

COAL TAR AUTOXIDATION - KINETIC STUDIES BY VISCOMETRIC
AND REFRACTOMETRIC METHODS

by

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INTRODUCTION

Coal tar is a complex mixture of hydrocarbons and organic compounds containing sulfur, oxygen and nitrogen. Some of these compounds are easily attacked by oxygen when they are exposed to air. This attack always results in the formation of high-molecular-weight compounds, thus reducing the value of the tar. The ability of coal tar to resist the changes in its composition and properties is referred to as its stability. In attempting to evaluate the stability, it was necessary to investigate the kinetics of coal-tar autoxidation. Because of the complexity of the coal-tar composition, it was very difficult to apply conventional methods to this kinetic study. The measurement of viscosity and refractive-index change were regarded as the most convenient ways to determine the extent of coal-tar autoxidation; hence, both of these methods were used in this study. Present-day theory of autoxidation is employed to explain the different mechanisms involved in the autoxidation of whole tar, neutral oils, tar acids, and tar bases respectively, under ambient storage conditions.

EXPERIMENTAL PROCEDURES

Sample Material

The coal tars used in this study were obtained from two processes: hydrogenation (at 650°C reactor temperature), and carbonization (at 700°C). The distillate boiling in the range of 110 to 300°C was used as the sample. Neutral oils, tar acids, and tar bases were chemically separated from this distillate. Samples of Hiawatha, and Spencer coals were selected for hydrogenation, and carbonization. Both coals are

bituminous coals and analyses for them are given in Table 1.

TABLE 1

Analyses of coals (% by weight, as received) which were used to produce coal tar.

	<u>Hiawatha</u>	<u>Spencer</u>
Volatile matter (DAF)	48.6	45.4
Fixed carbon (DAF)	51.4	54.6
Moisture	3.20	5.16
Ash	5.51	4.42
Sulfur	0.80	0.53

Oxidation of Tar Sample

50 ml of tar sample was stored and exposed to air (20°C) in a 100 ml beaker which was covered with a plastic sheet to prevent the evaporation of tar sample. The number of samples used in each different experimental run was 4 or 5, except tar acids, and tar bases, which were difficult to collect. After the sample had been oxidized for the desired period, it was taken from the beaker for measurements or analyses.

Measurement of Viscosity

The viscosity of the tar samples was measured with a Haake falling-ball viscometer. The measuring temperature was controlled by a constant temperature circulator at $25.0 \pm 0.1^\circ\text{C}$.

Measurement of Refractive Index

A Bausch & Lomb Model ABBE-3L refractometer was used to measure the

refractive index of tar samples at 25°C. The refractive index could be read to the fourth decimal place.

Determination of Iodine Number

The Hanus method was employed in this study to determine the iodine number of tar samples.

Analysis of Oxygen Content

Oxygen analyses were obtained from Gailbraith Laboratories, Inc. of Knoxville, Tennessee. Duplicate samples were run on the tars as prepared fresh by hydrogenation of Spencer coal.

Infrared Absorption Spectrum Analysis

The infrared absorption spectra were measured with a Beckman Model IR 20 Spectrometer over the wave-length interval 25 to 40 microns. In this study, a routine scan was selected, and the time required to scan the region was 30 minutes. After the tar sample had been stirred mildly, a liquid film of coal tar, approximately 0.015 mm thick, was spread on a KBr sample holder, and the spectrum was observed immediately.

Auxiliary Experiments

In order to understand the kinetics of the coal-tar autoxidation, some auxiliary experiments were carried out to determine the following:

- a. effect of stirring
- b. effect of oxygen pressure
- c. effect of temperature
- d. effect of light irradiation

RESULTS AND DISCUSSION

Viscosity

The viscosity-change behavior of the whole-tar samples oxidized in air is shown in Figures 1 and 2. It is apparent that the viscosity increases linearly with the reaction time. This indicates that a particular mechanism is involved in the whole tar autoxidation.

In the process of coal-tar autoxidation, some high-molecular-weight compounds are believed to be formed in the liquid, so the viscosity of coal tar increases continuously. The relations between the viscosity of tar sample, the concentration of new compounds, and the time of reaction is shown in Figure 3. In some small interval of reaction time, say, Δt , the viscosity of the tar sample increases from η to $\eta + \Delta\eta$, and the concentration of new compounds increases from C to $C + \Delta C$. If the tar sample with viscosity η at time t is considered as the solvent of new compounds formed from time t to time $t + \Delta t$, then, at the end of the time interval Δt , the relative viscosity is written as

$$\eta_r = \frac{\eta + \Delta\eta}{\eta}$$

and the specific viscosity becomes

$$\eta_{sp} = \eta_r - 1 = \frac{\eta + \Delta\eta}{\eta} - 1 = \frac{\Delta\eta}{\eta}$$

Also, according to definition, the intrinsic viscosity can be expressed as

$$[\eta] = \left(\frac{\eta_{sp}}{\Delta C}\right)_{\Delta C \rightarrow 0} = \left(\frac{\Delta\eta/\eta}{\Delta C}\right)_{\Delta C \rightarrow 0}$$

Substitution of the Mark-Houwink equation (1), which is applicable to a mixture, into the latter equation gives

$$\left(\frac{\Delta n/n}{\Delta c}\right)_{\Delta c \rightarrow 0} = K\bar{M}_v^a$$

in which K and a are constants, \bar{M}_v represents the viscosity average molecular weight of the high-molecular-weight compounds. It is true that as Δt approaches 0, Δc also approaches 0, so does Δn ; hence, division of both the numerator and the denominator by Δt at the left-hand side and taking the limit as Δt goes to 0 yields

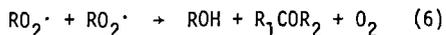
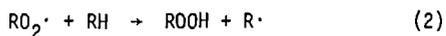
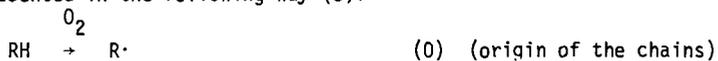
$$\frac{d \ln n / dt}{dc / dt} = K\bar{M}_v^a$$

After rearrangement, it becomes

$$\frac{d \ln n}{dt} = K\bar{M}_v^a \frac{dc}{dt} \quad (1)$$

This kinetic equation relates the viscosity-change rate with the chemical-reaction rate. Most products of coal-tar autoxidation are dimers, which can be considered roughly as a rigid spherical particle, so that the interaction between different new compounds is negligible, and the characteristic constants K and a can be assumed to be constant during reaction (2).

