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Occurrence of pyrophoric iron immune to chemical washing in vacuum distillation columns

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A R T I C L E I N F O

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A B S T R A C T

Pyrophoric iron deposits on vacuum distillation column internals can become immune to water and chemical washing, by coating with asphaltenes entrained in the flash zone vapors. This hypothesis was confirmed by obtaining and inspecting samples of a vacuum distillation column mist eliminator on which pyrophoric iron ignitions were observed that were not affected by the conventional washing procedures. Three conditions are highlighted whose fulfillment significantly increases the probability of persistent pyrophoric iron occurrence on vacuum distillation column internals. A handling strategy is outlined which was based on the experience gained from the described incident.

1. Introduction

Vacuum distillation of straight run fuel oil is the method for obtaining vacuum gas oils which can be used as feed for FCC (Fluid Catalytic Cracking), Hydrocracker or Lubricant production units. Pyrophoric iron i.e. iron sulfide deposits on the vacuum distillation column internals is a usual phenomenon for this process. Under the operating conditions of the distillation column, the sulfur contained in the feed, can combine with the iron of the equipment creating a fine layer of iron sulfides on the metal surfaces.

The sulfides remain attached on the metal walls of the equipment, as long as it remains in operation. During shutdowns, when the equipment is neutralized and opened to the atmosphere, the sulfides oxidize quickly to iron oxides. The oxidation reactions are significantly exothermic, (Walker, 1988) and they can cause ignition of other, hydrocarbon containing deposits, (Davie, Mores, Nolan, & Hoban, 1993a) or even of the internals themselves. Thin (0.1–0.2 mm) parts of metal structured packing can ignite, heating the equipment to temperatures close to 1500 °C, (Ender & Laird, 2003), (Roberts, Rogers, Mannan, & Ostrowski, 2003). In such cases, damage to the distillation column or even its collapse is possible, (Mannan, 2003).

Pyrophoric iron is not the only contaminant deposited on vacuum tower internals after some years of operation. Petroleum coke and bituminous matter are also usually present in amounts far greater than those of iron sulfide. Moreover, considerable amounts of liquid hydrocarbons adhere to the internals. The high temperature of a possible pyrophoric iron ignition can provide an ignition source for all these combustible materials. The consequences of such an incident can vary from minor falling behind maintenance schedule, to major vessel walls damage or even collapse, (Kister, 2006; Mannan, 2003; Woodward & Ketchum, 2001).

Various strategies are used by the refineries to remove the pyrophoric sulfide deposits prior to opening the vacuum distillation columns. However, sometimes the pyrophoric deposits are persistent even to proven methods, like $KMnO_4$ solution washing. There can be various reasons for the immunity of the sulfide deposits to chemical washing, like washing procedure errors, plugging of distributors etc.

This paper aims to indicate coating of the pyrophoric sulfide deposits with bituminous material as an additional cause of their persistency to chemical washing. A case study is presented, where parts of the persistent pyrophoric deposit containing column internals were retrieved in good condition. The inspection of those internals led to the conclusion that their chemical washing had failed, because the pyrophoric deposits where rendered waterproof due to bituminous matter layers enveloping them.

The following paragraph describes shortly the operation of a vacuum distillation column.

2. Theory

2.1. Vacuum distillation

In vacuum distillation units, the distillate yield depends strongly upon the flash zone pressure. In order to achieve the minimum possible pressure drop at the internals, structured and random

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packings are employed instead of trays. Moreover, due to the low absolute operating pressures, (10–30 mmHg(a)), the vapors have large specific volume. In order to keep the pressure drop of the column as low as possible, large diameters are employed.

The operating strategy of such a column is distillate maximization, LVGO (Light Vacuum Gasoil and HVGO (Heavy Vacuum Gasoil) up to the point of incipient asphaltene or/and metal entrainment in HVGO. For the de-entrainment of asphaltenes from the vapors of the flash zone, a "wash section" is provided, (Fig. 1). The wash zone contains some layers of grid. The grid is a special kind of structured packing, with wide openings, suitable for this specific use, because it does not coke – up easily. Some columns also contain at the wash section, some layers of structured packing laid over the grid, to ensure adequate asphaltene de-entrainment. The wash bed is being irrigated with a spray distributor. The wash oil comes into contact over the packing and the grid layers, with the vapors that leave the flash zone and de-entrains the contaminants. The excess of the wash oil dissolves the contaminants and is collected at a suitable trap-out tray, under the wash bed. This liquid, (slop cut), is recycled to extinction in the vacuum unit fired heater.

