

DETERMINATION OF HYDROXYL CONTENT OF COALS BY THE
FORMATION OF TRIMETHYLSILYL ETHERS

Sidney Friedman, Waldo A. Steiner, Raphael Raymond, and Irving Wender

U. S. Bureau of Mines, Bruceton, Pa.

Abstract

Although a number of methods for determining hydroxyl groups in coal have been used, a more reliable and independent method is needed to correlate and check the results obtained in various laboratories. This paper presents a new method for the determination of hydroxyl groups in coal based on the formation of trimethylsilyl ethers, $\text{ROSi}(\text{CH}_3)_3$, by treating coal with hexamethyldisilazane, $(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3$ and trimethylchlorosilane, $(\text{CH}_3)_3\text{SiCl}$, in pyridine at about 115°C . The resulting derivatives are analyzed for silicon to calculate the hydroxyl content in the coal samples. Experiments on model compounds have shown that hydroxycarbonyl compounds and even highly hindered phenols (2,6-di-*t*-butylphenol) form trimethylsilyl ethers quantitatively under reaction conditions.

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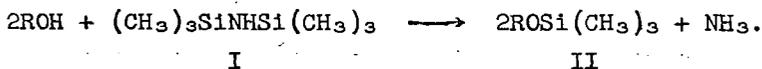
Sidney Friedman, Waldo A. Steiner, Raphael Raymond, and Irving Wender

U. S. Bureau of Mines, Bruceton, Pa.

Introduction

Although a number of methods have been used for determining hydroxyl groups in coals,* a more reliable and independent method is needed for correlating and checking the results of various laboratories. This paper presents preliminary work on the determination of hydroxyl groups in coal by the formation of their trimethylsilyl ethers. The method appears to offer an excellent way for determining the hydroxyl content of coals as well as providing a means for introducing a protective group which is easily removed.

Work in these laboratories has shown that hexamethyldisilazane (I) reacts quantitatively with hydroxyl groups, including even the most hindered ones, according to the following equation (1):



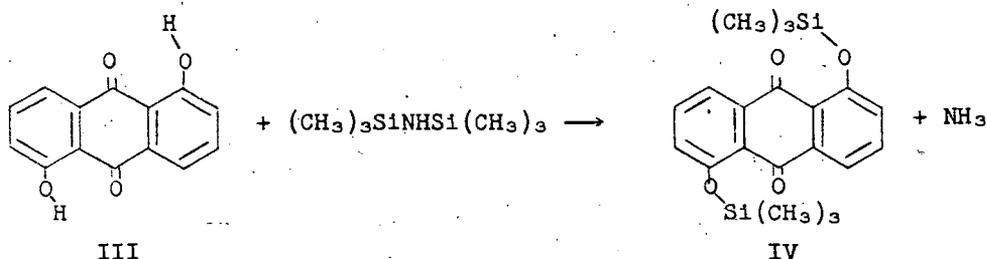
The resulting trimethylsilyl ether (II) is thermally stable and resistant to oxidation. The starting compound, however, is easily recovered from the ether by hydrolysis.

This reagent was first used for quantitative determination of hydroxylated compounds in the analysis of mixtures of Fischer-Tropsch alcohols, by mass-spectrometric analysis of their trimethylsilyl ethers (2). The mixture of ethers was more easily analyzed than the original alcohol mixtures. Reaction between these aliphatic alcohols and reagent (I) was rapid and quantitative.

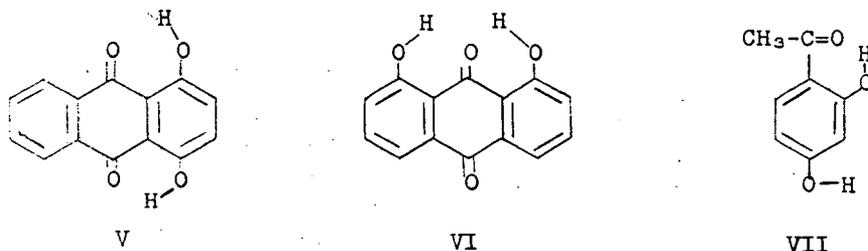
The reaction was equally adaptable to simple phenols; this prompted an investigation into its use for hydroxyl groups present in hydrogen-bonded hydroxycarbonyl compounds such as 1,5-dihydroxyanthraquinone (III). Hydrogen-bonded quinone groupings such as are found in this compound have been postulated to exist also in coal (3,4). This compound is reported to form a dimethyl ether only under rather severe

*/ For a review of these methods, see reference 6.

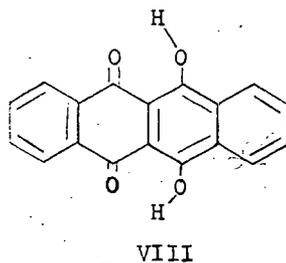
reaction conditions (5); i.e., when its dipotassium salt is heated with dimethyl sulfate at 140°C. It forms a bis(trimethylsilyl)ether (IV) readily on refluxing in hexamethyldisilazane; the reaction is essentially quantitative.



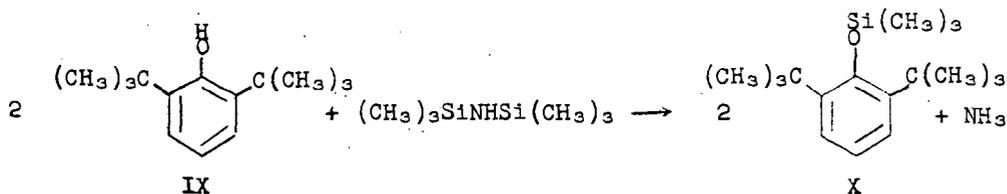
The related 1,4- and 1,8-dihydroxyanthraquinones (V, VI) as well as the hydrogen-bonded keto-phenol, 2,4-dihydroxyacetophenone (VII), also react readily to form trimethylsilyl ethers.



The compound 6,11-dihydroxynaphthacene-9,10-quinone (VIII), which is similar to 1,4-dihydroxyanthraquinone, was found to acetylate to the extent of only 10 percent, and methylate to the extent of 5 percent (6).



Further work has demonstrated that a highly-hindered phenol, 2,6-di-*t*-butylphenol (IX), reacts quantitatively with hexamethyldisilazane in the presence of trimethylchlorosilane and pyridine to form a stable trimethylsilyl ether (X) which can be used as a derivative of the phenol.



Reported attempts to form other derivatives of this hindered phenol indicate that it is necessary to form the sodium salt in liquid ammonia first before any reaction will take place (7). Thus, even in the case of a hindered phenol, reaction with hexamethyldisilazane represents a convenient and quantitative method for the formation of a derivative.

The same procedure has been applied to a series of coals, with the formation of the trimethylsilyl ethers of the hydroxyl groups in the coals. The derivatives have been analyzed for silicon to calculate the percentage of hydroxyl in the original coal.

Experimental Procedures and Results

Preparation of Trimethylsilyl Ether of 1,5-Dihydroxyanthraquinone

To 15 ml. of hexamethyldisilazane was added 2.5 g. of 1,5-dihydroxyanthraquinone (recrystallized, melting point 280°-284°C.) and one drop of trimethylchlorosilane. The mixture was refluxed for 24 hours. Hexamethyldisilazane and other relatively volatile substances were distilled off under vacuum, leaving 2.6 g. of solid which was recrystallized from petroleum ether (b.p. 60-68). The orange crystals, m.p. 138-142°C., had an infrared spectrum with absorption bands at 8.0, 9.45, 11.80, and 13.25 μ , all of which have been found to be common to phenyl trimethylsilyl ethers. In addition, the band at 12.70 μ , found in phenols, was absent, and the 6.12 and 6.23 μ bands of 1,5-dihydroxyanthraquinone, due to hydrogen-bonded carbonyl and aromatic absorptions, were shifted to 5.9 and 6.12 μ in the bis(trimethylsilyl)ether. These spectra are shown in Figure 1.

Analysis of the ether:

Calcd. for C ₂₀ H ₂₄ O ₄ Si	C, 62.46;	H, 6.29
Found	C, 62.81;	H, 6.45

Preparation of Trimethylsilyl Ethers of Other Hydrogen-bonded Hydroxycarbonyl Compounds

By the same procedure derivatives were prepared from 1,8-dihydroxyanthraquinone, 1,4-dihydroxyanthraquinone and 2,4-dihydroxyacetophenone. The infrared spectra of the last two compounds and their derivatives, Figures 2 and 3, showed the same changes in spectra which were noted in the case of the 1,5-dihydroxyanthraquinone.

Preparation of Trimethylsilyl Ether of 2,6-di-t-butylphenol

A 10 g. sample of 2,6-di-t-butylphenol was refluxed for 24 hours with 5 ml. of hexamethyldisilazane and 10 ml. of trimethylchlorosilane in 25 ml. of dry pyridine. Ammonium chloride sublimed into the condenser and the color of the solution changed from pale yellow to light pink during refluxing. Solvent and unreacted reagents were distilled off under vacuum, leaving 10.3 g. of straw-colored crystals which were recrystallized from petroleum ether (b.p. 60-68°). A second recrystallization gave colorless crystals of m.p. 109-110°C.

Calcd. for $C_{17}H_{30}SiO$	C, 73.31;	H, 10.86
Found	C, 73.30;	H, 10.90.

The infrared spectrum showed the complete disappearance of the hydroxyl band at 2.9μ and bands appeared at 8.0, 9.5, 11.8, and 13.25μ as in the other phenyl trimethylsilyl ethers. There were also other changes in the spectrum due to skeletal vibrations. The spectra are shown in Figure 4.

Unsuccessful attempts were made to prepare this trimethylsilyl ether with hexamethyldisilazane and trimethylchlorosilane without pyridine, trimethylchlorosilane and pyridine without hexamethyldisilazane, and hexamethyldisilazane and pyridine with only a drop of trimethylchlorosilane as catalyst; a trace of ether was found in the last case.

Formation of Trimethylsilyl Ethers of Coal Hydrogenation Asphaltene

To 20 ml. of hexamethyldisilazane was added 1.0 g. of coal hydrogenation asphaltene and one drop of trimethylchlorosilane. The solution was refluxed under nitrogen for 3 days, and then the reagents were distilled off under vacuum. As the dry residue was somewhat soluble in heptane, it could not be washed. Instead, the product was vacuum oven-dried to constant weight. Infrared analysis indicated that essentially all hydroxyl groups had reacted.

Analysis of asphaltene before treatment: C, 85.25;
H, 7.00; N, 1.15; O, 6.60.

The treated asphaltene contained 6.21% silicon, corresponding to a hydroxyl content equivalent to 64% of the oxygen present in the original asphaltene.

Formation of Trimethylsilyl Ethers of Coals

Reflux method. A 5 g. sample of the coal, ground to -325 mesh and dried to constant weight in a vacuum oven, was refluxed under nitrogen in a solution of 5 ml. of trimethylchlorosilane and 10 ml. of hexamethyldisilazane in 50 ml. of dry pyridine. Except where noted (Table 2), the reflux period was 4 days. At the end of this time, the reagents were distilled off under vacuum. The reacted coal was washed with petroleum ether (b.p. 60-68°) to remove the last traces of reagents and dried in a vacuum oven. Original ultimate analyses, silicon determinations, and calculated percentages of hydroxyl in the coals,

Table 1.- Trimethylsilyl ether formation of coals.

Coals	Percent, moisture- and ash-free basis				Percent silicon in original coal		Percent silicon in treated coal		Percent hydroxyl oxygen in original coal		Percent hydroxyl oxygen in treated coal	
	Carbon	Hydro-	Nitro-	Per- cent ash	Sulfur	0	Percent silicon in original coal	Percent silicon in treated coal	Percent hydroxyl oxygen in original coal	Percent hydroxyl oxygen in treated coal	Percent hydroxyl oxygen in original coal	Percent hydroxyl oxygen in treated coal
Colorado, Weld County	66.91	5.48	1.41	0.39	25.81	4.22	0.93	6.81	4.13	16.0	4.13	16.0
Alberta, Red Hot Mine, Edmonton	70.75	5.32	1.41	3.35	19.14	10.54	1.36	10.64	7.79	40.7	7.79	40.7
Illinois, Little Dog Mine	71.94	5.50	1.36	2.71	18.58	8.58	3.13	8.04	3.51	18.9	3.51	18.9
Jugoslavias, Rasez ^a	75.06	5.58	1.13	12.14	6.09	12.58	0.51	2.47	1.35	22.2	1.35	22.2
Illinois, Little John Mine, Knox County	76.47	5.66	1.38	3.35	13.13	7.42	1.57	8.80	5.15	39.2	5.15	39.2
Ohio, Dorothy Mine, Belmont County	77.42	5.47	1.36	4.18	11.57	4.18	1.42	6.71	3.81	32.9	3.81	32.9
Ohio, Hocking #6 Bed, Athens	77.52	5.33	1.59	1.07	14.48	6.92	1.53	7.74	4.53	31.3	4.53	31.3
Kentucky #11 Seam, Hopkins County	77.94	5.68	1.58	3.70	11.11	5.46	1.26	8.09	5.21	46.9	5.21	46.9
Kentucky, #12 Seam, Hopkins County	78.00	5.79	1.39	3.71	11.10	10.90	2.98	9.38	5.41	48.7	5.41	48.7
Indiana, #5 Red, Enos	78.15	5.74	1.54	3.82	10.74	9.05	1.98	8.38	4.78	44.5	4.78	44.5
Kentucky, #11 Seam, Muhlenberg County	78.37	5.62	1.60	3.56	10.00	7.87	2.11	7.05	5.61	56.1	5.61	56.1
Indiana, #5 Seam, Knox County	78.79	5.72	1.57	4.37	9.55	7.68	1.47	8.47	5.26	55.1	5.26	55.1
Illinois, #6 Seam, Jefferson County	78.87	5.57	1.83	1.47	12.24	7.06	2.03	8.94	5.34	43.6	5.34	43.6
Wyoming, Rock Springs	79.31	5.41	1.74	0.90	12.65	1.96	0.48	6.89	4.47	35.3	4.47	35.3
Utah, Sunnyside #1, Carbon County	79.79	5.73	1.74	1.01	11.72	5.42	1.86	6.98	3.56	30.4	3.56	30.4
Illinois, #5 Seam, Saline County	80.90	5.62	1.92	1.32	10.25	6.71	1.80	8.90	4.68	45.6	4.68	45.6
West Virginia, #8 Bed, Marion County	82.32	5.70	1.27	3.69	6.88	8.91	1.63	5.91	3.23	46.9	3.23	46.9
Pennsylvania, Princeton	82.68	5.51	1.61	1.18	9.02	4.93	1.17	6.17	3.45	38.2	3.45	38.2
West Virginia, #2 gas bed, Lady Dunn Mine	84.93	5.65	1.71	0.82	6.79	3.36	0.83	5.61	3.22	47.4	3.22	47.4
West Virginia, #8 Bed, Big Knob #A,	87.86	5.20	1.17	1.01	4.77	7.52	1.65	4.35	1.79	37.5	1.79	37.5
Pennsylvania, Jedo Anthracite	93.25	2.23	0.79	0.52	1.22 ^d	3.34	0.70	0.99	0.18	14.3	0.18	14.3
Pennsylvania, Brucston anthracite ^{a/b}	83.25	5.50	1.56	0.69	9.00	1.22	0.37	5.78	3.63	40.3	3.63	40.3
								5.78	3.36	46.3	3.36	46.3
								5.61	3.54	39.3	3.54	39.3

a/ Not in graph.
b/ Refluxed with water for 1 hour, dried, then treated.
c/ Reacted in bomb at 150°C.
d/ Direct oxygen determination.

based on the uptake of silicon, are shown in Table 1. Some of the data are also shown in Figures 5 and 6.

Pretreating coal (Bruceton anthraxylon) with boiling water had no effect on the determinable hydroxyl content (Table 1).

In more recent work reflux periods from 1 hour to 8 days were tried on one coal. As shown in Table 2, the reaction was essentially complete after only 1 hour. With this coal (14.5% O) the method was precise to $\pm 3\%$ of the oxygen content, based on the weight of total oxygen in the moisture- and ash-free coal.

Table 2.- Effect of time on formation of trimethylsilyl ethers in coal from Hocking #0 bed, Athens, Ohio.

Time, hours	Silicon in treated coal, %	Oxygen as OH in original coal, %	$\frac{O_{OH}}{O_{total}}$, %
1	8.08	5.07	35.0
4	7.97	4.97	34.3
24	8.35	5.33	36.8
96	7.90	4.60	31.8
96	7.57	4.91	33.9
<u>192</u>	<u>8.57</u>	<u>5.43</u>	<u>37.5</u>
Average	8.07	5.05	34.9

Bomb method. In a small stainless steel bomb (volume, 70 ml.) 4.861 g. of Bruceton anthraxylon, 5 ml. each of trimethylchlorosilane and hexamethyldisilazane, and 17 ml. of pyridine were heated to 150°C. for 5 hours. The product was treated as in the reflux method. Results are included in Table 1.

As the bomb method at elevated temperature did not increase the number of trimethylsilyl groups introduced into Bruceton anthraxylon, it showed that the reaction had been rapidly completed at reflux temperature in pyridine.

Silicon Analysis

Silicon was determined by peroxide bomb fusion of the samples, followed by treatment of residues with hydrofluoric acid to volatilize silicon. The analyses, done in duplicate, checked to within $\pm 0.1\%$.

Discussion

A recent article by Blom, Edelhausen, and Van Krevelen (6) reviews the various methods used for determining hydroxyl groups in coals. The uncertainties in each of these methods indicate the need for a more reliable method. Methylation by methyl sulfate in base (8) and by diazomethane (6) gives low values, presumably due to incomplete reaction. Ion-exchange, with barium hydroxide (9) may give rise to hydrolysis products and appears to suffer because of inaccessibility in high-rank coals. Potentiometric titration in ethylenediamine (10, 11) determines not only the acidic hydroxyl, but also such groups as quinones and acidic non-hydroxylic hydrogen; this method is also difficult to reproduce. Different procedures have been tried for acetylation as well as for estimating the extent of reaction (6, 12, 13, 14); each worker has reported different values for similar rank coals. The sources of these variations in results are still unexplained.

Comparison of the data in Table 1 and Figures 5 and 6 with published values shows the present ones to be higher than those found by methylation (6, 8), lower than those found by acetylation (6) and ion-exchange (9), and similar to those determined by titration (10, 11) and acetylation (12, 13, 14). Most of the other methods are indirect, and either known side reactions or difficulties in completing the reaction throw doubt on the reliability of the results. On the other hand, the present method is easy and direct, has no known side reactions, and is complete even where other reagents fail altogether.

As concerns the structure of coal, the ease of ether formation may indicate that few highly hindered phenolic groups, such as in 2,6-di-*t*-butylphenol, are present, since this phenol required 24 hours for complete reaction.

Acknowledgments

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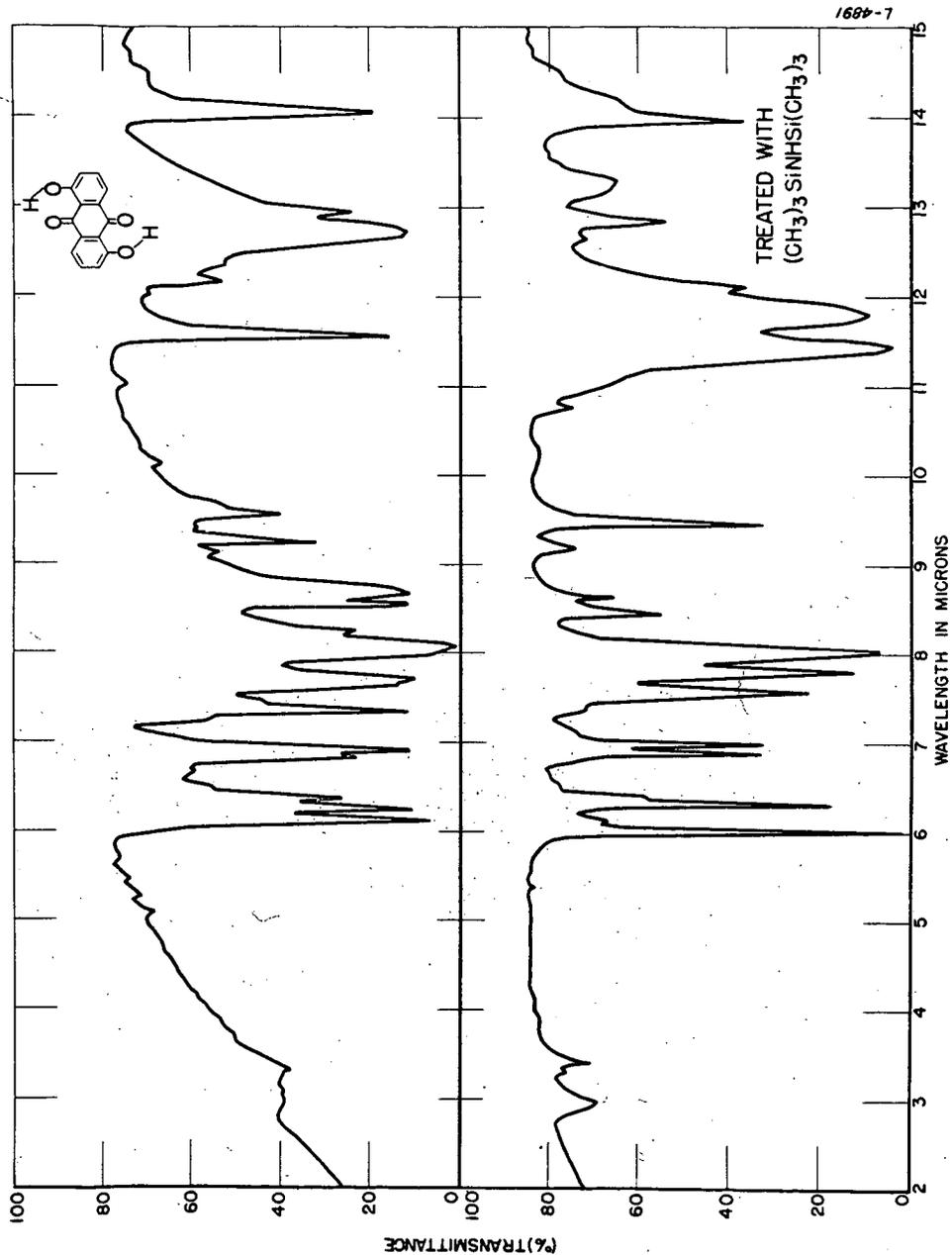


Figure 1 - Infrared spectra of 1,5-dihydroxyanthraquinone and its silyl ether.

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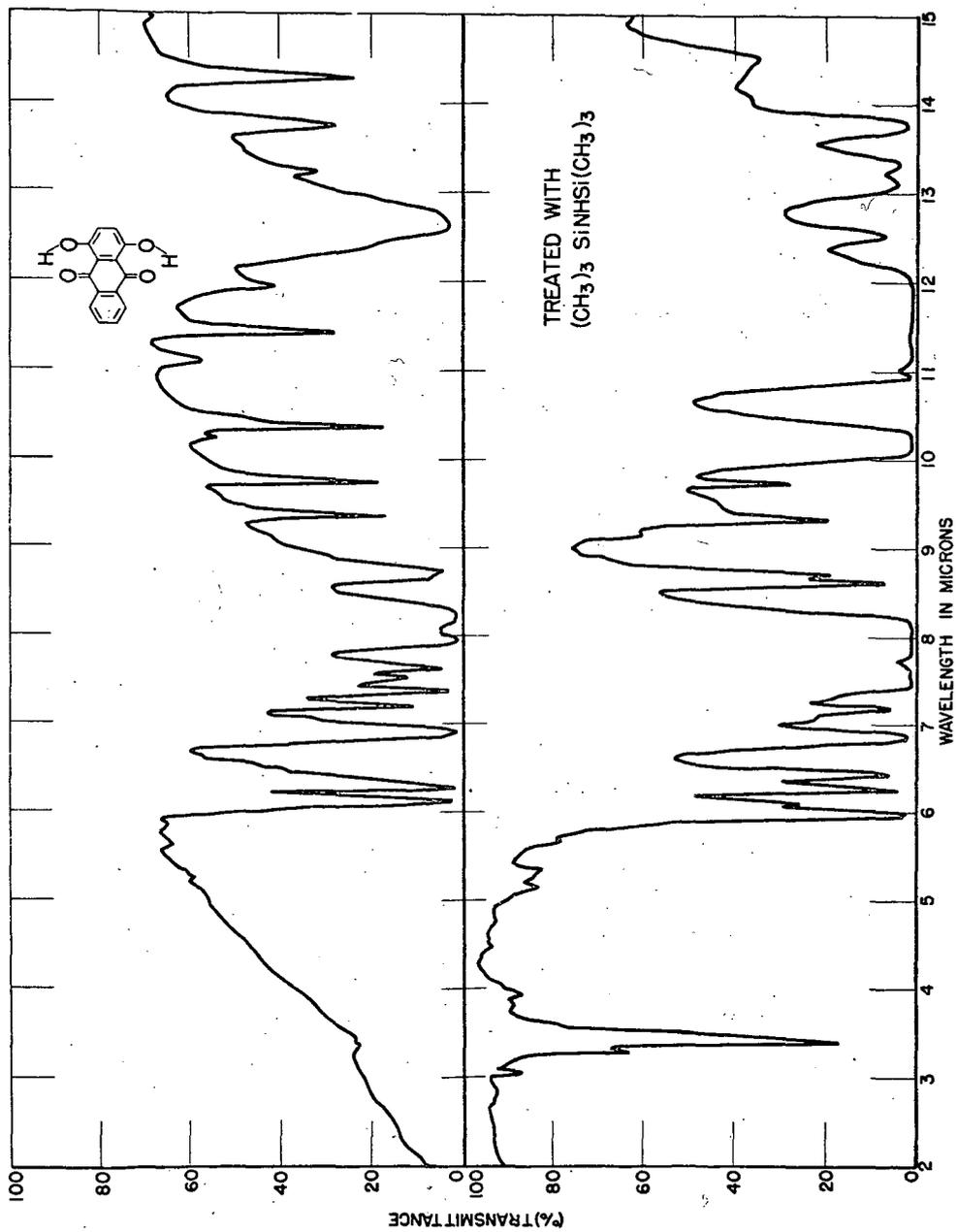


Figure 2.- Infrared spectra of 1,4-dihydroxyanthraquinone and its silyl ether

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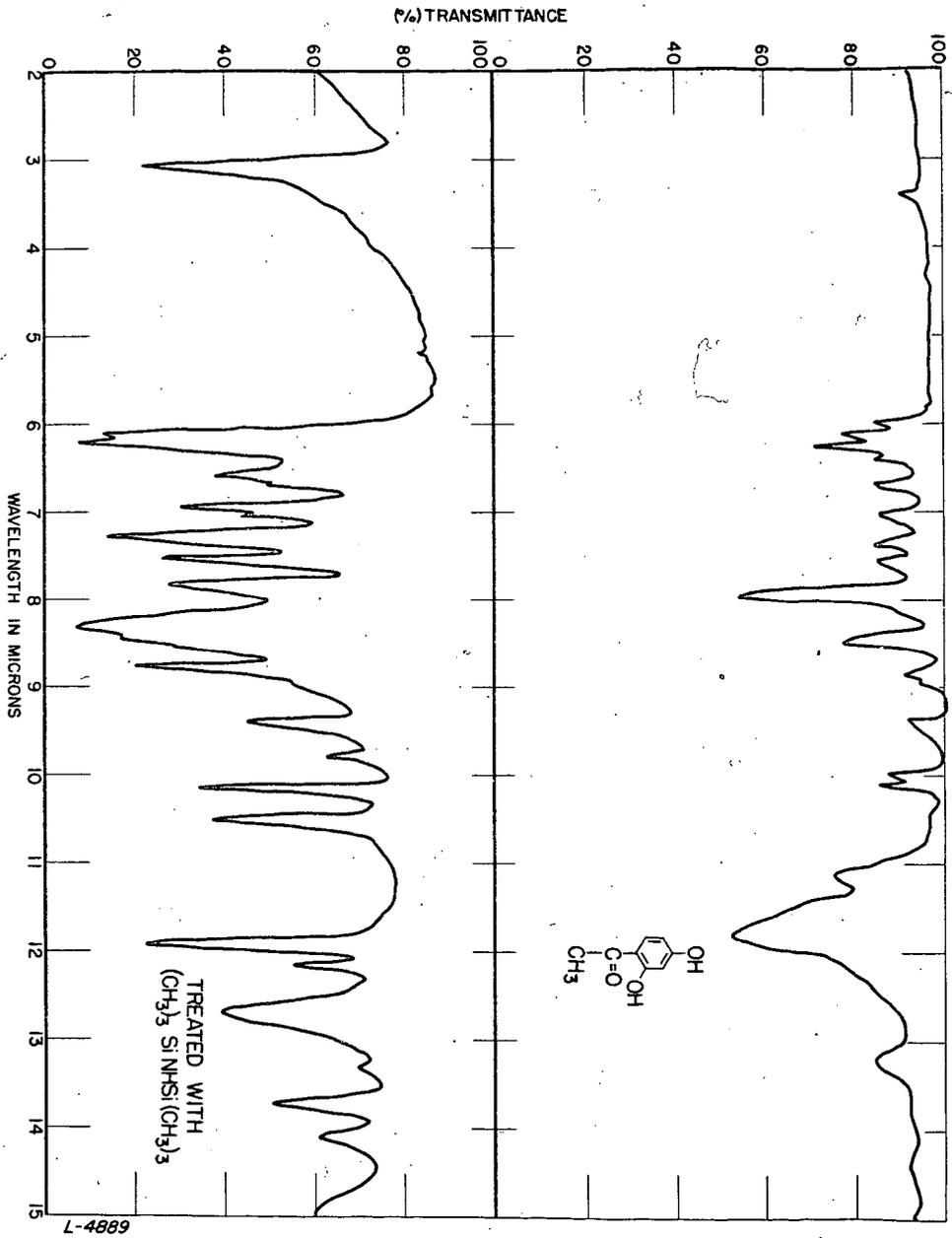


Figure 3.-Infrared spectra of 2,4-dihydroxyacetophenone and its silyl ether.

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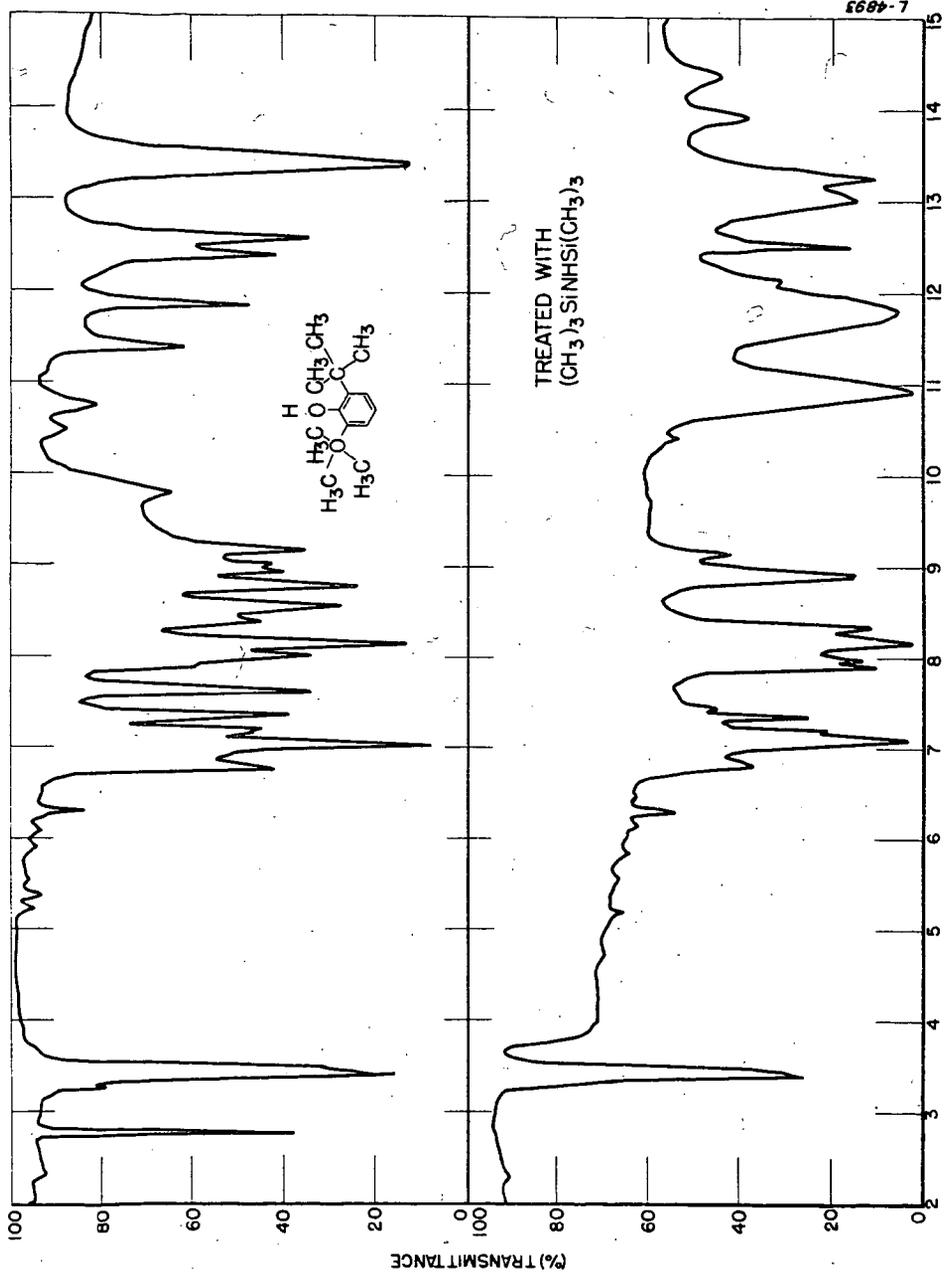


Figure 4.- Infrared spectra of 2,6-di-1-butylphenol and its silyl ether.

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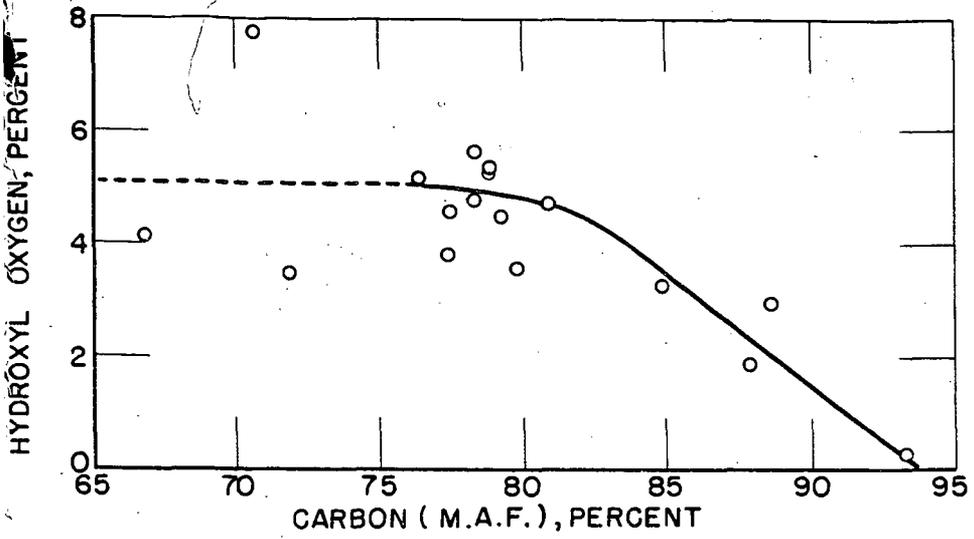


Figure 5.-Percent of hydroxyl oxygen in coals.

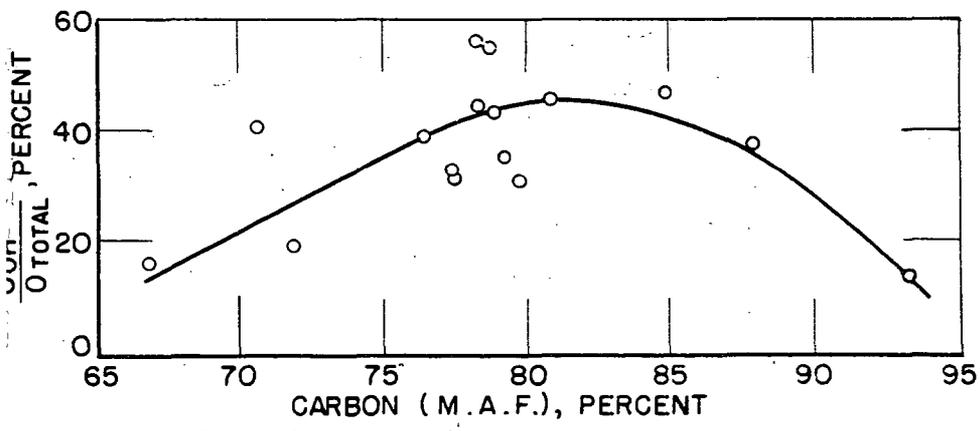


Figure 6.-Ratio of hydroxyl oxygen to total oxygen in coals.

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(4)

Sorption of Polar Vapors on Elastic Wall Gels

Paul Fugassi and George Ostapchenko

Coal Research Laboratory, Dept. of Chemistry
Carnegie Inst. of Technology, Pittsburgh 13, Pa.

From an investigation of the kinetics of methanol sorption on coal, a new sorption isotherm has been derived of the form,

$$W_c = \frac{AK\Sigma}{1 + K\Sigma}$$

$$\Sigma = \frac{K_1 p^0 c}{(1 + (K_1 p^0 - 1)c)(1 - c)}$$

In these equations, W_c is the sorption usually expressed as moles of sorbed vapor per gram of solid, c is the relative pressure of the vapor and p^0 is the vapor pressure of the liquified vapor at the temperature in question. The equation has three adjustable parameters; A , K , and K_1 .

The equation has been applied to the sorption of polar vapors by proteins, nylon and other gels of the elastic wall type. The equation agrees with experiment over a range of relative pressures from 0.1 to 0.9, and also accounts for the effect of temperature changes.

Since the equation was developed on the assumption that surface adsorption is negligible relative to interior absorption, it would appear that sorption of polar vapors by elastic wall gels of the protein and polysaccharide is mainly a solution process.

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Sorption of Polar Vapors on Elastic Wall Gels

Paul Fugassi and George Ostapchenko
Coal Research Laboratory, Dept. of Chemistry
Carnegie Institute of Technology, Pittsburgh (13), Pa.

Summary

From an investigation of the kinetics of methanol sorption on coal, a new sorption isotherm has been derived of the form,

$$W_e = \frac{AK\Sigma}{1+K\Sigma} \quad , \quad \Sigma = \frac{\pi_1 p^0 c}{(1 + (\pi_1 p^0 - 1)c)(1-c)}$$

In these equations, W_e is the sorption usually expressed as moles of sorbed vapor per gram of solid, c is the relative pressure of the vapor and p^0 is the vapor pressure of the liquefied vapor at the temperature in question. The equation has three adjustable parameters, A , K , and K_1 .

The equation has been applied to the sorption of polar vapors by proteins, nylon and other gels of the elastic wall type. The equation agrees with experiment over a range of relative pressures from 0.1 to 0.9 and also accounts for the effect of temperature changes.

Since the equation was developed on the assumption that surface adsorption is negligible relative to interior absorption, it would appear that sorption of polar vapors by elastic wall gels of the protein and polysaccharide types is mainly a solution process.

Introduction

Recent kinetic investigations made in this laboratory on the sorption of gaseous methanol by coal(1) and cellulose(2) have shown that both coal and

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1. P. Fugassi, G. Ostapchenko, and R. Trammell, Fuel
 2. P. Fugassi and G. Ostapchenko,
-

cellulose follow the same rate equation,

$$W = \frac{k_x W_e^2 t}{1 + k_x W_e t}$$

In this equation W is the weight of alcohol taken up by one gram of solid at time t , W_e is the corresponding weight at infinite time, t is the time and k_x is the experimental velocity constant. On the basis of fragmentary data in the literature and unpublished data from this laboratory it appears that a rate equation of this form would be expected if the gas is a polar compound and if the solid is an elastic wall gel composed of oxygen containing compounds.

For methanol sorption on cellulose the experimental velocity constant involves the fraction of surface sites holding two methanol molecules per site and from this fact the adsorption of methanol on the surface of cellulose is

known to be of the multilayer type. The dependence of k_x upon the surface sites holding two methanol molecules gave a new sorption equilibrium isotherm of the following type.

$$W_e = \frac{AK\Sigma}{1+K\Sigma} \quad (1)$$

$$\Sigma = \frac{K_1 p^0 c}{(1 + (K_1 p^0 - 1)c)(1-c)} \quad (2)$$

In equation 1, W_e is the equilibrium sorption in moles per gram of solid at some fixed temperature, A is a constant being moles of interior sites per gram of solid, and K is a dimensionless equilibrium constant. In equation 2, K_1 is an equilibrium constant (atm.^{-1}) for the adsorption of methanol on surface sites, p^0 is the vapor pressure (atm.) of the liquefied vapor at the temperature in question, and c is the relative pressure of the vapor.

The mechanism which leads to these equations is that vapor is rapidly adsorbed on the surface sites and then adsorbed molecules slowly migrate from the surface into the solid phase.

Equation 1 really gives the amount of vapor dissolved in the solid. The total amount of vapor held by the solid is obviously the sum of two terms; the adsorption on the surface and the absorption in the interior. Thus,

$$(W_e)_{\text{total}} = (W_e)_{\text{interior}} + (W_e)_{\text{surface}}$$

For the total amount of vapor held by the solid, which is the experimental quantity measured, the full equation is,

$$(W_e)_{\text{total}} = \frac{AK\Sigma}{1+K\Sigma} + Bf(c) \quad (3)$$

In equation 3, B represents moles of surface sites per gram of solid.

The nature of $f(c)$ is not completely known. If $f(c)$ is Σ , the full equation would have four parameters; A , B , K_1 and K . However, Σ is really the BET equation for an infinite number of layers and approaches infinity as c approaches 1. For this reason $f(c)$ must be a modified BET equation where adsorption is restricted to n layers. The use of a modified BET equation introduces five parameters and this number of parameters is meaningless when only equilibrium data are available. Kinetic data if available would permit independent evaluation of one of the parameters. However such data are not available for most of the systems to be discussed here.

In applying the full equation (3) to the data in the literature the assumption will be made that B approaches zero. Experimentally there is evidence that in the case of methanol sorption on cellulose this assumption is valid. In this case the amount of methanol adsorption on the surface appears to be less than ten percent of the total weight of methanol held by the cellulose. However an assumption of this type would be expected to effect the behavior of the equation at low values of c . Accordingly the discussion which follows uses the partial equation (1) and is limited to a range of relative pressures from 0.1 to higher values. Equation 1 will be applied to some of the data available in the literature on the sorption of polar molecules by elastic wall gels.

Sorption of Water by Proteins

A comprehensive study of water sorption by various proteins has been published by Bull(3). He showed that the experimental data fitted the BET

3. H. B. Bull, J. Am. Chem. Soc., 66, 1499 (1944)

equation up to relative pressures of 0.4-0.5 excepting salmin where two different sets of constants in the BET equation were required. In general application of the new equation shows that the experimental data are followed up to relative pressures of 0.9 or greater. A comparison of experimental and calculated values of W_e for the sorption of water on wool are given in Table I.

c	$W_e \times 10^3$ (expt.)	$W_e \times 10^3$ (calc.)	W_e (calc. - expt.)
0.1	2.36 moles/gram	2.06 moles/gram	-0.3 moles/gram
0.2	3.47	3.56	+0.09
0.3	4.57	4.54	-0.03
0.5	6.35	6.38	+0.03
0.7	8.67	8.71	+0.04
0.9	12.52	12.46	-0.06

As previously mentioned the use of equation 3 would give better agreement at low values of c .

