

## Incident

# Seven minutes to failure — the Tosco hydrocracker runaway

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## Summary

On 21 January 1997, a temperature excursion in a hydrocracker led to the rupture of a 12-inch reactor outlet pipe segment. The explosion that followed killed one person and injured 46.

The accident investigation found that it took only seven minutes between the onset of temperature excursion until failure of the outlet pipe. This accident makes a strong case for why automatic depressurisation should be an independent protection layer for hydrocracker units.

The fatality was an operator standing next to the reactor when the pipe ruptured. He was there to read temperature indicators that were monitored through a locally mounted panel. Remote monitoring of all key process indicators is needed to ensure no one is placed in danger.

**Keywords:** Hydrocracker, temperature excursion, explosion

## A brief history of hydrocracking

Upgrading low-value, heavy carbonaceous feedstock to lighter hydrocarbon fuels by hydrocracking dates to the Bergius process for coal liquefaction. In the Bergius process, a slurry of pulverised lignite coal underwent hydrogenation and hydrogenolysis reactions that broke down the high-carbon macromolecules into lighter hydrocarbons suitable for use as gasoline and diesel fuels.

Carl Bosch, who developed much of the metallurgical and mechanical engineering know-how for use of hydrogen at high pressures/temperatures during his famous work on the ammonia process, led I.G. Farben Trust's successful commercialisation of lignite hydrocracking in Germany. He joined Friedrich Bergius to share the 1931 Nobel Prize in Chemistry for this step-out refining technology.

Standard Oil of New Jersey (Exxon) adapted the process to hydrocrack heavy petroleum fractions in the U.S. through their technical exchange program with IG Farben<sup>1</sup>. Their hydrocracker operated at around 4,000 psig (277 bar) pressure with temperatures above 700°F (371°C). ICI developed a similar hydrocracking process in England to supply aviation gasoline during World War II. As a refining process, hydrocracking was abandoned in favour of fluidised catalytic cracking (FCC) in the 1940s and 50s.

Modern hydrocracking was developed by Standard Oil of California (Chevron) in the late 1950s and early 60s. Through

advances in catalysis, better conversion performance was achieved at lower pressures. Hydrocrackers today are used to upgrade a range of low-value, heavy petroleum fractions to gasoline, jet fuel, diesel, and intermediates for lubricant base oils—offering a feedstock and product flexibility that FCC does not have. Today over 200 hydrocrackers are in operation at refineries in 60 countries.

## Chemistry of hydrocracking

Hydrocrackers use bifunctional catalysts with both acidic and metal sites for simultaneous cracking and hydrogenation. Since more C-H bonds are formed than C-C bonds are broken, the reaction is exothermic.

An unusual feature of hydrocracking is that there is essentially no limitation on the degree of reaction. Larger molecules continue to crack into smaller molecules. Reactors are designed for monitoring and controlling temperatures within a relatively narrow operating band. A temperature excursion may lead to onset of a runaway reaction (sometimes referred to as demethylation)<sup>2</sup>.

## Previous hydrocracker incidents

The *Loss Prevention Bulletin* archives include two articles about accidents involving hydrocrackers. *LPB089* describes an incident at BP Grangemouth Refinery in 1987 that resulted in one fatality. While in standby mode, liquid level in the hydrocracker's high pressure separator vessel was lost. High pressure gas blew through, resulting in the explosion of the low-pressure separator drum.

*LPB116* tells of another deadly accident at the hydrocracker unit at Fiji Oil Sodegaura Refinery following a turnaround in 1992. During the unit start-up, the lock ring of a Breech-Lock feed-effluent exchanger burst. As operators and site workers heard the hissing sound of escaping gas and approached close enough to get a better look, an explosion occurred. Ten were killed and seven injured. According to the authors of the article, the root cause was likely a modification to the exchanger lock ring for it to fit better. The exchanger was not inspected during the turnaround to see how this modified lock ring had held up.

Although the refining industry is aware of several hydrocracker runaway incidents through various inter-company communication channels, there is very little about these in the public domain. An example of one such event is the 1970 hydrocracker vessel rupture and explosion at the Exxon Bayway Refinery (Linden/Elizabeth, NJ). The massive explosion was felt in towns 40 miles up the Hudson River and

across Staten Island<sup>3</sup>. Seventeen days before the accident, the hydrocracker developed a hot spot exceeding vessel design temperature. Since most of the reactor temperature indicators had already failed due to corrosion, the operators believed this was another faulty/corroded thermocouple and continued to operate normally until the catastrophic runaway. Despite the scale of the explosion/fires and the large number of injuries, there were no fatalities.

The Tosco Avon Refinery accident of January 1997 may be the only publicly investigated case of a catastrophic hydrocracker runaway. The EPA investigation report<sup>4</sup> is the source for most of the information contained in this article.

