II. SUMMARY OF BENCH-SCALE WORK

The Kellogg Coal Gasification Process has been investigated experimentally in a program carried out in the laboratories of The M. W. Kellogg Company with the support of the Office of Coal Research. It is the purpose of this section of the report to present a summary of the accomplishments and conclusions of this laboratory work. More detailed discussions of this work can be found in the Status Report submitted to the Office of Coal Research on June 19, 1967 and in the monthly Progress Reports.

The experimental work has been divided into two areas; namely, chemical process research and mechanical development in order to study the individual problems most effectively, but results from one area have been reviewed and used repeatedly in planning subsequent experimentation in the other area.

A. CHEMICAL PROCESS RESEARCH

The bench-scale process research work was designed to provide the data required to fix the process operating conditions needed to ensure attractive economics. The bulk of the effort was directed toward determining the effects of the major process variables on the rates of gasification and combustion of a broad range of coal feeds. Other work done included viscosity measurements of various melts, melt expansion as a function of gas flow, measurement of salt carryover and the development of a recovery procedure for sodium carbonate and for sulfur while removing ash.

1. Gasification Rates

The experimental work on gasification has been carried out in a reactor consisting of a 2-inch I.D. Inconel pipe having a length of 26 inches. The reactor is enclosed in an electric furnace and is equipped with two one-quarter inch tubes; one for a thermocouple and one for introducing process gases at a point 1/2 inch from the bottom.

Runs were made in the following manner: Sodium carbonate and ash were added to the reactor, the salt melted and the mix brought to temperature while nitrogen was flowing through the reactor. Steam flow at the desired rate and pressure was then started and held for 15 minutes. Steam was then briefly stopped

to permit the addition, under pressure, of the batch of coal, and steam flow was again started 5 minutes after coal addition. Gases evolved during the 5-minute devolatilization and the steam gasification period were analyzed. The carbon compounds in the gases evolved during a run accounted for some 95% of the carbon charged to a run as coal.

The results were plotted on semi-log paper (Figure 5) and were well correlated assuming gasification to be pseudo-first order with respect to carbon content of the carbonate melt. It is notable that deviations from pseudo-first order are in the direction of increased gasification rates as the degree of gasification of the coal particles increases. This is an interesting characteristic of gasification in the presence of molten sodium carbonate. The pseudo-first order constants were converted to volumetric rates of gasification since this factor controls the cost of the reaction vessels. The goal is to attain gasification rates of 20 pounds of carbon gasified per hour per cubic foot of melt volume.

Gasification data are shown in Figures 6 to 10. Figure 6 shows that the gasification rate varies substantially with the character of the coal. Low rank coals gasify much more rapidly than high rank coals except that the bituminous coal appeared abnormally slow. This coal was found to agglomerate when dropped into the hot molten salt in the small unit and its gasification rate could be increased substantially by coking and particularly preoxidation. In all cases, more than adequate gasification rates could be attained at temperatures in the 1700°F to 1750°F range under the test conditions. Furthermore, grinding of anthracite coal to 80/100 mesh was found to double the rate over that shown in Figure 6 for 12/20 mesh anthracite. The data also show a decreasing energy of activation as the coal becomes more active which is consistent with an increasing contribution of diffusional resistance to the overall gasification of the more reactive coals.

The effect of inlet steam pressure on gasification rate is shown on Figure 7. Gasification rates of economic interest have been obtained at even 1 atmosphere of inlet steam partial pressure. Increasing the steam partial pressure up to the limit permitted by the equipment provides substantial increases in gasification rate. For most of the runs in Figure 7, steam conversions are about 5% as a result of the low bed depth that can be used in the equipment. In several runs the inlet steam was diluted with nitrogen or hydrogen in order to permit increased steam conversions (up to about 60-70%) at reasonable gas velocities (to assure good mixing). In these runs
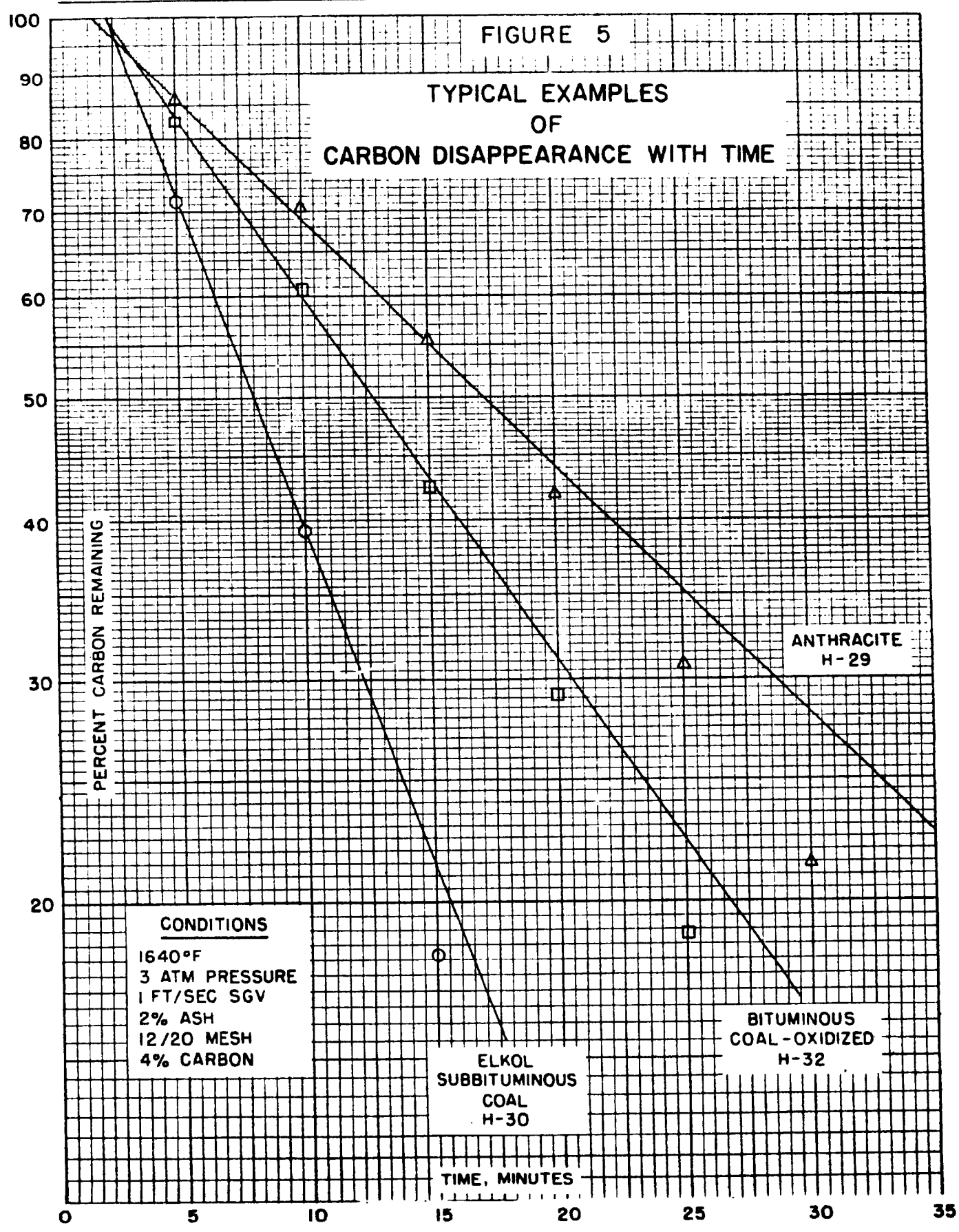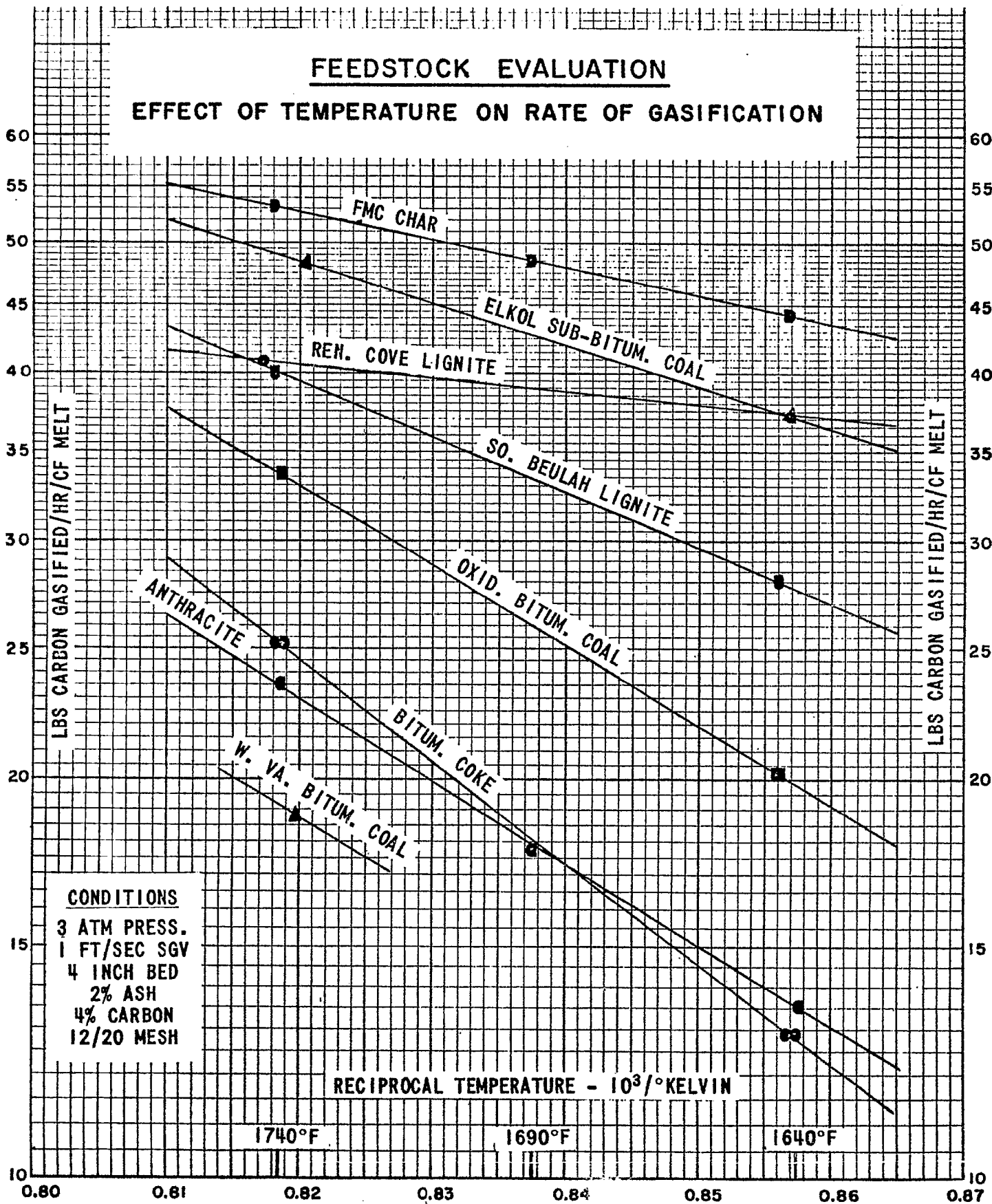
FIGURE 5

