

INSTABILITY OF MIDDLE DISTILLATE FUELS DURING STORAGE AND CHARACTERIZATION OF INSOLUBLES BY FTIR

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ABSTRACT

The problem of stability of diesel fuels has become more pronounced in recent years with the increasing use of cracked stocks in the diesel pool. These cracked products induce gum and sediment formation in fuels. In the present paper, the instability of total cycle oil (TCO) derived from FCC operation of Bombay High VGO, under accelerated and ambient storage conditions has been studied with and without additive doping. During ambient storage yield of the insolubles in TCO has been found to decrease after a period of about 18 months which may be attributed to the reformation of fresh oxidised species from insolubles. However during accelerated tests trend of increasing insoluble formation with time is revealed. The qualitative composition of insolubles obtained from ambient storage of additive doped and undoped fuels has been studied by FTIR and the role of additives on the composition of insolubles is discussed.

INTRODUCTION

Diesel fuels, particularly obtained from catalytically cracked stocks, start degradation right from production and on storage degrade to the extent that start giving application problems. The degradation mechanism and additive response depend on fuel composition, temperature, oxygen availability, static and dynamic conditions, storage time and type and size of storage vessels. In the present investigation, the instability of total cycle oil (TCO) derived from FCC stream of a refinery and doped with commercial additives has been studied under accelerated as well as ambient storage conditions. FTIR spectroscopy has been employed to explain the mechanism of additive functioning by comparing the spectra of sediments obtained under different conditions.

EXPERIMENTAL

The total cycle oil (TCO) was doped with 100 ppm of phenol (A1) and amine (A2) types additives. Various accelerated test methods viz modified ASTM D-2274, ASTM D-4625 along with ambient storage tests for 4, 8, 12, 18 and 24 months were performed on TCO as such and doped with additives. FTIR spectra of various insolubles were recorded in absorbance mode on Perkin-Elmer 1760 FTIR spectrometer by making thin films of samples on KBr plates by evaporating their dichloro methane solution.

RESULTS & DISCUSSION

The physico chemical properties of TCO determined by standard ASTM/IP test methods are reported in Table-1. The insoluble yields from TCO as such and doped with additives (TCO+A1, TCO+A2) under modified ASTM D-2274 test conditions are shown in Fig.1, while those obtained with ASTM D-4625 and ambient storage conditions are presented in Figs. 2 & 3 respectively. Typical FTIR spectra of sediments obtained after 18 months and 24 months storage of TCO as such and with additives (TCO + A1 and TCO + A2) are presented in Fig.4.

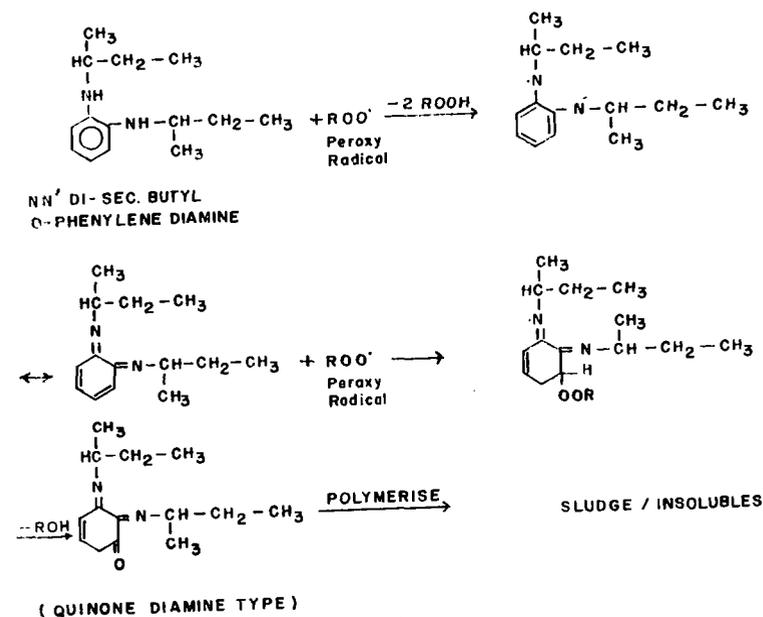
From Fig.1, it is evident that sediment yield, under accelerated test conditions (dynamic) in the presence of oxygen is reduced significantly after doping with additives due to better additive fuel interaction under these conditions. This reduction is more pronounced in case of amine type additive as compared to phenol type. But in case of

