

## Separation and Identification of Fischer-Tropsch Products

The Fischer-Tropsch process with reduced or carburized iron yields chiefly hydrocarbons containing small to moderate amounts of oxygenated organic molecules, but nitrated iron gives alcohols as a major portion of the product. Separation and identification, especially of the higher alcohols, are difficult in the presence of hydrocarbons. The mixtures cannot be analyzed quantitatively by infrared or mass spectrometer. A chemical method (phthalation) has been used but is time consuming and not quantitative.

A new procedure for rapid and accurate analysis of alcohols up to  $C_{13}$  consists essentially of reacting the alcohol-hydrocarbon mixture with hexamethyldisilazine to form the trimethylsilyl ethers of the alcohols. These ethers are generally more volatile than the original alcohols. The ether-hydrocarbon mixture can be analyzed by mass spectrometer as the ethers cleave at a silicon-carbon bond to yield characteristic fragments (ions) that differ from those derived from the parent alcohols as well as from any hydrocarbons present. The method also appears promising for the analysis of phenols in products from coal hydrogenation and low-temperature carbonization. In particular, the analysis of very reactive di- and trihydroxybenzenes may be facilitated by synthesis of the stable, more volatile trimethylsilyl derivatives.

## Structural Group Analysis Applied to Coal-Hydrogenation Oils

The complex nature of the higher boiling fractions of coal-hydrogenation oils makes quantitative characterization of the individual compounds impractical. Isolation of individual compounds is helpful, of course, but only a small fraction (about 5 percent) of the estimated number of individual compounds has been isolated so far. The applicability of structural analysis to coal-hydrogenation oils was investigated in a light oil used as a vehicle in high-temperature coal hydrogenation. Preliminary work indicated that the "n-d-M" method is suitable for the analysis of complex mixtures of hydrocarbons. The method is so called because it is based on the determination of refractive index (n), density (d), and molecular weight (M). Instead of indicating the nature and amount of molecules present in an oil, the method characterizes organic structures in terms of "carbon distribution" and ring content. Carbon distribution refers to the relative amounts of carbon atoms in aromatic, naphthenic, and paraffinic structures.

As part of this work, a modified Menzies-Wright apparatus was developed for the ebullioscopic determination of molecular weights. Rapid determination of molecular weights of oils to within 1 percent is now possible (see fig. 10).

## Mass Spectra of Alcohols and Ketones

Mass spectra of 65 alcohols, ranging from methanol to undecanol, and of 35 ketones, ranging from 2-propanone to tridecanone, have been obtained. Fragmentation peaks were correlated with molecular structures. Numerous rearrangement peaks were found. In many cases, these peaks were more intense than the lower molecular-weight parent peaks. General rules were derived for relating usual fragmentation peaks and rearrangement peaks to molecular structures.

## Mass Spectra of Oxides of Nitrogen

In a cooperative study with Consolidated Engineering Corp., mass spectrometric analyses have been developed for gaseous mixtures containing oxides of nitrogen. Determination of all components except nitrogen dioxide is routine. Analysis for this compound requires conditioning of the mass spectrometer. Reaction among the components of the blends was avoided by mixing at micron pressures. This procedure

