D. RATES OF CARBON FORMATION EXPERIMENTAL PROGRAM

1. Description of Experimental Equipment

During the period July - September, 1977, the design of the multiple fixed-bed reactor system was completed (see Figure IV-D-1 and IV-D-2). Equipmemt was ordered and a fabricator was commissioned to construct the reactor unit. The reactor design incorporates a removable, sectional catalyst basket which can be positioned inside the reactor tube. The baskets contain provisions for a central thermowell. The thermowell contains three stationary thermocouples for zone temperature controllers in addition to the traveling thermocouple necessary for the temperature profile.

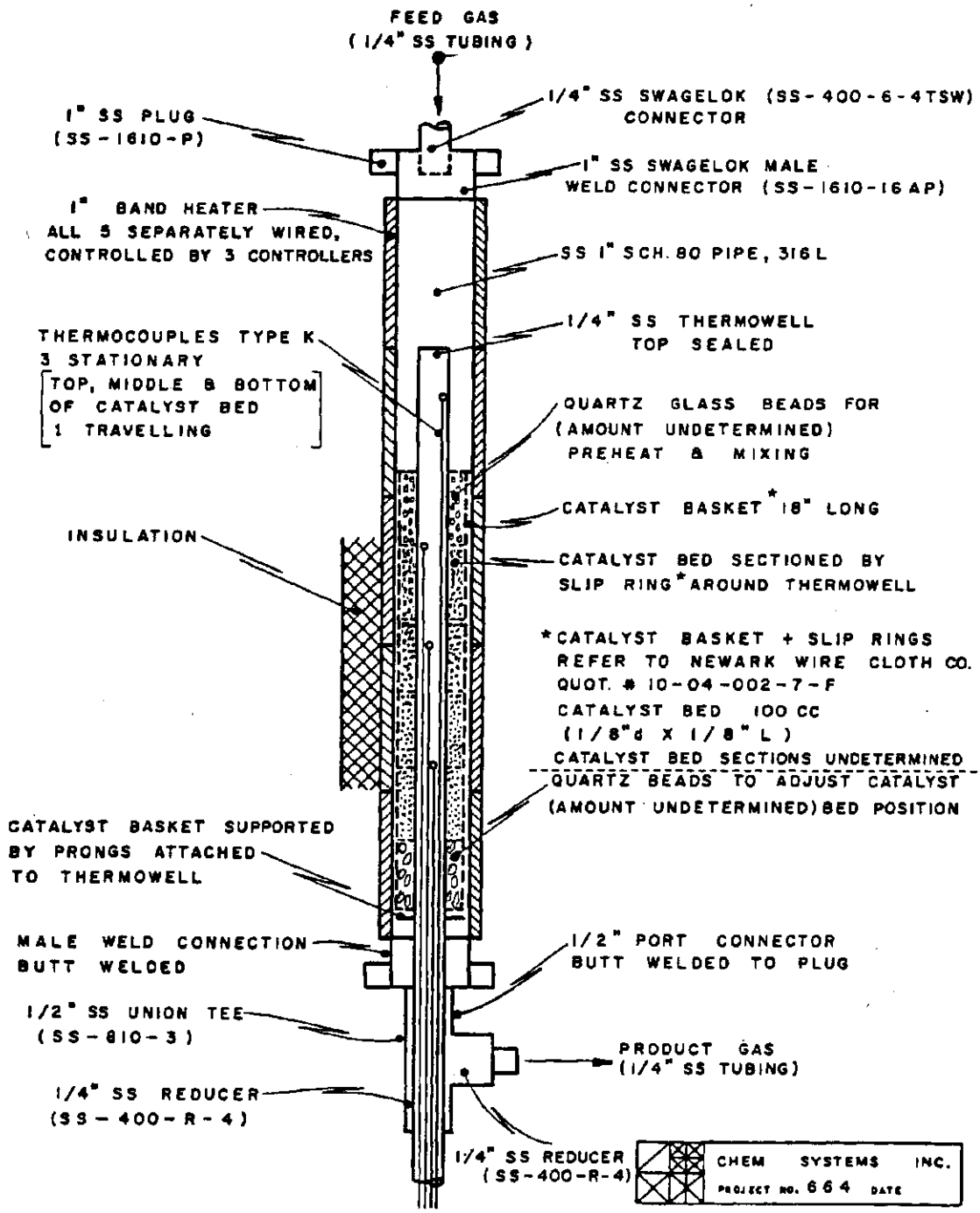
Construction of the test unit assembly (support structure and piping) started in October, 1977. The overall dimensions are 19 ft. long, 4 ft. wide, and 7 ft. high. It is subdivided into five identical units, one for each reactor system, and a master control panel to hold the temperature indicator and recorder.

The feed gas lines from the trailer to the reactor skid were completed in October. Construction began on a single prototype unit of the reactor system to study the feasibility of several instrument and piping arrangements. The remaining four units were later duplicated from this one.

During November, 1977, the reactor skid housing five individual reactor units was completed. Construction of a modular unit for two gas booster compressors, as shown in Figure IV-D-3, was also finished except for electrical wiring. Construction of a prototype of a single reactor system neared completion. The layout of the control panel of the prototype is shown in Figure IV-D-4.

