

OXYGEN AGING OF SRC-II HEAVY DISTILLATE

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Abstract—The aging of SRC-II heavy distillate has been studied under oxygen or nitrogen atmospheres at a temperature of 60°C for one month. IR spectra, viscosities, calorific values, and elemental analyses have been determined to characterize the aging behavior of samples. The oxygen aged samples exhibit a new IR band at 1700- cm^{-1} which is not shown in the nitrogen aged samples. The viscosity increases by 325% in oxygen, but only 18% in nitrogen, after one month of aging at 60°C. The sample aged in oxygen for one month shows a significant decrease in the heat of combustion, 106 cal/g. On the other hand, the decrease for the nitrogen aged sample is only 13 cal/g. Elemental analyses show that the content of carbon decreased by 1.03 wt% and that of hydrogen by 0.2 wt% in the oxygen aged sample compared with the unaged sample. No significant change occurs in the nitrogen aged sample. An examination has been made of the extent to which the experimental values of combustion heat can be fitted by various literature equations relating heats of combustion of coals to the elemental analyses. It is found that the equation of Mott and Spooner gives good absolute agreement (within 0.47% error) with our experimental values.

INTRODUCTION

Since SRC-II, which was used as starting material in this experiment, is a coal derived liquid in solvent refined process, its characteristics should be similar to those of coal and some petroleum fractions. It is for this reason that an attempt is made here to review the stability of coal and petroleum fuels on storage. Stability problems of coal and petroleum have been studied for many years. Significant changes in the physical and chemical properties of coal occur upon exposure to air even at ambient temperatures. These changes in coal properties are caused mainly by the interaction of coal with oxygen in the air [1,2]. Much has been published on petroleum fuel stability. Among them, Hazlett and Hall [3] has found the high amount of oxygen, nitrogen and sulfur in the deposits from jet aircraft fuel are remarkable; the deposits point to the importance of compounds containing hetero atoms. The stabilization of hydrocracked lubricating oils are reviewed by Yan and Espenscheld [4]. In case of exposure to light and oxygen, the hydrocracked lubricating oils darken and finally deposit heavy sediments. Such unstable oils can be stabilized by catalytically treating them with paraffins over shape selective zeolite catalysts.

With the increased interest in synfuels, the study of the stability of such coal derived products has been started. Aging studies of synthoil, which is the cen-

trifuged liquid product from the experimental runs of the PERC, have been done by Karn and Brown [5,6]. In this study, they have reported that aging is accelerated at higher temperature and exposure to an environment of oxygen rather than air or nitrogen. The presence or absence of ambient light appears unimportant. Stirred samples are more reactive to oxygen than unstirred samples. The stability of Synfuel also studied by Bowden and Brinkman [7,8]. The gums generated during the aging of refined synthetic fuels had considerable concentration oxygenated materials, presumably the result of oxidation, and some high molecular weight material suggesting that polymerization may have occurred. The results of aging SRC-II middle distillate in the presence of copper were obtained by Jones and Li [9]. They suggested that one of the aging reactions is the selective polymerization of phenolic compounds. Incorporation of oxygen and polymerization of nitrogen compounds also occur. Lacount Noceti [10] have found that phenol contents and molecular weight of coal derived asphaltenes affect the viscosity of their solutions. Intermolecular aggregation, probably involving hydrogen bonding, is a prime factor in the increase of viscosity. They suggest that an effective way of reducing the viscosity of coal derived liquids is to reduce the phenol content of the asphaltene fraction. The aging characteristics of 30/70 (wt%) blend of SRC-I and SRC-II have been investigated by Hara and

Jones [11]. There is a linear increase in viscosity with increasing wt% of toluene insolubles formed during oxygen aging. This indicates that the formation and content of larger molecular size toluene insolubles are mainly responsible for the increased viscosity of blend. Another series of experiments by Brown and Karn [12] shows that large increases in the amount of organic benzene insoluble materials appear with corresponding decreases in oil, pentane soluble components and a constant amount of asphaltenes under an oxygen containing environment. No change in these components appears under nitrogen. The increase of oxygen content in oxygen aged sample show that oxygen has been chemically incorporated into the oxygen aged sample; this was confirmed by the infrared spectra. The spectrum of the oxygen aged sample shows a new band at $1700\text{-}1\text{cm}^{-1}$ and increased generalized absorption in $1300\text{-}1\text{cm}^{-1}$ region. This indicates the formation of C = O groups in the samples. The data for oxygen consumption show that the asphaltene and organic benzene insolubles are much more susceptible to oxidation than oil components.