The mechanism of the chain oxidation of hydrocarbons can be represented in the following way (3):



Usually reaction 1 is believed to be a very fast reaction (4). However, in the process of the whole-tar autoxidation, the free radical $R\cdot$ reacts not only with oxygen, but also with the antioxidants such as phenols (belonging to tar acids), amines (belonging to tar bases), and sulfur-containing compounds. At the same time, the peroxy radical $RO_2\cdot$ is easily arrested by these antioxidants too. Thus, the concentration of free radicals is kept at such a low level that the propagation of free radicals fails to proceed eventually, and reaction 1 becomes a rate-determining step. For this study the tar sample was stored in a static container (cf. Figure 4), before collision with free radical $R\cdot$, the oxygen molecule had to diffuse from air through some media of the tar sample to meet the reactant; the overall reaction was therefore a diffusion-controlled reaction, which has been substantiated by the data shown in Figure 5. Thus, in accordance with Smoluchowski theory (5,6), the rate of the diffusion-controlled reaction can be written as

$$W = \frac{4\pi N_0 \sigma_{12} D}{1000} [R\cdot][O_2]$$

where $[R\cdot]$ and $[O_2]$ are the concentration of free radical $R\cdot$ and oxygen respectively, D is the diffusion coefficient, N_0 is Avogadro's number, and σ_{12} is the reaction radius, (the distance between the centers of the particles when they are reacted). For simplicity, the rate equation can be expressed as

$$W = \alpha D [O_2] \quad (II)$$

in which

$$\alpha = \frac{4\pi N_0 \sigma_{12} [R\cdot]}{1000} = \text{constant}$$

The autoxidation system used in this study and the oxygen profile in the coal-tar sample are also shown in Figure 4. Here A represents the oxygen in air, B represents the coal-tar sample to be oxidized, Z represents the depth of the sample, C_A is the concentration of oxygen and N_{AZ} is the molar flux of oxygen in the Z-direction. As gas A diffuses into liquid B and undergoes an irreversible reaction: $A + B \rightarrow AB$, the mass balance (input - output + production = 0) takes the form (7)

$$N_{AZ}|_Z^S - N_{AZ}|_Z + \Delta Z^S - D\alpha C_A S \Delta Z = 0$$

in which S is the cross-sectional area of the liquid. The quantity $\alpha D C_A$ represents the moles of oxygen disappearing per unit volume per unit time. Division of both sides by $S \Delta Z$ and taking the limit as ΔZ goes to zero gives

$$\frac{dN_{AZ}}{dz} + D\alpha C_A = 0$$

Since A and AB are present in small concentrations, the following approximation (Fick's first law) can be established:

$$N_{AZ} = -D \frac{dC_A}{dz}$$

Substitution of this relation into the preceding equation and division of both sides by D gives

$$-\frac{d^2 C_A}{dz^2} + \alpha C_A = 0$$

This is to be solved with the boundary conditions:

$$\text{at } z = 0, \quad C_A = C_{A0}$$

$$\text{at } z = L, \quad N_{AZ} = 0 \quad \text{or} \quad \frac{dC_A}{dz} = 0$$

Thus, the concentration profile of oxygen is obtained and expressed as

$$C_A = \frac{\cosh b[1 - (Z/L)]}{\cosh b} C_{A0}$$

in which $b = L\sqrt{\alpha}$

and the rate of oxygen consumption is

$$\begin{aligned} \frac{dQ_A}{dt} &= N_{AZ}|_{Z=0} S \\ &= -D \frac{dC_A}{dz}|_{Z=0} S \\ &= DS\sqrt{\alpha} C_{A0} \tanh b \quad (\text{III}) \end{aligned}$$

The rate of generation of high-molecular-weight compounds in this diffusion-controlled reaction is proportional to the consumption rate of oxygen. Therefore, substitution of the consumption rate of oxygen (III) into the preceding kinetic equation (I) gives

$$\frac{d \ln n}{dt} = K' K \bar{M}_v^a DS\sqrt{\alpha} C_{A0} \tanh b / (SL)$$

in which K' is a proportionality constant and SL is the volume of the sample. For simplicity, this can be written as

$$\frac{d \ln n}{dt} = \beta DC_{A0}$$

where

$$\beta = K' K \bar{M}_v^a \sqrt{\alpha} \tanh b / L$$

It may be noted that an approximate equation for the diffusion coefficient of a spherical molecule of radius σ is

$$D = \frac{RT}{6\pi N_0 \sigma \eta}$$

in which η is the viscosity of the medium, R is the gas law constant, T is the absolute temperature and N_0 is Avogadro's number (5). Sub-

stitution of the relation into the preceding equation yields

$$\frac{d\eta/\eta}{dt} = \beta \left(\frac{RT}{6\pi N_0 \sigma \eta} \right) C_{A0}$$

Because η is different from zero, multiplication of both sides by η gives

$$\frac{d\eta}{dt} = \beta \left(\frac{RT}{6\pi N_0 \sigma} \right) C_{A0} = \gamma$$

Under constant pressure and temperature, β and C_{A0} are assumed to be constant, therefore so is γ . Thus

$$\frac{d\eta}{dt} = \gamma = \text{constant}$$

After integration, it becomes

$$\eta = \eta_0 + \gamma t \quad (\text{IV})$$

where η_0 is a constant of integration. This accounts for the linear relation between viscosity and time as shown in Figures 1 and 2.

The total amount of oxygen which diffuses into the coal-tar sample from air during reaction, can be calculated by introducing the relation above (IV) into the rate equation of oxygen consumption (III), that is

$$\begin{aligned} \frac{dQ_A}{dt} &= DS\sqrt{\alpha} C_{A0} \tanh b \\ &= \frac{RT}{6\pi N_0 \sigma (\eta_0 + \gamma t)} S\sqrt{\alpha} C_{A0} \tanh b \\ &= \frac{\delta}{\eta_0 + \gamma t} \end{aligned}$$

where

$$\delta = \frac{RT}{6\pi N_0 \sigma} S\sqrt{\alpha} C_{A0} \tanh b = \text{constant}$$

Integration gives

$$\int_0^{Q_A} dQ_A = \int_0^t \frac{\delta dt}{\eta_0 + \gamma t}$$

$$\begin{aligned}
 Q_A &= \frac{\delta}{\gamma} \ln(n_0 + \gamma t) \Big|_0^t \\
 &= \frac{\delta}{\gamma} \ln\left(\frac{n_0 + \gamma t}{n_0}\right) \quad (V)
 \end{aligned}$$

When neutral oils are chemically separated from coal tar and oxidized in air, its viscosity-change behavior (Figure 6) is different from that of the whole tars. For neutral oils, olefins are usually regarded as the compounds which most easily react with the oxygen in air. Because most of the tar acids and the tar bases are absent in the neutral oils, few antioxidants compete with oxygen to consume the free radicals during autoxidation; thus the propagation reaction can be self-sustained, and the overall reaction becomes a long chain reaction. At relatively high pressure (> 100 mm) and high-chain length during autoxidation at the steady state the integrated equation is found to be:

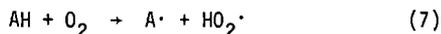
$$-\ln(\ln n_\infty - \ln n) = K_\infty t + \text{constant}$$

in which n_∞ is the viscosity of neutral oil as time approaches infinity.