Equation 1 has three parameters; A , K , and K_1 . A tabulation of the values of these parameters for the sorption of water on various proteins is given in Table II.

Protein	K_1 (atm. ⁻¹)		K		A (moles sites/gram)	
	25°C.	40°C.	25°C.	40°C.	25°C.	40°C.
	Wool	173.18	65.02	0.4133	0.4346	0.0155
Salmin	228.23	155.70	-0.0052	-0.0232	.8334	.1669
Gelatin	280.32	89.22	.2500	.3286	.0289	.0239
Collagen	315.56	85.04	.2473	.3057	.0317	.0273
β -Lactoglobulin (crystals)	182.67	71.99	.2117	.2157	.0240	.0225
Silk	213.53	80.03	.2772	.3038	.0127	.0113
C-Zein	305.67	114.72	.1842	.2401	.0148	.0118
B-Zein	283.47	132.86	.2308	.2363	.0128	.0115

The values of the equilibrium constant, K_1 , in Table II are for the reaction, $H_2O(g) + S \rightleftharpoons S \cdot H_2O$. In this equation S represents surface sites. It will be noted that K_1 always decreases as temperature increases. The heat of reaction associated with the change in K_1 can be calculated by conventional methods. When this is done it is found that the calculated heats of reaction range from 9,400 to 16,200 cal. per mole excluding salmin, and the average value is about 12,000 cal. per mole. It appears that the surface sites on various proteins are very similar as would be guessed from their similar chemical composition.

The values of K in Table II are for the reaction, H_2O (surface) + $D \rightleftharpoons D \cdot H_2O$. Here D represents interior sites. An increase in temperature gives an increase in K . However the change is not great so that the heat of reaction is close to zero or in the extreme case about 3,000 cal. per mole endothermic. The values of K for salmin are negative which is an impossibility. The behavior of salmin is stated by Bull(3) to be different from that of the other proteins. Salmin dissolves at a relative pressure of 0.7 and while for

the other proteins the BET equation is followed to a relative pressure of 0.5, for salmin two BET equations are needed. Pauling(4) suggested that for salmin

 L. L. Pauling, J. Am. Chem. Soc., 67, 555 (1945)

the number of sites increased with increasing sorption of water. The negative values for K could either be blamed on experimental errors in which case the true value of K is a small positive number or a modified sorption equilibrium isotherm must be used. From experience with the equation small values of K represent adsorption on a non-porous solid as will be shown later. It is improbable that experimental error is the cause of the negative value for K. Consequently the second possibility seems more probable.

In the derivation of the sorption equilibrium isotherm where K is the equilibrium constant of the reaction, $H_2O(\text{surface}) + D \rightleftharpoons D \cdot H_2O$, it was assumed that the effective concentrations to be used were Σ , $(1 - \phi)$, and ϕ for adsorbed water, empty interior sites (D), and filled interior sites ($D \cdot H_2O$) respectively. These formulations for D and $D \cdot H_2O$ are equivalent to the assumption that the number of sites is independent of the amount of adsorption as found experimentally for the sorption of methanol by cellulose. If the Pauling suggestion is adopted that the number of interior sites per gram increases as sorption increases then the effective concentration of unoccupied sites should be given by $1 - \phi + f(\phi)$. The nature of $f(\phi)$ is unknown but if $f(\phi)$ is expressed as $\alpha\phi$ where α is an adjustable parameter then the resulting values of K for salmin are positive and the equation for the sorption equilibrium isotherm becomes,

$$W_e = \frac{AK\Sigma}{1 + K\Sigma(1 - \alpha)}$$

To date only one example, that of salmin, has been found where K is negative with $\alpha = 0$ and until other examples are found it seems unnecessary to introduce the additional parameter,

The values of A, which is moles of interior (D) sites per gram of solid show a small decrease with increase in temperature. Excluding salmin the maximum change in A for a 15 degree temperature interval is of the order of 20%. The average change in A is about half of this. It would be anticipated that A would be independent of temperature or change slightly with the temperature.

In discussing Bull's results, Pauling (4) correlated the number of water molecules held in the first layer as calculated from the BET equation with the number of polar side groups present in the protein chain and found approximately a one to one correspondence. Taking Pauling's values for the moles of polar side groups per gram of protein and dividing these values into the previously listed values for A, ratios are obtained ranging from 3 to 5. These ratios are interpreted as meaning that each polar side group introduces sufficient disorder into a protein lattice that 3 to 5 water molecules are held in these disordered regions. With this modification the mechanism of the sorption of polar molecules by proteins as deduced from the new isotherm is essentially identical with the concepts of Bull and Pauling.

Sorption of Polar Molecules by Nylon

Nylon is a condensation polymer of the polypeptide type with no polar side groups. In Table III are listed the values of A, K, and K_1 calculated for the sorption of various polar vapors on Nylon 66.

Table III
Sorption of Polar Vapors on Nylon 66

Ref.	Vapor	State	T	K_1 (atm. ⁻¹)	K	A (moles sites/gram)
3	H ₂ O	Unstretched	25°C.	105.42	0.2184	0.00688
3	"	"	40	27.63	0.3336	0.00551
3	"	Stretched	25	95.56	0.3717	0.00473
3	"	"	40	31.24	0.4235	0.00417
5	"	?	40	32.65	0.1825	0.00754
5	CH ₃ OH	"	25	12.66	0.1128	0.01412
5	C ₂ H ₅ OH	"	25	22.96	0.2240	0.00695
5	C ₂ H ₅ CN	"	25	30.15	0.2797	0.00116

5. J. A. Cutler and A. D. McLaren, *Tappi*, **36**, 423 (1953)

For the results in Table III it will be noted that the sorption of water by nylon is much less than the sorption of water by proteins as indicated by the lower values for A. The lower values for A for nylon indicate as is known from other evidence that nylon has a high degree of order or a low degree of disorder. Part of the disorder in nylon must arise from the fact that the chain length of the nylon polymer is much smaller than that in natural polymers. Each chain end can be considered as a disturbance center in the vicinity of which disorder must occur. The molecular weights of the particular nylon samples are not known but if the chains have an average molecular weight of 10,000 then the number of disturbance centers would be 2×10^{-4} centers per gram of nylon. From the protein data it appears that each polar side group or one disturbance center furnishes sorption sites for 5 molecules of water. If we use the same assumption, the value of A for nylon would be 1×10^{-3} sites per gram in comparison with the experimental value of 4 to 5×10^{-3} sites per gram. Exact agreement would require an average molecular weight for nylon of 2,000 to 2,500.

In the disordered regions complete hydrogen bonding between adjacent chains has not taken place. Sorption is probably limited to such regions as it is unlikely that molecules of any vapor can permeate any region having high order. As shown from the data in Table III, stretched nylon has lower disorder than the unstretched material.

It is interesting to note that the values of A vary with the nature of the vapor undergoing sorption. The value of A decreases in going down the series; CH₃OH, C₂H₅OH, and C₂H₅CN. This change in A is probably caused by the increase in molecular size in going from CH₃OH to C₂H₅CN. In other words all types of disordered regions are present ranging from those which can only be permeated by CH₃OH to those sufficiently disarranged to accommodate all polar molecules whose size is equal to or less than that of the C₂H₅CN molecule. Although H₂O as a small molecule would be expected to permeate as many disordered regions as any other molecule nevertheless the A values indicate that it is not as good as CH₃OH but is better than C₂H₅OH. The reason for this discrepancy is not known but it may involve the fact that the H₂O molecule can be considered multifunctional with respect to hydrogen bonding if the spacial configuration is just right.

Sorption of Methanol on Various Polymers

The sorption of methanol on coal and other natural polymers has been under investigation in this laboratory for several years. These data fit the sorption equilibrium isotherm. The values of A, K, and K_1 are tabulated in Table IV.

Table IV
Sorption of Methanol on Natural Polymers

Ref.	Solid	T	K_1 (atm. ⁻¹)	K	A (moles sites/gram)
2	Cotton linters	30°C.	14.51	0.7472	0.00261
"	" "	35	13.60	0.6505	0.00265
"	" "	45	9.91	0.5844	0.00264
6	Kincaid Lignite	45	44.13	0.5229	0.09444
"	Wyoming Coal	45	16.04	0.9037	0.00648
1	Pittsburgh Coal	30	21.61	1.8941	0.00170
1	" "	35	29.55	1.1859	0.00172
1	" "	40	32.00	1.1700	0.00180

6. P. Fugassi and G. Ostapchenko, unpublished

The solids in Table IV have been listed in order of decreasing oxygen content. Cellulose is considered a precursor of coal and if cellulose is considered as the lowest rank coal having zero geologic age, then the solids are listed in order of increasing rank. It will be noted that A has at first a low value, rises to a high value and then decreases. The low value of A for cellulose is due to high order being present. With increasing age and rank order is destroyed and simultaneously oxygen content decreases. The low values of A for Pittsburgh Seam coal is not due to order but arises from the small amount of oxygen containing gel present in the coal. For Pittsburgh Seam coal the values of K_1 increase as temperature increases. This is the only system for which this behavior has been found.

Other Systems

Data are in the literature for a wide variety of possible combinations such as polar and non-polar gases on non-porous solids, polar compounds on porous, inelastic wall gels, etc. The sorption equilibrium isotherm has been applied to such systems although the properties of these systems are not in agreement with those assumed for the derivation of the equation. It is found that the experimental data can be fitted to relative pressures of 0.9. A tabulation of these data are given in Table V.

Table V
Values of Parameters for Various Systems

Ref.	Adsorbent	Adsorbate	T	K_1 (atm. ⁻¹)	K	A (moles sites/gram)
7	Charcoal	n-caproic acid-H ₂ O	25°C.	266.1	0.3439	0.00112
"	"	n-amyl alcohol-H ₂ O	"	68.8	0.5221	0.00093
"	"	phenol-H ₂ O	"	27.3	0.7416	0.00112
8	Ag	n-C ₄ H ₁₀	-78°	336.6	0.0282	0.00034
"	"	CHCl ₂ F	"	1398.5	0.0161	0.00052

7. R. S. Hanson, Y. Fu, and F. E. Bartell, J. Phy. Chem., 53, 769 (1949)
8. R. T. Davis, Jr.; T. W. DeWitt, P. H. Emmett, J. Phy. Chem., 51, 1232 (1947)

For such systems the equation must be considered as empirical. Ag is a non-porous solid and has a low value for A. Increased polarity of the gas increases K_1 (n C₄H₁₀ relative to CHCl₂F). While the sorption equilibrium isotherm

must be considered as empirical for these systems, it is possible that such an equation might be valid for non-porous solids if the surface is heterogeneous and composed of two types of sites having properties similar to the S and D sites postulated for elastic wall gels.

3

The Kinetics of the Sorption of Methanol on Cellulose

Paul Fugassi and George Ostapchenko

Coal Research Laboratory, Dept. of Chemistry,
Carnegie Institute of Technology, Pittsburgh 13, Pa.

The sorption of gaseous methanol on cellulose has been studied at 30, 35, and 45°C. The process follows a second order equation and has an activation energy of 5,700 cal per mole. A mechanism for the sorption process is suggested involving adsorption of methanol on the surface followed by permeation of the solid by methanol molecules. The kinetic data require that the surface adsorption be of the multilayer type. From the kinetic data a new sorption equilibrium isotherm is derived which fits the experimental equilibrium data over the entire pressure range studied, from a relative pressure of 0.1 to a relative pressure of 0.9. From this equation and from equilibrium data for the adsorption of tertiary butyl alcohol on cellulose it is shown that most of the methanol held by cellulose is dissolved in the cellulose.

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The Kinetics of the Sorption of Methanol on Cellulose

Paul Fugassi and George Ostapchenko
Coal Research Laboratory, Dept. of Chemistry
Carnegie Institute of Technology, Pittsburgh (13), Pa.

Summary

The sorption of gaseous methanol on cellulose has been studied at 30, 35, and 45°C. The process follows a second order equation and has an activation energy of 5,700 cal. per mole. A mechanism for the sorption process is suggested involving adsorption of methanol on the surface followed by permeation of the solid by methanol molecules. The kinetic data require that the surface adsorption be of the multilayer type. From the kinetic data a new sorption equilibrium isotherm is derived which fits the experimental equilibrium data over the entire pressure range studied, from a relative pressure of 0.1 to a relative pressure of 0.9. From this equation and from data for the adsorption of tertiary butyl alcohol on cellulose it is shown that most of the methanol held by cellulose is dissolved in the cellulose.

Introduction

For the sorption of methanol on coal, it was found that the weight of methanol taken up at time t at some constant pressure and at constant temperature was given by the equation

$$W = \frac{k_x W_e^2 t}{1 + k_x W_e t}$$

In this equation W is the weight of methanol held by one gram of coal at time t , k_x is the experimental velocity constant, and W_e is the maximum weight of alcohol held by one gram of coal at the given temperature and pressure. The experimental velocity constant, k_x , was found to be independent of the pressure over a considerable range of pressure and hence is a true velocity constant in the sense that it is a function of the temperature only.

Limited data in the literature appeared to show that the same equation was valid for the sorption of polar gases on elastic wall gels such as cellulose. As cellulose is considered one of the precursors of coal it was thought desirable to investigate the kinetics of methanol sorption on cellulose in detail.

Experimental

Apparatus: The sorption of methanol on cellulose was measured gravimetrically, using a McBain-Bakr type adsorption balance. The spring was made of Ni-Span-C wire and had a sensitivity of 1.57 milligrams per millimeter extension. Spring lengths were measured by a cathetometer to 0.1 mm. The sample, in the form of fibers, was carried in a glass bucket weighing around 200 milligrams. Sample weights were about 300 milligrams. The apparatus consisted of the balance, a

2-liter flask to add sufficient volume to the system so that during sorption experiments the methanol pressure did not vary more than 1 mm. Hg., a Hg manometer, and a storage flask for the methanol. Mercury sealed stopcocks were used throughout. The pumping system was a two-stage Hg diffusion pump backed by a mechanical pump. The entire apparatus was housed in an air thermostat whose temperature could be held to $\pm 0.1^\circ\text{C}$.

Chemicals: Absolute methanol, Mallinckrodt A.R. was used as received. It was stored over Drierite. Tertiary butanol was redistilled. The sample of cellulose was prepared for us by the Hercules Powder Co. Cotton linters were washed with NaOH solution, bleached with Cl_2 and then washed with distilled water. No further treatment of the material was made except that before the start of kinetic experiments a cellulose sample, after evacuation to constant weight, was allowed to remain in contact with methanol vapor for several days. The sorption of methanol on cellulose is isothermally reversible; evacuation of the system always caused the cellulose to return to a weight practically identical with the starting weight.

Procedure: After evacuation of the system until the cellulose sample showed constant weight, methanol vapor was admitted to the system and readings of the spring length taken at various times. The spring lengths were converted into weights making no correction for buoyancy which can be shown to be negligible or for adsorption of methanol on the glass bucket and spring. Experiments using an empty bucket showed that methanol adsorption on the glass bucket and the metal spring could be neglected up to relative pressures as high as 0.9. The fundamental data, then, are weights at known time intervals including the equilibrium weights characteristic of each pressure.

Calculation of Velocity Constants

From the experimental data, a value of the fraction of the reaction, f , could be calculated for each value of the time. f is defined as $\frac{W_t - W_0}{W_e - W_0}$ where W_0 is the sample weight at time, $t = 0$, W_t is the weight at $t = t$, and W_e is the equilibrium weight at time $t = \infty$. The value of $\frac{t}{1-f}$ was plotted against the time giving straight lines through the origin. The slope of this straight line is $k_x W_e$ and since W_e is measured for each pressure and temperature k_x can be calculated. In general, points fell on a straight line and the line passed through the origin. In all experiments readings were taken until at least 80% of the equilibrium sorption was attained. At low pressures, $c = 0.1$, experimental points corresponding to the initial stages of the reaction were above the straight line. This behavior will be discussed later.

Experimental Data

The experimental values of k_x and W_e are tabulated in Table I.

T (°C.)	Table I Experimental Values, k_x and W_e		
	c	k_x ($\frac{\text{gr. cellulose}}{\text{moles CH}_3\text{OH-hrs.}}$)	W_e ($\frac{\text{moles CH}_3\text{OH}}{\text{gr. cellulose}}$)
30	0.894	5.8×10^3	22.6×10^{-4}
	0.700	16.3 "	18.1 "
	0.500	19.2 "	13.6 "
	0.306	7.9 "	10.0 "
	0.125	2.5 "	5.3 "
35	0.848	16.4 "	21.1 "
	0.669	21.4 "	17.3 "
	0.486	29.0 "	12.9 "
	0.268	13.0 "	8.8 "
	0.119	1.9 "	5.1 "
45	0.863	9.3 "	21.2 "
	0.697	26.7 "	16.9 "
	0.491	31.0 "	13.1 "
	0.294	13.1 "	8.8 "
	0.088	1.9 "	4.5 "

It will be noted that the value of the experimental velocity constant passes through a maximum as the relative pressure, c , decreases.

Since a true velocity constant, k , must be a function of temperature only, the experimental velocity constant, k_x , must be equal to k multiplied by some function of the relative pressure, c . Separation of k from k_x requires that a mechanism of the process be formulated. Even such an operation does not insure that k is actually known because both velocity constants and equilibrium constants have a similar dependence on temperature. In other words, independent equilibrium data are needed to make sure that the term k is really not k multiplied by an equilibrium constant.

It will be necessary to anticipate the discussion of the mechanism for the sorption process to be given later. It is postulated in brief that the mechanism of the sorption process is a two-step process. The first step, known experimentally and theoretically to be rapid, is the adsorption of methanol molecules on the surface of the cellulose. The second step, which determines the reaction rate as the slower step, is the migration of methanol from the surface into the interior. From this type of a mechanism it is necessary that in the simplest case

$$k_x = k \Theta$$

where k_x is the experimental velocity constant, k is the true velocity constant and Θ is the fraction of the surface sites covered.

Now the surface adsorption of methanol on cellulose can be of two types: monomolecular with one methanol molecule on one site or polymolecular with more than one methanol molecule on one site. For monomolecular adsorption, the Langmuir adsorption isotherm holds and it can be shown that Θ increases as c increases for all values of c . Since k_x goes through a maximum, Θ likewise must go through a maximum as c increases. Consequently the surface adsorption of methanol on cellulose cannot be monomolecular. For polymolecular adsorption, the only alternative, the surface adsorption at a given temperature will be shown to be given by the equation

$$\Theta_n = \frac{(K_2)^{n-1} K_1 (c p^0)^n (1 - K_2 p^0 c)}{1 + K_1 p^0 c - K_2 p^0 c}$$

In this equation Θ_n is the fraction of surface sites covered by n molecules and K_1, K_2 are equilibrium constants whose significance will be discussed later. c is the relative pressure and p^0 , the vapor pressure of methanol at the temperature in question. The product, cp^0 , is the pressure of methanol vapor actually present. Insertion of values of one, two, or three for n gives $\Theta_1, \Theta_2, \Theta_3$, the fraction of surface sites covered by one, two, or three molecules. It will be noted that the expression for Θ_n contains two parameters, K_1 and K_2 . From three kinetic experiments at different values of c but at the same temperature, k, K_1 , and K_2 can be evaluated in turn for $\Theta_1, \Theta_2, \Theta_3$.

In figure I is shown a plot of Θ_n as a function of c for $n = 1, 2, 3, 4$. It was found that the experimental values of k_x used in the equation, $k_x = k \cdot \Theta_2$ gave the best fit of the experimental data. Figure II is a plot of $k \cdot \Theta_2$ against c . The points are the experimental points. The solid line is the calculated line using 8.1×10^4 as the value of k (k_{true}) at 30°C .

The values of $K_2 p^0$ evaluated at three temperatures are 1.07, 1.03, and 1.05. These values of $K_2 p^0$ are sufficiently close to one that these kinetic data are experimental evidence for the correctness of the assumption, $K_2 p^0 = 1$, made in the derivation of the BET equation.

With this assumption, the equation for Θ_2 simplifies into

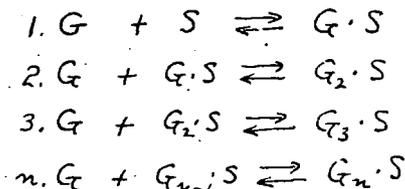
$$\Theta_2 = \frac{K_1 c^2 p^0 (1-c)}{1 + (K_1 p^0 - 1)c}$$

From this equation and from the equation, $k = k_x \Theta_2$, the values of K_1 and k can be obtained. However the values of K_1 can also be obtained from the equilibrium isotherm and as the equilibrium measurements have the higher precision, it seems desirable to use these values in calculating k . The values of $K_1 p^0$, as evaluated from the equilibrium isotherm at 30, 35, and 45°C . are 3.0, 3.6 and 4.2 respectively. The corresponding average values of k in units of $\frac{\text{grams cellulose}}{\text{moles CH}_3\text{OH} \cdot \text{hours}}$ for the three temperatures are: at 30°C ., 8.1×10^4 ; at 35°C ., 10×10^4 ; and at 45°C ., 12.7×10^4 . These values substituted in the Arrhenius equation give 5,700 cal. per mole as the average energy of activation. This low value for the energy of activation is evidence that the sorption process is physical in nature.

Equilibrium Sorption Isotherm

The full solution of the kinetic problem in closed equation form requires that W_e , the equilibrium sorption, be expressed as a function of the relative pressure, c , and the temperature, T . The kinetic data are informative and permit the derivation of an equation for the equilibrium sorption isotherm. The sorption of methanol by cellulose can be visualized as a two-step process: 1. Adsorption of methanol on the surface, and 2. Migration of methanol from the surface into the interior.

For the surface adsorption, the following equations hold:



In these equations G represents the gas molecule; S the surface sites; G·S, the surface sites holding one gas molecule; G₂·S, the surface sites holding two gas molecules, etc.

If θ_1 represents the fraction of surface sites holding one molecule; θ_2 , the fraction of surface sites holding two molecules; θ_n , the fraction of surface sites holding n molecules; then the equilibrium constants would be expressed as

$$K_1 p^0 = \frac{\theta_1}{(1 - \theta_1 - \theta_2 - \dots - \theta_n) c}$$

$$K_2 p^0 = \frac{\theta_2}{\theta_1 c}$$

$$K_n p^0 = \frac{\theta_n}{\theta_1^{n-1} c}$$

where p^0 is the vapor pressure of the liquid and c is the relative pressure.

Further manipulation of these equations requires some simplifying assumptions connecting the equilibrium constants. If it is assumed that $K_1 > K_2$ and $K_2 = K_3 = K_n$, two assumptions similar to the ones made in derivation of the BET equation (1), then it can be shown that

 1. S. Brunauer, P. H. Emmett, and E. Teller, J. Am Chem. Soc., 60, 309 (1938)

$$\theta_1 = \frac{K_1 p^0 c (1 - K_2 p^0 c)}{1 + (K_1 - K_2) p^0 c}$$

$$\theta_2 = K_2 p^0 c \theta_1$$

$$\theta_n = (K_2 p^0 c)^{n-1} \theta_1$$

These equations were applied to the kinetic data and it was shown that the kinetic data make two facts obvious: 1. The adsorption of methanol on cellulose involves more than one molecule for one surface site, and 2. $K_2 p^0 = K_3 p^0 = K_n p^0 = 1.0$.

To determine the adsorption isotherm a term, Σ , will be defined as

$$\Sigma = \theta_1 + 2\theta_2 + 3\theta_3 + \dots + n\theta_n$$

Σ is a concentration unit representing moles of adsorbed molecules for 6.02×10^{23} occupied sites or one mole of sites. It has been shown (1) that Σ is given by the equation,

$$\Sigma = \frac{\theta_1}{(1 - K_2 p^0 c)^2}$$

and using the condition that $K_2 p^0 = 1$ this equation reduces to

$$\Sigma = \frac{\theta_1}{(1-c)^2} = \frac{K_1 p^0 c}{(1 + (K_1 p^0 - 1)c)(1-c)}$$

which is essentially the BET equation, for multiplying Σ by a constant representing moles of sites for one gram of solid gives w_e , the equilibrium adsorption in moles per gram.

The second stage of the sorption process involves the migration of molecules adsorbed on the surface into the interior. This reaction can be represented by the equation,



In this equation D represents interior sites. Calling ϕ the fraction of D sites holding methanol molecules, the equilibrium constant, K, for the above reaction can be written as

$$K = \frac{\phi}{(1-\phi)\Sigma}$$

and solution of this equation for ϕ gives

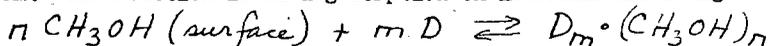
$$\phi = \frac{K\Sigma}{1+K\Sigma}$$

and the amount of sorption, W_e , is given by the equation

$$W_e = \frac{AK\Sigma}{1+K\Sigma}$$

where A is moles of interior sites for one gram of solid. In setting up the last equation it has been assumed that the measured equilibrium sorption is the sorption on interior sites or, in other words, the surface adsorption contributes very little to the total sorption. An experimental and theoretical justification of this assumption will be given later.

It should be pointed out that the particular equation for W_e is not the general form. The reaction involving sorption on internal sites might be,



In all cases examined to date, $n = m = 1$. Furthermore it has been assumed by using $1 - \phi$ for the concentration of empty internal sites that the number of sites is independent of the amount of sorption. If sorption leads to the formation of new sites, by expansion of the gel, then the concentration of empty internal sites would be of the form, $(1 - \phi + f(\phi))$. To date, no definite experimental evidence has been found which requires the use of a site-expansion term.

The sorption isotherm derived here, which is

$$W_e = \frac{AK\Sigma}{1+K\Sigma}$$

$$\Sigma = \frac{K_1 p^0 c}{(1 + (K_1 p^0 - 1)c)(1-c)}$$

is an equation involving three parameters, A, K, K_1 . It has been found to fit the equilibrium data in the literature for the sorption of polar gases by elastic wall gels. The extension of this equation to other systems will be the subject of a subsequent paper. But it can be stated that in general it will fit many systems up to relative pressures of 0.9 or greater.

The equation fits the equilibrium data for methanol sorption on cellulose also to 0.9. Application of the equation to the methanol-cellulose system gives the constants listed in Table II.

Table II
Constants for Methanol Sorption on Cellulose

Temp.	K_1	K	A
30°C.	14.51 atm. ⁻¹	0.75	2.61×10^{-3} moles D sites/ gram
35	13.60	0.65	" " " " "
45	9.91	0.58	2.64 " " " " "

The values of K in Table II, are dimensionless because Σ , used in K, represents a dimensionless quantity, the average number of adsorbed molecules held by one occupied surface site. It will be noted that A is independent of the temperature

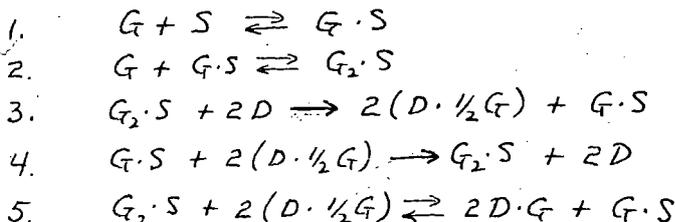
as would be expected. K_1 and K vary in the normal manner with the temperature. Using the equation, $\Delta F^\circ = -RT \ln K$, and evaluating ΔH from a plot of $\ln K$ against the reciprocal of the absolute temperature ΔF° , ΔH and ΔS for surface adsorption (K_1) and for interior sorption (K) can be evaluated. These quantities have been tabulated in Table III.

Equilibrium	Temp.	ΔF°	ΔH	ΔS
	30°C.	-1610 cal./mole	-5080 cal./mole	-11.5 cal./degree
Surface	35 "	-1600 " "	" " "	-11.3 " "
K_1	45 "	-1450 " "	" " "	-11.4 " "
Interior	30°C.	530 cal./mole	-1830 cal./mole	-7.8 " "
K	35 "	600 " "	" " "	-7.9 " "
	45 "	660 " "	" " "	-7.8 " "

Thermodynamic data derived from measurements over limited temperature ranges would be expected to have low precision so that conclusions drawn from such data cannot be too definite. The heat of condensation of methanol vapor in the temperature range from 30° to 45°C. is known to vary but assuming a constant value over this temperature range the heat of condensation is approximately -8,600 cal. per mole. The fact that the value of ΔH for the interior sorption (D sites) differs greatly from the heat of condensation indicates that the interior sorption cannot consist of a large number of methanol molecules clustered near one site. In general, clustering of methanol molecules so that interaction of methanol molecules with methanol molecules takes place should lead to higher values of the heat of reaction for the interior sorption than those observed.

Reaction Mechanism

The following reaction mechanism is suggested for the kinetics of methanol sorption on cellulose:



Reactions 1 and 2 represent the adsorption of the gas on S (surface) sites. Obviously additional reactions leading to the formation of species like $G_3 \cdot S$, $G_4 \cdot S$ are also involved but are not necessary for explanation of the kinetic data. All reactions involving surface adsorption of the physical type are known to be rapid both on theoretical and experimental grounds. The double arrow is used to indicate that these reactions are in equilibrium.

Reaction 3 is the slow rate-determining reaction for the sorption process. A molecule from a site of the $G_2 \cdot S$ type migrates into the interior and is held on two D (internal) sites. Two internal sites are required to explain

the second order kinetics found experimentally. The nature of these sites will be discussed later. Reaction 4 is the reverse of reaction 3 and is necessary to account for the reversibility of the sorption process. Reaction 5 is a rapid equilibrium type reaction. It is postulated to have one G molecule held on one D site, which is indicated to be the case from the previously derived sorption isotherm.

Using W to be $W_t - W_0$ or the increase in weight at time, t , and W_e to be $W_\infty - W_0$ or the increase in weight at infinite time, the differential equation for the process is,

$$-\frac{dW}{dt} = k_3 \theta_2 (w_e - w)^2 - k_4 \theta_1 (w)^2$$

Since f , the fraction of reaction, is $\frac{W}{W_e}$, this equation can be arranged to give

$$\frac{df}{dt} = k_3 \theta_2 w_e (1-f)^2 - k_4 \theta_1 w_e f^2$$

Let B designate the term, $\frac{k_4 \theta_1}{k_3 \theta_2}$. Introduction of B gives

$$\frac{df}{dt} = k_3 \theta_2 w_e [(1-f)^2 - Bf^2]$$

which on integration and substitution of limits gives,

$$k_3 \theta_2 w_e t = \frac{1}{2\sqrt{B}} \ln \frac{1-f(1-\sqrt{B})}{1-f(1+\sqrt{B})}$$

Unfortunately, this equation is difficult to handle numerically because of the appearance of B in the \ln term. However, the experimental data indicate, that at higher pressures corresponding to higher values of c , B becomes smaller since θ_1/θ_2 is $1/c$. If B can approach a small number then the differential equation simplifies to

$$\frac{df}{dt} = k_3 \theta_2 w_e (1-f)^2$$

which on integration and substitution of limits give

$$k_3 \theta_2 w_e t = f/1-f$$

This latter equation was used for the calculation of rate constants setting $k_3 \theta_2 = k_x$. The experimental work indicates that at low pressures ($c = 0.1$) the full equation should be used. For single experiments it has been shown that the experimental data fit the full equation using the trial and error method for the evaluation of B . However, the low pressure region from $c = 0$ to $c = 0.1$ is the region for which the experimental precision of the apparatus is low. This is the reason for limiting the experimental work to the region, $c > 0.1$.

It will be noted that the data suggest only $G_2 \cdot S$ species on the surface furnish G molecules for the interior sites. The question naturally asked is why other types of surface species such as $G \cdot S$ and $G_3 \cdot S$ are not involved in the reaction. For the $G \cdot S$ configuration it appears that the G molecule is held more firmly on the S (surface) site than on the D (internal) site. The standard free energy differences at 30°C. for the reactions $G + S \rightleftharpoons G \cdot S$ and $G + D \rightleftharpoons G \cdot D$ are about -1600 and -1450 cal. per mole, or a difference of 1150 cal. Two reasons can be advanced for the relatively little participation of $G_3 \cdot S$, $G_1 \cdot S$ species in the adsorption reaction. In the first place the fractions of surface, θ_1 , θ_2 , occupied by each type are related by the equation,

$$\theta_1 : \theta_2 : \theta_3 : \theta_4 = 1 : c : c^2 : c^3$$

and except at high values of c , the relative concentrations of $G_3'S$ and higher species are low. See Figure I. In the second place the adsorption sites on polymeric materials need not, as in the case of metals, be restricted to areas essentially equal to the area occupied by an atom. The area of the surface sites on cellulose could be much larger than the area of a single atom. Such sites could be visualized in the case of methanol adsorption on cellulose, as cooperative and hence adjacent functional groups such as hydroxyl. If this is true then the orientation of the surface units is of importance and the different types of sites correspond to adsorption on a heterogeneous surface. It is very probable that gaseous methanol molecules cannot penetrate the crystalline lattice of cellulose and where such a lattice is present on the surface, adsorption on such crystalline sites will not lead directly to sorption on the interior sites.

The reversibility of the sorption process is obviously dependent on the relative values of θ_1 , and θ_2 , which in turn depend on the pressure. If in the system at equilibrium the pressure of methanol is decreased, θ_2 approaches zero faster than θ_1 , and the reverse reaction predominates.

Desorption Experiments

The rates of desorption of methanol from cellulose have been measured in a number of experiments but with the experimental conditions used here the data are not significant and have not been reported. The desorption data follow the same rate equation as the sorption data. This can be shown by plotting t/W against t . The slope of the straight line should be $1/W_e$. In desorption experiments all data fit on such a line. However the experimental slope is always lower than $1/W_e$, where W_e has been determined from equilibrium measurements. Desorption experiments are made under high vacuum and as desorption is an endothermic process it is believed that in the present procedure the temperature of the sample is appreciably lower than the thermostat temperature. The present technique must be modified in some manner to get better heat transfer, probably by pelletizing the cellulose sample. Experimental work on this phase of the problem is continuing. It should be mentioned that in the sorption experiments W_e as determined from the plot of t/W against t always checked the value of W_e obtained from equilibrium measurements to 1% or better. As the equilibrium measurement is free from thermal effects caused by the evolution of heat it was concluded that the sorption measurements were being made sufficiently close to thermostat temperatures so as to be significant. The low energy of activation for the sorption process indicates that the change in k with change in temperature is about 3% per degree in comparison to a change of greater than 6% per degree usually encountered in kinetic work.

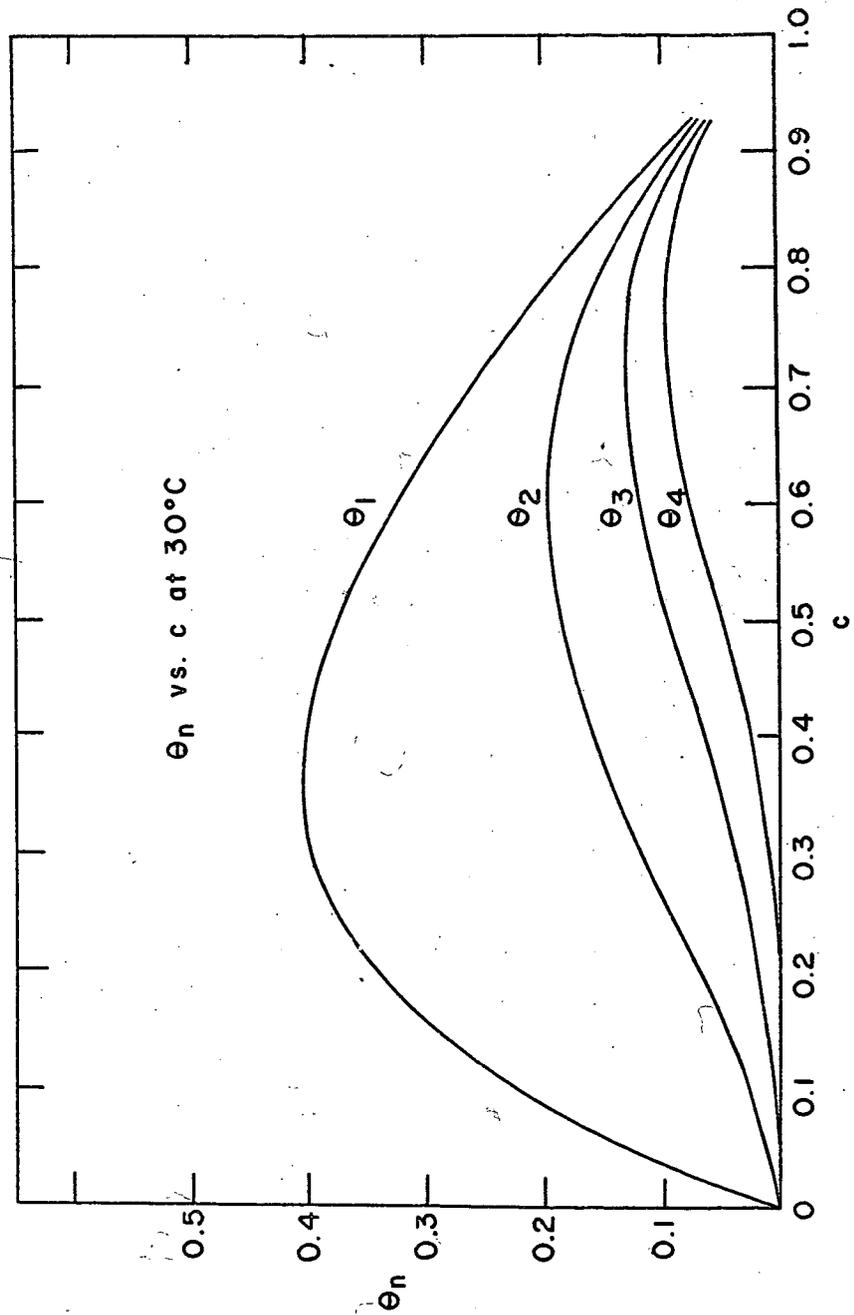
Number of Surface Sites

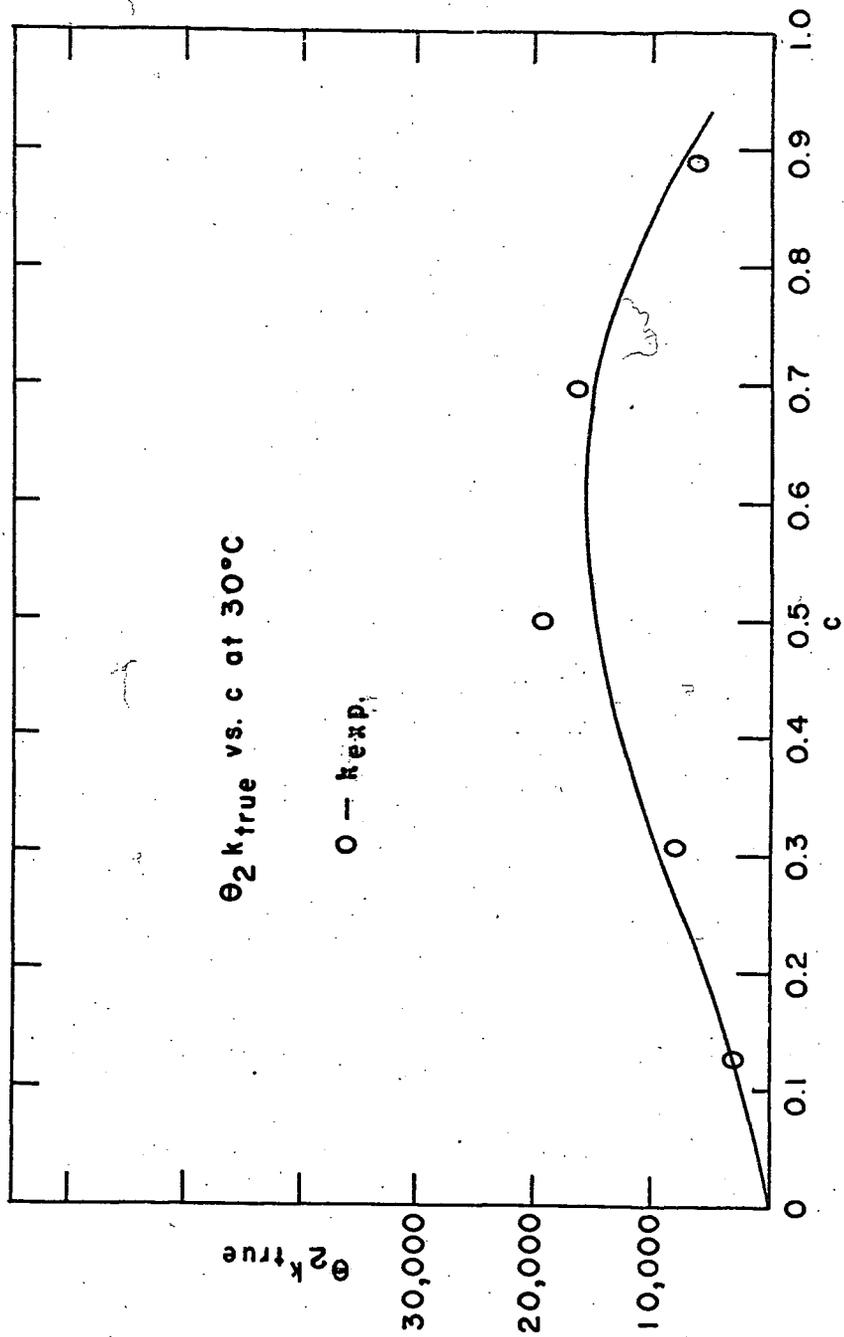
The kinetic data indicate that the number of surface sites on cellulose is small. The total weight of methanol held by cellulose at a given time must be equal to the weight of methanol on the surface plus the weight of methanol held in the interior. The experimental quantity is, of course, the total weight. Kinetically, it would appear that the only manner in which the total weight could follow the experimental kinetic equations would be that the weight of the methanol held in the interior is essentially equal to the total weight or that the weight of methanol adsorbed on the surface is small. If this is true, the number of surface sites on cellulose must be small. Experimental confirmation of this point is desirable.

The adsorption of tertiary butyl alcohol on cellulose has been measured at 45°C. Tertiary butyl alcohol was selected as a molecule having relatively large dimensions along the x, y, and z axis. The sorption of tertiary butyl alcohol by cellulose is a very slow process, and equilibrium values were not obtained because of the slowness of the system to come to equilibrium. The following procedure was adopted assuming that surface adsorption had reached its equilibrium value in one hour. For non-porous solids ten minutes suffices. The cellulose sample was exposed for one hour to a known pressure of tertiary butyl alcohol and the increase in weight recorded. The sample was then evacuated overnight and a new weight increase measured for a new pressure. Under these conditions, the cellulose sample returns to its initial weight on pumping so that the adsorption is reversible. Measurements of this type were made from relative pressures 0.1 to 0.8 and gave a Langmuir type isotherm. Tertiary butyl alcohol adsorptions ranged from 1.4×10^{-5} to 7.9×10^{-5} moles alcohol per gram cellulose. Except at low values of c, these values for tertiary butyl alcohol are much smaller than those obtained with methanol (see Table I). These data are considered experimental evidence that the number of surface sites on the cellulose is small and that most of the methanol held by the cellulose is dissolved in the cellulose.

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The Interaction of Organic Vapors With Coal. II. The Irreversible Sorption of Amines

Ruth Trammell¹ and Paul Fugassi

Coal Research Laboratory, Dept. of Chemistry
Carnegie Institute of Technology, Pittsburgh 13, Pa.