FIGURE IV-D-1

SCHEMATIC DIAGRAM OF REACTOR ASSEMBLY CARBON FORMATION STUDY IN METHANATION



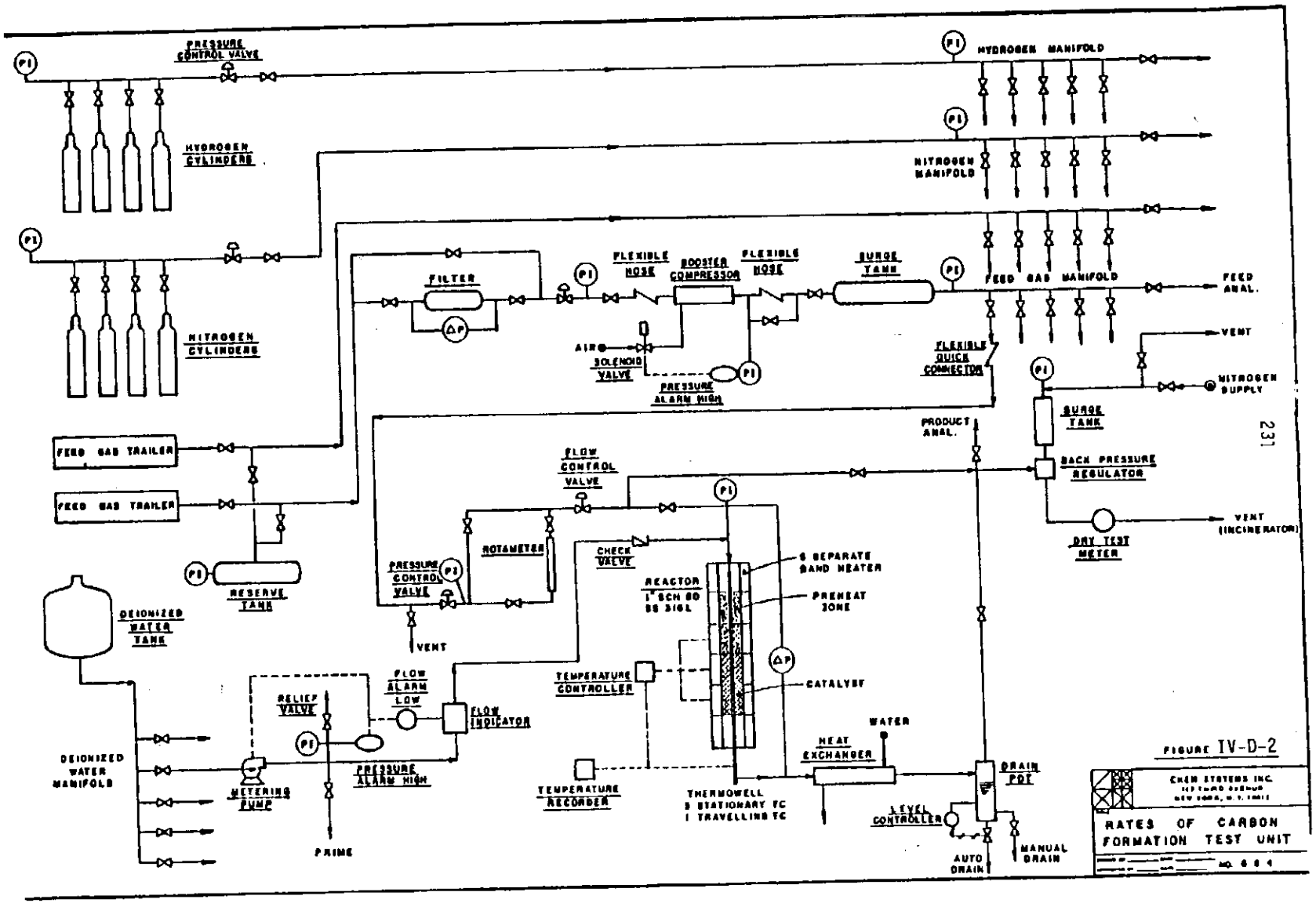

PRESSURE CONTROL VALVE
HYDROGEN CYLINDERS
HYDROGEN MANIFOLD
NITROGEN MANIFOLD
NITROGEN CYLINDERS
FILTER
FLEXIBLE HOSE
BOOSTER COMPRESSOR
FLEXIBLE HOSE
SURGE TANK
FEED GAS MANIFOLD
FEED ANAL.
VENT
AIR
SOLENOID VALVE
PRESSURE ALARM HIGH
FLEXIBLE QUICK CONNECTION
NITROGEN SUPPLY
SURGE TANK
PRODUCT ANAL.
BACK PRESSURE REGULATOR
FEED GAS TRAILER
FEED GAS TRAILER
FLOW CONTROL VALVE
ROTAMETER
CHECK VALVE
6 SEPARATE BAND HEATER
PREHEAT ZONE
CATALYST
VENT (INCINERATOR)
DRY TEST METER
RESERVE TANK
PRESSURE CONTROL VALVE
VENT
REACTOR 1" SCH 80 SS 316L
DEIONIZED WATER TANK
FLOW ALARM LOW
RELIEF VALVE
FLOW INDICATOR
TEMPERATURE CONTROLLER
WATER
HEAT EXCHANGER
DEIONIZED WATER MANIFOLD
METERING PUMP
PRESSURE ALARM HIGH
PRIME
TEMPERATURE RECORDER
THERMOWELL 5 STATIONARY TC 1 TRAVELLING TC
DRAIN POT
LEVEL CONTROLLER
AUTO DRAIN
MANUAL DRAIN
CHEM SYSTEMS INC.
RATES OF CARBON FORMATION TEST UNIT
NO. 6 6 4

FIGURE IV-D-2

FIGURE IV-D-3

CARBON FORMATION BOOSTER CONTROL PANEL

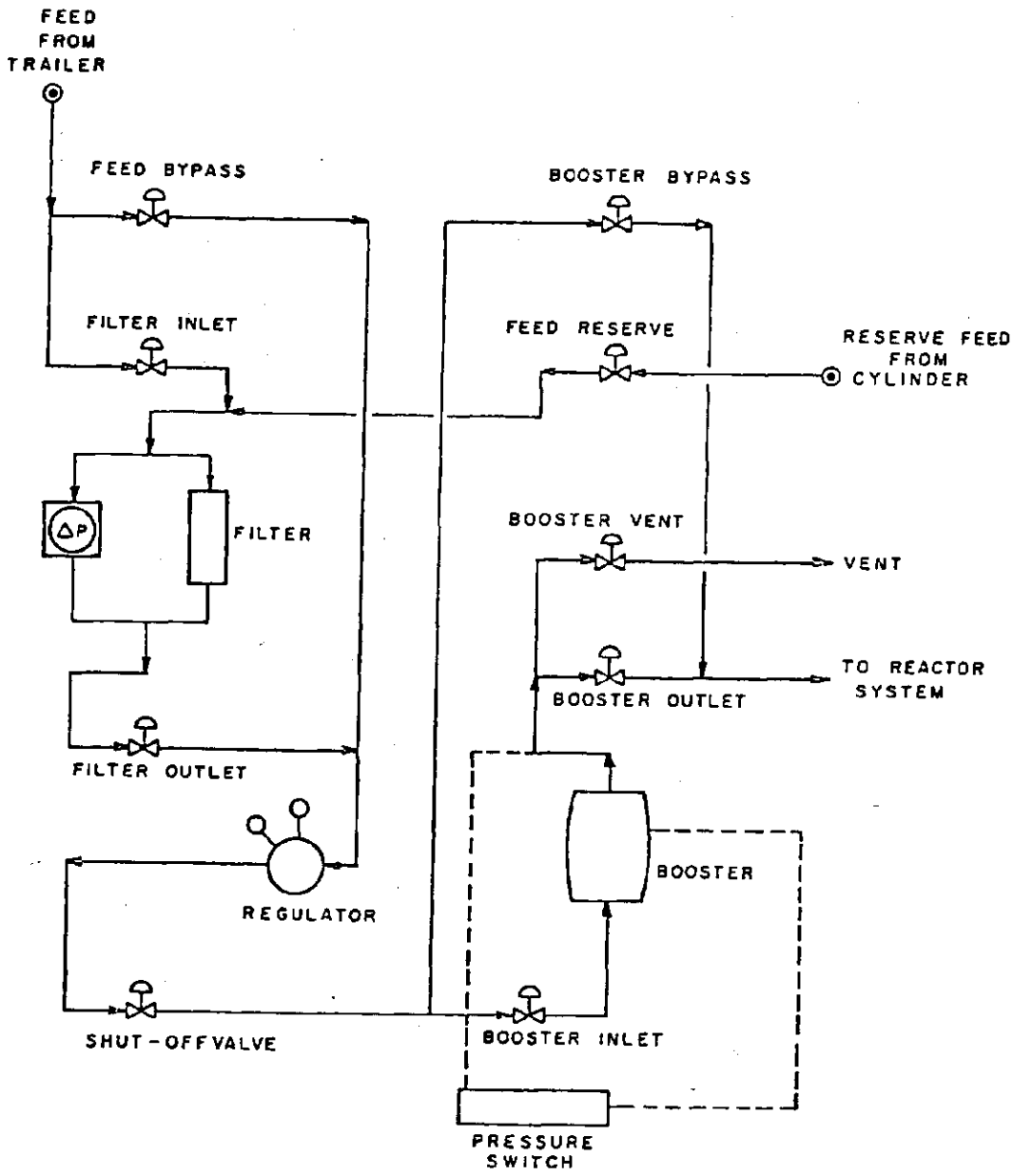
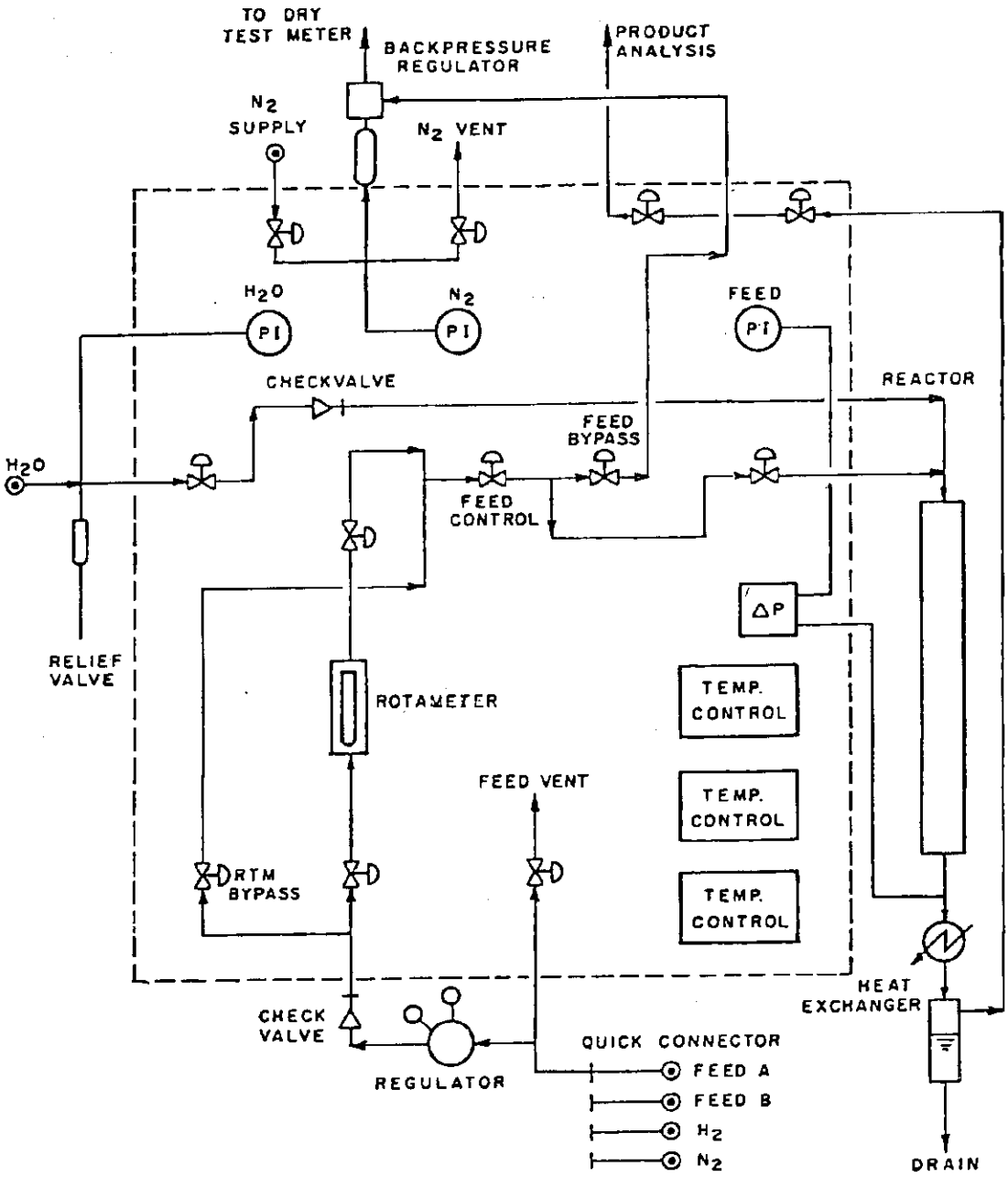