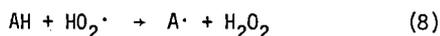
When the quantity $\ln(\ln n_\infty - \ln n)$ is plotted against the reaction time t , a straight line is obtained as shown in Figure 7. The slope of the linear plot represents the rate constant of the overall autoxidation reaction. The rate constant thus obtained for the neutral oil from Hiawatha coal by carbonization is $4.56 \times 10^{-2}/\text{hr.}$, and that for the neutral oil from hydrogenation is $2.62 \times 10^{-2}/\text{hr.}$ The reason for this difference is perhaps that the neutral oil from carbonization contains more diolefins than that from hydrogenation because the unsaturation of coal tar is reduced in the hydrogenation reactions.

The viscosity-change behavior of tar acids and tar bases during autoxidation are shown in Figures 8 and 9. Although these are quite

similar to that of neutral oils, both autoxidation mechanisms of tar acids and tar bases are somewhat different. Some workers reported that inhibitors (AH) may react directly with oxygen (8) in the following way:



Tar acids contain a large amount of phenols, and tar bases contain various amines. Both phenols and amines are generally used as inhibitors for hydrocarbon autoxidation. Hence, reaction (7) must be the main reaction involved in the autoxidation of tar acids and tar bases. In the absence of other hydrocarbon radicals, the following reaction is also believed to take place in the tar acids and tar bases (8):



Finally the reaction may be terminated by dimerization of A· radicals:



Hence, assuming steady state, the rate equation can be expressed as

$$\frac{-d[\text{AH}]}{dt} = 2k_7[\text{O}_2][\text{AH}]$$

Here the concentration of oxygen ($[\text{O}_2]$) can be considered as constant because tar acids and tar bases are oxidized in air. Thus, the autoxidations of tar acids and tar bases become a pseudo-first reaction, which is similar to the rate equation of the neutral oil autoxidation. The linear plots for $-\ln(\ln n_\infty - \ln n)$ vs. time are shown in Figures 10 and 11. The apparent rate constant of tar-acid autoxidation is $2.88 \times 10^{-2}/\text{hr}$ for samples from both carbonization and hydrogenation and that for tar bases from both processes is $3.75 \times 10^{-2}/\text{hr}$. It

is evident that the composition of active compounds contained in either tar acids or tar bases is independent of the coal liquefaction process.

The dependence of the viscosity-change rate for the whole-tar autoxidation on the partial pressure of oxygen is shown in Figure 12. It can be seen that at oxygen pressures greater than 50 mm Hg, the rate of oxidation is independent of the oxygen partial pressure. This corresponds with the inhibited oxidation theory (9).

The temperature effect on the viscosity-change behavior for the whole-tar autoxidation is shown in Figure 13. At higher reaction temperatures the viscosity changes faster. If the slopes of these curves near zero time are taken as the apparent rate constants for the initial reaction period, a linear plot for the Arrhenius equation (Figure 14) gives an activation energy of 9.07 kcal/mole. Usually, the activation energy of a physical-process-controlled reaction is less than this value; therefore, the autoxidation of whole tar is probably not a purely physical-process-controlled reaction.

The effect of light on the viscosity-change behavior during the autoxidation of whole tar is shown in Figure 15. The viscosity-change of the sample under continuous irradiation of fluorescent light is higher than that of the sample isolated from light. In photochemical oxidation, the rate of formation of radicals W_i is directly proportional to the density of the light (3); hence, some compounds contained in the coal tar may be subjected to photochemical oxidation.

Refraction

The refractive-index change behavior accompanying the viscosity change during the whole-tar autoxidation is shown in Figures 1 and 2. For a pure substance, the Lorenz-Lorentz refraction equation is expressed as (10)

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4}{3} \pi N \bar{\alpha}$$

in which n represents the refractive index, N represents the number of particles per unit volume and $\bar{\alpha}$ is the polarizability of the particle. Coal tar is a complex mixture; therefore, for simplicity the assumption is made that the internal field strength is homogeneous throughout the liquid, and the polarizability of the individual particle is independent of its environment, so the Lorenz-Lorentz refraction equation for coal tar can be roughly written as

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4}{3} \pi (\sum N_i \bar{\alpha}_i)$$

in which N_i represents the number of particles of i per unit volume and $\bar{\alpha}_i$ is the polarizability of particle i . Since whole-tar autoxidation appears to be a diffusion-controlled reaction, the number of reactant molecules disappearing and the number of product molecules generated are proportional to the number of oxygen molecules consumed in the reaction, which is small compared to that of whole tar; thus, substitution of equation (V) into the Lorenz-Lorentz refraction equation for coal tar the following relation is obtained:

$$\left(\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d} \right)_t = \left(\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d} \right)_o + \zeta \ln \left(\frac{n_o + \gamma t}{n_o} \right) \quad (\text{VI})$$

in which ζ is a constant, subscript o indicates the initial state, and subscript t indicates the state at time t . According to equation (VI), if the refraction $(n^2 - 1)/[(n^2 + 2) \cdot d]$ is plotted against $\ln[(n_o + \gamma t)/n_o]$, a straight line is obtained (Figure 16). The negative slope of the linear plot is a good evidence for polymerization reaction involved in coal-tar autoxidation. The polarizability of the product is not much

larger than that of the reactant, however the difference between the number of reactant molecules which disappeared and that of the product molecules generated during the reaction is tremendously big. Thus, the net gain of the polarizability per unit volume is negative, and the value of the proportional constant ζ of equation (VI) is negative.

Oxygen Content

The oxygen content of the whole tar during autoxidation is shown in Figure 17. The continuous increase of oxygen content indicates that autoxidation is a main factor leading to deterioration of coal-tar properties.

Iodine Number

Iodine number is the common designation for the determination of unsaturation via the addition of iodine monohalides. The iodine-number change for the whole-tar autoxidation is shown in Figure 18. The decrease of iodine number with reaction time indicates that olefins in the coal tar are attacked by oxygen and saturated by polymerization reactions and therefore play an important part in coal-tar autoxidation.