The sorption of different amines on coals of various ranks has been investigated. In all cases examined to date, the sorption is isothermally irreversible. Different hypotheses for explanation of the irreversible sorption are discussed and it is concluded that the most probable explanation is the formation of solvates stabilized by mechanical trapping of amine molecules in the gel structure of the coal. Experimental evidence in support of a trapped molecule hypothesis is presented.

1. Present address: Dept. Chemistry, Chatham College, Pittsburgh (13) Pennsylvania

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The Interaction of Organic Vapors With Coal.
II. The Irreversible Sorption of Amines¹

Ruth Trammell² and Paul Fugassi
Coal Research Laboratory, Dept. of Chemistry
Carnegie Institute of Technology, Pittsburgh (13), Pa.

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1. Submitted by Ruth Trammell in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Carnegie Institute of Technology.
 2. Present address: Dept. of Chemistry, Chatham College, Pittsburgh (13), Pa.
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Summary

The sorption of different amines on coals of various ranks has been investigated. In all cases examined to date the sorption is isothermally irreversible. Different hypotheses for explanation of the irreversible sorption are discussed and it is concluded that the most probable explanation is the formation of solvates stabilized by mechanical trapping of amine molecules in the gel structure of the coal. Experimental evidence in support of a trapped molecule hypothesis is presented.

Introduction

Amines have been used frequently in extraction studies on coal. It has been found that it is difficult to remove the last traces of amines from both extract and residue, and this behavior might be considered evidence that the amines have reacted chemically with coal. It is the purpose of this investigation to study the sorption of gaseous amines on coal, to determine whether chemisorption has taken place, and if chemisorption is involved to find the nature of the functional groups in coal responsible for the chemisorption.

Experimental

Apparatus: Sorption measurements were made gravimetrically using McBain-Baker balances. The apparatus had six tubes connected in series so that six different samples of coal could be studied at the same time under the same experimental conditions. The springs were made from Ni-Span-C wire, 0.005 inches in diameter. The sensitivities of the springs ranged from 1.55 to 2.98 milligrams per millimeter extension. With a cathetometer reading to 0.1 mm. and a sample weight of 200 milligrams the precision of measurement was about 0.1%. The pumping system was composed of a two-stage mercury diffusion pump backed by a mechanical pump. The system included a storage chamber for storing the liquid whose sorption was to be measured and a mercury manometer for reading the pressure. Mercury sealed stopcocks were used for isolating the balance chambers and the storage chamber. The entire apparatus was mounted in an air thermostat. The temperature of the thermostat could be varied from 35°C. to 50°C. and held at a given temperature $\pm 0.10^\circ$ for a period of weeks.

Chemicals: The samples of coal used were obtained in part from the stock of the Coal Research Laboratory and were furnished in part by the Pittsburgh-Consolidation Coal Company. Samples in the form of coarsely-grained material were ground by passage through a hammer mill. The samples thus ground were used unsieved in order to avoid separation of the petrographic components of the coal. Samples of pale crepe natural rubber, GRS-1502 synthetic rubber, pulverized rubber peels (reclaimed rubber) and hard rubber dust were furnished by the General Tire and Rubber Company. Samples of natural and synthetic rubber in the form of gum (unvulcanized) stock were washed repeatedly with methanol. Cured (vulcanized) rubber samples were refluxed with a mixture of ether, toluene, and methanol. Anhydrous Drierite was used as a sample of calcium sulfate. The iron pyrites used was a mineralogical specimen consisting of small cubes of pyrites held in a stone matrix. Some of the cubes were freed from the matrix and ground to provide the sample.

Pyridine, Baker, C.P., was redistilled and stored over Drierite. Methylamine, Eastman, was obtained and used as a 25% solution in water. Ethanolamine, Eastman, and ethylenediamine, Matheson, Coleman and Bell, were redistilled before use. 2-Methoxyethylamine, Eastman, was received as a 56-70% solution in water; potassium hydroxide was added and the mixture refluxed. 2-Methoxyethylamine was distilled from the mixture and then redistilled over sodium metal.

Procedure: The samples of coal were weighed out to 0.1 mg. and allowed to stand overnight in a desiccator. The samples, after being reweighed and placed in the apparatus, were allowed to stand for one hour, with an atmosphere of air present, to come to the thermostat temperature. A reading of the spring length was taken. It was assumed that the weight of the sample had not changed during the hour waiting period. The next step was to evacuate the apparatus and to follow the sample weight (spring length) until constant weight was attained. Coal samples were allowed to stand in the vacuum for a minimum of one day although the samples usually attained constant weight in shorter periods of time.

Following evacuation, the balance compartments were isolated from the vacuum line and the chosen vapor admitted to the system at a pressure equivalent to a relative pressure of about 0.5. The samples were kept under these conditions until a constant weight was reached. Usually periods of 3 to 5 days were needed to get complete adsorption although in some cases several weeks exposure was required. Plots of weight, W , vs. time, t , made for each experiment aided in the determination of the weight at equilibrium. After determination of the equilibrium weight, the system was evacuated until the sample came again to a constant weight. Figure 1. is a schematic drawing of a typical plot of W as a function of time. W_0 is the initial weight of the sample. After vapor has been admitted to the system the weight of sample increases to some constant value. The increase in weight is called W_e , the equilibrium sorption. When the system is evacuated the weight of the sample rapidly decreases at first and then gradually falls to a constant value. For all the work described here the final sample weight was always greater than the initial weight, W_0 . The increase in weight after a completed cycle of sorption and desorption is called W_p (permanent sorption).

Experimental Results

As previously mentioned, all coals investigated showed an irreversible adsorption of amines. The values of the permanent sorption, W_p , in moles per gram for the sorption of 2-methoxyethylamine are given in Table I.

Table I
Permanent Sorption of 2-Methoxyethylamine on Coals

Coal	35°C. moles/gram	50°C. moles/gram
Pocahontas	3.7×10^{-4}	3.6×10^{-4}
Pittsburgh (Edenborn)	5.9	7.1
Spitsbergen	5.9	9.2
Anthracite (Pa.)	7.2	6.6
Cannel	10.5	9.2
Clover Splint	15.7	14.4
Illinois No. 6	19.1	18.3
Wyoming	29.3	30.2
Lignite (Kincaid)	34.6	36.7
Brown (German)	41.7	36.0

In examining these results it will be noted that for the higher rank coals the values of W_p do not parallel the rank. However, for lower rank coals the values of W_p parallel the rank, increasing as the rank decreases. The high values of W_p for low-rank coals is noteworthy, being around 4×10^{-3} moles per gram of coal; this figure corresponds to a permanent sorption of 0.3 grams of 2-methoxyethylamine per gram of coal or about 30% of the original weight of the dry coal. It will also be noted that W_p does not change much as the temperature is changed, and that W_p does not increase or decrease uniformly with increase in temperature.

The tenacity with which amines are held by the coal even under prolonged evacuation suggests that the amine is chemically combined with the coal. To check this hypothesis, additional experiments were made to determine the nature of the functional groups responsible for the irreversible adsorption. The following possibilities were considered:

1. The formation of solvates with the inorganic constituents present in the coal.
2. The reaction of amines with acidic groups (COOH, OH) present in the coal.
3. The reaction of amines with elemental sulfur in the coal.
4. The reaction of amines with thioether or disulfide groups.
5. A reaction of amines with conjugated systems such as C=C-C=O.
6. The formation of solvates stabilized by trapping.

Each of these possibilities will be considered in turn.

Inorganic Constituents: All coals contain mineral matter and the compounds which comprise the bulk of this mineral matter are iron pyrites, silicates, and iron and calcium salts (1). Since calcium salts are known to form ammoniates there

1. C. B. Marson and J. W. Cobb, Gas J., 171, 39 (1925)

is a possibility that amines form similar complexes. Several sorption experiments were made using ferrous sulfide (synthetic), iron pyrites (mineralogical) and calcium sulfate. The results are tabulated in Table II. All measurements were made at 35°C.

Table II
Sorption of Amines on Selected Mineral Constituents

Amine	Mineral	W_e (moles/gram)	W_p (moles/gram)
Ethylenediamine	FeS	0.2×10^{-4}	0.09×10^{-4}
"	FeS ₂	0.13	0.13
2-Methoxyethylamine	FeS ₂	0	0
"	CaSO ₄	6.64×10^{-4}	0.63

Inspection of the results in Table II shows that W_p is essentially zero for all samples although W_e is large for CaSO₄.

Acidic Groups: The acidic groups in coal are probably COOH and OH. As the carbonyl frequency in the infrared spectra is very weak (2) it may be concluded that

2. R. A. Friedel and J. A. Queiser, Anal. Chem., 28, 22 (1956)

the concentration of COOH in coal is very low. The reaction with amines would be of the type, $RH(s) + B NH_2(g) \rightarrow RNH_3 B(s)$

The equilibrium constant for this reaction is the product of a number of equilibrium constants involving solution in water, neutralization, etc. and data are insufficient for its evaluation. However, it can be shown that the equilibrium constant for the reaction involves the basic dissociation constant of the amine in water. Amines with large dissociation constants would be expected to have a large K for the above reaction and a greater probability that the salt formed would not be pumped off under high vacuum. The above fact suggests the following procedure. If a given type of coal is picked then treatment of this coal with amines of different basicity should give values of W_p paralleling to some extent the dissociation constant.

Experiments were made with Pittsburgh Seam (Edenborn) coal at 35°C. using amines dissolved in water or containing water. Under these conditions the coal samples are simultaneously adsorbing water and amine. The results are shown in Table III.

Table III
Permanent Sorption (W_p) of Amines on Pittsburgh Seam Coal (35°C.)

Amine	pK (H ₂ O-25°C.)	W_p (moles/gram)
Methylamine - H ₂ O	3.4	4.3×10^{-4}
Ethanolamine - H ₂ O	4.3	3.9 "
2-Methoxyethylamine - H ₂ O	4.6	6.0 "
Pyridine - H ₂ O	8.6	7.0 "

These data show that W_p actually increases as the basic strength decreases or the result opposite to that expected. The oxygen content of the coal is about 4×10^{-3} moles of oxygen atoms per gram of coal. Consequently adequate oxygen is present and salt formation cannot be eliminated on the basis of insufficient oxygen in coal.

Reaction with Sulfur: Amines are known to react with elemental sulfur but data on the nature of the reactions are not available. Although the content of elemental sulfur in coal is supposed to be small, it seemed desirable to do a few experiments on the amine-sulfur reactions. Accordingly the sorption of various amines on rhombic sulfur were measured. Sorption does occur and the color of the sample changes from yellow to deep orange and then to black during the course of the sorption. The reaction product appears to form a very tight coating over the unreacted sulfur as, even after reaction periods of six to seven weeks, the yellow color of unreacted sulfur can be seen through the bottom of the glass bucket carrying the sample. None of our experiments have gone to completion. Most of the sorption, 75% or more, is irreversible and values ranging from 0.72 grams of amine to 0.016 grams of amine per gram of sulfur were obtained. Methylamine showed the lowest permanent sorption and ethylenediamine the highest permanent sorption. Sorption of ethylenediamine corresponds to 0.5 moles of amine per mole of sulfur. Unless the elemental sulfur content of the coal is high, it does not seem possible to explain the irreversible sorption of amines on coal in this manner.

Reaction with Sulfide or Disulfide Bonds: If thio-ether or disulfide bonds are present in coal, such bonds might react with amines. To check this possibility the sorption of 2-methoxyethylamine on a series of Pittsburgh Seam coals of known sulfur content was measured. The coal samples used were from the following mines: Hendrix, Edenborn, Montour, Waterman, Pursglove and Moundsville. The total sulfur content of these coals ranged from 0.90% to 4.25%. The permanent sorption for these samples ranged from 5.1×10^{-4} to 15.1×10^{-4} moles of amine per gram of coal. The experimental values of W_p showed no correlation with the total sulfur, pyritic sulfur, sulfate sulfur or organic sulfur contents of the coals.

To determine whether any reaction of this type did occur under the experimental conditions used, the sorption of 2-methoxyethylamine on samples of cured and uncured rubber stocks was measured. The data are tabulated in Table IV.

Table IV

Sorption of 2-Methoxyethylamine on Rubber (35°C.)

Rubber	W_p (moles/gram)
Pale crepe (vulcanized)	1.8×10^{-4}
" " (unvulcanized)	0.8×10^{-4}
GRS-1502 (vulcanized)	$0.5 \times "$
GRS-1502 (unvulcanized)	$0.4 \times "$
Rubber peels (reclaim)	$1.4 \times "$
Hard, rubber dust	$3.8 \times "$

The permanent sorption on all samples is low. As vulcanized samples contain more sulfur than unvulcanized samples and as in vulcanized samples some of the sulfur is present as thioether or disulfide bonds it can be concluded that the reaction between amines and sulfur links is very slow at 35°C.

Reactions with Conjugated Systems: The system of particular interest is the quinones. Many different reagents are known to react with quinones under rather mild conditions. If the reagent being added is designated as RH, the reaction can be written as,

$$C=C-C=O + RH \rightarrow RC-C=C-OH$$

Among the compounds which undergo this reaction are amines, alcohols, and bisulfites. The sorption of methanol on coals of various ranks has been under investigation in this laboratory for several years. Although in these experiments coal samples have been exposed for periods of time as much as several weeks and at temperatures ranging from 30° to 45°C., all methanol sorptions determined to date have been reversible to better than 1%. These data indicate that the experimental conditions are not correct for methanol addition to coal or that the concentration of conjugated systems of the quinone type in coal is very small. Additional experiments have been made where samples of coal were treated with liquid reagents under conditions which would be expected to lead to the addition of bisulfites or methanol to quinones. No evidence of appreciable reaction as measured by increase in weight of the coal sample has yet been obtained. In these experiments, reacting, say coal with liquid methanol, the system is two-phased and this fact might explain the slowness of the reaction. On the basis of the data at hand, it does appear that the concentration of quinones in coal is small.

Solvates Stabilized by Trapping: As mentioned before, most solvates would be unstable at the low pressures prevailing during the desorption process. However, such solvates might show sufficient stability if the molecules are trapped in the gel structure. On this hypothesis the permanent sorption of amines is analogous to clathrate formation found with crystalline compounds. The values of W_p hence are kinetic and not equilibrium values for amine sorption.

Two types of experimental evidence can be sought to support such a hypothesis. First, if it can be shown that an inert organic molecule of high volatility is irreversibly held by the coal, then the trapped molecule hypothesis appears probable. Second, other polymer systems with functional groups of known inertness to amines might be expected to show the same behavior.

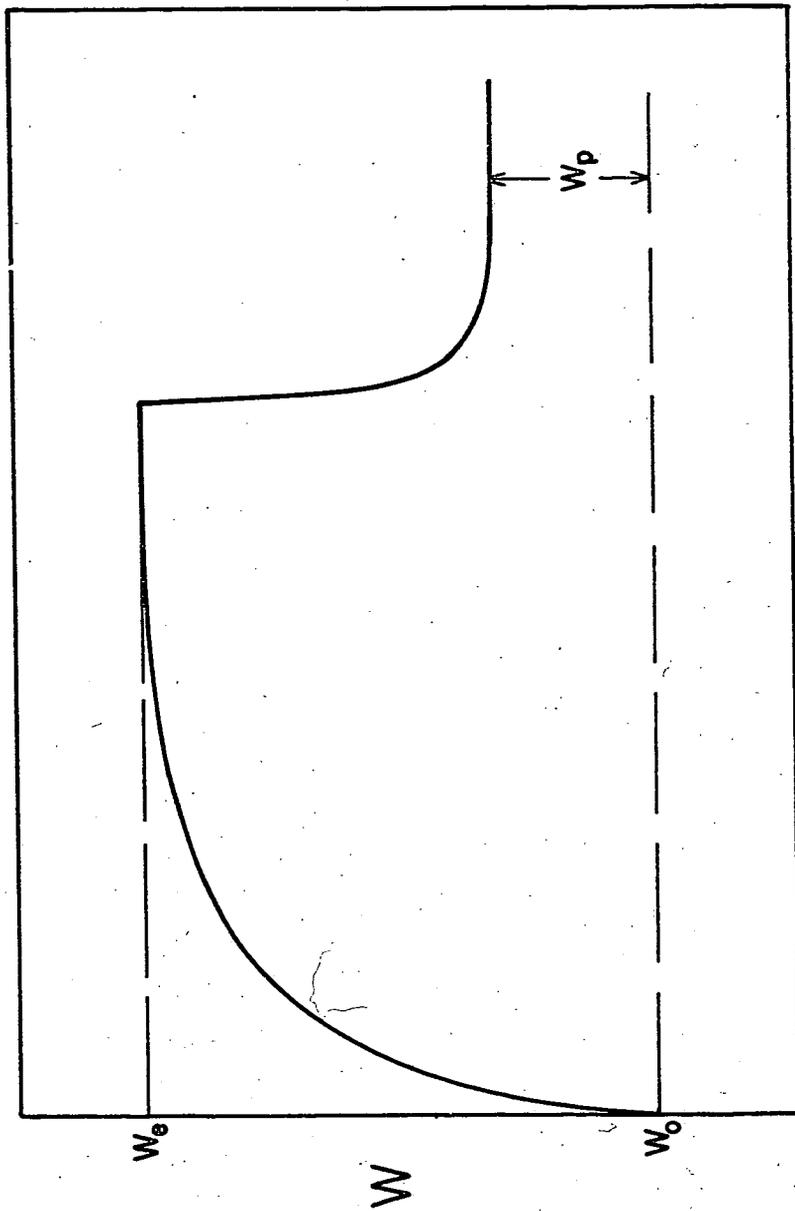
For an experiment of the first type diethylether was selected as the molecule which could be considered inert. Accordingly, the sorption of diethyl ether on Wyoming coal was measured at 35°C. The value of W_p for ether was 10×10^{-4} moles for gram coal, and while this value is substantially less than W_p for 2-methoxyethylamine, nevertheless ether is held by this coal very tenaciously. For an experiment of the second type the sorption of 2-methoxyamine on two natural polymers was measured at 35°C. The results are tabulated in Table V.

Polymer	W_e (moles/gram)	W_p (moles/gram)
Cotton linters	13.8×10^{-4}	5.1×10^{-4}
Raw silk	10.5 "	5.5 "

One other piece of evidence may be cited as supporting the trapped molecule hypothesis. For a series of coals, W_p was measured at 25°C. Keeping the samples under high vacuum, the thermostat temperature was changed successively to 40, 45 and 50°C. allowing the samples to remain at each new temperature for a minimum period of 24 hours. Under this procedure, W_p decreased slightly as the temperature increased. For a given coal, the values of $\log W_p$ when plotted against $1/T$ gave a straight line whose slope is related to the heat of reaction. Of the six coals on which this procedure was tried, anthracite gave the lowest heat of reaction, 1.3 kcal. per mole, and Clover Splint gave the highest heat of reaction, 3.3 kcal. per mole. These thermal values are much too low to be associated with anything but a very low order of bonding.

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TIME

PRODUCTS FROM SULFONATION OF PETROLEUM RESIDUA

(1) (2)

Mayer B. Goren and I. Dean Elkins

Kerr-McGee Oil Industries, Inc.

Oklahoma City, Okla.

A B S T R A C T

In a search for new applications for resinous fractions derivable from asphalt, studies of sulfonation reactions of these substances have led to the development of an intermediate product which can be utilized to prepare either strong acid cation exchange materials or an activated gas-adsorbent carbon.

The cation exchange materials have operating characteristics and stability resembling the commercial sulfonated coals, while adsorbent carbons of very high activity have been prepared.

(1) Present address: Kerr-McGee Oil Industries, Inc.
Mining and Ore Processing
Denver, Colo.

(2) Present address: Kerr-McGee Oil Industries, Inc.
Cushing, Oklahoma

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PRODUCTS FROM SULFONATION OF PETROLEUM RESIDUA

Mayer B. Goren and I. Dean Elkins
Kerr-McGee Oil Industries, Inc.
Oklahoma City, Okla.

Processing of low gravity crudes at the Wynnewood, Oklahoma refinery of Kerr-McGee Oil Industries, Inc., affords asphalt as a major product, and among the major efforts of the Kerr-McGee research group has been the investigation of new uses for asphalt and asphalt fractions. The development of commercially feasible methods for separating vacuum reduced crude into the asphaltic components usually referred to as asphaltenes, resins, and oils afforded us ample quantities of these materials for investigation in a search for new uses for these substances as raw materials in the chemical and allied industries.

By proper control of the conditions of separation it is possible to prepare resinous fractions of varying physical properties as reflected by ring and ball softening point, hardness, penetration, etc.

Although these resin fractions have industrial uses of their own as for example in paints, rubber, tile, emulsions, and others, projects were undertaken for the chemical modification of these fractions in search of entirely new utilization of these components as chemical raw materials.

The higher molecular weight fractions of these resins are relatively complex, highly condensed mixed aromatic-aliphatic-naphthenic materials, largely hydrocarbon in nature, but containing minor percentages of sulfur and oxygen most probably present as heterocyclic function. Without extensive fractionation by extremely tedious and expensive processes it appeared that only simple chemical treatment of the resins might result in desirable changes in the properties of these substances, which might give rise to useful products.

Among the reactions investigated which did, indeed, afford useful intermediates or end products was that of treating higher melting resin fractions with a variety of sulfonating agents. The course of the reactions with these reagents apparently involves sulfonation, sulfation, and oxidative condensation and is probably as complex as the somewhat analogous well-known "sulfonation" of coal. However, unlike coal, the asphaltic fractions investigated are fusible at (relatively) low temperatures, and so in the mechanical processing of the latter, dust and fines arising from grinding operations are not lost to chemical processing, inasmuch as the dust and fines can be melted, cast, and reground.

A single sulfonation (the term sulfonation is used with the understanding that the reactions involved are considerably more complex than is implied by this term; however, it is convenient to use this rather than "complex reaction with sulfonating-sulfating agents" which is what it is intended to imply) with, for example, ordinary concentrated sulfuric acid yields, with a variety of asphaltic resinous materials, a product which is readily wet by water and infusible, whereas it will be recognized that the starting material is essentially hydrophobic in nature and is readily fused without more than minor decomposition. The sulfonated product is harder and (from asphaltenes) less friable than the starting material. It possesses poor cation exchange properties, as will be seen from the "Experimental" section.

However, a retreatment of this product with additional sulfonating agents⁽⁴⁾ does afford products useful as cation-exchange materials operative in both the

hydrogen and sodium cycle, and of capacity and operating characteristics essentially indistinguishable from commercial "sulfonated coal" cation exchange products, with which the better products were compared. Thus granular materials were prepared having satisfactory ion exchange capacity, good physical stability and resistance to attrition; they are economically regenerated, are free from color throw-off in the alkali metal forms and are washed free of excess regenerant with a reasonable volume of wash water.

The hardness and infusibility of the once sulfonated "intermediate product" led to the testing of these substances as coking materials for the preparation of an activatable adsorbent char(5). It may be pointed out that slow coking of asphaltic resin fractions (resins or asphaltenes) is preceded by fusion, evolution of gaseous pyrolysis products with concomitant profuse foaming until the material is well carbonized, whereupon a light porous friable product is left having essentially no utility as an activatable char. On the other hand, slow charring of a properly-sulfonated intermediate product derivable from the same resinous material affords in good yield a hard granular carbon, the granules of a size essentially the same as the starting material. No fusing or foaming occurs, and the char is readily activated by the usual well-known methods to give a very active adsorbent of satisfactory hardness characteristics.

The relationship of the original resinous material to the "sulfonated" product is largely that of binder to base material as defined by Morgan and Fink(7). These investigators classified binders as substances which, on carbonization, "swell, become macroporous and yield a lustrous char." During the carbonization the material goes through a plastic, or even a liquid stage, during which effervescence accompanying the expulsion of volatile matter gives rise to the swelling with building of the macroporous structure. Base materials, on the other hand, should not become plastic or fluid during carbonization, but rather should have a rigid oriented structure. Other desirable characteristics of a base material are that it should be "a large ring-chain molecule with oxygen or other volatile constituents in the ring."

Inasmuch as binder materials carbonize to give (after activation) carbons of low activity, these investigations conclude that such substances are in the main not very desirable as raw materials for activated carbon.

Similar, though perhaps not as broad, conclusions were reached by Bureau of Mines Investigators(2) who found that certain bituminous and sub-bituminous coals, natural cokes, pitch cokes and petroleum cokes did not yield satisfactory adsorbent carbons by methods which, with desirable raw materials, were successful.

Apparently the reactions attending the sulfuric acid treatment of the asphaltic resins - e.g., sulfonation, sulfation, and oxidative condensation serve to transform these asphaltic resinous materials from a binder (quality unknown) into a very satisfactory base material. The amount of sulfuric acid which is required to effect the conversion depends upon the relative binder/base characteristics of the asphaltic resin, and is most economically a quantity which will effect enough oxidative condensation to minimize fusion during charring. With pentane-precipitated asphaltenes, about 3.5 parts of 95% sulfuric acid per part of resin effects, during a two-hour "sulfonation" period, conversion into a satisfactory base material. For conversion into an activatable char, the sulfonation product, without isolation or washing is slowly heated to coking temperature (about 550-600°C) in the absence of air. During the heating period, excess acid, some sulfur dioxide, H₂S, and even elementary sulfur are evolved along with water, and later, as temperatures in excess of about 400-450° are attained, carbonaceous pyrolytic decomposition products are evolved. The char can be satisfactorily activated by the usual methods (steam) to afford active adsorbent chars in good yield.

Thus examination of sulfonating reactions on asphaltic resin fractions leads to a product which may be resulfonated to yield useful cation exchange materials or which

can be carbonized and activated to give a good activated carbon.

EXPERIMENTAL

Preparation of Cation Exchange Materials

The reaction between hard asphalts or asphaltic resins and simple sulfonating agent such as concentrated sulfuric acid is very slow at ambient temperatures, becoming more rapid as the temperature rises to about 70°C. Above this temperature the reaction proceeds rapidly, accompanied by vigorous evolution of SO₂ as the acid oxidizes part of the asphaltic material. The mixture foams persistently and in consequence the reaction must be carried out in oversize equipment with adequate stirring. Useful starting materials for preparation of either the cation exchange materials or the activated char were found to be blown asphalts of softening point in excess of about 270° and asphaltic resins, asphaltenes, or mixtures thereof having similar softening point properties. Simple asphaltenes were very useful as starting materials.

1. Sulfonation of Asphaltenes

Fused and subsequently ground pentane-precipitated asphaltenes derived from a vacuum reduced asphalt (penetration 89, softening point 120°F) were screened, and the 20/40 mesh fraction retained. Fines were remelted, cast to solidify and reground. For the preliminary sulfonation 100 parts of the 20/40 mesh material were treated with 540 parts by weight of 95% sulfuric acid in a resin reaction flask equipped with an efficient stirrer and vented for the escape of gases. The sulfuric acid was added to the ground material slowly, the mixture was allowed to reach its equilibrium temperature (about 45°C) and was then slowly heated on a steam bath. Because of the violent foaming which ensues, the temperature must be raised slowly - one-half to one hour being required to reach maximum steam bath temperature which is maintained for a period of about two hours. The reaction had largely moderated at the end of this time under these conditions and most of the acid appeared to be absorbed. The mixture was cooled and poured into a large excess of cold water. Fines produced in the sulfonation were removed by backwashing in a large cylinder. Washing of excess acid from the solid product is a tedious operation and is at best not wholly successful.

To test the product for ion exchange capacity, twelve grams of the washed and dried material was transferred to a half-inch diameter glass column and alternately exhausted and regenerated by treatment with dilute sodium hydroxide followed by dilute hydrochloric acid. After several cycles of this sort, the product was regenerated with 4 Normal hydrochloric acid. To wash out the excess acid required over a liter of water (about fifty column volumes) and the material in the hydrogen form was found by standard column testing methods to have an exchange capacity of only about 0.35 m.e.q./gram. (Twelve grams exchanged hydrogen for the cations in about 550 ml of hard water containing 400 ppm hardness expressed as CaCO₃). Thus this product is a very poor ion exchange material.

2. Resulfonation of Intermediate Product

The intermediate sulfonated product prepared (above) was further activated by treating 150 parts of the dried material with 80 parts of 20% oleum in similar equipment. The oleum was added slowly while the mixture was cooled in order to prevent excessive heating and foaming. Again when equilibrium temperature was established, the mixture was heated slowly to steam bath temperatures and maintained for two hours. The product was "drowned out" after cooling and thoroughly washed, finally in the sodium form with hot water. A twelve-gram sample of this product required somewhat less than 100 ml of wash water to free it of excess acid after regeneration, and in standard column operation exchanged hydrogen for the cations in 2,150 ml of 400 ppm hard water before leakage reached 5% of the original total hardness. This much-improved product had a working capacity of approximately 1.43 m.e.q. per gram.

3. Double Sulfonation without Intermediate Isolation of Product

A quantity of 20/40 mesh asphaltene was sulfonated with 5.5 times its weight of concentrated sulfuric acid as in the first example. After the initial sulfonation the mixture was cooled and a quantity of 20% oleum equal in weight to the original sulfuric acid charged was slowly added, after which heating was resumed. More SO_2 was evolved and the mixture again foamed as badly as during the original sulfonation. After an additional two hours at steam bath temperature the reaction was terminated and the product was washed. The material possessed high exchange capacity but exhibited color throw-off on lengthy standing in the sodium form in contact with water. This was believed due to small amounts of lower molecular weight sulfate/sulfonates. To eliminate these, the washed material was soaked in hot (90°C) 20% sodium hydroxide for about six hours and then was thoroughly washed with hot water.

This material exhibited ion exchange capacity in both the hydrogen and sodium cycles comparable with that of commercially available sulfonated coals. Color throw-off was not noticeable, regeneration and washing requirements were essentially those of commercial sulfonated coal. Yield of the twice-sulfonated material was about 1.4 times the weight of pentane asphaltene charged. Quite similar products were obtained from similar sulfonations carried out on an oxidized asphalt and air oxidized asphaltic resins.

Preparation of Activated Carbons

A special apparatus was constructed of fused quartz for preparing and activating chars from sulfonated materials. The major components of this apparatus were a steam superheater and a carbonizing and activating vessel, both constructed of fused quartz. The superheater was a quartz macro combustion tube $3/4" \times 30"$ with ball joints at the ends and heated by a standard electric combustion furnace.

The activating vessel was somewhat similar but arranged in a vertical position. This vessel was larger in diameter (2") and shorter (10"). It was also heated electrically by furnace elements which fit closely for most of its length. Temperature was controlled by a large variable transformer. The lower end was closed and a socket joint attached near the bottom at right angles to its axis. This joint received superheated steam from the combustion tube. A grating of quartz was included just above the steam inlet. This helped distribute the steam uniformly. The upper end of the tube was bottle shaped with a socket joint finish. This socket accepted a ball joint fitting carrying a thermocouple and a condenser.

Steam rate was measured by pressure drop across a calibrated orifice between the supply line and the inlet to the superheater tube.

Approximately 40 grams of dry, granular, sulfonated material was charged to the vessel and carbonized without steam at $500-550^\circ\text{C}$. The temperature was then raised to that desired for activation, and steam admitted at a rate sufficient to suspend or fluidize the bed of carbon. At the end of the time of activation, heating of the activation vessel was discontinued but superheated steam was continued until the temperature of the carbon had fallen below 500°C at which time the steam was shut off. The carbon was allowed to cool thoroughly before disconnecting the apparatus.

1. Activated Carbon from Asphaltene

Two-hundred grams of pentane precipitated asphaltene were slowly coked in the absence of air. Foaming was severe because of fusion and evolution of volatile matter, so that the rate of heating required careful monitoring to avert mechanical loss of material. The final temperature of coking was 500°C and heating was continued for about ten minutes after essentially all pyrolysis products had been evolved. The cooled porous, friable residue (104 g.) was crushed and screened, the 20/40 mesh fraction (54 g.) being retained. Activation for 30 minutes at 975°C with excess of

superheated steam afforded 19.7 grams (4.8% based on asphaltenes) of an "activated carbon" which had a CCl_4 service time(1,3,8) of 36 seconds. Thus, the activated asphaltene coke would be considered worthless as an active char.

2. Activated carbon from Sulfonated Asphaltenes

100 g. of 20/40 mesh asphaltenes was treated with 200 ml (370 g.) of concentrated sulfuric acid, heated to water bath temperature and maintained for two hours. The temperature was slowly raised until a final temperature of 400°C was attained. Copious evolution of SO_2 attended the whole operation. The dry product was screened to eliminate a small amount of fines and the 20/40 mesh fraction coked at $500\text{--}550^\circ\text{C}$ until evolution of gases had ceased. Half the char (38.5 g.) was activated with steam at 800°C for 35 minutes to yield 36 g. of activated carbon having a CCl_4 service time of 185 seconds. The other half of the char was steam-activated at 950°C for 35 minutes to yield 24 g. of activated carbon having a CCl_4 service time of 1028 seconds. The once-tested carbon was regenerated for seven minutes at 975°C and exhibited a CCl_4 service time of 1050 seconds. The products are granular, of fairly satisfactory hardness and have been prepared under conditions which yield carbons having CCl_4 service times as high as 1600 seconds.

The activity of the carbon increased with increasing temperature of activation up to about $850\text{--}875^\circ\text{C}$. Thus, carbon activated at temperatures above 900°C was no more active than that obtained at 850°C . At these temperatures, yield of activated carbon decreased rapidly with increased retention time and with increasing temperature. These facts are in general accord with and confirm observations made by previous investigators.(6)

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DETERMINATION OF TOTAL PYRIDINES AND TOTAL QUINOLINES
IN LOW TEMPERATURE COAL-TAR DISTILLATES BY
ULTRAVIOLET SPECTROPHOTOMETRY

Ta-Chuang Lo Chang and Clarence Karr, Jr.

Low-Temperature Tar Laboratory
Bureau of Mines
U. S. Department of the Interior
Morgantown, W. Va.

ABSTRACT

An ultraviolet spectrophotometric method for determining total pyridines and total quinolines in coal-tar distillates is described. The bases are extracted from the sample with 10% sulfuric acid. The pH of the acid extract is adjusted to 12 by adding potassium hydroxide. The free bases are extracted from the alkaline solution with isooctane, and the ultraviolet spectrum is obtained from the isooctane solution. The total quinolines and total pyridines are determined from the spectrum by using the following average absorptivities from 10 quinolines and 13 pyridines: 15.95 for quinolines at 316.5 $m\mu$ and 23.24 and 21.25 for quinolines and pyridines at 260 $m\mu$. This method needs only a small amount of sample and can be applied to similar materials, such as petroleum distillates.

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Ta-Chuang Lo Chang and Clarence Karr, Jr.
Low-Temperature Tar Laboratory
Bureau of Mines
U. S. Department of the Interior
Morgantown, West Virginia

Pyridine bases as derived from coal tar are complex mixtures of pyridine, quinoline and their homologs (5,7). For the analysis of these bases according to chemical type, (that is, as pyridines and quinolines), it was desired to develop an ultraviolet spectrophotometric method that would apply to low temperature coal-tar distillates and crude tar bases.

Previously LeRosen and Wiley (6) had attempted to determine pyridines in petroleum products by extracting the sample with phosphoric acid wherein the pyridines were determined by ultraviolet spectrophotometry and expressed as pyridine by referring to a standard graph of pyridine itself. Another paper (4) described a similar process.

In the method described in this paper, pyridine and alkyl derivatives are estimated as "total pyridines," not as pyridine itself, as done by LeRosen and Wiley. Similarly, quinoline and its alkyl derivatives are estimated as "total quinolines." Briefly, the procedure is as follows: The sample is extracted with 10% sulfuric acid and the acid layer is adjusted to pH 12 by adding potassium hydroxide. The tar bases in the alkaline solution are then extracted with isooctane. The total pyridines and total quinolines are determined by the composite spectrum of the isooctane extract.

The selected wave length for calculating total quinolines is 316.5 $m\mu$, at which pyridines show no absorbance. The empirical absorptivity for total quinolines at this wave length is 15.95, the average coefficient of 10 quinolines chosen for this study. The wave length selected for total pyridines is 260 $m\mu$, at which quinolines show considerable absorbance. Their absorbance can be calculated from their concentration, as determined by the absorbance at 316.5 $m\mu$, and a correction applied to total absorbance from which pyridines may be calculated. The empirical absorptivity for total quinolines at 260 $m\mu$ is taken as 23.24, the average of 10 quinolines; that for total pyridines is taken as 21.25, the average coefficient of 13 pyridines.

APPARATUS

Beckman DK-2 Spectrophotometer with hydrogen discharge lamp.
Matched pair 1-cm. silica cells.
Separatory funnels.
Pipettes and volumetric flasks.

CHEMICALS

Pyridine bases:
Pyridine, Fisher certified reagent.
2-Methylpyridine, C. P. Eimer and Amend.

3-Methylpyridine, 98%, Eastman Kodak Co., yellow label.
4-Methylpyridine, Eastman Kodak Co., white label.
2,3-Dimethylpyridine, Matheson, Coleman and Bell.
2,4-Dimethylpyridine, 95%, Eastman Kodak Co., yellow label.
2,6-Dimethylpyridine, 90%, Eastman Kodak Co., yellow label.
3,5-Dimethylpyridine, pure grade, Aldrich Chemical Co.
2-Ethylpyridine, 95% purity minimum, Reilly Tar & Chemical Corp.
4-Ethylpyridine, 95% purity minimum, Reilly Tar & Chemical Corp.
5-Ethyl-2-methylpyridine, Eastman Kodak Co., white label.
3-Ethyl-4-methylpyridine, pure grade, Aldrich Chemical Co.
2,4,6-Trimethylpyridine, Eastman Kodak Co., white label.
Quinoline, synthetic, Eastman Kodak Co., white label.
2-Methylquinoline, Quinaldine 95%, Eastman Kodak Co., yellow label.
4-Methylquinoline, Lepidine, Eastman Kodak Co., yellow label.
6-Methylquinoline, Eastman Kodak Co., white label.
7-Methylquinoline, pure grade, Aldrich Chemical Co.
8-Methylquinoline, Eastman Kodak Co., white label.
2,4-Dimethylquinoline, pure grade, Aldrich Chemical Co.
2,6-Dimethylquinoline, Eastman Kodak Co., white label.
Isoquinoline, Eastman Kodak Co., white label.
3-Methylisoquinoline, Eastman Kodak Co., yellow label.
Acridine, pure grade, Aldrich Chemical Co.
Sulfuric acid, 10%, analytical reagent.
Sodium hydroxide, 10%, analytical reagent.
Potassium hydroxide pellets, analytical reagent.
Isooctane (2,2,4-trimethylpentane), spectro-grade.

EXPERIMENTAL

Procedure for Synthetic Mixtures. The ultraviolet spectra of the 23 bases used for this study were determined individually in isooctane. The spectra agreed well with those in the literature (1,3). The absorptivities of the bases and their averages at 260 $m\mu$ and 316.5 $m\mu$ were then calculated and are presented in Table I.

Stocks of synthetic mixtures containing bases listed in Table II were prepared in 10% sulfuric acid solution. Their concentrations were exactly three times those shown in the table.

The stocks to which neutral oil was added were washed three times with isooctane, which was discarded. The volume of isooctane used each time equaled that of the stock. Ten ml. of the acid layer was adjusted to pH 12 by slowly adding KOH pellets. The alkaline solution was then extracted three times with 10 ml. of isooctane. The extracts were combined, and the ultraviolet spectrum of the 30-ml. extract was determined. The concentrations of total quinolines and total pyridines were determined by the absorbances and average absorptivities at 316.5 $m\mu$ and 260 $m\mu$, respectively.

Table III shows the recovery of bases by this method. In this table, the "present" concentrations were one-third of their stocks and the "found" were the concentrations of the 30-ml. isooctane extract of the corresponding mixtures. For example, synthetic mixture number 1 in Tables II and III has a total pyridine concentration of 0.0202 g/l. to correspond to the dilution of the original stock from 10 to 30 ml. The concentration found, as shown in Table III, was 0.0201 g/l.

Procedure for Tar-Base Samples. (a) For tar distillate: For samples containing 1-2% base by weight, 10 ml. of distillate was weighed in a separatory funnel and extracted three times with 10% sulfuric acid, 20 ml. the first time and 10 ml. each the second and the third times. The acid layers were collected in a 100-ml. volumetric flask. The oil residue remaining in the funnel was extracted three times with 10 ml. of 10% sodium hydroxide each time. This extraction removes any tar acids

Table I

Absorptivities of Pyridine Bases

<u>Pyridine Bases</u>	<u>Wave Length</u>	
	<u>260 mμ</u>	<u>316.5 mμ</u>
Pyridine	17.44	0
2-Methylpyridine	25.43	0
3-Methylpyridine	23.47	0
4-Methylpyridine	14.22	0
2,3-Dimethylpyridine	26.86	0
2,4-Dimethylpyridine	22.41	0
2,6-Dimethylpyridine	26.74	0
3,5-Dimethylpyridine	22.87	0
2-Ethylpyridine	24.47	0
4-Ethylpyridine	13.07	0
5-Ethyl-2-methylpyridine	20.99	0
3-Ethyl-4-methylpyridine	18.87	0
2,4,6-Trimethylpyridine	<u>20.33</u>	<u>0</u>
Average	21.25	0
<u>Quinoline Bases</u>		
Quinoline	24.23	9.84
2-Methylquinoline	23.90	24.71
4-Methylquinoline	27.69	8.97
6-Methylquinoline	17.79	12.39
7-Methylquinoline	19.16	18.95
8-Methylquinoline	12.56	12.87
2,4-Dimethylquinoline	24.24	17.25
2,6-Dimethylquinoline	21.25	13.56
Isoquinoline	28.67	27.27
3-Methyl-isoquinoline	<u>27.08</u>	<u>13.69</u>
Average	23.24	15.95

Table III

Recovery of Total Pyridines and Quinolines from Synthetic Mixtures by Using Average Absorptivities^{a/}

<u>Mixture No.</u>	<u>Total Pyridines Present, g/l.</u>	<u>Total Pyridines Found, g/l.</u>	<u>Recovery, Percent</u>	<u>Total Quinolines Present, g/l.</u>	<u>Total Quinolines Found, g/l.</u>	<u>Recovery, Percent</u>
1	0.0202	0.0201	99.3	0.0155	0.0155	100.0
2	0.0282	0.0281	99.7	0.0093	0.0091	97.8
3	0.0081	0.0080	99.8	0.0248	0.0245	98.7
4	0.0181	0.0181	100.0	0.0171	0.0166	97.3
5	0.0179	0.0173	96.2	0.0184	0.0201	109.0
6 ^{b/}	0.0179	0.0192	107.0	0.0184	0.0206	112.0
7	0.01875	0.0193	103.0	0.01238	0.0116	93.7
8 ^{b/}	0.01875	0.0206	109.8	0.01238	0.0117	94.5
9	0.01875	0.0208	111.0	0.01238	0.0117	94.5
10 ^{b/}	0.01875	0.0199	106.0	0.01238	0.0119	96.1
11	0.02203	0.01905	87.0	0.01354	0.0135	99.0
12 ^{b/}	0.02203	0.01868	85.0	0.01354	0.0135	99.0

a/ At 316.5 m μ , a for quinolines = 15.95; at 260 m μ , a for quinolines = 23.24; at 260 m μ , a for pyridines = 21.25.

b/ These mixtures contained 0.03 g/l. neutral oil obtained from low temperature tar; their acid solutions (pH = 2) were extracted with isooctane to remove the neutral oil.