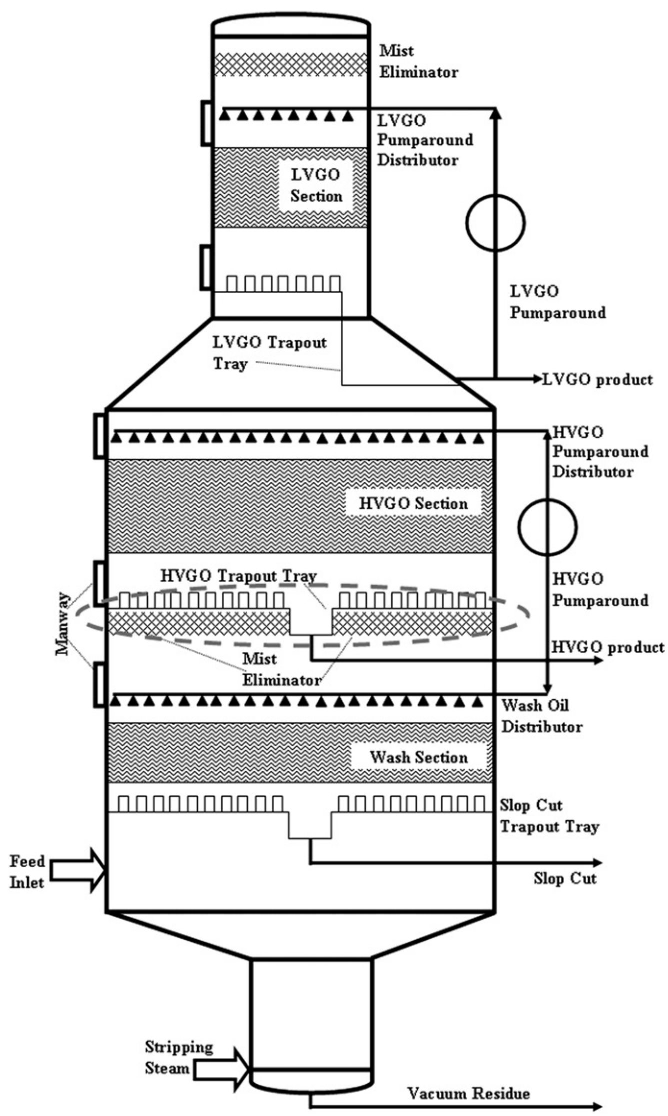

Fig. 1. Typical layout of a vacuum distillation column. The location of the mist eliminator with the persistent pyrophoric deposits is marked in gray oval.

Some distillation columns have also a mist eliminator located over the spray distributor and underneath the HVGO trap-out tray, to effect the complete de-entrainment of contaminants.

The following paragraph outlines shortly the simplified mechanism of the pyrophoric iron sulfides deposition during operation and ignition at contact with the atmospheric air.

2.2. *Pyrophoric iron occurrence and chemical washing*

The present work does not aim to elaborate on the chemical phenomena. However, a short discussion of the occurrence and the oxidation of pyrophoric iron sulfides would help the better understanding of the rest of this work.

Under the operating conditions of a vacuum distillation column, both the organic sulfur and the H_2S contained in the feed can combine with the iron of the equipment, according to the chemical reaction (1), creating a fine layer of iron (II) sulfide on the metal surfaces.

$$Fe + S \rightarrow FeS, \tag{1}$$

The compound remains attached on the metal walls of the equipment and on the internals, as long as it remains in operation. During shutdowns, when the equipment is neutralized and open to the atmosphere, the iron sulfide oxidizes quickly to iron oxide, according to chemical reaction (2).

$$4FeS + 7O_2 \rightarrow 2Fe_2O_3 + 4SO_2, \tag{2}$$

The oxidation of iron sulfide is highly exothermic. The heat of reaction can be calculated as −608.91 kJ/mol (Castellan, 1983). Other iron sulfides, such as pyrite can also be produced, (Walker, Steele, & Morgan 1987), (Li, van Santen, & Weber, 2008). Those compounds can also oxidize exothermically, (Yang Wu, & Li, 2011), (Somot and Finch, 2010). For simplicity reasons, only the chemical species of reactions (1) and (2) will be considered.

In most cases, the internal surface area of the equipment is small related to its mass, absorbing thus the heat of the reaction without much increase in the temperature. Of course in cases that the equipment has not been thoroughly steamed and flushed before opening, hydrocarbons may be absorbed or deposited upon the iron sulfide layer and they may ignite, triggered by the heat of reaction (2), (Li, Li, Zhao, Kong, & Zhai., 2005).

In order to avoid such incidents, certain procedures are usually followed after the shut down of a vacuum distillation unit and before air ingress.

- The column is steamed excessively, so as to make sure that the internals are free from all liquid hydrocarbons.
- Next, the column is thoroughly washed with ambient temperature water, in order to remove as much pyrophoric deposits as possible and in the same time to achieve a complete soaking of the internals which will prevent iron sulfide ignition for sufficient time. High flows of wash water are essential to ensure efficient soaking of all parts of the internals.
- Finally, the tower is blinded, the manholes are opened, entry permits issued and the works and inspections are carried out.

A most effective removal of pyrophoric deposits can be achieved with chemical washing (Ender & Laird, 2003), (Sahdev, 2010). This procedure calls for washing of the internals with a dilute solution of an oxidizing agent, usually 1–2% wt. solution of $KMnO_4$, after the water washing. Alternatively, $K_2Cr_2O_4$, H_2O_2 or other oxidizing agents can be utilized. The chemical oxidizes the iron sulfide according to the reaction (3). The reaction heat is absorbed by the heat capacity of wash water, raising its temperature 15–25 °C, in the short amount of time till the reaction's completion.