static conditions (ASTM D-4625) as the oxygen availability is limited and agitation is also not there, the overall sediment formation and reduction after doping with additives are relatively small (Fig.2). In case of ambient storage (Fig.3) sediment formation is low in the beginning which increases significantly with time up to 18 months. Here also the reduction in sediment formation after doping with additive is significant. An appreciable reduction in sediments after ambient storage of 18 months in TCO as such as well as in doped with additives is observed (Fig.3). This observed pattern may be due to the formation of fresh oxidized species after 18 months storage. This has further been confirmed from the comparison of FTIR spectra of sediments from TCO, TCO+A1 and TCO+A2 after 18 and 24 months storage (Fig.4).

The appearance of two carbonyl band around 1740 and 1710 cm^{-1} (having comparable intensity) in all the sediments obtained after 24 months reveals that on longer duration, hydrolysis of ester type structures in sediments takes place forming the carboxylic and phenolic structures which are soluble in fuels. Thus the sediment yield is reduced. This is supported by the enhancement of bands at 3270 and 1600 cm^{-1} due to stretching and bending vibrations of OH groups.

FTIR spectroscopy has also been employed to explain the higher effectiveness of amine type additive compared to phenol type in inhibiting the sediment formation. The comparison of FTIR spectra of sediments from TCO, TCO+A1 and TCO+A2 after ambient storage of 18 months (Figs.4 A,B,C) reveals that while there is no appreciable qualitative variation in the spectra of TCO and TCO+A1, the spectrum from TCO+A2 (Fig.4C) is quite different in nature.

The sediment from TCO as such shows an appreciable amount of ester type carbonyl 1740 cm^{-1} (Fig.4A), while this is reduced considerably in sediment from TCO+A2 (Fig.4C). Further, the structures like quinone diamine type which forms during controlling the peroxy radicals also appears in the sediments due to sludge formation during storage. This may probably occur in sediment through polymerisation as per following mechanism of action of amine type additive².



This is also supported from the FTIR spectra of sediment from TCO+A2 (748 cm^{-1} band due to 3-adjacent protons on aromatic rings). The strong and broad absorptions at 3260 and 1600 cm^{-1} in sediment of TCO+A2 (Fig.4C) as compared to those of TCO and TCO+A1 (Figs.4 A & B) show the dominance of structures containing OH functionalities (phenolic type). Aromatic structures are confirmed by the appearance of 3052 cm^{-1} band (aromatic C-H stretching) and enhanced absorption at 1600 cm^{-1} . Thus, amine type additive is more effective in inhibiting the formation of sediment containing ester type structures during ambient storage of total cycle oil.

REFERENCES

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Table-1 Characteristics of Total Cycle Oil

Density D15	0.8821
Kinematic viscosity, at 40 °C, cSt	2.46
Pour point, °C	18
Molecular weight	177
Maleic anhydride value	5.56
Diene value	1.44
Sulphur, %wt	1.46
Nitrogen, ppm	125
Boiling range, °C (5-95% vol)	158-441