Infrared Absorption Spectra (numbers in parentheses indicate wave numbers where infrared absorption takes place)

For the whole tar autoxidation, the oxygen-containing groups such as phenols ($3200-3600\text{ cm}^{-1}$), hydroperoxides (3400 cm^{-1}), carboxylic acids ($1960-1760\text{ cm}^{-1}$), and esters (1250 cm^{-1}) increase; however, the double bonds ($3020-3080\text{ cm}^{-1}$) diminish (Figures 19 and 20). This corresponds very well with the decrease of iodine number, indicating

that the unsaturated hydrocarbons become saturated during oxidation. Furthermore, the reduction of amines (1474 cm^{-1}) indicates that they take part in the whole-tar autoxidation. Finally, the decrease of monosubstituted aromatic compounds ($690\text{-}710, 730\text{-}770\text{ cm}^{-1}$) and the increase of m-disubstituted aromatic compounds ($750\text{-}810\text{ cm}^{-1}$) indicate that some aromatic molecules enlarge by addition or polymerization reactions.

CONCLUSION

Coal tars are easily attacked by oxygen when they are exposed to air. The ease and extent of this attack are determined by a number of factors, among which are the composition of the coal tar, the reaction temperature and the oxygen pressure.

According to the viscosity-change behavior, it is believed that the whole-tar autoxidation is a diffusion-controlled reaction; the autoxidation of neutral oils is a long-chain, radical reaction, the rate of which is proportional to the concentration of hydrocarbon reactants; the oxidation of tar acids, and tar bases is a second-order reaction, the rate of which is proportional to the concentration of tar acids or tar bases, and the partial pressure of oxygen.

The decrease of refraction of coal tars as reaction with oxygen proceeds indicates that some polymerization reactions are involved in coal-tar autoxidation.

The decrease of iodine number with reaction time reveals that the olefins play an important part in coal-tar autoxidation. The same conclusion is drawn from the results of the infrared absorption analyses.

To prevent deterioration of coal-tar properties, coal tars should be isolated from oxygen and light; otherwise significant quantities of

good oxidation inhibitors are required for stability.

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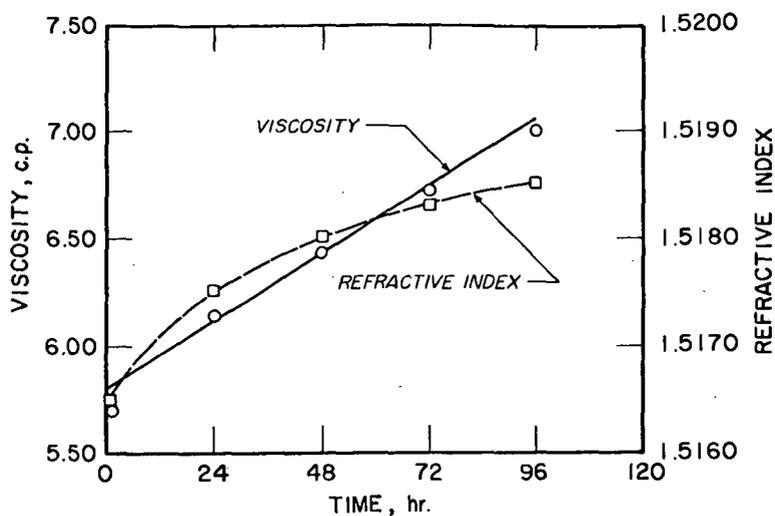


Fig. 1. Viscosity and refractive-index change as a function of time for the autoxidation (at 20°C) of whole tar obtained from Hiawatha coal by carbonization.

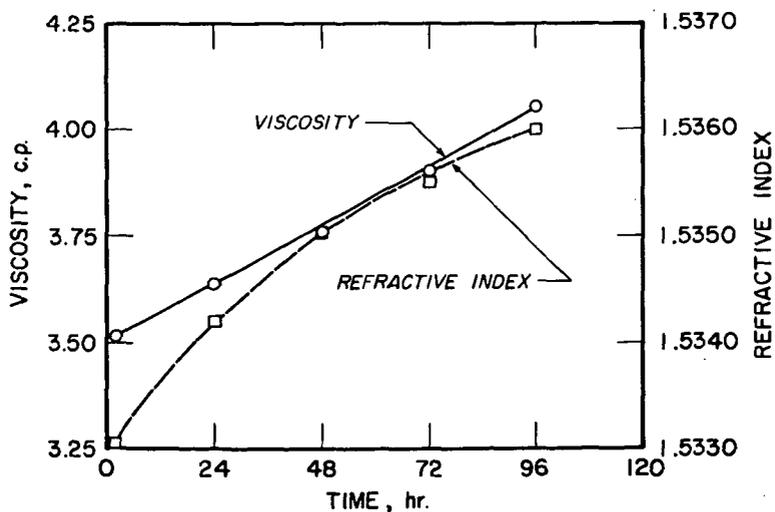


Fig. 2. Viscosity and refractive-index change as a function of time for the autoxidation (at 20°C) of whole tar obtained from Hiawatha coal by hydrogenation.

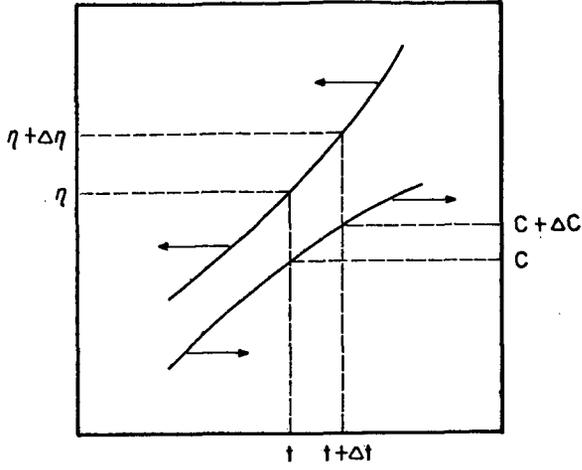


Fig. 3. Relation among viscosity, concentration and time..

