

INVESTIGATION OF THE FOULING MECHANISMS IN THE HEAT EXCHANGERS OF A HYDROTREATER

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ABSTRACT

The problem of fouling on heat exchanger surfaces has been one of the major unresolved problems of the hydrotreatment unit at the Homs oil refinery in Syria. In this unit, a feed stream of straight-run naphtha is preheated in a series of four heat exchangers prior to the hydrotreater. Severe fouling conditions led to an overall reduction in the performance of the unit as a result of lower temperatures at the heat exchangers outlet and increased pressure drop. An investigation of the cause or causes of this problem was called for. For this purpose, deposits from the heat exchanger surfaces were analyzed in order to identify the fouling mechanism(s). Such analysis pointed unmistakably to fouling due to polymerization in general and oxygen-initiated polymerization in particular. Various laboratory tests were also conducted on the naphtha feed stream, which provided indications of the stream's polymerization potential. Since the naphtha feed stream was drawn from blending tanks that are not very well blanketed, the naphtha must clearly be exposed to atmospheric oxygen. It was concluded that a gaseous protective layer, composed of nitrogen or refinery gas, is essential for the amelioration of the fouling conditions encountered in the heat exchangers.

I. INTRODUCTION

Despite great technical achievements in the design and manufacture of heat exchangers in the past two decades, the problem of fouling on heat exchanger surfaces remains one of the major unresolved problems in Thermal Science. The costs of fouling in heat recovery and transfer equipment is estimated at about \$5 billion per year in the United States alone [1].

Fouling is generally defined as the accumulation of unwanted materials on the surfaces of processing equipment. The two main effects of fouling are production losses and increased maintenance costs.

Fouling may be divided into six distinctively different mechanisms [1]:

1. Crystallization, usually observed in process equipment cooling towers and steam generation plants.
2. Particulate sedimentation and deposition of particles on heat exchanger surfaces.
3. Chemical reaction and polymerization leading to the formation of oil sludge, organic oxidation products, etc.
4. Coking and hydrocarbon depositions. This usually occurs at high temperatures.
5. Biological and organic material growth. This occurs in seawater, and in types of waste treatment systems.
6. Corrosion, a mechanism which is dependent on thermal resistance and surface roughness.

In general, several of these fouling mechanisms may occur at the same time and each requires a different prevention technique.

In the present work, the fouling mechanisms in the heat exchangers of the naphtha hydrotreater plant at the Homs Oil refinery were investigated. This plant is one of the most important units at the Homs Oil Refinery, with an annual capacity of 480,000 tons/yr. It is used to remove impurities such as sulphur, nitrogen, oxygen, halides and trace metal impurities that may deactivate reforming catalysts. Furthermore, the quality of the naphtha fractions is also upgraded by reducing potential gum formation as a result of the conversion of olefins and diolefins into paraffins. The process utilizes a catalyst (Hydrobon) in the presence of substantial amounts of hydrogen under high pressures (50 bars) and temperatures (320°C) (Fig. 1). The feedstock for this unit is a blend of light and heavy straight-run naphtha fractions from four different topping units. The resulting naphtha is left in a blending tank for a

sufficient period of time to allow for equilibrium conditions to be realized. A series of four heat exchangers (A, B, C and D) is used to preheat the naphtha feed [2].

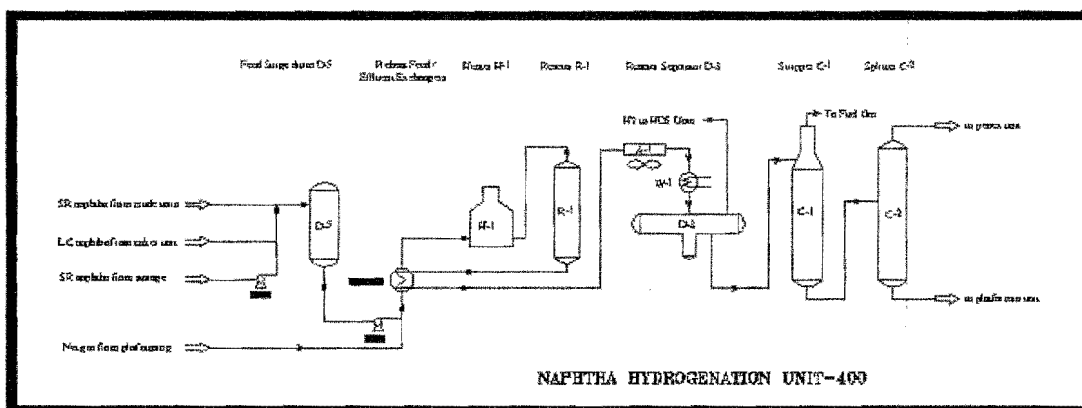


Figure 1: Naphtha Hydrotreating Unit

A major fouling problem was encountered early on in the heat exchangers used for pre-heating the unit feedstock. This was indicated by an increased pressure drop in the reactor (to about 7 bars), decreased flow rate and lower temperatures at the heat exchangers outlet. As a consequence, fuel consumption increased and the unit operation had to be interrupted at frequent intervals for cleaning and maintenance purposes.