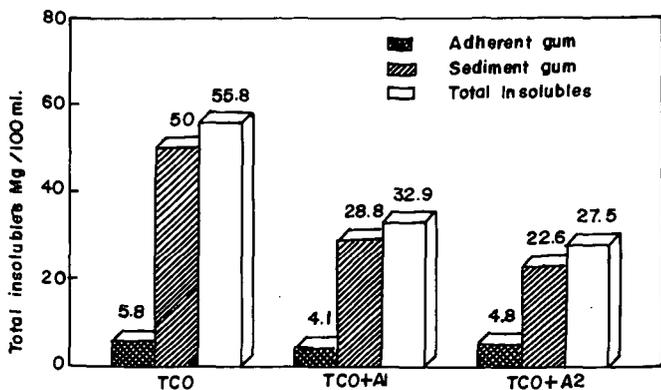


Fig. 1 : Response of Additives in TCO on stability under Modified ASTM D-2274

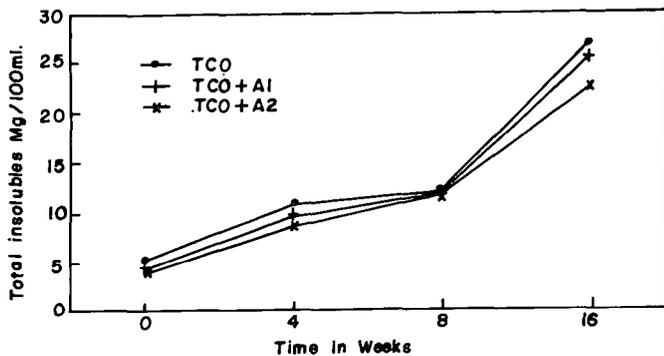


Fig. 2 : Response of Additives in TCO on long storage stability in non vented conditions at 43.3°C

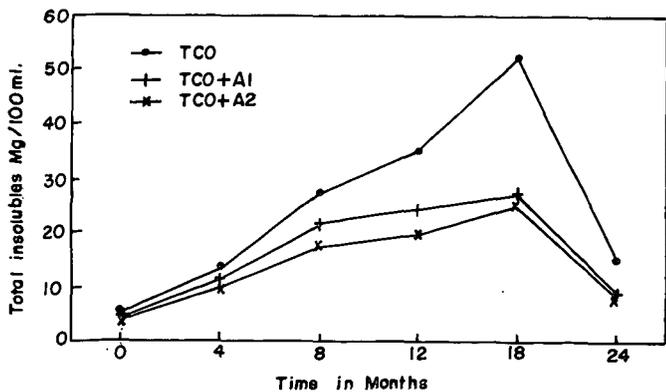


Fig. 3 : Response of Additives in TCO on Ambient storage stability.

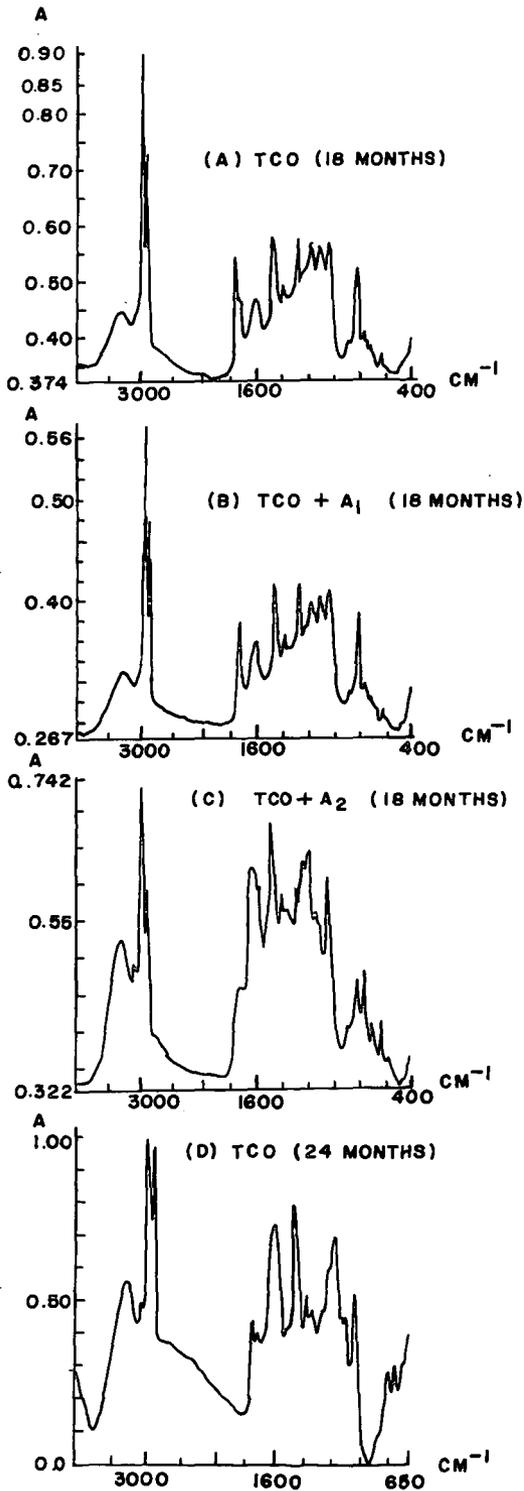


FIG. 4. FTIR SPECTRA OF SEDIMENTS