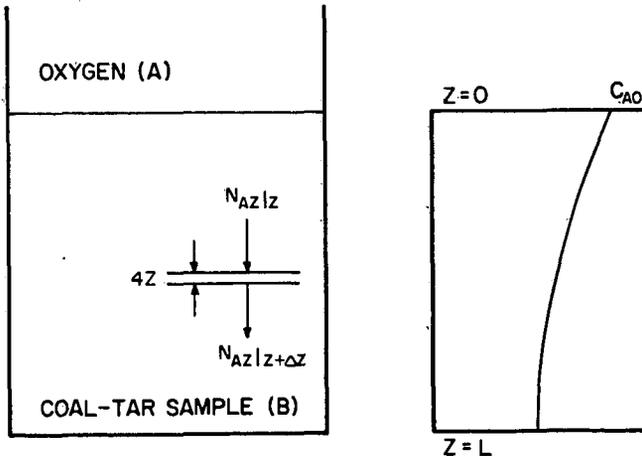


Fig. 4. Autoxidation system and oxygen profile in coal tar sample.

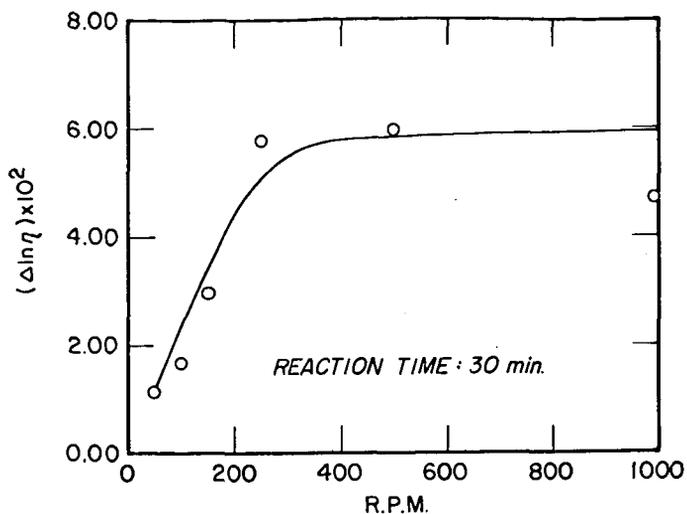


Fig. 5. Viscosity increase as a function of stirring speed for the autoxidation (at 20°C) of whole tar obtained from Hiawatha coal by carbonization.

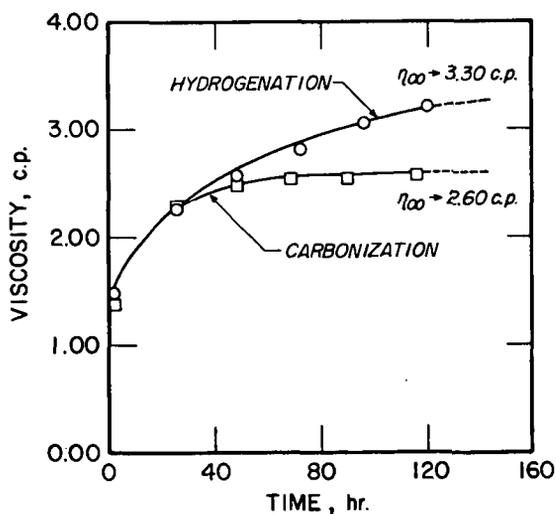


Fig. 6. Viscosity change as a function of time for the autoxidation (at 25°C) of neutral oils from Hiawatha coal.

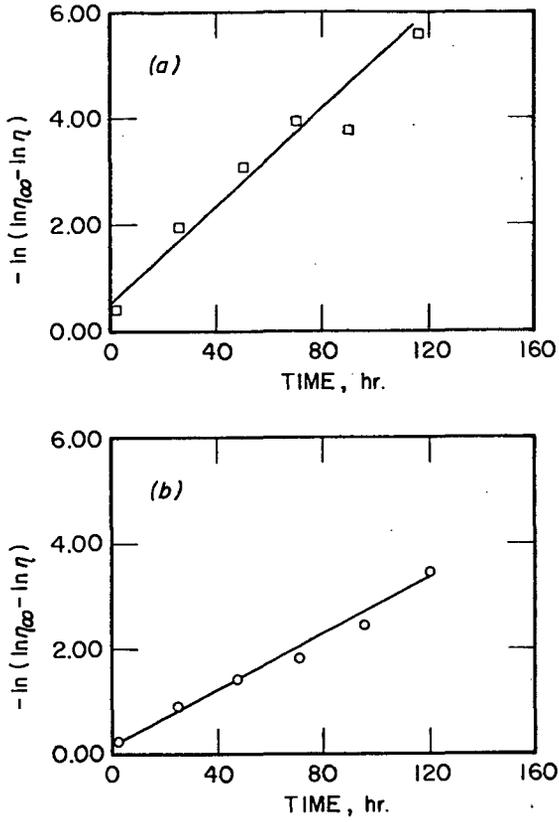


Fig. 7. Linear plot for a first-order autoxidation reaction of neutral oils obtained from Hiawatha coal by (a) carbonization and (b) hydrogenation.

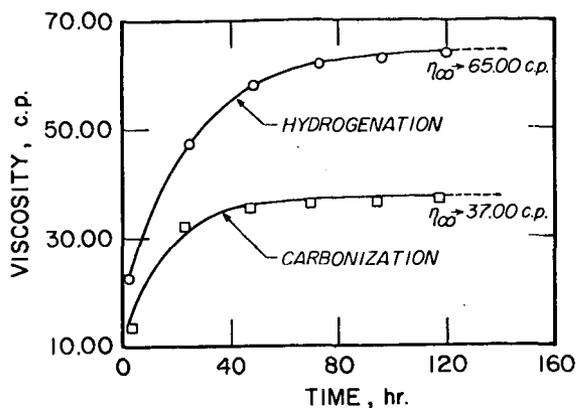


Fig. 8. Viscosity change as a function of time for the autoxidation (at 25°C) of tar acids from Hiawatha coal.

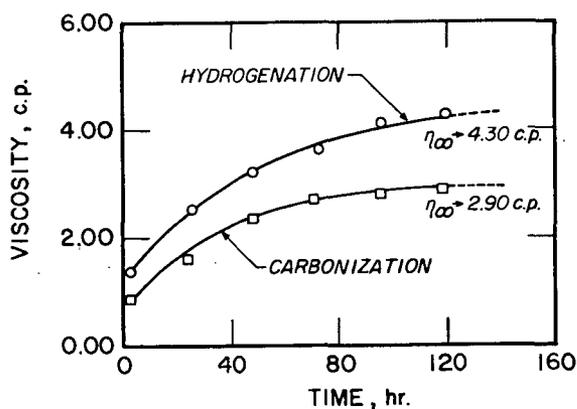


Fig. 9. Viscosity change as a function of time for the autoxidation (at 25°C) of tar bases from Hiawatha coal.