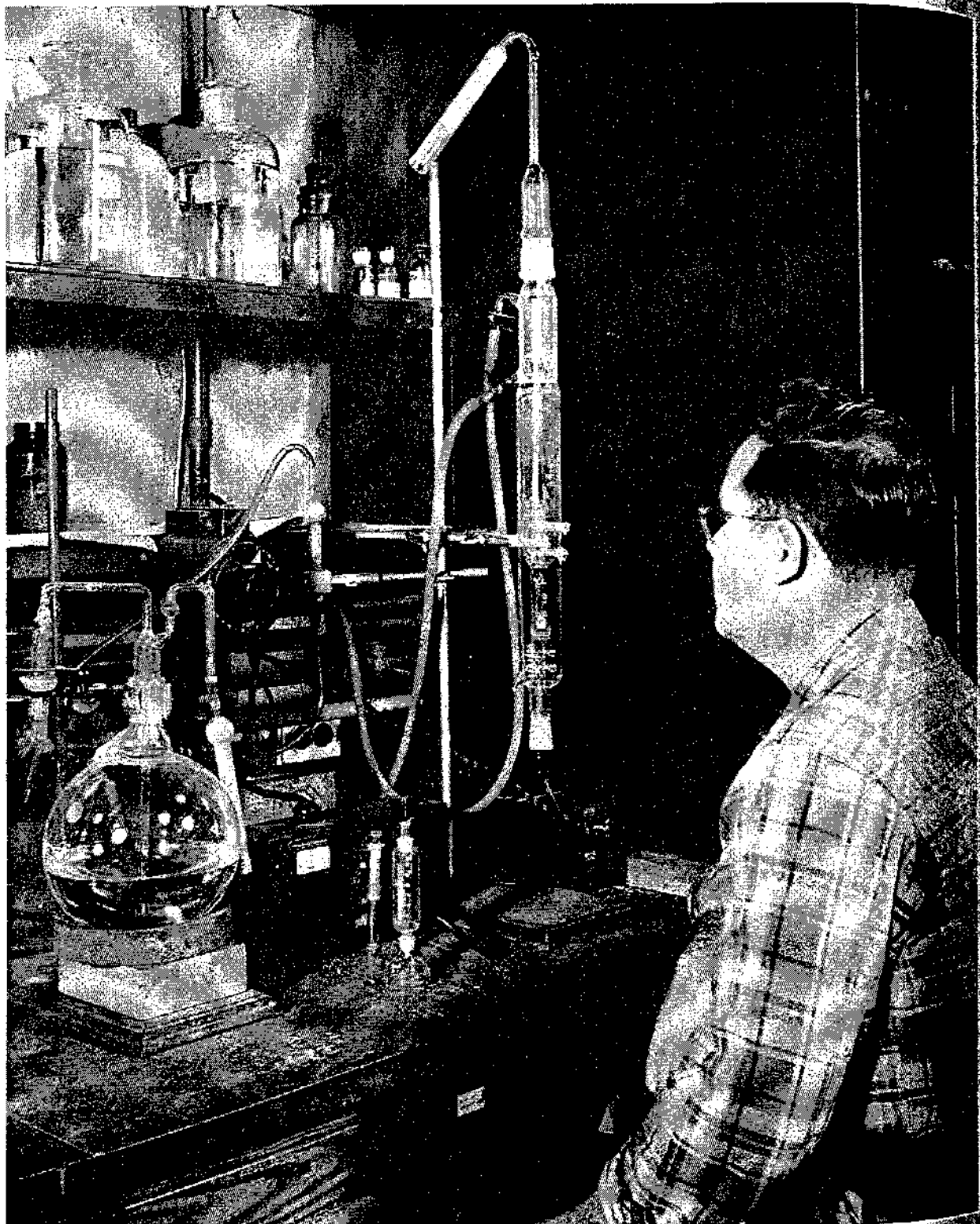


Figure 10. - Improved Menzies-Wright apparatus for accurate determination of molecular weight.

suggests an approach to sampling of mixtures in high-temperature systems, such as jet engines and rockets. If samples containing nitrogen dioxide, water, nitric oxide, oxygen, etc., are collected at or near atmospheric pressure, the cooling process will result in condensation of water, solution of nitrogen dioxide in condensed water, reaction between nitric oxide and oxygen, formation of nitrogen trioxide, and other difficulties depending on the particular mixture. If, however, such samples are collected at micron pressures, all of these difficulties are avoided, and the sample can be truly representative. The accuracy of analysis of nitrogen dioxide depends upon its concentration and on the other components in the mixtures.

## SYNTHESIS GAS FROM COAL PILOT PLANTS, MORGANTOWN, W. VA.

Experimental Development of Processes for Producing  
Synthesis Gas From Coal

Synthesis gas, consisting essentially of carbon monoxide and hydrogen, is a large item in the end cost of gasoline, alcohol, pipeline gas, and other such products when manufactured synthetically. The work of the Morgantown Experiment Station has been to develop practical processes that will lower the cost of manufacturing this gas. The approach has been to react oxygen and steam with pulverized coal.

A process of this kind, carried out at approximately atmospheric pressure, has advanced to the point where the design of practical large-scale plants is possible, and development work was stopped at the end of the 1954 fiscal year.

Investigations are continuing on a similar but apparently more economical process, operating at pressures up to 450 p.s.i.g. This process reduces costs by using much smaller equipment and eliminating the need for compressing the gas before synthesis to oil. During the past year the effects of residence time and heat loss on the coal and oxygen requirements of a gasifier were determined more exactly. The equipment was moved to the new Morgantown Experiment Station and is being rebuilt and improved so that these studies may be continued with those to determine better methods of feeding pulverized coal to gasification equipment operating under high pressures.

Several new fields of experimental work and process development are now under study: Use of metallic oxides to supply oxygen for gasification, use of refractory solids to supply heat required for the steam-carbon reaction, and methods for obtaining oxygen from the air other than the standard air liquefaction process.

