Copper Catalyzed Aging Reactions of a SRC II Middle Distillate

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INTRODUCTION

Stability of synfuels is an important consideration in direct utilization or upgrading processes. The tendency of synfuels to form gums and sediments and to increase in viscosity poses a serious detriment in handling procedures and burning efficiency. Recently, investigators have studied the aging characteristics of shale (1) and coal-derived liquids (2-5) in an attempt to identify the reactive components and to postulate mechanisms. In aging studies of a Synthoil product in an oxygen atmosphere, the viscosity increase was accompanied by a decrease in the content of oil components and in increase in the content of benzene-insoluble components (4). Similar results were observed in a study of a SRC I/SRC II blend aged by bubbling oxygen directly into the sample (6). These studies indicate that during oxidative degradation, the oil components 'react' to form benzene-insoluble components which are primarily responsible for the increased viscosity.

The oxidative degradation of a SRC-II middle distillate, which is an oil, free of asphaltenes and benzene-insolubles was investigated in this study. The objective was to determine the molecular types of compounds responsible for the viscosity change and postulate mechanisms. Since the middle distillate is relatively stable to oxidative degradation, copper shavings were added to accelerate the process.

EXPERIMENTAL

SRC II middle distillate (b.p. range, 170-276°C) from Illinois no. 6 coal was obtained from Gulf R&D Co., and from a process run operated at 2000 psi hydrogen pressure at 454°C for 1 hr residence time. The coal liquid was placed in a 3-necked flask, equipped with a gas bubbling inlet and a condenser to minimize the loss of volatiles. Oxygen was bubbled through the sample (1-2 ml/min) and copper shavings, 2 wt %, were added to accelerate the degradation. The flask was immersed in a thermostat bath at 62°C, and samples were withdrawn at time intervals, for viscosity and other measurements.

Separation of Aged Coal Liquid into Pentane-Soluble and Pentane-Insoluble Components:

Pentane, 20-fold by volume, was added to the aged coal liquid, mixed (magnetic stirring bar) for 1 hr at room temperature and then filtered through a 0.5 micron millipore styrene membrane. The precipitate was dried in a vacuum oven at 80° for 12 hr to remove pentane (94% of the precipitate is soluble in benzene). Pentane from the pentane-soluble fraction was removed by distillation at 40°C. The sample was then subjected to rotary evaporation at 70° for 5 min to insure complete removal of pentane.

INSTRUMENTATION

Viscosity data were obtained at 30° using a Brookfield Synchrolectric

viscometer with a small sample adaptor. Infrared spectra of CS_2 solutions (5g/L) in a 5 mm KBr liquid cell were obtained with a Beckman IR-20 spectrometer. NMR spectra were obtained with a 60-MHz or 600-MHz spectrometer as $CDCl_3$ solutions with TMS as internal reference. Gel permeation chromatograms were obtained with a Waters HPLC and three μ-styragel columns in series: 10^3, 500, and 100 A using THF as solvent at a flow rate of 1 ml/min.

RESULTS AND DISCUSSION

Viscosity of the coal liquid increased exponentially with time when aged at 62°C with oxygen and copper. Aging with copper or oxygen alone at 62° does not affect the viscosity in a 5-day period. Thus, the loss of volatiles which undoubtedly occurs with oxygen bubbling through the sample does not contribute to the observed viscosity change.

Infrared spectra of dilute solutions of the coal liquid before and after aging 5 days at 62° were obtained. The unaged coal liquid shows a prominent free hydroxyl stretching band at 3600 cm^{-1}. The intensity of this band is not significantly affected by aging with copper or oxygen alone. Aging with both copper and oxygen, however, reduces the intensity of this band. This indicates that the hydroxyl group is modified during aging.

The unaged coal liquid is completely soluble in pentane. After aging 5 days, 30% of the aged coal liquid becomes insoluble in pentane. Therefore, pentane was used to separate the aged material into two fractions: the pentane-soluble and pentane-insoluble fractions.