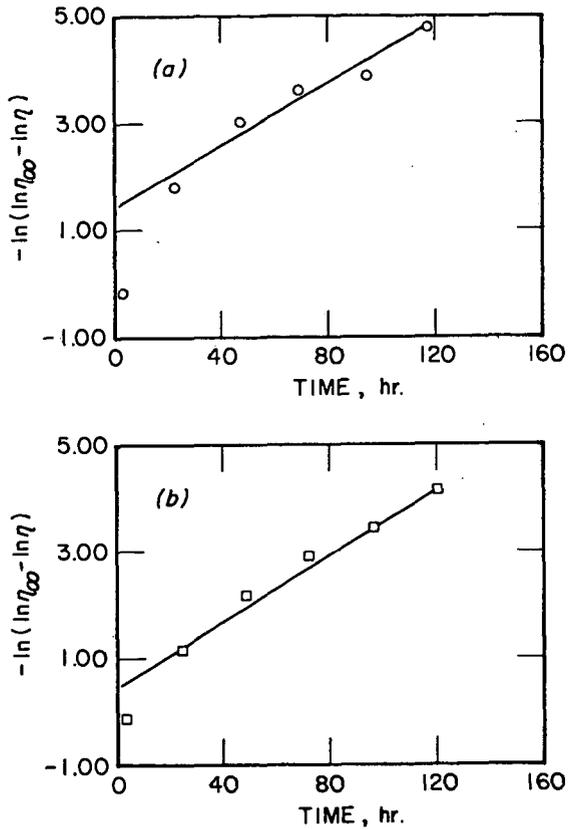


Fig. 10. Linear plot for a pseudo-first-order autoxidation reaction of tar acids from Hiawatha coal by (a) carbonization and (b) hydrogenation.

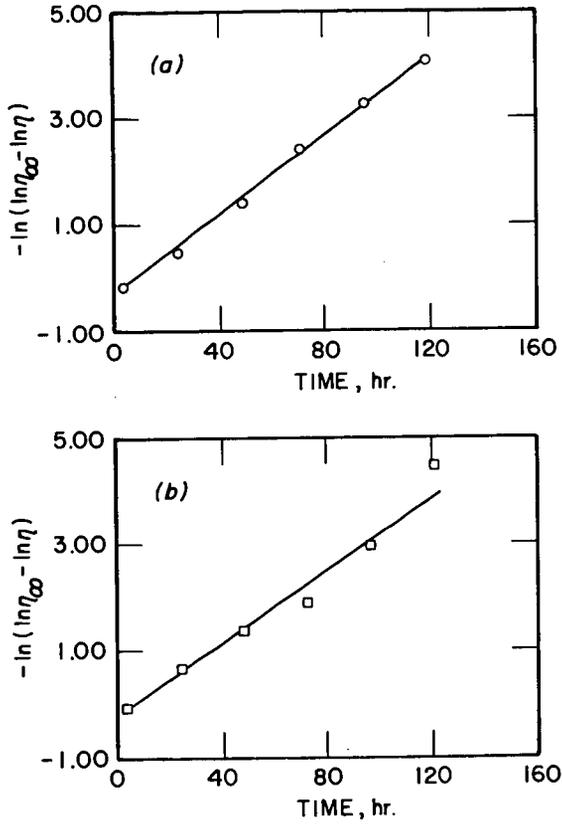


Fig. 11. Linear plot for a pseudo-first-order autoxidation reaction of tar bases obtained from Hiawatha coal by (a) carbonization and (b) hydrogenation.

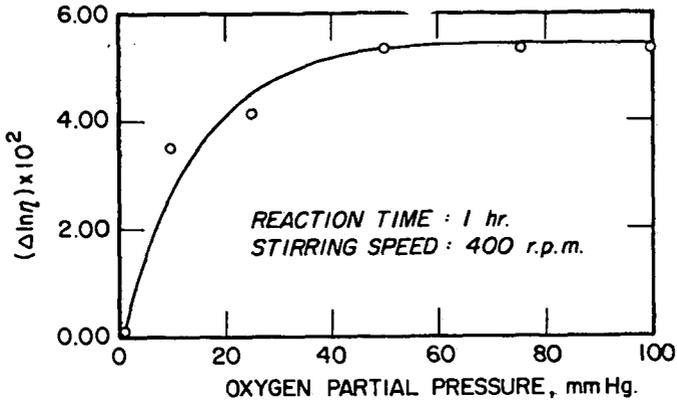


Fig. 12. Dependence of the viscosity-change rate on the oxygen partial pressure for the autoxidation (at 20°C) of whole tar obtained from Hiawatha coal by hydrogenation.

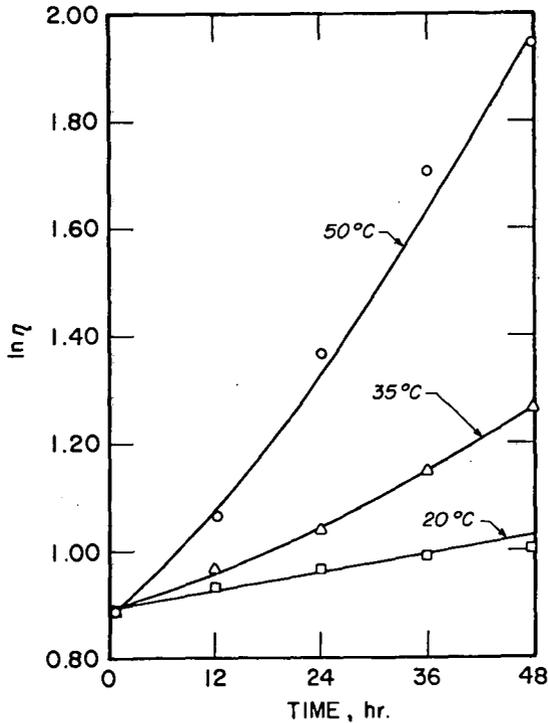


Fig. 13. Logarithm of viscosity vs. reaction time for the whole-tar autoxidation at various temperatures. (Sample obtained from Hiawatha coal by hydrogenation)

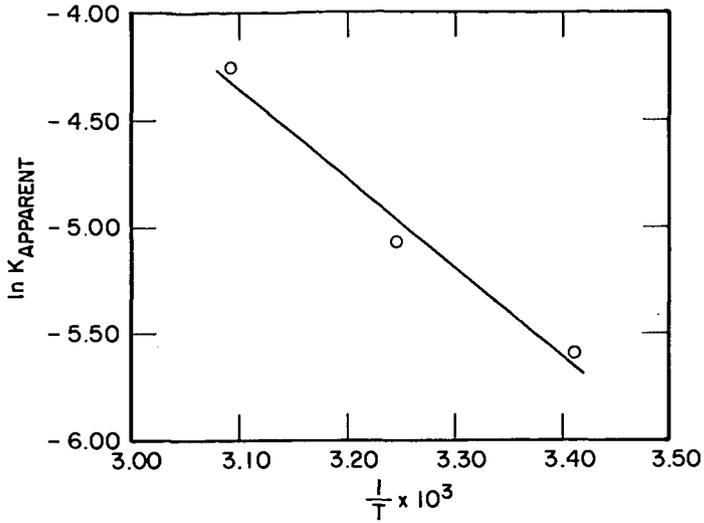


Fig. 14. Linear plot of Arrhenius equation for evaluation of activation energy for initial reaction of whole tar with air.

