Fire in an isomerisation unit and domino effects on a benzene saturation unit, in a refinery

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Rome

Italy

Fire
Refinery
Paraffin
Compressor
Domino effect
Material failure
Material losses
Benzene

THE INSTALLATIONS IN QUESTION

The refinery started its operation in 1965. The current plant asset is the result of an important reconditioning and technological modernization that was completed in 1995. The refinery produces a wide range of petroleum products with a capacity of over 5 million tons per year, and 130 storage tanks with a total storage capacity of 1300000 m^3.

The establishment covers an area of about 100 ha and is located in a high density industrial area, near a river. The plant is under Seveso II Directive (upper tier plant).

A map and a general functional flow-scheme of the refinery are showed respectively in fig. 1 and fig. 2.

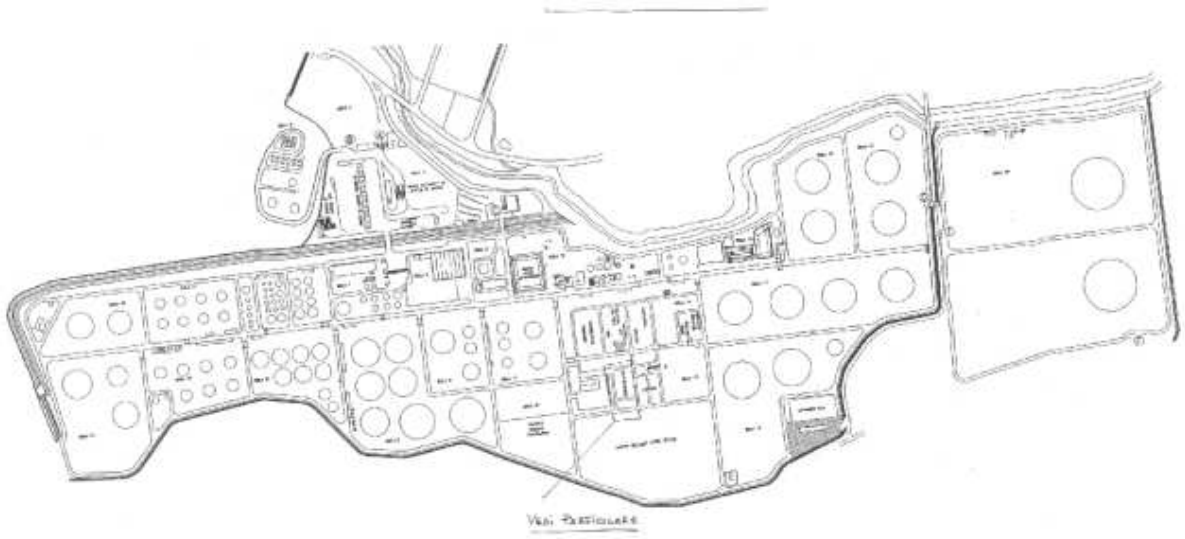


Fig. 1

The main steps of the process are detailed in the following diagram and correspond to classical units of a refinery.