Table II. Composition of Synthetic Mixtures

	Mixture No.											
	1	2	3	4	5	6 ^a	7	8 ^a	9	10 ^a	11	12 ^a
Total Base, g/l.	0.03565	0.0375	0.02286	0.03519	0.0363	0.0363	0.03113	0.03113	0.03113	0.03113	0.03557	0.03557
Pyridine	0.00155	0.00217	0.00062	0.0014			0.0016	0.0016	0.0016	0.0016		
2-Methylpyridine	0.00155	0.00217	0.00062	0.0014			0.00348	0.00348	0.00348	0.00348		
3-Methylpyridine	0.00155	0.00217	0.00062	0.0014	0.0066	0.0066	0.00202	0.00202	0.00202	0.00202		
4-Methylpyridine	0.00155	0.00217	0.00062	0.0014			0.00176	0.00176	0.00176	0.00176	0.00705	0.00705
2,3-Dimethylpyridine	0.00155	0.00217	0.00062	0.0014			0.00284	0.00284	0.00284	0.00284		
2,4-Dimethylpyridine	0.00155	0.00217	0.00062	0.0014			0.00199	0.00199	0.00199	0.00199		
2,6-Dimethylpyridine	0.00155	0.00217	0.00062	0.0014	0.0071	0.0071						
3,5-Dimethylpyridine	0.00155	0.00217	0.00062	0.0014								
2-Ethylpyridine	0.00155	0.00217	0.00062	0.0014								
4-Ethylpyridine	0.00155	0.00217	0.00062	0.0014								
5-Ethyl-2-methylpyridine	0.00155	0.00217	0.00062	0.0014			0.00204	0.00204	0.00204	0.00204	0.00816	0.00816
3-Ethyl-4-methylpyridine	0.00155	0.00217	0.00062	0.0014	0.0042	0.0042	0.00131	0.00131	0.00131	0.00131	0.00682	0.00682
2,4,6-Trimethylpyridine	0.00155	0.00217	0.00062	0.0014	0.0179	0.0179	0.00171	0.00171	0.00171	0.00171	0.02203	0.02203
Total Pyridines, g/l.	0.02015	0.0282	0.00806	0.01814	0.0179	0.0179	0.01875	0.01875	0.01875	0.01875	0.02203	0.02203
Quinoline	0.00155	0.00093	0.00248	0.001705			0.00327	0.00327	0.00327	0.00327		
2-Methylquinoline	0.00155	0.00093	0.00248	0.001705								
4-Methylquinoline	0.00155	0.00093	0.00248	0.001705			0.00242	0.00242	0.00242	0.00242	0.0097	0.0097
6-Methylquinoline	0.00155	0.00093	0.00248	0.001705								
7-Methylquinoline	0.00155	0.00093	0.00248	0.001705								
8-Methylquinoline	0.00155	0.00093	0.00248	0.001705	0.00432	0.00432	0.00135	0.00135	0.00135	0.00135		
2,4-Dimethylquinoline	0.00155	0.00093	0.00248	0.001705	0.00518	0.00518	0.00162	0.00162	0.00162	0.00162	0.00384	0.00384
2,6-Dimethylquinoline	0.00155	0.00093	0.00248	0.001705			0.00096	0.00096	0.00096	0.00096		
Isocoumarin	0.00155	0.00093	0.00248	0.001705	0.00582	0.00582	0.00182	0.00182	0.00182	0.00182		
3-Methyl-isocoumarin	0.00155	0.00093	0.00248	0.001705	0.03708	0.03708	0.00094	0.00094	0.00094	0.00094		
Total Quinolines, g/l.	0.0155	0.0093	0.0248	0.01705	0.0184	0.0184	0.01238	0.01238	0.01238	0.01238	0.01354	0.01354
Total Pyridines in Base Mixture, Wt. %	56.52	75.2	24.53	51.55	49.3	49.3	60.2	60.2	60.2	60.2	62.0	62.0
Total Quinolines in Base Mixture, Wt. %	43.48	24.8	75.47	48.45	50.7	50.7	39.8	39.8	39.8	39.8	38.0	38.0

^a These mixtures contained 0.03 g/l. neutral oil from low-temperature coal tar.

that may make complete extraction of tar bases difficult. The alkaline layer was discarded, and the oil layer was then extracted again three times with 10% sulfuric acid as before. These acid extracts were added to the 100-ml. volumetric flask, and the final volume of the acid solution was diluted to 100 ml. with 10% sulfuric acid.

(b) For crude tar base: About 0.1 gram of crude tar base was weighed and dissolved in 10% sulfuric acid in a 50-ml. volumetric flask. The solution was diluted to the mark with 10% sulfuric acid.

Twenty-five ml. of either of the above acid solutions was washed three times with isooctane. The volume of isooctane used each time equaled that of the acid solution. After washing, the volume of the acid solution was adjusted to 25 ml. with water if necessary. Two ml. of the acid solution was pipetted into a small beaker that contained a few milliliters of water and placed in an ice-water bath. Potassium hydroxide pellets were added to the acid solution with constant stirring until the pH of the solution reached 12. The solution was transferred quantitatively to a 25-ml. volumetric flask and was diluted to the mark with distilled water. Five ml. of the alkaline solution was extracted three times with 10 ml. of isooctane each time. The isooctane extracts were combined, and an ultraviolet spectrum was determined.

Calculation of Tar Bases in Sample.

Average absorptivity for quinolines at 316.5 m μ = 15.95

Average absorptivity for quinolines at 260 m μ = 23.24

Average absorptivity for pyridines at 260 m μ = 21.25

$$Q = \frac{A_{316.5}}{15.95} \times F_1 \times F_2 \quad (1)$$

$$P = \frac{A_{260} - \left(\frac{A_{316.5}}{15.95} \times 23.24 \right)}{21.25} \times F_1 \times F_2 \quad (2)$$

where Q = total quinolines in grams,

P = total pyridines in grams,

A_{316.5} = absorbance at 316.5 m μ ,

A₂₆₀ = absorbance at 260 m μ ,

F₁ = dilution factor for final isooctane extract, if any,

F₂ = dilution factor for the sample.

In the procedure described above, there is no further dilution for the final isooctane extract. Therefore, F₁ equals 1. F₂ is equal to (30/1000 x 25/5 x 100/2) = 7.5 for the distillate and (30/1000 x 25/5 x 50/2) = 3.75 for the crude tar base.

If the tar-base content in the sample is too high, further dilution of the final isooctane extract is necessary to obtain a satisfactory spectrum with absorbances at 316.5 and 260 m μ within a range of 0.1 - 0.9. The dilution factor F₁, therefore, has to be found by the actual dilution made.

If the tar-base content in the sample is so low that the composite spectrum of the final 30 ml. of isooctane extract is unsatisfactory, either of the following two procedures can be used: (a) Increase the volume of alkaline solution for final isooctane extraction from 5 to 10 ml. In this case, F₁ is still 1, and F₂ is changed to 3.75 instead of 7.5; (b) increase the volume of isooctane-washed

acid extract from 2 ml. to any desired volume up to 20 ml. In this case, the dilution factor F_2 has to be changed to a value depending on the actual volume of the acid solution used.

From the weight of total pyridines, total quinolines, and weight or volume of the sample used, the percentage of total pyridines and total quinolines can be calculated.

DISCUSSION

Selection of Wave Lengths and Absorptivities for Calculating Total Pyridines and Total Quinolines. The pyridine bases of tar distillates contain a great number of pyridine and quinoline derivatives, and the exact composition varies with the type of tar and manner of distillation. To represent all possible compositions an unlimited number of synthetic mixtures would be required. For this study, the best one can do is to make a synthetic mixture containing the main bases found in tar distillates (5,7) as representatives. Thirteen pyridines and ten quinolines have been selected. However, several other important alkyl pyridines and quinolines, such as tetramethylpyridines and trimethylquinolines, were not included in this work because of their unavailability in this laboratory when this work was done. It is expected that these bases will not appreciably change the pattern of the composite spectrum and also that their absorptivities will not be far from the average values of the 23 bases.

Table II shows the compositions of the synthetic mixtures. The spectra of six typical synthetic mixtures, as shown in Figures 1 to 4, follow a general pattern that also applies to the spectra of pyridine bases extracted from two tar distillates (Fig. 5).

To select suitable wave lengths for calculating total pyridines and total quinolines, several key wave lengths (256, 260, 265, and 270 $m\mu$ for pyridines and 304.5, 308, 313, 316.5, and 318 for quinolines) were tried. Best recoveries for the bases in the above synthetic mixtures have been found at wave lengths of 260 $m\mu$ and 316.5 $m\mu$, respectively, for pyridines and quinolines. The recovery at these wave lengths is shown in Table III. For the first four mixtures, which contained all of the available pyridines and quinolines, recoveries were within 0.7%, or better, for total pyridines, and 2.7%, or better, for total quinolines. Based on the recovery and the assumption that the reference mixture of equal amounts of individual bases better represents the tar bases in the samples than other mixtures would, the following average absorptivities were chosen for calculating the total pyridines and the total quinolines in tar distillates: 21.25 for total pyridines and 23.24 for total quinolines at wave length 260 $m\mu$, and 15.95 for total quinolines at wave length 316.5 $m\mu$.

As the average absorptivity is based on the presence of many bases, the chances of its failing to be applicable will increase as the number of bases decreases. For example, if only 4-ethylpyridine with an absorptivity of 13.07 is present, the error incurred by using the average value of 21.25 will be the greatest. Likewise, the error in the quinoline determination increases as the number of quinolines in the sample decreases. However, coal-tar bases are complex mixtures, and this situation will be unlikely to happen; also, in most instances the true absorptivities of the base mixtures are expected to fall in the neighborhood of the average values.

Of the two types of bases, it is noted that the recovery for quinolines is better than that for pyridines. This is due to the fact that pyridines do not interfere with quinolines at 316.5 $m\mu$, while quinolines interfere with pyridines at 260 $m\mu$.

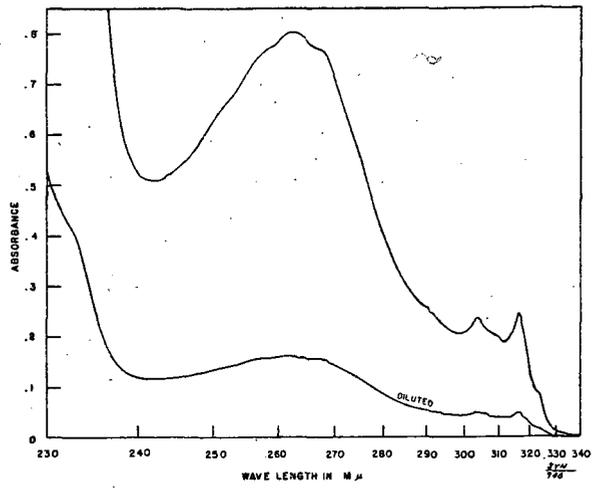


Figure 1. Spectrum of synthetic mixture 1.

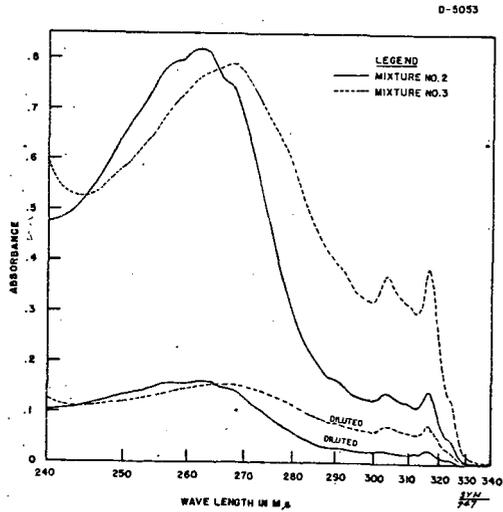


Figure 2. Spectra of synthetic mixtures 2 and 3.

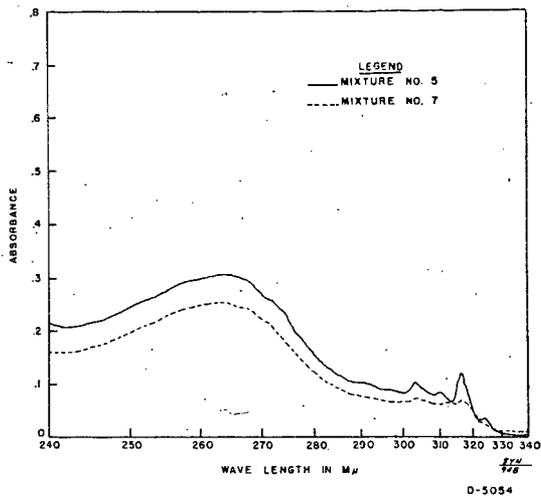


Figure 3. Spectra of synthetic mixtures 5 and 7.

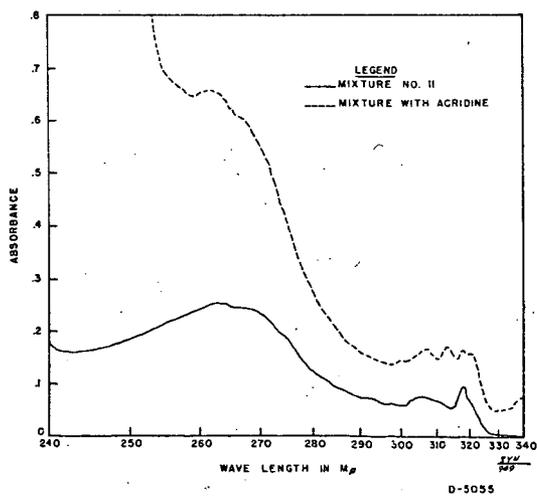


Figure 4. Spectra of synthetic mixture 11 and mixture containing acridine.

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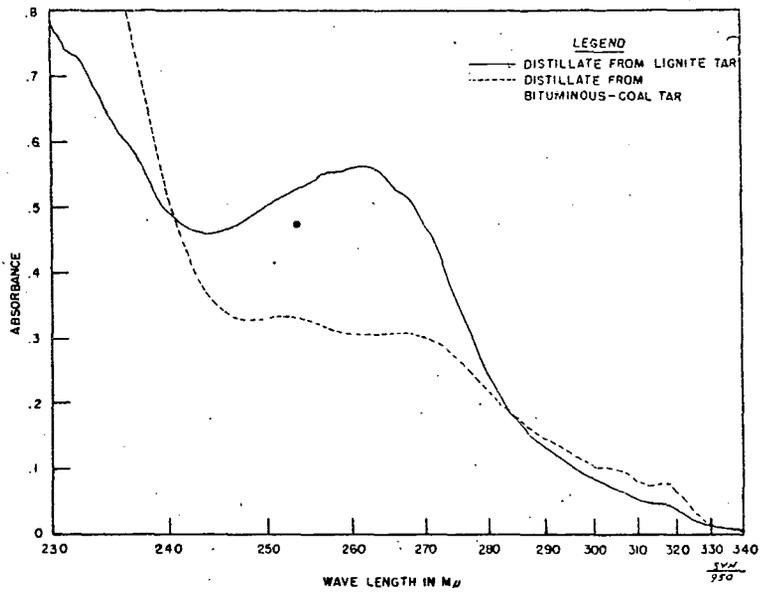


Figure 5. Spectra of base mixtures from two tar distillates

To obtain a good composite spectrum, the best concentration of the bases in isooctane is 0.03 - 0.04 gram per liter. However, this method can also be satisfactorily applied to a final isooctane extract containing a total base content as low as 0.015 gram per liter, if the quinoline content roughly equals that of the pyridines.

Interference. In extracting the bases from the distillate, a small amount of acid-soluble phenols and hydrocarbons that also possess an absorption for ultraviolet energy at 250 to 260 $m\mu$ is carried over to the acid solution and eventually will interfere with the determination of the bases. However, this interference can be overcome by washing the acid extract with isooctane and by holding all phenols in the alkaline solution during the final extraction of the bases with isooctane. Synthetic mixtures 6, 8, 10, and 12, which were contaminated purposely with hydrocarbons from tar distillate, demonstrate the fairly good removal of the hydrocarbons by treating the acid extract with isooctane.

Although the tar bases in distillates consist mainly of pyridines and quinolines, they also may contain some other nitrogenous compounds, such as pyrroles, indoles and anilines (5,7). However, pyrroles and indoles are very weak bases. Their pK_b values are so close to 14 that they are not extractable with dilute mineral acids. Anilines are basic in property and are extractable with dilute mineral acids. Some of the aniline derivatives, such as toluidines, have been identified in tar bases. By examining their ultraviolet spectra (1,3), it was shown that the highest absorbance appears from 235 - 250 $m\mu$ while the lowest is from 260 - 270 $m\mu$. Fortunately, their presence usually is in a small percentage in comparison with pyridine bases (7). In this method, the interference of this small amount of anilines can be assumed to be negligible insofar as the composite spectrum of the tar bases follows the general pattern of the synthetic mixtures. On the other hand, if the composite spectrum shows an unusual pattern with a peak at 240 to 250 $m\mu$, it might indicate that the tar base might contain a rather higher amount of anilines than usual. Should this happen, the small amount of anilines is included as pyridines at 260 $m\mu$, although the interference is not considered to be appreciable.

The two composite spectra (Fig. 5) of two tar distillates (Table IV) followed the general pattern of those of the synthetic mixtures. One of these distillates was obtained from a low temperature Wyoming lignite tar and the other from a low temperature bituminous coal tar. The spectrum of tar bases from the bituminous coal tar shows a small additional peak at 252 $m\mu$. This might be due to an unusually high amount of aniline derivatives or an unusually high percentage of a certain alkyl pyridine. For example, 3-ethyl-4-methylpyridine present in a comparatively larger amount than other pyridines would give a small individual peak at around 250 $m\mu$. A crude tar base, consisting of a mixture of neutral oil, tar bases, and small amounts of benzene and tar acids, was recovered as a by-product in the liquid-liquid countercurrent extraction of tar acids from the bituminous coal tar distillate using aqueous methanol (8). This crude tar base upon analysis was found to contain 70 weight-percent of total pyridines and 30 weight-percent of total quinolines. The proportion of total pyridines to total quinolines is quite similar to that for the base obtained directly from the distillate.

Analysis of Distillates Containing Acridine. High-boiling tar distillates may contain some acridines. Acridine, qualitatively and quantitatively, can be measured by a similar procedure. Its ultraviolet spectrum shows a significant peak at 339 $m\mu$ which is suitable for its quantitative analysis and also shows an unusual high absorbance at around 250 $m\mu$ which can be used as a confirmation for this compound.

A synthetic mixture, which contained six pyridines, three quinolines and acridine was analyzed in the same manner as the other synthetic mixtures. The composite spectrum of the mixture and the recovery of the bases by this method are shown in Figure 4 and Table V. The absorptivity for acridine at 339 $m\mu$ is 42.2, at 316.5 $m\mu$, 13.9, and at 260 $m\mu$, 17.2

Table IV

Determination of Total Pyridines and Total Quinolines in Tar Distillates

	Distillate	
	Lignite Tar	Bituminous Coal Tar
Distillation Endpoint, °C.	125.0	125.0
Pressure, mm. Hg	0.1	0.1
Volume of Sample Used, ml.	10.0	10.0
Weight of the Sample, g.	9.35	9.55
Total Pyridines Found, g.	0.103	0.104
Total Quinolines Found, g.	0.012	0.05
Total Base, g.	0.115	0.154
Total Pyridines in Base, wt. %	89.5	67.5
Total Quinolines in Base, wt. %	10.5	32.5
Total Base in Sample, wt. %	1.23	1.62
Total Pyridines in Sample, wt. %	1.1	1.1
Total Quinolines in Sample, wt. %	0.13	0.52

Table V

Recovery of Bases from a Synthetic Mixture Containing Acridine

Bases	Present, gram/liter	Found, gram/liter	Recovery, percent
Total Pyridines	0.0184	0.020	109.0
Total Quinolines	0.00989	0.0081	82.0
Acridine	0.0017	0.00175	103.0

Other Applications. This method can also be applied to tar refinery streams, such as the extract and raffinate, from the countercurrent liquid-liquid extraction of tar distillates with aqueous methanol and hexane (8). The bases in the hexane phase can be analyzed by this procedure directly, and the bases in the methanol phase can be purified by distillation and extraction as described elsewhere (2).

Pyridine bases present in samples from petroleum refining can also be determined by this method.

CONCLUSION

An ultraviolet spectrophotometric method developed to determine total pyridines and total quinolines in their mixtures has been shown to give satisfactory analysis of these two types of bases in coal-tar distillates. This method should work equally well for the bases in similar materials.

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IDENTIFICATION AND DETERMINATION OF LOW-BOILING
PHENOLS IN LOW TEMPERATURE COAL TAR

Clarence Karr, Jr., Paul M. Brown, and Patricia A. Estep
Low-Temperature Tar Laboratory
Bureau of Mines
U. S. Department of the Interior
Morgantown, W. Va.

George L. Humphrey
West Virginia University
Morgantown, W. Va.

ABSTRACT

Low-boiling phenols in a low temperature bituminous coal tar distillate have been identified and quantitatively determined by gas-liquid partition chromatography. These phenols were also determined by the conventional technique of fractional distillation, followed by infrared analysis. Comparison of the two independent techniques of GLPC and IR was made. Phenol, cresols, xylenols and ethylphenols were included in the analyses.

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Clarence Karr, Jr., Paul M. Brown, and Patricia A. Estep
Low-Temperature Tar Laboratory
Bureau of Mines
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Morgantown, West Virginia

George L. Humphrey
West Virginia University
Morgantown, West Virginia

As part of an extensive program on separating and characterizing components in tar resulting from low temperature carbonization of bituminous coal, it was desired to identify and determine quantitatively the low-boiling phenols in a certain tar distillate. Examination of the literature published within the last ten years showed that information on identification of phenols in low temperature tar mostly represents work done outside of the United States (3,6,7,8,9,10). The best conventional quantitative procedure involves fractional distillation of the mixture of phenols, followed by infrared analysis. This technique has been recently described by Fair and Friedrich (2), who, however, do not give any actual examples of analysis of coal-tar distillates. An example, using essentially the same technique, is provided by Jones and Neuworth (4).

To complement as well as check the results obtained by distillation and infrared analysis, a completely independent method of separation and analysis was chosen. This was a gas-liquid partition chromatographic technique for phenols which had been previously described (5).

EXPERIMENTAL

Isolation of Mixture of Low-Boiling Phenols. A distillate was obtained from a sample of low temperature (500°C.) bituminous coal tar, furnished by the Pittsburgh Consolidation Coal Company, Library, Pa., under very mild temperature conditions, so as to reduce structural alterations of tar components to a minimum. For this purpose, a rotary vacuum stripper was constructed.

The stripper consisted of a 12-liter-capacity, stainless-steel, spherical flask, which was rotated at about 6 r.p.m. in a 20-gallon-capacity oil bath. A mechanical vacuum pump with a free-air flow rate of 375 liters per minute was used to reduce the pressure, and oxygen-free nitrogen was employed to maintain an inert atmosphere in the system. An ionization vacuum gauge with a range of 1000 mm. to 1 micron was used for continuous pressure indication. The main distillate was recovered with a cold-water Friedrichs condenser. A small portion of distillate, representing components distillable at room temperature and about 133 microns pressure (equivalent to very approximately 215°C. at 1 atmosphere), was recovered with a trap cooled with a mixture of trichloroethylene and solidified carbon dioxide. A similar trap was used to protect the sensing head of the ionization gauge. In operation, the bulk of the distillation takes place from the fresh film of hot tar, which is continually drawn up the wall at one side of the flask owing to the slow rotary motion. At about 125°C. and 133 microns about 21 weight-percent of the tar was distillable.

A Claisen alkali extraction was performed on the cold-trap portion of the distillate, following the procedure described by Woolfolk et al. (12). From this extraction the tar-acid content of the low-boiling distillate appeared to be about 20 volume-percent. This cold-trap material did not necessarily represent complete recovery of any of its components from the tar. It was, however, considered to be a good mixture for evaluation of a vapor-phase chromatographic technique because of its high volatility and relatively simple composition.

Distillation of Low-Boiling Phenols. A 37.25-g. portion of the low-boiling mixture of phenols isolated from the tar was fractionated in a Piro-Glover micro-spinning-band vacuum still. All air was flushed out of the still with oxygen-free dry nitrogen before the distillation was started. The still was operated at a head pressure of 50 mm. Hg, which very nearly represents the pot pressure, since the pressure drop in the spinning-band column is almost negligible. The boilup rate was approximately 30 to 40 ml. per hour, and the reflux ratio was 10 to 1. The speed of the band was fixed at 1800 r.p.m. Seven fractions were isolated, with a recovery of 96.2 weight-percent. All fractions were initially colorless, but fraction 7 developed a slight color on standing two days. The results of this distillation are shown in Table I and Figure 1. The temperature readings in Figure 1 are for an iron-constantan thermocouple in the still head as recorded on a 10-millivolt, 5-inch-span recorder, the cold junction being at room temperature, which was essentially constant. The weights of each component in each fraction were determined by conventional infrared spectrophotometry, using the following analytical wave lengths, in microns:

Compound	Fraction						
	1	2	3	4	5	6	7
Phenol	14.55	14.55					
o-Cresol	11.86	11.86	13.35				
2,6-Xylenol			11.02				
p-Cresol				12.24			
m-Cresol			14.57	14.57			
o-Ethylphenol				13.34	13.34	13.34	
2,4-Xylenol				12.47	10.27	12.27	
2,5-Xylenol					10.03	10.03	
2,3-Xylenol					11.11	14.17	
p-Ethylphenol						12.07	
m-Ethylphenol						11.04	
3,5-Xylenol						9.73	14.64, 10.56
3,4-Xylenol							12.33, 12.53

Gas-Liquid Partition Chromatography of Low-Boiling Phenols. The low-boiling mixture of phenols obtained from the tar was fractionated in a vapor phase chromatographic apparatus. A 12-foot column of $\frac{1}{8}$ -inch tubing packed with Johns-Manville C-22 firebrick, 30-60 mesh, containing 31 weight-percent di-n-octyl phthalate was used at 160°C., with a carrier gas flow rate of 150 cc. helium per minute (15 psig. inlet, outlet at 1 atm.), and a 250 microliter sample. The efficiency of this column was determined using a charge of o-cresol and the equation given by Wiebe (11):

$$p \approx 2 \left(\frac{V_m}{V_m - V_e} \right)^2 \quad (1)$$

where p = number of theoretical plates.

V_m = volume of effluent that has passed through the column when the zone maximum appears in the effluent.

V_e = volume of effluent that has passed through the column when a point on the elution curve has been reached where the solute concentration is 1/eth of the maximum.

A value of 966 theoretical plates was obtained.

Table I

Fractionation of Low-Boiling Phenol Distillate in Spinning-Band Still

Fraction No.	Weight, Grams	Refractive Index, n_D^{20}	Components by Infrared Analysis		
			Major	Minor	Trace
1	8.00	1.5243	Phenol, 5.2 g.	o-Cresol, 2.8 g.	
2	7.84	1.5224	o-Cresol, 4.8 g.	Phenol, 3.0 g.	2,6-Xylenol, 0.8 g.*
3	7.88	1.5190	m-Cresol, 3.4 g.	p-Cresol, 2.3 g.	
4	3.39	1.5180	m-Cresol, 1.35 g.	o-Cresol, 1.4 g.	o-Ethylphenol, 0.15 g.
5	3.07	1.5173	2,4-Xylenol, 1.3 g.	p-Cresol, 0.6 g.	2,3-Xylenol, 0.12 g.
6	4.76	1.5150	2,4-Xylenol, 2.1 g.	2,5-Xylenol, 0.74 g.	o-Ethylphenol, 0.1 g.*
7	0.90	1.5152	2,4-Xylenol, 1.5 g.	3,5-Xylenol, 0.9 g.	2,3-Xylenol, 0.3 g.
			3,4-Xylenol, 0.3 g.*	p-Ethylphenol, 0.8 g.	c-Ethylphenol, 0.1 g.*
			3,5-Xylenol, 0.3 g.*	m-Ethylphenol, 0.6 g.	
				2,5-Xylenol, 0.6 g.	
				m-Ethylphenol	
				2,3-Xylenol	
				2,3,5-Trimethylphenol	

* Estimated quantities.

The results of fractionating the tar phenols are shown in Figure 2. As can be seen, there are eight obvious concentration maxima. Traps consisting of a short length of 12-mm. I. D. glass tubing fitted with a rubber serum bottle cap and syringe needle were filled with about 1 ml. of spectro-grade cyclohexane and used in an attempt to isolate the components producing the major peaks in the elution curve. Infrared analysis of the solutions corresponding to peaks 1 and 2 showed beyond any doubt that the compounds responsible for these peaks were phenol and o-cresol, respectively. However, contamination of subsequent solutions with residual phenol and o-cresol in the collection system made positive identification of the components responsible for other peaks impossible. Further identification was made possible by comparing the relative retention times of the various peaks with the relative retention times of individual pure low-boiling phenols under identical operating conditions. This comparison is presented in Table II; in addition, the retention times of the individual pure phenols are indicated in the lower portion of Figure 2.

Table II

Comparison of Experimental Relative Retention Times with Times for Individual Phenols

Peak No.	Relative Retention Time to Peak 2 (o-Cresol)	Compound	Relative Retention Time (Compared to o-Cresol)
1	0.75	Phenol	0.79
2	(1.00)	o-Cresol	(1.00)
3	1.13	2,6-Xylenol	1.12
4	1.31	m-Cresol	1.29
		p-Cresol	
5	1.53	o-Ethylphenol	1.53
6	1.67	2,5-Xylenol	1.66
		2,4-Xylenol	1.70
7	2.01	2,3-Xylenol	1.98
		p-Ethylphenol	2.02
8	2.16	3,5-Xylenol	2.08
9	2.42	3,4-Xylenol	2.47

The areas under each of the peaks in Figure 2 were obtained by means of a planimeter and the weight-percentages of phenols were calculated from these areas and the total area. For this calculation it is assumed that the thermal conductivities of the components are about the same, being homologs, and that therefore, areas under the recorded curves are directly proportional to the weight percent of the components (1). These values are given in Table III, which also includes the weight percents calculated from the infrared data given in Table I.

Table III

Comparison of Infrared and Vapor-Phase Chromatographic Analysis of Low-Boiling Mixture of Phenols

Compound	Weight-Percent by IR	Weight Percent by VPC
Phenol	22.5	21
o-Cresol	25	26
m-Cresol	13	} 26
p-Cresol	8	
2,4-Xylenol	13	} 13
2,5-Xylenol	3.5	
2,6-Xylenol	> 2	5
3,5-Xylenol	3	3
o-Ethylphenol	~1	2
m-Ethylphenol	1.5	} 3
p-Ethylphenol	2	
2,3-Xylenol	1	
3,4-Xylenol	~0.8	< 1
	~96	~99

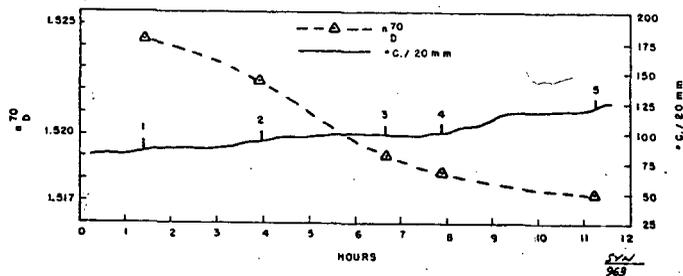


Figure 1. Fractionation of low-boiling phenol distillate in spinning band still.

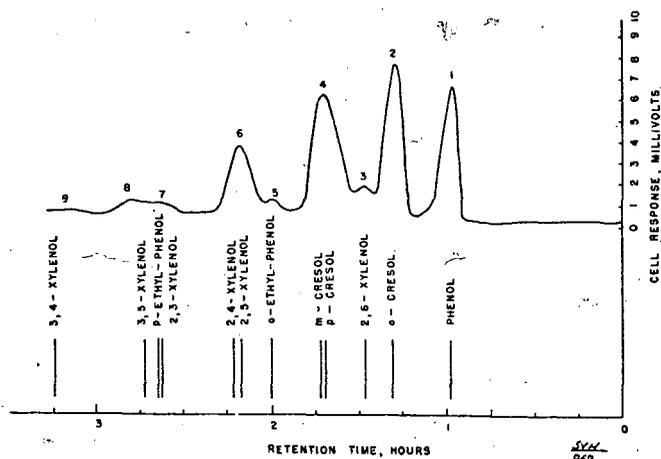


Figure 2. Vapor phase chromatography of low-boiling mixture of phenols and retention times of individual pure phenols.

DISCUSSION

Figure 2 demonstrates that by means of gas-liquid partition chromatography alone a low-boiling mixture of phenols with as many as a dozen components can be fairly well characterized, both qualitatively and quantitatively. There can be no question about the identity of a component for those retention times for which calibrations have been made on all theoretically possible phenols and where the peaks for individual phenols are essentially isolated in time. Examples of this would be peaks 1, 2, 3, and 5. In addition, the quantitative analysis is always obtainable with acceptable accuracy from the areas under these peaks. In fact, the vapor-phase chromatographic analysis is undoubtedly much less subject to qualitative and quantitative errors, being such a simple and direct technique. However, it is limited in scope by the difficulty of resolving certain phenols which have very similar partition coefficients.

As can be seen in Table III the agreement between weight-percentages of phenols by infrared analysis and vapor-phase chromatographic analysis is fairly good. In the case of two compounds, 2,6-xyleneol and o-ethylphenol, only an estimate of the quantity could be made by IR analysis, whereas in the VPC analysis these two compounds gave two distinct peaks whose areas could be obtained with fair accuracy. The extent of fractionation of higher boiling phenols will be described in a future paper.

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FLUID-BED PRETREATMENT OF BITUMINOUS COALS
AND LIGNITE AND DIRECT HYDROGENATION
OF THE CHARs TO PIPELINE GAS

by
K. C. Channabasappa and H. R. Linden
Institute of Gas Technology
Chicago, Illinois

ABSTRACT

The fluid-bed pretreatment of low-rank coals in nitrogen, air, carbon dioxide and steam atmospheres was investigated in a bench-scale unit at atmospheric pressure, and at maximum temperatures of 400° to 720°F, in a study of the production of non-agglomerating, reactive chars suitable for fluid-bed hydrogenation to pipeline gas. Reactivities of the chars in respect to methane and ethane production were determined in batch hydrogenation tests at 1350°F, approximately 17 standard cubic feet of hydrogen per pound of char and approximately 3000 psig maximum pressure.

The results of this study indicated that the optimum pretreatment temperature is 600°F for bituminous coal and 500°F for lignite, and that there is little variation in the reactivity of the chars produced in nitrogen, air and steam atmospheres. The chars produced in a carbon dioxide atmosphere showed consistently lower reactivity. Substantial agglomeration during pretreatment or hydrogasification occurred only with high-volatile bituminous coal. The extent of agglomeration increased with increases in pretreating temperature, and in steam and carbon dioxide atmospheres. Under the routine test conditions, the chars produced 50 to 55 weight percent (moisture-ash-free) of pipeline gas containing 70 to 80 mole percent of methane plus ethane upon reaching a hydrogasification temperature of 1350°F. At higher hydrogen/char ratios, substantially higher conversions of pretreated lignite were attained.

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Studies of methods for supplementing base-load natural gas requirements have indicated that conversion of coal to high-methane content gas, in areas where long-distance transmission lines pass through coal fields near the major market areas, may be the most economical method for transporting this source of energy to the domestic consumer in readily usable form. One method for the production of pipeline (900 Btu/SCF*) gas is direct hydrogenation of low-rank coals to methane.^{3,4,5,7-11,27} In such a process, the residual char may be used for hydrogen production by suspension-gasification with steam and oxygen, or for meeting fuel requirements. Essentially complete hydrogasification of lignites and some sub-bituminous coals may also be feasible; in this case hydrogen could be produced by reforming of product gas or of a relatively small portion of the primary natural gas supply.

Hydrogasification has three major advantages over the production of pipeline gas by the two-step partial coal oxidation-synthesis gas methanation process:^{1,24} (1) large reduction, or potential elimination, of oxygen requirements, (2) elimination of the extreme synthesis gas purification requirements prior to catalytic methanation and (3) greater thermal efficiency through reduction of exothermic heats of reaction.²⁸ These potential advantages should constitute adequate justification for attempting to determine whether the design of a hydrogasification reactor suitable for large throughput rates, and with facilities for residual char removal, is feasible. On the basis of batch reactor tests, engineering studies and operation of pilot plant-scale models, it appears that the optimum design requires fluid-bed operation with parallel upward flow of dry pulverized coal and hydrogen at temperatures of 1300° to 1400°F and pressures of more than 1000 psig. A thorough knowledge of the agglomeration and hydrogasification characteristics of available coal feeds would be essential for successful operation of such a reactor.

In the first phase of this investigation, it was demonstrated in batch reactor tests that essentially olefin-free gases containing 60 to 80 volume percent methane could be produced by hydrogasification of an Illinois bituminous coal,²⁸ a Wyoming subbituminous coal and North Dakota lignite at 1350°F and 2500 to 3500 psig. By adjustment of hydrogen/coal ratios, gasifications on an ash- and moisture-free basis up to 80 weight percent were obtained with bituminous coal, and over 90 weight percent with lignite. It was also noted that after

- Standard cubic foot at 60°F, 30 inches of mercury pressure, saturated with water vapor.

preheating of these coals in the batch reactor to 600° to 700°F at atmospheric pressure in a nitrogen atmosphere, substantially higher rates of high heating value gas production were obtained at the expense of converting a relatively small portion of the coal to low heating value gases during pretreatment. However, the residues obtained at the end of hydrogasification were agglomerated, the degree of agglomeration being most severe with bituminous coal. Since this would be detrimental to the smooth operation of a continuous fluid-bed hydrogasification unit, the need for a pretreatment step yielding non-agglomerating, reactive chars was indicated.

Much of the published information useful in selecting pretreatment conditions has been obtained in the development of processes for the production of smokeless fuels, and in studies of upgrading of high-moisture content, low-rank coals for power plant, carbonization and metallurgical uses.^{16, 20-23, 25} Of particular interest are the results of investigations concerned with reducing the caking or agglomeration tendencies of coal. For this purpose, thermal pretreatment at temperatures up to 800°F for partial removal of volatile constituents, often in the presence of an oxidizing atmosphere, is generally practiced.^{6, 17, 19, 25} Control of agglomeration by dilution with recycle char¹⁵ and with inert solids¹³ has also been recommended. Preheating in inert atmospheres before hydrogenation has been found to result in the elimination of a considerable fraction of the oxygen content in the form of carbon oxides, thereby raising the "available" hydrogen content of the coal.²⁹

The effects of temperature, residence time and atmosphere on the quantity and composition of the gas evolved in the distillation of low-rank coals have been investigated extensively.^{12, 14} These studies show that as the temperature is raised, oxygen-containing substances break down to form water, carbon dioxide and carbon monoxide. Highest rates of carbon dioxide evolution occur between 400° and 600°F. As temperatures are increased further, hydrocarbon and hydrogen evolution represents the major portion of the increasing gas yields from bituminous and subbituminous coals; lignites tend to evolve mainly carbon oxides.

A considerable volume of literature also exists on pretreatment of coal with various acids, acid salts, nitric oxide, sulfur or sulfur compounds and caustic prior to hydrogenation.¹⁸ However, the relative effects of these chemical pretreatment procedures on coal reactivity are not clearly defined.

APPARATUS AND PROCEDURE

The laboratory-scale coal pretreatment unit used in this study consisted of a pyrex fluid-bed retort, 1-3/4 inches inside diameter and 30-1/2 inches long with a 3-1/8 inch inside diameter, 15-inch long disengaging section. The retort closure was equipped with an 11/32 inch outside diameter thermocouple well which protruded very nearly to the bottom of the reaction zone.

The retort was heated by two circular electric furnaces. The lower one was 5 inches inside diameter and 12 inches long and had a rating of 2.5 kilowatts; the upper one was 2-3/8 inches inside diameter and 12 inches long and had a rating of one kilowatt. The disengaging section was heated with an electro-thermal tape. The unit was also equipped with a cyclone separator and a water-cooled condenser. A diagrammatic sketch of the apparatus is shown in Fig. 1.

Three-quarter pound batches of powdered coal (88-98 weight percent through 100-mesh) were dried at 110°C according to ASTM method D 271-48;² the dry coal was charged to the reactor at room temperature and was heated to the desired temperature at a rate of about 12°F per minute.

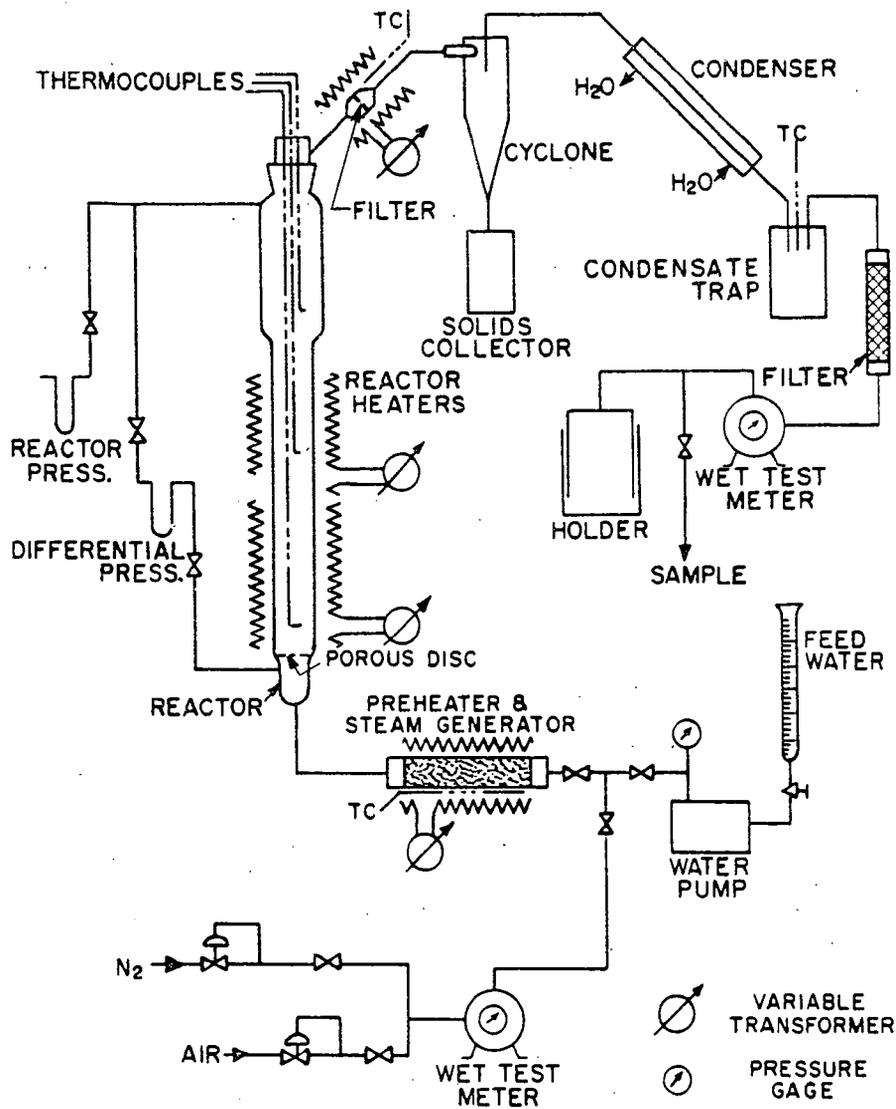


Fig. 1.-FLOW DIAGRAM OF FLUID-BED COAL PRETREATMENT LABORATORY UNIT

Measured volumes of nitrogen, air, carbon dioxide or steam, at rates sufficient to keep the coal bed in a fluidized state, were preheated in an electric furnace to 800° to 1000°F and introduced at the bottom of the retort.

Temperatures at the bottom, center and upper zones of the retort were sensed with chromel-alumel thermocouples and measured by a Wheelco temperature indicator. Pressures were read from a 15-inch standard mercury manometer.