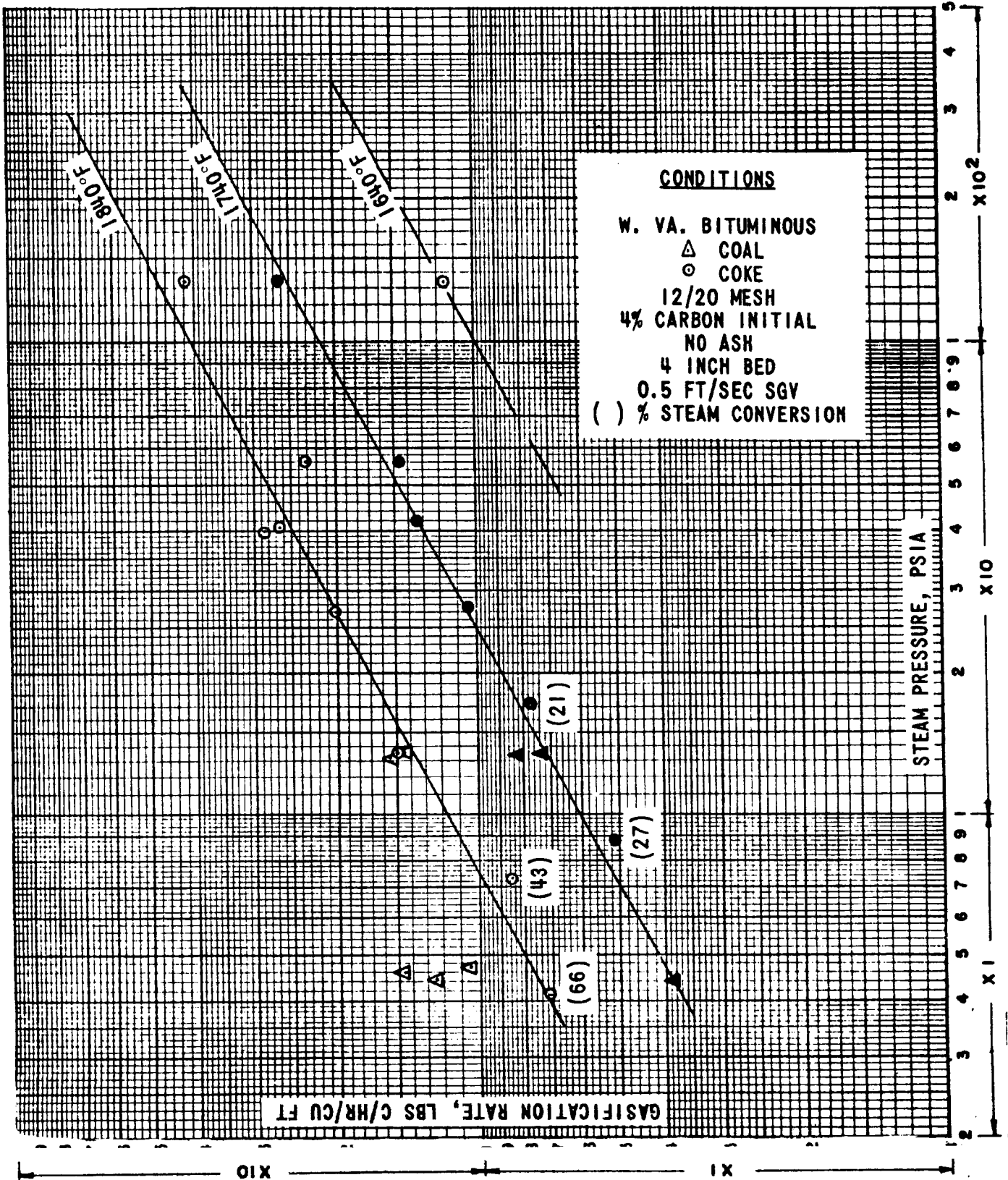TYPICAL EXAMPLES
OF
CARBON DISAPPEARANCE WITH TIME

PERCENT CARBON REMAINING

ANTHRACITE
H - 29

CONDITIONS

1640°F
3 ATM PRESSURE
1 FT/SEC SGV
2% ASH
12/20 MESH
4% CARBON

BITUMINOUS
COAL-OXIDIZED
H-32

ELKOL
SUBBITUMINOUS
COAL
H-30

TIME, MINUTES

FIGURE 6

FEEDSTOCK EVALUATION
EFFECT OF TEMPERATURE ON RATE OF GASIFICATION

CONDITIONS
3 ATM PRESS.
1 FT/SEC SGV
4 INCH BED
2% ASH
4% CARBON
12/20 MESH

FIGURE 7

EFFECT OF STEAM PRESSURE ON GASIFICATION RATE

CONDITIONS

W. VA. BITUMINOUS
△ COAL
⊙ COKE
12/20 MESH
4% CARBON INITIAL
NO ASH
4 INCH BED
0.5 FT/SEC SGV
( ) % STEAM CONVERSION

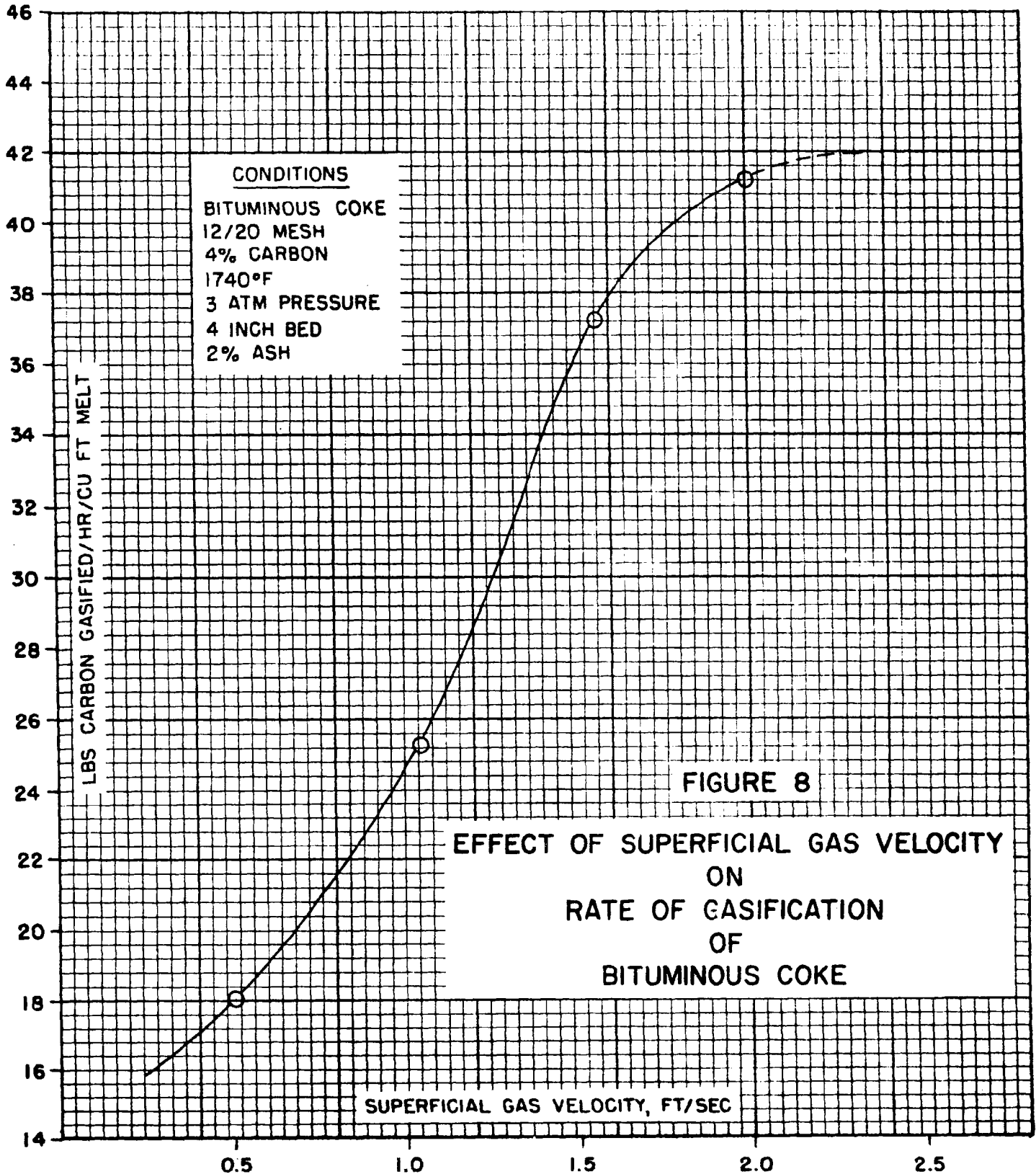STEAM PRESSURE, PSIA

GASIFICATION RATE, LBS C/HR/CU FT

the gasification rates fell right on the curve showing that
inlet steam pressure was the correlating variable and that hydro-
gen in the gasifying medium caused no decrease in gasification
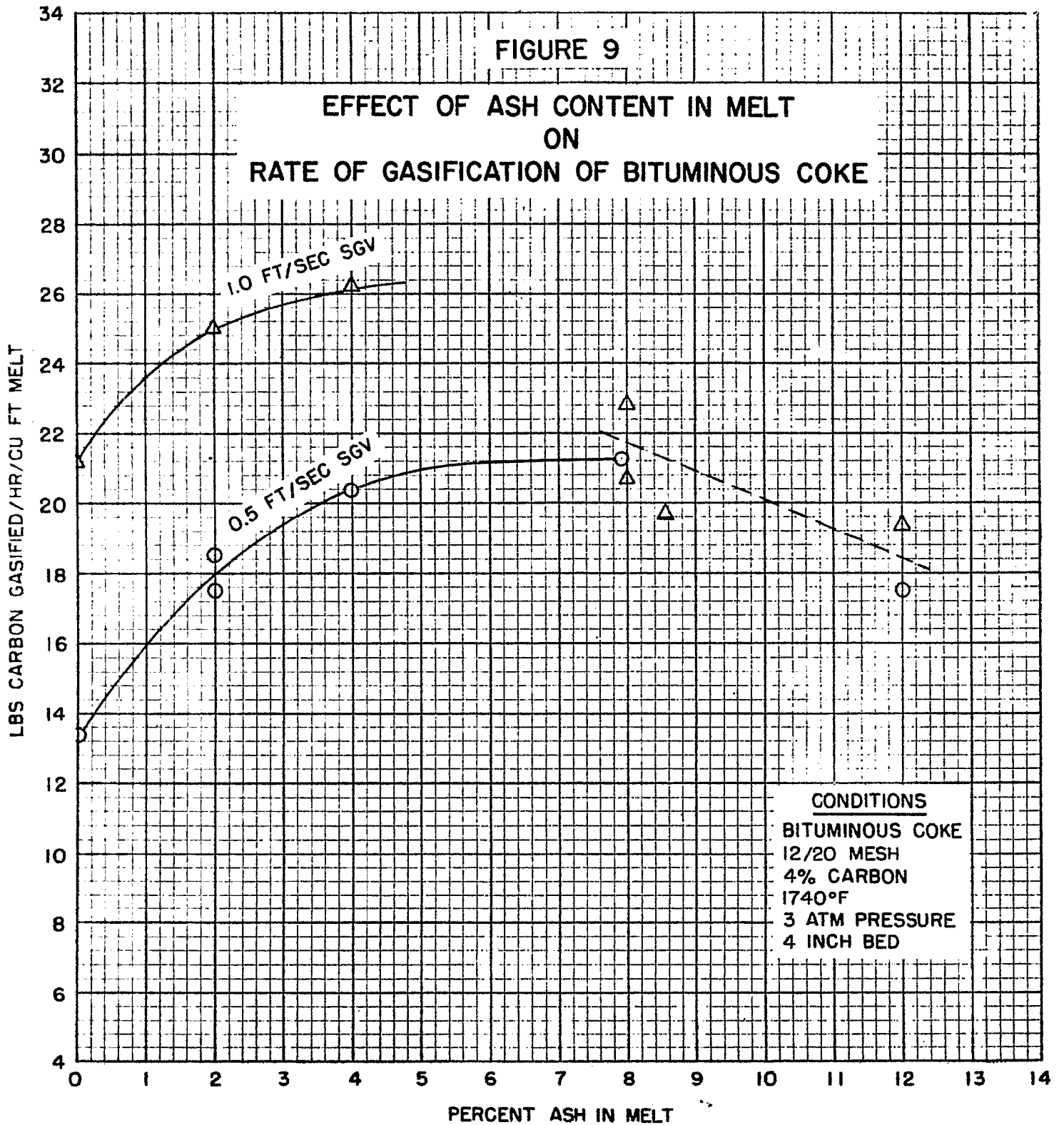rates observed in the molten salt system.

The beneficial effect of gas velocity up to about 2
feet per second is shown on Figure 8 and the effect of ash content
of the melt is illustrated in Figure 9. The latter figure shows
that the presence of ash yields some improvement in gasification
rate in the range between about 4% and 10% ash.

The effect of the remaining factor—melt height—studied
on the bench scale is shown on Figure 10. The data show that the
gasification rate decreases significantly as melt height increases
from 2 inches to 6 inches which covers the range that can be
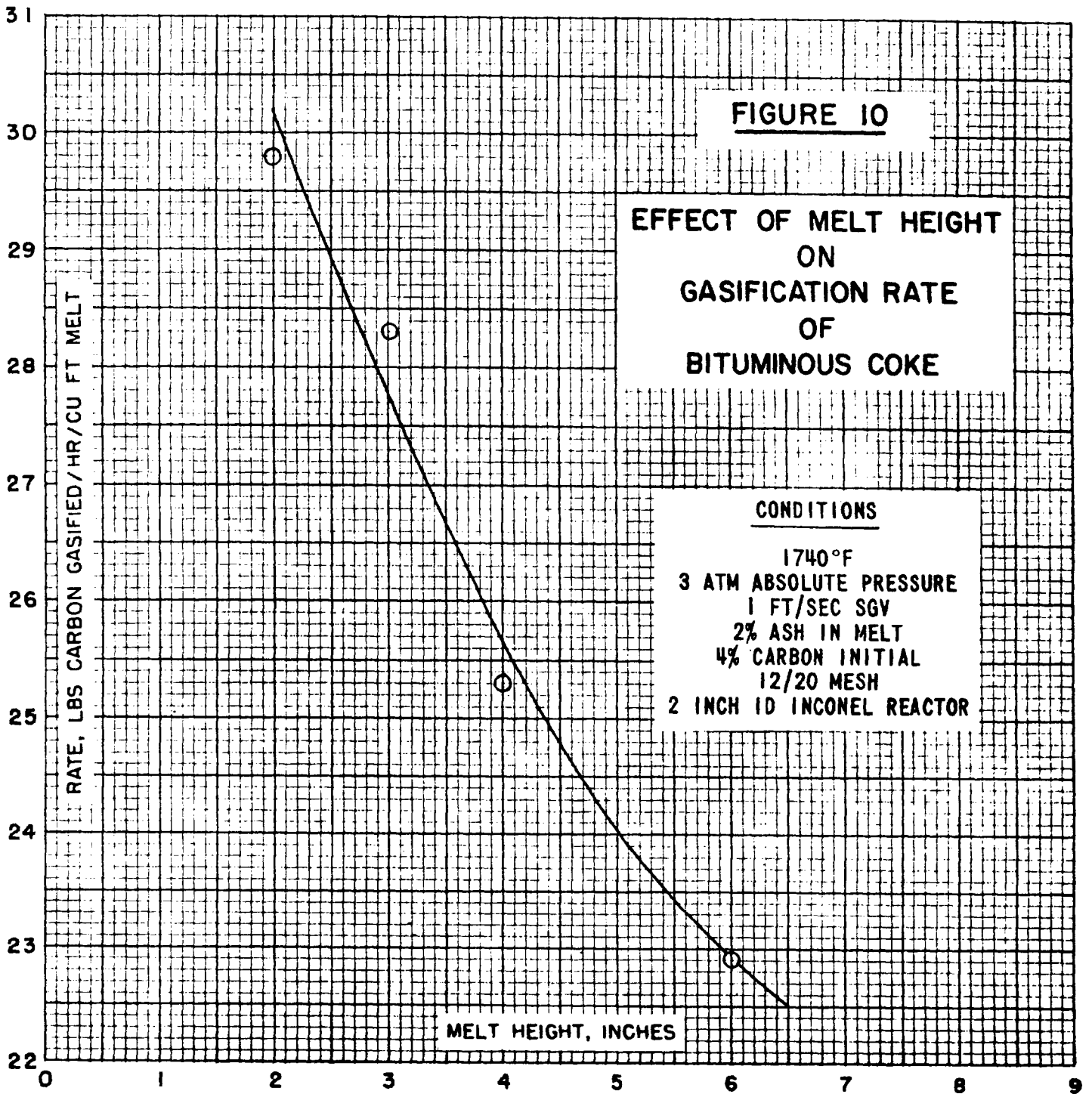studied in the current equipment.

The experimental data on gasification cover as wide a
range of each factor as is practical in the bench-scale equipment.