FIGURE IV-D-4

CARBON FORMATION REACTOR SYSTEM CONTROL PANEL



2. Planning and Experimental Procedures

C. F. Braun was requested to perform a series of computer runs to establish the thermodynamic carbon formation boundaries in the C-H-O system for both graphite and non-equilibrium carbon. The following process conditions were identified:

- 600°, 900° and 1200°F @ 500 psig
- 600°, 900° and 1200°F @ 1000 psig

This information was received in October, 1977 in the form of computer calculation printouts of thermodynamic equilibrium boundaries of carbon formation in C-H-O system for both graphite and non-ideal carbon at 600, 900, 1200°F for 500 and 1000 psig. Atomic C-H-O boundaries for both carbons are plotted in Figures IV-D-5 through IV-D-10.

A meeting was held on January 11, 1978 to define the overall scope of the experimental program and to update the program time schedule. The following paragraphs describe the experimental program and procedures formalized at that time:

a. Of the many variables involved in determining a set of experimental conditions for methanation, the most important are feed gas consumption, operating temperature and pressure, catalyst, duration of test and amount of steam injected into the reactor system.

b. Gases simulating three different coal gasification process sources (scrubbed nonshifted HYGAS, scrubbed nonshifted Lurgi gas and shifted conventional methanator feed gas) were to be used to represent different regions in the atomic C-H-O boundaries of both graphite and nonideal carbon formation (see Figure IV-D-11). The final composition, however, would be determined by a series of exploratory runs conducted with 2 percent, 4 percent and 6 percent CO with $3H_2/CO$ and nitrogen balanced feed gases. Results would indicate to what extent reactor temperatures can be controlled and dictate the maximum allowable carbon oxide content in the feed gas. Too high a concentration of carbon oxides causes excessive hot spots, which subsequently foul the catalyst because of the highly exothermic nature of methanation.