The feed gases used as fluidizing media together with the fixed gas evolved from the distillation of the coal charge were passed through a 60-millimeter outside diameter fritted glass disc kept at 400°F, and a cyclone separator, to remove the suspended coal particles from the outgoing gas. The gas, after passing through a water-cooled condenser, was measured by wet-test meter and was stored in a gas-holder. Simultaneous readings of temperatures, pressures and volumes of inlet and outlet gases were recorded at intervals throughout the progress of the run.

Gas samples were taken at intervals by bleeding the sample into an evacuated 200 cc gas analysis bottle. At the conclusion of the run, the electric current was shut off and a composite gas sample was taken from the gas holder. After the retort cooled, it was opened and the solid residue recovered. The weights of the liquid condensate and of the solid residue were recorded.

Product gas samples were analyzed with a Consolidated Engineering Co. Model 21-103 mass spectrometer and specific gravities and heating values were calculated from the analyses. Product gas volumes and heating values were calculated for the conditions of 60°F, 30 inches of mercury absolute pressure and saturation with water vapor, assuming the ideal gas law. Specific gravities were calculated on a dry basis from the average molecular weight of the gas referred to air of molecular weight 28.972.

Since the gas samples taken at intervals during the test period differed in composition, the properties of the composite sample taken from the gas-holder at the end of the run were used to determine the weight fraction of the coal charge gasified during pretreatment. The material balance was calculated from the weights of liquid and solid products obtained at the end of the run, and from the weight of the fixed gas (total weight of outlet gas less the total weight of the feed gas) collected in the gas-holder.

The solid residue was subjected to a screen analysis to determine the extent of agglomeration and was analyzed in accordance with ASTM method D 271-48.

An average sample of the residue from pretreatment was crushed to minus 60-mesh and was charged to a one-liter capacity batch hydro-gasification reactor to determine the gas yields and compositions obtainable at 1350°F and about 3000 psig, employing a hydrogen/char ratio of about 17 SCF/lb. The apparatus and procedure employed in the hydrogasification tests were described previously.^{2a}

Solid residues obtained in these tests were again subjected to screen analyses to determine the extent of agglomeration.

YIELDS AND CHARACTERISTICS OF FLUID-BED PRETREATMENT PRODUCTS

The proximate, ultimate and screen analyses of the pulverized coals used in the pretreatment studies are shown in Table 1. Before charging to the bench-scale fluid-bed unit the samples were dried at 110°C. The product yields and compositions after pretreatment for 50 to 75 minutes in nitrogen, air, carbon dioxide and steam at flows of 4 to 6 SCF/lb dry coal-hour and at maximum temperatures of 400° to 720°F, are summarized in Table 2.

Table 1.-PROXIMATE, ULTIMATE AND SCREEN ANALYSES OF COALS USED IN TESTS

<u>Coal</u>	<u>High-Volatile "B"</u>	<u>Subbitu- minous "A"</u>	<u>Lignite</u>
Proximate Analysis, wt %			
Moisture	4.1	11.0	22.0
Volatile Matter	34.6	38.7	29.0
Ash	6.2	4.7	8.1
Fixed Carbon	55.1	45.6	40.9
Total	100.0	100.0	100.0
Heating Value, Btu/lb (Dry Basis)			
	13,790	12,760	10,800
Ultimate Analysis, wt % (Dry Basis)			
Ash	4.70	5.30	10.40
Carbon	72.50	66.60	65.30
Hydrogen	4.57	4.65	4.29
Sulfur	1.16	2.46	0.31
Nitrogen + Oxygen (By Difference)	17.07	20.99	19.70
Total	100.00	100.00	100.00
Screen Analysis, wt %			
+ 40 Mesh	0.1	--	--
+ 60 Mesh	2.5	0.8	1.0
+ 80 Mesh	0.9	1.0	1.0
+100 Mesh	8.4	--	0.1
+120 Mesh	9.1	3.2	2.7
+200 Mesh	20.7	5.9	9.6
-200 Mesh	58.3	89.1	85.6
Total	100.0	100.0	100.0

Table 2.-EFFECTS OF PRETREATMENT CONDITIONS ON PRODUCT YIELDS AND CHARACTERISTICS

Coal No.	HIGH VOLTAGE VAPOR PRETREATMENT										LOW VOLTAGE										
	PR-24	PR-25	PR-26	PR-27	PR-28	PR-29	PR-30	PR-31	PR-32	PR-33	PR-8	PR-9	PR-10	PR-11	PR-12	PR-13	PR-14	PR-15	PR-16	PR-17	
Operating Conditions																					
Original Charge (Before Drying), grams	340.2	340.2	340.2	340.2	340.2	340.2	340.2	340.2	340.2	340.2	340.2	340.2	340.2	340.2	340.2	340.2	340.2	340.2	340.2	340.2	
Original Charge (After Drying), grams	330.8	330.8	330.8	330.8	330.8	330.8	330.8	330.8	330.8	330.8	330.8	330.8	330.8	330.8	330.8	330.8	330.8	330.8	330.8	330.8	
Gas Type	Steam										Air										
Gas Prod., Avg. 500/Abbr. hr	6.03	5.17	4.80	5.96	4.13	5.96	4.80	4.67	3.98	5.85	5.85	4.70	4.70	5.85	5.85	4.70	4.70	5.85	5.85	4.70	
Maximum Temperature, °F	610	720	510	610	705	605	580	620	750	620	620	620	610	620	400	620	510	520	510	620	
Operating Medium	N ₂																				
Water and Other Condensates, wt % Dry Coal	4.7	5.1	5.2	2.2	3.8	2.1	2.1	4.2	6.4	2.5	7.3	4.2	6.2	3.0	7.2	5.2	4.3	7.1	9.4	6.3	
Residue (Char), wt % Dry Coal	91.7	85.0	89.8	89.6	94.3	91.4	95.1	90.2	87.9	86.5	86.5	89.6	91.9	81.5	81.5	89.7	89.1	86.5	89.1	86.5	
Material Balance, %	101.1	98.8	99.3	98.1	101.2	99.9	98.9	99.2	98.6	100.4	101.7	99.9	99.9	98.5	101.5	101.5	101.5	101.5	101.5	101.5	
Composition, mole %																					
H ₂	95.2	75.5	57.1	48.2	61.2	1.1	---	---	---	73.8	86.4	3.1	---	---	---	84.5	27.3	1.9	---	---	
CO	2.4	3.3	28.2	2.4	4.7	93.7	23.6	10.9	17.4	19.0	7.9	96.7	---	---	---	61.0	2.1	10.4	93.2	79.2	
H ₂ S + CH ₄	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Paraffins	0.1	0.1	0.1	0.2	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Olefins	1.7	10.0	1.5	0.3	1.1	3.3	19.4	54.0	42.6	2.8	0.2	---	---	---	---	12.1	0.7	0.9	1.6	2.2	2.7
A ₂ Total	0.4	2.8	0.2	0.2	0.1	0.1	0.2	0.3	0.1	---	---	---	---	---	---	0.1	---	---	---	---	---
Heating Value, Btu/SCP	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Residue Properties, Air - 1	0.968	0.929	1.012	0.990	0.995	1.479	1.023	0.732	0.788	1.076	1.023	1.500	---	---	---	1.276	0.969	1.026	1.472	1.451	1.347
Screen Analysis, wt %																					
+100 - Mesh	15.8	9.7	6.6	23.8	40.7	31.6	5.7	16.2	22.4	7.9	1.5	1.1	---	---	---	0.6	---	---	---	0.5	0.8
+200 - Mesh	31.0	37.5	41.5	23.9	17.7	35.6	23.0	28.1	31.2	20.9	2.9	4.0	---	---	---	2.2	1.6	2.7	21.0	14.1	12.8
+40 - Mesh	54.4	21.7	31.9	54.3	41.2	24.4	62.2	56.1	46.4	68.2	80.9	80.9	---	---	---	75.6	78.5	90.0	62.3	85.4	84.3
Proximate Analysis, wt % (Dry Basis)																					
Moisture	28.4	22.4	28.7	29.3	28.9	26.6	24.2	28.8	25.8	28.1	28.4	31.1	---	---	---	25.6	27.5	29.9	35.6	28.6	31.7
Volatile Matter	65.0	68.2	60.4	66.2	60.3	63.0	29.4	60.3	62.5	61.4	61.3	62.5	---	---	---	65.3	62.5	52.5	55.4	53.1	62.3
Fixed Carbon	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	---	---	---	100.0	100.0	100.0	100.0	100.0	100.0
Total	8.60	10.90	9.50	10.30	10.30	10.50	10.90	10.90	10.90	10.90	10.90	10.90	---	---	---	10.90	10.90	9.60	10.90	10.90	9.20
Ultimate Analysis, wt % (Dry Basis)																					
Carbon	75.10	72.60	73.00	73.70	73.60	73.60	73.20	73.20	73.20	73.20	73.20	73.20	---	---	---	72.20	73.50	73.50	71.60	71.60	71.60
Nitrogen	1.57	0.72	0.88	0.98	1.34	1.34	1.17	1.17	1.17	1.17	1.17	1.17	---	---	---	1.40	1.19	1.40	1.40	1.40	0.90
Hydrogen	10.80	11.14	12.19	10.64	10.45	10.55	10.55	10.55	10.55	10.55	10.55	10.55	---	---	---	12.20	11.80	12.20	11.80	11.80	13.84
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	---	---	---	100.00	100.00	100.00	100.00	100.00	100.00

1. Fired according to ASTM Method D 271-46
 ** Net Wt of Fixed Gas
 ** Net Wt of Dry Coal Charged
 ** Wt. of Residue, Net Wt. of Water, and Other Condensates + Net Wt. of Fixed Gas
 ** Wt. of Dry Coal Charged
 * Analysis of composite sample not available.
 * Flare gases evolved during pretreatment.
 * Analysis of average sample from the boiler containing SCP - Gas volume in standard cubic feet at 60°F, 30 inches of mercury pressure and saturated with water vapor.

Fixed Gases

In all of the runs the cumulative volume of fixed gas evolved increased with increases in pretreatment temperature as illustrated by the steam atmosphere data for lignite and bituminous coal shown in Fig. 2. The evolved gases consisted primarily of carbon dioxide in case of lignite and subbituminous coal, and of gaseous hydrocarbons and hydrogen in case of bituminous coal. After attainment of constant temperature, the rate of gas evolution decreased markedly with residence time as shown in Fig. 3 for steam atmosphere runs with lignite and bituminous coal at maximum pretreatment temperatures of 520°F and 620°F, respectively.

The effects of pretreatment atmosphere on the rate of fixed gas evolution from bituminous coal at approximately 600°F maximum pretreatment temperature are shown in Fig. 4. Carbon dioxide evolution was lowest in a steam atmosphere, probably as a result of substantial carbon monoxide formation, and was very rapid in an air atmosphere after attainment of maximum temperature. The highest hydrocarbon evolution occurred in a steam atmosphere and the lowest hydrocarbon evolution occurred in an air atmosphere.

Carbon dioxide evolution for subbituminous coal and lignite was higher than from bituminous coal in all of the pretreatment atmospheres investigated. Total carbon dioxide evolution for subbituminous coal in the 600°F runs was approximately 0.5 SCF/lb (dry basis) and carbon dioxide evolution from lignite in the 500°F runs was about 0.3 to 0.4 SCF/lb (dry basis). Hydrocarbon evolution for these relatively high oxygen content coals under the above conditions was low and normally ranged from 0.1 to 0.2 SCF/lb (dry basis) with the hydrocarbon formation being even lower in an air atmosphere.

Residual Chars

The chars showed relatively uniform decreases in volatile matter with increases in pretreatment temperature, independently of other pretreatment conditions (Table 2); the effects of pretreating atmosphere composition on the quantity and composition of fixed gases evolved were not reflected in the proximate analyses. The ultimate analyses of selected chars (Table 2) also showed little variation with pretreatment conditions in the 500° to 700°F temperature range. However, the extent of agglomeration varied considerably with the composition of the pretreatment atmosphere as well as with pretreatment temperature. This is shown in Fig. 5 which indicates a well-defined trend of increases in agglomeration with increases in temperature for the pretreatment of bituminous coal in a steam atmosphere, and a tendency for considerably greater agglomeration in carbon dioxide and steam atmospheres as compared to nitrogen and air atmospheres. The greater agglomeration of bituminous coal in steam and carbon dioxide appeared to be related to the large evolution of hydrocarbon gases under these pretreatment conditions.

In contrast to this behavior, subbituminous coal and lignite did not agglomerate significantly over the entire range of pretreating conditions. This follows the trend of decreases in agglomeration with decreases in hydrocarbon evolution. However, subbituminous coal and lignite exhibited some tendency towards increased agglomeration at the higher temperatures, and in steam and carbon dioxide atmospheres.

In all the pretreatment runs, the amount of dried coal converted to gases was quite small (2.5 to 9.9 weight percent of charge). The heating values of the total product gases was low, normally less than 200 Btu/SCF, except in steam pretreatment runs in which gases with heating values in the 200 to 1000 Btu/SCF range were evolved.

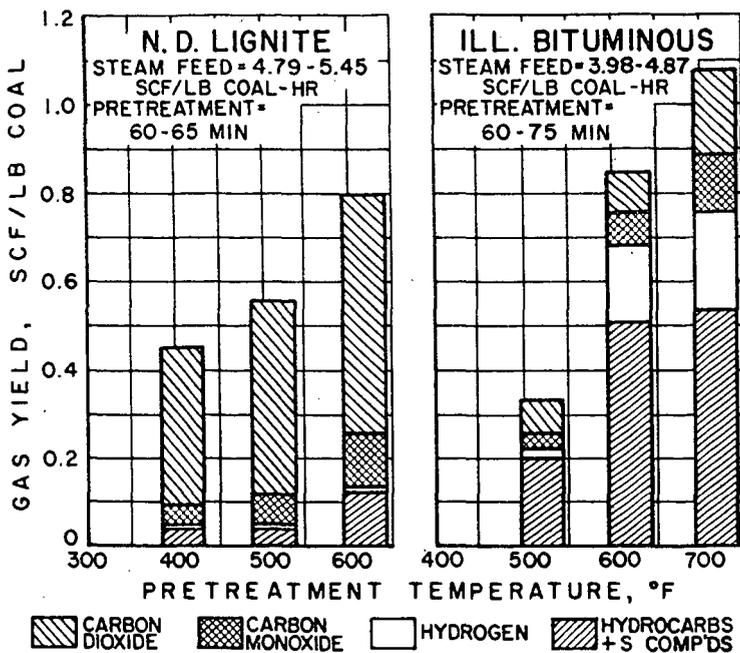


Fig. 2.-COMPOSITION AND YIELD OF GASES FROM FLUID-BED PRETREATMENT OF DRIED LIGNITE AND BITUMINOUS COAL IN STEAM

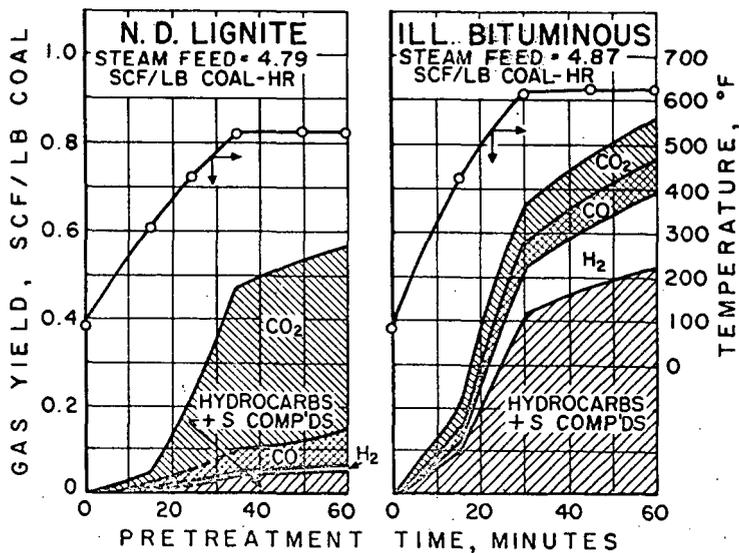


Fig. 3.-RATE OF EVOLUTION, AND COMPOSITION, OF GASES FROM FLUID-BED PRETREATMENT OF DRIED LIGNITE AND BITUMINOUS COAL IN STEAM

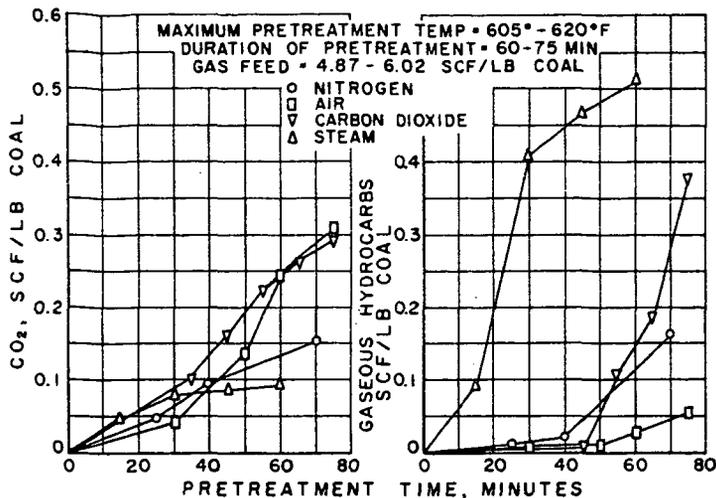


Fig. 4.-EFFECT OF GAS ATMOSPHERE ON RATE OF EVOLUTION OF CARBON DIOXIDE AND GASEOUS HYDROCARBONS FROM DRIED ILLINOIS HIGH-VOLATILE "B" BITUMINOUS COAL

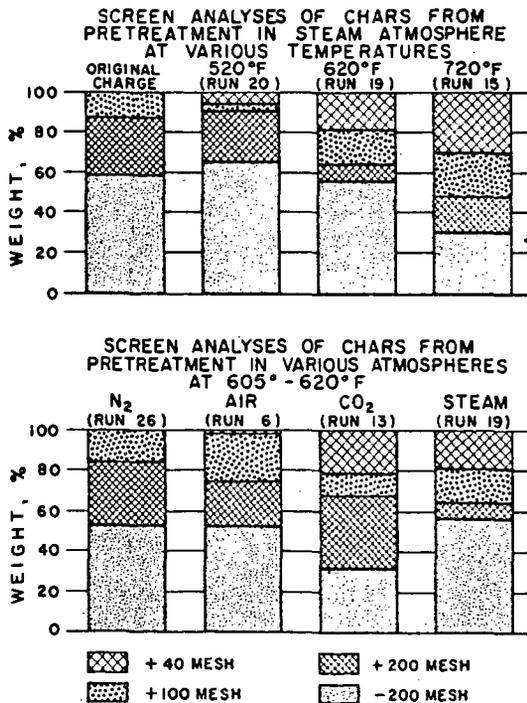


Fig. 5.-EFFECTS OF PRETREATMENT TEMPERATURE AND GAS ATMOSPHERE ON PARTICLE SIZE DISTRIBUTION OF DRIED ILLINOIS HIGH-VOLATILE "B" BITUMINOUS COAL

HYDROGENOLYSIS CHARACTERISTICS OF PRETREATED COAL

The reactivities of the chars in respect to gaseous hydrocarbon formation were evaluated in batch hydrogasification tests. Test conditions were: 1000 to 1010 psig initial hydrogen pressures at room temperature, approximately 60-gram sample size, 1350°F maximum reaction temperature and 25 minutes run duration at maximum temperature. These charge quantities corresponded to a hydrogen/coal ratio of 17 SCF/lb and gave maximum reactor pressures of 2900 to 3300 psig (Table 3). The char charge to the reactor was obtained by sampling the residual chars from the pretreatment runs with a small riffle sampler and crushing to minus 60-mesh size.

The threshold temperatures reported in Table 3 correspond to the point at which the number of moles of gas in the reactor passed through a maximum due to initiation of the hydrogenolysis reactions. Reactor pressures increased nearly linearly with increases in temperature up to the threshold temperature (approximately 950° to 1050°F) and passed through a maximum at temperatures of 1100° to 1200°F. As the reactor attained the maximum run temperature, the pressures decreased rapidly and then continued to decrease at a lower rate during the remainder of the run. These characteristics of batch hydrogenolysis were similar to those reported previously.²⁵

Effects of Pretreatment Conditions on Hydrogenolysis Yields

It can be observed from Table 3 that the net Btu recoveries and gaseous hydrocarbon yields for each of the three coals investigated fell within relatively narrow limits because of the similarity in char properties. (Net Btu Recovery is defined as the product of gas yield and heating value, minus the initial hydrogen heat of combustion.) However, there was a clear indication that optimum conversion to hydrocarbons at the time the reactor attained 1350°F occurred with bituminous and subbituminous coal chars prepared at 600°F, and with lignite char prepared at 500°F. Further, when comparing the results with the chars prepared at these optimum temperatures in the four different atmospheres (nitrogen, air, carbon dioxide and steam) the net Btu recoveries of the chars prepared in a carbon dioxide atmosphere were lower for each of the three coals.

These data indicate that the occurrence of optimum pretreatment conditions insofar as hydrogasification yields are concerned are the result of two factors: (1) increase in reactivity of the char to a maximum value as pretreatment temperature is increased, followed by reactivity decrease as low-temperature carbonization temperatures are approached and (2) continuous decrease in the content of relatively easily hydrogenable materials as pretreatment temperature is increased. The increased quantities of coal converted to liquid products with increases in pretreatment temperature (Table 2) are an indication of the loss of the more reactive coal constituents which eventually offsets any general increase in reactivity due to pretreatment.

In Fig. 6 the rates of methane-plus-ethane production from 720°F air-pretreated, and from dried bituminous coal, are compared. It can be seen that at least ten additional minutes of residence time at 1350°F would be required for the dried coal to yield product gases similar to those obtained with pretreated coal at the time the reactor attained 1350°F. In Table 4 the effects of steam and air pretreating on hydrogasification rates are shown for bituminous coal and lignite. The increase in the reactivity of the bituminous coal is illustrated by the fact that a gas of 67.5 mole % methane plus ethane content was produced from the pretreated sample (Run 112) upon attainment of a reactor temperature of 1275°F, or 15 minutes before reaching the maximum reaction temperature of 1350°F, whereas

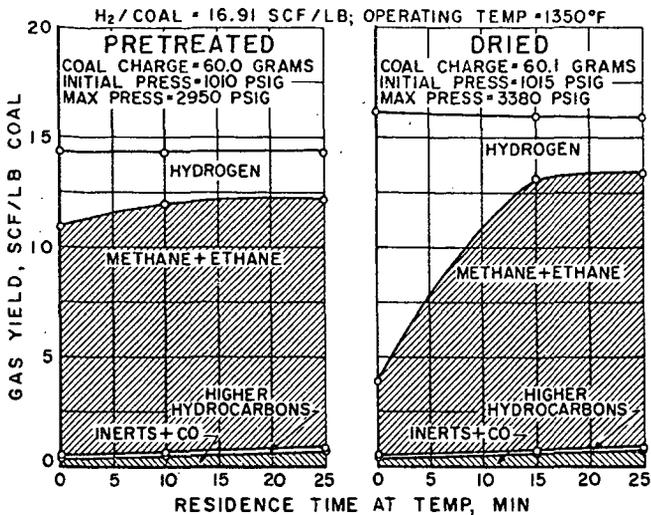
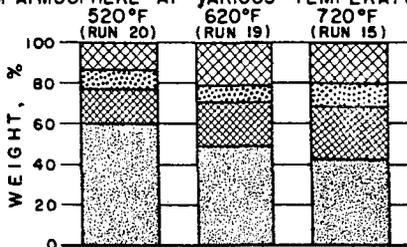


Fig. 6.-EFFECT OF RESIDENCE TIME ON HYDROGASIFICATION YIELDS FROM DRIED AND PRETREATED (AIR AT 720°F) ILLINOIS HIGH-VOLATILE "B" BITUMINOUS COAL

SCREEN ANALYSES OF RESIDUES FROM HYDROGASIFICATION OF CHAR PRETREATED IN STEAM ATMOSPHERE AT VARIOUS TEMPERATURES



SCREEN ANALYSES OF RESIDUES FROM HYDROGASIFICATION OF CHAR PRETREATED IN VARIOUS ATMOSPHERES AT 605°-620°F

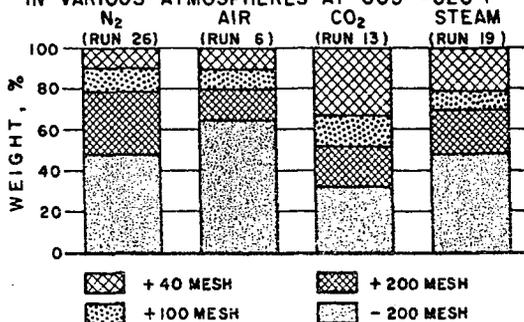


Fig. 7.-EFFECT OF PRETREATMENT TEMPERATURE AND GAS ATMOSPHERE ON PARTICLE SIZE DISTRIBUTION OF RESIDUES FROM HYDROGASIFICATION OF ILLINOIS HIGH-VOLATILE "B" BITUMINOUS COAL CHAR

in the comparable test with the dried coal (Run 67) the product gas contained only 21.1 mole % methane plus ethane at the time a reactor temperature of 1350°F was attained.

Pretreatment Losses

Because of evolution of substantial amounts of gaseous hydrocarbons and of liquid products during pretreatment of bituminous coal (Table 2) the increase in reactivity to hydrogenation was accompanied by a decrease in ultimate gaseous hydrocarbon yield and net Btu recovery. However, a substantial portion of these pretreatment losses can be recovered in the form of fuel gases produced during pretreatment; steam pretreatment of bituminous coal yields high heating value product gases suitable for addition to the pipeline gas formed in the hydrogasification step. Further, pretreatment is essential in reducing or eliminating agglomeration of coking or caking coals to be used as feeds to moving-bed or fluid-bed hydrogasification processes so that pretreatment losses must be considered a characteristic of bituminous coal operation.

The effects of steam pretreatment on the hydrogasification product distribution for dried Illinois high volatile "B" bituminous coal are illustrated by Runs 67 and 112, Table 4. Net Btu recoveries and gas yields are reported on an as received basis as well as on the basis of the actual dried or pretreated coal charge to permit direct comparisons of the results. It can be seen that for approximately equal product gas compositions (after 25 minutes at 1350°F for the dried coal and at 0 minutes at 1350°F for the pretreated coal) substantially higher conversions were obtained with the dried coal. A clearer picture of the relative yields with and without pretreatment can be gained from the following data summary based on 100.0 weight units of moisture-ash-free bituminous coal and on char or residue yields corrected to 100% material balance (the lower conversion of the pretreated coal was probably in part due to the somewhat lower hydrogen/coal ratio employed):

<u>Pretreatment</u>	<u>Steam, 620°F</u>	<u>None</u>
<u>Product</u>	<u>(Run PR-19)</u>	
Char (Moisture-Ash-Free)	90.4	--
Net Water and Other		
Condensates	4.4	--
CO, CO ₂	1.8	--
Hydrogen	Trace	--
Gaseous Hydrocarbons	3.4	--

<u>Hydrogasification</u>	<u>0 Minutes at 1350°F</u>	<u>25 Minutes at 1350°F</u>
	<u>(Run 67)</u>	<u>(Run 112)</u>
<u>Feeds</u>		
Char or Coal (Moisture-Ash-Free)	90.4	100.0
Hydrogen	8.9	9.4
<u>Products</u>		
Residue (Moisture-Ash-Free)	43.1	39.8
Condensates	1.9	5.0
CO, CO ₂ , N ₂	3.4	4.7
Hydrogen	1.5	1.4
Gaseous Hydrocarbons	49.4	58.5

The comparative performance of dried and air-pretreated (520°F maximum temperature) lignite is shown in Run 71 and 140, Table 4. In these runs the quantity of sample was reduced to correspond approximately to 60 grams on an as-received basis. This was done to demonstrate that essentially complete conversion of lignite to a high heating gas is possible at short residence times if sufficient amounts of hydrogen are provided. In spite of the high initial reactivity of the lignite, pretreatment resulted in further increases in reactivity although these increases were relatively small; methane plus ethane contents and gaseous hydrocarbon yields, upon attainment of 1350°F reactor temperature before and after pretreatment were 60.0 and 74.7 mole %, and 11.45 and 12.25 SCF/lb (as received basis), respectively. However, there were only minor differences in ultimate net Btu recoveries and gaseous hydrocarbon yields for the dried and pretreated lignite. The higher volumetric gas yields and weight percent hydrogasification yields for the dried lignite were primarily the result of substantial carbon dioxide evolution; the pretreated sample had already evolved most of the carbon dioxide prior to hydrogasification. Thus, it appears that the major benefit of lignite pretreatment would be the increase in product gas heating value (80 to 90 Btu/SCF on the basis of the data of Table 4), due to reduction of carbon dioxide content; increases in reactivity would probably not justify pretreatment and lignite has little agglomeration tendency. The behavior of subbituminous coal appeared to fall between that of bituminous coal and lignite on the basis of less complete data than presented for the other two coals.

Agglomeration of Hydrogasification Residues

One of the objectives of the hydrogenolysis tests with pretreated coals was to determine if variations in agglomeration of the hydrogasification residue could be related to pretreatment conditions. As noted before, a sample of the char from each pretreatment run was ground to minus 60-mesh to approximate constant initial conditions. Although this procedure was probably inadequate insofar as the size distribution of minus 60-mesh particles is concerned, it can be seen from Fig. 7 that the degree of agglomeration indicated by the percentage of plus 40-mesh particles in the hydrogasification residue followed the degree of agglomeration of dried bituminous coal during pretreatment (Fig. 5). Increases in pretreatment temperature resulted in increased agglomeration of the residue, and agglomeration during hydrogasification increased with various pretreatment atmospheres in the following order: air, nitrogen, steam and carbon dioxide.

Hydrogasification Characteristics of Low-Temperature Chars

An indication of the reactivities of low-temperature chars and cokes produced with the Bureau of Mines^{22,23} and Disco¹⁵ processes can be obtained by comparison of the batch hydrogasification test results shown in Table 5 with the data for the pretreated coals reported in Table 3. It can be seen that over 40 weight percent of these low-temperature carbonization products were converted to gases with heating values of 760 to 880 Btu/SCF at 1350°F and 2400 to 3100 psig, employing a hydrogen/charge ratio of 17 SCF/lb. Although the coal conversions in these tests are quite low, the data nevertheless serve to indicate the possibility of obtaining high-heating value gases from non-agglomerating chars from which a major portion of reactive coal constituents have been removed under the relatively severe pretreating conditions employed in low-temperature carbonization processes.

Table 5.-OPERATING RESULTS FOR THE HYDROGASIFICATION OF LOW-TEMPERATURE CHARs

	BITUMINOUS CHAR		SUBBITUMINOUS CHAR		LIGNITE CHAR	
	82	84	84	85	85	85
Coal Run No. Source	Pittsburgh Consolidation Coal Co.		U. S. Bureau of Mines		U. S. Bureau of Mines	
Proximate Analysis, wt %	0.9 Moisture; 21.2 Vol. Matter; 6.2 Ash 60.0		1.3 Moisture; 19.3 Vol. Matter; 4.6 Ash 60.0		1.9 Moisture; 25.2 Vol. Matter; 11.3 Ash 60.0	
Charge, gram						
Operating Conditions						
Initial Pressure, psig	1010	1010	1010	1010	1010	1010
Hydrogen/Coal Ratio, SCF/lb	16.91	16.83	16.83	16.80	16.80	16.80
Threshold Temperature, °F	875	745	745	790	790	790
Time to Reach Threshold Temp., min	36	31	31	36	36	36
Total Time Elapsed, min	90	100	94	104	100	125
Run Time at Temp., min	0	10	0	10	0	25
Reactor Pressure, psig	2430	2430	2690	2700	3060	3120
Reactor Temp. of	1350	1350	1350	1350	1350	1350
Operating Results						
Net Btu Recovery, MBtu/lb	0.862	4.820	4.914	5.224	6.083	6.273
Product Gas Yield, Total SCF/lb	11.97	11.97	11.90	13.28	15.04	15.33
Gaseous Hydrocarbon Space-Time Yield, SCF/CF-hr ¹	14.9	36.1	29.7	34.0	26.9	33.7
Net Moisture-Ash Free Coal Hydrogasified, wt % ²	13.1	37.7	39.9	41.9	46.3	47.7
Material Balance, % ³				42.5	102.2	98.5
Product Gas Properties						
Gas Composition, mole %						
N ₂ + CO	1.5	2.5	2.9	5.2	5.3	6.5
CO ₂	0.3	0.3	0.3	1.6	2.5	1.1
H ₂	71.6	20.2	17.9	26.7	19.6	25.7
H ₂ S	--	0.1	--	--	--	--
CH ₄	23.5	75.5	77.3	63.5	71.6	66.6
C ₂ H ₆	2.7	0.7	0.2	2.4	0.4	0.1
C ₂ H ₆ plus Olefins	0.2	--	0.1	--	--	--
Benzene	0.1	0.7	1.2	0.6	0.6	0.3
Toluene plus Total	--	--	0.1	--	--	--
Heating Value, Btu/SCF	100.0	100.0	100.0	100.0	100.0	100.0
Specific Gravity, Air = 1	523	854	881	798	804	768
	0.2333	0.4873	0.5118	0.4846	0.5185	0.4349

1. Based on time after the reactor attained threshold temperature. SCF - Gas volume in standard cubic feet at 60°F, 30 inches of mercury pressure and saturated with water vapor.

2. 100 Wt of Product Gas - Wt of Hydrogen In Wt of Moisture-Ash Free Charge

3. Based on product gas volume calculated from reactor pressure, volume and temperature.

CONCLUSIONS

The results of this study indicated that a representative sub-bituminous coal and North Dakota lignite showed relatively little agglomeration when pretreated in a fluid-bed retort with 4 to 6 SCF/lb-hr of nitrogen, air, carbon dioxide and steam at temperatures of 400° to 600°F and atmospheric pressure. A high-volatile "B" bituminous coal agglomerated to an increasing degree with increases in pretreatment temperature from 500° to 700°F. This agglomeration tendency was greatest in carbon dioxide and steam atmospheres, and relatively small in air and nitrogen atmospheres. The amounts of fixed gases evolved (2.5 to 9.9 wt % of the dry charge) increased with increases in pretreatment temperature, and at any constant temperature, the rate of fixed gas evolution decreased with increases in residence time. The predominant constituents in the gaseous pretreatment products of the bituminous coal were paraffins and olefins, whereas the subbituminous coal and the lignite evolved primarily carbon dioxide.

Reactivities of the pretreated chars, as determined in batch hydrogasification tests at a maximum reactor temperature of 1350°F and a maximum pressure of approximately 3000 psig, first increased to an optimum value with increases in pretreatment temperature, and then decreased as a result of increased evolution of easily hydrogenable tar and other volatile combustibles. The optimum pretreatment temperature appeared to be 600°F for bituminous and subbituminous coal, and 500°F for lignite. Chars produced at constant pretreatment temperature in nitrogen, air and steam atmospheres showed little variation in reactivity. However, carbon dioxide-treated chars showed consistently lower reactivities than nitrogen, air and steam-treated chars.

The chars, in general, produced 50 to 55 weight percent of (moisture-ash-free basis) of pipeline gas containing 70 to 80 percent of methane plus ethane at the time 1350°F was reached when using a charge of approximately 17 SCF of hydrogen per pound of char. At higher hydrogen/char ratios, substantially higher weight percent conversions of lignite to gaseous hydrocarbons were obtained.

The particle size distribution of the residues obtained at the end of hydrogasification tests in general followed the trends of the pretreated chars. Steam and carbon dioxide treatments, and high pretreating temperatures, caused greater agglomeration during hydrogasification.

These data indicate that the production of non-agglomerating, reactive chars from lignite and subbituminous coal for fluid-bed hydrogenation to pipeline gas will be feasible. Although substantial agglomeration during pretreatment or hydrogasification was noted with bituminous coal, the data also show that chars suitable for conversion in a continuous fluid-bed hydrogenation unit could be produced by treating the bituminous coal in a fluid-bed at 600°F, in atmospheres of air, nitrogen and possibly steam.

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INFRARED SPECTROSCOPY AS A MEANS FOR EVALUATING
PITCHES FOR USE AS BINDERS IN THE PREPARATION OF
ELECTRODES FOR THE ALUMINIUM INDUSTRY. D. S. Montgomery
and F. E. Goodspeed. Department of Mines and Technical Surveys,
Ottawa, Canada.

The infrared absorption spectra of 28 coal tar and petroleum pitches were measured to discover the factors responsible for the quality of pitch when used as a binder in the manufacture of electrodes for the aluminium industry. The good pitches whether derived from coal or petroleum were associated with a high background absorption, and the poor pitches were associated with large proportions of CH_2 and CH_3 groups. Coal tar pitch quality improved with an increase in aromaticity of the type which gives rise to absorption bands at 6.25 and 11.4μ , and a decrease in the hydroaromatic structure associated with the 6.95μ band. Among the petroleum pitches the background absorption was as satisfactory a measure of pitch quality as the absorption at 6.25μ .

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INFRARED SPECTROSCOPY AS A MEANS FOR EVALUATING PITCHES
FOR USE AS BINDERS IN THE PREPARATION OF ELECTRODES FOR
THE ALUMINIUM INDUSTRY

By

D. S. Montgomery and F. E. Goodspeed
Department of Mines and Technical Surveys, Ottawa, Ontario.

INTRODUCTION

The perfection that has been achieved in the development of instruments for measuring infrared absorption has enormously extended the use of this physical property for characterizing substances which cannot be obtained in crystalline form. Coals and pitches have recently been studied by this technique to secure information relating to the chemical structure of these complex substances (1) (2). This type of structural information should be capable of giving an insight into the reasons for the differences in behaviour of different pitches which have hitherto been difficult to explain. The following work was undertaken to see if infrared spectroscopy was capable of revealing the structural features in a pitch which are responsible for its capacity to act as a binder of petroleum coke in the manufacture of electrodes used in the aluminium industry.

Before discussing the infrared spectra in detail it may be helpful to review briefly some of the properties of commercial pitches. The pitch which is used to bind together the petroleum coke aggregate on carbonization is itself composed of a solid and a liquid phase. The solid phase consists of coke dust and high molecular weight hydrocarbons with a low hydrogen to carbon ratio which together make up what is known as the quinoline insoluble portion of the pitch. The balance of the pitch may be composed of a very wide variety of hydrocarbons and hetero compounds, but both these phases play an important part in determining the quality of the bond. On heating the coke aggregate and pitch binder, a portion of the binder is volatilized during the baking process. The portion of the binder that distills out not only makes no contribution to the bond, but creates undesirable porosity and cracks in the process of disengaging itself. For this reason a very small amount of volatile material and a high pitch coke yield have been considered as important criteria of pitch

binder quality (3). However the coke dust and other quinoline insoluble components in pitch are by themselves incapable of making a good bond owing to the lack of mobility that is necessary to wet the petroleum coke surfaces and to form a link on carbonization.

Infrared spectroscopy could not be expected to distinguish between the coke dust, consisting of amorphous and graphitic carbon, and the high molecular weight hydrocarbons which comprise the quinoline insoluble fraction, but it might give some indication of the total quantity of this class of structure that is present due to the intense continuous background absorption that is characteristic of this class of substance. On the other hand it was expected that the contribution which infrared absorption spectroscopy would make would be in the estimation of the quantity and type of aliphatic alicyclic and aromatic material present which in turn would determine the quantity of gas liberated and the amount of order in the carbon frame work produced on carbonization. Presumably a higher concentration of large fused aromatic clusters would lead to a larger quantity of graphitic structure on carbonization.

The attempts of L. P. Charette and G. T. Bischofberger (4) to find a simple laboratory test which would define binder quality seemed to present an unusual opportunity to conduct a parallel infrared study to test the validity of some of the assumptions just mentioned, and to see if infrared spectroscopy could reveal some new aspect of the problem of the characterization of pitch binders.

EXPERIMENTAL

The infrared absorption spectra of all the pitch samples were measured using the potassium bromide pellet technique. The potassium bromide used for this purpose was secured from the Harshaw Chemical Company. As the pitches varied considerably in tarriness no uniform method of sample preparation was suitable. To reduce the particle size of the pitches which were hard and dry a small high speed vibration mill supplied by Research and Industrial Instruments London was used. The disintegration of the pitch was accomplished in a cylindrical tool steel capsule 3/8" I.D. x 1-1/4" in length which was attached to a spring blade oscillating in a magnetic field. The charge in the capsule consisted of 0.3 g of pitch and two chromium plated steel ball bearings. To ensure reduction the sample was vibrated for two hours. The pitches which were too soft to be ground were simply weighed onto the top of the appropriate amount of

potassium bromide. The potassium bromide pellets were prepared by weighing .004 g of pitch to the nearest 0.0001 g together with the appropriate quantity of potassium bromide to make the pitch concentration 0.4 percent by weight. The mixture was then transferred to an agate mortar where enough benzene was added to cover the mixture. The mortar was subsequently covered with a watch glass and allowed to stand for a few minutes prior to being uncovered and ground to dryness. The benzene facilitated the dispersal of the pitch throughout the potassium bromide and aided the grinding and mixing operation conducted in the mortar. After grinding to dryness the mixture was transferred to a small beaker and dried to 110°C for at least one hour to remove all traces of the benzene. The final traces of moisture were removed by placing the sample in an evacuated desiccator over phosphorous pentoxide. Half a gram of the pellet mixture was then transferred to a die and pressed.

The spectrometer employed was a Perkin-Elmer Model 21 double beam instrument which recorded the absorption in percent transmission versus wavelength. To eliminate any absorption arising from the medium used to form the pellet a blank pellet was used in the reference beam.

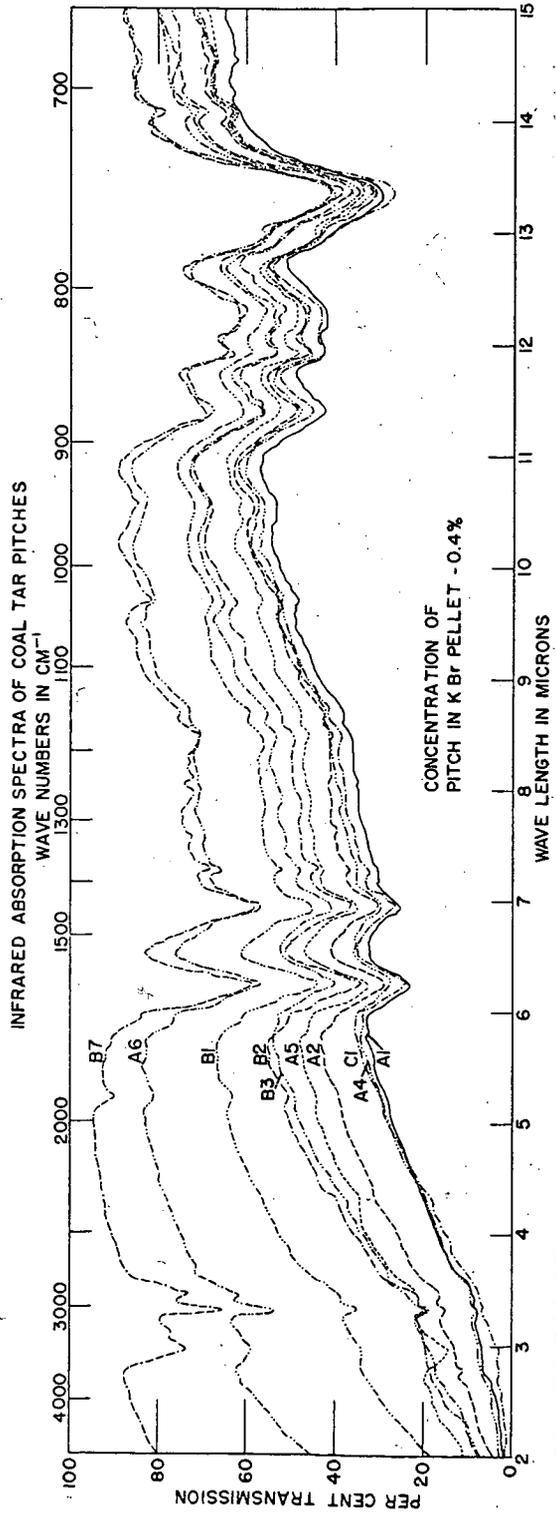
DISCUSSION OF RESULTS

On examining all 28 samples of coal tar and petroleum pitch in a cursory fashion it was evident that the coal tar pitches differed substantially from the petroleum pitches, and this suggested that the two types of pitch be discussed separately.