Limitations in the equipment, however, make it impossible to run
experiments under all the conditions to be expected in the proposed
commercial plant. An attempt to project the present data to commer-
cial scale is shown on Figure 11 which depicts the scale-up problem
with respect to melt height. The current data are shown as circles
and these points are converted to flow sheet conditions and shown
as squares. Extrapolation of these points to the necessary melt
height (or depth) of 10 feet show that the design gasification rate
of about 21 pounds of carbon per hour per cubic foot of melt is
attainable but the extrapolation is great.

To minimize the risk of extrapolation from the present
data, a number of attempts have been made to design equipment and
experiments that might provide data at some intermediate melt height.
Such design is complicated by the large heat requirements for gasi-
fication at about 20 pounds of coal per hour per cubic foot, the high
temperature at which heat must be supplied and by the limitations on
design imposed by the special ceramic materials in the case of ves-
sels of modest size. Heat supply by using the electric resistance
of the melt, by induction heating or by use of a furnace were all
considered. It was found that any design that appeared adequate for
generation of satisfactory data was quite expensive (approaching the
cost of about $100,000 - $200,000) and such designs also appeared
incapable of generating data that could significantly improve the
confidence of pilot plant design or of extrapolation to commercial
scale at the desired gasification rates. It was decided, therefore,
to eliminate gasification rate studies at an intermediate scale and,
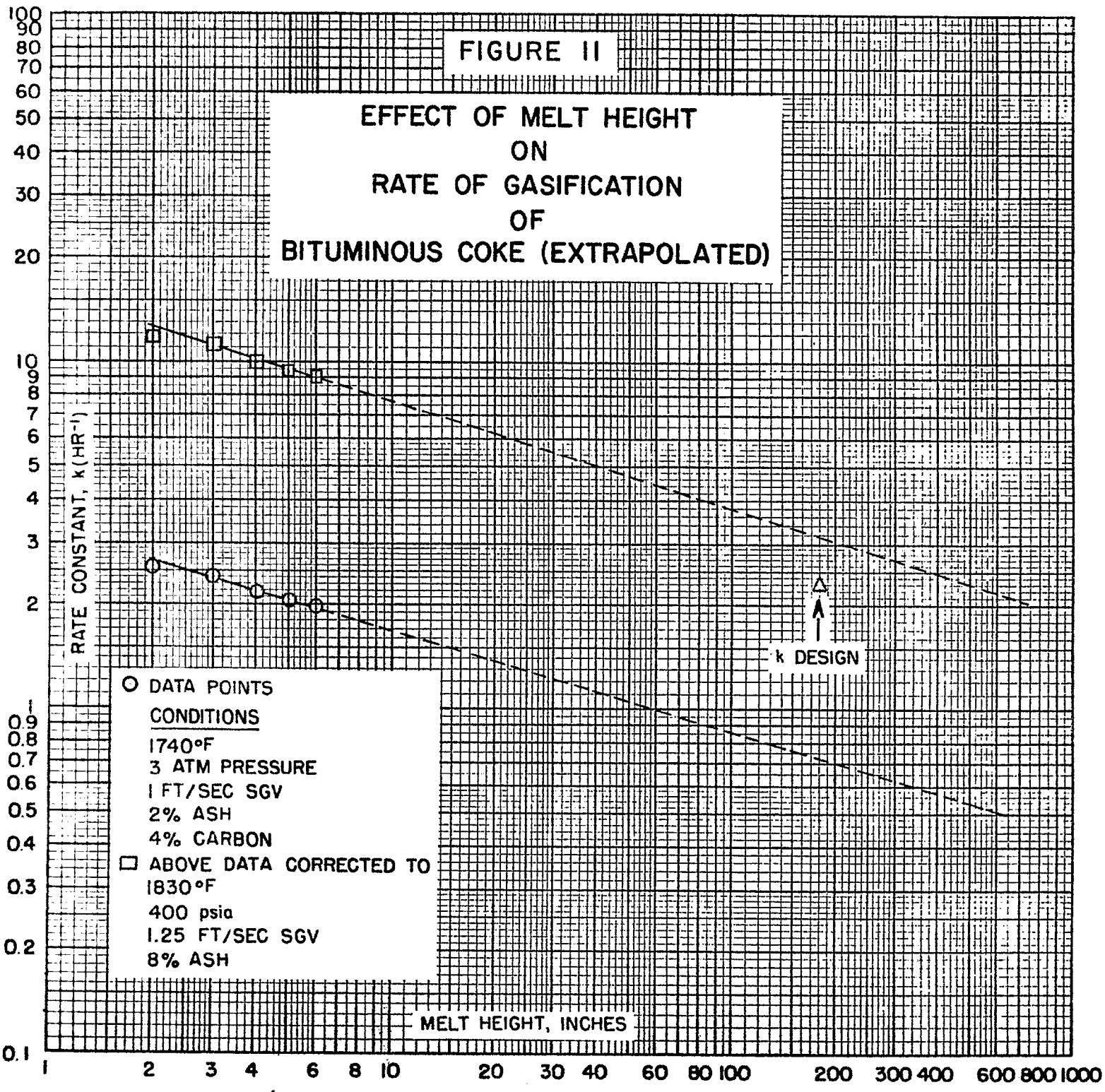
CONDITIONS