## Atmospheric-Pressure Gasifier

The pilot plant described in the 1953 annual report was operated until June 30, 1954. Forty individual test runs, involving over 220 periods of varying conditions, were made during the 6 months. These experiments were designed to determine the effect of the following operating variables on the coal and oxygen required per unit of gas produced and on the percentage of carbon utilization: Oxygen-carbon ratio, steam-carbon ratio, throughput rate in pounds carbon per hour per cubic foot of reaction space, and coal rank. The solid fuels used were a bituminous coal from the Sewickley bed, Monongalia County, W. Va.; a subbituminous C coal from Lake de Smet, Wyo.; and an anthracite from a Pennsylvania colliery. Typical analyses of these coals are given in table 2.

TABLE 2. - Typical analyses of coals used in gasification tests

Kind of coal	Ultimate analysis, percent							Calorific value, B.t.u. per lb.	
	Moist.	Ash	H <sub>2</sub>	C	S	N <sub>2</sub>	O <sub>2</sub>	Gross	Net
Lake deSmet sub-bituminous C . . . .	8.1	11.8	4.1	57.9	0.9	1.2	16.0	9,790	9,330
Anthracite . . . . .	1.0	10.1	2.8	82.2	.6	1.1	2.2	13,550	13,280
Sewickley-bed bituminous . . . . .	1.5	12.8	4.5	72.1	1.0	1.5	6.6	12,900	12,470

With the rebuilt gasifier, using a silicon carbide refractory to line the primary reaction zone and more complete water cooling of that zone, the heat losses

were higher than in previous designs and were not fairly representative of what will be obtained in large-scale plants. However, it was possible to maintain a reasonably constant reaction volume, as refractory erosion was negligible.

The results obtained in the tests are summarized in figures 11, 12, and 13. The runs were carried out as a factorial experiment, using the same oxygen-carbon and steam-carbon ratios and the same carbon-input rate for the three coals. After determining significant effects at the 5-percent probability level, the values were calculated that would have been found had the nonsignificant effects been zero. Smooth curves were drawn through the resulting points. The generally higher level of heat loss from the gasifier used in these tests is reflected in the results.

Figures 11 and 12 show for Sewickley-bed coal the effects of coal-input rate and steam-carbon ratio on the percentage of carbon gasified and oxygen required, both as functions of the oxygen-carbon ratio. The variation of percentage carbon gasified and of oxygen required with coal-input rate is a linear function and may be attributed mainly to heat loss. As the throughput increases, the heat loss per unit decreases because the hourly heat-loss rate is essentially constant. If the effect of heat loss were eliminated, the variation with coal rate probably would be in the opposite direction, as is shown later for the pressure-gasifier results. The variation of the oxygen requirement with steam-carbon ratio is not linear. In fact, the slope of variation of the oxygen requirement with oxygen-carbon ratio is negative at the highest steam-carbon ratio and positive at the lower steam-carbon ratios.

Figure 13 compares the percentage of carbon gasified and the oxygen requirement for the three coals used - Lake deSmet, Sewickley-bed, and anthracite. A highly significant difference was found between the three types, for the amount of carbon gasified in Lake deSmet coal was definitely higher and in anthracite definitely lower than that of Sewickley-bed coal at the same oxygen-carbon ratio. The slope of the variation of oxygen-carbon ratio is much steeper for Lake deSmet than for Sewickley-bed, showing that the optimum operating conditions will vary with the type of coal.

Accurate control of the coal-feed rate is, of course, important. Using a pneumatic feeder that injects the coal in a dense fluidized state, the flow rate was measured and controlled by determining the pressure drop across a previously calibrated coil placed in the feed line (see figs. 14 and 15). At best the accuracy of this method was plus or minus 3 percent and, unless close control of the gasifier pressure is possible, even that accuracy is not obtained in practice (the effect of pressure variations in the gasifier is even more pronounced when operating in the range 100 to 450 p.s.i.g.). A new type of weighing instrument, a Monsell pneumatic weight transmitter, was placed in the "low-pressure continuous feeder" system after test G4-57. This instrument functioned well within limits of the installation. Owing to the small capacity of the continuous feeder, the time interval between transfers of coal to it from the batch feeder was short, about 15 to 20 minutes. Consequently, the feed rate could not be checked over a long period. However, use of this instrument helped to improve control of the feed rate, and arrangements are being made to use it on coal-feeding systems for the high-pressure-gasification investigation.

These test runs again demonstrated the versatility of this gasifier design. Fuels varying widely in both ash content and ash-melting-point temperature were gasified successfully. Tests were made in which none of the ash was slagged. In others 40 percent of the ash in the coal was removed as molten slag.