## Tosco Avon Refinery

Located in the San Francisco Bay area near the city of Martinez, the Avon Refinery was built in 1913. The hydrocracker unit was commissioned in 1962. Tosco purchased the refinery in 1976. The facility is currently owned by Marathon Petroleum.

## Hydrocracker operation

A simplified flow diagram of the 35,000 BPD Tosco hydrocracker unit is provided in Figure 1.

In that process, heavy petroleum feed (heavy gas oil and light/heavy cycle oils from FCC) entered the first stage hydrotreating unit (three reactors in parallel) through preheaters. The hydrotreaters remove the heteroatoms that

could poison the second stage hydrocracker catalyst. Nitrogen compounds are the main concern for the second stage hydrocracker catalyst as these can neutralise the acid sites of the catalyst. The "nitrogen slip" (concentration of nitrogen in the hydrocracker feed) was maintained below 14 wppm.

The feed to the three parallel hydrocracker reactors was preheated and combined with H<sub>2</sub> before entering the three parallel hydrocrackers. The H<sub>2</sub> was heated through a "trim heater" (the fired heaters shown in Figure 1) to control reactor inlet temperatures. The reactors operated under a pressure of between 1350 and 1735 psig (94-121 bar).

Tosco hydrocrackers had five catalyst beds each, with cold hydrogen quench between the beds. The quench gas system ensured that the temperature rise across the reactors was kept below a target maximum. An Emergency Depressurisation System (EDS) could be activated by the operators to depressure the reactor to flare in case of a temperature excursion. Depressurisation stops the reaction through a rapid drop in hydrogen partial pressure.

To prevent an excursion from becoming a runaway, the operating procedure called for the following actions.

1. If any reactor Temperature Indicator (TI) is 5°F (2.8°C) above normal, change reactor controls to return the TI to normal. This may include reducing the trim heater temperature (reactor inlet) or increasing quench H<sub>2</sub> to the bed where the TI is located.

