B. Experimental Program at the HYGAS Pilot Plant

1. Run #1

During the week of March 6, 1977, the Calsicat Ni-230-S catalyst was reduced using the HYGAS hydrogen stream containing 1-2% CO. Heat-up of the hydrogen was accomplished without the use of the hydrogen exchanger. The reactor was heated to 800°F. Since the catalyst was pre-reduced, hydrogen was fed at this temperature for only four hours. The bed was then cooled to 550°F.

The circulating oil system was started up and heated to 550°F and oil slowly introduced to the reactor. The system was stabilized with low flows of oil and remained in this "ready state" awaiting either HYGAS gasifier product or hydrogen reformer gas. A complete summary of events for Run #1 is presented in Table IV-B-1.

During the first 600 hours of hot oil circulation, three sets of filters plugged with catalyst fines carried out of the reactor. This was estimated to have caused a ten percent loss, normal for fresh catalyst. There was considerable dust when the catalyst was charged to the reactor, which eventually worked its way out of the system. After the first 300 hours, no further catalyst losses were observed.

At hour 138, it was learned that both HYGAS and the hydrogen plant would be shut down for repairs. Gas feed was, therefore, switched to a low flow of HP nitrogen and the system was maintained at 200 psi.

While waiting for gas, liquid only catalyst fluidization studies were performed. The fluidization curves at four temperatures ranging from 450°F to 600°F are shown in Figure IV-B-1. Oil velocities ranged from 0.1 to 0.2 ft/sec. These curves are generally similar to those

TABLE IV-B-1

SUMMARY OF EVENTS FOR PILOT PLANT RUN #1

Hour	Accumulated Reaction Time (Hrs.)	
0	0	Nitrogen heat-up of catalyst to 500°F on 3/9/77.
15	0	Catalyst bed at 680°F. Start hydrogen reduction with 20,000 SCFH of hydrogen.
29	0	Reached 800°F in catalyst bed.
33	0	Reduction completed. Cooling bed to 550°F with hydrogen...
47	0	Lowered hydrogen flow to 10,000 SCFH.
66	0	Integrated heated oil into reactor and stabilized at 500°F, 100 psi and 182 gpm oil flow.
75	0	First filter plugged. Approximately 25 lbs. of catalyst was removed. Switched to second filter, lowered gas flow to 6,000 SCFH and oil flow to 144 gpm.
110	0	Second filter plugged with approximately 30 lbs. of catalyst and oil. Cracked bypass to keep pressure drop at 10 psi.
118	0	Third filter on-stream and bypass closed.
138	0	Switched to HP nitrogen flow at 5,000 SCFH and shutdown reduction system. Increased pressure to 200 psi.
158	0	Started liquid-only fluidization studies.
185	0	Completed fluidization studies.
190	0	Reduced system pressure to 100 psi and switched to L.P. nitrogen. Reactor gas by-pass line installed and in use.
282	0	Third filter plugged. Switched to fourth filter.

TABLE IV.B.1 (Continued)