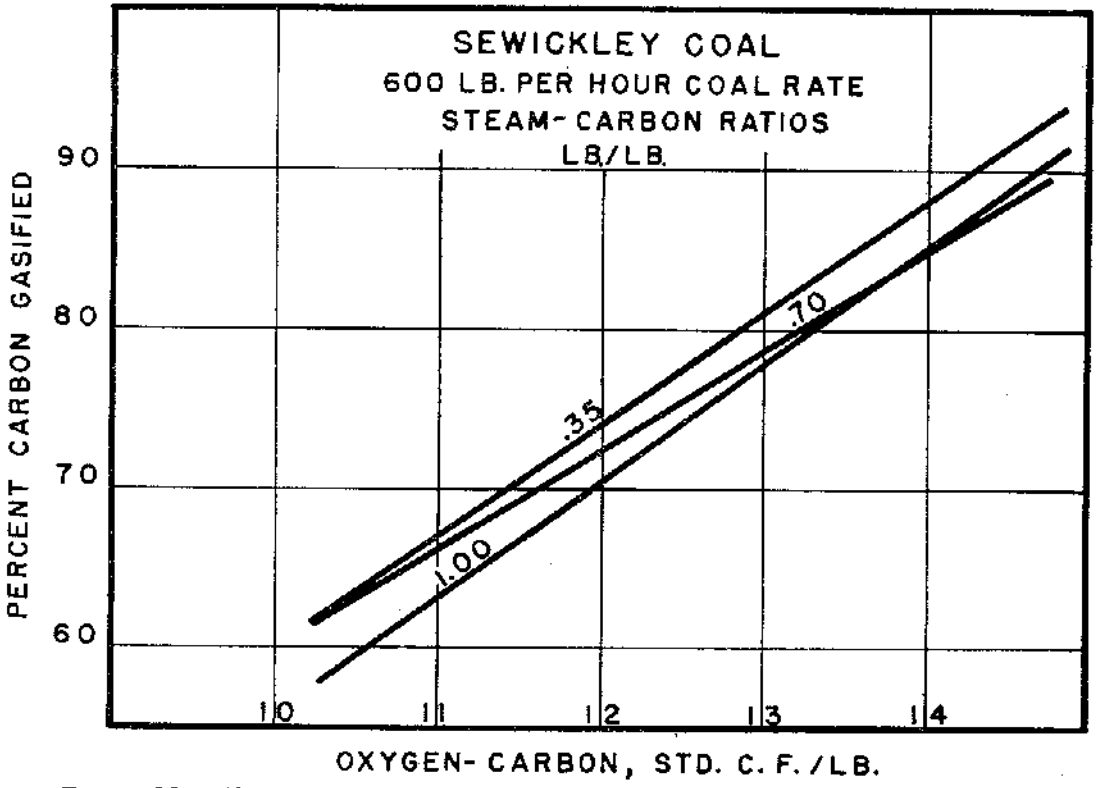
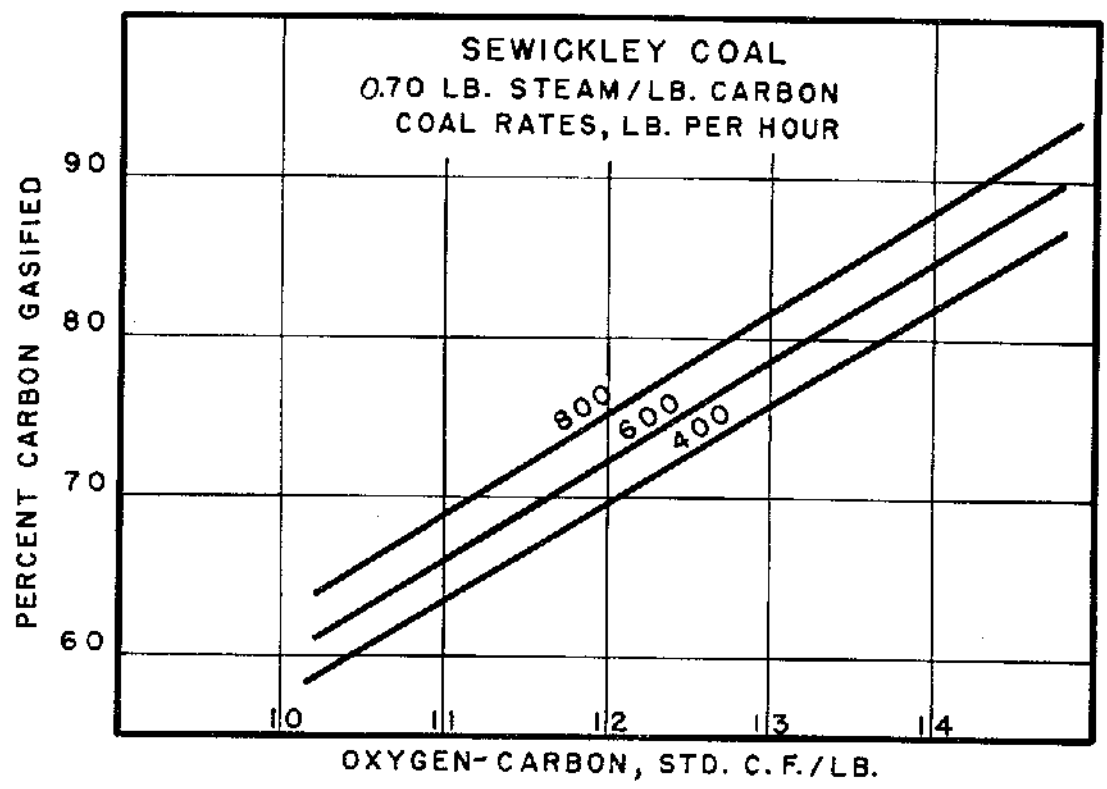