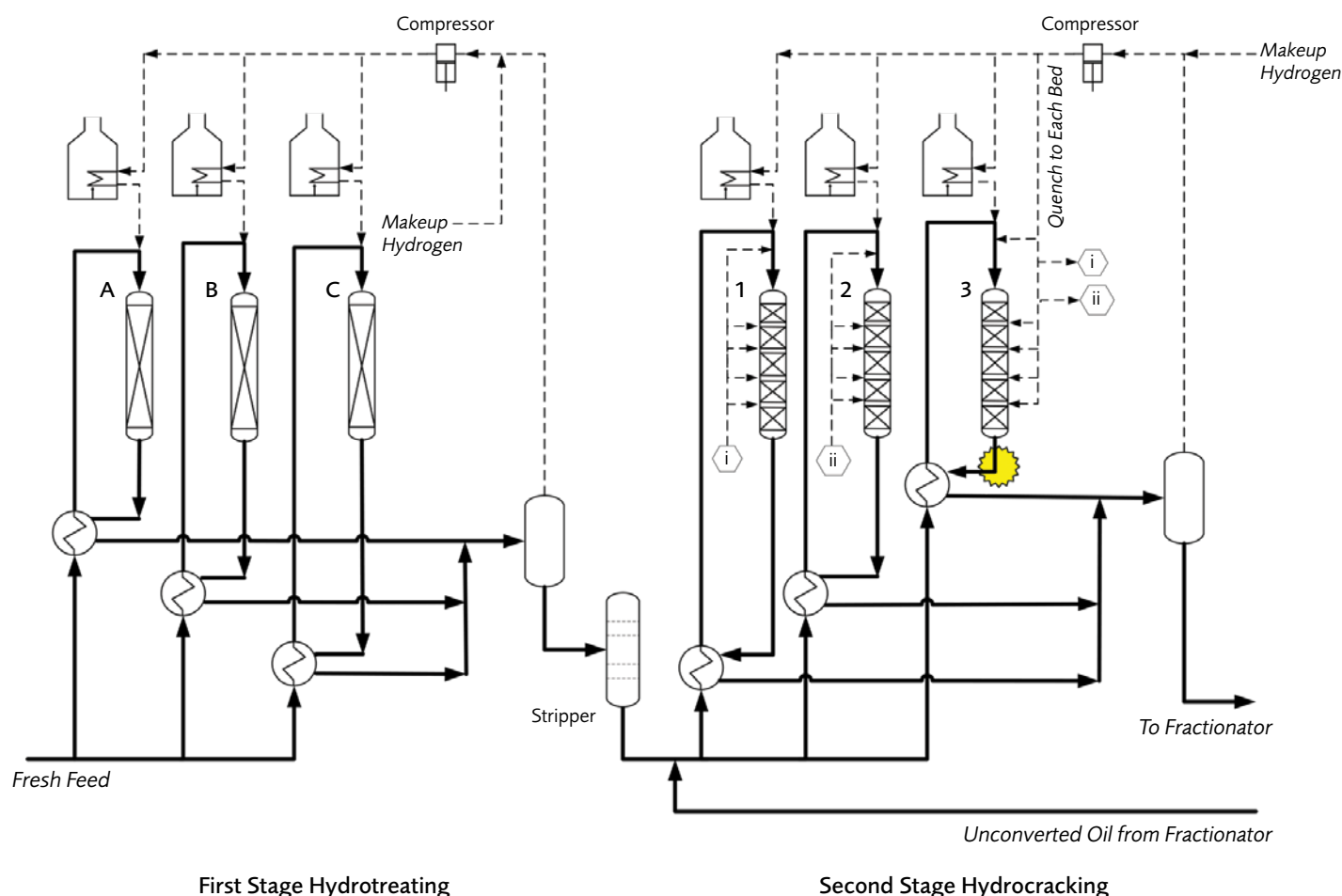


Figure 1 – Simplified process flow diagram for the Tosco hydrocracker with the location of the pipe rupture highlighted.

2. If any reactor TI is 25°F (14°C) above normal, close the oil feed control valve, reduce trim furnace firing, circulate maximum H<sub>2</sub> through hot reactor, and maintain normal unit pressure.
3. If any reactor TI is 50°F (28°C) above normal, or if any TI exceeds 800°F (427°C), immediately activate the EDS. (The reactor design temperature was 845°F or 452°C.)

Audible alarms alert the operators to conditions requiring action. Recovering from an EDS, i.e. re-establishing conditions for on-spec fuels production, takes about two days<sup>4</sup>.

During the January 1996 turnaround (a year before the incident), the thermocouples were replaced with 12-point array style thermometry which provided more TI's per reactor. Some of these new TI's were monitored locally through a panel by the hydrocracker reactors.

In addition, a new, more active catalyst was loaded in the hydrocrackers during that turnaround.

### *Prior incidents of temperature excursion at the unit*

On 23 July 1992 (four and half years before the accident), a temperature excursion occurred in the hydrocracker unit. The operators responded as specified in the procedure and activated the EDS. The depressurisation stopped the temperature excursion—but also led to a grass fire at the flare. Refinery management expressed concern that future depressurisations to flare may risk a fire in the adjacent wildlife preserve. This may have been interpreted by the operators to mean that EDS should be avoided.

On 19 March 1996, another temperature excursion occurred. The operators responded by stopping oil feed, reducing trim heater firing rate, and increasing quench. Before the temperatures started to decrease, the reactor outlet had reached 921°F (494°C). Despite exceeding the 800°F (427°C) trigger temperature, EDS was not activated. There was no disciplinary action or re-training for not following the SOP.

Another such event took place just two days before the accident. In response to an excursion in hydrocracker Reactor 1, quench gas was added manually to Beds 2-4. Then the oil feed was stopped and fuel gas to trim heater was cut back. About five minutes after stopping oil feed, a Bed 4 TI reached 998°F (537°C) before starting to decrease. Again, EDS should have been activated but was not. There is no mention of how management responded to this second known deviation from the procedure.

### *The day of the runaway*

At 4:50 a.m. on 21 January 1997, a clamp on the feed-effluent exchanger of hydrotreater Reactor A began to leak. The Reactor A feed was diverted to Reactors B and C at about 5:20 a.m. while repair work began on the heat exchanger clamp. With increased flow, nitrogen removal performance suffered in Reactors B and C. Laboratory analysis showed that nitrogen slip to the hydrocrackers increased from 5 wppm to 352 wppm through the morning. (Recall that the upper limit for the second stage hydrocracker catalyst was 14 wppm nitrogen.)

With high nitrogen slip poisoning its catalyst, the hydrocracker performance declined. This was evidenced by a decline in conversion performance, as well as reductions in hydrogen consumption and quench gas requirement.

The repair of the leaking heat exchanger involved adding a

sealant that needed a day to cure. With hydrotreater Reactor A isolated, the decision was made to reduce throughputs by a third to re-establish proper nitrogen removal.

At the reduced rates and higher hydrotreater temperatures, nitrogen removal performance recovered quickly. The 1:30 p.m. sample showed 40 wppm nitrogen slip. Meanwhile, the hydrocracker reactor temperatures were maintained at 612-640°F (322-338°C)—higher than typical values around 600°F (315°C)—to help drive off the nitrogen. The automatic quench H<sub>2</sub> temperature control valves were at 10% output (i.e. almost closed).

A morning lead operator was asked to stay for the swing shift (2-10 p.m.) to help get the unit lined out at proper hydrocracker conversion operation. There were now two lead operators directing the hydrocracker.

