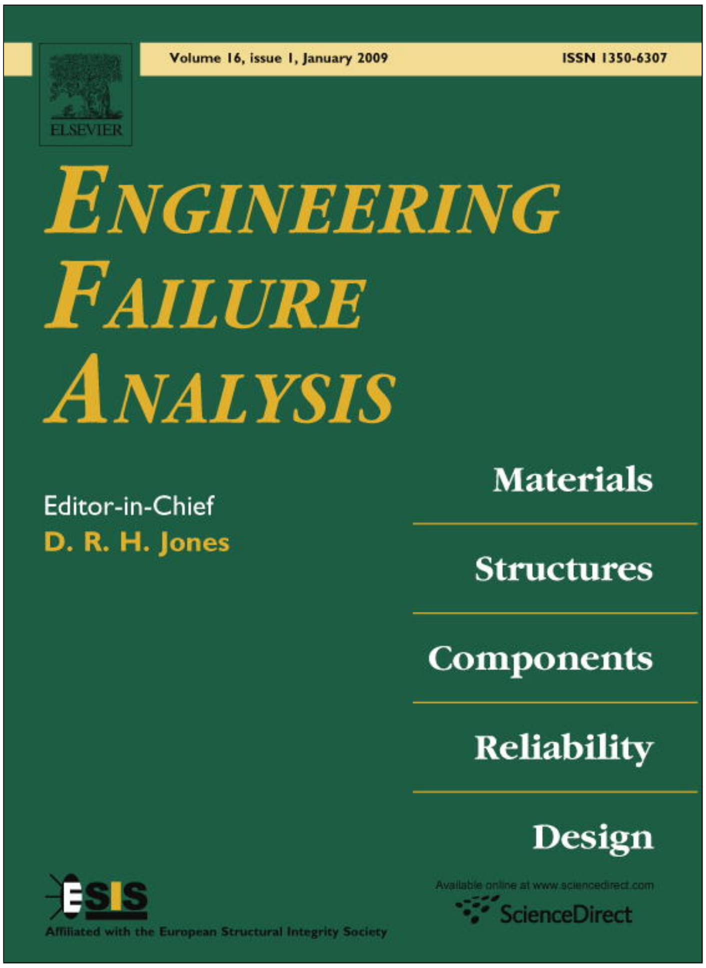
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Self-ignition of natural gas inside pipes at a regulation station

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Abstract

Expert investigations were developed for a leak followed by fire in a natural gas measurement and regulation station, located in the Southern part of South America. Field inspections, chemical and microstructural tests, mechanical tests and models, and models for deflagration and detonation are presented and discussed. The fire was due to air that got into the pipes, when mounting valves at the pig traps. Venting and bleeding failed to be properly carried out while the line was pressurized, and the filling rate was not regulated properly either. In order to reduce the probability of recurrence of the event, the procedure for the filling and the pressurization of the pipeline was redesigned, safety features added, and personnel trained.

Keywords: Self-ignition; Pipe; Failure; Fire; Natural gas

1. Introduction

The explosion and fire in a skid-type natural gas measurement and regulation station, located in the Southern part of South America, occurred during the process of re-pressurization of the system, after a prolonged plant shutdown. The station operates at a maximum of 65 bar, pipe diameters are 8 in. and 6 in., flanges are series 600. During the programmed shutdown, in the zone affected by the incident work was done to disassemble and repair spherical ∅ 8 in. valves mounted on Scrapper traps. Then the maneuvers to pressurize the pipe began, during which the valves operated according to the pre-established diagram. The volume splitter valve was opened gradually until pressure became stabilized in 36 bar. When checking the joints at one end of the gas pipeline, an explosion took place at the other end. Immediately the operators managed to cut gas provision and extinguish the fire.

Fig. 1 shows the container of the separating filter, and the first horizontal and vertical portions of the suction pipe. The first bend is indicated, the vertical pipe ends in a Tee to the 8 in. collector pipe, see detail (A) in Fig. 2. Also indicated in this figure are (B) the end flange, (C) strongly deformed intermediate pipe tract, (D)

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Fig. 1. Separating filter and upper suction pipe.