Comparison of the 60 MHz NMR spectra of the coal liquid before and after aging 4 days shows that for the aged pentane-soluble fraction: (a) there is a decrease in the intensity of the signal at 2.3 ppm attributed to the methyl protons attached to benzylic groups, (b) the hydroxyl signal at 5 ppm is absent, and (c) the higher-field aromatic signals from 6.3 to 6.8 ppm are also absent. The 600-MHz spectra of the unaged coal liquid and its acid-free fraction (obtained by ion exchange chromatography) are presented in Fig. 1. The acid-free spectrum is identical to that of the aged pentane-soluble fraction (not shown). Obviously, during aging, acidic methyl substituted phenols are modified and are no longer soluble in pentane.

The gel permeation chromatography of the unaged coal liquid shows three peaks (retention times of ~28, 29 and 30 min.) After aging for three days, profiles of the pentane-separated fractions (Fig. 2) show that the aged pentane-soluble fraction (top), which constitutes 70 wt % of the aged coal liquid, contains components which elute at 29 and 30 min. Components of the unaged coal liquid which elute at 28 min are no longer present after aging. As comparison, the acidic and basic components of the unaged coal liquid (isolated by ion-exchange chromatography) also elute at 28 min. The profile of the pentane-insolublefraction (Fig. 2 bottom) shows that this fraction is composed of large molecular size components. These results suggest that the polar constituents of the coal liquid are reacting during aging to form large molecular aggregates which are pentane-insoluble.

The coal liquid was also enriched 10 wt % with acidic and basic fractions which were isolated by ion-exchange chromatography. The effect of these additives on the formation of pentane-insoluble material is shown in Table 1. The enriched coal liquids were aged at 62°C for 1 day with oxygen and 1% copper. Clearly, enrichment with the acid II fraction

yields the largest amount of pentane-insoluble material (46 wt %). The acid-II fraction consists of alkyl substituted phenols, the base II fraction contains quinoline type compounds and the acid I fraction contains carbazoles, indoles, anilines and xylenols (5).

The elemental composition of the coal-liquid before and after aging 4 days is presented in Table 2. The aged pentane-soluble fraction contains 23% less oxygen and 50% less nitrogen than the unaged coal liquid. The decrease in oxygen content is consistent with IR, NMR, and GPC results showing a reduction in the amount of phenolic compounds during aging. The large amount of oxygen contained in the pentane-insoluble fraction indicates: (a) oxygen containing compounds of the coal liquid have been concentrated in this fraction and (b) the oxygen bubbled into the coal liquid has been incorporated into the structure of this fraction. This is confirmed in FTIR spectra (not shown). The increased nitrogen content of the pentane-insoluble fraction indicates that nitrogen containing compounds are involved in the aging reaction.

Significant characteristics of the aged pentane-soluble fraction are that the viscosity and the atomic H/C ratio are similar to those of the unaged coal liquid, but the oxygen and nitrogen contents are less (Table 2). A low heteroatom content is required in syncrude upgrading procedures to prevent fouling of the catalyst. Our experiments have shown that a reduction in heteroatom content can be achieved with metallic copper under mild conditions.

The results of this study suggest that at least one of the aging reactions is the selective polymerization of phenolic compounds. Incorporation of oxygen and polymerization of nitrogen compounds also occur. In oxidative coupling of phenols, -OH groups give way to ether linkages, in the formation of polymers. The distinctly smaller retention time of the pentane-insolubles in the GPC profiles and the increased VPO molecular weight of the pentane-insolubles are consistent with the formation of polymers.