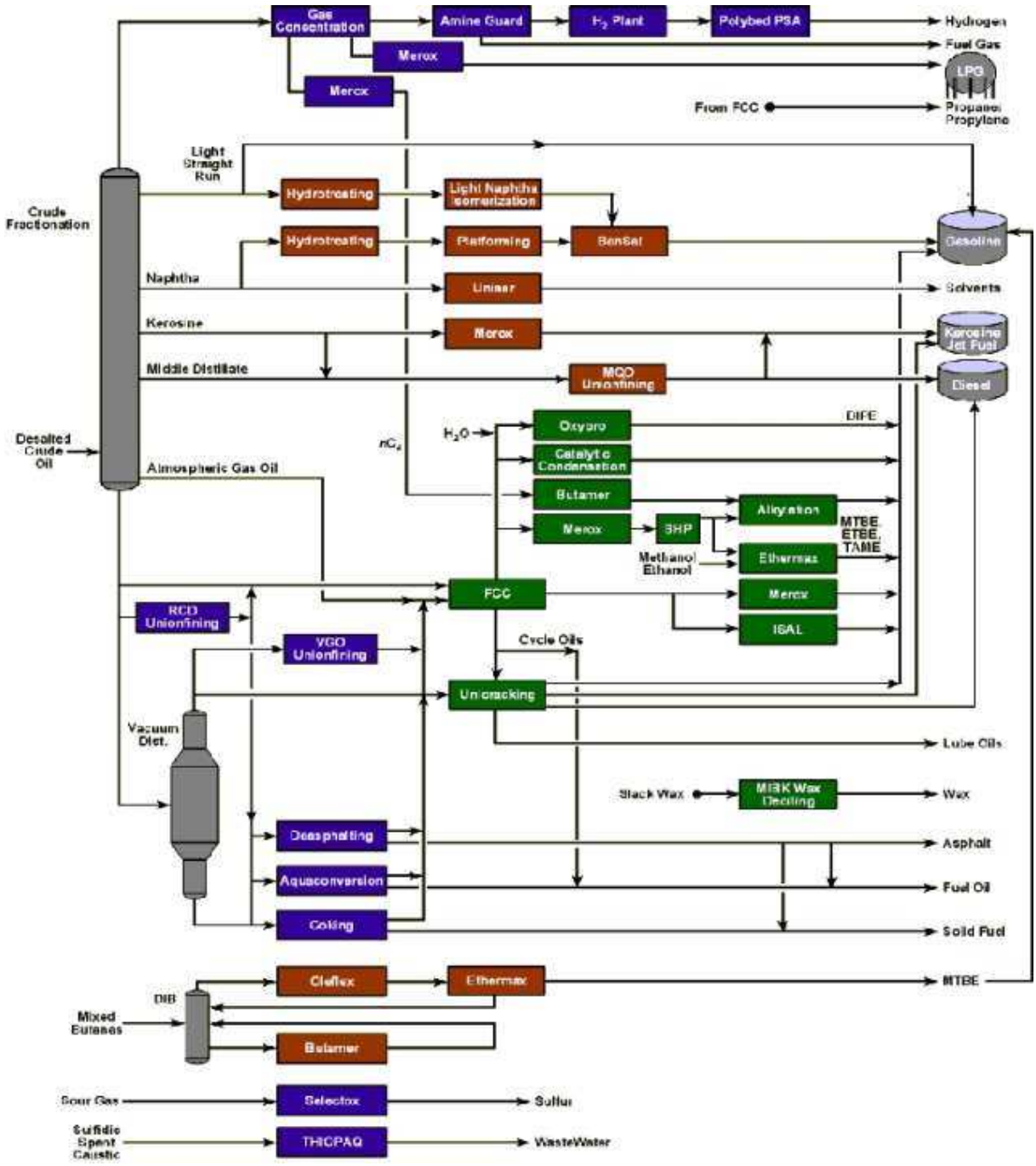


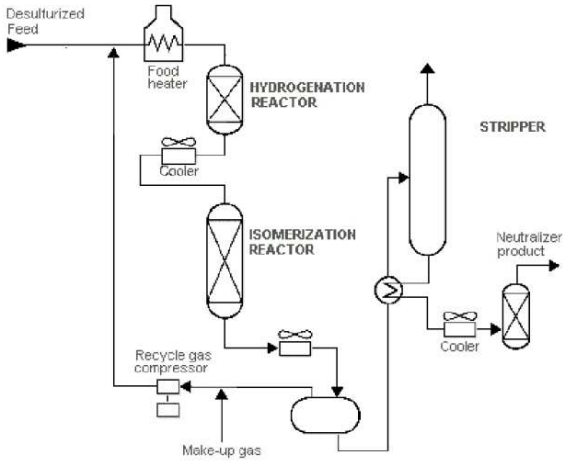
Fig. 2

In the accident, two units were involved : the isomerisation unit (TIP), used for the pentanes and hexanes transformation, and the benzene saturation unit (bensat), that converts aromatics to saturated compounds. The initiating event occurred in the TIP unit and extended to the near benzene saturation unit (BenSat). Both the sections belong to the isle 129 of the plant.

TIP unit :

In the isomerisation unit N-paraffins are transformed into iso-paraffins, with a higher octane number. The reaction takes place at temperatures in the range of 250 - 300 degrees C, in presence of a catalyst, and at pressures in the range of 15-22 bar. The catalyst requires an atmosphere of hydrogen to minimize coke deposits (hydro-isomerisation process). The unit produces light naphtha with a C5/C6 content about 97% or better, relative to the feeding, and octane upgrading between 8 and 10 points.