The ultimate analyses of fuel have an interesting relation with the calorific values. This relation holds not only for coal but also for other organic compounds. Various formulas [13-17] have been based on the ultimate analysis. The relations are generally modifications of the Dulong formula.

The purpose of this study was to investigate changes in the physical and chemical properties of SRC-II heavy distillate upon storage. Changes in IR spectra, viscosity, elemental analysis, and calorific value were followed. Another goal was to try to account for changes in calorific value in terms of changes in elemental composition.

EXPERIMENTAL

1. Materials

SRC-II heavy distillate sample was obtained from Westinghouse Electric Corporation. The analytical characterization of SRC-II is shown in Table 1.

2. Apparatus

The flow diagram of the apparatus used for aging is shown in Figure 1. The SRC-II heavy distillate samples were placed in two gas washing bottles. The fritted glass end of the gas inlet tubes was located close to the bottom of the washing bottle. The fritted glass (coarse porosity) resulted in improved dispersion of gas (oxygen or nitrogen) through the sample. The 125 ml samples of SRC-II were placed in each of two 250 ml washing bottles; the bottles were kept in a temperature controlled water bath during one month at 60°C . Oxygen was supplied continuously to one washing

Table 1. Analytical characterization of SRC-II heavy distillate

Physical and Chemical Properties	
Gravity $^\circ\text{API}$	0.2
Flash Point $^\circ\text{F}$	285
Pour Point $^\circ\text{F}$	0
Gross Heat of Combustion $\frac{\text{BUT}}{\text{lb}}$	17071
Kinematic Viscosity $\text{cs @ } 40^\circ\text{C}$	44.54
Kinematic Viscosity $\text{cs @ } 100^\circ\text{C}$	4.05
Carbon Residue % wt	2.15
Aromaticity % C_a	77
Elemental Analysis wt %	
Hydrogen	7.13
Sulfur	0.42
Nitrogen	0.98
Oxygen	2.04
Ash	0.14
Trace Metals ppm wt %	
Titanium	7.1
Sodium	31.0
Potassium	63.0
Calcium	25.0
Vanadium	2.3
Lead	0.54
Iron	155.0
Phosphorus	< 0.01

*This analysis was supplied by Mobil

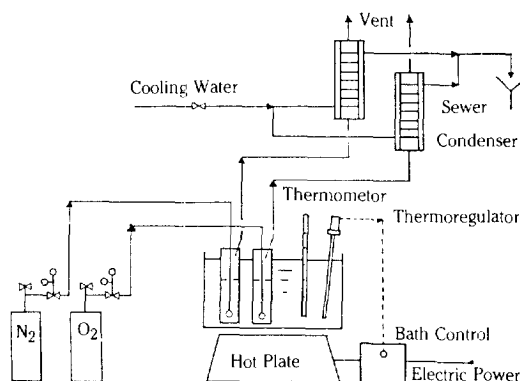


Fig. 1. Flow diagram of aging.

bottle and nitrogen to the other at a flow rate of 6 l/hr through each. The gas flow rate was measured with soap bubble flowmeter everyday. The gas outlet of bottle was connected to a reflux condenser. The water

cooled condensers help to prevent loss of volatile components, and to prevent any overflow because of any sudden changes of flow rate.

3. Instruments

The viscosity was measured with an ASTM 300 Cannon Fenske viscometer at 20°C water bath. The viscometer is calibrated by measuring the efflux time of the ethylene glycol. IR spectra were taken with a 727 B Perkin Elmer spectrophotometer. Elemental analysis was done with a 240°C Perkin Elmer elemental analyzer. The analyzer is calibrated by measuring the sensitivities of N, C, and H using acetanilide as the standard sample. The heat of combustion was measured with an Parr 1241 adiabatic oxygen bomb calorimeter. It is calibrated by measuring the energy equivalent with benzoic acids pellets.