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Table 1. Aging of Enriched Coal Liquids

(62°C, 1% Cu, O_2, 1 Day)

	Pentane Insolubles
Ill #6	14%
10% Acid-Free Enriched	10
10 Acid I Enriched	11
10% Acid II Enriched	46
10% Base II Enriched	12

Table 2. Elemental Composition and Characterization of SRC II Middle Distillate, Before and After Aging 4 days, 2 wt % Copper and Oxygen at 62°C

	Unaged	Aged Pentane-Soluble	Aged Pentane-Insolubles
C	85.58	86.67	75.48
H	9.12	9.33	6.00
N	0.85	0.43	1.80
O	4.29	3.31	12.78
S	0.19	0.27	0.27
	100.03	100.00	96.29
Copper			3.7
MW	172*	170**	570***
Viscosity+	4.3	3.6	
Atomic H/C	1.28	1.28	0.96

*VPO method, toluene, 37°C 2-15 g/l
**VPO method, methylene chloride, 28°C, 4-7 g/l
***VPO method, pyridine, 86°C, 4-7 g/l
+Centipoise at 30°C

FIG. 1

600 MHZ ^{1}H NMR SPECTRA

ILL NO. 6

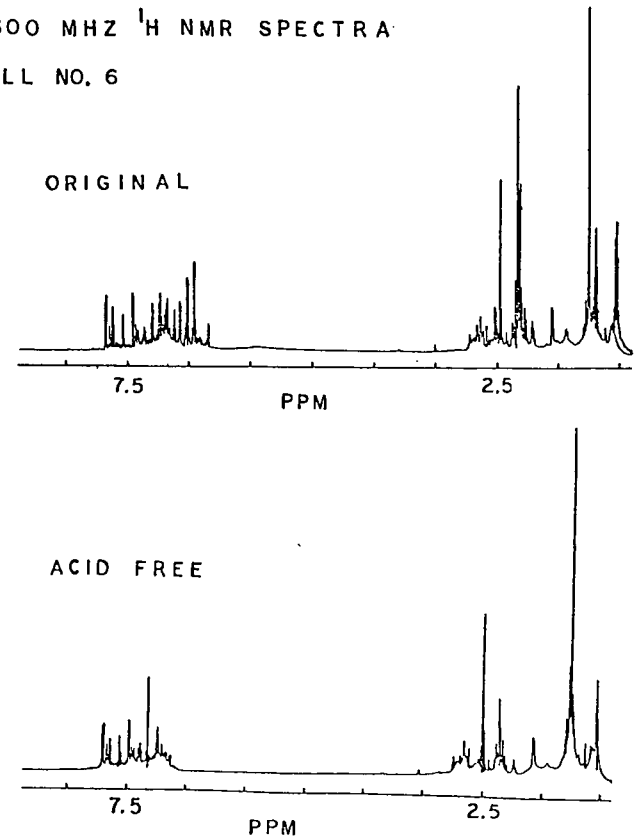
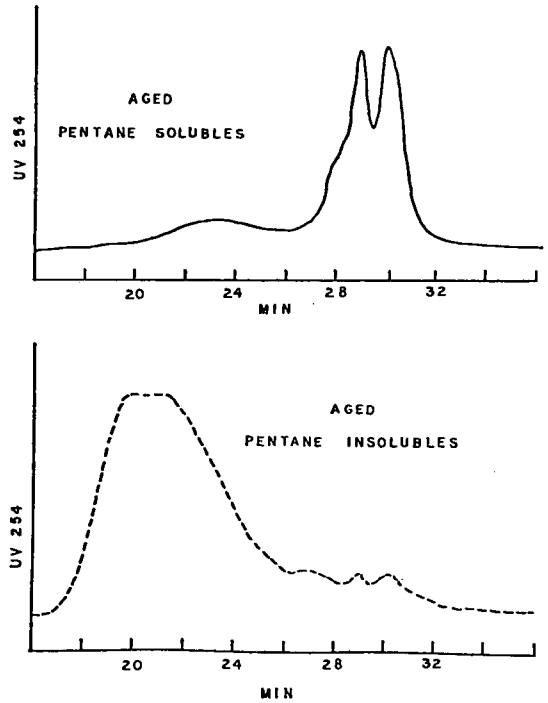


FIG. 2

GPC PROFILES AGED ILL NO. 6