In order to identify the main mechanisms responsible for the fouling conditions observed in the heat exchangers, the naphtha feed and deposits on heat exchanger surfaces and in the reactor were analyzed. The results of this analysis are shown in Tables 1 and 2.

II. DISCUSSION

It is apparent from the examination of the deposit analysis shown in Table 2 that most deposits are organic in nature, as the loss reported on heating the deposit samples to 840°C was greater than 80 % in both the "B" and "C" heat exchangers, where working temperatures are rather high. Since organic deposits result mainly from polymerization reactions, the high organic content observed in the deposit analysis could be taken as an indication that the fouling in these two heat exchangers is due mainly to polymerization, which could take place in the heat exchangers themselves or it could occur prior to the heat exchangers either during storage or in transport. The presence of carboxylic compounds in the deposit is also consistent with a mechanism of peroxide formation and polymerization propagation.

As is well known, polymerization reactions are often initiated by free radicals or certain transition metals. Free radical polymerization occurs when a free radical is formed and continues to react with other molecules. Such radicals are easily formed at the temperatures found in the preheat exchangers. The formation of free radicals has been investigated extensively and it is known that some compounds form free radicals more readily than others [3]. Once formed, the free radicals continue to propagate in the feed stream producing longer chain polymers. These polymers will continue to be produced as long as free radicals are being formed. Free radical polymerization is easily initiated in the presence of light and heat and its rate for polymer formation increases exponentially with temperature. A general rule is that for every 10°C increase in temperature, the rate of polymer formation doubles. Free radical polymerization, leading to the formation of organic sediments or polymers, readily takes place in storage tanks [3].

There are numerous types of free radicals which can be formed in a feed stream. These include the breaking of a double bond, or an unsaturated bond to produce an alkyl radical or other types of polymerization precursors such as nitrogen and sulphur radicals. The presence of unsaturated components in the feed stream contributes significantly to polymerization reactions, particularly at high temperatures. The significant effect of the hydrogenation process in

decreasing the content of unsaturated components is apparent from an examination of the results shown in Table 1, where the unsaturated components decreased from 0.35 to 0.09 %.

Table 1: Analysis of Naphtha Feed (Straight Run Naphtha)

Source of sample	Feedline	Blending tank	Pump dish	Storage for 6 months	Hydro-treated
Saybolt Colour	12	12	> 20	12	> 20
Gum mg/100 ml	0.7	1.0	0.5	2.2	2.0
Acidity mg KOH/g	0.004	0.008	0.009	0.026	0.015
Bromine No. g/100g	0.35	0.36	0.34	0.33	0.09
Total Sulphur (wt %)	0.070	0.050	0.042	0.035	0.00
Nitrogen mg/l	0.32	0.36	0.36	0.48	0.08
Aromatics (wt %)	9.38	9.74	8.55	9.27	0.00
Olefins (wt %)	0.35	0.26	0.42	0.31	0.00

Table 2: Analysis of Naphtha Feed Deposits

Year	1999	2000		2001				
		Heat Exchanger	Top of reactor	A	B1	B2	C	D
Loss at 105°C (wt %)	0.00			1.17	1.03	1.05	1.15	1.14
Loss at 550°C (wt %)	0.00		84.72	79.70	95.10	90.17	94.42	57.17
Loss at 840°C (wt %)	99.76	85.81	85.81	80.00	95.29	90.19	94.48	57.99
Ash (wt %)	0.04	15.19	15.19	20.00	4.71	9.81	5.52	42.01
Carbon (wt %)	0.00		19.01					
Chloride (wt %)	56.93	Trace	Trace	170	435	0	664	50800
Sulphate (ppm)	0.00		Trace	Trace	Trace	Trace	Trace	129
Sulphur (wt %)	2.58	11.00	11.00	17.00	13.50	13.80	10.20	13.00
Ammonium (ppm)	33		Trace	42	1184	43	134	4969
Iron (wt % of ash)	0.05	10.14	10.40	19.30	2.83	1.70	2.80	15.58
Sodium (ppm of ash)	138		1628	1473	1047	825	3301	914
Calcium (ppm of ash)	0		159	459	179	78	377	1431
Magnesium (ppm of ash)	31		25	90	41	19	102	1431
Chromium (ppm of ash)	851		995	231	107	1166	196	1096
Copper (ppm of ash)	0		296	511	319	74	443	126
Nickel (ppm of ash)	0		268	378	129	63	0	521
C/H ratio		19.01						