Fig. IV-D-5 Atomic C-H-O boundaries for graphite and non-ideal carbon formation

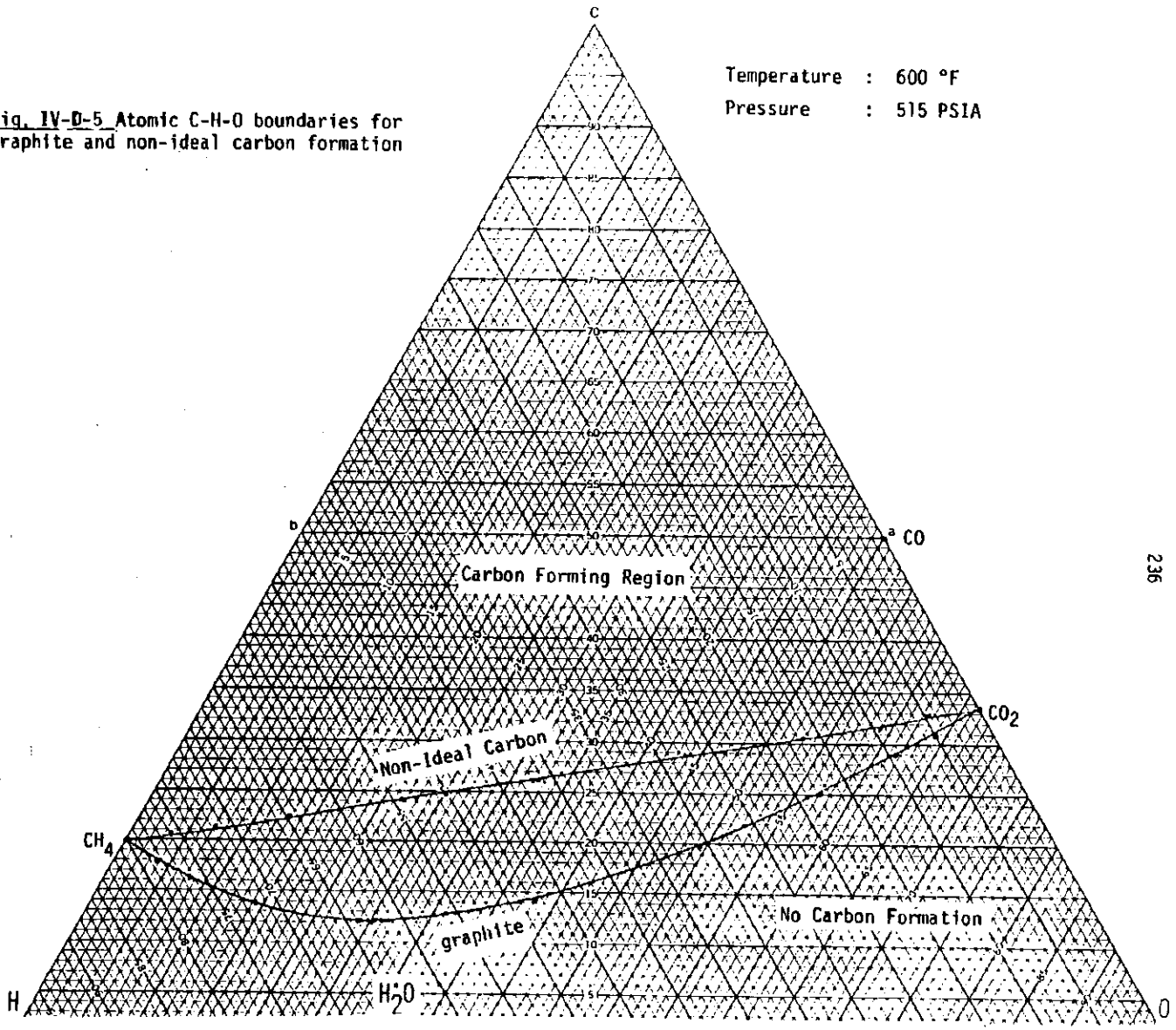


Fig. IV-D-6: Atomic C-H-O boundaries for graphite and non-ideal carbon formation

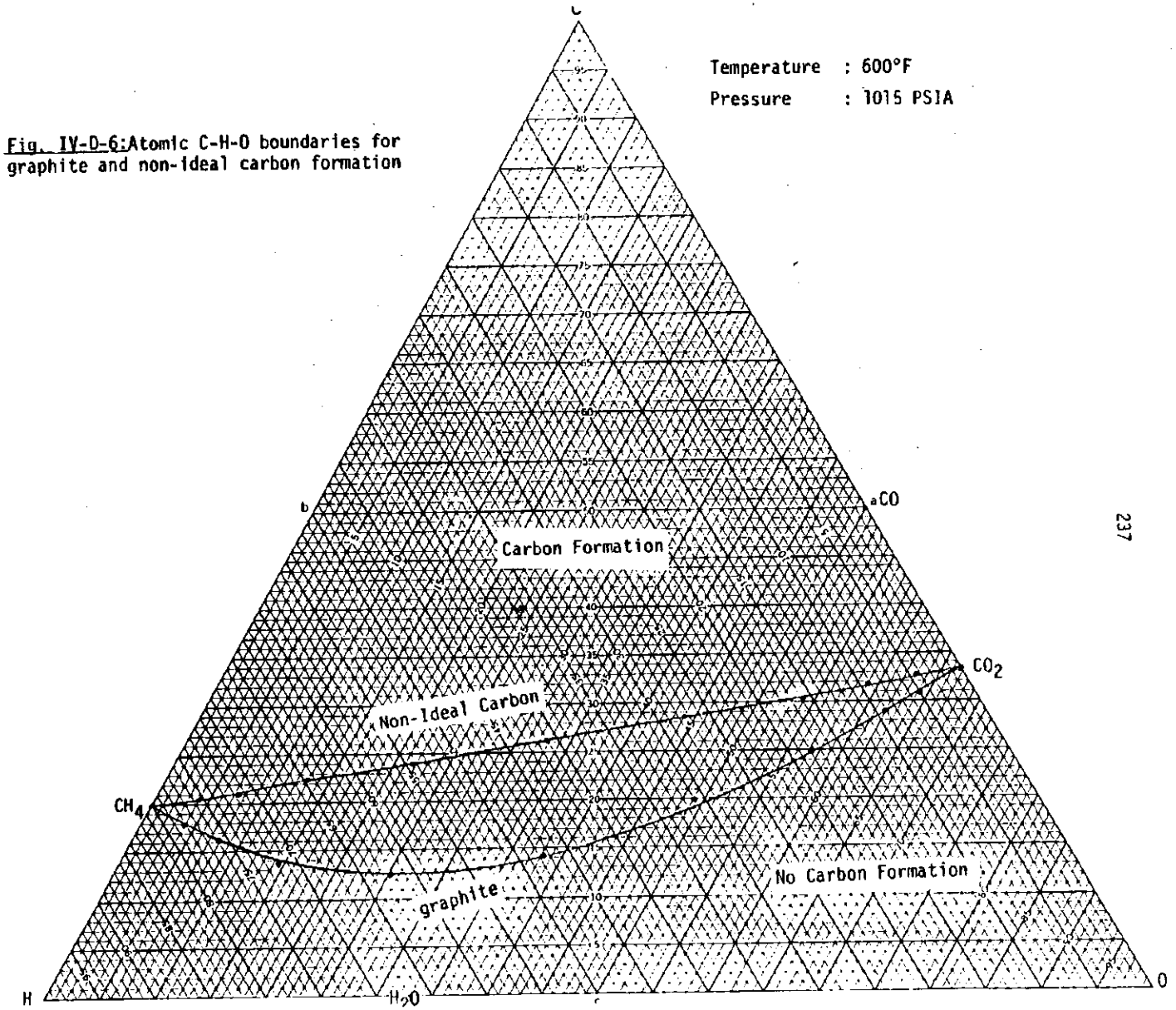