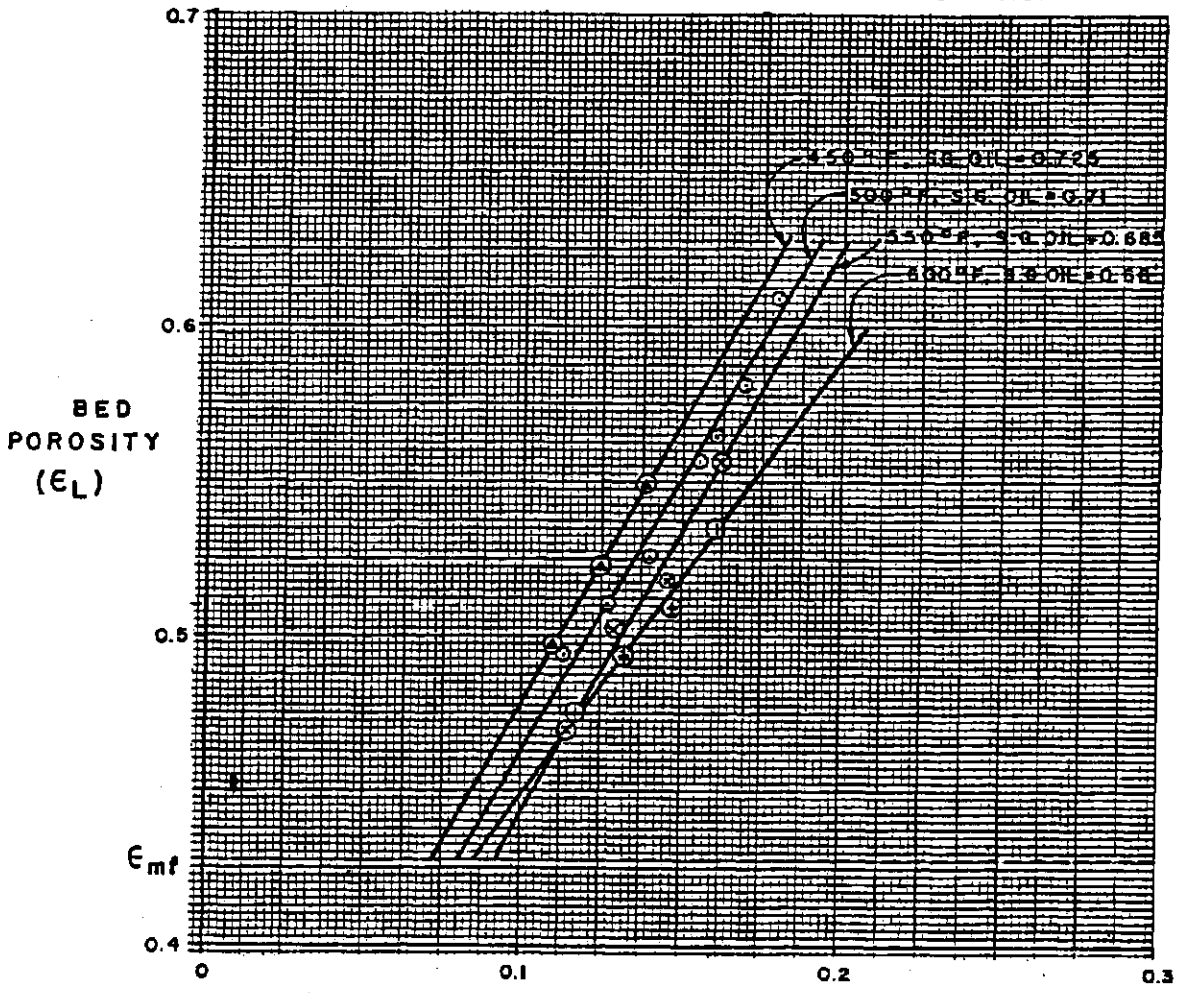
572	0	Switched to HP nitrogen and maintained at 465°F and 100 psi.
615	0	Raised reactor to 550°F and 300 psig.
626	0	Started HYGAS feed to system.
629	3	At 570°F and 500 psig, HYGAS upset sent DGA through system.
781	3	Raised reactor to 550°F and 300 psig.
788	3	Started feeding hydrogen reformer gas to system.
813	28	Stopped Feeding hydrogen reformer gas to system. Stopped reformer gas flow and began cooling down unit. End of Run #1.

FIGURE IV-B-1

BED POROSITY VS. LIQUID VELOCITY

LPM PILOT PLANT RUN #1

FREEZENE - 100 OIL
CALSICAT Ni-2305 CATALYST



SUPERFICIAL OIL VELOCITY (U_L)

(Ft. / Sec.)

CHEM SYSTEMS INC.
PROJECT NO. 664 DATE

generated earlier during fluidization studies in the Process Development Unit. Combined gas-oil fluidization was to be studied concurrent with with the process variable scans.

At hour 190, it was learned that HP nitrogen would also be blocked off throughout the HYGAS plant. System pressure was reduced to 100 psi and held by LP nitrogen. Simultaneously, a gas by-pass line around the reactor was installed so that gas would not disturb the catalyst until process gas became available.