BITUMINOUS COKE
12/20 MESH
4% CARBON
1740°F
3 ATM PRESSURE
4 INCH BED
2% ASH

FIGURE 8

EFFECT OF SUPERFICIAL GAS VELOCITY
ON
RATE OF GASIFICATION
OF
BITUMINOUS COKE

LBS CARBON GASIFIED/HR/CU FT MELT

SUPERFICIAL GAS VELOCITY, FT/SEC

FIGURE 9

EFFECT OF ASH CONTENT IN MELT
ON
RATE OF GASIFICATION OF BITUMINOUS COKE

CONDITIONS

BITUMINOUS COKE
12/20 MESH
4% CARBON
1740°F
3 ATM PRESSURE
4 INCH BED

FIGURE 10

EFFECT OF MELT HEIGHT
ON
GASIFICATION RATE
OF
BITUMINOUS COKE

CONDITIONS

1740°F
3 ATM ABSOLUTE PRESSURE
1 FT/SEC SGV
2% ASH IN MELT
4% CARBON INITIAL
12/20 MESH
2 INCH ID INCONEL REACTOR

RATE, LBS CARBON GASIFIED/HR/CU FT MELT

MELT HEIGHT, INCHES

FIGURE 11

EFFECT OF MELT HEIGHT
ON
RATE OF GASIFICATION
OF
BITUMINOUS COKE (EXTRAPOLATED)

O DATA POINTS
  CONDITIONS
    1740°F
    3 ATM PRESSURE
    1 FT/SEC SGV
    2% ASH
    4% CARBON
□ ABOVE DATA CORRECTED TO
    1830°F
    400 psia
    1.25 FT/SEC SGV
    8% ASH

k DESIGN

RATE CONSTANT, k(HR⁻¹)

MELT HEIGHT, INCHES

instead, to recommend proceeding directly to the pilot plant design so as to have sufficient flexibility to handle variations in gasification rate.

2. Combustion Rates

Dependence of combustion rate in the presence of molten salt with respect to the primary process variables was investigated in the same equipment that was used for gasification investigations. Again, batch runs were made following the consumption of coal by combustion as reflected in the gas analyses. The combustion was found to be pseudo-first order with respect to carbon content for 50% consumption of the coal. In addition, the volumetric rate of combustion was found to increase directly with carbon content from 2.0% to 8.0% of the melt by weight, as shown in Figure 12. It may be seen that combustion and gasification behave similarly with respect to carbon concentration.

The effect of temperature and rank of coal are shown in Figure 13, indicating comparable effects as observed for gasification. In the case of combustion, however, Figure 13 contains no points for FMC char, Elkol subbituminous coal and South Beulah lignite. These three materials burned at such a high rate that the measured rate was limited by the availability of oxygen to the very high level of 70 pounds per hour per cubic foot.
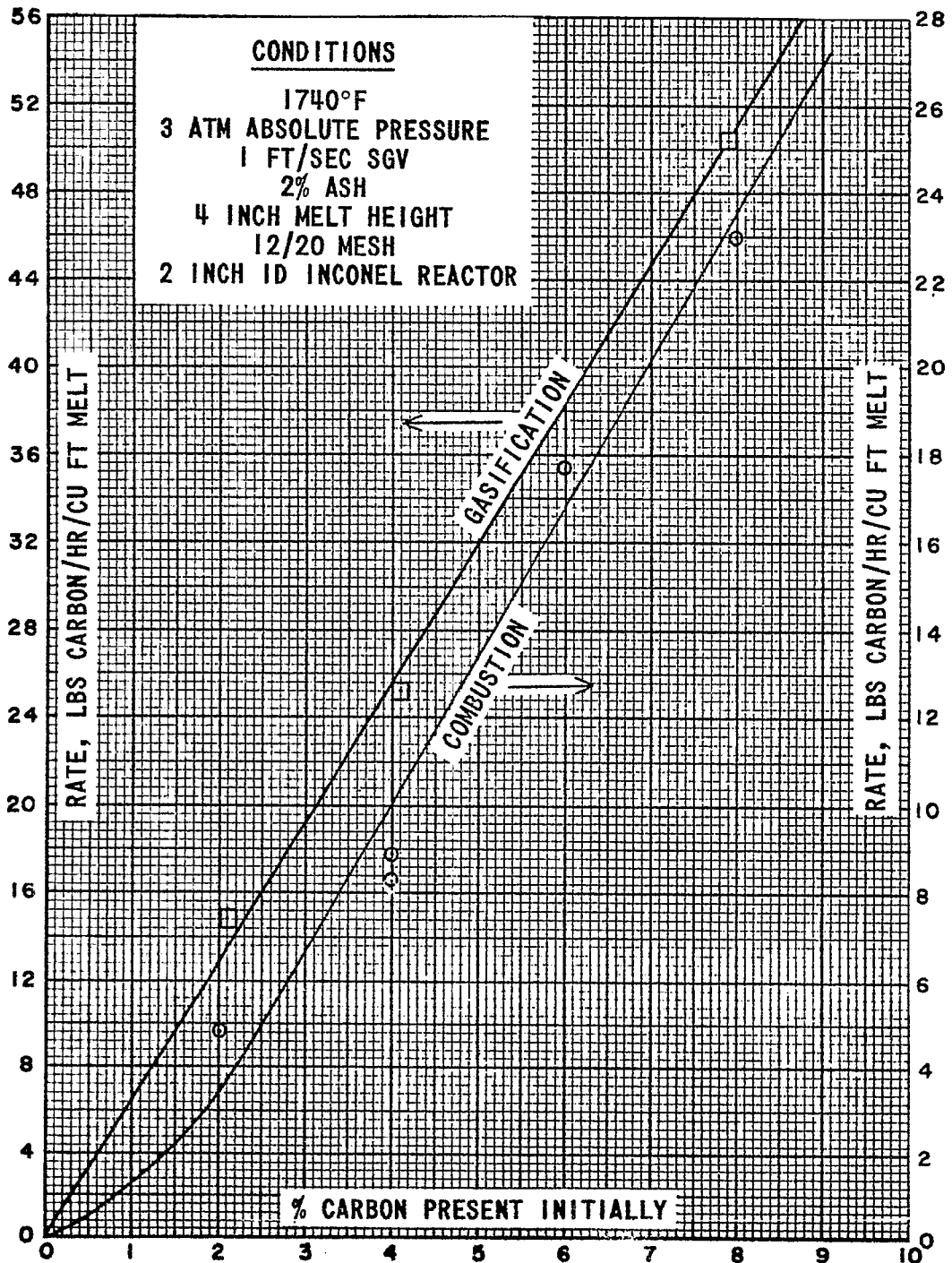
No variation in combustion rate was observed in experiments in which air pressure was varied between 15 and 120 pounds per square inch absolute or air velocity was varied between 0.5 and 1.5 feet per second. These two factors are, therefore, different than in the case of gasification.
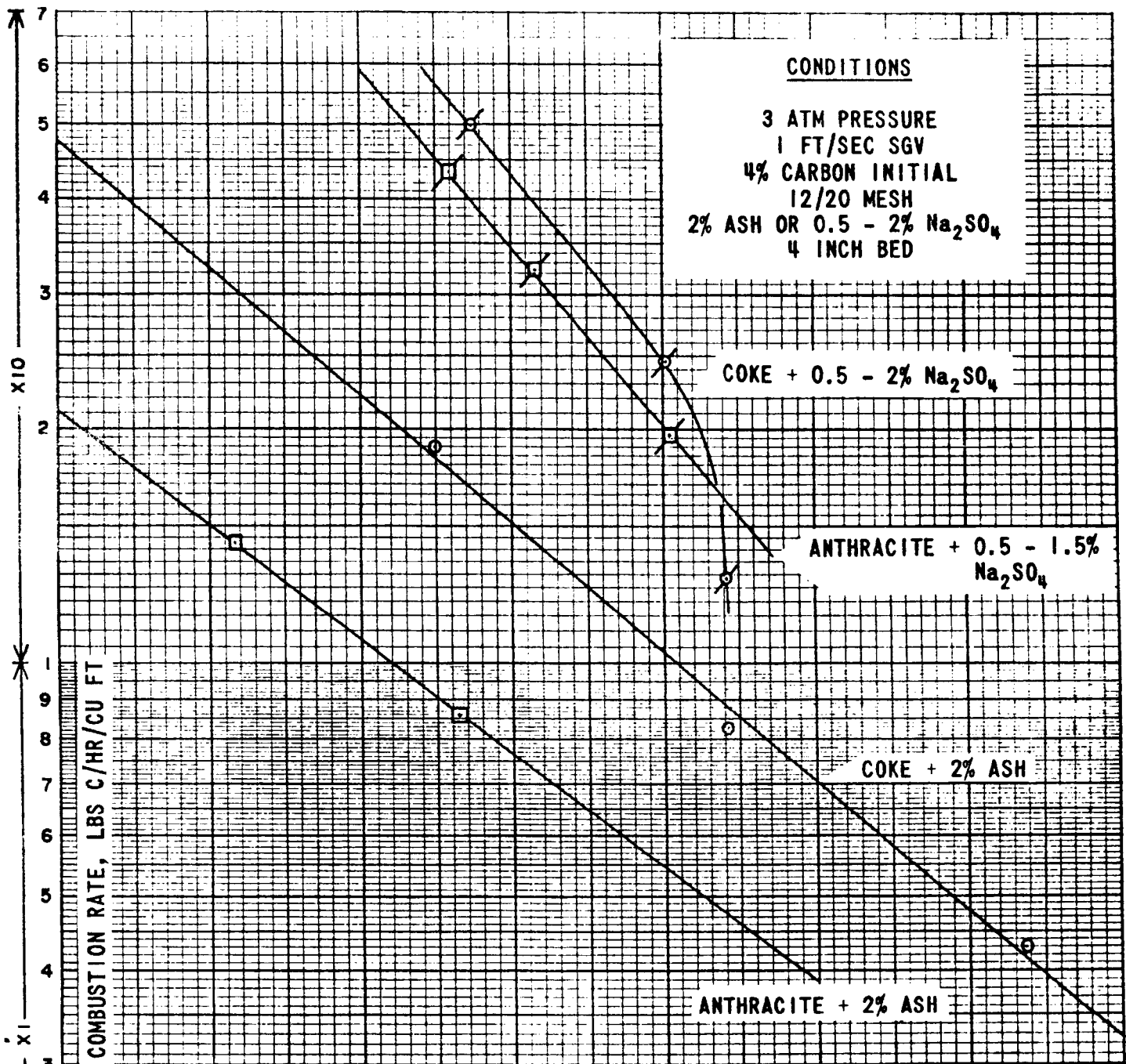
The addition of sodium sulfate to the melt was found to yield important increases in combustion rate, as shown on Figure 14 for bituminous coke and for anthracite. Grinding of coal to smaller particle sizes is also beneficial to combustion rate as shown in Figure 15.