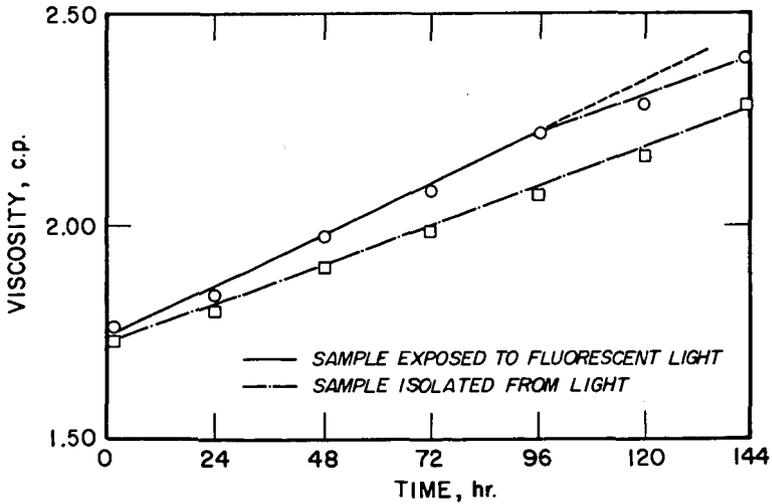


Fig. 15. Fluorescent light effect on viscosity change for the autoxidation (at 20°C) of whole tar obtained from Spencer coal by hydrogenation.

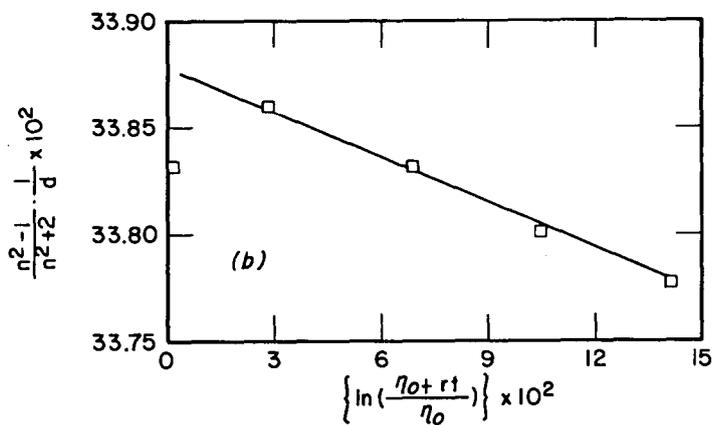
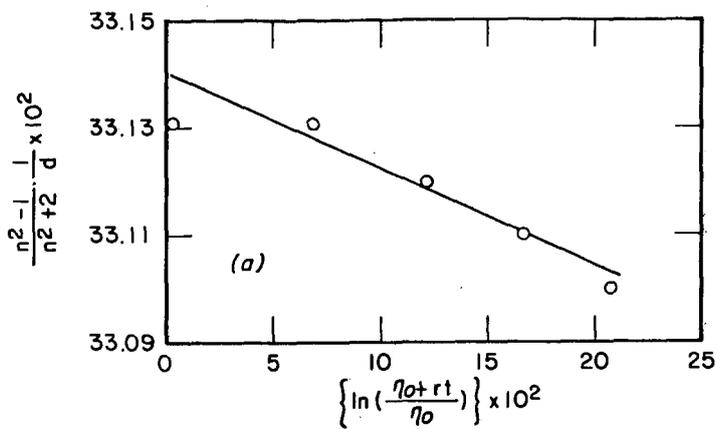


Fig. 16. Refraction as a function of time for the autoxidation (at 20°C) of whole tars obtained from Hiawatha coal by (a) carbonization and (b) hydrogenation.

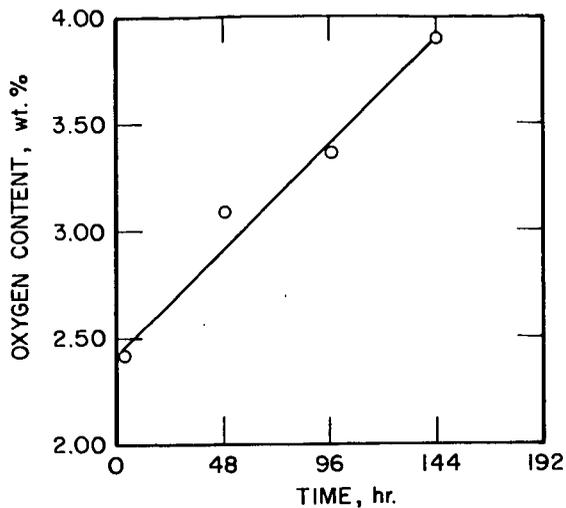


Fig. 17. Oxygen content as a function of time for the autoxidation (at 20°C) of whole tar obtained from Spencer coal by hydrogenation.

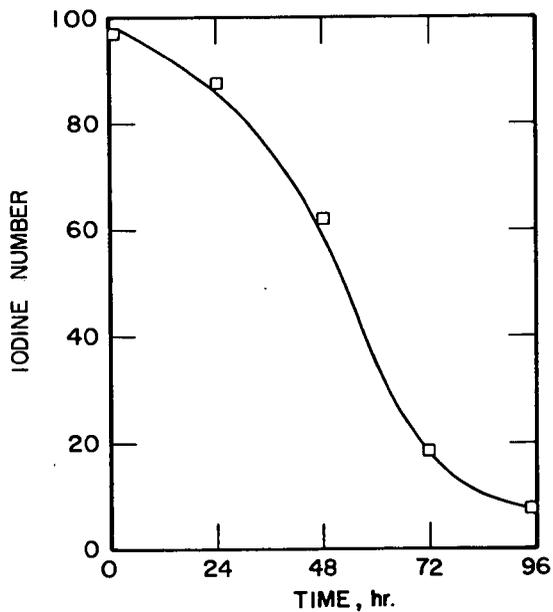


Fig. 18. Iodine number vs. time for the autoxidation (at 50°C) of whole tar obtained from Spencer coal by hydrogenation.