Fig. 2. 8 in. lower suction pipe. (A) End Tee for vertical pipe, (B) end flange, (C) strong deformation, (D) cap to thermometer, (E) cap to manometer.

joint to a thermometer, and (E) joint to manometer, whose clock was taken off. The gas leak from the end flange B caused the small hole seen at the bottom right of the picture.

2. Inspection and evaluation of evidence

Diameter variations due to plastic deformation are seen in tube section between the Tee and the end flange, and in the section between manometer and thermocouple. Fig. 3 shows the strongly deformed tract C, as seen

Fig. 3. Deformed tract (detail C in Fig. 2), as seen immediately after the fire.

immediately after the fire was extinguished. Dark parts correspond to burned coating. Atmospheric corrosion soon turned into orange color all parts seen white in this picture, in which the coating was totally destroyed by the fire.

The damages due to the overpressure in the ∅ 8 in. pipe not only include increased diameter. The threaded connection of the manometer broke and the gauge flew almost 20 m. Its gauge got stuck in 28 bar, see Fig. 4. The needle was stopped by a rivet when pressure dropped.

Site inspection and analysis of available data allow the following hypotheses on the possible causes of the accident:

Fig. 4. The manometer flew 20 m, the needle was stopped by a rivet at 28 bar.

(1) Over pressure.
(2) Leak in end flange and explosion by friction with stones.
(3) Inner explosion.

The possibility of an overpressure was discarded, since the pressure downstream the skid was 41 bar, much less than previous operating pressure (between 45 and 60 bar). The hypothesis of a leak in the end flange followed by outer explosion was originally considered unlikely. The burst disk in the filter was activated; its rupture pressure is 95 bar. The switch for high level of liquid in the filter also failed. Burst disk (a), safety valve (b) and switch (c) are shown in Fig. 5.

Once repairs were finished, all failed parts and critical areas were analyzed, including verification of geometry and dimensions, angles and radii. All accessories flange, tube, end flange, by-pass, and curves correspond in material and schedule with design data. Thicknesses were normal in all accessories.

All deformed sections remained practically round, except the region where the tubes were supported and moored on concrete. Minimum thickness in the most deformed pipe tract next to the end flange is 6.81 mm, its diameter is 270.5 mm (Fig. 3). This implies a radial displacement of the outer surface of 25.73 mm (nominal diameter 8.6 in., nominal thickness 8.18 mm). The deformation in the section between the pressure gauge and the thermometer is also important, with a resulting radial displacement of 14.92 mm.

Fig. 6 shows the bent section of the line connecting the by-pass. Sections indicated in the sketch sustained symmetrical deformations, with radial displacements of 8.71, 8.4 and 5.37 mm for sections 1, 2 and 3, respectively. The straight sections are thinner than the accessories (curve and Tee), but these also sustained plastic deformations. The flat plate of the end flange also bent, indicating it also underwent important plastic deformations due to pressures above its yield strength. Its fixing bolts were also plastically bent, those in the lower