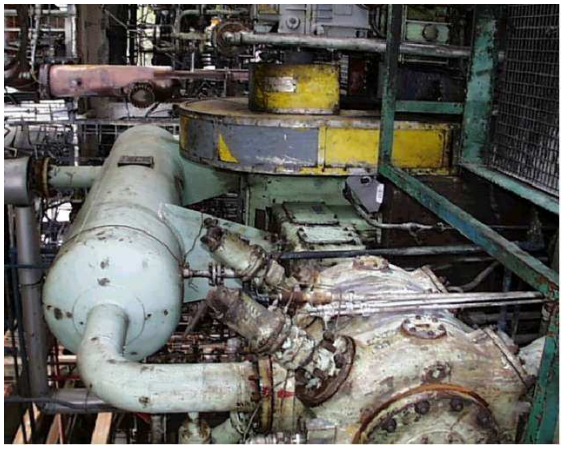
The liquid feedstock is pentane/hexane from light naphtha. The light naphtha (C5/C6) is combined with the recycle gas/ fresh gas mixture. The resultant combined reactor feed is routed to a feed/ effluent heat exchanger, where it is heated and completely vaporised by the effluent of the reactor. The vaporised combined reactor feed is further heated to the desired reactor inlet temperature in the reactor charge heater. The hot charge enters the isomer reactor at the top and flows downwards through the catalyst bed, where a portion of normal and mono-branched paraffins is converted into higher branched (high octane) components. Temperature rise from the heat of reaction release is controlled by a cold quench gas injection into the reactor. Reactor effluent is cooled and subsequently separated in the product separator into two streams: a liquid product (isomerate) and a recycle gas stream returning to the reactor via the recycle gas reciprocating compressor. A technical scheme of the process is showed in the scheme here beside.

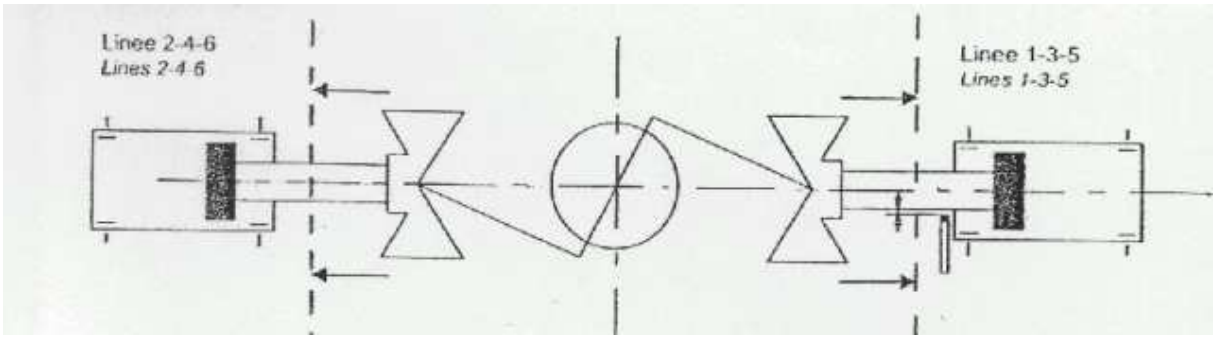


Reciprocating compressor K-2901B:

The accident was originated by one of compressor of the recycle gas compressors group (reciprocating compressor K-2901B), located in isomerisation unit, used to recycle a gas mixture to the isomerisation and Bensat units.

The compressor works in parallel with a twin compressor (K-2901A), at pressures from 15 to 21 bar and a thermal range from 40 to 60 Celsius degree. The gas mixture recycled consists mainly in hydrogen (70% vol), with the remaining part of methane, ethane, propane and butane.