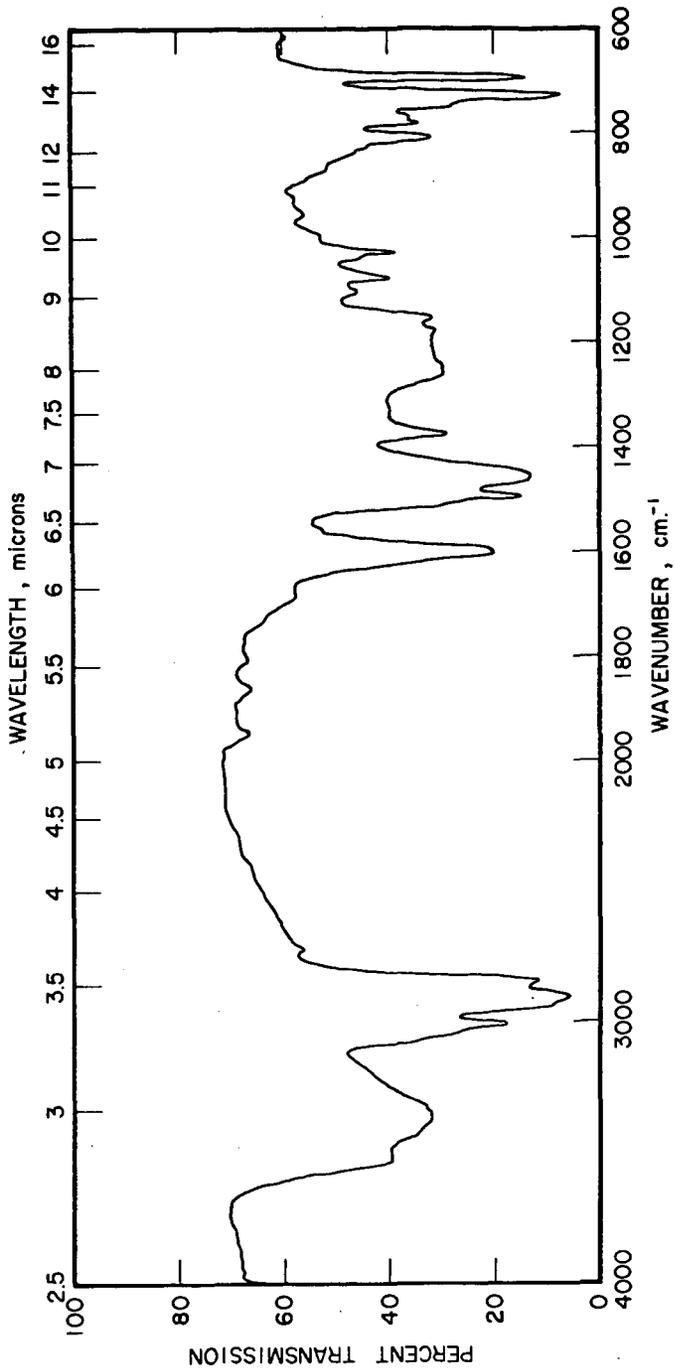


Fig. 19. Infrared absorption spectrum of whole tar before oxidation (Sample obtained from Hiawatha coal by hydrogenation)

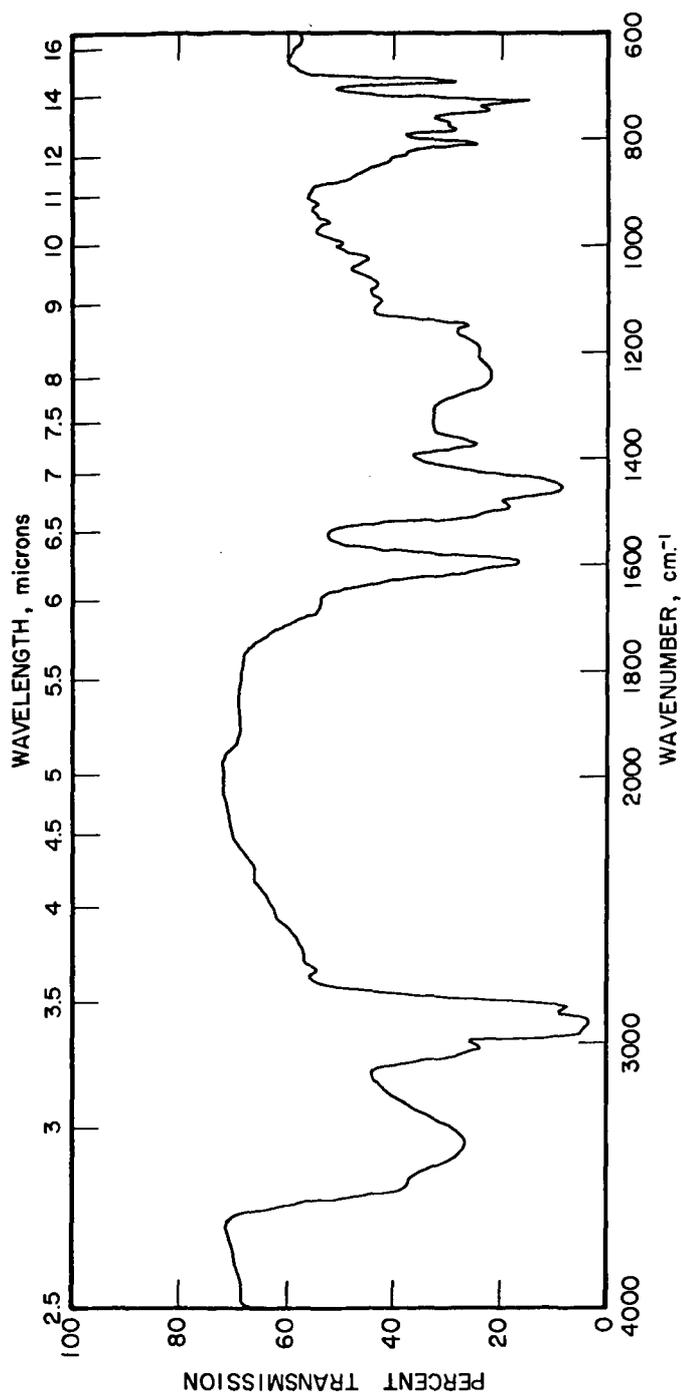


Fig. 20. Infrared absorption spectrum of whole tar oxidized (at 50°C) for 48 hr.
(Sample obtained from Hiawatha coal by hydrogenation)