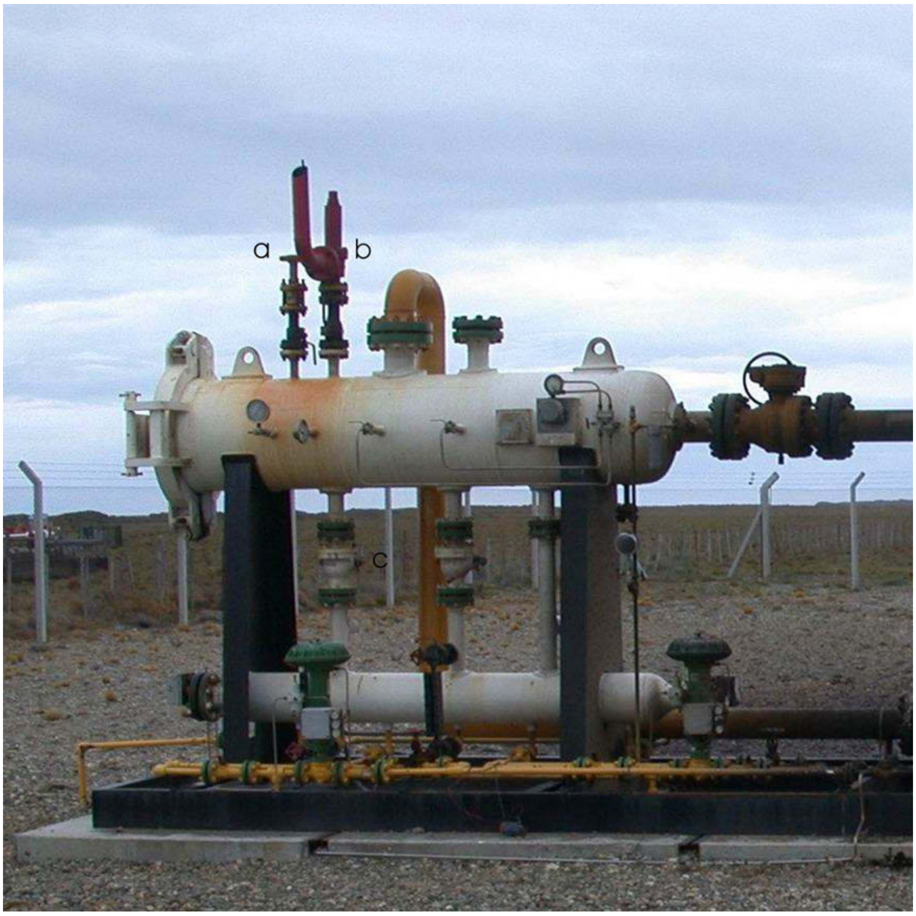

Fig. 5. Burst disk in the filter, safety valve and switch for high level of liquid.

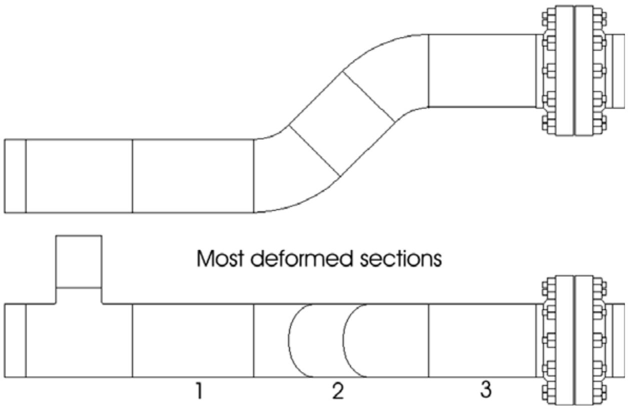

Fig. 6. Sketch of bent section of the line connecting the by-pass.

part of the end flange were more stretched than those in the upper part. This pattern is compatible with the occurrence of a leak in the lower part of the flange. In the middle region of the bolts are remnants of the seal, changes in thread color were due to different temperatures and environment during the fire.

Several elements were found inside the collector pipe. A small rolling stone, similar to those in nearby soil, it was probably introduced during manipulation subsequent to the failure. Fibrous pieces were found to be fiber glass remnants from coatings used during construction, repair and replacement. These were carried by the gas flow, probably from the filter separator. Oily dirt could have contributed to lower the ignition point of these pieces of coating.

The thermocouple tube, located in D in Fig. 2, was bent in the direction of gas flow. No marks of damage due to impacts with hard objects were found, bending was probably caused by a large volume of gas, an explosion or the impact with a soft object. In any case, this indicates larger than normal flow speed.

The threaded joint of the manometer was fractured at the weldolet. Fig. 7 shows that approximately half of the fracture took place in one thread within the weldolet, and the rest in another thread, outside the weldolet. The threads are worn away in the inner diameter of the female thread. These fracture surfaces do not show

Fig. 7. Fracture at thread in weldolet of manometer (E, Fig. 2).

indication of previous fatigue or corrosion defects. This uncommon flaw is related to the weldolet being too large, so that a male–female intermediary was placed. In spite of the poor quality of this accessory, its failure shows large plastic deformation, due probably to an important increase of internal pressure. This accessory is downstream the bent thermocouple tube (Fig. 2).

Metallographic specimens were cut, polished and Nital etched. Optical microscopy (X10 – X1000) revealed through-the-thickness pipe microstructure. In the figures that follow the inner surface is in the superior part, the outside in the inferior part.

Fig. 8 (X250) shows as an example the microstructure near the inner surface of the deformed tract B (Fig. 2). The microstructure shows a ferrite matrix (clear) with reasonably equi-axial pearlite islands, with characteristic banding. There is no evidence of aligned nonmetallic inclusions. No relevant or unusual surface conditions were observed, except for a slight reduction of pearlite and de-carburization in the outer surface, probably due to the action of fire.