Figure 11. - Effects of oxygen-carbon ratio, steam-carbon ratio, and coal rate on percentage of carbon gasified for Sewickley-bed coal, atmospheric gasifier.

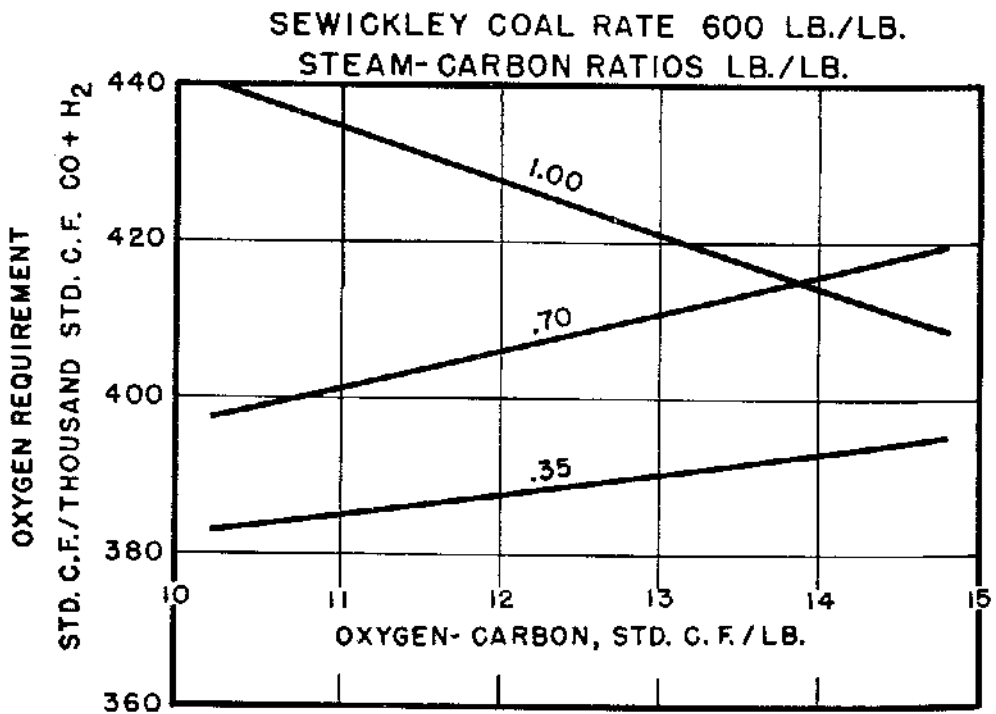
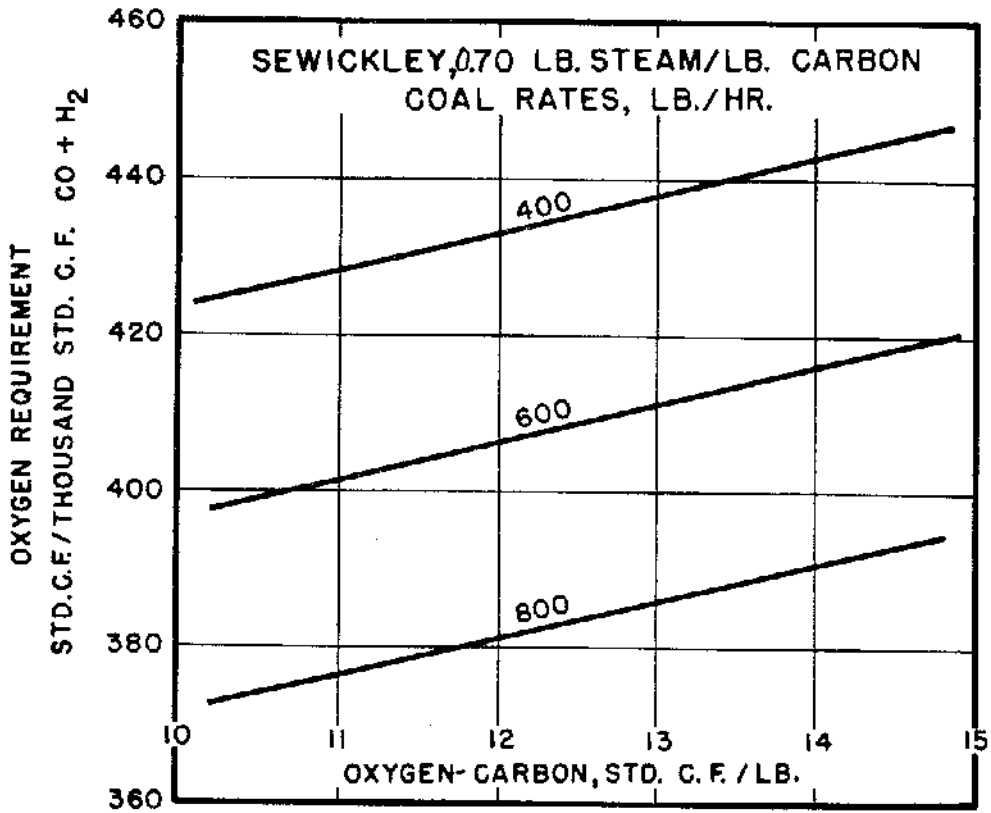