One type of free radical polymerization is that of oxygen-initiated polymerization. Oxygen reacts with a hydrocarbon to form a peroxide free radical. The free radicals increase in chain length as more hydrocarbons are attached. Air is the main oxygen source in non-blanketed storage tanks, but oxygenated compounds in the feed stream may provide another source of oxygen, which become more reactive as the feed stream is heated [3].

Metal-initiated polymerization may be considered as a special case of free radical polymerization. The metal ion has the ability to catalyze reactions by making it easier to form free radicals at lower temperatures. This occurs when a ligand is broken from a metal complex. The unshared electrons resulting from this break react with an unsaturated hydrocarbon or oxygen to form a free radical [4].

There are numerous metals which, in very low concentrations, can act as a catalyst and initiate polymerization reactions. The metals may be in the form of metal salts or metal complexes. Metal salts may themselves contribute to deposit formation or disassociate at higher temperatures to catalyze some polymerization reactions. Some of these catalytically reactive metals are iron, copper, nickel, vanadium, chromium, calcium and magnesium [3].

A further type of polymerization reactions involves a non-free radical mechanism in which the formation of a polymer is not through the formation of a free radical, but results from the reaction of two different molecules under the right conditions. One of the reactive components may be a radical or a compound from a free radical-initiated polymerization step. An example of non free radical polymerization is condensation polymerization. In this type of polymerization, two large radicals, or compounds, react together to form an even larger compound, but in their reaction also generate a smaller compound, such as water. This new larger compound can continue to react with other reactive species in the feed stream to make higher molecular weight polymers. At some point, the polymer will either get so large in size that it is no longer able to stay entrained or soluble in the fluid stream and deposit, or all the different compounds that can react with it are consumed, and no further polymer is formed [3].

Analysis of the naphtha feed indicates the presence of many species that may cause fouling. Although straight run naphtha does not in general contain enough unsaturated compounds to generate a serious fouling problem, this may well happen with certain types of feedstock. There are several tests which can be used to determine if certain organic precursors, which are known to contribute to polymerization mechanisms, are in the feed. The bromine number is one such test in which the degree of unsaturation in a feed stream is measured. The unsaturated bonds react with bromine, and the amount of bromine reacted is an indication of the degree of unsaturation [4]. The more unsaturated a feed is, the greater its potential to form polymers by oxidative or free radical polymerization mechanisms. It is apparent from Table 1 that the olefins content as measured by the bromine number of the naphtha feed is rather low (less than 0.5%), and no significant changes are to be observed in their values even after storing the naphtha for a period of six months. This could indicate that the polymerization reactions are not, in the main, initiated by the presence of unsaturated compounds in the feed.

Apart from the hydrocarbon compounds, of which naphtha is primarily composed, the presence and concentration of trace elements such as sulphur, nitrogen and oxygen can significantly contribute to a stream's fouling potential. Organic sulphur, nitrogen and oxygen compounds increase the potential for various polymerization reactions, depending on the form in which they exist. The basic nitrogen test determines the amount of basic compounds in a sample, such as amines, which are organic bases. This method can, however, overestimate the basic nitrogen content which can react with other compounds or with themselves to form polymers by several different polymerization mechanisms. The presence of sulphur in the feed may contribute to the activation of polymerization reactions. Additional polymerization precursors that can be analyzed for and should be taken into consideration include carbonyls, mercaptans, and pyrrole nitrogen. All of these compounds are known to contribute to free radical and non-free radical (condensation) polymerization mechanisms. In the present case neither the sulphur content (less than 0.1%) nor the nitrogen content (less than 0.5%) are high enough to contribute significantly to polymerization reactions Table 1.

Analysis for metals in the hydrotreater feed samples does indicate the presence of individual metals in the stream (Table 2). Although, some of these metals may only be found in very low concentrations, this may be sufficient for catalyzing different polymerization mechanisms.