Grain size is relatively large. Sliding bands are seen throughout the thickness, preferentially circumferential in the collector pipe, which are associated with particular lattice directions. These bands are indicative of plastic deformations. The pearlite grains have straight faces and acute angles, also typical in plastically deformed microstructures. Impurity (P, S) contents are low.

Chemical and tensile test results are included in Table 1. Mechanical and chemical parameters indicate that deformed pipe tracts fulfill the requirements for an API 5L X52 steel, and could even be classified as X56.

Fig. 8. (X250) microstructure near inner surface of deformed tract B (Fig. 2).

Table 1
Chemical and tensile test results for collector pipe base material (deformed pipe tracts)

Sample	Elongation (%)	Section reduc. (%)	YS (MPa)	UTS (MPa)
#1	22	46	408	517

Elements (% m/m)

C	Si	Mn	P	S	Cr	Ni	Mo
0.20	0.21	0.56	0.014	0.010	0.05	0.03	0.02

3. Mechanical models: maximum pressure reached

Normal operation loads on the critical points of the tube and flange previous to the leak are due to pressure and piping support conditions. To model the plastic deformations undergone by the collector pipe and the flange requires analyzing the displacements and loads generated during failure, that is, a limit load analysis. The elastic plastic behavior of the model should be modeled using the true stress – true strain tensile properties of the material. As the material has little work hardening capacity, we can consider an elastic – perfectly plastic behavior.

Relatively small plastic deformations allow using the principle of invariability of initial dimensions. This is done here as a first approach, and then it is verified if elastic and plastic deformations are of the same order.

During plastic bending of the flat plate at the end flange the neutral plane is approximately at mid thickness. To find the maximum pressure underwent by the plate. it is modeled a circular plate of diameter d and thickness h, subjected to a uniform pressure in its surface, see Fig. 9, supported in its perimeter. Its solution is well known, given for instance in Table 19.1 of Ref. [1]. If simply supported, radial (S_r) and tangential (S_t) components of the stress state at the center of the plate are

$$S_r = S_t = -\frac{3W}{8\pi m t^2}(3m+1) \tag{1}$$

where W is total transversal load (pressure times section), $m = 3$ ($1/v$, inverse of Poisson coefficient), and a and t are diameter and thickness, respectively. Considering fully supported edges, stresses are 1/3 of the previous ones. The sum of diameters of all bolts is less than half the perimeter of flange plate, therefore, their bending rigidity is much smaller than the rigidity of the plate. It is reasonable therefore to neglect the rigidity of the bolts, and consider the simply supported case (Eq. (1)). The maximum principal stresses at the center of the plate are $S_r = S_t = 0.398W/T$. Then, the Von Mises equivalent stress S_{VM} is

$$S_{VM} = S_r[1/2\{(1-1)^2 + (1-0)^2 + (1-0)^2\}]^{1/2} = S_r \tag{2}$$

When the plate begins to yield this stress is equal to the yield stress S_{and}, of the steel, this is, 408 MPa. The plate underwent important plastic deformations, thus its resistance to deformation is better represented by the flow stress, if taken as the average between yield and ultimate stresses, S_y and UTS, this is about 462 MPa. Then, the pressure necessary to deform the flange plate is

$$p = 37.5 \text{ MPa}$$

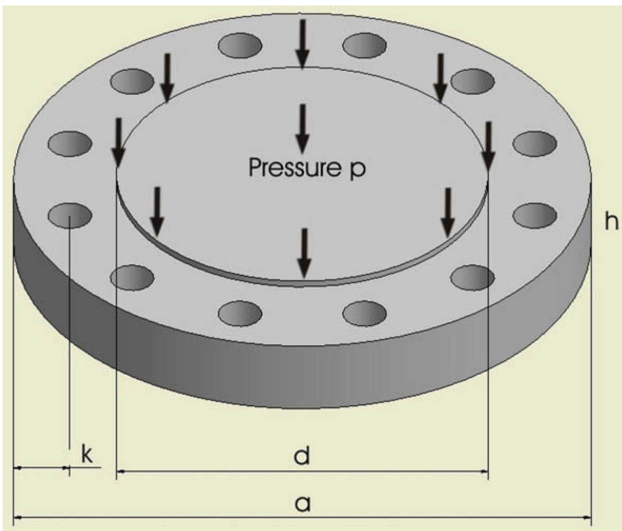

Fig. 9. End flange as a circular plate supported in its perimeter, subjected to uniform pressure.