Figure 12. - Effects of oxygen-carbon ratio, steam-carbon ratio, and coal rate on oxygen requirement for Sewickley-bed coal, atmospheric gasifier.

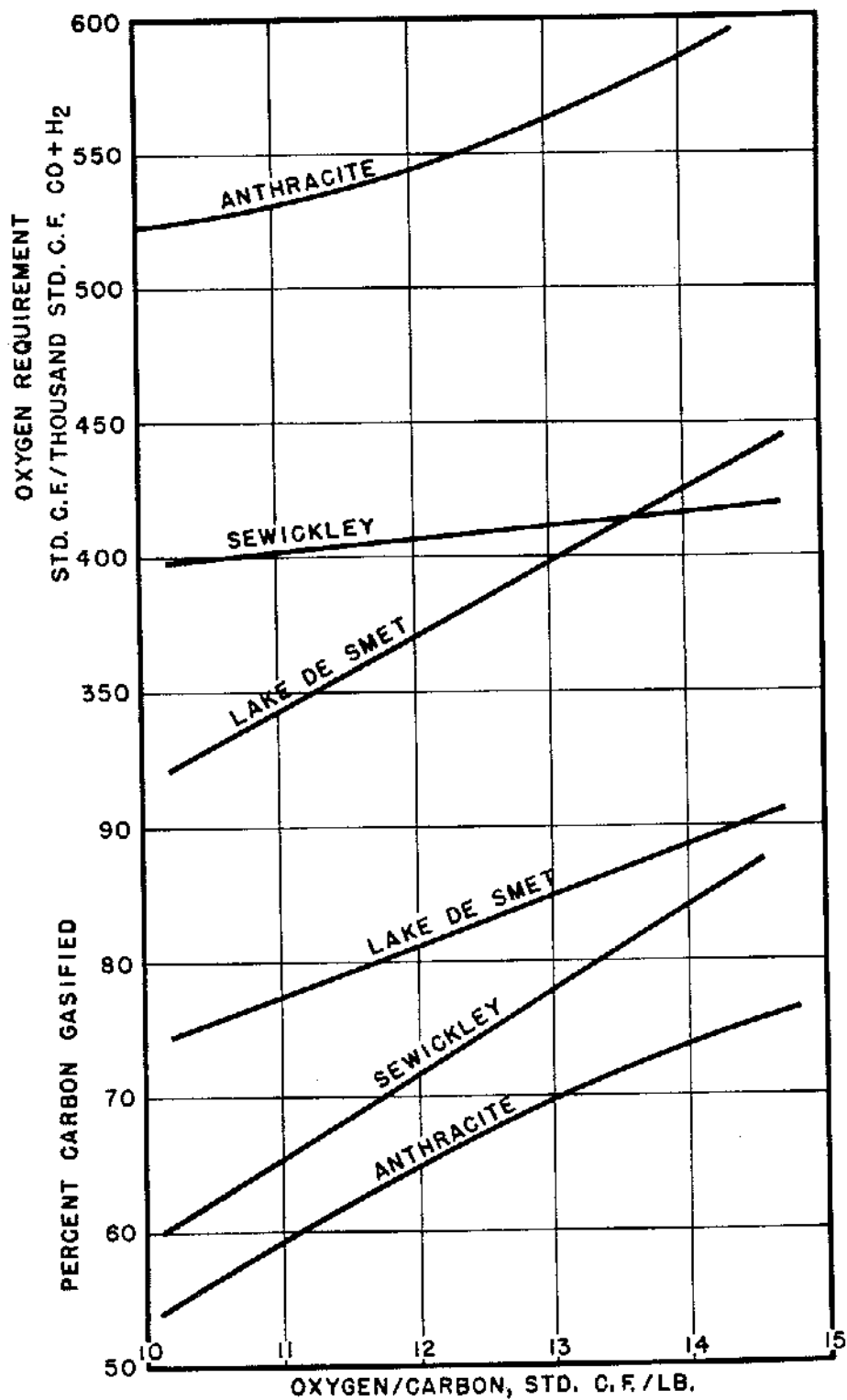


Figure 13. - Comparison of oxygen requirement and percentage of carbon gasified for Lake deSmet and Sewickley-bed coals and anthracite at constant steam-carbon ratio of 0.70 lb./lb. and at constant carbon-input rate of 430 lb./hr., atmospheric gasifier.