The potential for polymerization increases significantly, when naphtha is routed through intermediate blending tanks, even with good blanketing and reduced oxygen presence. This is because of the increase of residence time, which allows free radicals generation reactions to progress even if the reaction rate is slow. With long reaction times some reactions are bound to take place.

When blanketing is not efficient, and oxygen can find its way to contaminate naphtha, the potential for polymerization is definitely increased. This is a two steps process. First, oxygen reacts with some molecule to generate a peroxide, a step occurring in the tank. Second, when heat is applied as in the pre-heat exchangers, peroxides start fast polymerization reactions, leading to the formation of the polymers that eventually deposit on hot surfaces of the heat exchangers [5]. A similar effect may also result from increased transfer time and exposure to oxygen.

As can be seen from Table (1), the nitrogen content of the naphtha feed increased during storage from 0.36 to 0.48 mg/l, a fact which indicates air leakage into the tank. It is to be expected that an improved blanket layer could reduce significantly this effect. Since nitrogen is not available in the refinery in a sufficient quantity, fuel gas is used instead for blanketing the storage tanks.

The potential gum test is a method of determining a sample's oxidative polymerization potential. This test provides a very good indicator of whether or not oxygen contamination will increase the fouling potential of the fluid. The gum content in the naphtha feed after storage for six months increased from 0.7 to 2.2 mg/100 ml. Similarly, the gum content for the hydrotreated naphtha increased on storage as can be clearly seen from Table 1. This also points to insufficient blanketing of the storage tank.

The neutralization number, or acid number, is an indication of fouling tendency, where the more acidic the feed stream, the greater is its tendency to foul. This is most likely due to the fact that acidic compounds can promote free radical polymerization by initiating free radicals through the formation of a positive ion or cation. The acidity in the naphtha after storage increased from 0.0035 to 0.026 mg KOH/g.

All these observations tend to confirm that storing the naphtha feed for longer periods of time is a major cause of polymerization reactions, and hence of fouling in the heat exchangers under study. This was demonstrated in fact when the naphtha feed was taken directly from the topping unit bypassing thereby the blending tanks. A dramatic decrease in the organic content of the deposits was immediately observed, indicating decreased polymerization activity, along with a corresponding improvement of the fouling situation in the heat exchangers (Table 3).

Table 3: Analysis of Naphtha Feed Deposits when the Naphtha was taken directly to the Heat Exchangers without Prior Storage

	B1	B2	C1	C2	D1	Top of reactor
Loss at 105°C (wt %)	5.55	1.12	2.63	2.49	1.59	0.10
Loss at 550°C (wt %)	55.48	40.60	44.00	44.34	38.17	20.05
Loss at 840°C (wt %)	68.19	40.76	45.16	55.34	40.36	20.07
Ash (wt %)	31.81	59.24	54.14	55.34	59.64	79.30
Carbon (wt %)	8.85	11.48	9.65	18.80	1.30	11.12
Chloride (wt %)	0.31	0.10	0.84	0.65	0.71	305
Sulphur (wt %)	21.33	24.43	27.90	24.10	45.04	25.28
Ammonium (ppm)						963
Iron (wt % of ash)	23.31	43.85	28.53	36.00	37.15	50.14
Sodium (ppm of ash)	6342	2080	1247	533	413	516
Calcium (ppm of ash)	935	660	182	86	120	0
Magnesium (ppm of ash)	608	408	176	89	121	0
Chromium (ppm of ash)	3366	5644	1147	1065	2049	
Copper (ppm of ash)	2525	1970	967	664	496	
Nickel (ppm of ash)	1772	977	345	224	369	

Similar arguments to the above apply in the case of the "A" heat exchanger, where polymerization may account for about 80% of the total fouling associated with it. Further, fouling by corrosion may not be negligible, with about 19% of the total fouling may be due to corrosion, as is clearly indicated by the iron content of the deposits obtained from the A heat exchanger (Table 2). Polymerization, however, could not be the sole mechanism responsible for fouling in the "D" heat exchanger, where fouling by polymerization accounts for no more than about 50%. Some other mechanism must no doubt contribute a not insignificant part to the overall fouling situation. Examination of the data points unmistakably to particulate fouling as the second major contributor to fouling in this particular heat exchanger.

III. CONCLUSION

In conclusion it can be said that the amelioration of the fouling conditions observed in the heat exchangers under study can to a considerable extent be reduced by dispensing with naphtha storage and taking the feed directly from the topping unit. Where this is not feasible or possible, better blanketing conditions for the storage tanks are essential, where a gaseous protective layer, composed of nitrogen or refinery gas, may be used to the best advantage.

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