The material of the collector pipe was subjected to a plane state of circumferential and longitudinal principal stresses S_C and S_L, easily calculated with Barlow's equation and the condition $S_L = 0.5S_C$. S_{VM} in elastic conditions is

$$S_{VM} = \{1/2[S_L^2 + S_{CL}^2 + (S_C - S_L)^2]\}^{1/2}$$

The yield condition $S_{VM} = S_y$ is reached when

$$Sc = S_{VM}/0.87 = 531 \text{ MPa},$$

For which an inner pressure p is required:

$$p = 43 \text{ MPa}$$

Both calculations agree remarkably; the internal pressure reached in the section of the collector pipe during the event that triggered the failure was of the order of 40 MPa, that is, around 400 bar. This pressure is 10 times the normal operating pressure.

4. Models for deflagration, detonation and self-ignition

The high pressure required can be reached by a phenomenon of internal deflagration followed by gas detonation. The minimum energy for detonation depends on the concentration and the type of fuel. When a combustible cloud ignites, the flame can propagate in two different ways through the inflammable parts of the cloud. The most common is deflagration, which propagates at a subsonic velocity relative to the non-burning gas [2]. The pressure attainable depends on flame speed. In confined conditions a high speed of flame is not a requirement for generation of high pressure. Considering the well-known laws of gases, the temperature increase and the chemical reaction involved in this combustion, a pressure increase factor of 8 is attainable in a situation of confinement at constant volume. Whereas in a situation of constant pressure, the gaseous cloud can reach a volume 8 times larger than the original one.

The pressure in combustion at constant volume is not the maximum attainable pressure in a gas explosion. Dynamic effects such as a pre-compression can cause much higher local explosion pressures. The energy released in the initial part of the explosion can pre-compress the gas still not burned, which allows pressure to surpass the attainable value from the original pressure [2]. A deflagration propagating in a collector pipe leads to the situation shown in Fig. 10.

A detonation is defined as a wave of supersonic combustion. The gas in the front of the wave stays without disturbances. The speed of detonation is typically 1500–2000 m/s. The transition of deflagration to detonation depends upon geometry and combustible mixture. When the deflagration becomes sufficiently intense, a sudden transition to detonation can happen. In a long pipe, the pressure generated by the flame can propagate far from the combustion front. If pipe ends are open, a high speed flame is required to generate an explosion [2].

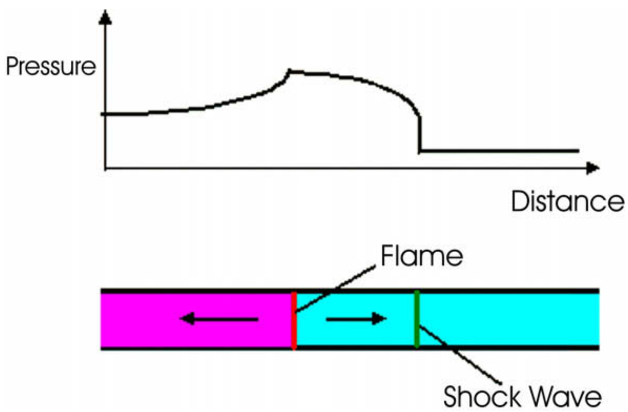

Fig. 10. Deflagration propagating in a collector pipe.

Turbulence is the main mechanism by which the flame is accelerated in collector pipes. When the gas is burned, it expands and pushes the gas without burning ahead of the flame front. The flow in the front can cause a boundary layer of increasing turbulent flow and this way the turbulence can reach burn speed. Experiments in literature [2] show the importance of edge conditions in a collector pipe (Fig. 11).

Transition from deflagration to detonation is characterized by very high local pressures, up to 50 times the initial pressure. In accidents, great damage can be observed in the place of transition. When detonation propagates the so called CJ (Chapman–Jouguet) condition develops, with smaller pressures than the maximum just defined [3], see Fig. 12.