Fig. IV-D-7 Atomic C-H-O boundaries for graphite and non-ideal carbon formation

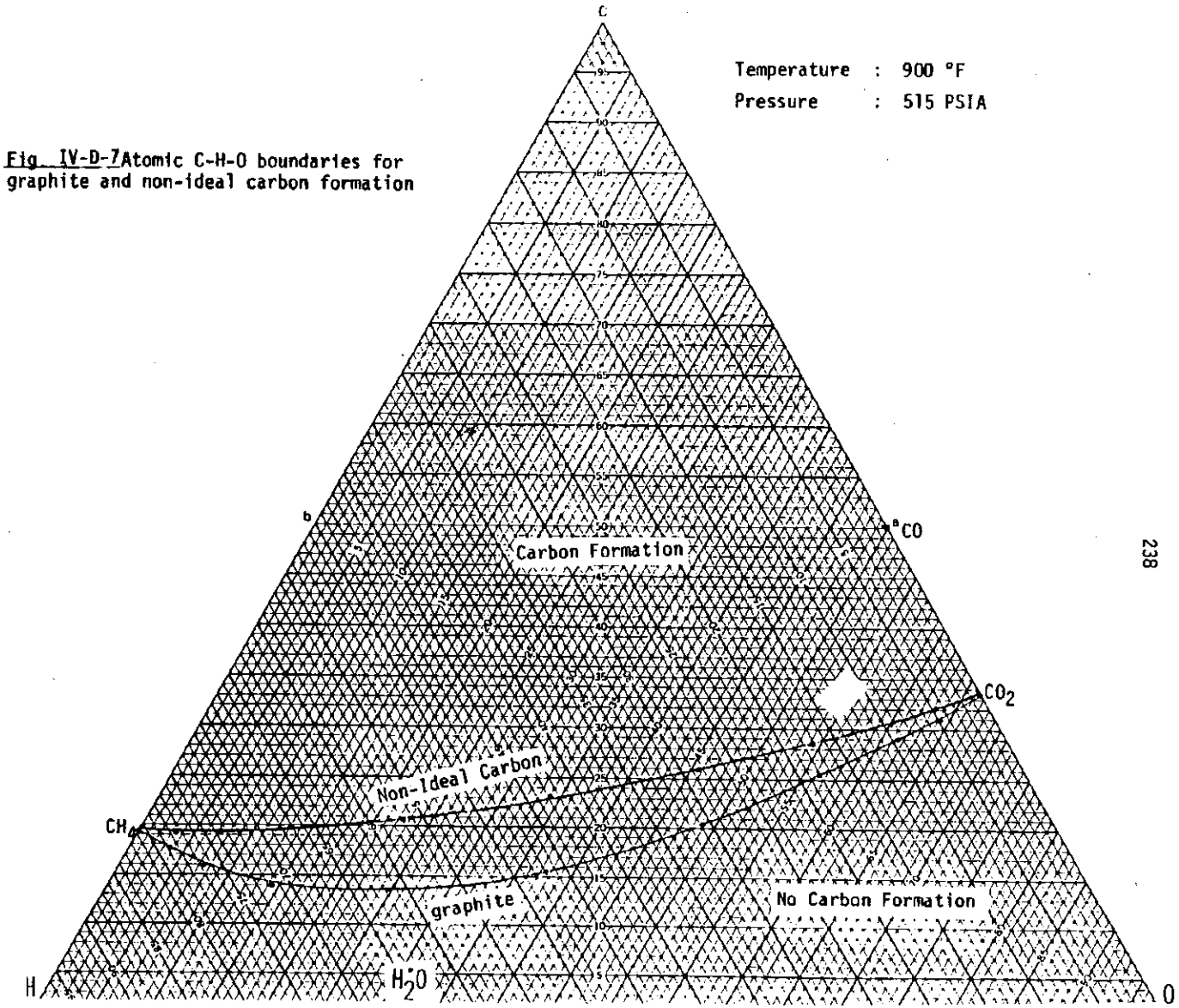


Fig. IV-D-8 Atomic C-H-O boundaries for graphite and non-ideal carbon formation

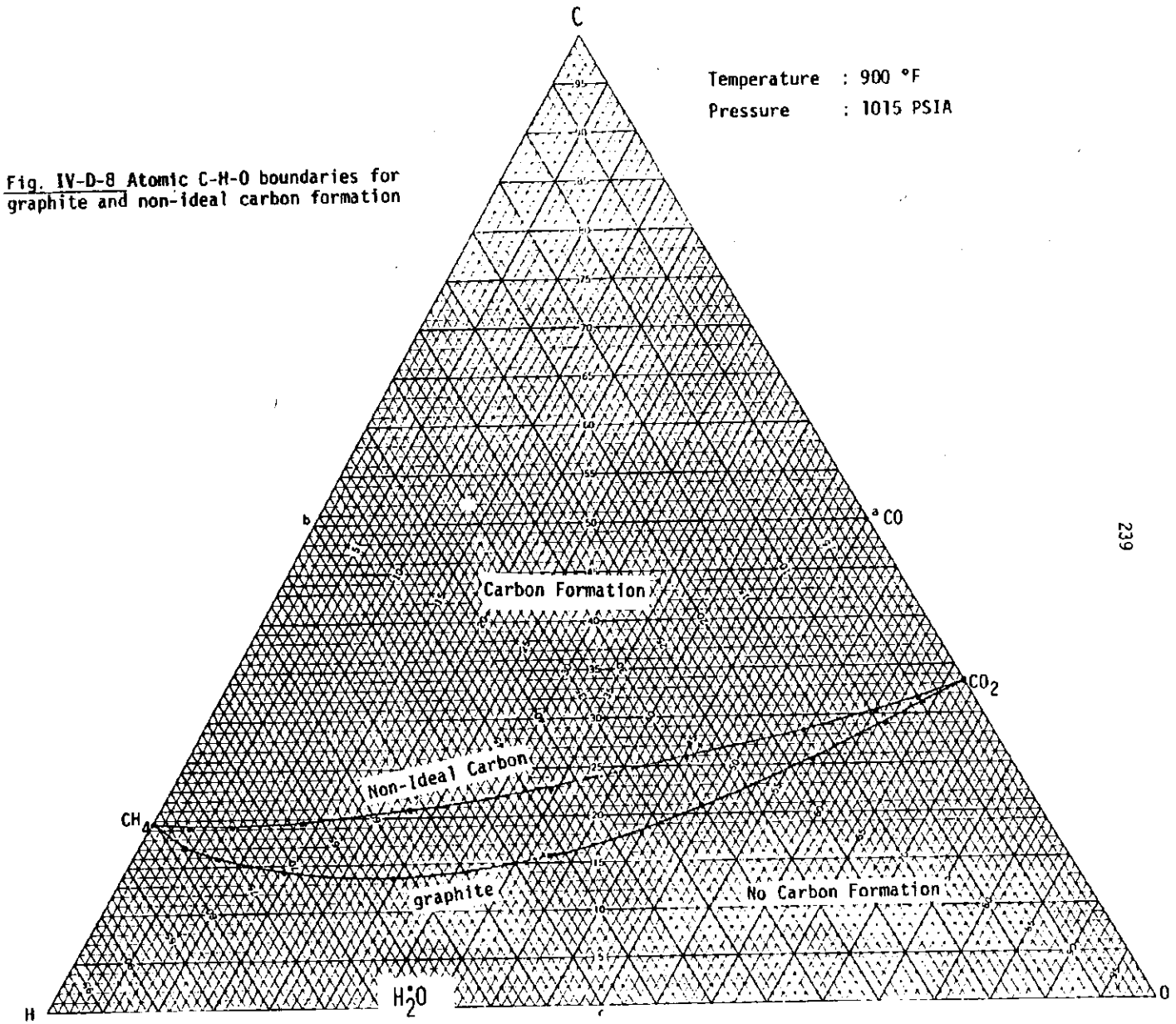
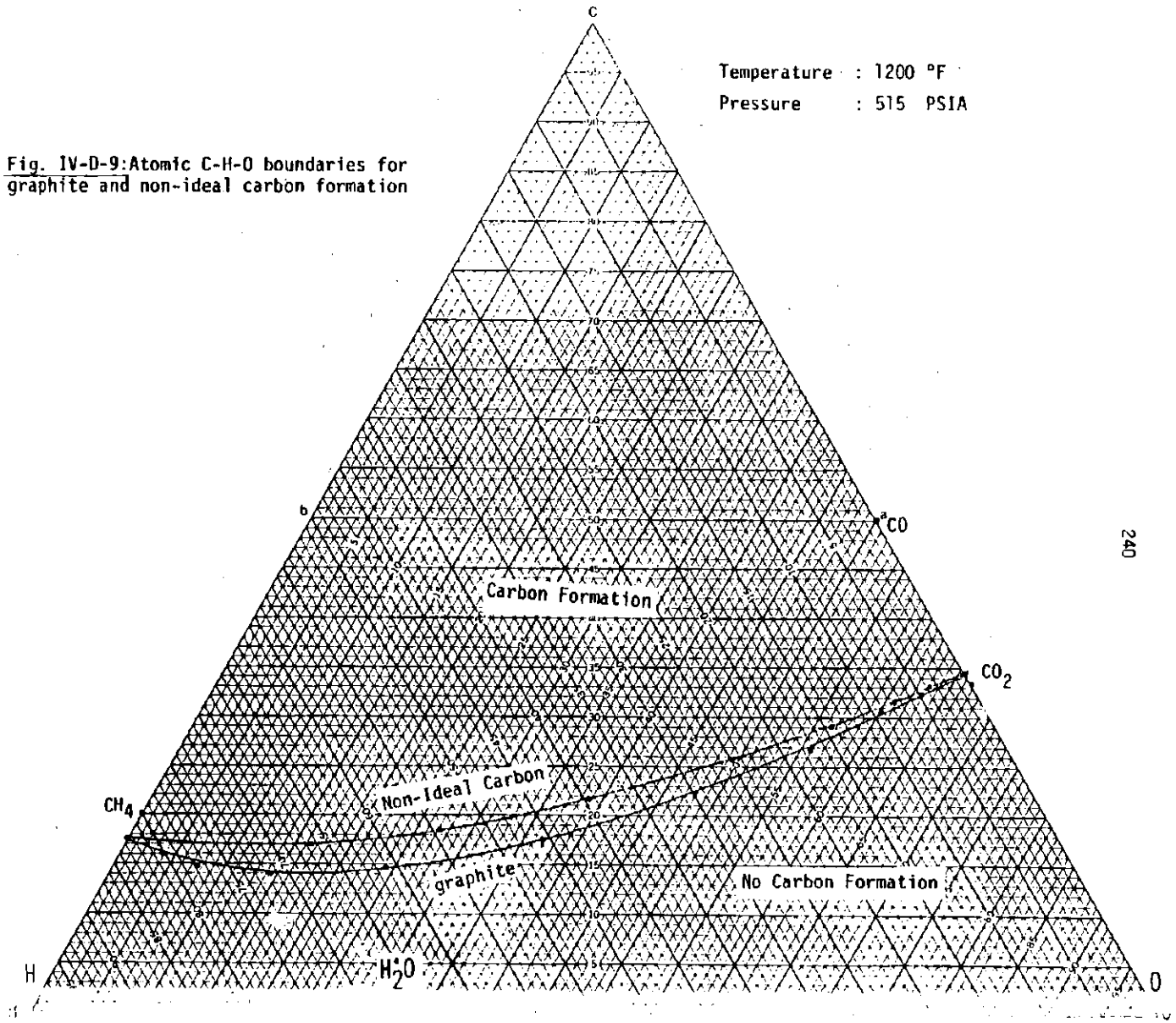