The effect of melt height for combustion and gasification is shown on Figure 16 which again shows the scale-up problem. The lowest combustion rate, after correction for the factors discussed above to the levels chosen for commercial operation, still appears satisfactory after allowing for scale-up, but this problem must await the pilot plant because no useful experiments of intermediate scale can be devised at costs sufficiently low to warrant the intermediate step.

FIGURE 12

EFFECT OF CARBON CONCENTRATION IN MELT ON GASIFICATION AND COMBUSTION RATES OF BITUMINOUS COKE

CONDITIONS

1740°F
3 ATM ABSOLUTE PRESSURE
1 FT/SEC SGV
2% ASH
4 INCH MELT HEIGHT
12/20 MESH
2 INCH ID INCONEL REACTOR

RATE, LBS CARBON/HR/CU FT MELT

GASIFICATION

COMBUSTION

% CARBON PRESENT INITIALLY

CONDITIONS

3 ATM PRESSURE
1 FT/SEC SGV
4% CARBON INITIAL
12/20 MESH
2% ASH OR 0.5 - 2% Na_2SO_4
4 INCH BED

COKE + 0.5 - 2% Na_2SO_4

ANTHRACITE + 0.5 - 1.5% Na_2SO_4

COKE + 2% ASH

ANTHRACITE + 2% ASH

COMBUSTION RATE, LBS C/HR/CU FT

RECIPROCAL TEMPERATURE, 10^3/°K

1940°F   1840°F   1740°F   1640°F

0.73   0.75   0.77   0.79   0.81   0.83   0.85   0.87

FIGURE 13

EFFECT OF TEMPERATURE ON COMBUSTION RATES
OF
ANTHRACITE AND BITUMINOUS COKE

FIGURE 14

EFFECT OF SODIUM SULFATE IN MELT ON COMBUSTION RATES OF
BITUMINOUS COKE AND ANTHRACITE

CONDITIONS

1740°F (CORRECTED)
3 ATM PRESSURE
1 FT/SEC SGV
4 INCH BED
4% CARBON INITIAL
12/20 MESH

COMBUSTION RATE, LBS C/HR/CU FT

PERCENT SODIUM SULFATE IN MELT
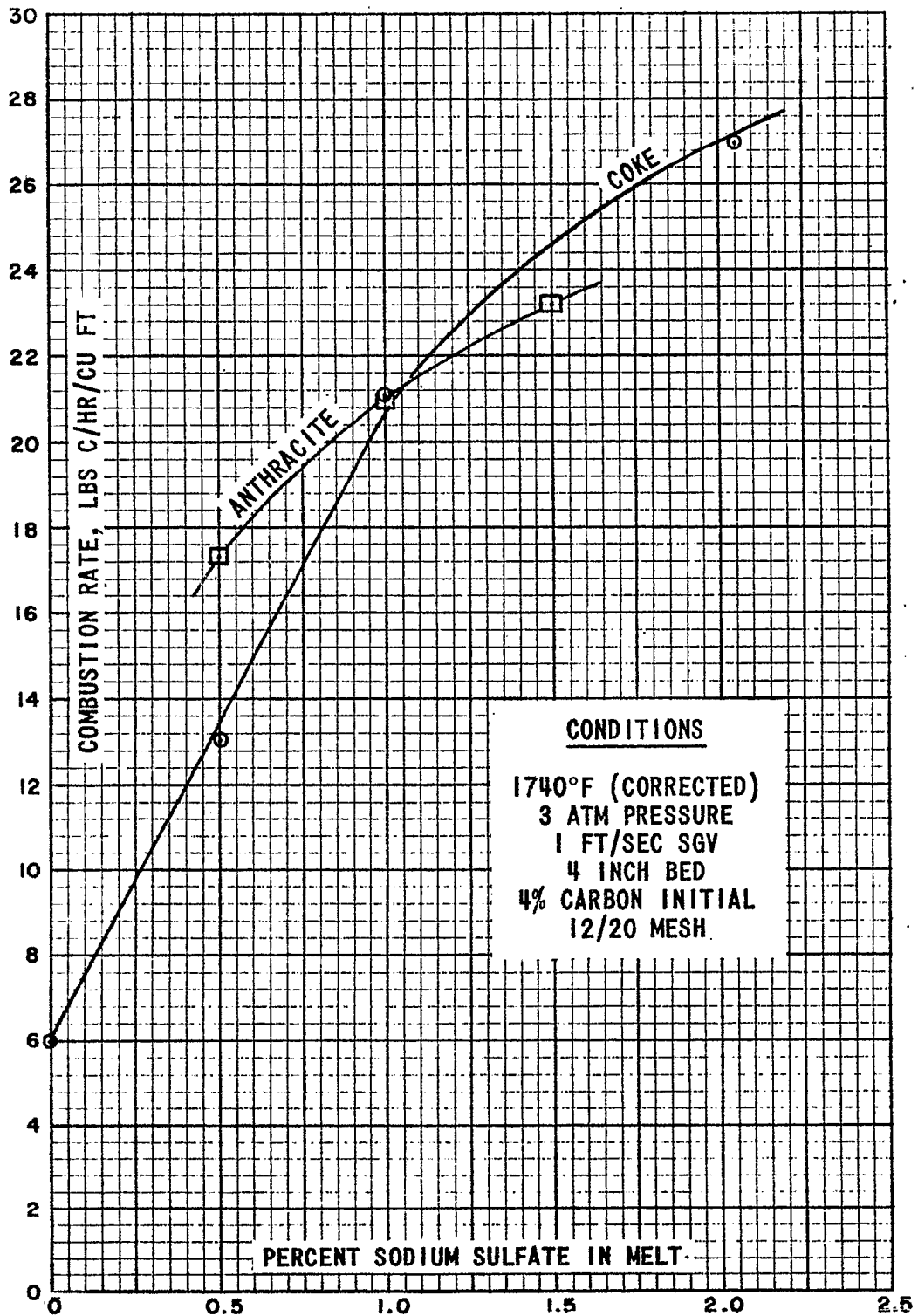
FIGURE 15

