

# DEPOSIT FORMATION IN HEAT EXCHANGER FROM COAL DERIVED NAPHTHA

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## INTRODUCTION

Coal derived naphthas have been observed to produce deposits in hydrotreaters, heat exchangers, heaters, and reactor inlets which operate at approximately 400°C. These deposits are black in appearance and cause plugging of the reactor components. This results in a shutting down of the system. Such downtime is expensive due to both production losses and repair costs. If causes for deposit formation can be identified and a probable mechanism found, it should be possible to decrease or eliminate this expensive reactor downtime.

There are two main objectives for this study. 1) Determine what classes of compounds are responsible for deposit formation. This involves concentrating various classes of compounds by both distillation and chromatographic means and developing a way to indicate their potential for deposit formation. 2) Indicate a possible mechanism for deposit formation. This includes an examination of the deposit and the identification of secondary products of deposit formation.

## EXAMINATION OF DEPOSIT

A deposit was formed in a pilot plant heat exchanger from a coal derived naphtha. The heat exchanger was run at approximately 400°C in an atmosphere consisting of vaporized naphtha and hydrogen. The formation of the deposit had resulted in shutting down the pilot plant. It was estimated that 10g of deposit was formed from 50 gallons of full range (66-204°C) naphtha. Therefore, only 0.006% of the original material was involved in deposit formation.

The deposit was drilled out of the plugged heat exchanger. It was insoluble in pentane, dichloromethane, chloroform, methanol, dimethyl sulfoxide, and pyridine. The elemental analysis of the deposit is given in Table 1, along with that of a typical naphtha feed. These analyses were performed by Micro-Analysis of Wilmington, Delaware.

The N/C ratio in the deposit relative to the feed increased by a factor of 15.0 while that of S/C and O/C increased by 9.9 and 1.8, respectively. Therefore, the nitrogen and sulfur compounds were heavily involved in deposit formation. The S/N ratio of the deposit was 0.11.

This indicates that the deposit was not comprised predominantly of ammonium polysulfides. These polysulfides have been observed as deposit materials in hydrotreatment runs.

The fact that the O/C ratio only increased by a factor of 1.8 partially rules out an oxidative mechanism. The increase in oxygen could have been due to a small amount of oxidation which occurred after the deposit was collected. No precautions were taken at the time of collection to blanket it with nitrogen, and the deposit was several months old at the time of analysis.

#### CONCENTRATION OF DEPOSIT PRECURSORS

Coal liquid naphtha is a complex mixture. In order to identify the deposit precursors, they had to be concentrated. A combination of distillation and ion exchange chromatography was used to do this. The effect of these two concentration techniques was tested using TGA. From these experiments it was possible to identify the structural types responsible for much of the deposit formation.

The TGA experiment used to test concentrates for deposit formation consisted of heating the sample in a platinum boat from 25°C to 400°C, under nitrogen, at 20°/min. At 400°C the weight was recorded and the atmosphere switched to oxygen. The temperature was then increased to 700°C, and the material in the pan was burned off. This latter step allowed the tare of the balance to be checked.

It was determined that the residue remaining in the pan at 400°C was insoluble in common organic solvents. Herein, the insoluble residue is designated as "deposit."

It was shown in the pilot plant that the 177-204°C naphtha produced more deposit than the full range (66-204°C) naphtha. Therefore, various distillate cuts of the 177-204°C sample were prepared and tested for deposit formation. From these experiments it was found that the bottom 40% of the 177-204°C naphtha contained essentially all of the deposit precursors. The bottom 40% of the naphtha was used in the remainder of the experiments. It formed 1.73+ .04 Wt.% deposit on heating to 400°C.

Because of the large amount of nitrogen seen in the deposit, the nitrogen containing compounds were concentrated on an ion exchange resin. Basic nitrogen compounds such as quinolines, pyridines and amines have been reported to be removed by Amberlyst-15 ion exchange resin. (2,3) The resin was prepared as described elsewhere (3) and it was used to remove the basic nitrogen compounds. It was ultimately decided that a ratio of 2.3:1:resin:bottom 40% was needed to lower the basic nitrogen content from 1.4% to 88 ppm, as determined by nonaqueous titration. This was the lowest basic nitrogen level that could be achieved.