RESULTS AND DISCUSSION

1. Changes in IR spectra

IR spectra were determined for the aged samples and unaged sample of SRC-II heavy distillate. The IR spectra is shown in Figure 2. There is no difference in spectrum among the samples except one. A new absorption band at 1700 cm^{-1} appears in the oxygen aged sample. This band is characteristic of carbonyl or carboxyl group. The appearance of such a band has been reported [12] for a synthoil product aged in oxygen.

2. Changes in viscosity

Figure 3 shows the change in viscosity of SRC-II heavy distillate with storage time in flowing oxygen or nitrogen at 60°C. Increases in viscosity occur in both samples. By far the largest viscosity increase was ob-

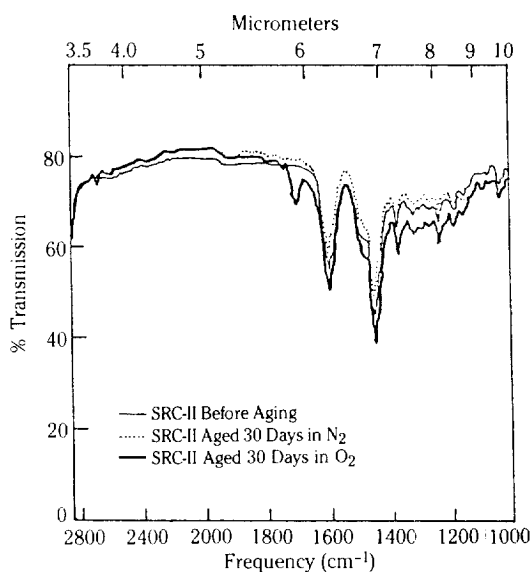


Fig. 2. IR absorption spectra.

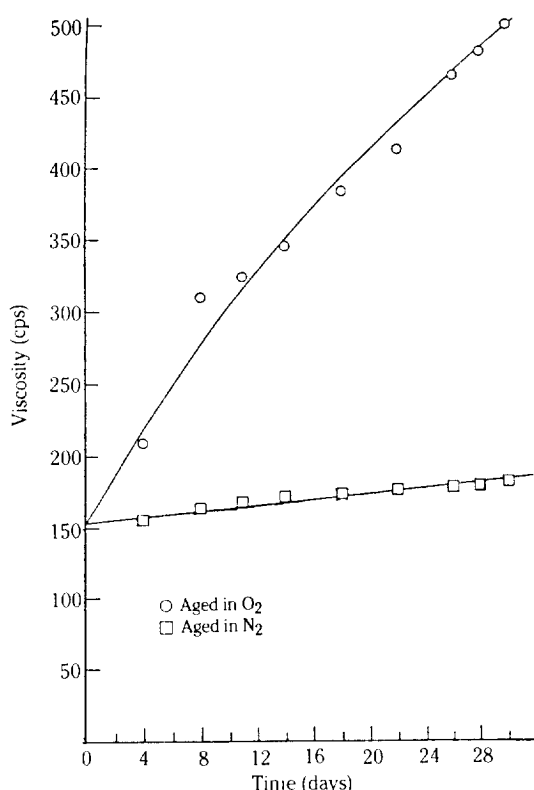


Fig. 3. Change in viscosity on aging at 60°C.

served by 325% (from 153 cp to 500 cp) after one month of storage in oxygen. The increase in viscosity which was observed in nitrogen aged samples was only 18% (from 153 cp to 181 cp) after one month. The viscosity increase during aging under oxygen may have some contributing cause. Carbonyl groups are known to be formed in samples during oxygen aging; these can form hydrogen bonds with phenols and thus increase the viscosity. In any event, intermolecular aggregation involving hydrogen bond seems to be an important factor determining the viscosity increase.