EFFECT OF PARTICLE SIZE ON COMBUSTION RATE
OF
BITUMINOUS COKE

CONDITIONS

1740°F

3 ATM PRESSURE

1 FT/SEC SUPERFICIAL AIR VEL

4% CARBON INITIAL

2% ASH

4 INCH BED

COMBUSTION RATE, LBS C/HR/CF

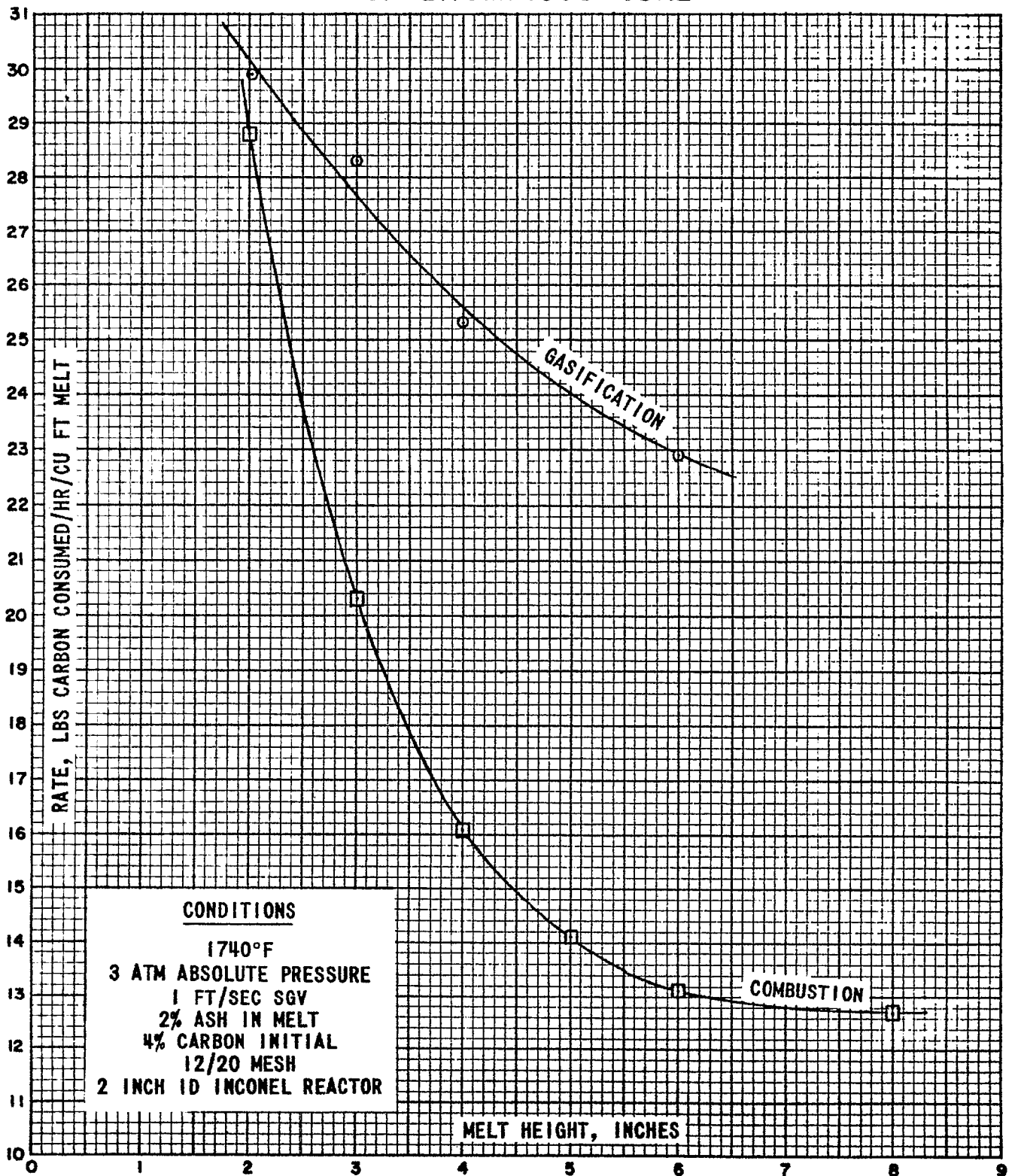COMBUSTION RATE, LBS C/HR/CF

SURFACE/VOLUME RATIO, mm^{-1}
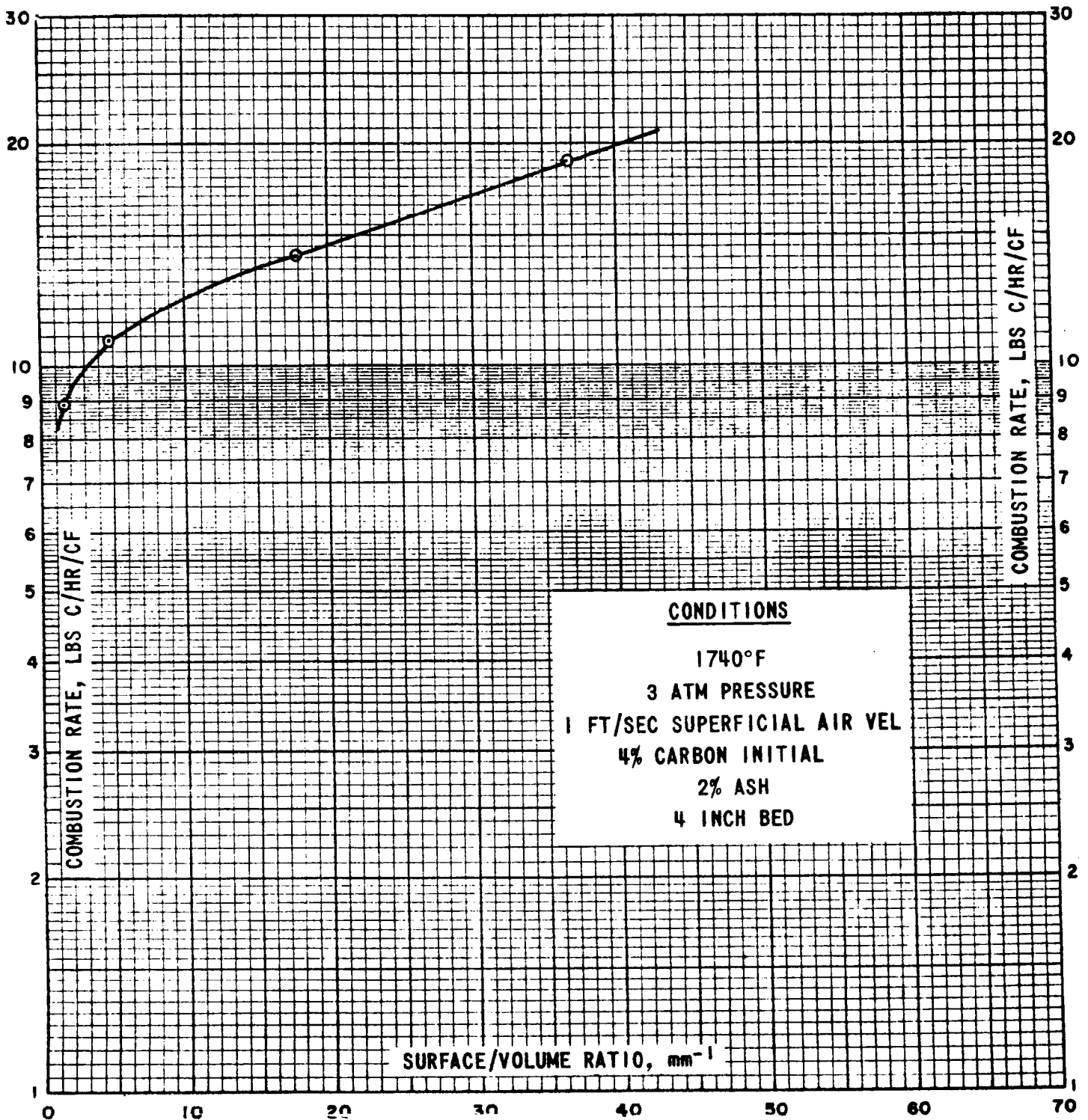
FIGURE 16

EFFECT OF MELT HEIGHT ON GASIFICATION
AND COMBUSTION RATES
OF BITUMINOUS COKE

3. Combustion Efficiency

Several runs have been made to determine the efficiency with which the carbon in the melt is burned to carbon dioxide. The conceptual flow sheet shows a 300°F temperature difference between the flue gas and the melt. This could be caused either by inefficient heat transfer or by incomplete combustion of the coal (15 percent of carbon oxides present as carbon monoxide). Carbon monoxide, in turn, could afterburn in the gas space and result in the elevated temperatures. This thermal inefficiency of course, results in an increased coal requirement.

For the purpose of determining this efficiency, a gas-cooled probe sampler was used to obtain gas samples just above the melt surface before any afterburning could occur. These experiments were carried out with top-feeding of coal to the same equipment used for the gasification and combustion studies. The probe samples thus obtained were analyzed for carbon monoxide, carbon dioxide and oxygen. When the coal first contacts the melt with no air being fed, the coal undergoes a devolatilization period where the gas is rich in CO (70 to 80 percent of total carbon oxides). This, however, is an acceptable situation since the fresh coal will be fed to the gasifier while only devolatilized coal will circulate to the combustor. After this initial period air is introduced and the carbon monoxide level drops from 8 to 13 percent of the carbon oxides to only trace quantities as the carbon concentration drops from 6 to 3 percent. Since the design carbon level in the combustor is 4 percent, these experiments support the assumption made for combustion efficiency in the commercial design.

4. Chemistry of Ash Removal

The laboratory work carried out to test the ash removal system consisted of the following program.

A sample of ground melt containing about 8 percent bituminous coal ash was leached with 9 percent sodium bicarbonate solution at the boiling point for ten minutes. The slurry was filtered on either a 25 micron stainless steel crucible or filter paper to separate the undissolved ash and filtrate. The residue, after washing, and the original melt were dried, weighed and analyzed for Na, SiO_2, Al_2O_3, and Fe_2O_3. The filtrate was then saturated with carbon dioxide and the precipitated sodium bicarbonate was filtered on a Buchner funnel. The residue was air dried, weighed and analyzed for sodium content. In addition, SiO_2 and Al_2O_3 analyses were obtained as required. The filtrate was also measured and its sodium content determined.

It has been found that the sodium losses in the first filter can be reduced by keeping one atmosphere of carbon dioxide pressure over the molten carbonate and ash mixture in order to minimize the extent of carbonate-ash reactions (mineralization) to form sodium compounds. Data have shown sodium losses up to 19 percent when nitrogen was used to aerate the molten salt but only 9 percent when carbon dioxide was used. X-ray patterns of these ash cakes have shown $Na_2CO_3 \cdot H_2O$ to be present which indicates that the wash treatment was insufficient. When these residues were washed again with a large amount of hot water, the sodium loss was only about 3 percent. It is felt that countercurrent, multi-stage washing that can be used on a plant scale will be considerably more efficient, so that sodium losses will be approximately at the design point of 2.4 percent.

Additional experiments have shown that even if mineralization does occur in the melt forming soluble silicates and aluminates, the silica and alumina will precipitate out upon treatment with sodium bicarbonate solution. However, from the standpoint of ease of filtration, it is preferred that no mineralization occur in the melt since a gelatinous silica or alumina can be formed. Hence, care should be taken to keep a pressure of carbon dioxide above the melt at all times.

The same factors which affect sodium mineralization also effect silica and alumina insolubility in the quench solution. In addition, if the sodium bicarbonate solution used to quench the melt can be maintained below pH of 9.8, carryover of silica in the first filtrate will be about 20 percent rather than 35 percent as assumed in design. Under these conditions, none of the alumina or Fe_2O_3 will be carried through the first filter.

The carbonation step has been studied somewhat less quantitatively than the dissolving and ash filtering steps. This step is very similar to the carbonation step used in the Solvay process for the manufacture of soda except that there is ammoniated brine present and that the carbonation is carried out between 20 and 40°C in the Solvay process. In general, laboratory results have shown that sodium not lost in the ash filtering step can be completely recovered as sodium bicarbonate after carbonation with twice the stoichiometric carbon dioxide. The conceptual flow sheet shows 8.5 times the stoichiometric carbon dioxide in order to assure a high driving force for mass transfer. The residence times and operating conditions required for good sodium bicarbonate crystal growth have not yet been determined.