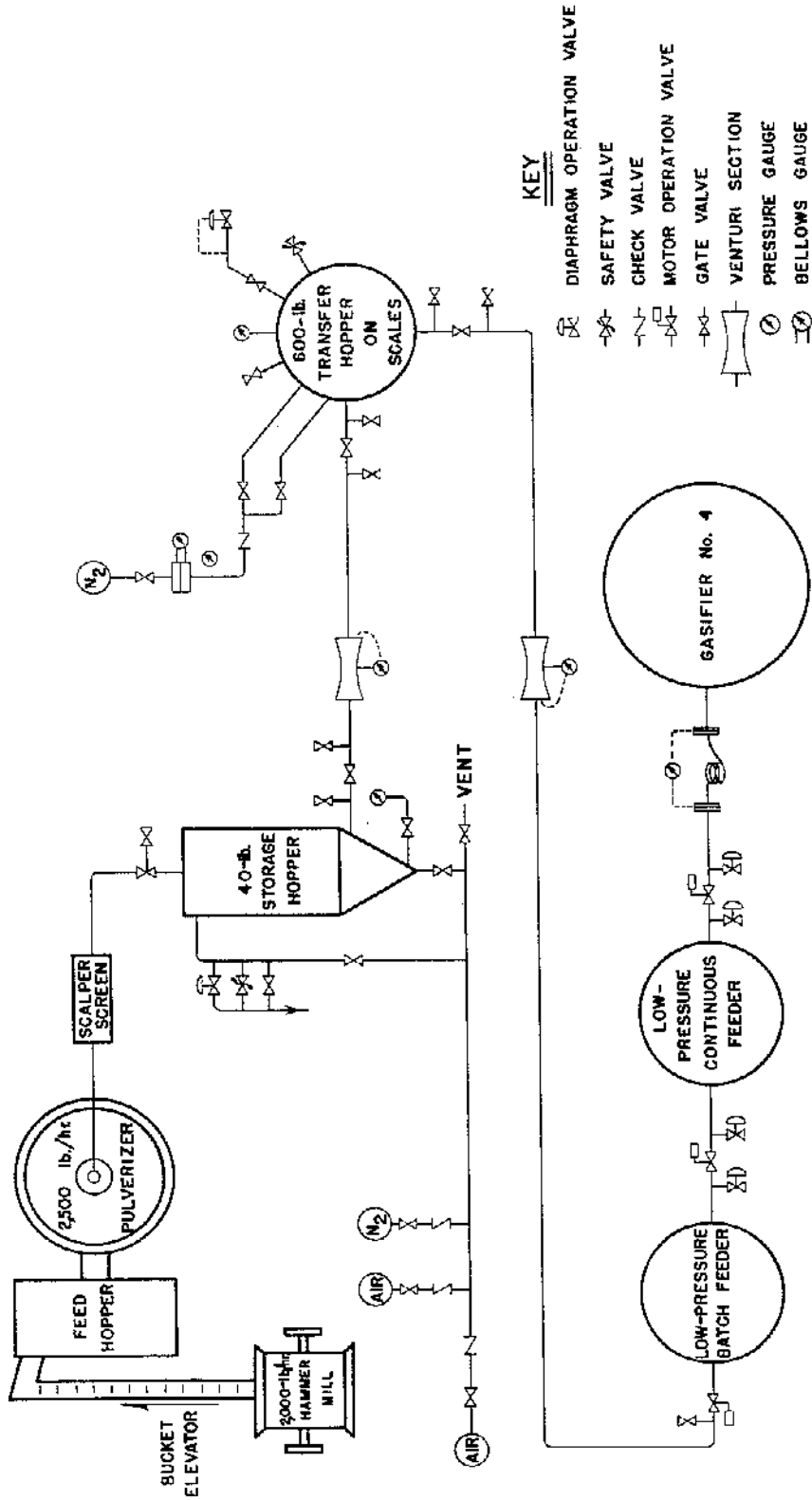


Figure 14. - Coal-handling flowsheet for atmospheric pressure gasifier No. 4.