The 5:40 p.m. nitrogen analysis showed 47 wppm slip. What happens next suggests that this may not have been reflective of the actual nitrogen slip to the hydrocracker and a new sample may have had to be taken for re-analysis.

At 7:34 p.m., the hydrocracker Reactor 3 Bed 4 outlet temperature increased from 628°F (331°C) to 823°F (439°C) in 40 seconds. At the same time, Bed 5 top inlet TI rose from 627°F (330°C) to 860°F (460°C). Alarms sounded as the quench valves to Bed 5 had automatically opened to 100% output in response. However, the makeup hydrogen to the hydrocracker began to decrease.

As the catalyst recovered its activity, the expectation was to see an increase in hydrogen consumption. Therefore, the decrease in makeup hydrogen was incorrectly interpreted as an indication that the catalyst had not yet returned to its active state. Of course, there was plenty of hydrogen in the loop (especially at the bottom beds of the last reactor) to support a runaway without the need for makeup hydrogen.

We now know that the runaway reaction had started at this point, forming methane and other light gases that increase the density of the hydrogen recycle gas. The compression of this higher density gas resulted in a higher hydrogen compressor discharge pressure. Since hydrogen supply was controlled off the compressor discharge pressure, makeup H<sub>2</sub> flow stopped.

The recycle hydrogen GC analyser had a significant lag time. The operators did not have the online GC data, recorded later, that indicated the onset of demethylation.

At 7:37 a lead operator put the quench gas to Bed 5 in manual and reduced the flow. A minute later another operator corrected the mistake and put that in automatic; however, the flow did not return to the full-open position flow of 25 MMSCFD (27,900 Nm<sup>3</sup>/h) and hovered around 8 MMSCFD (8,900 Nm<sup>3</sup>/h).

Between 7:38 and 7:39, all Bed 5 temperatures were above 780°F (415°C), and one over 1200°F (649°C). Three Bed 5 temperatures then defaulted to zero while a fourth was at 890°F (477°C). This behaviour may have confused and distracted the operators who may have not noticed the reactor outlet temperature above 980°F (527°C) and rising steadily.

Puzzled by the bouncing temperature readouts, one of the two lead operators called to request an instrument technician to check on the data logger. At the same time, a team member was sent to read the temperatures from the locally mounted panel in the field.

By 7:40, Reactor 3 inlet was at 889°F (476°C) and its outlet at

1220°F (660°C). The other lead operator proceeded to reduce the fuel gas to the trim heater.

The operator who was sent to read the temperature from the panel by the reactor radioed, "1250" (677°C). The board operator radioed him back to make sure he heard correctly but received no response. It was thought that the outside operator's radio batteries had died, so two other operators went out to check on the field temperature reading.

No one activated the EDS.

At 7:41, the 12" outlet pipe on Reactor 3 ruptured. The explosion that immediately followed killed the operator who was sent there to read the temperature.

### Some of the key lessons

From automation to operations management and human factors, the Tosco Hydrocracker tragedy offers many lessons.

First, EDS needs to be automated as an Independent Protection Layer with all the requirements an IPL entails. It took only seven minutes from the time the temperature started to rise (from what was thought to be a deactivated catalyst state) until the explosion. This is too short of a response time for reliable operator action.

Layers of Protection Analysis had not been adopted by the industry in 1997. This accident makes a strong case for LOPA and IPL considerations (or a comprehensive HAZOP/PHA that considers runaway scenario in detail).

Recovery of bifunctional catalysts from temporary nitrogen deactivation can occur quickly. A rapid decrease in nitrogen slip from the upstream hydrotreater can result in an equally fast reactivation of the hydrocracking catalyst.

During a reactor temperature excursion, no one should be around the reactor. All instrumentation for monitoring the reactor needs to be placed a distance away, preferably in a blast proof control room.

Management should include operations, maintenance and safety personnel in the design phase of projects. The field temperature panel would very likely have not been located at the base of the runaway reactor if operations personnel would

have been involved in the design, construction and location of the field temperature panel.

Finally, management should ensure safety-critical procedures are followed. Refresher training needs to emphasise the following message: When in doubt, a high temperature reading should be believed and acted on as specified in the procedures.

Looking at how excursions were handled prior to the accident, it seems that deviation from SOP (not activating EDS as specified) was tolerated. What steps were taken to manage the excursion were not documented as these likely differed among different lead operators. Reading through the operator actions during the fateful seven minutes prior to the 21 January 1997 explosion leaves one with a sense that there may have been conflicting approaches at play in the control room. The presence of two lead operators there may have contributed to this. However, the root cause is found in a management culture that tolerated deviation from SOP when it came to emergency depressurisation.

### Acknowledgment

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