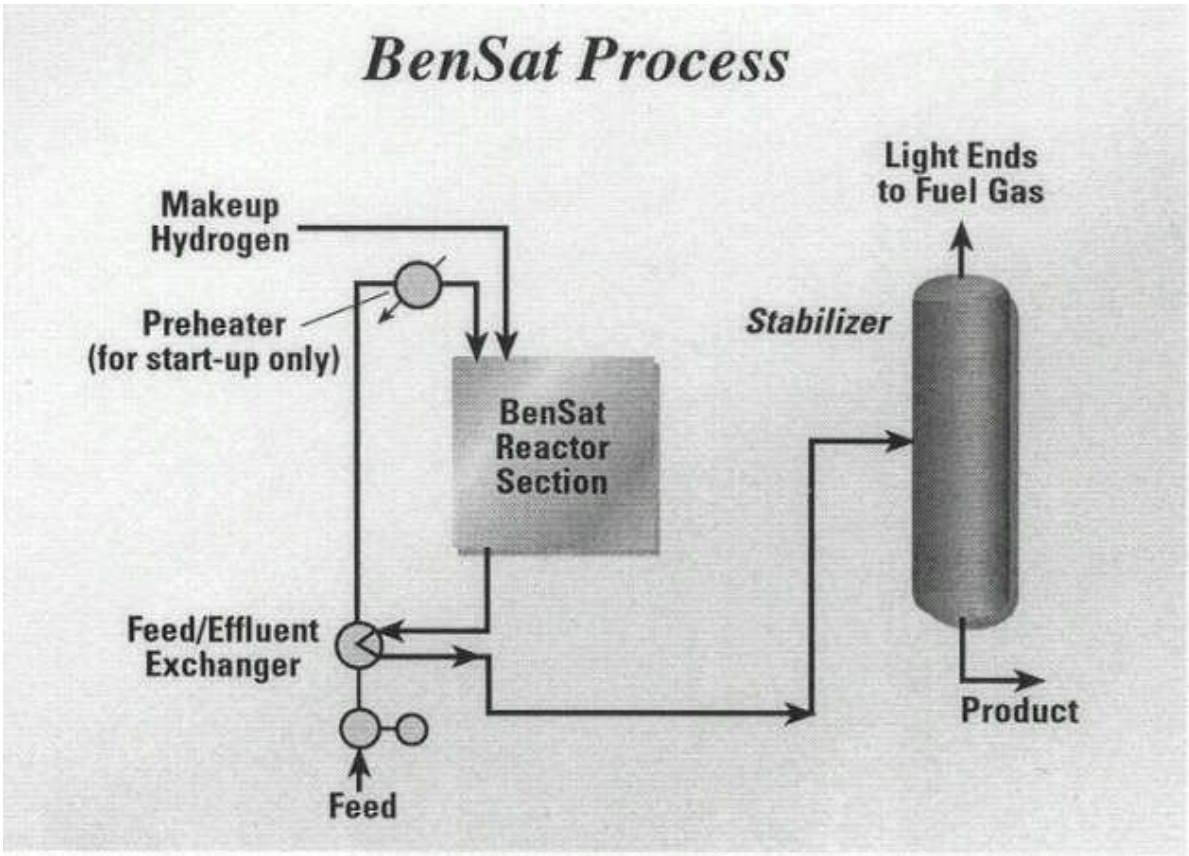
The reciprocating compressor (cf scheme here above) with horizontal balanced opposed cylinders is designed to handle gas mixture complex. The packings are lubricated. The gas is compressed in one stage by two cylinders. The cylinders are of double acting type. The crank mechanism has two opposed cranks in order to completely balance all inertia forces. The compressor is driven by an electric asynchronous motor. The rotation is anticlockwise facing the compressor from non driving end.

Bensat process :

This process consists in aromatics saturation catalysts to reduce the benzene contained in the distillate, in order to avoid product contamination and catalyst poisoning.

It is realised to complete the C5-C6 isomerisation, to remove the natural benzene concentrated by aggressive reformer feed pre-fractionation, and also to remove the benzene that has been produced in the reformer.

The process handles up to 30 vol-% or more benzene in the feed. Benzene is saturated to C6 naphthenes so that the reactor effluent contains less than 0.5 vol-% benzene. The catalyst used in this process is highly selective. The unit receives about 12 ton/h of gasoline from the plat-former. The heat of reaction from benzene saturation is carefully managed to control the temperature rise across the reactor.



Makeup hydrogen to the BenSat process is provided in an amount slightly above the stoechiometric level required for benzene saturation. The liquid feed stream is pumped to the feed-effluent exchanger and then to the pre-heater, used only for start-up purposes. Once the unit is operating, the heat of reaction provides the required heat input to the feed via the feed-effluent exchanger.

Benzene is saturated to C6 naphthenes in the presence of hydrogen using a noble metal catalyst. The effluent passes through the feed effluent exchanger and is then sent to a stabilizer for removal of light ends.

THE ACCIDENT, ITS BEHAVIOUR, ITS EFFECTS AND CONSEQUENCES

The accident :

In December 2002, at 03.00 p.m. a strong abnormal noise from the reciprocating compressors area was heard by the field operators in the TIP unit. The operators recorded a high temperature alarm in the 2nd cylinder of the compressor K2901B and a low pressure oil alarm in the crankshaft. Field operators went near the compressor, where the noise was increasing. One of them pushed the stop-emergency button of the compressor on the local control panel. At the same

time, a strong burst was heard, followed by a jet-fire starting from the compressors area of the TIP unit (at the bottom of K2901B compressor), impinging the near bensat unit (14 m apart).