Fig. IV-D-9:Atomic C-H-O boundaries for graphite and non-ideal carbon formation



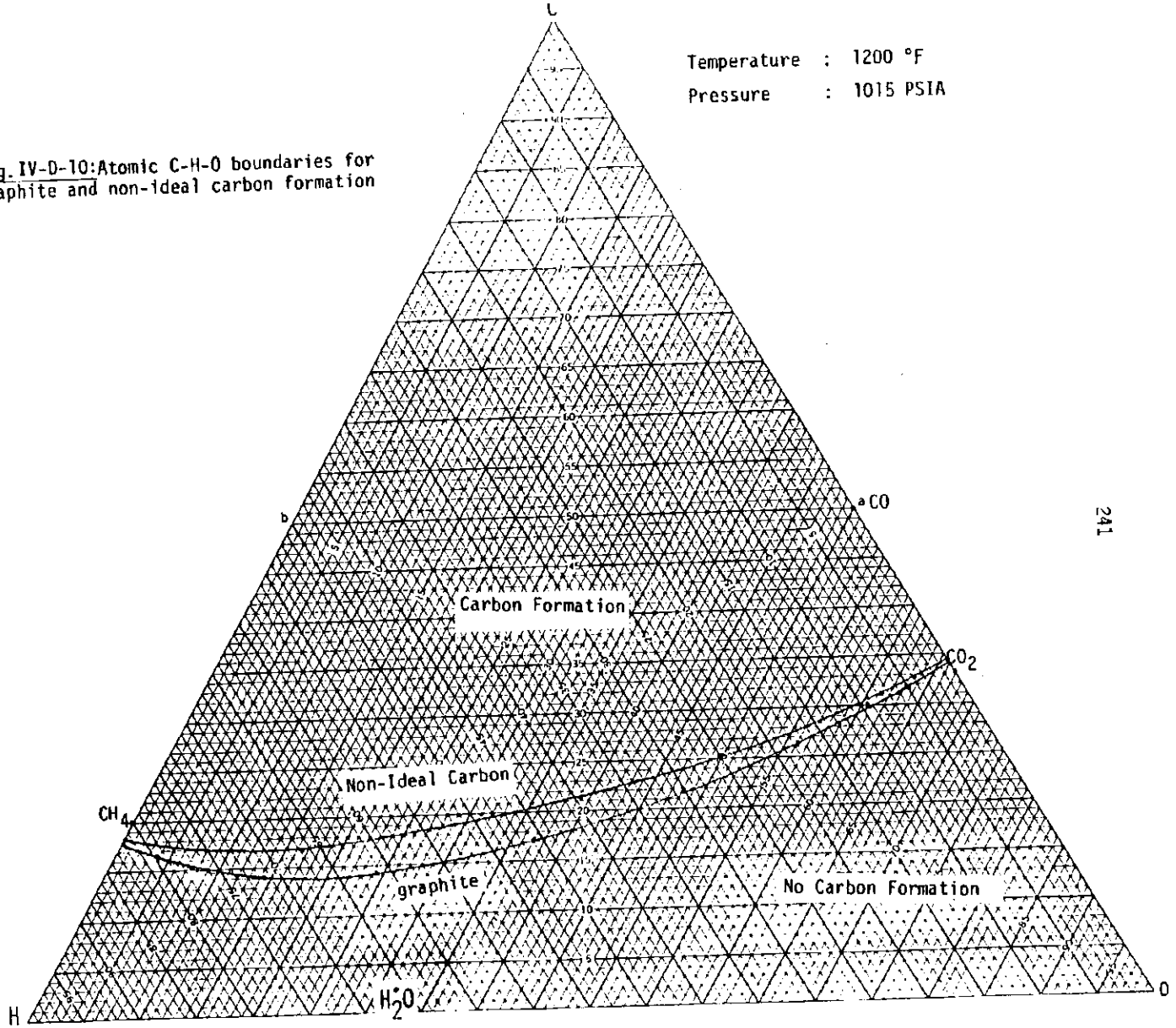


Fig. IV-D-10: Atomic C-H-O boundaries for graphite and non-ideal carbon formation

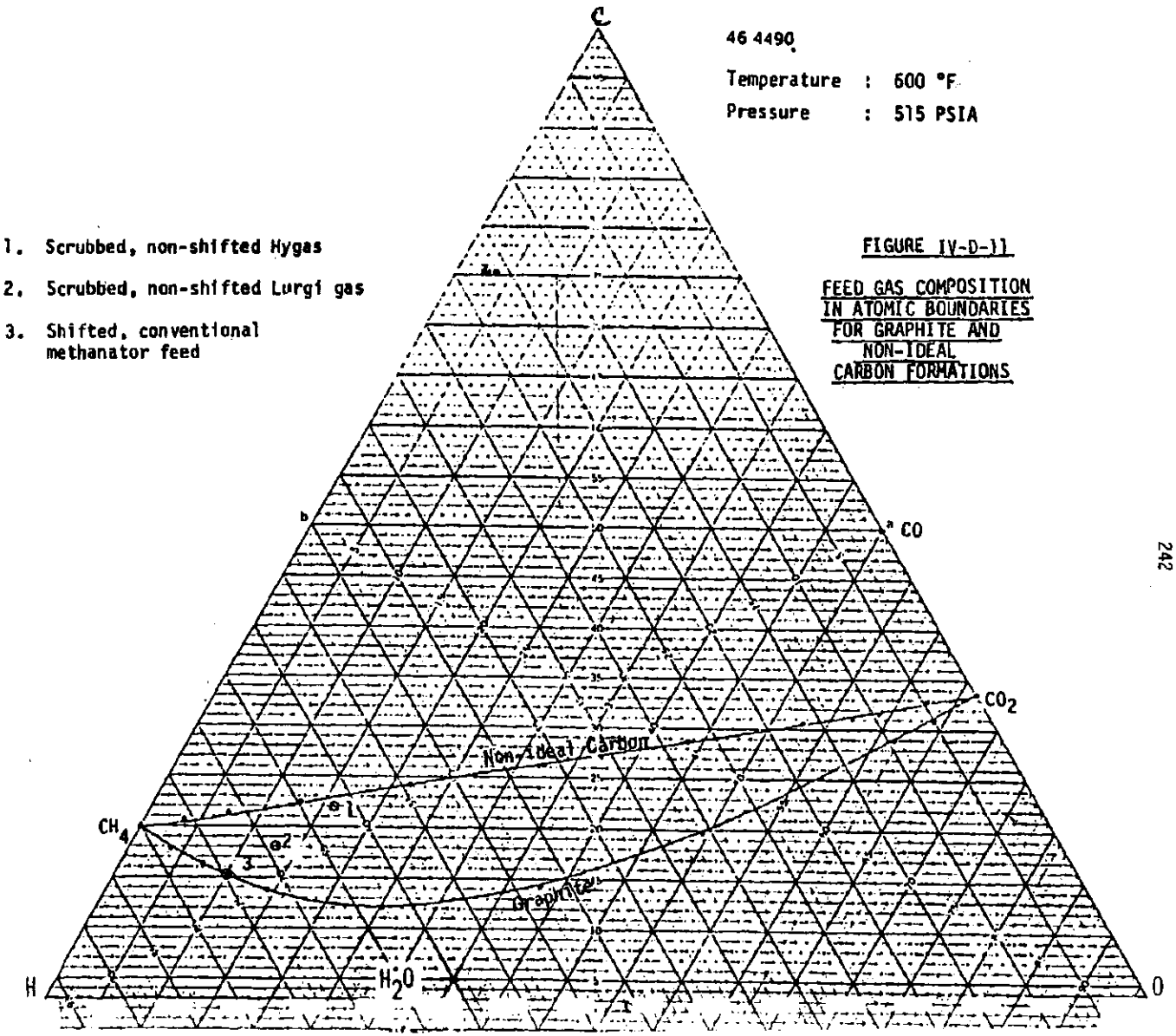


FIGURE IV-D-11

FEED GAS COMPOSITION IN ATOMIC BOUNDARIES FOR GRAPHITE AND NON-IDEAL CARBON FORMATIONS

In formulating the feed composition, it may be necessary to shift the proportions of CO, CO_2 and CH_4, depending upon the carbon oxide limitations. The atomic C-H-O distribution would remain unchanged.

c. Tests were to be carried out at 600, 900 and 1200°F. It was throught that a problem might arise at the 1200°F operating temperature because of the physical limitations of most currently available methanation catalysts. In this case, special high-temperature catalyst, if available, would have to be used. Initially, all tests would be run at 500 psi since the atomic C-H-O boundaries of carbon formation are far less sensitive to pressure than to temperature. Each test would be limited to 500 hours of continuous operation. After the first series of tests was completed, a second and third series would be run to investigate the effects of time (up to 1200 hours) and pressure (up to 1000 psi) on the rate of carbon deposition.

d. Tentatively, two different catalysts would be tested in the carbon formation study. The first would be G-87P by United Catalyst (previously Girdler). The second catalyst would be Ni-104T by Harshaw Chemical. Both catalysts would be analyzed for Ni content and Ni crystallite size, which will be the criteria for catalyst characterization.

e. Steam injection is needed to bring the feed gas composition out of nonideal carbon or graphite forming regions. As shown in Figure IV-D-11, under operating conditions of 600°F and 500 psi, all three feed gases are outside of the nonideal carbon formation region but within the graphite formation region. Operating without steam injection will theoretically form graphite for all feed gases. Graphite-free operation is achieved by injecting enough steam to the feed gas so that the atomic

C-H-O fraction is moved outside the graphite formation boundary. It is possible that nonideal carbon will form at higher pressures and temperatures using the same feed gases, since the region between nonideal carbon and graphite formation boundaries become narrower.