The distance from ignition to transition to detonation in pipes is an experimental value, which is related to the probability of detonation. This distance increases when the collector diameter. In smaller pipes the layer of turbulent flow in front of the flame fills a relatively larger portion of the tube than in the larger collector pipes. This distance decreases when increasing initial pressure, diminishing temperature and increasing turbulence (due to obstructions). Tests in stoichiometric methane–air mixtures with circular obstructions show that the transition to detonation of flames initiated with a weak ignition source can occur in less than 10 m [3].

The mechanisms of transition to detonation are not yet completely understood. Fuel concentration is also an important factor. After the detonation front the combustion products expand and pressure drops, see Fig. 13. Pressure drop depends on edge conditions. The expansion of combustion products forms a propagating blast wave in the tube.

The failure analysis is at this stage centered in three basic events:

1. formation of a combustible mixture,
2. ignition of this mixture, and
3. propagation of the flame with the consequent rise in pressure.

In-field inspection results to support the hypotheses are:

1. There were two zones of highest deformation:
   - Pipe tract in the 8 in. collector line between the discharge tee from filter and the end flange.
   - Collector pipe between the discharge tee from filter and the by-pass tee.

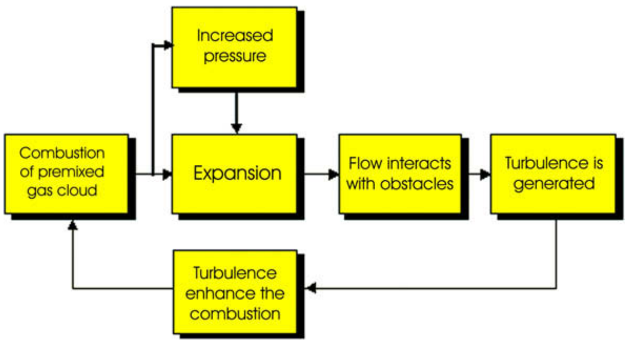

Fig. 11. Transition from deflagration to detonation in a collector pipe.

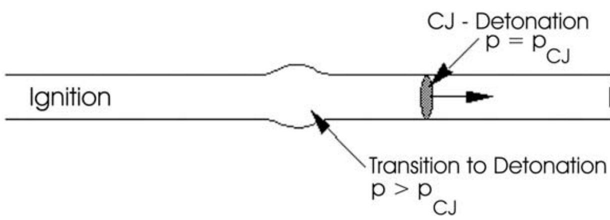

Fig. 12. High local pressures in transition from deflagration to detonation, Chapman–Jouguet condition.

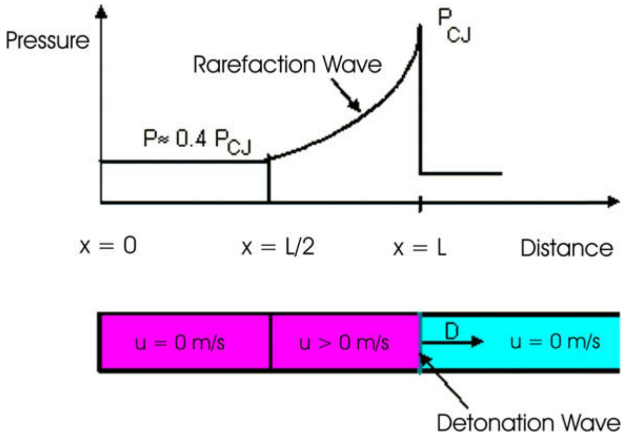

Fig. 13. Expansion of combustion products and detonation front.

2. Leak in the end flange plate and generalized burning on the outer surface of the pipe.

Flammability limits of methane volume concentration are 5–15%. The re-pressurization carried out without having vented the air introduced in the line during maintenance made it possible for a fuel–air mixture to cause an internal explosion. The minimum ignition energy for this mixture is between 0.3 and 2 mJ [2].

No evidence of possible friction of hard elements inside the pipe against the walls was found, but pieces of glass fiber and wool from insulating material were found inside the pipe. A spark from static charges accumulated in fibrous materials involves an energy between 0.5 and 20 mJ, One or several static discharges between these materials and the metallic filter (which did not have earthing) were the most probable source for ignition. Note however that ignition did not take place in the analyzed sections of pipe, so an ignition generated by a spark from some kind of impact of a hard body against the walls or some element of the filter cannot be completely discarded.