Absorption Spectra of Coal Tar Pitches

The coal tar pitch spectra shown in Figure I were characterized by eight significant absorption bands which were as follows:- 3.3 μ aromatic C-H 3.45 μ naphthenic and aliphatic CH, CH₂ and CH₃, 6.25 μ aromatic C=C 6.95 μ naphthenic and heterocyclic CH₂ 7.27 μ aliphatic CH₃, and the three substituted aromatic absorption bands at 11.4 12.3 and 13.35 μ . The 3.3 μ aromatic C-H band was prominent in pitches of poor quality; however as the pitch quality improved the background absorption increased and the band became so small that it was extremely difficult to measure accurately. The 3.5 μ naphthenic and aliphatic band and the 7.27 CH₃ band also suffer from the same defect in that they are readily measured when the pitches were of poor quality, but became so small in the good pitches that they could no longer be measured.

FIGURE - I



The 13.35 μ substituted aromatic absorption band was very prominent in all the coal tar pitch spectra. However, the difference in the intensity of the absorption between the best and the poorest of the pitches was much less than was found in the 11.4 μ absorption band. The standard deviation of the electrode compressive strength predicted from the absorptivity at 13.35 μ was also greater than that obtained from the predictions based upon the 11.4 μ band. These observations discouraged the use of this absorption band. The substituted aromatic absorption band between 11.95 μ and 12.5 μ appeared to be composed of a number of bands super-imposed on each other; consequently the shape of the absorption curve in this region changed considerably, and the location of the maximum was difficult to determine. As the order in which the absorption in this region placed the pitches was the same as that of the 11.4 μ absorption band which was more clearly defined, there seemed to be little merit in selecting this region for making correlations with the electrode compressive strength. These observations reduced the number of absorption bands for detailed examination to three, the 6.25 μ aromatic C=C, the 6.95 μ naphthenic or hydroaromatic CH₂ and the 11.4 μ substituted aromatic absorption band. At each of these wavelengths and at several background points the absorptivity was measured at three pitch concentrations 0.5%, 0.4% and 0.25% by weight as shown in Tables I, II and III.

To test the measure of agreement of these spectra with Beer's Law, the optical density at specific wavelengths was plotted against the sample concentration for individual pitches. Graphs showing this data for pitches A-1, A-2 and B2 are shown in Figure 2. The optical densities plotted at one wavelength for a given sample should give a straight line passing through the origin if Beer's Law is obeyed. The results seemed reasonably satisfactory with the largest deviations occurring at 2 microns where the variations in pellet quality would be expected to have the greatest effect upon the absorption spectrum due to the scatter of radiation in this region.

A cursory examination of the absorption spectra in Figure I in conjunction with the electrode compressive strength data suggested that the quality of the pitch improved with increasing background absorption. As intense background absorption was associated with the quinoline insoluble fraction this result was in accord with the view that the pitch quality improved with increasing pitch coke yield and increasing quinoline insoluble content. This background absorption was of a continuous nature upon which were superimposed the characteristic absorption bands of the atomic groups

TEST OF APPLICABILITY OF BEER'S LAW AT VARIOUS WAVELENGTHS FOR COAL TAR PITCHES

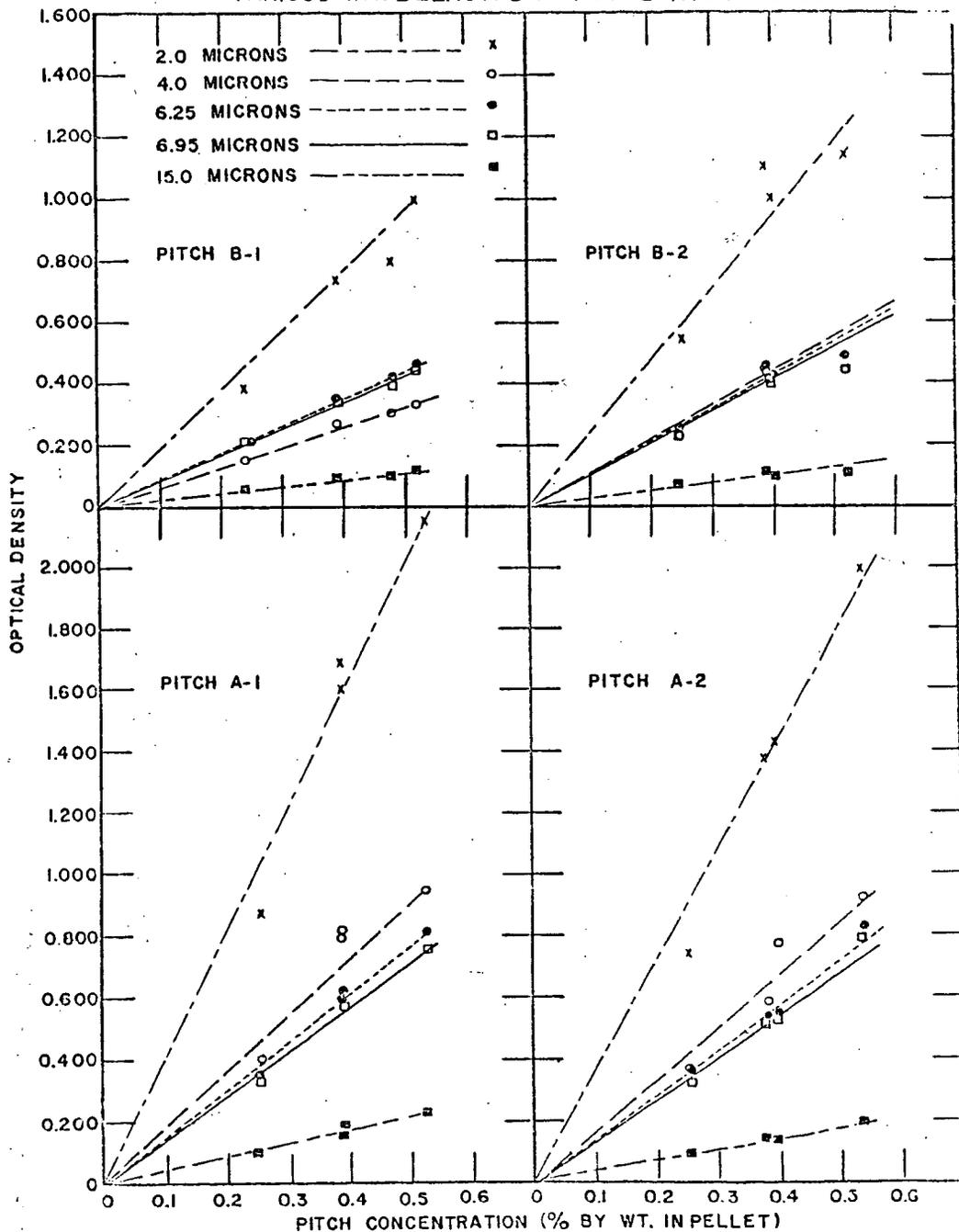


FIGURE 10

TABLE I

PER CENT TRANSMISSION AND ABSORPTIVITIES
OF COAL TAR PITCHES
(0.4% CONCENTRATION PELLETS)

Sample No.	Concentration gm. pitch per gm. pellet	Per Cent Transmission						
		2.0 μ	4.0 μ	6.25 μ	6.95 μ	11.4 μ	13.35 μ	15.0 μ
A-1	0.0039	2.5	16.3	23.6	25.6	42.7	29.9	64.8
C-1	0.0039	1.0	16.6	26.4	28.7	47.0	30.2	72.9
A-2	0.0040	3.7	25.0	28.3	31.5	50.0	33.0	72.7
A-4	0.0040	2.8	16.8	27.5	30.0	48.0	31.8	70.7
B-3	0.0040	8.3	37.0	39.4	41.5	57.9	33.7	78.2
B-2	0.0040	8.9	38.3	38.0	40.3	58.0	39.2	81.3
A-5	0.0039	14.0	38.1	37.8	40.3	57.7	38.1	78.0
A-6	0.0040	45.7	74.7	56.5	58.3	68.2	40.0	87.7
B-1	0.0039	18.2	53.2	44.0	45.7	61.0	40.7	80.0
B-7	0.0038	79.2	90.8	58.8	57.0	69.8	39.2	88.0

	Compressive Strength Kg/cm	Absorptivity A						
		2.0 μ	4.0 μ	6.25 μ	6.95 μ	11.4 μ	13.35 μ	15.0 μ
A-1	440	411	202	161	152	95.0	134	48.2
C-1	366	512	200	147	139	84.1	133	35.1
A-2	352	358	151	137	126	75.2	120	34.5
A-4	340	388	194	140	131	79.8	125	37.5
B-3	320	270	108	101	96	59.5	118	26.8
B-2	300	263	104	105	99	59.0	102	22.5
A-5	289	219	107	108	101	61.3	107	27.7
A-6	273	85	32	63	59	41.5	100	14.3
B-1	263	190	70	91	87	54.9	100	24.9
B-7	181	27	12	58	64	41.1	107	14.7

TABLE II
PER CENT TRANSMISSION AND ABSORPTIVITIES
OF COAL TAR PITCHES
(0.4% CONCENTRATION PELLETS)

Sample No.	Concentration grm. pitch per grm. pellet	Per Cent Transmission						
		2.0 μ	4.0 μ	6.25 μ	6.95 μ	11.4 μ	13.35 μ	15.0 μ
A-1	0.0039	2.5	16.3	23.6	25.6	42.7	29.9	64.8
C-1	0.0039	1.0	16.6	26.4	28.7	47.0	30.2	72.9
A-2	0.0040	3.7	25.0	28.3	31.5	50.0	33.0	72.7
A-4	0.0040	2.8	16.8	27.5	30.0	48.0	31.8	70.7
B-3	0.0040	8.3	37.0	39.4	41.5	57.9	33.7	78.2
B-2	0.0040	8.9	38.3	38.0	40.3	58.0	39.2	81.3
A-5	0.0039	14.0	38.1	37.8	40.3	57.7	38.1	78.0
A-6	0.0040	45.7	74.7	56.5	58.3	68.2	40.0	87.7
B-1	0.0039	18.2	53.2	44.0	45.7	61.0	40.7	80.0
B-7	0.0038	79.2	90.8	58.8	57.0	69.8	39.2	88.0

	Compressive Strength Kg/cm ²	Absorptivity A						
		2.0 μ	4.0 μ	6.25 μ	6.95 μ	11.4 μ	13.35 μ	15.0 μ
A-1	440	411	202	161	152	95.0	134	48.2
C-1	366	512	200	147	139	84.1	133	35.1
A-2	352	358	151	137	126	75.2	120	34.5
A-4	340	388	194	140	131	79.8	125	37.5
B-3	320	270	108	101	96	59.5	118	26.8
B-2	300	263	104	105	99	59.0	102	22.5
A-5	289	219	107	108	101	61.3	107	27.7
A-6	273	85	32	63	59	41.5	100	14.3
B-1	263	190	70	91	87	54.9	100	24.9
B-7	181	27	12	58	64	41.1	107	14.7

TABLE III

PER CENT TRANSMISSION AND ABSORPTIVITIES OF
COAL TAR PITCHES
(0.25% CONCENTRATION)

Sample No.	Concentration gm. pitch/gm. pellet	Per Cent Transmission					
		2.0	4.0	6.25	6.95	11.4	15
A-1	0.0026	13.4	39.8	44.1	46.1	62.5	79.7
C-1	0.0025	13.2	42.2	48.6	52.2	66.5	84.0
A-2	0.0026	18.0	43.3	43.1	48.5	64.7	81.0
A-4	0.0025	12.0	34.9	45.6	47.7	63.3	81.0
B-3	0.0025	26.8	57.5	60.0	60.1	72.4	87.2
B-2	0.0025	28.0	60.0	55.3	57.8	72.0	86.6
A-5	0.0025	24.5	50.0	52.1	53.7	68.3	85.2
A-6	0.0025	60.0	82.3	72.2	70.8	78.6	92.7
B-1	0.0024	41.1	71.0	61.5	62.1	74.3	87.6
B-7	0.0025	95.0	96.3	70.8	74.3	82.6	93.1

	Compressive Strength Kg/cm ²	Absorptivity, A					
		2.0	4.0	6.25	6.95	11.4	15
A-1	440	342	157	140	132	80.0	38.4
C-1	366	355	151	127	114	71.4	30.7
A-2	352	292	143	143	123	74.6	36.1
A-4	340	363	180	134	126	78.0	36.2
B-3	320	229	96	89	88	56.0	24.0
B-2	300	224	90	105	97	57.8	25.6
A-5	289	244	120	113	108	66.4	27.6
A-6	273	89	34	57	60	42.0	13.2
B-1	263	161	61	88	86	53.6	24.1
B-7	181	9	7	59	51	32.6	12.2

OH, C=C, CH₂, CH₃ and C=O. These absorption bands were thought to be more intense in the quinoline soluble portion of the pitch and a base line technique was tested to see if the background could be subtracted from the band height so that the contribution of the soluble portion of the pitch might be more clearly discerned. This did not turn out to be a fruitful approach. A more satisfactory correlation was obtained between the absorptivity at certain characteristic absorption band positions.

As a first approximation it was assumed that there was a linear dependence between the electrode compressive strength and the absorptivity at various wavelengths. The equation of correlation was obtained by the method of least squares and the standard deviations and the correlation coefficient were calculated as shown in Table IV. The standard deviations and correlation coefficients indicate that the best results are obtained with a pitch concentration of 0.4 percent at the two aromatic absorption bands occurring at 6.25 μ and 11.4 μ respectively.

The standard deviation values of the correlations between the absorptivities at the three background positions at 2, 4 and 15 μ , and the electrode compressive strength were 32.2, 28.6 and 27.3 Kg./cm² respectively. These values indicated a slight improvement in the correlation with increasing wavelength. This might be anticipated in view of the smaller contribution to the scattered radiation made by the pellet at longer wavelengths. On comparing the above standard deviations obtained at the aromatic absorption band positions 6.25 μ and 11.4 μ , which are 26.2 and 25.5 kg./cm², there is a suggestion that this improvement in standard deviation is due to the improved correlation between the background absorption and the electrode compressive strength at longer wavelength. On the other hand the poor correlation between the electrode compressive strength (E. C. S.) and the absorption at 13.35 μ suggest strongly that the chemical structure giving rise to this band has an undesirable influence upon the E. C. S.

In Table V are shown the results obtained from the correlation of the absorptivities at more than one wavelength with the E. C. S. In all the correlations it has been assumed that the E. C. S. could be expressed as a linear combination of the absorptivities at various wavelengths. This can at best only be considered to be a first approximation. The best correlation giving the lowest value of the standard deviation (23.6 kg./cm²), was obtained between the E. C. S. and the absorptivities at the 6.95 μ hydroaromatic CH₂ band and the 11.4 μ aromatic absorption band. The next best correlation was obtained between the absorptivities at the 6.95 μ hydroaromatic band and the 6.25 μ aromatic band. Both these correlations were superior to those which only involved aromatic absorption bands such as the 6.25 and the 11.4 μ bands. The correlation between these two absorption bands and the E. C. S.

TABLE IV

CORRELATION OF THE E. C. S. WITH INFRA-RED
ABSORPTIVITIES OF COAL TAR
PITCHES

Wavelength Correlated	Pellet Conc. %	Equation of Correlation *	Standard Deviation	Correlation Coefficient
2 μ	0.5	$y=0.506x + 191$	25.6	0.92
	0.4	$y=0.404x + 202$	32.2	0.872
	0.25	$y=0.53 x + 191$	30.7	0.885
4 μ	0.5	$y=0.935x + 210$	30.7	0.883
	0.4	$y=0.92 x + 204$	28.6	0.903
	0.25	$y=1.04 x + 204$	34.4	0.852
6.25 μ	0.5	$y=1.64 x + 140$	32.0	0.874
	0.4	$y=1.83 x + 110$	26.2	0.916
	0.25	$y=1.82 x + 120$	37.0	0.829
6.95 μ	0.5	$y=1.87 x + 122$	32.1	0.874
	0.4	$y=2.01 x + 101$	28.5	0.901
	0.25	$y=2.19 x + 97$	32.9	0.867
11.4 μ	0.5	$y=3.13 x + 109$	30.7	0.883
	0.4	$y=3.59 x + 79$	25.5	0.925
	0.25	$y=3.92 x + 73$	30.8	0.886
13.35 μ	0.5	$y=3.20 x - 49$	40.8	0.787
	0.4	$y=4.23 x - 172$	39.3	0.802
15 μ	0.5	$y=5.49 x + 182$	30.6	0.898
	0.4	$y=6.03 x + 140$	27.3	0.910
	0.25	$y=6.6 x + 136$	33.7	0.860

* y = Electrode Compressive Strength in Kg/ cm².
 x = Absorptivity A at Wavelength Indicated.

TABLE V

MULTIPLE CORRELATIONS OF E. C. S. WITH INFRA-RED
ABSORPTIVITIES OF COAL TAR PITCHES

Wavelength Correlated	Pellet Conc. %	Equation of Correlation *	Standard Deviation
2 μ and 15 μ	0.5	$y = 0.37 x_1 + 1.61x_2 + 211$	24.8
	0.4	$y = 0.160x_1 + 4.06x_2 + 152$	24.7
4 μ and 15 μ	0.5	$y = 0.84 x_1 + 0.50x_2 + 208$	31.8
	0.4	$y = 0.425x_1 + 3.44x_2 + 174$	25.4
6.25 and 6.95 μ	0.5	$y = 1.38 x_1 + 0.31x_2 + 136$	32.0
	0.4	$y = 5.53 x_1 - 4.16x_2 + 136$	23.9
6.25 and 11.4 μ	0.4	$y = 1.26 x_1 + 1.00x_2 + 109$	25.7
6.95 and 11.4 μ	0.4	$y = 4.52 x_1 + 11.4 x_2 + 46$	23.6
4 μ , 15 μ , 6.25 μ and 6.95 μ	0.4	$y = 0.515x_1 + 4.175x_2 + 1.060x_3$ $-1.631x_4 + 186$	23.9

* y = Electrode compressive strength; x_1, x_2, x_3, x_4 are the absorptivities measured at the wavelengths recorded in the first column in order of their presentation.

was slightly inferior to that obtained when using the absorption at the two background positions at 4 and 15 μ . From this result it was inferred that within this group of coal tar pitches the background absorption and the absorption at 6.25 and 11.4 μ were probably related.

Using the 0.4 percent concentration pellets which give the lowest standard deviations the multiple correlations involving the absorptivities at 6.25 with 6.95 μ and 6.95 with 11.4 μ it was noted that the coefficient of the 6.95 μ absorptivity is negative while the others are both positive. From this it can be concluded that the presence of hydroaromatic hydrogen atoms responsible for the 6.95 μ absorption tend to reduce pitch binder quality while the group causing absorption at 6.25 and 11.4 μ tend to improve pitch quality.

To summarize the findings up to this point, aromaticity associated with isolated benzene rings giving rise to a 3.3 μ band or substituted benzene rings yielding a 13.29 μ band are undesirable aromatic structures. The presence of hydroaromatic rings associated with absorption at 6.95 μ also reduce pitch binder quality. The chemical structures associated with absorption at 6.25 μ and 11.4 μ are the preferred aromatic structures.

The  absorption band at 11.4 μ is considered to be due to structures of the type  and the 12.3 μ band is interpreted as being due to the structure  that is to say two adjacent hydrogenations on a tetra substituted benzene ring, while the 13.35 μ band is due to ortho substitution on the benzene ring . A prominent absorption band in the 11.4 μ region implies a large number of condensed aromatic platelets. The observation that the background absorption increased with increasing absorption in the 11.4 μ region is consistent with what might be expected on increasing the number of platelets and the number of stacks of platelets. It was therefore inferred from the relation between the electrode compressive strength and the background absorption as well as the 11.4 μ absorption band, that the basic requirement for a satisfactory coal tar pitch binder was that a large proportion of the carbon atoms must be involved in highly condensed aromatic platelets.

The estimation of the E. C. S. from infrared spectroscopy appears to be somewhat less satisfactory than the method devised by Charette (4) as the standard deviation reported for both petroleum and coal tar pitches was 19 kg./cm², whereas the lowest value of the standard deviation obtained from the correlation of the infrared absorption band intensities was 23.6 kg./cm². This value will be recalled only applied to the coal tar pitches.

On examining a "cut back pitch" which possessed an intense background absorption, erroneous values were predicted for the E. C. S. The reason for this discrepancy was thought to be due to the fact that the low molecular weight solvent used to dilute the pitch contained undesirable aromatic structures whose absorption bands were obscured by the intense background.

Absorption Spectra of Petroleum Pitches

The infrared absorption spectra of the petroleum pitches are shown in Figure (3) and Tables VI. Much greater variations were encountered in these pitches than among the coal tar pitch spectra. The electrode compressive strength again appeared to be closely linked with the background absorption, but certain chemical structural groups appeared to have greater influence upon the E. C. S. than observed in the coal tar pitches. The petroleum pitches appeared to fall into roughly two classes, those pitches which possess an E. C. S. of 225 or less which transmit approximately 70 percent of the radiation at 4.0μ and those which have a much higher background absorption in this region. The pitches possessing an E. C. S. of 225 or less may be readily determined by visual inspection of the absorption curve. These pitches all possess a weak aromatic CH band at 3.3μ in relation to a strong aliphatic CH band at 3.45μ , a low background absorption in the 4.0μ region, and a relatively strong aliphatic CH_2 band at 7.25μ . The absorption band at 6.95μ , which was found to be common to all the coal tar pitches, was found to shift to 6.85μ in the petroleum pitches as the E. C. S. decreased. This shift in absorption spectrum was interpreted as being due to the increase in aliphatic CH_2 groups. On the other hand the better pitches possess an aromatic CH band of greater intensity than the aliphatic 3.45μ band. Also the background absorption in the 4.0μ region was relatively high.

Calculations were made following the procedure adopted for the coal tar pitches. Correlations were made between the E. C. S. and the absorptivity at 2μ , 6.25μ and 11.4μ and 15μ because of the success of this technique with the coal tar pitches and the undesirability of having too many special treatments for different classes of pitch. The correlation equations relating to the E. C. S. and the absorptivity at each of the above wavelengths gave the following standard deviations 31.7, 32.4, 40.5, 34.1, 33.2 kg./cm^2 as shown in Table VII. Many of the standard deviations exceed the values obtained with coal tar pitches at similar wavelengths. The petroleum pitches differed from those derived from coal in that the correlation between the absorptivity at the 6.25μ aromatic band and the E. C. S. was not significantly better than obtained at the 2μ background position. The implication was that the magnitude of the E. C. S. was not as closely related to the aromaticity in the petroleum pitches as measured by the absorption at

TABLE VI

PER CENT TRANSMISSION AND ABSORPTIVITY OF
PETROLEUM PITCHES
(0.4% CONCENTRATION)

Sample No.	Concentration gm. pitch/gm. pellet	Per Cent Transmission					
		2.0 μ	4.0 μ	6.25 μ	6.95 μ	11.4 μ	15.0 μ
D-1	0.0041						34.3
F-1	0.0038	9.2	23.1	26.0	26.0	44.3	67.5
G-1	0.0040	36.4	69.9	53.3	49.9	57.1	87.0
H-1	0.0040	43.0	76.0	55.4	55.8	67.2	87.0
F-2	0.0040	14.0	41.4	43.9	44.7	60.0	82.8
D-2	0.0040	72.5	89.7	60.4	51.0	72.0	91.2
D-3	0.0040	80.0	91.9	61.8	52.0	73.9	90.2
E-2	0.0040	77.7	91.7	62.8	51.0	72.7	89.6
I-1	0.0041	63.3	86.4	61.8	52.1	64.9	92.0

	Compressive Strength Kg/cm ²	Absorptivity A					
		2.0 μ	4.0 μ	6.25 μ	6.95 μ	11.4 μ	15.0 μ
D-1	319						11.3
F-1	315	273	167	154	154	93.2	45.0
G-1	255	111	38.8	68.2	75.5	61.0	15.0
H-1	254	91.5	30.0	64.0	63.3	43.3	15.0
F-2	242	214	95.8	89.2	87.5	55.5	20.5
D-2	210	35.0	11.8	54.8	73.0	35.5	10.0
D-3	169	24.3	9.0	52.2	71.0	32.4	11.3
E-2	167	27.5	9.5	50.5	73.0	34.5	12.0
I-1	135	48.5	15.6	51.0	69.0	45.9	8.8

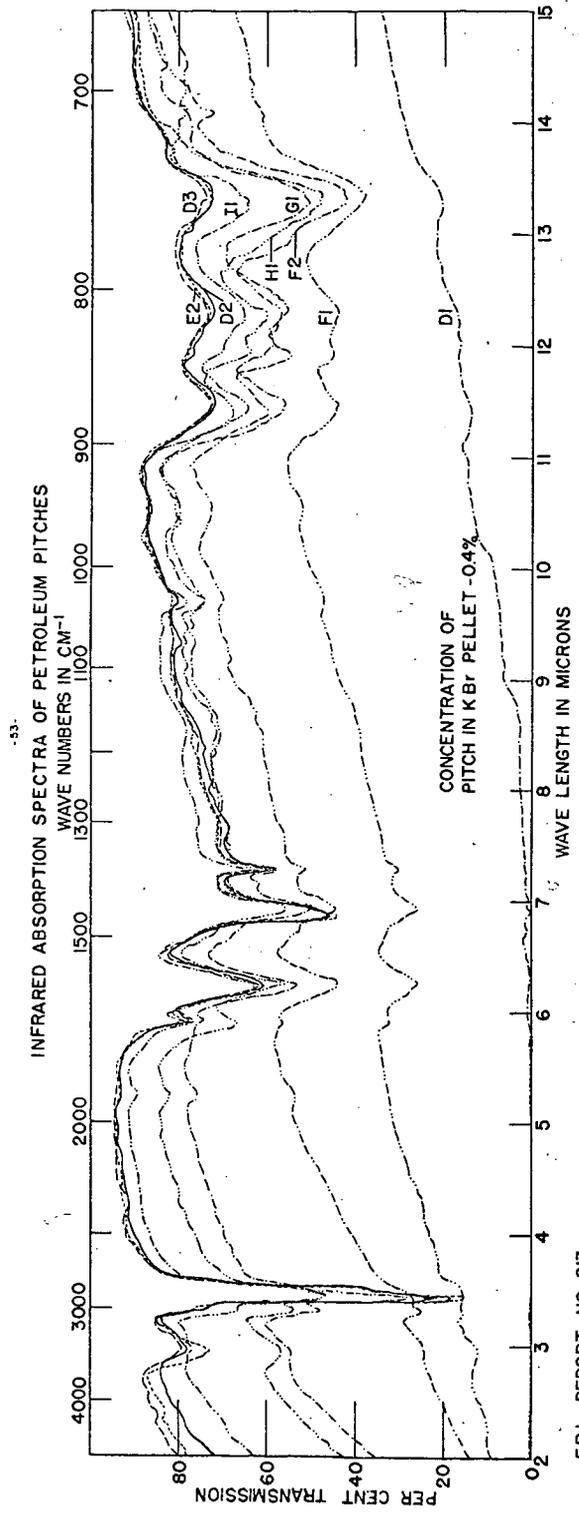
TABLE VII

CORRELATIONS OF PETROLEUM
PITCHES *

Wavelength Correlated	Pellet Conc. %	Equation of Correlation	Standard Deviation	Correlation Coefficient
2 μ	0.5	$y=0.428x + 182$	32.2	0.814
	0.4	$y=0.524x + 164$	31.7	0.821
6.25 μ	0.5	$y=1.23 x + 134$	31.5	0.821
	0.4	$y=1.37 x + 118$	32.4	0.813
6.95 μ	0.5	$y=1.28 x + 109$	39.6	0.698
	0.4	$y=1.42 x + 100$	40.5	0.701
11.4 μ	0.5	$y=2.13 x + 109$	34.9	0.774
	0.4	$y=2.33 x + 101$	34.1	0.790
15.0 μ	0.5	$y=3.49 x + 167$	34.4	0.727
	0.4	$y=3.98 x + 150$	33.2	0.796

* Pitch D-1 Not Included.

FIGURE - 3



6.25 μ or 11.4 μ . The correlation between the E.C.S. and the absorptivity at 11.4 μ was not as satisfactory as that noted in the coal tar pitches. The large background absorption suggests that large molecular aggregates are present, but there is nothing to suggest that the number of large aromatic platelets increases with increasing E.C.S. On the contrary there was a suggestion that the 13.35 μ band becomes more prominent relative to the other aromatic bands at 11.4 μ and 12.3 μ as the background absorption increases and the pitch quality improves. If the presence of carbon black is excluded this may be interpreted to mean that the high molecular weight components derived from oil tend to polymerize in a manner which does not yield a large number of large aromatic platelets, but yields a more chaotic carbon frame work associated with a slight preponderance of ortho substituted benzene rings.

To secure an insight into the effect of molecular weight upon the electrode compressive strength, a series of hard pitches prepared from Lloydminster crude oil were examined. It was previously shown that these pitches were derived from this petroleum under conditions where there was virtually no thermal cracking, and the increase in hardness was a reflection of the increase in average molecular weight resulting from the evaporation of the more volatile components. The softening point of these pitches varied from 145°F to 288°F (Ring and Ball), increasing with increasing molecular weight as may be seen in Table VIII.

The infrared absorption spectra of this series of pitches shown in Figure 4 possessed all the prominent absorption bands associated with poor pitch quality, that is to say too little aromaticity and too much aliphatic CH₂ and CH₃. This poor quality was confirmed for the measured value of the E.C.S. of pitch sample 1-5 was 73 kg./cm². While the precision obtainable at this low level of compressive strength was poor it did indicate that the test electrode was extremely weak. The background absorption from 2 to 15 μ increased with increasing molecular weight as might be expected, however the increase was quite small.

The indications from this work are that even if the molecular weight of the pitch is of approximately the right order, as indicated by the softening point 203-221°F (Ring and Ball) the quality of the pitch may be very poor. The structure of the macromolecules in the pitch appeared to play the dominant role in determining pitch quality.

FIGURE - 4

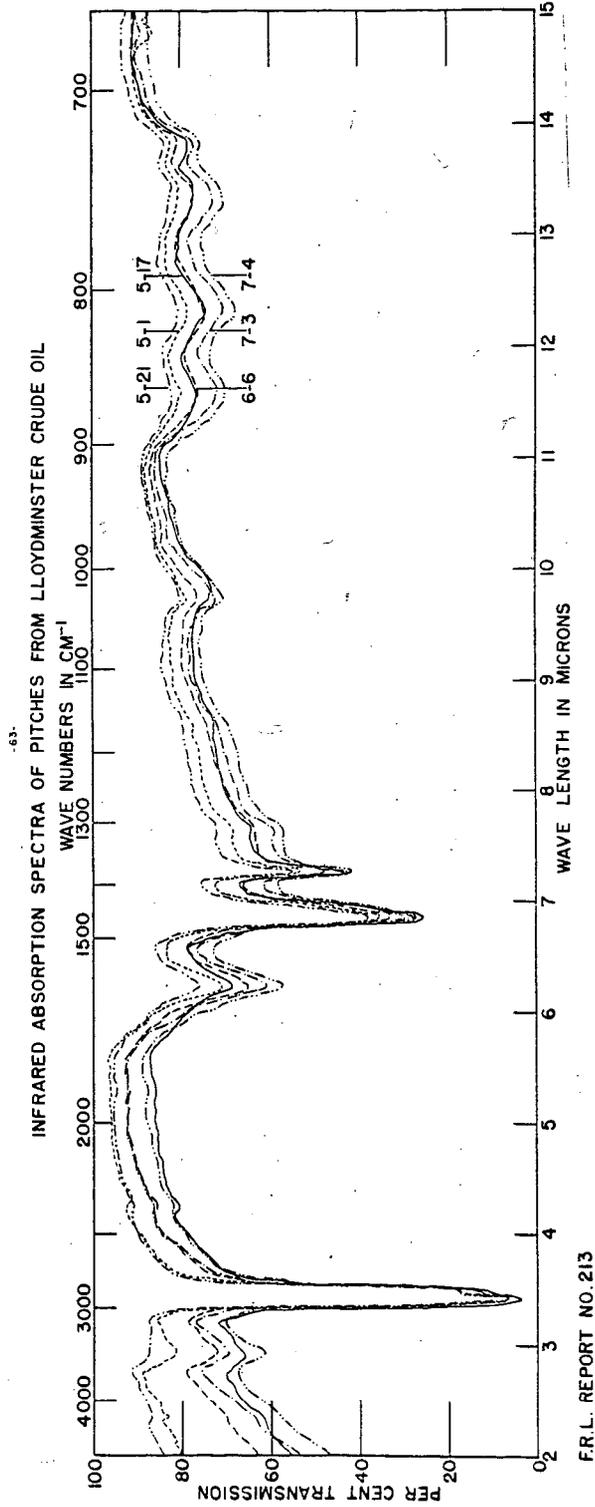


TABLE VIII

PER CENT TRANSMISSION AND ABSORPTIVITY
LLOYDMINSTER PETROLEUM PITCHES

Sample No.	Concentration gm. pitch/gm. pellet	Per Cent Transmission				
		2 μ	4 μ	6.25 μ	6.85 μ	15 μ
5-17	0.0057	50.8	78.6	68.0	25.2	92.2
5-21	0.0050	85.0	89.8	75.8	37.8	93.0
5-1	0.0055	80.6	90.0	70.7	35.4	88.0
6-6	0.0051	62.8	83.2	64.8	33.0	92.0
7-3	0.0061	53.7	83.8	60.7	27.1	90.9
7-4	0.0058	47.0	79.2	57.1	27.8	87.8

Sample No.	Softening Point °F.	Absorptivity				
		2 μ	4 μ	6.25 μ	6.85 μ	15 μ
5-17	145	51.6	18.4	29.5	105	6.3
5-21	170	14.0	9.4	24.2	84.6	6.4
5-1	197	17.1	8.4	27.5	80.2	10.2
6-6	223	39.6	15.7	37.1	94.5	7.1
7-3	252	44.3	12.6	35.6	93.0	6.9
7-4	288	56.6	17.6	42.1	95.8	9.8

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COMPARISON OF THE THERMAL DECOMPOSITION OF THE COPPER SALTS WITH THE
COPPER-QUINOLINE DECARBOXYLATION METHOD

R. S. Montgomery and E. D. Holly
The Dow Chemical Company

ABSTRACT

The copper-quinoline decarboxylation method has produced appreciably different results than has the thermal decomposition of copper salts of the acids obtained by the controlled oxidation of bituminous coal. Therefore, a study was made of these two decarboxylation methods in order to determine their reliability. Essentially complete decarboxylation was obtained with the copper-quinoline method while the other method produced only partial decarboxylation. A portion of the naphthalene obtained by the decarboxylation of naphthoic acid, however, was converted to methylnaphthalene during the course of the copper-quinoline decarboxylation. The thermal decomposition, on the other hand, produced the lactone of 2-hydroxy-2'-biphenylcarboxylic acid and probably other oxygenated nuclei. These peculiarities of the methods must be taken into account in interpreting the results of the decarboxylations of the coal acids.

* * * * *

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COMPARISON OF THE THERMAL DECOMPOSITION OF THE COPPER SALTS WITH
THE COPPER-QUINOLINE DECARBOXYLATION METHOD

R. S. Montgomery and E. D. Holly
The Dow Chemical Company

The structures of the acids obtained by the controlled oxidation of bituminous coal have been investigated by decarboxylation followed by separation and identification of the nuclei. The results of decarboxylation by the copper-quinoline method^{1,2} and by thermal decomposition of the copper salts^{3,4} were appreciably different. Much larger yields of oxygenated nuclei and less complete decarboxylation of the acids resulted when the thermal decomposition of the copper salts was used. In the present study a model mixture that approximated the coal acids as closely as possible was decarboxylated by both of the methods and the products and their amounts were compared.

EXPERIMENTAL

A mixture of aromatic acids was made that would resemble the mixture obtained by the controlled oxidation of bituminous coal. The approximate proportions of acids possessing the benzene, naphthalene, and biphenyl nuclei were the same although the functionalities of the naphthalene and biphenyl carboxylic acids were lower than the acids of the same nuclei in the coal acid mixture. Furoic acid and an aliphatic acid containing a pyrene nucleus were included in the model mixture although there is no evidence that these nuclei are actually present in the coal acid mixture. This was done because it has been suggested that these types of nuclei were present but not detected owing to the experimental techniques used. The composition of the model mixture is given in Table 1.

TABLE 1

Nucleus	Acid	Proportion, %
Benzene	Benzoic acid	0.94
	o-toluic acid	0.54
	m-toluic acid	0.47
	p-isopropylbenzoic acid	0.47
	o-phthalic acid	12.19

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TABLE 1 (cont'd)

Nucleus	Acid	Proportion, %
	m-phthalic acid	3.96
	p-phthalic acid	2.89
	trimellitic acid	20.07
	trimesic acid	9.79
	pyromellitic acid	8.87
Naphthalene	1-naphthoic acid	9.59
	2-naphthoic acid	9.48
Biphenyl	diphenic acid	18.85
Propylpyrene	α -(1-pyrene) butyric acid	0.94
Furan	furoic acid	0.94
		<u>100.00</u>

Decarboxylation using the Copper-Quinoline Method. - A 40.0 g. portion of the model mixture was mixed with 12.0 g. of anhydrous copper sulfate and 120.0 g. of freshly distilled quinoline and allowed to stand overnight. The flask that contained the mixture was fitted with a reflux condenser and the condenser vented through a cold trap. It was maintained at 160° overnight and then heated under slow reflux for nine days. The reflux temperature had gone down to 205° after three days but after four days had risen again to 218° where it remained for the duration of the decarboxylation. This was doubtless caused by the formation of benzene and other low-boiling nuclei and the subsequent loss of some of these products. After the reaction mixture had been cooled to room temperature, carbon tetrachloride was added and the resulting solution washed with 325 ml. of 20% hydrochloric acid. The insoluble tar was filtered out of the mixture and the layers separated. The aqueous layer was washed with carbon tetrachloride and discarded. A total of about 575 ml. of carbon tetrachloride was used.

The carbon tetrachloride layer was extracted with 100 ml. of 5% sodium hydroxide solution and the basic extract, in turn, acidified and extracted with about 100 ml. of ether. After the ether had been allowed to evaporate at room temperature, a residue of 0.03 g. of a viscous yellow oil was obtained. This oil was examined by means of a 200° inlet mass spectrometer and the results are given in Table 2.

TABLE 2

Component	Weight, g.
Mass 170 (phenylphenol)*	0.002
Mass 142	0.0006
Mass 136 (C ₃ phenol)**	0.0002
Mass 122 (C ₂ phenol)	0.002
Mass 108 (cresol)	0.001
	<u>0.006</u>

* Tentative identifications are given in parenthesis

** This notation designates phenol substituted with three saturated carbon atoms, i.e. propylphenol, methylethylphenol, or trimethyl phenol.

The mass spectrum also indicated that in addition to the components listed, the oil contained a complex mixture of high molecular weight materials.

The low-boiling material obtained from the cold trap was also analyzed by means of a mass spectrometer. In addition to sulfur dioxide and water, it contained 0.09 g. of furan, 0.9 g. of benzene, and 0.04 g. of toluene.

Most of the solvent was removed from the carbon tetrachloride solution containing the neutral components using a 12 inch Vigereux column. In addition to the carbon tetrachloride, the distillate contained 4.5 g. of benzene and 0.09 g. of toluene. The residue was examined using a 200° inlet mass spectrometer and the results are tabulated in Table 3.

TABLE 3

<u>Component</u>	<u>Weight, g.</u>
Biphenyl	4.66
Methylnaphthalene	0.37
Naphthalene	5.78
C ₃ benzene	0.16
Toluene	0.13
	<hr/>
	11.1

Decarboxylation using Thermal Decomposition of the Copper Salts. - A 40.0 g. portion of the model mixture was mixed with 16.0 g. of basic copper carbonate ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$) in enough water to produce a solution volume of about 160 ml. The mixture was heated for 2 hours on a steam bath and then charged to a 320 ml. stainless steel autoclave. The autoclave was heated at 150° for about 2 hours and then maintained at 250 - 260° for 26 hours. After this length of time, the pressure had reached 750 psi. The autoclave was carefully vented and the contents washed out with both water and carbon tetrachloride. The mixture was made basic and the dark colored, insoluble residue filtered out and discarded.

The aqueous, basic extract was then acidified thereby precipitating a tan-colored material. The composition of this tan, insoluble material was investigated using a 200° inlet mass spectrometer. It contained 3.7 g. of benzoic acid and 2.6 g. of naphthoic acid. A significant amount of a mass 73 fragment ($-\text{CH}_2-\text{CH}_2-\text{COOH}$) was also found but no peak was detected at the molecular weight of this component. The mixture also contained small amounts of mass 198 (α -phenylbenzoic acid), 196, 170 (phenylphenol), 168, and 164 (isopropylbenzoic acid).

Most of the solvent was removed from the carbon tetrachloride solution of the neutral components using a 12 inch Vigereux column. The distillate contained 0.65 g. of benzene, 0.1 g. of toluene, 0.18 g. of naphthalene, and 0.21 g. of biphenyl in addition to the carbon tetrachloride. The composition of the residue as determined by its mass spectrum is given in Table 4.

TABLE 4

Component	Weight, g.
Biphenyl	3.5
Naphthalene	3.2
C ₃ benzene	0.05
Toluene	0.05
	<u>6.8</u>

In addition to the nuclei listed, small amounts of masses 202, 196, and 168 were also found.

Since small amounts of unexpected nuclei were found in the residue, it was chromatographed so that they could be more positively identified. A 9.60 g. portion was chromatographed using a 1 x 14 inch column filled with about 150 g. of alumina. The solvents used to elute the column are tabulated in Table 5.

TABLE 5

Fraction	Solvent	Volume, ml.
1	Carbon tetrachloride	225
2	" "	500
3	Acetonitrile	225
4	"	500
5	"	100
6	95% ethanol	250
7	"	450

The first part of the solvent was removed on a steam bath under reduced pressure and the remaining solvent removed by means of a jet of air at room temperature. Fractions 1 and 2 were not taken to dryness to avoid losing the more volatile components. The fractions were examined by means of a 200° inlet mass spectrometer. The first two fractions contained only biphenyl and naphthalene. Fraction 3 contained a mixture of small amounts of many components while the later fractions contained almost exclusively mass 196. This mass 196 was shown to be the lactone of 2-hydroxy-2'-biphenyl carboxylic acid by its infrared spectrum. The total weights of the various components of these fractions based on the total weight of the residue rather than the 9.60 g. actually chromatographed are tabulated in Table 6.