It was originally proposed to adopt three different steam injection levels to each feed gas for operation in each of three regions (nonideal carbon, graphite, and non-carbon forming). The revised steam injection levels include: (1) 0 percent steam (dry basis); (2) 5 percent steam, to study the effect of low-level steam while still operating in the carbon forming region; and (3) 30 percent (or more if needed), to bring the final feed composition out of the carbon forming regions. Using scrubbed nonshifted Lurgi gas, the feed composition with three different steam levels are illustrated in Figure IV-D-12 at 500 psi and 600°F. To operate in the graphite-free region requires more than 30 percent steam injection. Operating at higher temperatures requires less steam to bring the feed composition out of the carbon forming region as illustrated in Figure IV-D-13.

f. After the proper carbon oxide content in the feed gas has been determined, the following series of tests would be conducted:

1. Scrub nonshifted Lurgi gas (C:H:O: = 0.18:0.69:0.13) to be run at 500 psi for 500 hours of continuous operation with G-87P catalyst. Five sets of conditions are run simultaneously in the five reactor units:

	Temperature		
Steam	600°F	900°F	1200°F
0%	X	X	
5%	X	X	
30%		X	

1-A. Scrubbed, non-shifted Lurgi gas -- 0% steam

1-B. 5% steam

1-C. 30% steam

1-D. 40% steam

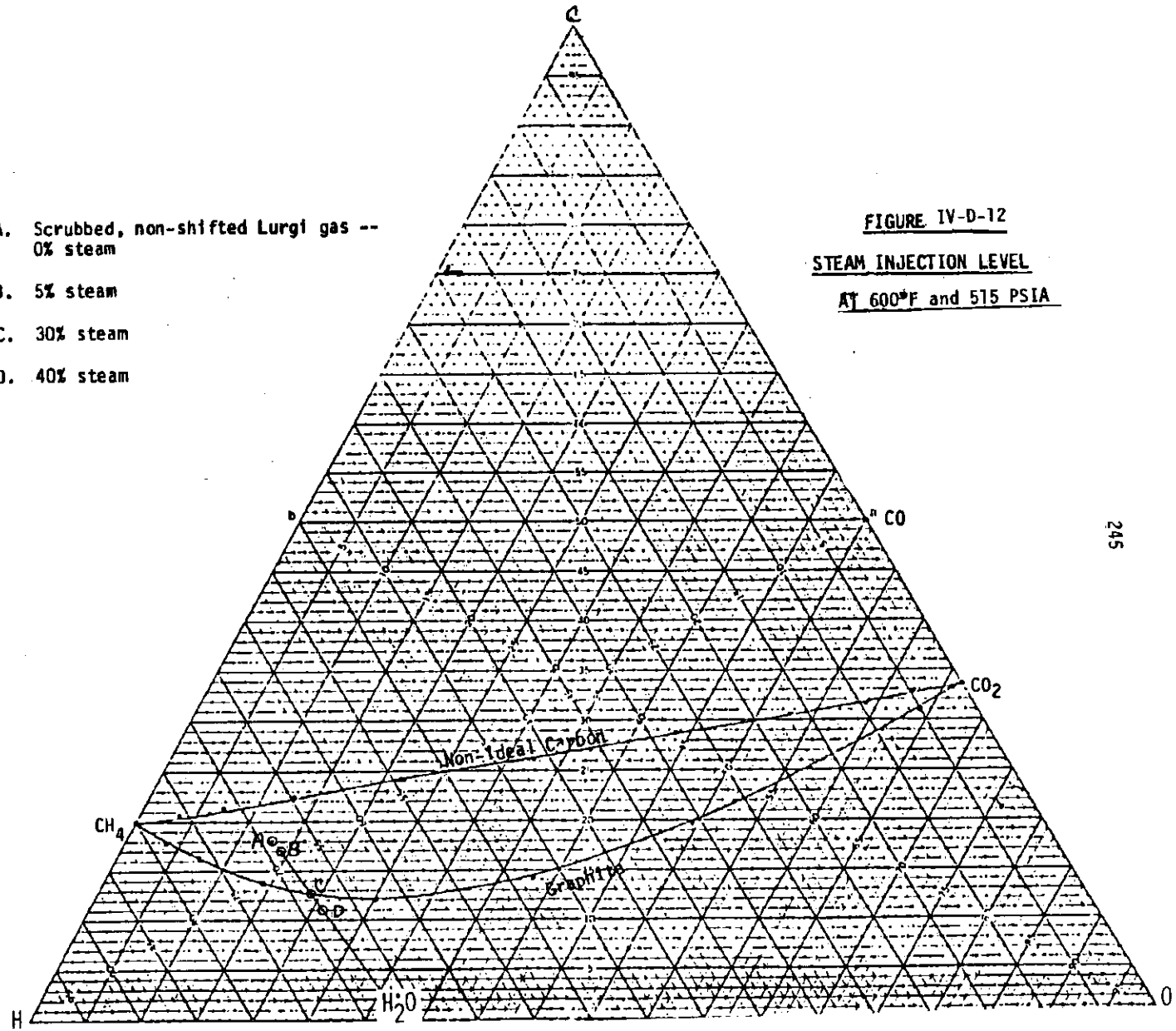
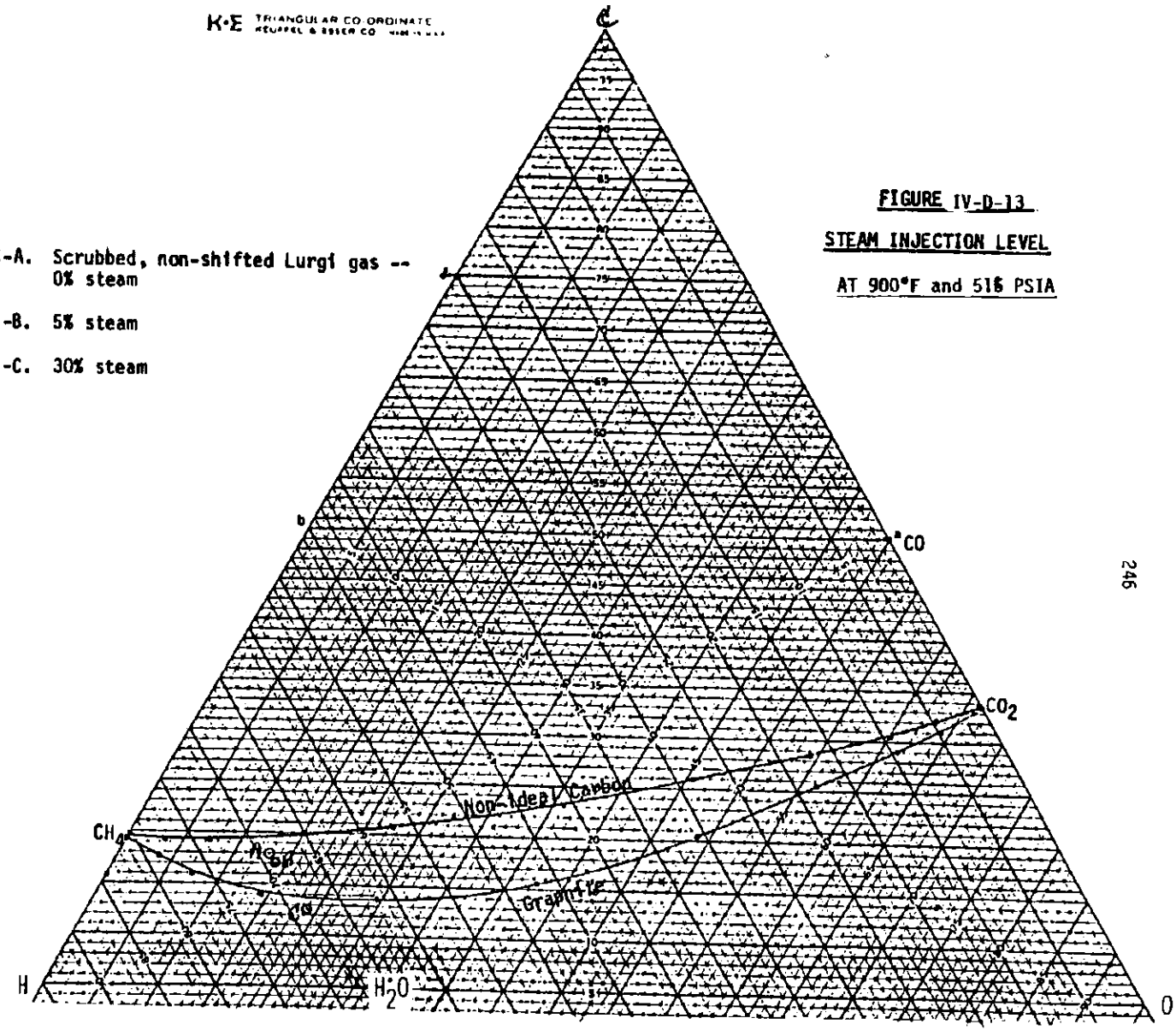