3. Changes in elemental composition

The results are given in Table 2, along with 95% probability level confidence limits. The content of both carbon and hydrogen in oxygen aged samples show a decrease. The average weight percent of carbon decreased by 1.03 wt% and that of hydrogen decreased by 0.2 wt% in oxygen aged samples after one month, compared with the unaged samples. No decrease in carbon or hydrogen content was observed in nitrogen aged samples. No change is expected in sulfur or nitrogen content of the SRC-II sample upon aging, and they were assumed to be constant. The content of oxygen in the sample is obtained by difference, and the increase in oxygen is deduced from the decrease in car-

Table 2. Elemental analysis of SRC-II heavy distillate

	Carbon	Hydrogen	Oxygen (wt %)
Unaged	88.82 ± 0.13	7.53 ± 0.03	2.11
Oxygen-Aged	87.79 ± 0.10	7.33 ± 0.06	3.34
Nitrogen-Aged	88.85 ± 0.07	7.48 ± 0.04	2.13

*The values of carbon and hydrogen are based on 95% probability level confidence limit.

*The value of oxygen was calculated from following formula: $O = 100 - C - H - N - S$. C, H, O, N, and S are denoting the percentages by weight of carbon, hydrogen, oxygen, nitrogen, and sulfur.

bon and hydrogen on aging in oxygen. Another approach to confirm the increase in oxygen content in oxygen aged SRC-II heavy distillate was carried with IR absorption spectra study.

4. Changes in calorific value

The mean value of combustion heat is 9541 cal/g for unaged sample and 9528 cal/g for nitrogen aged sample. On the hand, the combustion heat of the sample aged in oxygen for 30 days is 9435 cal/g. To know if the decrease of heat of combustion is significant, a t-test was carried out. Table 3 gives the results. The calculated value of t, 3.3 for oxygen aged sample for 30 days, is much greater than the critical t value, 2.4 at a 95% probability level. From the t-test result, it is obvious that the decrease of combustion heat of oxygen aged 30 days at 60°C SRC-II is significant. The calculated t value of nitrogen aged 30 days, 0.4, is less than the critical t value. Therefore there was no significant change after nitrogen aging. The heat of combustion are summarized in Table 4.

The calorific value equation is generally expressed in the following general form. $Q = aC + bH + cS - dO$,

Table 3. t-values for combustion heats of SRC-II

	Calculated t Value	Critical Value at 95% Probability
Nitrogen-Aged (30 days)	0.36	2.4
Oxygen-Aged (21 days)	2.67	2.5
Oxygen-Aged (30 days)	3.27	2.4

D.F. = $n + m - 2$

$$t\text{-value} = \frac{x - y}{s} \sqrt{\frac{nm}{n + m}}$$

where x and y are two averages, m and n are the number of individual value to obtain x and y. s is the overall standard deviation. D.F. is degrees of freedom.

Table 4. Summary of combustion heats

Unaged	9541.2 ± 28.5	cal/g
Nitrogen-Aged (30 days)	9528.4 ± 20.8	cal/g
Oxygen-Aged (21 days)	9447.9 ± 10.6	cal/g
Oxygen-Aged (30 days)	9435.1 ± 9.0	cal/g

*These values are based on 95% probability level confidence limit.

where a, b, c and d are the coefficients of carbon, hydrogen, sulfur, and oxygen. The equation of Mott and Spooner, for example, is $Q = 80.3 C + 330 H + 22.5 S - 34.7 O$, where C, H, O, and S denote the weight percent of elements carbon, hydrogen, oxygen, and sulfur. From this equation, it can be understood that the decrease of carbon and hydrogen, and the increase of oxygen will correspond to a loss of calorific value.

5. Formulas of calorific values

An attempt has been made to find the best calorific equation to fit our experimental values for SRC-II samples. The formulas and calculated calorific values, relating combustion heat of coal to elemental analyses, are given in Table 5 and Table 6. Among these formulas, Dulong, Seyler, Boie, and Mott & Spooner equations give reasonable agreement to our values. The Mott and