5. Viscosity Studies

Measurement of viscosities of various melts was made with a Brookfield viscometer which employed a specially constructed Inconel spindle. Calibration liquids were employed to check the accuracy of measurement. Results established the non-Newtonian, pseudo-plastic nature of the molten sodium carbonate containing ash and coke. That is, in a system with increasing shear, the apparent viscosity decreases. A summary of these results, along with literature data for pure sodium carbonate is given in Figure 17. As can be seen a melt containing 8 percent ash and 4 percent carbon should have an apparent viscosity below 200 centipoise in the temperature range of interest. Simulation studies have indicated that such viscosities should be low enough to ensure good mixing and permit melt transfer in the manner proposed commercially.

6. Salt Carryover

Consideration of the salt carryover (or entrainment) problem from the bench-scale unit has led to several conclusions. Presence of ash in the melt has been shown to be beneficial in decreasing salt carryover as shown in Figure 18. Apparently, the ash constituents react rapidly with the more volatile sodium oxide and hydroxide to prevent their loss. Pressure has also been shown to reduce the sodium volatility in gasification studies as has the presence of a small amount of steam in combustion studies. Presumably, this steam reacts with sodium oxide to form the somewhat less volatile hydroxide.

7. Mineralization Studies

Experiments were carried out to determine whether mineralization (reaction) of the ash constituents with the sodium carbonate melt would be a problem under commercial conditions. In addition, since one of the constituents, alumina, is also proposed as the material of construction in contact with the melt, information thus obtained is useful in helping to explain corrosion results. Figures 19 and 20 show the effect of carbon dioxide pressure on the solubility of alumina and silica as evidenced by freezing point depression. As can be seen about 0.4 atmospheres of carbon dioxide are adequate to prevent mineralization of these constituents. Therefore, under commercial conditions where carbon dioxide pressure may be as high as 3 to 4 atmospheres, there should be little possibility of either ash solubility or Monofrax A corrosion.
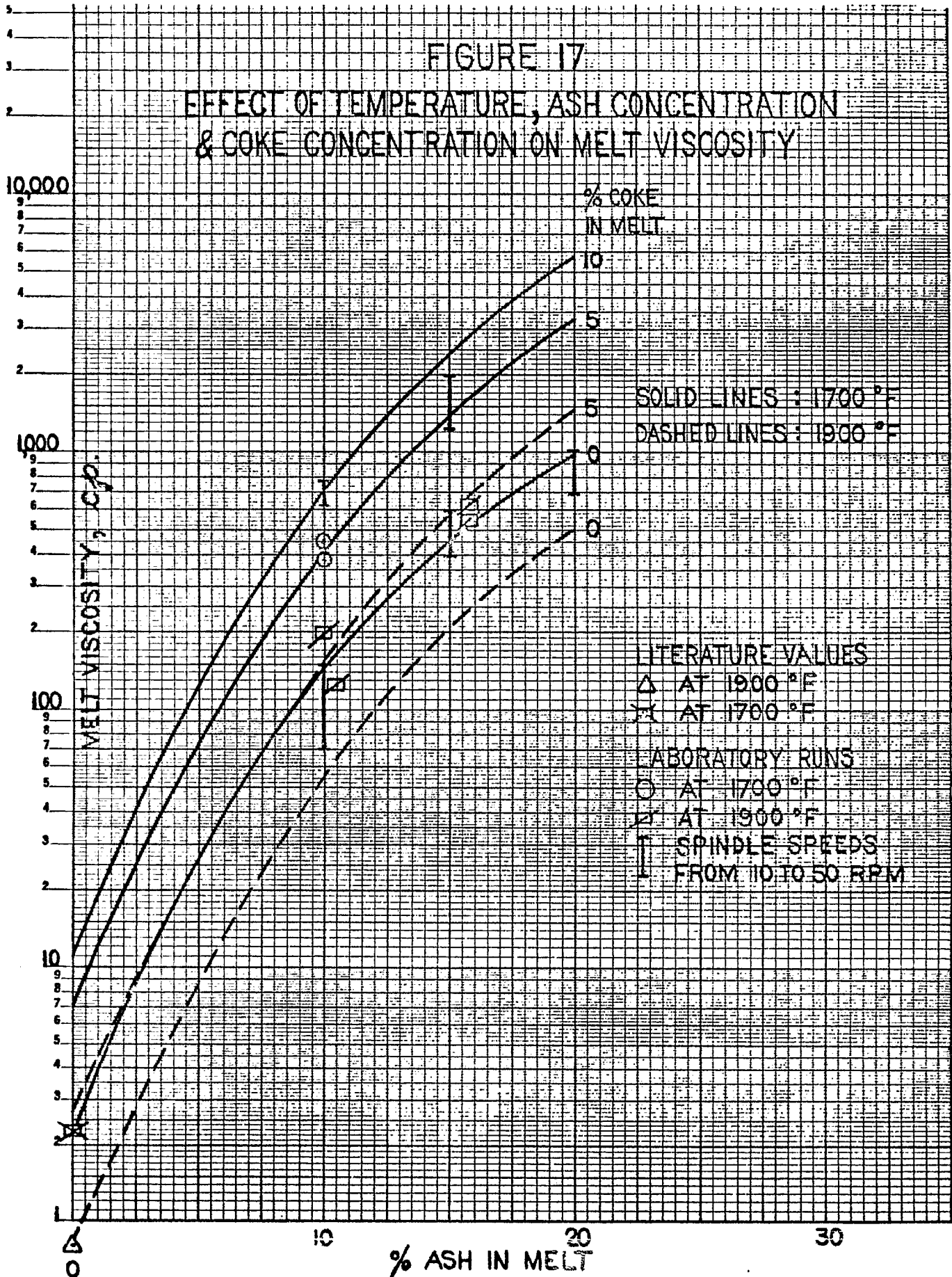
FIGURE 17
EFFECT OF TEMPERATURE, ASH CONCENTRATION
& COKE CONCENTRATION ON MELT VISCOSITY

% COKE IN MELT

SOLID LINES : 1700 °F
DASHED LINES : 1900 °F

LITERATURE VALUES
△ AT 1900 °F
⋈ AT 1700 °F

LABORATORY RUNS
○ AT 1700 °F
⊿ AT 1900 °F
⊥ SPINDLE SPEEDS
FROM 10 TO 50 RPM

MELT VISCOSITY, cp.