A big quantity of highly flammable gas mixture was released and immediately found ignition. Under the effect of the jet-fire, parts of the bensat unit failed causing the release of gasoline and hydrogen, which led to the extension of the fire.

TIP and bensat units were isolated. The TIP unit was immediately shut down and depressurised and the fuel gas was drained to the net. The emergency alarm started and the internal emergency measures, cooling and spread-foam systems activation, were immediately applied. After 25 minutes from the internal emergency alarm, the external Fire Brigades arrived. All the plants of the refinery were put in safety shut down condition. After about 1 hour the fire was controlled, and at about 30 minutes later the emergency was closed.

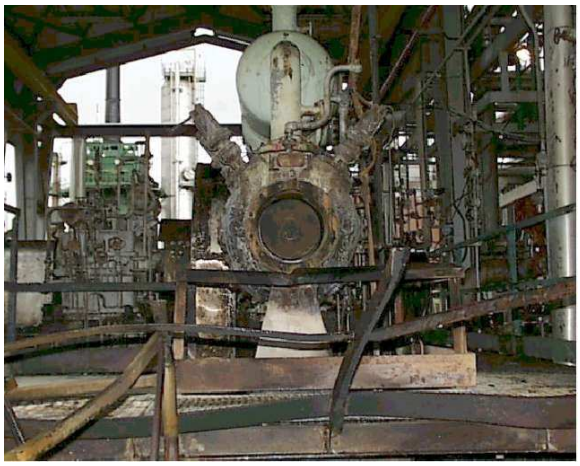
The consequences :

The accident did not cause effects to people or to environment. The estimated damage to property was about 3 million euros, corresponding to the total rebuilding of the bensat unit and to the substitution of the compressor K2901B. The damages are listed here under :

TIP unit

✓ About 3 tons of gas mixture rich in hydrogen and about 6 tons of gasoline were released.

✓ The cylinder liner and the bottom-head of the compressor were found at distances of respectively 8 and 14 m from the compressor. Some of the structures near the compressors area were damaged by the fire and the direct impact of parts of the compressors.



Bensat unit

✓ Most of the structures invested by the jetfire were protected by a fire-proofing layer; they were damaged but didn't have mechanical failure. Pipe connections and process units lost their sealing and released some gasoline and hydrogen that contributed to the extension of the fire and the destruction of the unit.

✓ About 0,3 tons of gas mixture and 6 tons of gasoline were released.

The total quantities of flammable substances released were estimated as follows:

- 3,3 tons of gas mixture (70% hydrogen, 30% methane, ethane, propane and butane);
- 12 tons of gasoline.

Seveso II directive – Annex VI

The accident has been considered a 'major accident' according to the criteria set in Annex VI of the Seveso II Directive, in particular:

✓ Substances involved

- Any fire or explosion or accidental discharge of a dangerous substance involving, a quantity of at least 5 % of the qualifying quantity laid down in column 3 of Annex I.

=> About 3,3 tons of highly flammable gas mixture have been released through the compressor and from the bensat unit, so exceeding the limits for the highly flammable substances according to the Annex VI: 2,5 tons (5% of 50 tons).

✓ Damage to property

- Damage to property in the establishment at least euros 2 million,
- Damage to property outside the establishment; at least euros O,5 million.

⇨ Damage to property was estimated more than 3 millions Euros, exceeding the 2 millions Euros that represents the limit in Annex VI.

European scale of industrial accidents

By applying the rating rules of the 18 parameters of the scale made official in February 1994 by the Committee of Competent Authorities of the Member States which oversees the application of the 'SEVESO' directive, the accident can be characterised by the following 4 indices, based on the information available.

The parameters which comprise these indices and the corresponding rating method are indicated in the appendix hereto and are available at the following address: http://www.aria.environnement.gouv.fr

ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

The first phase of the accident consisted in the mechanical failure of the bottom of one of the cylinders of the compressor K2901B.

Nevertheless, the original causes of the event are not yet well identified. One of the hypothesis is the rupture of the crankshaft-rod mechanism in the compressor, with a consequent hitting action of the piston on the bottom of the cylinder 2. The combined effects of hitting-action with the internal pressure (20 bar) led to the failure of the nuts, which hold the bottom.

The relevant last maintenance operations on the compressor unit were:

- Pumping part revision in October 1999

- Substitution of 9 valves in July 2001
- Substitution of valve of cylinder 1 East side in September 2001
- Pumping part revision, substitution of speedy joint in November 2001
- Compressor general revision in May 2002
- Revision of sealing packages in November 2002
- Revision of pumping part of cylinder 2 West Side, in December 2002

The maintenance operations of the compressor, according to registers, were regular.