Table 5. Formulas for calorific value from elemental analysis

Author	Formula
Vondracek	$(81.1 - .062C)C + 270(H - 1/10 O) + 25S$
Schuster	$(254 + .355O)(C/3 + H - (O - S)/8)$
Steuer	$81(C + 3/8 O) + 57(3/8 O) + 345(H - 1/16 O) + 25S$
D'huart	$81C + 342.5H + 22.25S - 30.4O$
Strache-Lant	$81.37C + 342.2H - 36.6O + 25S$
Gumz	$81.3C + 297H + 15N + 45.6S - 23.5O$
Grumell-Davies	$(3.635H + 235.9)(C/3 + H - (O - S)/8)$
Dulong	$80.80C + 344.6(H - 1/8 O) + 25S$
Seyler	$123.92C + 388.12H - 4269 + 1/4 O^2$
Boie	$84C + 277.65H + 15N + 25S - 26.5O$
Mott-Spooner	a) $80.3C + 339H - 34.7O + 22.5S$ b) $80.3C + 339H - (36.6 - .172O)O + 22.5S$

Note: * C, H, O, and S are denoting the percentages by weight carbon, hydrogen, oxygen and sulfur.

* In Mott-Spooner, formula a) is the case of oxygen content less than 15 percent, formula b) is the case of oxygen content is more than 15 percent.

* Unit of calorific value = cal/g.

Table 6. Application of calorific value formulas

Formula	Calculated Calorific Value (cal/g)	
	Unaged SRC-II	Oxygen-Aged SRC-II
Vondracek	9411.37	9143.67
Schuster	9407.88	9242.84
Steuer	9738.28	9548.26
D'huart	9718.66	9566.73
Strache-Lant	9737.32	9540.06
Guniz	9441.74	9269.70
Grun-ell-Davies	9722.56	9509.20
Dulong	9691.11	9485.98
Seyler	9661.22	9457.65
Boie	9520.86	9346.22
Mott-Spooner	9624.15	9427.96

Note: *Elemental analysis data:

Unaged C: 88.82 H: 7.53 O: 2.11 S: .42

Oxygen-Aged C: 87.79 H: 7.33 O: 3.34 S: .42

*Experimental calorific value:

Unaged 9541. cal/g

Oxygen-Aged 9435. cal/g

Spooner equation was found the best of equations tested for oxygen aged samples.

In the Dulong formula, the oxygen of the coal is assumed to be associated with hydrogen to form water, the excess hydrogen being available for combustion together with carbon and sulfur. Boie [13] modified Dulong's formula to apply to fuels other than coal. He examined fuels such as peat, wood, benzene, and petroleum, and he found that the derivation from the experimental results is less than 1 percent in most cases. Mott and Spooner [15] suggest that only two thirds of the oxygen of bituminous coals may be considered to be in combustion with hydrogen, one third of the oxygen being associated as CO and CO₂ groups. It was found that a single linear equation over the whole composition range is impossible owing to the increase in the proportion of oxygen as CO₂ groups in coals. For this reason, two equations were developed according to the oxygen content. The empirical equations do not consider a relationship between the structural properties and calorific values. The formula which takes into account the structure properties is that of Schuyer and Van Krevelen [17]. The formula in which the evaporation heat of liquid fuel, the dissociation heat of molecules into atoms, and the heat of formation of the combustion products should be added to get the molar heat of combustion. Therefore the molar heat of combustion can be developed as follows: $Q = 90.0 C_{ar} + 98.9 C_{al} + 35.5 H_{ar} + 28.7 H_{al}$, where the unit of Q is Kcal/mole, C_{ar} and C_{al} represent the number of aromatic carbon and aliphatic carbon atoms per mole. H_{al}

and H_{ar} represent the number of aliphatic hydrogen and aromatic hydrogen atoms per mole. The above formula can be applied in case of oxygenaceous, nitrogenous, and sulfurous compounds. In this case the heat of combustion can be given by $Q = 95.0 C_{ar} + 98.9 C_{al} + 35.5 H_{ar} + 28.7 H_{al} - 39 O + 15 N + 100 S$.

CONCLUSION

The aging behavior of SRC-II heavy distillate could be detected by IR spectra, viscosity, elemental composition, and calorific value. The oxygen atmosphere leads to viscosity increase, new IR band, elemental composition change, and calorific value decrease in aged samples. These changes are correlated. As a result, oxygen environment is a main factor of degradation of SRC-II heavy distillate.

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