While it was not possible to get the basic nitrogen content below 88 ppm, the deposit formation from the sample of ion exchange treated effluent was reduced to 34.7% of its original level. The correlation between deposit formation as measured by TGA and basic nitrogen level is shown in Table 3.

The material retained by the Amberlyst-15 ion exchange resin was desorbed by a solution of ammonia saturated methanol. The methanol was stripped off at 50°C under a stream of nitrogen. The resultant material was called the basic nitrogen concentrate. Examination of this material by <sup>13</sup>C NMR showed it to contain nitrogen heterocycles, such as pyridines and quinolines, and phenols. When heated to 400°C, the basic nitrogen concentrate gave 4.95% deposit as compared with 0.60% deposit from the effluent from the ion exchange resin. The weighted sum of the amounts of deposit from the basic nitrogen concentrate and that of the base-free material was 1.74%, which compares well with 1.73% deposit in the unseparated material. This indicates that there is no interaction between the basic and base-free material. The basic nitrogen concentrate was used in the remainder of this work.

The elemental analysis of the basic nitrogen concentrate, base-free material and bottom 40% of the 177-204°C naphtha is shown in Table 2. While the Amberlyst-15 concentrated the basic nitrogen compounds, it also carried along a large amount of oxygen in the basic nitrogen concentrate. An examination of the material boiling above 200°C by both <sup>13</sup>C NMR and Mass Spectrometry showed no evidence for molecules containing both basic and phenolic functionalities on the same molecule. It was not possible to completely separate this residual oxygen by caustic extraction.

#### EFFECT OF HEATING ON STRUCTURE

In order to arrive at an understanding of the mechanism of deposit formation, the effect of heating on the structure of the basic nitrogen concentrate was observed using FT-IR. Due to small amounts of deposit (~1-5mg) formed in the TGA pan, the use of other analytical techniques was not possible.

Samples were prepared by heating the basic nitrogen concentrate in the TGA at 400°C for a desired length of time. The deposit was recovered from the pan by soaking the pan with its contents in methylene chloride and evaporating the methylene chloride under nitrogen. (4) The deposit was then made into KBr pellets as described previously. Spectra were run on a Digilab 15B FTS System. Two hundred co-added interferograms at 2cm<sup>-1</sup> resolution were taken for each sample.

Visual observation of the spectra showed changes in aromatic C-H, aliphatic C-H and hydroxyl bands at 3000-3100cm<sup>-1</sup>, 2820-3000cm<sup>-1</sup>, and 3100-3600cm<sup>-1</sup>, respectively. These three bands were curve resolved and integrated using the methods of Painter, et al. (4) The integrated intensities for the three regions were plotted against heating time at 400°C and are shown in Figure 1. Substantial decreases were seen in all three of these regions with increased sample heating time.

#### MECHANISTIC CONSIDERATIONS

The decreases in aromatic C-H, aliphatic C-H, and hydroxyl bands described above have substantial implications for deposit formation. The loss of aliphatic C-H indicates a pyrolysis type of reaction. An analysis by gas chromatography of the TGA gaseous effluent shows the presence of light alkanes and alkenes as would be expected from a pyrolysis reaction.

The loss of aromatic C-H indicates a cross-linking of free radicals formed during pyrolysis with the subsequent formation of higher molecular weight molecules. The addition of octahydrophenanthrene to the basic nitrogen concentrate lowered the amount of deposit formed by 52%. Presumably, this is due to the capping of free radicals formed during pyrolysis.

The loss of O-H indicates either a loss of adsorbed water or a condensation reaction with a subsequent loss of water. The amount of water formed during heating was measured by gas chromatography. The adsorbed water in the feed was also measured. The amount of water produced during heating was substantially larger than the amount of adsorbed water on a molar basis. This indicates that some deposit formation occurs through condensation (phenol coupling) reactions. Reactions like these have been shown to occur upon heating naphthol to 400°C.<sup>(5)</sup> Silylation of the phenols with BSTFA resulted in a 24% decrease in the amount of deposit formed.