TABLE 6

Component	Weight, g.
Mass 232 (phenylnaphthylketone)	0.05
Pyrene	0.09
Lactone of 2-hydroxy-2'-biphenylcarboxylic acid	0.4
Biphenyl	3.0
Naphthalene	3.1
Mass 149 (fragment)	0.08

Very small amounts of the following components were also found: Mass 220, mass 208, mass 182 (benzophenone), mass 180 (fluorenone), Mass 168 (biphenylene oxide), and possibly Mass 280. The pyrene was identified by its mass and ultraviolet spectra.

RESULTS

The amounts of the various nuclei found using each of these decarboxylation methods are tabulated and compared with calculated amounts in Table 7. The amounts found using the copper-quinoline method generally agreed very well with the calculated amounts. This agreement would probably be even better if a larger amount of the mixture had been decarboxylated. The amounts of the most volatile components, benzene and furan, that were obtained were substantially below the calculated amounts. This was doubtless due to the long reaction time that was used. Low yields of benzene were also obtained when the acids obtained by the controlled oxidation of bituminous coal were decarboxylated using this method and a long reaction time.² It is interesting to note that the furan nucleus survived the decarboxylation. This indicates that since no furan was found in the decarboxylation products of the coal acids, the furan ring is probably not present in the coal acids. Neither pyrene nor any derivative of pyrene was found in the neutral decarboxylation products indicating that α -(1-pyrene) butyric acid was not decarboxylated. This is not unexpected since it is an aliphatic acid and not an aromatic acid as are the others.

An unexpected product of the copper-quinoline decarboxylation of the model mixture was methylnaphthalene. Apparently about six per cent of the naphthalene was converted to methylnaphthalene during the decarboxylation. This presence of methylnaphthalene where there should be none casts doubt on the large amounts of methylnaphthalene obtained from the coal acids and reported in our earlier paper.² The amounts of methylnaphthalene found in the decarboxylation products of the coal acids have been much more variable than have the amounts of any other nucleus. It is likely that some of the methylnaphthalene that was found in the decarboxylation products was actually present as naphthalene in the original acid mixture.

TABLE 7
Copper-Quinoline Method Thermal Decomposition Method

Component	Calc. Amount, g.		Amt. found, g.		Amt. found, %		Amt. found, g.		Amt. found, %	
	9.3	0.27	5.4	0.26	58	96	0.65	7.	---	---
Benzene	0.14	0.16	0.15	0.05	114	36.	0.15	56.	---	---
Toluene	5.7	4.8	5.8	4.7	102	77.	3.4	60.	---	---
Isopropylbenzene	4.8	0.23	4.7	0.09	98	39	3.7	77.	---	---
Naphthalene	0.23	0.32	0.09	0.0	39	0	0.0	0.	---	---
Biphenyl	0.32	0.0	0.0	0.37	0	---	0.0	0.	---	---
Furan	0.0	0.0	0.0	0.0	---	---	0.0	---	---	---
n-propylpyrene	0.0	0.0	0.0	0.0	---	---	0.0	---	---	---
Methylnaphthalene	0.0	0.0	0.0	0.0	---	---	0.09	---	---	---
Pyrene	0.0	0.0	0.0	0.0	---	---	0.05	---	---	---
Mass 232 (phenylnaphthylketone)	0.0	0.0	0.0	0.0	---	---	0.05	---	---	---
The lactone of 2-hydroxy-2'-biphenylcarboxylic acid	0.0	0.0	0.0	0.0	---	---	0.40	---	---	---

In addition to the above components, very small amounts of phenols were found in the products of the copper-quinoline method and probably were also present in the products of the thermal decomposition method. Complex, oxygenated nuclei were also found in the products of the thermal decomposition method.

Very small amounts of phenols were also found in the copper-quinoline decarboxylation products of the model mixture. Because of this, it is doubtful if much can be concluded from the small amounts of phenols found in decarboxylation products of the coal acids.

The thermal decomposition of the copper salts of the model mixture resulted in a much less complete decarboxylation. No furan and no propylpyrene were found in the products although a small amount of pyrene itself was detected. A significant amount of the lactone of 2-hydroxy-2'-biphenylcarboxylic acid was found doubtless arising from the diphenic acid. Small amounts of mass 232, probably phenylanthracenylketone, and other oxygenated products were also obtained by using this decarboxylation method. Therefore, the lactone of 2-hydroxy-2'-biphenylcarboxylic acid and probably the 9-fluorenone and the biphenylene oxide reported by Entel³ and by us in a previous paper⁴ are artifacts of the decarboxylation method and not present as such in the coal acids. These nuclei were found by using the thermal decarboxylation method but not by using the copper-quinoline method. Larger amounts of benzophenone were also found by using the thermal decomposition of the copper salts and so probably some of this oxygenated nucleus is also an artifact of the method. Small amounts of phenols are probably also present in the decarboxylation products as they were when the copper-quinoline method was used but they were masked by the large amounts of undecarboxylated and partially decarboxylated acids recovered.

CONCLUSION

The copper-quinoline decarboxylation method seems to be quite reliable and to provide a good estimate of the amounts of the various nuclei present. Significant amounts of methylanththalene, however, were found where only naphthalene should have been found. Therefore, some of the methylanththalene and perhaps some of the other methyl substituted aromatics reported in the previous papers^{1,2} as occurring in the acids obtained by the controlled oxidation of bituminous coal may be artifacts and not actually present. The thermal decomposition of the copper salts resulted in a much less complete decarboxylation of the model mixture and, in addition, resulted in the formulation of oxygenated nuclei. The lactone of 2-hydroxy-2'-biphenylcarboxylic acid which is present in the thermal decarboxylation products of the coal acids^{3,4} is probably obtained from a diphenic acid type precursor since it was also found in the decarboxylation products of the model mixture. It also seems likely that the 9-fluorenone and the biphenylene oxide and some of the benzophenone that was found when this decarboxylation method was used are also artifacts of the method.

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STRUCTURES OF THE ACIDS OBTAINED BY OXIDATION OF BITUMINOUS COAL-
THERMAL DECARBOXYLATION OF THE COPPER SALTS

R. S. Montgomery and E. D. Holly
The Dow Chemical Company

ABSTRACT

The chemical structures of the aromatic acids obtained by the controlled oxidation of bituminous coal were investigated by thermal decarboxylation of the copper salts followed by separation and identification of the products. This decarboxylation method allows the identification of the nitrogen-containing nuclei. The use of this method, however, resulted in a less complete decarboxylation and much greater yields of oxygenated nuclei than did the copper-quinoline method.

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STRUCTURES OF THE ACIDS OBTAINED BY OXIDATION OF BITUMINOUS COAL-
THERMAL DECARBOXYLATION OF THE COPPER SALTS

R. S. Montgomery and E. D. Holly
The Dow Chemical Company

In our previous papers^{1,2} the chemical structure of bituminous coal was studied by investigating the nuclei of the aromatic acids obtained on controlled oxidation. The mass spectrometer was found to be ideally suited to this work because with it very small amounts of hydrocarbons can be identified in rather complex mixtures. In the previous work the decarboxylations were carried out using the copper-quinoline method. This method was found to be generally satisfactory but with it the small amounts of the basic, nitrogen-containing nuclei could not be detected owing to the large quantities of quinoline that are used in the reaction. Therefore, the coal acids have been decarboxylated using an alternate method. The thermal decomposition of the copper salts of the acids will bring about decarboxylation without the use of quinoline and so allow the determination of the nitrogen-containing nuclei in addition to the neutral and acidic nuclei. Another reason for investigating this alternate decarboxylation method was that Entel³, by using this method, found significant amounts of 9-fluorenone, biphenylene oxide, and the lactone of 2-hydroxy-2'-biphenylcarboxylic acid that we were unable to detect using the copper-quinoline method although we had been able to account for substantially all of the nuclei.

EXPERIMENTAL

The acids used in this study were obtained from The Coal Research Laboratory of the Carnegie Institute of Technology and were the same as those investigated in our previous papers. They were obtained by the oxidation of an aqueous alkaline suspension of Pocahontas No. 3 bituminous coal by gaseous oxygen at 270° and total pressures of about 900 psig.

Decarboxylation. - The decarboxylation was carried out by the method used by Entel. A solution of 1.0 kg. of the coal acids in 1.0 l. of water was made and 380 g. of basic copper carbonate (1.7 mole $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$) was added in small quantities with stirring. To ensure the completion of the reaction, after cessation of the evolution of carbon dioxide the reaction mixture was stirred and heated for one and a half hours on a steam-bath.

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- (1) R. S. Montgomery, E. D. Holly, and R. S. Gohlke, *FUEL*, Lond. 35, (1956) 49
 - (2) R. S. Montgomery and E. D. Holly, *FUEL*, Lond. 36, (1957) 63
 - (3) J. Entel, *J. Amer. Chem. Soc.* 77, (1955) 611

This aqueous suspension of the copper salts of these acids was made up to a volume of 2.0 l. and charged to a four-liter, stainless steel, externally heated, shaking autoclave. The autoclave was flushed with nitrogen and heating and shaking of the autoclave was started and maintained for 24 hours after reaching a temperature of 250°. The pressure after this length of time was 3180 psig. After cooling to room temperature, the autoclave was vented through two Dry Ice-methylene chloride-filled cold traps. Just 3.6 g. of a very low-boiling liquid was obtained in the cold traps.

Initial Separation. - The autoclave contained two layers. The aqueous layer was almost clear and colorless while the oil layer was rather dark-colored and tarry appearing. The residue on the bottom of the autoclave was washed well with both water and carbon tetrachloride before discarding it. About 2 l. of carbon tetrachloride was used.

The acidic products of the decarboxylation were separated by making the reaction mixture basic and separating the aqueous layer. This aqueous layer was in turn acidified and the acidic nuclei extracted by means of carbon tetrachloride. A large amount of solid material was obtained that was not soluble in either water or carbon tetrachloride. This was presumably the partially decarboxylated acids.

The original carbon tetrachloride solution from which the acidic material had been removed was then extracted with water to which had been added a little sulfuric acid. The basic nuclei were obtained by making this extract basic and then extracting it with carbon tetrachloride. The original carbon tetrachloride solution from which both the acidic and basic components had now been removed contained only the neutral decarboxylation products.

Work-up of the Carbon Tetrachloride Extracts. - Most of the solvent was removed from the carbon tetrachloride solutions of the neutral, acidic, and basic decarboxylation products at atmospheric pressure using a 30 inch concentric-rod type column. The distillation fractions were examined by means of a 200° inlet mass spectrometer and in some cases an ultraviolet spectrometer. The residue from the atmospheric distillation of the carbon tetrachloride solution containing the acidic components was vacuum distilled in order to obtain more accurate estimates of the amounts of the various components. The weights of the components are given in Table 1.

TABLE 1

Compound	Weight, g.
Mass 198 (carboxybiphenyl)*	1.
Mass 196	2.
Mass 172	0.3
Mass 170 (phenylphenol)	1.
Biphenylene oxide	0.2
Mass 166 (phthalic acid)	0.1
Biphenyl	0.1
Toluic acid	3.2
Naphthalene	0.7
Benzoic acid	11.7
Cresol	0.03
Phenol	2.3

* Tentative assignments are given in parenthesis.

The carboxylic acids present represent 0.8 g. of biphenyl, 1.9 g. of toluene, and 7.2 g. of benzene.

The weights of the various basic decarboxylation products are given in Table 2.

TABLE 2

Compound	Weight, g.
Phenanthridine	0.2
Phenylpyridine	4.1
Quinoline	0.3
Pyridine	present

The phenanthridine was identified by means of its ultraviolet spectrum.

The solvent that was stripped from the carbon tetrachloride solution containing the neutral decarboxylation products contained a total of 75.9 g. of benzene, 1.9 g. of toluene, and 18.9 g. of methylethylketone. The total weight of the residue from this distillation was 165 g. A 106.6 g. portion was vacuum distilled. The results are tabulated in Table 3.

TABLE 3

Fraction	Temperature	Weight, g.
1	35°/160 mm. to 48°/160 mm.	10.60
2	76°/1.0 mm. to 97°/0.6 mm.	10.85
3	87°/0.3 mm. to 141°/0.6 mm.	15.68
4	139°/0.7 mm. to 181°/0.6 mm.	20.67
residue		44.55
loss		4.2

These fractions were examined by means of a 200° inlet mass spectrometer and the results given in Table 4. The weights are based on the entire 165 g. rather than the 106.6 g. actually distilled.

TABLE 4

Component	Fract. 1	Fract. 2	Fract. 3	Fract. 4
Terphenyl	---	0.02 g.	0.05 g.	0.6 g.
α -phenyl naphthalene	---	0.07	0.3	4.1
Mass 196	---	0.2	0.2	3.8
Benzophenane	---	0.5	6.4	6.7
9-Fluorenone	---	---	---	7.0
Phenanthrene	---	---	---	6.7
Biphenylene oxide	---	1.7	12.6	1.3
Biphenyl	---	6.5	7.9	0.3
Mass 152	---	---	---	1.
Methylnaphthalene	---	0.2	---	---
Naphthalene	0.02 g.	7.6	0.9	---
C ₂ benzene	0.03'	---	---	---
Toluene	0.6	---	---	---
Benzene	0.3	---	---	---

** This notation indicates benzene substituted with two saturated carbon atoms, i.e. ethylbenzene or xylene.

There were also small amounts of masses 198, 146, 134, 122 and 120. The residue was about 80% non-volatile in the mass spectrometer. It contained terphenyl, biphenyl, and masses 204, 202, 196, 182, 180, 178 and 168.

Chromatography. - An 18.7 g. portion of the fourth fraction of the above vacuum distillation was chromatographed. A 1-1/8 x 20 inch column packed with alumina was used. The material to be chromatographed was applied to the column from 172 g. of carbon tetrachloride. All of the material with the exception of 1.5 g. of a dark-colored tar was soluble. One hundred milliliter fractions of the eluate were taken. The fractions were evaporated under vacuum at room temperature and the residues weighed. Some representative fractions were examined by means of a mass spectrometer. Some of the fractions were also examined by means of an infrared spectrometer and an ultraviolet spectrometer. A total of 14.01 g. was collected but it was estimated that 3.5 g. of this was residual solvent. Therefore quite a bit of the material that was originally absorbed on the column was lost and judging from the fact that the lower molecular weight, more volatile components were considerably reduced in the fractions of the eluate, it was lost by evaporation or sublimation during the removal of the solvent.

The amounts of the various components and the solvents used to elute them are plotted as a function of fraction number in Figures 1 and 2. After the last fraction, a small amount of additional material was obtained by heating the alumina from the column with benzene. The position and shape of the

curves if very informative about the structure of the components. The amounts of the components were estimated by graphically intergrating the areas under the curves, and are tabulated in Table 5. The weights are based on the entire 20.67 g. rather than the 18.7 g. actually chromatographed.

TABLE 5

Component	Weight, g.
Mass 258	0.12
Mass 244	0.078
Mass 232	0.011
Terphenyl	0.48
Mass 228	0.033
Mass 218	0.024
α -phenyl naphthalene	0.77
Mass 202	0.19
The lactone of 2-hydroxy-2'-biphenylcarboxylic acid	2.0
Methyl benzophenone	0.18
Mass 184	0.53
Benzophenone	2.6
9-Fluorenone	2.4
Phenanthrene	2.1
Mass 170	0.004
Total	11.5 g.

Traces of the following masses were also found: 246, 220, 210, 208, and 150.

Identification of Masses 204, 196, 180 and 168. - All of the important components found in the previous papers were identified with the exception of mass 204. This mass was tentatively identified as phenylnaphthalene. This component was concentrated from chromatographic fraction number two by crystalization and its mass and infrared spectra compared with that of an authentic sample of α -phenylnaphthalene. The spectra were found to be identical and so it was concluded that mass 204 is indeed α -phenylnaphthalene.

In the present work three new components were found. Mass 196 was identified as predominately the lactone of 2-hydroxy-2'-biphenyl carboxylic acid by its mass and infrared spectra. A small portion of mass 196 was identified as methylbenzophenone by its mass spectrum and its position in the eluate (see Fig. 1). Mass 180 and mass 168 were identified as 9-fluorenone and biphenylene oxide respectively by their mass and infrared spectra. This lactone, 9-fluorenone, and biphenylene oxide were all found by Entel using the same decarboxylation method.

Total Amount of Nuclei Found. - The total amount of the various nuclei can be computed by summing up the components in each of the fractions. The various carboxylic acids that were found were calculated as neutral nuclei and included in this sum. The nitrogen-containing nuclei are tabulated in Table 6 and the neutral and acidic nuclei tabulated in Table 7.

TABLE 6

Compound	Yield, g./kg.	Portion of total nitrogen, % *	Portion of total nuclei, % **
Phenanthridine	0.2	1.	0.04
Phenylpyridine	4.1	19.	0.9
Quinoline	0.3	6.	0.07
Pyridine	present	---	----
Total	4.6	26.	1.0

* Based on 0.2% nitrogen in the original acids.

** Based on a theoretical yield of 453 g. of nuclei per kilogram of coal acids.

TABLE 7

Compound	Yield, g./kg.	Compound	Yield, g./kg.
<u>Neutral Nuclei</u>			
Mass 258	0.12	Mass 184 (C ₁₄ H ₁₆)	0.53
Mass 246	present	Benzophenone	13.6
Mass 244	0.078	9-Fluorenone	8.2
Mass 232	0.011	Phenanthrene	9.9
Terphenyl (m- and p-)	0.82	Biphenylene oxide	16.6
Mass 228	0.033	Biphenyl	19.0
Mass 220	present	Mass 152	0.95
Mass 218	0.024	Mass 150	present
Mass 210 (C ₁₄ H ₁₀ O ₂)	present	Methylnaphthalene	
Mass 208	present	(α- and β-)	0.17
α-phenylnaphthalene	4.5	Naphthalene	10.6
Mass 202	0.19	C ₂ benzene	0.03
Lactone of 2-hydroxy-2'-biphenylcarboxylic acid	7.4	Toluene	3.8
Methylbenzophenone	0.18	Benzene	83.1
<u>Acidic Nuclei</u>			
Mass 170 (phenylphenol)	1.0	Phenol	2.3
Cresol	0.03		

In addition to these nuclei, 18.9 g. of methylethylketone was obtained. This was doubtless a residue of the solvent used to isolate the coal acids from the original aqueous reaction mixture.

DISCUSSION

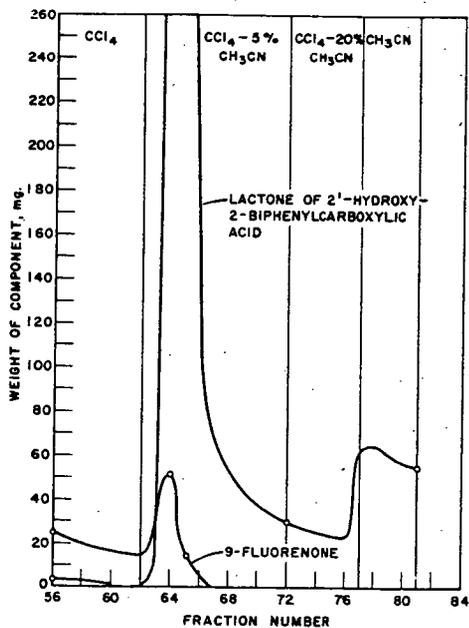
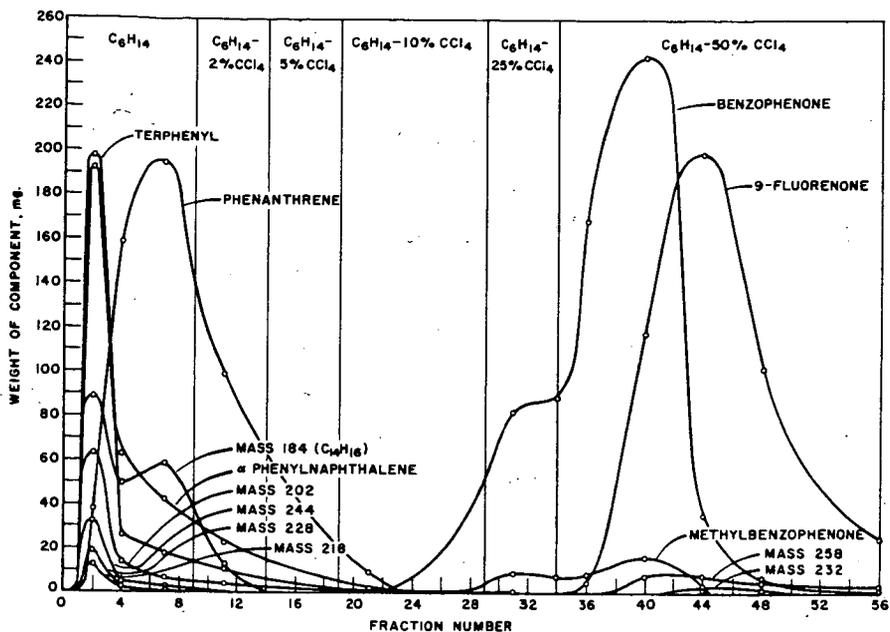
By using the thermal decomposition of the copper salts of the coal acids it has been possible to identify about 26% of the nitrogen containing nuclei. The nitrogen-containing nuclei probably amount to only about 4% of the total nuclei of the coal acids but their structures are important in that they provide information about the condition of the nitrogen atoms in the original coal structure. Phenanthridine, phenylpyridine, quinoline, and pyridine have been found. Entel found similar amounts of phenylpyridine, quinoline, and pyridine but the more highly condensed structure, phenanthridine, has not been reported before. The presence of these compounds in the decarboxylation products demonstrates the presence of nitrogen-containing condensed aromatic systems in bituminous coal.

In the present work, mass 204 which occurs in significant amounts in the decarboxylation products was definitely identified as phenyl-naphthalene. It was also possible to definitely identify methylbenzophenone.

This decarboxylation method yielded smaller amounts of nuclei than did the copper-quinoline method used in our previous papers. This is due to a less complete decarboxylation as evidenced by the relatively large amounts of carboxylic acids present in the products. In addition, this decarboxylation method yielded greatly increased amounts of oxygenated nuclei. The oxygenated compounds amounted to about 48 per cent of the neutral nuclei (excluding benzene) where by the copper-quinoline method they amounted to only 3 per cent. Almost twice as much benzophenone was obtained and large amounts of three oxygenated nuclei that did not occur in the products of the other decarboxylation method were found. These three nuclei were the lactone of 2-hydroxy-2'-biphenylcarboxylic acid, 9-fluorenone, and biphenylene oxide. With the exception of these oxygenated nuclei, the decarboxylation products were similar to those found previously by the other method.

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PERFORMANCE OF AN AGITATOR ABSORBER IN
REMOVING CO₂ FROM A GAS

A Statistical Investigation by Albert S. Moore and Sidney Katell
U. S. Bureau of Mines, Branch of Coal Gasification
Morgantown, West Virginia

ABSTRACT

The effects of process pressure, carbon dioxide content of the feed gas, solution throughput, and liquid-to-gas ratio on the performance of an agitator absorber at levels of 200-300 p. s. i. g., 10-20 mol-percent, 60-90 gal. /hr., and 16.5-55 gal. /hr. solution per 1000 std. cu. ft. gas/hr., respectively, have been determined. The absorbent used was 40 weight-percent diethanolamine in water; the gas used was inert gas with carbon dioxide added.

The data and results from three sets of sequential factorial experiments are presented. The experiments were designed to test each of the four factors at three levels of operation.

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"Performance of an Agitator Absorber in Removing CO₂ From a Gas"
A Statistical Investigation
Albert S. Moore and Sidney Katell
U. S. Bureau of Mines, Branch of Coal Gasification
Morgantown, West Virginia

During the last fifteen years, processes for removing carbon dioxide and hydrogen sulfide from industrial gases by scrubbing with various amines have become generally accepted. To date, these processes have employed conventional gas-liquid contactors, packed columns and bubble-cap towers.

It has been shown that the absorptive capacities of the amines increase markedly with increased concentration, but because of the operating difficulties encountered when conventional scrubbers are used to process liquids of even moderate viscosity, the limiting concentration has been about 15 percent amine in water. Thus, for these processes to realize full commercialization, methods of gas-liquid contacting able to tolerate more viscous scrubbing media must be developed.

This paper describes studies of the absorption of carbon dioxide in 40 weight-percent diethanolamine in water utilizing an agitator-type contactor. Figure 1 shows a vertical cross section of the absorber. The action within the absorber is as follows: The lean solution is fed into the vessel through a sparger ring. The liquid is raised in the lift tube by the centrifugal action of the turbine and propelled from the absorber impeller in the form of a fine spray. This spray of liquid droplets moves at a high speed relative to the gas stream, which passes through the spray curtain in upward flow through the absorber. Inasmuch as this is a relatively novel gas-liquid contactor, it is to be expected that its mode of action would be distinctive.

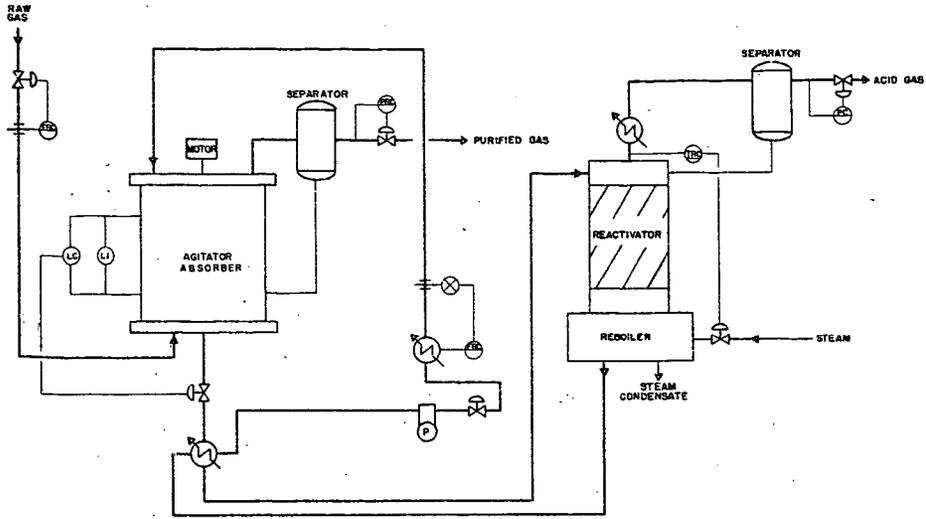
The work described here was undertaken to determine the characteristics of the agitator-absorber with respect to: (1) Process pressure, (2) carbon dioxide content of the feed gas, (3) absorbent solution rate, and (4) liquid-to-gas ratio.

DESCRIPTION OF GAS-PURIFICATION PILOT PLANT

Figure 2 is a flow diagram of the pilot plant. For this study the absorber was installed to operate with existing solution-regeneration facilities.

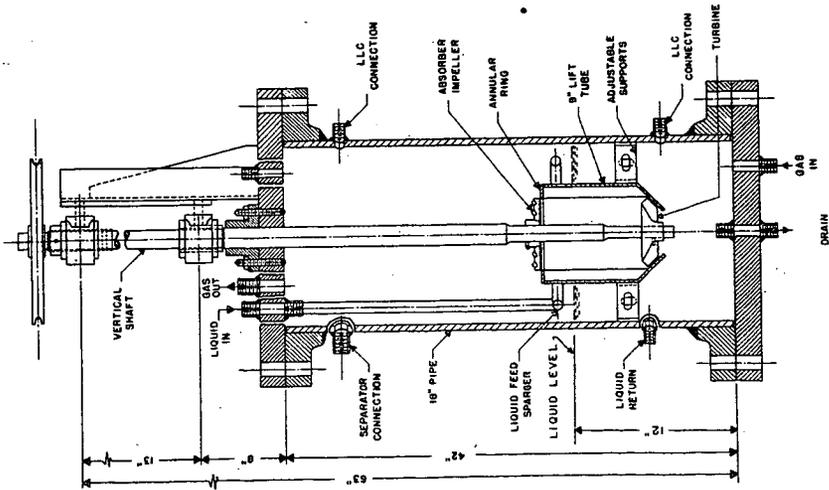
The Absorber

The absorber is shown in figure 1. The essential internal parts are the annular ring and lift tube and the turbine and impeller. The turbine imparts a centrifugal action to the absorbent solution, which is directed by the annular ring and lift tube onto the impeller, where the spray is formed. The latticed faces of the impeller are beveled to about 38° off horizontal so



FLOW DIAGRAM OF (GAS - PURIFICATION PILOT PLANT)

D-3853
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74



THE AGITATOR ABSORBER

Fig. 1.-The agitator absorber

Fig. 2.-Flow diagram of (gas-purification pilot plant)

that the principal portion of the spray is directed toward the walls of the absorber vessel rather than the top. A 1-hp. motor (1,750 r. p. m.) connected to the shaft through sheave pulleys is used to drive the turbine. A constant turbine speed of 750 r. p. m. was used for these tests.

The Reactivator

The reactivator tower is a 17-foot length of 10-inch, schedule 40 pipe, which is packed to a depth of 15 feet with 3/4-inch Raschig rings and direct-connected to the reboiler by 10-inch diameter flanges. The reboiler is 10-feet in length and 16 inches in diameter. It is fitted with a pressure connection, connections for adding makeup condensate and for draining the solution, and a thermocouple connection installed near the end of the tube bundle. Steam for reactivation is controlled by a pressure controller and is measured by weighing the condensate. The entire unit is lagged with 2 inches of magnesia insulation and 1/4 inch of "Insulcote".

Auxiliary Equipment

The solution heat exchanger, solution cooler, and acid-gas cooler are all similar. Each consists of two Griscom-Russell twin G-fin sections connected in series. The heat exchanger and solution cooler each contain four, schedule 40, 3/4-inch, G-fin pipes about 10 feet long. The fin pipes in the acid-gas cooler are about 5 feet long. Thermocouple connections are installed so that all inlet and outlet temperatures can be recorded.

A 1-1/4 by 4-inch triplex, single-acting power pump circulates the solution. The flow of the solution to the absorber is controlled by an air-operated bypass valve.

The gas is stored, before compression, in a wet-type gas holder having a capacity of 1,000 cubic feet. The 2-stage gas compressor can deliver 7,200 standard cubic feet per hour at 350 p. s. i. g.

Solution and Gas Flow

The flow of solution and gas in the pilot plant is typical of most gas-purification systems. Inert gas, varying in CO₂ content from 7 to 10 mol-percent, is taken from the gas holder, compressed to about 350 p. s. i. g., and fed to the absorber.

The carbon dioxide necessary to bring the carbon dioxide content of the unpurified gas to the level of predetermined experimental conditions is added to the suction line of the compressor.

The lean diethanolamine solution enters through the top of the absorber. It is distributed by a sparger ring directly above the liquid level and just below the top of the lift tube and leaves the absorber through a side connection 6 inches from the bottom. The level of solution in the absorber is maintained to a depth of 12 inches (indicated by the broken line in figure 1).

The diethanolamine is forced up into the lift tube by the turbine; baffles in the lift tube eliminate any swirling action. The rising solution contacts the absorber impeller, a deflector designed to give maximum spray commensurate with the dimensions of the absorber vessel. Three distinct spray patterns are formed--(1) the initial spray from the absorber impeller, consisting of small droplets moving at very high velocities, (2) impact spray formed when the initial spray rebounds from the walls of the vessel, and (3) conjunctive spray formed when the initial spray and impact spray collide.

The feed gas enters at the base of the absorber to the right of the lift tube. It bubbles through the diethanolamine, passes through the spray pattern, and leaves the top of the absorber into an entrainment separator as purified gas. It is then returned to the gasholder for feed-gas makeup.

The fouled amine solution leaving the bottom of the absorber is heated by heat exchange with lean amine solution and regenerated in the reactivator with indirect heat from low-pressure steam. The acid gas leaves the top of the reactivator and passes through a cooler where entrained steam is condensed and returned to the column. The acid gas is then returned to the holder for feed-gas makeup.

The reactivated diethanolamine leaves the reactivator, flows through the heat exchanger where it gives up a portion of its heat to the fouled solution leaving the absorber, and is pumped through a water-cooled solution cooler back to the absorber.

EXPERIMENTAL PROCEDURE

The agitator gas-liquid contactor is a novel piece of equipment. To evaluate it in terms of more conventional gas-cleaning apparatus, packed columns and bubble-cap towers, optimum operating conditions for the agitator absorber process must first be found.

Eight obvious factors will affect performance of the absorber: (1) Process pressure, (2) carbon dioxide content of the feed gas, (3) absorbent-solution throughput, (4) liquid-to-gas ratio, (5) concentration of the absorbent solution, (6) feed-gas throughput, (7) the speed of the turbine, and (8) carbon dioxide content of the lean absorbent solution. Although the operational levels of all of these factors are easily controlled within relatively narrow limits, there is no reason to suppose that the efficiency of the process is an additive function of any two of them. Consequently, the complete exploration of the causal relations among these factors would require that the effect of each factor be observed under all combinations of values of the other factors. Such a procedure would require a relatively large number of tests.

To overcome this difficulty, a series of sequential factorial experiments, each concerned with a group of relevant factors, was initiated. Such a procedure allows for maximum flexibility in planning and has the inherent advantage that, as each factorial is developed, the factors involved may be directed toward optimum conditions relevant to all other factors.

Process pressure, carbon dioxide content of the feed gas, absorbent solution throughput, and liquid-to-gas ratio were chosen as the independent variables for the initial experiment; the levels chosen for these factors were 200-300 p. s. i. g., 10-20 mol-percent, 60-90 g. p. h., and 16.4-55 respectively.

Liquid-to-gas ratio in this instance is defined as gallons of solution per 1,000 std. cu.ft. of feed gas per hour. The dependent variable in the process is the total carbon dioxide absorbed, since all other variables for these experiments were predetermined.

As dictated by subsequent operation, a second factorial was designed at new operational levels for the four factors. The purpose of the second set of experiments was to investigate further the interactions among the various factors revealed in the initial set of tests. The block design for each factorial is presented in Appendix 1.

DATA AND RESULTS

Table 1 presents typical operating conditions prevalent throughout the 30 tests performed for this study; table 2 presents the cumulative data from these tests.

Table 1. - Typical operating range for all runs

Gas temperature, °F.	
Before agitator	75-85
After agitator	140-155
Solution temperature, °F.	
Before agitator	100-110
After agitator	140-160
Reboiler pressure, p. s. i. g.	6.5-8
Reboiler temperature, °F.	265-275
Agitator motor	
Ammeter, amps	1.2-1.4
Voltmeter, volts	470 (constant)
Steam pressure, p. s. i. g.	22-30
Steam consumption, lb. /gal. amine	0.6-0.8
Turbine speed, r. p. m.	750 (constant)

A statistical analysis of the data from experiment "A" is made and an analysis of the cumulative data from experiments "A" and "B" is presented.

An empirical equation relating the independent variables to the performance of the agitator absorber is developed. The effect of the same variables on the performance of the agitator is presented graphically in chart 1.

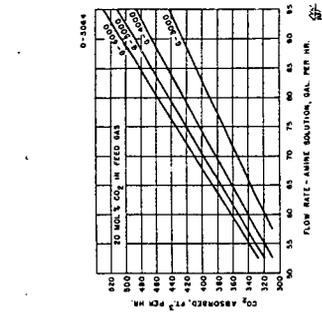
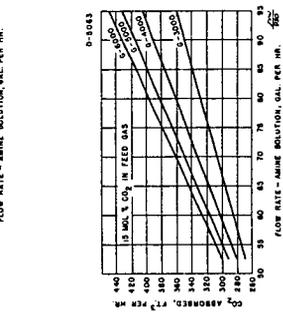
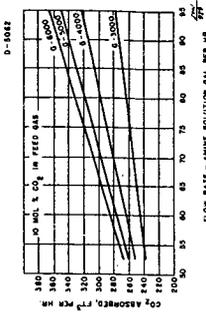
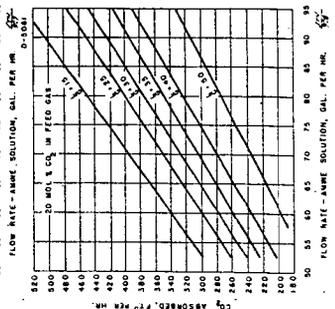
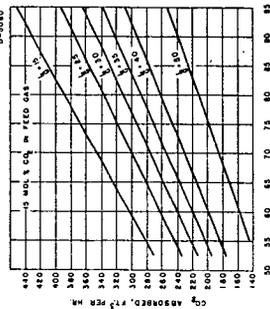
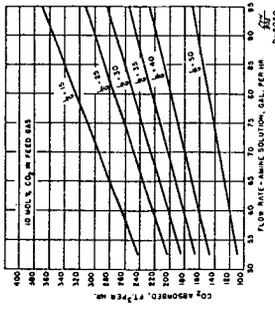


Chart 1. - An expression of the scrubbing capacity of the agitator absorber as a function of solution throughput and CO₂ content of feed gas with L/G ratios and gas rates as parameter.
 G = gas rate, std. ft. ³/hr. L/G = ratio of solution throughput, gal/hr. to gas rate 1000 std. ft. ³/hr.

The following nomenclature is used in these presentations:

- Y = total CO₂ absorbed, cubic feet per hour
L = L/G = liquid-to-gas ratio, $\frac{\text{gallons per hour solution}}{1,000 \text{ std. cu. ft. gas/hr.}}$
S = solution throughput, gallons/hr.
C = CO₂ content of feed gas, mol-percent
P = process pressure, p.s.i.g.
D²/16 = sum of the squares of the dependent variable accounted for by a given factor, divided by the number of tests involved.
n = number of tests, contingent to a given calculation.

EVALUATION OF DATA

Table 3 presents an analysis for significance of the 16 runs of experiment "A" in which the factors involved were tested at the high and low levels. This analysis was made using the method of Yates.

The error mean square was determined using data from the runs at which the factors were tested at the median levels. The calculation was made using this relationship:

$$\text{E. M. S.} = \frac{\sum Y^2 - \frac{(\sum Y)^2}{n}}{n-1} = 33.2$$

The standard deviation by definition is the square root of the error mean square. In this instance the standard deviation was ± 6 cu. ft./hr. of CO₂ absorbed.

The interactions between the carbon dioxide content and solution throughput, and between the carbon dioxide content and liquid-to-gas ratio revealed in the analysis of the data from experiment "A", were evaluated further by solving the normal equations using matrices set up from the cumulative data of experiments "A" and "B". Using the methods of Davies, the coefficients of table 4 were determined and an empirical equation relating the significant factors to the dependent variable was set up.

Table 3. - Factorial analysis - Experiment A

<u>P</u>	<u>C</u>	<u>S</u>	<u>L</u>	<u>Run</u>	<u>Y</u>	<u>Factor</u>	<u>D²/16</u>	<u>Significance</u>
-1	-1	-1	-1	A-11	296	Total	1,211,100	
-1	-1	-1	1	A-4	96	L/G	136,900	0.001
-1	-1	1	-1	A-10	373	S	41,820	0.001
-1	-1	1	1	A-13	132	S L/G	2,601	0.05
-1	1	-1	-1	A-3	350	C	51,984	0.001
-1	1	-1	1	A-14	189	CL	812	nil
-1	1	1	-1	A-19	496	CS	5,625	0.01
-1	1	1	1	A-7	303	CSL	462	nil
1	-1	-1	-1	A-9	260	P	289	nil
1	-1	-1	1	A-15	91	PL	756	nil
1	-1	1	-1	A-16	342	PS	324	nil
1	-1	1	1	A-2	155	PSL	210	nil
1	1	-1	-1	A-18	309	PC	56	nil
1	1	-1	1	A-6	201	PCL	225	nil
1	1	1	-1	A-1	515	PCS	2	nil
1	1	1	1	A-17	294	PCSL	676	nil
							<hr/>	
0	0	0	0	A-5	263		1,453,842	
0	0	0	0	A-8	270		1,211,100	
0	0	0	0	A-12	271		242,742	
0	0	0	0	A-20	275			

Table 4. - Empirically determined coefficients

<u>Factor</u>	<u>Coefficient</u>
Constant	267.3
C	+57.0
S	+57.125
L/G	-92.5
S L/G	-12.75
CS	+18.75

By substituting these real for the coded factors:

$$P = \frac{P-250}{50}$$

$$C = \frac{C-15.2}{5}$$

$$S = \frac{S - 75}{15}$$

$$L = \frac{L/G - 35.7}{19.3}$$

and by affixing the proper coefficients and reducing, equation (1) resulted.

$$(1) Y = 178.3 - 7.35 C + 1.18 S - 1.49 L - 0.044 SL + 0.25 CS$$

An analysis for variance was made by solving the inverted matrix set up from the cumulative data of experiments A and B, again using the methods of Davies. This revealed that the empirical equation would account for 98.5 percent of the total sum of squares of the dependent variable.

A further analysis for significance was made using Student's "T" test as presented by Villars. By this calculation, the empirical equation contains only those terms significant at less than the 5 percent level.

The comparison of observed and calculated values for the rate of adsorption of CO₂ in the agitator absorber, included in table 2, was made employing equation (1).

Chart 1 presents graphically the absorbing capacity of the agitator as a function of solution throughput and CO₂ content of feed gas with gas rates and liquid-to-gas ratios as parameters. The data for plotting chart 1 was evolved by solving equation (1).

DISCUSSION OF RESULTS

The dependent variable for these experiments was taken as total carbon dioxide absorbed per hour. The effect of the independent variables -- pressure, carbon dioxide content of the feed gas, solution throughput, and liquid-to-gas ratio on the performance of the agitator absorber was determined on that basis.

Significant Effects

The factors of these experiments are tabulated in the fourth column of table 3; the coefficients that give these factors quantitative meaning are tabulated in table 4. Examination of these tables shows that the performance of the agitator absorber will appreciate with higher solution throughput, higher CO₂ content in the feed gas and lower liquid-to-gas ratios. The effect of these factors and of the interactions among them on the performance of the agitator absorber is given explicit quantitative meaning in the correlation afforded by equation (1). Using this equation the performance of the agitator, in terms of cubic feet per hour of carbon dioxide absorbed, can be predicted to an accuracy of plus or minus 13 cubic feet per hour within the range of these tests.

Operating requirements commensurate with feed gas composition may be observed directly by reference to chart 1.

Comparison with Conventional Scrubbers

Using the methods of Coulson and Richardson, the over-all mass-transfer coefficients for the agitator absorber were calculated at three sets of conditions, runs A-1, A-2, and A-12.

Until strict criteria for the choice of agitator volume are resolved, it is not possible to make a generalized comparison of the performance of the agitator absorber with conventional scrubbers on the basis of over-all mass-transfer coefficients. The principle of operation, and hence the flow mechanics in the two systems, are quite different; indeed, the flow mechanics in the agitator are extremely complex. However, it is possible to compare the performance of the two types of equipment for specific operating conditions and to describe the performance of the agitator in terms of a physical tower required to effect the same degree of scrubbing at those operating conditions. This comparison has been made and is presented in table 5. It shows the size towers that would have to be employed in place of the agitator absorber for the specified runs.

Table 5. - Data for comparing agitator absorber to packed tower

<u>Run No.</u>	<u>KgA *</u>	<u>Packing</u>	<u>Cross Tower section, sq. ft.</u>	<u>Packing height, ft.</u>
A-1	0.227	3/4 Raschig rings	0.5	5
A-2	.262	3/4 Raschig rings	.5	6
A-12	.111	3/4 Raschig rings	.5	10

*KgA for agitator absorber = $\frac{\text{lb. - mol of CO}_2 \text{ absorbed}}{(\text{hr.})(\text{atm. CO}_2 \text{ partial pressure})(\text{cu. ft. solution})}$

Cubic feet of solution is taken as that volume of the absorber actually occupied by solution; irrespective of the spray. For these calculations, that volume was considered to be a cylinder 18 inches in diameter by 12 inches in height. The actual absorber has a cross section of 1.42 sq. ft. and an inside height of 3.5 ft.