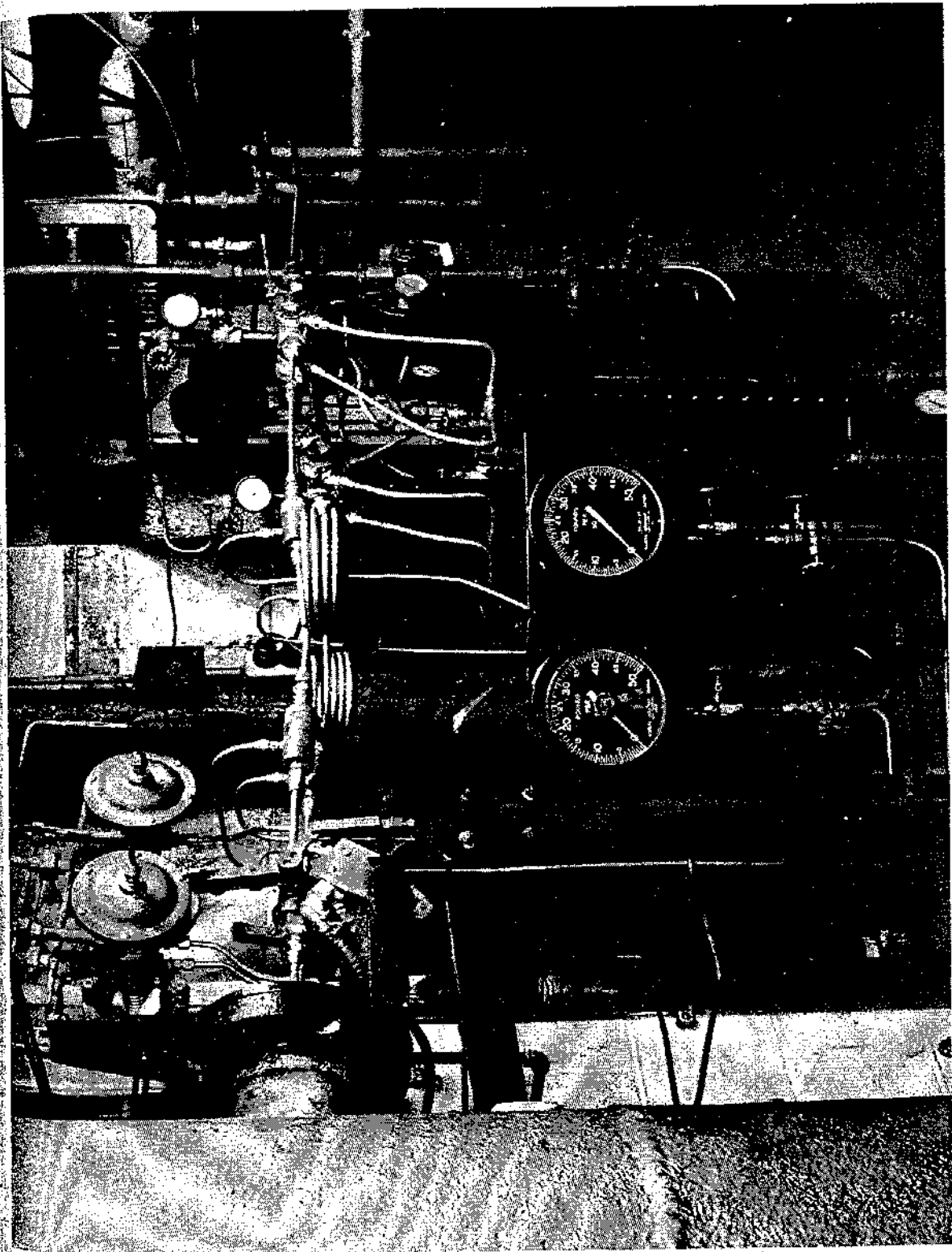


Figure 15. - Control-coil arrangement for low-pressure coal feeder, gasifier 4.