#### CONCLUSIONS

The heat exchanger deposit precursors are concentrated in the basic nitrogen concentrate obtained from the naphtha bottoms. This concentrate contains both heterocyclic nitrogen compounds and phenols. The primary reactions responsible for deposit formation were: 1) condensation of phenols, and 2) pyrolysis of alkylated nitrogen heterocycles.

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TABLE 1  
ELEMENTAL ANALYSIS OF FEED AND DEPOSIT

<u>ELEMENTAL</u>	<u>FEED</u>	<u>DEPOSIT</u>
%C	83.92	73.63
%H	10.86	5.74
%O	5.14	8.22
%N	0.52	6.86
%S	0.23	1.83
%Ash	0.00	3.73
H/C	1.55	0.94

TABLE 2  
ELEMENTAL ANALYSES OF BASIC NITROGEN CONCENTRATE,  
 BASE FREE MATERIAL, AND BOTTOM 40% FRACTIONS

	<u>Bottom 40%</u>	<u>Basic Nitrogen Concentrate</u>	<u>Base Free Material</u>
% Carbon	79.67	78.25	80.30
% Hydrogen	8.44	7.95	8.94
% Nitrogen	1.54	3.54	0.14
% Oxygen	9.59	10.04	10.03
% Sulfur	0.65	0.22	0.58
H/C	1.27	1.22	1.34

TABLE 3  
EFFECT OF BASIC NITROGEN ON DEPOSIT FORMATION

<u>Basic N Content</u>	<u>Wt.% Deposit</u>
88 ppm	.60%
173 ppm	.83%
280 ppm	1.40%
1.39%	1.73%

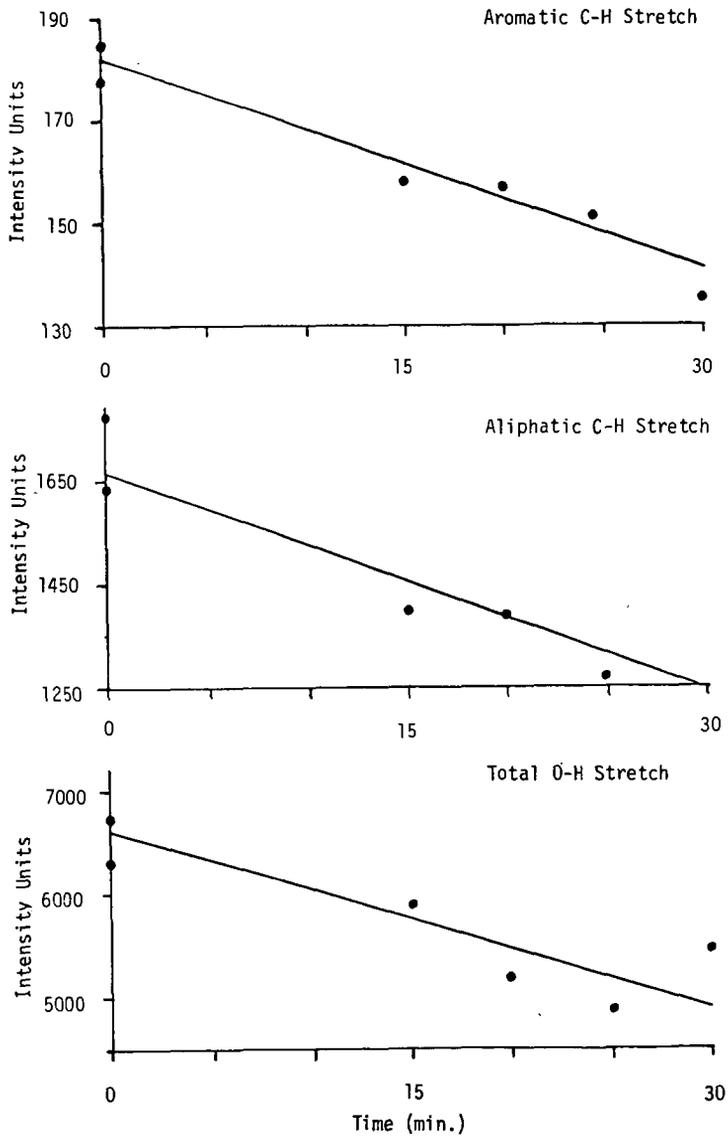


Figure 1. Integrated Intensities vs. Time at 400°C