FACTORS TO BE INVESTIGATED

It has been shown that the performance of an absorber of centrifugal design is greatly affected by the characteristics of the spray pattern it develops. The spray pattern in turn is almost totally a function of the turbine design and speed, the impeller design, and the viscosity of the absorbent. The viscosity of the absorbent is dependent on the concentration of the diethanolamine and on the heat of absorption developed. Consequently, this factorial will be expanded to include the factors (1) turbine speed, (2) concentration of absorbent, and (3) heat of absorption.

APPENDIX I

THE BLOCK DESIGN FOR FACTORIAL EXPERIMENTS A AND B

Factorial Experiment A

Factorial Experiment B

Set I				Set II			
A	B	C	D	A	B	C	D
-1	-1	-1	-1	1	-1	-1	-1
-1	-1	-1	1	1	-1	-1	1
-1	-1	1	-1	1	-1	1	-1
-1	-1	1	1	1	-1	1	1
-1	1	-1	-1	1	1	-1	-1
-1	1	-1	1	1	1	-1	1
-1	1	1	-1	1	1	1	-1
-1	1	1	1	1	1	1	1
0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0

A	B	C	D
0	0	0	1.2
0	0	0	-1.2
0	0	$\sqrt{2}$	0
0	0	$-\sqrt{2}$	0
0	$\sqrt{2}$	0	0
0	$-\sqrt{2}$	0	0
$\sqrt{2}$	0	0	0
$-\sqrt{2}$	0	0	0
0	0	0	0
0	0	0	0

In which:

LEVELS

	LEVELS				
	Factorial A			Factorial B	
	Interactions			Curved Effects	
	High	Medium	Low	High	Low
A = pressure, p. s. i. g.	300	250	200	321	179
B = CO ₂ content of foul gas, mol-percent	20	15	10	22.4	8
C = solution throughput gal. /hr.	90	75	60	96.2	53.8
D = liquid-to-gas ratio, gal. /1000 std. cu. ft. /hr.	55	35.7	16.4	58.8	12.6

The level designations: 1, -1, 0, $\sqrt{2}$, $-\sqrt{2}$, 1.2 and -1.2 may be defined as the value of the variable in question minus the mean value of that variable divided by the interval for that variable. The interval in turn may be defined as the value of the variable designated as 1 minus the value of that variable designated as 0.

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DIFFERENTIAL INFRARED SPECTROMETRY TECHNIQUE
USED FOR THE STUDY OF COALS

Raymond V. Smith, Milton E. Wadsworth and George Richard Hill
Departments of Fuel Technology and Metallurgy
University of Utah

ABSTRACT

For the technique described in this paper, two specimens of coal were prepared for runs in the infrared double beam spectrometer. One specimen was prepared for the coal as received from the mine and this was placed in the reference beam. The other sample was prepared from coal which had been heated in a pressure-tight container to the softening temperature. This was placed in the sample beam. The differential infrared spectrometer pattern thus obtained enables one to observe the changes in the chemical bonds of coal which may be detected in the infrared range. Most of the tests were conducted with a coal used for blending in the coking process because of its high fluidity.

The coal samples were prepared by grinding and then casting in a potassium iodide plate.

Samples from coke buttons made from this coal were run in the infrared spectrometer and x-ray diffraction patterns were obtained from these coke samples also. In addition to this some infrared spectra were run on this coal heated in a closed crucible to various temperatures in the softening range.

The results of these tests show positive and negative changes in almost all of the spectral band assignments for coals. Data obtained from the use of this technique should provide valuable information for use in the study of coal coking mechanism.

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INFRARED SPECTROPHOTOMETRIC STUDY OF THE COKING OF COAL

Raymond V. Smith, Milton E. Wadsworth and George Richard Hill
Departments of Fuel Technology and Metallurgy
University of Utah

In order to understand fully the coking mechanism one must trace the chemical changes which occur as the coal undergoes the change from coal to coke. The technique described in this paper provides a means for a more precise study of the chemical changes which occur in coal, particularly those changes which occur in the coal as it is heated to the softening or fluid range. Fluidity is a key factor in the coking mechanism as evidenced by the rather good correlation of coke quality predictability from free swelling and plastometer tests and more recently by the work of Dryden and Panchurst¹. In the latter case a chloroform soluble product was found in the softening temperature range which proved to be a significant factor in the coking process.

Coal specimens were prepared for evaluation by means of infrared spectrophotometry. The samples were ground to a very fine powder and then thoroughly mixed in carefully weighed proportions with potassium iodide. (usually 6 mg coal per gram KI) A measured quantity of this mixture was then pressed in an evacuated die into plates for examination. The reliability of this technique has been well established in other systems^{2,3,4}. Infrared spectra were obtained using a Perkin Elmer Model 21 double beam recording spectrophotometer.

The coal used for most of the tests was a blending coal used in coke ovens.* The physical properties of this coal are shown in Table I. One sample was prepared from the coal as received from the mine. The other sample of coal was heated in a pressure tight container to the fluid range; this required approximately 20 minutes. The temperature in the fluid range was held for periods of time from 10 to 30 minutes. The sample was then quenched and prepared as previously described.

The plate containing the untreated coal was placed in the reference beam of the spectrophotometer and the plate containing the coal which had been heated was placed in the sample beam. A differential absorption spectra was thus obtained. A typical pattern obtained by this method is shown in Figure 1.

Discussion of Data

Most of the spectral assignments have been made in previous studies.^{5,6} Table II lists the spectral assignments used in this study. Since the coal sample which had been heated was placed in the sample beam, peaks downward on the pattern indicated vibrational spectra for bonds greater in number in the heated coal and peaks upward indicated the presence of a greater number of bonds in the untreated coal sample. Increases were noted in the 2.7 to 3 μ range (OH stretching), 3.3 to 3.4 μ (aromatic hydrocarbon), 7.25 μ (hydrocarbon

* Coal samples were obtained from the Columbia-Geneva Steel Division, U. S. Steel Corporation.

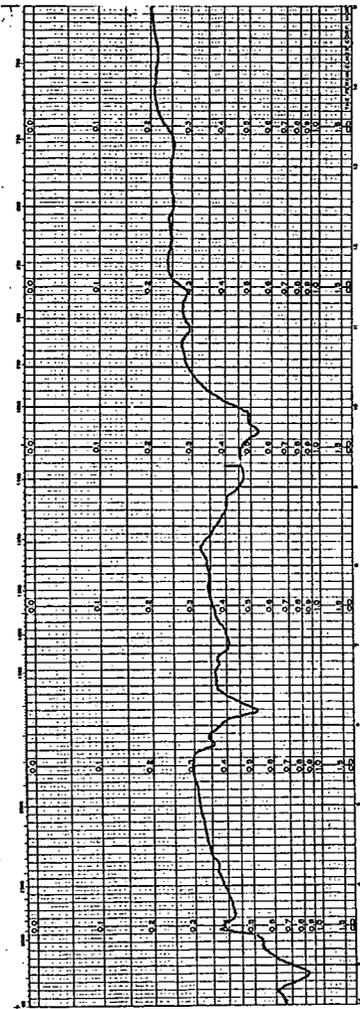
Table I. Physical Properties of Coal Used in Differential Infrared Spectrophotometer Tests

<u>Proximate Analysis</u>		<u>Ultimate Analysis</u>		<u>Gieseler Type Plastometer</u>
H ₂ O	2.94	C	75.20	Initial Soften. Temp. 341°C
V. M.	30.53	H ₂	5.23	Max. Fluidity Temp. 422°C
F. C.	58.17	N ₂	1.63	Max. Dial Div./Min. 2,977
Ash	11.30	Ash	11.30	Solidification Temp. 469°C
Sulfur	0.82	S	0.82	
		O ₂	5.82	

Table II. Spectral Assignments for Coal

Microns

3.00	Hydrogen-bonded OH or NH (see discussion in text)
3.30	Aromatic CH, weak
3.42	Naphthenic and/or aliphatic CH bonds
3.49	
5.87	C==O band, weak shoulder
6.19	Very intense band; may be partly caused by a conjugated carbonyl structure such as in quinones.
6.90	CH ₂ groups
7.25	CH ₃ groups
9.67	Aromatic band, intense in aromatic ethers



WAVELENGTH IN MICRONS

Figure 1. Differential infrared spectrophotometric pattern. Untreated coal in the reference beam; coal heated to the softening range in the sample beam.

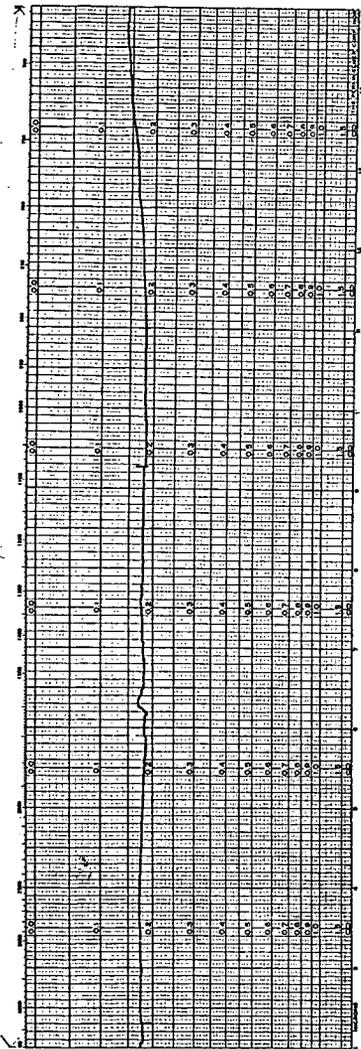
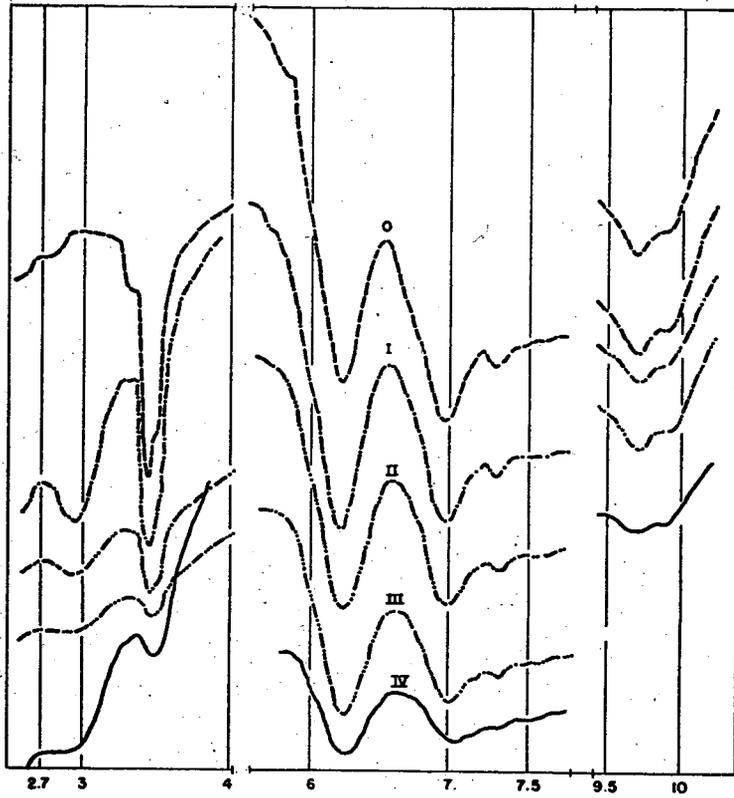


Figure 2. Differential infrared spectrophotometric pattern to prove technique. Untreated coal from the same sample in both the reference and sample beams.

WAVELENGTH IN MICRONS



---0 - Furnace at 500°F, coal sample 1 gram ---II - In furnace 2 minutes
 ---I - In furnace 1 minutes ---III - In furnace 3 minutes
 ---IV - In furnace 5 minutes (max. coal temperature approximately 475°C.

Figure 3. Infrared spectrophotometric pattern of coals heated in a closed crucible.

the softening stage because it provides a means for examining the bonds as they occurred in that stage before subsequent decomposition.

Samples prepared from coke buttons made from this coal were run on the infrared and in the x-ray diffraction camera. In the infrared the sample showed a very high background but a reliable pattern was obtained using 3 mg of sample in a 1 g plate. The pattern showed no indication of bands, indicating the edge groups are completely decomposed. The x-ray pattern showed a graphitic structure.

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LAMINAR BURNING VELOCITIES OF METHANE-
OXYGEN-DILUENT GAS MIXTURES

by

S. A. Weil, E. F. Searight, and R. T. Ellington
Institute of Gas Technology
Chicago, Illinois

ABSTRACT

The burning velocities of methane-oxygen-diluent mixtures were determined at atmospheric pressure by use of bunsen flames under laminar flow conditions. The fuel-lean region was investigated at theoretical flame temperatures of 2000, 2250 and 2500°K employing nitrogen, helium and argon as diluents. By maintaining constant calculated flame temperatures for the different mixtures, evaluation of the effects of the properties of the diluent and of O_2/CH_4 ratio was greatly simplified. The dependence of burning velocity on O_2/CH_4 ratio was not in accord with the approximate theories of combustion. Therefore, an empirical expression was developed to describe the effect of diluent, O_2/CH_4 ratio, and flame temperature on burning velocity. The evaluation of this expression is discussed in terms of effective transport properties and concentrations.

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INTRODUCTION

The laminar burning velocity of a fuel-oxidant mixture is an important parameter in the expressions which have been developed to describe such combustion phenomena as ignition energies and flame stability.⁴ Many relationships for turbulent flames have been developed which require knowledge of the laminar burning velocity of the same reaction system. Therefore, it would be extremely useful if the laminar burning velocity of a given fuel-oxidant system could be predicted with good accuracy from knowledge of the composition of the reactant system and quantities calculable from the composition and conditions of the system.

The prediction of burning velocities by use of the approximate theories of flame propagation developed by Semenov⁸, and Tanford and Pease¹⁰ has been only partially successful^{2,9,11}. These relationships adequately describe experimental data only in those cases in which flame temperature is the major variation in flame conditions. The effects of variations in unburned gas compositions on burning velocity cannot as yet be defined with accuracy², presumably because of the approximations of mechanism and transport properties which are necessary to obtain analytical expressions. The more rigorous theories of combustion in flames do not readily lend themselves to prediction of the functional dependence of burning velocity upon composition. The ability of rigorous theories to predict absolute burning velocities for the few cases that have been treated, is not as valuable as their potential ability to describe the internal structure of the flame from knowledge of the burning velocity.

An analytical expression would best suit the practical purpose of predicting burning velocities, even if it were determined empirically. As its contribution to a better understanding of the combustion process, an empirical expression could be used as a basis for speculation on kinetic expressions that might be used in the integration of the fundamental equations of flame propagation.

To achieve such a goal, an empirical equation must show the functional dependence of burning velocity on unburned gas composition. If the data, upon which the expression is based, are restricted to fuel-air systems in which fuel concentration is the only variable, the dependence of burning velocity on composition cannot be distinguished from its far greater dependence on flame temperature. In divariant systems consisting of fuel, oxygen and diluent, the equivalence ratio (actual fuel/oxygen ratio divided by stoichiometric ratio) can be varied while the theoretical flame temperature is held constant. In this manner the functional

relationship between burning velocity and equivalence ratio can be investigated with temperature effects being held to a minimum. Because of the significant effect of the surrounding atmosphere on the chemistry of the combustion of fuel-rich bunsen flames, and the additional complexities introduced thereby, this initial study was limited to fuel-lean flames.

EQUIPMENT AND PROCEDURES

Burning velocities were determined by the total area method using shadowgraphs of bunsen flames. It is recognized that burning velocities determined in this manner are not absolute values. The literature shows that no experimental method is free of some question in this respect, and that the absolute burning velocities obtained may show a strong dependence upon the experimental method used.⁵ However, in some instances, radically different methods have yielded the same absolute values.⁶ It is of major significance that different methods indicate the same functional dependence upon the composition variables.² The method used in this work does yield reproducible relative values that can be used to establish the functional dependence of burning velocity on unburned mixture composition. It is this dependence that is of greatest value in efforts to determine the mechanism of flame propagation from experimental results. Furthermore, the method used is simple and duplicates conditions encountered in many practical applications.

A gas metering and mixing panel was used to obtain the desired burner feed compositions, and contained four separate metering systems, each of which utilized a carefully calibrated critical-flow jewel orifice. From its cylinder, each gas passed through activated alumina driers and sintered bronze filters to Nullmatic pressure regulators, capable of accurately maintaining the desired pressure upstream of the orifice. Inlet pressure to the orifices was measured precisely by means of ten-foot mercury manometers. The orifice assemblies consisted of special companion flanges supporting removable brass plates; each plate contained a synthetic sapphire drilled to closely conform to the standard configuration for a round-edged orifice. Downstream from the orifices the individual gas streams were joined and valves were provided so that it was possible to direct the mixture to a wet test meter or the burner. Each orifice was calibrated before each run, and with this system measurements of the relative flow of the gas streams were accurate to within $\pm 0.2\%$, the absolute flows to within $\pm 0.5\%$.

The optical system used for photographing the flame was of the "Z" type, incorporating two paraboloidal mirrors.³ A 2-watt zirconium concentrated arc lamp was used as a light source. The two front-surfaced parabolic mirrors were 6 inches in diameter, with a focal length of 48 inches. A flat front-surfaced mirror, used to increase the angle of reflection and enable easier recording of the image, was placed at the same angle with respect to the second mirror as the light source was placed with respect to the first. The image was recorded by means of a camera, with the lens removed, on Contrast Process Panchromatic film.

The burners, for obtaining the bunsen flames used in this study, were cylindrical tubes at least 30 inches long. The upper portion was surrounded with a waterjacket connected to a constant temperature bath and circulating pump. Three burners were necessary for the range of burning velocities encountered. The coolest flames

(2000°K) were studied using a burner of 0.375-inch inside diameter. For the 2250°K and 2500°K temperature levels, burners with inside diameters of 0.250 and 0.188 inches, respectively, were used.

The relative amounts of fuel, oxygen, and diluent gas fed to the burner tube were adjusted to obtain the desired adiabatic reaction temperature. The necessary quantities of these gases were calculated with the usual assumptions of chemical equilibria using the thermodynamic properties as tabulated in the National Bureau of Standards Circular C461.⁷ The results of these calculations are presented in Table 1.

Representative mass spectrometer analyses of the gases used in these studies are given in Table 2.

TABLE 2
ANALYSES OF GASES

<u>Methane</u>		<u>Propane</u>		<u>Oxygen</u>	
CH ₄	99.2%	C ₃ H ₈	99.4%	O ₂	99.5%
C ₂ H ₆	0.4	C ₂ H ₆	0.6	N ₂	0.4
C ₃ H ₈	0.2			CO ₂	0.1
N ₂	0.1				
CO ₂	0.1				
 <u>Nitrogen</u>		 <u>Argon</u>		 <u>Helium</u>	
N ₂	99.9%	A	99.9%	He	100%
A	0.1	N ₂	0.1		
O ₂	0.05				

EXPERIMENTAL RESULTS

The observed values of burning velocity of fuel-lean methane flames are presented in Figs. 1-3. The diluents used to control calculated flame temperatures were nitrogen, argon and helium. The abscissa is the reciprocal of the more generally used equivalence ratio since the fuel-lean region is of greatest interest.

In these plots, the maximum amount of diluent occurs at the stoichiometric point, and the extreme lean limits represent binary mixtures of fuel and oxygen. The general behavior of these curves in the leaner regions is reasonable in that the slopes agree with expectations based on the simplest consideration of transport phenomena. Thus with increasing (O_2/CH_4), the transport coefficients would be expected to decrease in the helium system, increase in the argon system and remain essentially constant in the nitrogen system.

The maximum in the 2000°K curve of Fig. 1 is based on differences slightly greater than the reproducibility of the data. Contention that the burning velocity is approaching a limiting value cannot be rejected on the basis of these data. From the appearance of the curves in Fig. 1 it would appear that at a lower temperature level, with the greater range of (O_2/CH_4) to be encountered, a maximum would be accentuated. Attempts to achieve this at 1800°K failed due to formation of cellular flames.

Table 1.-OBSERVED BURNING VELOCITIES AND CALCULATED REACTANT COMPOSITIONS FOR THE SYSTEMS INVESTIGATED

METHANE-OXYGEN-NITROGEN 2000°K Burner Diam = 0.375 in.					METHANE-OXYGEN-HELIUM and METHANE-OXYGEN-ARGON 2000°K Burner Diam = 0.375 in.					
O ₂ /CH ₄ Stoich. Ratio	Reactant Composition			Burning Velocity ft/sec	O ₂ /CH ₄ Stoich. Ratio	Reactant Composition			Burning Velocity (ft/sec)	
	CH ₄	O ₂	N ₂			CH ₄	O ₂	Inert	CH ₄ -O ₂ -He	CH ₄ -O ₂ -A
1.00	7.82	15.63	76.55	0.65*	1.50	5.51	16.52	77.79	1.14*	0.96*
1.50	7.81	23.43	68.76	0.74*	2.00	5.74	22.96	71.30	1.07*	0.98*
2.00	7.87	31.48	60.65	1.03*						1.29*
2.50	7.91	39.59	52.49	1.00*	2.50	5.97	29.84	64.19	2.53	1.29*
				1.10						1.09*
				1.21	3.00	6.22	37.34	56.44	2.37	1.24*
				1.22						1.27*
				1.17	3.50	6.50	45.48	48.02	2.23	1.15
				1.20	4.00	6.30	54.38	38.83	1.91	1.12
				1.21						1.18
3.00	7.96	47.75	44.29	1.21						1.25
3.50	7.99	55.97	36.04	1.30						1.17
				1.36						1.19
4.00	8.09	64.70	27.21	1.37	4.50	7.12	64.03	28.85	1.84	1.22
				1.41						1.26
				1.36						1.20
4.50	8.04	72.32	19.64	1.37						1.22
				1.35						1.23
				1.39						1.23
5.25	8.05	84.50	7.45	1.30	5.00	7.49	74.86	17.65	1.55	1.32
				1.30						1.23
5.70	8.05	91.95	0	1.21	5.70	8.06	91.94	0	1.22	1.26
				1.24						
				1.21						
				1.28						
2250°K Burner Diam = 0.25 in.					2250°K Burner Diam = 0.25 in.					
1.00	9.72	19.45	70.83	1.43	1.00	6.92	13.84	79.24	2.50†	1.29
				1.49	1.50	6.85	20.57	72.58	3.74	1.38
				2.03					3.57	1.47
1.50	9.54	28.63	61.82	2.00	2.00	7.21	28.85	63.94	3.70	1.51
				2.38					3.75†	1.92
2.00	9.61	38.46	51.93	2.64	2.50	7.61	38.04	54.36	3.91	1.91
2.50	9.70	48.49	41.82	2.83					3.66	2.11
3.00	9.76	58.57	31.67	2.75	3.00	8.02	48.14	43.83	3.57	2.23
				2.95					3.78	2.28
3.50	9.81	68.67	21.52	2.94	3.50	8.51	59.58	31.91	3.62	2.40
4.00	9.85	78.77	11.38	2.81					3.34	2.42
4.60	9.81	90.19	0		4.00	9.04	72.34	18.62	3.18	2.44
					4.60	9.81	90.19	0	2.90	2.38
										2.54
										2.52
										2.94
2500°K Burner Diam = 0.188 in.					2500°K Burner Diam = 0.188 in.					
1.00	12.61	25.22	62.16	2.50	1.00	9.17	18.33	72.50	5.02	2.42
1.50	12.04	36.14	51.82	3.31	1.50	9.07	27.21	63.72	6.09	3.09
				3.34					5.76	3.13
2.00	12.13	48.52	39.35	4.08	2.00	9.61	38.45	51.94	5.57	3.50
2.50	12.24	61.18	26.58	4.13	2.50	10.31	51.55	38.14	5.36	3.94
				4.31	3.00	11.12	66.74	22.14	5.17	3.94
3.00	12.31	73.88	13.80	4.60					5.03	3.62
				4.52						3.75
3.58	12.25	87.75	0	4.56						
				4.37						

* These values were obtained from flames showing a large degree of instability and are of doubtful validity.

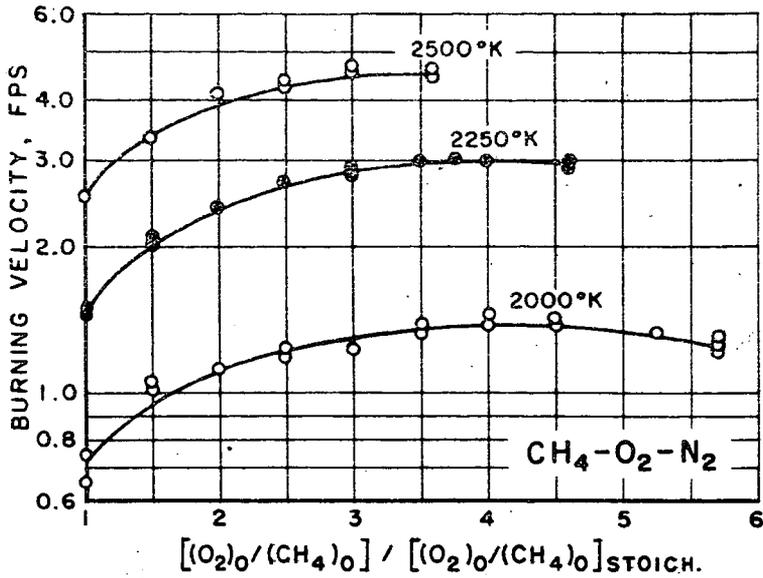


Fig. 1.-BURNING VELOCITIES OF THE METHANE-OXYGEN-NITROGEN SYSTEM AT ATMOSPHERIC PRESSURE AND THEORETICAL FLAME TEMPERATURES OF 2000°, 2250° AND 2500°K

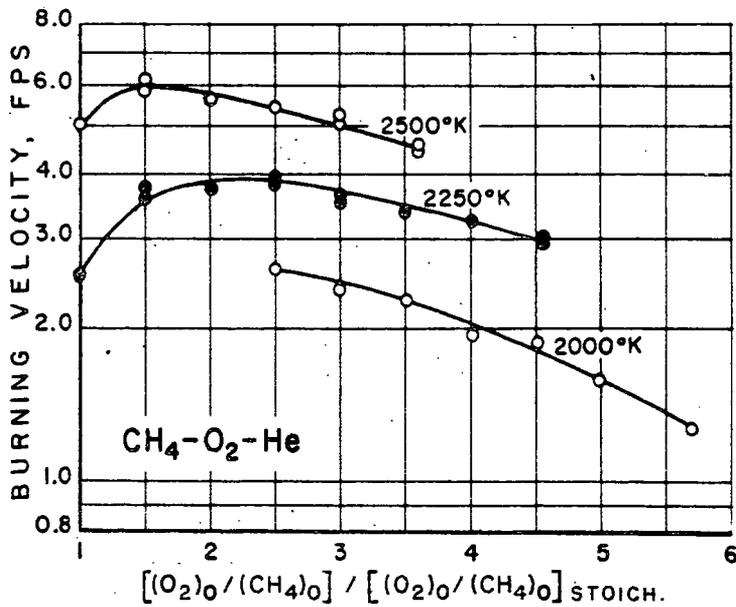


Fig. 2.-BURNING VELOCITIES OF THE METHANE-OXYGEN-HELIUM SYSTEM AT ATMOSPHERIC PRESSURE AND THEORETICAL FLAME TEMPERATURES OF 2000°, 2250° AND 2500°K

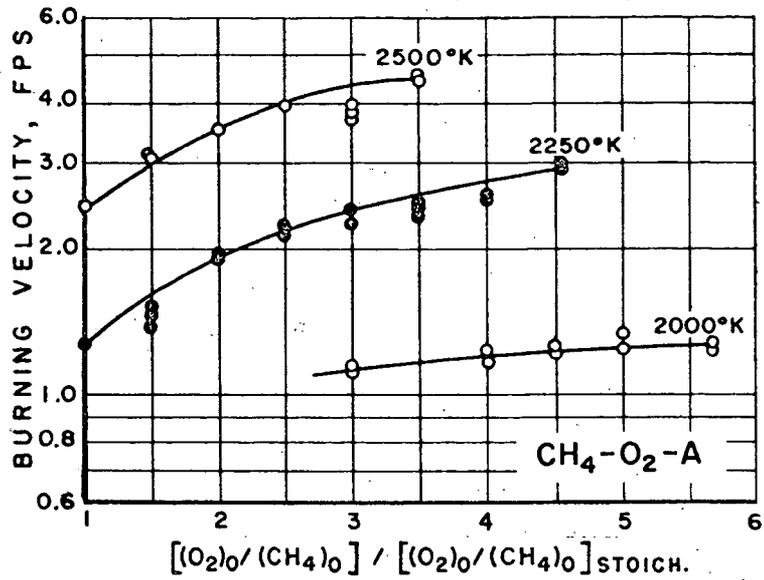


Fig. 3.-BURNING VELOCITIES OF THE METHANE-OXYGEN-ARGON SYSTEM AT ATMOSPHERIC PRESSURE AND THEORETICAL FLAME TEMPERATURES OF 2000°, 2250° AND 2500°K

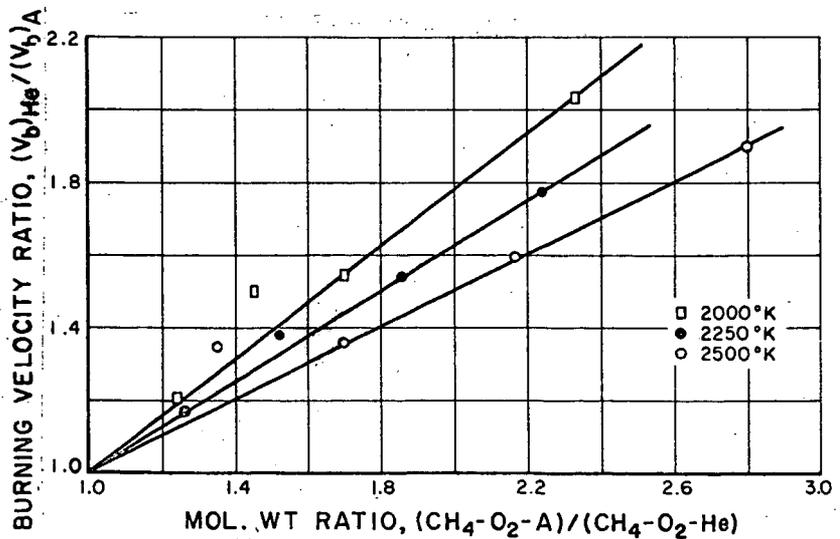


Fig. 4.-COMPARISON OF BURNING VELOCITIES OF METHANE-OXYGEN-HELIUM AND METHANE-OXYGEN-ARGON SYSTEMS AT THE SAME THEORETICAL FLAME TEMPERATURE AND OXYGEN/FUEL MOLE RATIO

DISCUSSION

To develop a method for the prediction of burning velocities based on the properties of the primary gases, it is necessary to determine "effective" values of the flame properties in terms of the primary gas properties. An obvious initial attempt was to correlate the effect of the diluent in terms of its effect on the transport properties. If it is assumed that the chemical processes are independent of the diluent, comparison of the helium and argon systems offers the most direct level to the contribution of transport phenomena. For this type of investigation, the simplest method of computing the transport properties of the mixtures can be used. Therefore, the reciprocal of the mean molecular weight was used as a measure of transport properties. In Fig. 4, where results are compared at the same temperature and O_2 /fuel ratio, distinct curves for the different temperature levels appear. Superficially none of the properties of the primary gases except those affecting the transport properties differ between the two systems being compared and one would expect no temperature dependence if this simple treatment were correct. The separation of these curves may be traced to the oversimplification in the use of density alone, or it may be attributed to differences in the microscopic description of the flame front. Since something in the nature of a mean or integrated transport property is desired, such differences in the internal flame structure may be sufficient to prevent the use of the simplest expressions for the transport property. However, unless the variation of the transport properties through the flame is considered, using the greatest rigor possible, there is little justification for a more complex expression. Thus, an empirical expression for prediction of burning velocity appears adequate.

A simple empirical correlation showing the effect of diluent is shown in Figs. 5 and 6 where the systems of different diluents are compared at the same theoretical flame temperature and oxygen-fuel ratio. The equations represented by the lines in these figures are:

$$\frac{V_{b,He}}{V_{b,A}} = \exp (0.0859 M_{He}) \quad (1)$$

$$\frac{[\frac{V_b}{(CH_4)_0}]_{He}}{[\frac{V_b}{(CH_4)_0}]_{N_2}} = \exp (0.0930 M_{He}) \quad (2)$$

At the present time, no theoretical explanation is offered to account for the interdependence of $\log V_b$ and diluent/fuel ratio at constant O_2 /fuel ratio and temperature. However, since the diluent content accounts for the major variation in transport properties, some form of dependence on the diluent content is to be expected. The particular form of that dependence, shown in Figs. 5 and 6, must be considered as the expression of a mean or effective evaluation of the effect of transport properties. Some contribution to the particular form obtained probably comes from certain mathematical relationships among the reactant compositions, resulting from the temperature calculations. Thus for any given temperature level at a given oxygen-to-fuel ratio, the following approximate relations hold in the fuel-lean region:

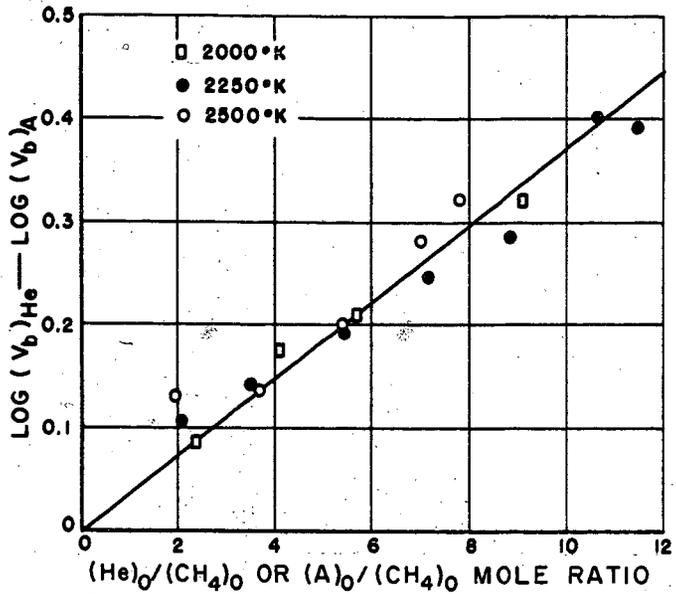


Fig. 5.-CORRELATION OF BURNING VELOCITIES OF THE METHANE-OXYGEN-HELIUM AND METHANE-OXYGEN-ARGON SYSTEMS AT ATMOSPHERIC PRESSURE AND THEORETICAL FLAME TEMPERATURES OF 2000°, 2250° AND 2500°K

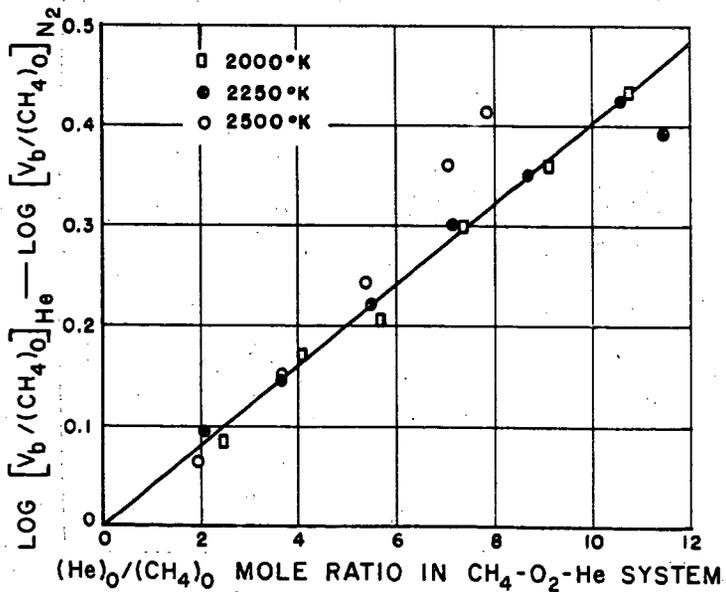


Fig. 6.-CORRELATION OF BURNING VELOCITIES OF THE METHANE-OXYGEN-NITROGEN AND METHANE-OXYGEN-HELIUM SYSTEMS AT ATMOSPHERIC PRESSURE AND THEORETICAL FLAME TEMPERATURES OF 2000°, 2250° AND 2500°K

$$M_{\text{He}} = M_A \quad (3)$$

$$M_{\text{He}} = 1.69 M_{\text{N}_2} \quad (4)$$

$$M_{\text{He}} = 1.71 (M_{\text{O}_2} - M_{\text{O}_2}^0) \quad (5)$$

Since $M_{\text{O}_2}^0$ is a function of temperature only, any empirical expression involving M_T cannot be distinguished from one involving a linear combination of M_T and M_{O_2} . The proportionality between the logarithm of the burning velocity and the diluent/fuel ratio, therefore, can also be expressed as one between $\log V_b$ and a linear combination of M_T and M_{O_2} . In this manner, the proposed effective transport term can be converted to one involving all components of the reactant mixture, which might be preferable. However, no particular linear combination was indicated and, therefore, the simplest expression was used.

To predict the dependence of burning velocity on reactant composition, an expression must also be found to describe the effect of oxygen/fuel ratio shown in Fig. 1. In the nitrogen system, there is little change in transport properties, and the system should be dependent only on the chemical effects of changing reactant composition. Examination of the curves of Fig. 1 indicates that they may be superimposed through the use of a proportionality constant. That is, the functional dependence of burning velocity on the oxygen/fuel ratio appears independent of temperature over the range investigated, which includes those usually encountered in fuel-air flames. Thus, an expression for the burning velocities of the systems investigated can be obtained which consists of only three factors. One is temperature dependent; one expresses the dependence on the oxygen/fuel ratio; and the last expresses the effect of transport properties in terms of the inert diluent. However, because only two of the three factors are independent, the mathematical expression relating the three factors must be arbitrary.

The following expression with four empirical parameters was used to describe the burning velocity of the $\text{CH}_4\text{-O}_2\text{-N}_2$ system:

$$\begin{aligned} [V_{b, \text{N}_2}]^2 &= [-1.75 + 1.99 M_{\text{O}_2} - 0.119 (M_{\text{O}_2})^2] \times 10^5 \\ &\times \left[\exp(-50.6 \times 10^3 / RT_f) \right] \end{aligned} \quad (6)$$

This equation can be used to describe systems of the other diluents, by means of Equations 1 and 2. To avoid the appearance of the CH_4 concentration in the N_2 system when applying the general equation to another diluent, it is necessary to introduce the approximate relationship:

$$(\text{CH}_4)_0 = 3.26 \times 10^{-7} (T_f - T_0)^{5/3} \quad (7)$$

for the systems containing nitrogen as diluent. This relationship was obtained by fitting a curve to the reactant methane concentration-flame temperature points in the theoretical flame temperature calculations. Combining Equations 1, 2, 6, and 7 yields an expression capable of describing the data of Figs. 1, 2, and 3.

$$\begin{aligned}
 [V_{b,I}]^2 &= 0.982 \left[(O_2)_O - 0.934(CH_4)_O \right] \left[(CH_4)_O - 0.0634(O_2)_O \right] \\
 &\times 10^{10} \times \left[\frac{T_O}{T_f - T_O} \right]^{10/3} \left[\exp(-50.6 \times 10^3 / RT_f) \right] \left[\exp(\alpha_I M_I) \right]
 \end{aligned}
 \tag{8}$$

with the values

$$\begin{aligned}
 \alpha_{He} &= 0.186 \\
 \alpha_A &= 0.0142 \\
 \alpha_{N_2} &= 0.0
 \end{aligned}$$

Similarities between the empirical Equation 8 and one proposed by Semenov⁸ in his approximate thermal theory offer the possibility of viewing the empirical equation in terms of "effective" quantities in a manner analogous to that used by Semenov. From this view, 50.6 Kcal is the effective activation energy of the overall reaction. This can be compared to the value of 51 Kcals used in other investigations.² The terms $(O_2)_O - 0.934(CH_4)_O$ and $(CH_4)_O - 0.0634(O_2)_O$ can be viewed as the effective oxygen and fuel concentrations, respectively, in the reaction zone which permit description of the reaction as being a single step reaction between those components. As presented above, the term $\exp(\alpha_I M_I)$ represents an effective transport term.

Another interesting aspect of Equation 8 is that, on extrapolation to lower temperatures, it predicts the existence of flammability limits, i.e. $V_b = 0$, when $(O_2)_O = 0.934(CH_4)_O$ (the upper limit) and when $(CH_4)_O = 0.0634(O_2)_O$ (the lower limit). These agree in order of magnitude with the observed values.¹

A more tenuous interpretation of the effective oxygen and fuel concentration terms is that they correspond to quantities controlling or determining the slow step of the reaction path. For example, the term $(O_2)_O - 0.934(CH_4)_O$ corresponds to the remaining oxygen after the oxidation of the fuel to formaldehyde and water or their chemical equivalent. An equally simple evaluation of the effective fuel term was not obtained.

CONCLUSIONS

In the use of burning velocity studies to add to the knowledge of the combustion process, it is necessary to know the manner in which burning velocity depends upon fuel gas composition as a function of stoichiometry, transport properties and flame temperature. When a single oxidant, such as air, is employed to study the variation of burning velocity with fuel-to-air ratio, flame temperature is a variable and overshadows all other factors. To minimize the effect of temperature, the concentration of the components of CH_4-O_2 -diluent systems were adjusted in this investigation to give flames of varying equivalence ratio but constant adiabatic reaction of 2000, 2250 and 2500°K. To the extent that the actual flame temperature can be identified with these theoretical flame temperatures, the process is then being studied under the same thermal conditions.

In the $\text{CH}_4\text{-O}_2\text{-N}_2$ system at the 2000°K temperature level; the burning velocity apparently passes through a maximum with increasing feed gas oxygen/methane ratio. Since the occurrence of this maximum is not predicted by the approximate theories of combustion which assume the rate-determining step to be the reaction between O_2 and CH_4 ,⁸ or that between the free radicals, H, OH, and O, and the fuel,¹⁰ an empirical correlation was developed relating the burning velocity to the composition of the feed gas and the flame temperature. This relationship describes all three isotherms and the effect of the diluents N_2 , He and A. It contains five experimental parameters, four of which are independent of the inert gas, and indicates, 1) the existence of mixtures for which $V_b = 0$, that is, flammability limits, which are of the correct order of magnitude, and 2) an energy of activation of $50.6 \text{ Kcal/moles-}^\circ\text{K}$ for the methane flames, which is in good agreement with that found by others.² The only term showing dependence on the inert gas is assumed to represent the effect of variation in transport properties.

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NOMENCLATURE

$(N)_O$	= mole fraction of component in burner gas mixture.
M_N	= $(N)_O / (\text{CH}_4)_O$
$M_{\text{O}_2}^O$	= $(\text{O}_2)_O / (\text{CH}_4)_O$ for the lean, diluent-free mixture.
$V_{b,I}$	= Experimental burning velocity (ft/sec) of ternary system $\text{CH}_4\text{-O}_2\text{-I}$.
R	= $1.986 \text{ cal/mole-}^\circ\text{K}$
T_O	= Initial temperature (300°K)
T_f	= Calculated adiabatic reaction temperature
α_I	= Empirically evaluated constant for the ternary system $\text{CH}_4\text{-O}_2\text{-I}$

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