% ASH IN MELT

FIGURE 18
SALT CARRYOVER IN GASIFICATION AND COMBUSTION RUNS
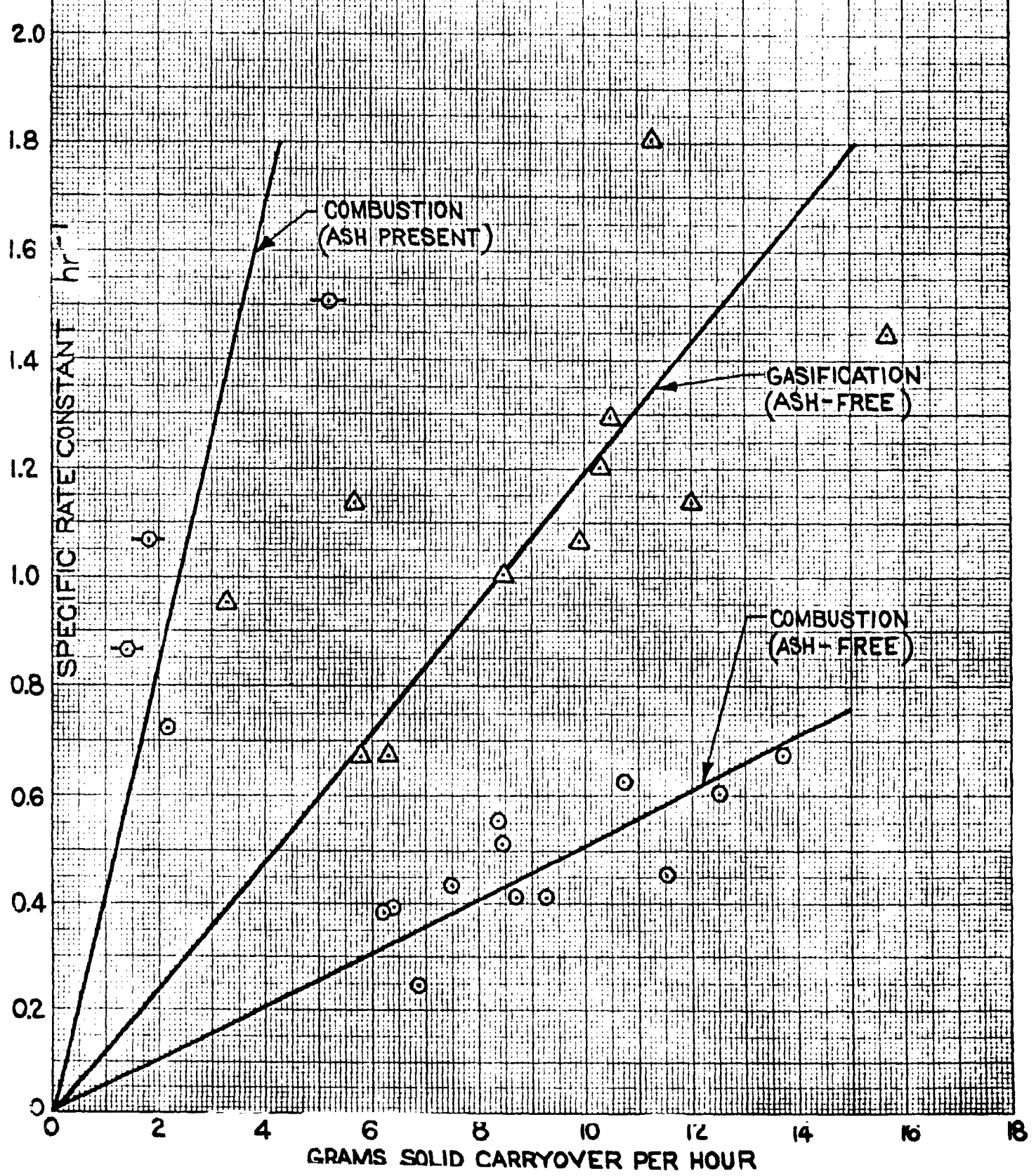
FIGURE 19
EFFECT OF CARBON DIOXIDE IN NITROGEN ON FREEZING POINT
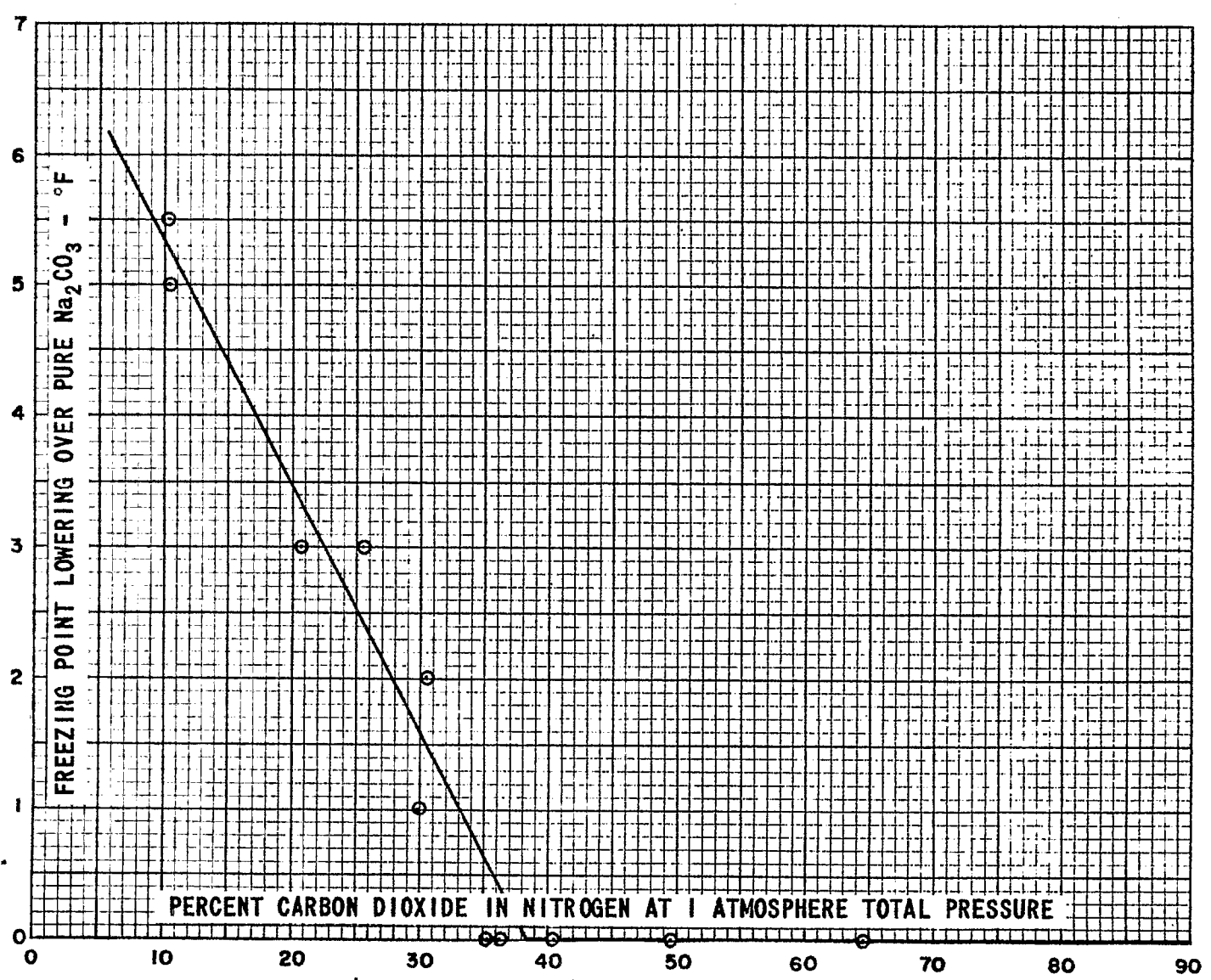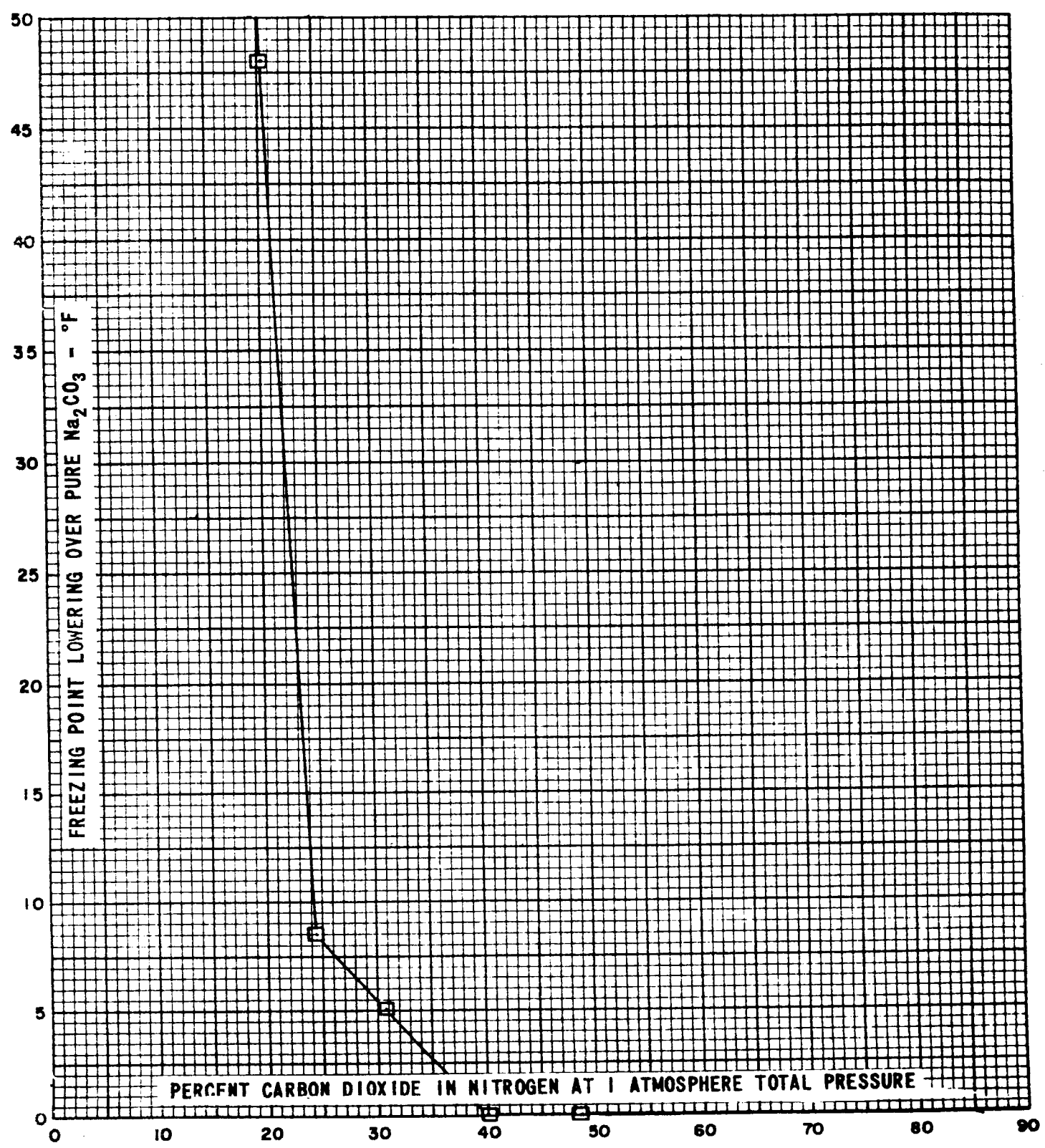OF
8% ALUMINA IN Na_2CO_3 MELT

FIGURE 20

EFFECT OF CARBON DIOXIDE IN NITROGEN ON FREEZING POINT
OF
8% SILICA IN Na_2CO_3 MELT

Y-axis: FREEZING POINT LOWERING OVER PURE Na_2CO_3 - °F

X-axis: PERCENT CARBON DIOXIDE IN NITROGEN AT I ATMOSPHERE TOTAL PRESSURE

8. Disposition of Sulfur in the Process

Two types of bench-scale experimentation have indicated that all of the sulfur brought in with the coal will be retained by the melt. First, a melt containing sodium sulfate was subjected to simulated gasification conditions and no sulfur could be detected in the off-gases. Second, during continuous gasification of oxidized bituminous coal feeding coal beneath the melt surface no sulfur compounds could be detected in the product gas.

The form of the sulfur in the two zones, gasification and combustion, has also been established. Under steady state conditions with 4% carbon present in the melt, the sulfur in the gasifier will be present mainly as sulfide. Carbon reduces sulfate sulfur to sulfide sulfur very readily at gasification conditions. It was also established that oxygen in air oxidizes sulfide to sulfate extremely fast at combustion conditions. Therefore, sulfur will exist as sulfate in the combustion zone. Experiments also established that carbon dioxide and steam oxidize sulfide sulfur in a sodium carbonate melt but that the oxidation is quite slow.

Removal of sulfur from the system must be done in the ash removal-sodium carbonate recovery section. Removal of the sulfur as sodium sulfate was tried and found not to be possible due to its high solubility. Thus the removal of ash and melt from the system cannot be done by tapping the combustor but must be done on the gasifier where the predominant form of sulfur is sulfide. Here experiments established that the sulfur, if present in the sulfide form, will be liberated as hydrogen sulfide during the carbonation step. It was further shown that the hydrogen sulfide is mainly liberated near the end of carbonation allowing the off-gas to contain about 20% or more hydrogen sulfide which can be readily converted to sulfur in the Claus Process.

9. Ash Settling Studies

Several experiments were carried out to determine the feasibility of concentrating the ash in the melt stream entering the ash removal section by means of settling caused by density difference. A six-inch bed depth in a 2-inch I.D. reactor was used and samples were taken over a period of time at the bottom and five inches from the bottom. These experiments showed that most of the settling took place in the first ten minutes and not much thereafter. Addition of calcium carbonate in an attempt to enhance the coal ash settling rate indicated that it did not have any effect on this rate and that it behaves like coal ash itself.

Temperature was found to have a beneficial effect on the ash settling rate as indicated below. The experiments were carried out with a mixture of 8 percent ash in sodium carbonate and the samples were taken after ten minutes of settling.

TEMPERATURE °F	WT. PERCENT ASH IN SAMPLE	
	4-5" FROM BOTTOM	BOTTOM
1740	3.1	9.2
1840	2.1	12.9
1940	5.0	10.8

As can be seen, the extent of settling begins to diminish at 1940°F. Along with this observation, carbon dioxide was also seen to evolve indicating that a reaction of ash with melt was interfering with the separation. Thus, the optimum temperature seems to be about 1840°F.

An experiment with 4 percent coke in the melt indicated that it did not affect the ash settling rate. Also, as predicted by density difference, the coke was observed to float on the melt and would be recycled back to the reaction zone with the ash-depleted melt.

Inclusion of such a step in the process would have to await testing on a larger scale in order to determine whether the ash-rich melt can be handled (due to its high viscosity) and processed to yield a high percentage recovery of sodium.