Local deformations and corresponding pressures agree with a deflagration with a transition to detonation in the zone adjacent to the filter discharge Tee. Line pressure at the time of the event was 36 bar, so local transition to detonation need only lead to a 10 times increases of pressure, 5 times less than maximum possible. Some important conclusions for the analysis:

- The low energy ignition caused by a spark due to static charge or friction only allow initial deflagration.
- The ignition site was located several meters away from the plastically deformed zone, which is the place of transition to detonation.

The "pressure pile up" effect considers two comparable volumes joined by a pipe, see Fig. 14. In our case, these are the filter and the portion of pipe from the Tee. With this configuration, different tests demonstrate that when ignition takes place within one of the volumes, pressure increase in the second volume is much larger than expected for an explosion at constant volume. When the flame enters volume 2, it does it as a "Jet" into the non-burning, pre-compressed gas mixture. The pressure developed in the deflagrations depends on pressure and on the speed of the flame front. The configuration at the failed collector does not allow the total development of the phenomenon, but does allow for an increase of pressure in the zone of the filter discharge Tee.

These conclusions allow discarding the hypothesis of leak in the end flange and subsequent outer gas ignition. An increase of internal pressure could be caused by the flame re-entering the pipe, In this case, gas pressure inside the line should have been atmospheric pressure, and in such case the maximum pressure in the transition to detonation would have been less than 50 bar, clearly not enough to produce plasticity.

The dynamics of the filling procedure is now analyzed to evaluate the possibility for self-ignition. When a gas is compressed at a high rate in an adiabatic compression, the temperature of the system is increased quickly. According to the first law of thermodynamics, the expression of Poisson is

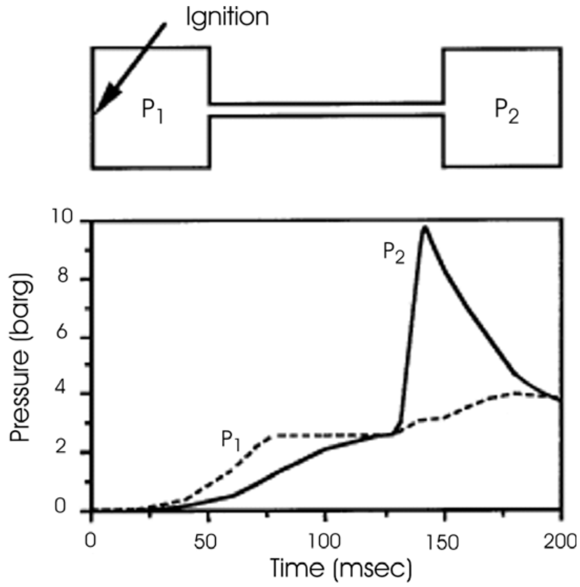

Fig. 14. Pressure pile up effect in two comparable volumes joined by a pipe.

$$T = T_0\left(\frac{p}{p_0}\right)^{R/\mathrm{Cp}} \tag{3}$$

where R is the universal constant of gases and Cp the heat capacity of the gas. The temperature for spontaneous combustion (AIT) varies with pressure increase, following a hyperbolic curve characteristic for each fuel. The octane value for methane mixtures vary between 120 and 130 [4]. The compression ratio necessary for self-ignition is then 38:1. At this pressure, Poisson expression defines the reached temperature. Using a Cp according to the rule of the mixtures and considering a 10% methane in air,

$$\mathrm{Cp}_{\text{it mixes}} = \mathrm{Cp}_{\text{air}} \cdot X_{\text{air}} + \mathrm{Cp}_{\text{methane}} \cdot X_{\text{methane}} \rightarrow \mathrm{Cp}_{\text{it mixes}} = 1122j\ (\text{kg K}) \quad R = 287j\ (\text{kg K})$$

An adiabatic increase of pressure from 1 to 38 bar at an initial temperature of 40 °C would elevate the temperature of the gas to 520 °C. This temperature is near the AIT of the mixture, which would allow self-ignition. The AIT of the mixture at 1 bar is 537 °C, and decreases with pressure, making self-ignition more likely.