FIGURE IV-D-12

STEAM INJECTION LEVEL

AT 600°F and 515 PSIA



1-A. Scrubbed, non-shifted Lurgi gas -- 0% steam

1-B. 5% steam

1-C. 30% steam

FIGURE IV-D-13

STEAM INJECTION LEVEL

AT 900°F and 516 PSIA

After 500 hours, each section of all five catalyst beds would be analyzed for carbon deposition and Ni crystallite size change.

2. Under experimental conditions at which carbon formation is observed, tests would be repeated for time variations of 100, 300, 600, 900 and 1200 hours.

3. In order to follow the level of activity during carbon laydown, one unit would be set up as an incremental nonequilibrium reactor using a high space velocity and operated as in item 2. above.

4. A catalyst sample that has lost activity because of carbon laydown would be selected from the above experiments and carefully regenerated. The reaction would then be repeated under the same conditions and the catalyst activity compared to that in the initial test.

5. Appropriate conditions for a test at 1000 psi would be selected and run.

6. If a high-temperature catalyst is available, a test would be conducted at 1200°F.

Steps 1 thru 8 will be repeated with the second catalyst.

g. Two more similar series of tests would be carried out using scrubbed nonshifted HYGAS (C:H:O: = 0.22:0.62:0.16) and shifted conventional methanator feed gas (C:H:O = 0.15:0.75:0.10).

The first series of exploratory runs was conducted to test the stability and performance of the individual reactor units and the system as a whole.

Reactors 1, 2, 3 and 4 were loaded with 100 ml catalyst (3//32" dia. X 3/32" tablets), equivalent to a 12" bed in the 18" long catalyst basket. The remaining space was filled with inert alumina beads from Rhodia, (SCS-9, 2-4 mm dia.) to form a pre-heat and pre-mix zone. The catalyst was then reduced in a manner similar to that used in the PDU. All reactors were then kept under nitrogen flow at 2 L/min, and the reactor temperature was maintained at 315°C, well above the initiation temperature of the methanation reaction.

The feed gases for these runs contained only hydrogen, carbon monoxide and nitrogen. Reactors 1 and 2 were switched to 2 percent CO (6 percent H_2, N_2 balance) feed gas, and Reactors 3 and 4 were switched to 4 percent CO (12 percent H_2, N_2, balance) feed gas at 2 L/min and 1 atm. Both reactor pressure and feed rate were gradually raised. The final reactor pressure was set at 500 psig, with a feed rate of 6.7 L/min (equivalent to 4000 v/v/hr versus the intended 10,000 v/v/hr). Reactor 2 developed a serious leak along the feed inlet line, and Reactor 3 ruptured the high pressure regulator diaghram. Both reactors were shut down for repair.

The temperature profile was monitored via three stationary thermocouples at the top, middle and bottom of each of each catalyst bed. The feed and product gases were continuously analyzed throughout the run. Total conversion of CO was obtained. Visual examination showed no signs of spent catalyst deterioration.

A standard operating procedure for each reactor unit was established in the course of these runs. The hot spot, usually located at the entrance region of the catalyst bed, could not be precisely detected with the stationary thermocouple probe although a temperature rise at this entrance area was measured. No attempt was made to control the exothermic heat release. All reactors were insulated with 2" thick Tempa-Mat blanket to simulate adiabatic conditions.

The second series of runs was conducted with 4 percent and 6 percent CO ($3H_2/CO$, N_2 balance) feed gas in order to measure the temperature profile in detail and to control the temperature rise within the operating limits. Reactors 1 and 2 were loaded with 100 ml fresh catalyst and reduced accordingly. The preheat zone temperature was adjusted to 260-280°C, just over the catalyst initiation temperature. The feed rate was increased stepwise to the final rate of 8820 v/v/hr at 500 psig. A travelling thermocouple measured the temperature profile at 2" intervals from the top of the inert zone to the bottom of the catalyst bed.

With 6 percent CO, the initial profile was measured at 4800 v/v/hr. The hot spot (460°C) was located at 2" from the top of the catalyst bed. Increasing the feed rate to 6600 v/v/hr caused the hot spot temperature to rise sharply to well over 600°C. The insulation covering the catalyst bed section was taken off to dissipate the exothermic heat. The profile then stabilized, and after 30 minutes the hot spot temperature was 450°C. Next, when the preheat zone temperature was lowered about 50°C and the feed rate increased to 8820 v/v/hr, the hot spot temperature dropped to about 400°C. It is conceivable that the catalyst may have been damaged by the extremely high temperature, which surpassed the manufacturer's suggested limit. However, the constant location of the hot spot at 2" from the top of the catalyst bed seemed to indicate otherwise.

With 4 percent CO, the feed rate was raised to 5700 v/v/hr. The hot spot measured 430°C with the insulation on and 360°C with the insluation removed. The profile resembled that of 6 percent CO feed. The lower hot spot temperature was due primarily to the lower flow rate and the lower CO concentration in the feed. At the end of these tests, both reactors were depressurized and kept under a low nitrogen flow.

The third and last series of preliminary runs attempted to increase the space velocity to the desired level of 10,000 v/v/hr. An effort was made to inject some steam into the reactor merely to prime the metering pumps and establish the operating procedure.

First, Reactor 1 was pressurized to 500 psig and the space velocity increased gradually to 10,000 v/v/hr. A stabilized profile measured at 1" intervals showed that the hot spot was 460°C, 2" below the top of the catalyst bed. Increasing the feed inlet temperature from 270°C to 320°C raised the hot spot temperature to 510°C and shifted its location to 1" below the top of the bed. Decreasing the feed inlet temperature to 200°C (with water injected at 19 mol percent) moved the hot spot 4" below the top of the catalyst bed and stabilized its temperature at 400°C.

Reactor #2, operating at 500 psig and 10,000 v/v/hr exhibited a similar initial profile. When the temperature at its feed inlet was lowered stepwise, the hot spot moved progressively down through the catalyst bed but maintained a constant temperature of 420°C, indicating that part of the catalyst bed was functioning as a preheat zone to raise the feed inlet temperature above the ignition temperature of methanation reaction. No significant change in profile was observed when water was pumped in at 21 mol percent.

The spent catalyst taken from Reactor #1 showed some effects of the excessive temperature in the top section of the catalyst bed, which was probably the result of previous runs with 6 percent CO feed. The spent catalyst from Reactor #2 showed no sign of damage.

At the conclusion of these runs, the following points were noted so they would be implemented in future runs:

a. The maximum reactable carbon oxide content in the feed should be no more than 4 percent to maintain the desired temperature profile of the reactor.

b. In order to maintain a more uniform temperature profile, the insulation must be taken off the catalyst zone. This will dissipate some of the exothermic heat of reaction.

c. The feed inlet temperature at the entrace of the catalyst bed should not be used to control the temperature profile but must always be maintained above the ignition temperature of methanation, i.e., 260-280^{o}C. If not, part of the catalyst bed will act as a preheat zone that raises the feed temperature to the ignition temperature.

d. The most effective method of starting a reactor after catalyst reduction is to pressurize with nitrogen to the operating pressure before switching to feed. The feed rate should be raised slowly to the final 10,000 v/v/hr.

e. The temperature profile should be measured at 1" intervals to pinpoint the hot spot.