After the accident, in order to make a detailed assessment on the causes of the failure, a careful examination of the damage compressor has been planned.

ACTIONS TAKEN

Internal Emergency Plan

3 minutes after the loud noise, field operators, who were near the compressor to check the situation, pushed the stop-emergency button of the compressor on the local control panel. They isolated the 2 units and activated the emergency systems. The TIP unit was immediately shut down and depressurised, and the fuel gas was drained to the net. The emergency alarm started.

The internal Emergency Control Centre immediately organized and activated cooling and foam systems in the involved units and in the near ones. The actions were coordinated with the Internal Advanced Control Centre.

The internal team faced the fire from South-East, through a fixed high-flow monitor, two fire-hoses UNI45 from south, another fixed monitor in south-west site, a truck with monitor jets and two fire-hoses UNI70 from north west.

External Emergency Plan:

At 03.16 p.m. the general emergency shut down of the establishment was disposed, and the actions for the activation of the external emergency plan were started.

Before the arrival of the external fire brigades, also the Major of the town, police and prefect were informed of the accident. An ambulance immediately arrived at the refinery and doctors were available for first aid if needed.

After 25 minutes from the internal emergency alarm, the external Fire Brigades arrived, taking charge of the coordination of the emergency actions.

With the arrival of the external fire brigades, the fire was soon (after 20 minutes) under control. After 25 minutes the fire was completely extinguished and at 04.50 the emergency was closed.

Official Actions taken:

A detailed investigation to understand the causes of the accident is still in course. A consultant, nominated by the civil law-court, is working together with the compressor provider and the maintenance team of the refinery. The investigation will focus on the causes and the dynamic of the mechanical failure, also through labs tests and analysis of the materials of the mechanical parts found broken.

LESSONS LEARNED

It is not clear if there is a direct link between the real causes of the accident and possible Safety Management System procedure deficiencies, in particular for those related to inspections, controls and maintenance of installations.

However, the accident put in evidence some issues that, even if general and already identified in other cases, still had an important role in the event occurred:

Equipment / devices issues:

- Improvement of lay-out of installations
- Definition of appropriate control parameters precursor of anomalies/failures in the installations (malfunction status)

Management:

- Performance of the emergency devices (flow and autonomy of water stock , number and position of water/foam suppliers and monitors, etc.)
- Accessibility of the critical areas to the emergency teams / fire Brigades (in terms of adequate ways-spaces for adequate devices, and of number of intervention points)
- Improvement of communications during the emergency actions.

The establishment, in consideration of the experience matured and of the up-to-date studies in course, intends to adopt the following plant-management measures:

- Substitution of the current reciprocating compressors by a single centrifugal compressor in order to potentiate the TIP unit.
- Use of interception electro commanded valves in suction lines, to be inserted near the compressor in order to limit strongly possible gas release (currently these valves are hand-commanded).
- Improvement of the location of hydrants and fixed monitors.
- More frequent personnel training for the emergency situation, to improve the response to accident.
- Revision of the emergency procedures in order to better define the emergency tasks of teams and the operators involved.
- Revision of the shut-down procedures of plants and of electrical systems.
- Up-date of safety analysis in safety report, in particular for aspects relative to potential domino effects.
- Start of the needed procedures to specialize the internal emergency plan for the incidental scenarios individuated in safety report.

The inspection Commission found that in the risk analysis conducted for the establishment a jetfire scenario in the TIP unit was considered, but the parameters used in the analysis were not such to cause damage to the near units. In particular, the timing of the real accident caused a domino effect with the involvement of the bensat unit 14 m apart.

Thank to the internal emergency team intervention and the Fire Brigades, the release of flammable substances was limited with almost no damages to the other units. The bensat unit was anyway completely destroyed.

The Commission suggested that a revision of the risk analysis, with the adoption of more ‘realistic’ hypothesis (timings, duration, intervention, etc.), should be done.

In addition and following the risk analysis, the criteria for the identification of critical units should be revised as well, and the process of their optimisation for reduction of risks should be better defined.

Operative procedures should also be revised, with particular reference to instructions in normal, abnormal and emergency conditions.

In consideration of the difficulties encountered during the intervention in emergency, the Commission also suggested:

- A review of the internal emergency procedures with particular attention to the detailed definition of role and responsibilities of personnel;
- More frequent training of personnel for the emergency situation, in order to improve their response to the accident.