Pressure having been stabilized at 36 bar, the line not having a needle valve, the filling rate could have been quite high. Under these circumstances it is possible that during filling much higher local pressures could have been reached, at rates sufficiently elevated to be considered adiabatic. Therefore, it is not possible to discard this possibility of self-ignition, especially if the gas has traces of heavier hydrocarbons that could have contributed to lower the AIT.

5. Discussion of results

The series of events validated by the models previously discussed is as follows:

- Re-pressurization of the pipe without venting formed an inflammable mixture within the line.
- Sparks generated by static discharge fibrous material or the impact of some hard piece within the filter, or the temperature reached during pressurization, caused ignition and deflagration.
- This deflagration was accelerated when entering the between the filter and the discharge Tee. The overpressure wave traveled in the mixture at speed of sound, whereas the flame travelled more slowly.
- When deflagration reached the Tee a transition to detonation took place. This was due to a layer of turbulent flow of mixture without burning.

- The overpressure due to the deflagration that approached the zone of transition could have generated the leak in the end flange and in the manometer joint. The venting effect generated by these leaks could have generated a flow acceleration, contributing this way with mixture turbulence and therefore accelerating deflagration, and eventually allowing the transition to detonation.
- These leaks justify flow acceleration in that zone of the line. The preexistence of these leaks, is not essential, although otherwise the confinement of the gaseous mixture could have restrained the propagation. This way the transition of deflagration to detonation produced a severe damage in the pipe and the complete rupture of the seal the end flange and the manometer.
- Detonation continued until total combustion of the mixture, at a pressure CJ, much smaller than the developed during transition.
- Continuing fuel intake, now outside a rank of flammable concentrations, allowed a persistent fire in the outside of the pipe. This generated the degradation of the outer coating and the oxidation of the metal.
- Deflagration advanced towards the suction pipe of the filter without developing turbulent flow, thus no transition to detonation occurred, until fuel exhausted and propagation extinguished.

6. Conclusions

This study allowed identifying the origin of the failure, ant to discard other alternative hypotheses. The cause of the explosion and fire was an internal explosion produced in the 8 in. collector line. Deformations were caused by an increase in internal pressure due to gas detonation, which surpassed 400 bar, more than 10 times the normal operating pressure. Probably the first leak in the flange and the loss of the manometer at its threaded joint occurred at a smaller pressure, around 150 bar, during the deflagration stage.

This study also allowed discarding a possible ignition of leaking gas in the atmosphere. The maximum attainable pressure in this case is only 50 bar, far below the necessary pressure to produce the deformation seen in the collector pipe, end flange and bolts. The material of the collector pipe comfortably fulfills the requirements for an API 5L X52 steel. No previous manufacturing or service defects in the deformed end flange, bolts and collector tube were found.

The main causes and events that led to the explosion and fire are:

1. When mounting the trap valves air entered the gas pipeline, which was not vented when re-pressurizing the line.
2. No bleeding was made in the dust filter, nor was the filling volume and rate regulated, due to the lack of elements.
3. A spark inside the tubes, possible due to friction of fiber glass debris or impact of some element of the filter could have produced the ignition of the gas–air mixture. Probably these elements were not introduced during the replacement of the valves, but rather were there much before.
4. The high rate of pressurization limited the temperature exchange, leading to an almost adiabatic condition, in which the air contained in the pipe could have reached temperatures above 500 °C, enough to justify self-ignition of.

The analysis concluded that the explosion and fire in the plant was due to an important amount of air that got into the pipes, when mounting valves at the pig traps. Venting in the receiving trap was not made while the line was filled and pressurized; neither was bleeding in the dust filter. The filling volume was not regulated due to the lack of elements, with which the rate of filling was likely high. In order to reduce the probability of recurrence of the event, the procedure for the filling and the pressurization of the pipeline was redesigned, safety features added, and personnel trained. Recommendations include:

(1) Follow a strict operative procedure for filling and pressurization.
(2) Within the procedure, enforce the need to inject an inert agent such as nitrogen and a water interphase.
(3) Install adequate valves and a connection for the injections.
(4) Review the procedure and the Roll of Emergencies.

(5) Improve electrical earthings (resistivity of soil) for all the elements of the plant.
(6) Enforce procedures in all sectors, train personnel.

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