On April 4th, HYGAS product was fed to the unit for the first time. This gas contained approximately 40%, H_2, 32% CH_4, 19% N_2 and 9% CO. The reactor was in the process of heating up when, after three hours, the HYGAS feed abruptly stopped due to malfunctions in the HYGAS clean up section. This was followed by a large slug of diglycol amine which entered the LPM unit without warning. Feed to the LPM unit was immediately halted and the unit was returned to a standby mode until the extent of the damage could be determined. Meanwhile, a single data point was salvaged for on-stream hour #2 (Table IV-B-2). At 500 psig and 560°F, the temperature was still rising, but a CO conversion of 81.5% was obtained. The gas space velocity was 2,060 Hr^{-1} and the H_2/CO mole feed ratio was 4.6. A kinetic rate constant corrected to 650°F of 1.47×10^{-6} lb-mol/(atm-lb catalyst-sec) resulted from the analysis which is comparable to the kinetics obtained in the Process Development Unit.

Immediately after the DGA upset, a liquid sample from the inlet feed gas line and a circulating oil sample were sent to outside contacts* for independent rapid sulfur analysis. The DGA in the feed line contained 1,000 ppm sulfur, whereas the circulating oil showed 0.5 ppm sulfur.

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* The analytical Department of Peoples Gas Light & Coke Co. SNG Plant, at Elwood, Illinois was most helpful in providing these analyses.

TABLE IV-B-2

LPM PILOT PLANT

RESULTS FROM RUN #1

CALSICAT Ni 230 S* /FREEZENE 100 OIL

Hour	Accumulated Reaction Time (Hrs)	Temp. (°F)	Pressure (PSIG)	Oil Flow Rate (GPM/FT^2)	VHSV (HR-^{1})	CO Conversion (%)	FEED H_2/CO Ratio	K_{T_R} (X10^6)	K_{650} (X10^6)
628	2	560	500	51.6	2,060	81.52	4.56[2]	0.72	1.47
789	4	559	500	51.6	3,000	78.66	9.83[3]	0.44	0.68
790	5	573	500	51.8	3,010	80.80	10.31	0.41	0.59
792	7	599	500	52.5	2,990	82.53	10.10	0.44	0.56
793	8	600	500	52.5	2,980	80.98	10.00	0.44	0.55
794	9	598	500	52.5	2,970	79.42	10.00	0.42	0.53
796	11	599	500	52.5	2,950	77.66	10.08	0.40	0.51
799	14	581	500	52.0	2,900	72.74	9.03	0.37	0.51
802	17	574	500	51.8	2,940	71.08	9.28	0.35	0.51
803	18	559	500	51.6	2,950	71.72	9.34	0.35	0.55
804	19	569	500	51.8	2,940	72.91	9.34	0.37	0.54
805	20	550	500	51.6	2,930	74.11	9.40	0.38	0.62
806	21	551	500	51.6	2,930	76.44	9.43	0.41	0.66
807	22	550	500	51.6	2,920	76.44	9.43	0.41	0.67
808	23	552	500	51.6	3,450	71.52	9.43	0.41	0.64
809	24	590	500	52.2	3,450	77.59	9.39	0.49	0.64
810	25	650	500	53.6	3,450	85.63	9.32	0.65	0.65
811	26	647	500	53.6	2,920	84.03	9.22	0.51	0.51
812	27	649	500	53.6	3,000	83.00	9.26	0.50	0.50
813	28	SHUTDOWN							

* 496 LBS. OF CATALYST LOADED (8.3 FT^3).

1 REACTOR ID = 22.5 INCHES

2 HYGAS FEED: 39.8% H_2, 19.4% N_2, 31.7% CH_4, 8.5% CO AND 0.6% C_2H_6 (AVERAGE ANALYSIS).

3 REFORMER FEED: 89.0% H_2, 0.9% N_2, 0.7% CH_4, AND 9.4% CO (AVERAGE ANALYSIS).

The latter indicated that any sulfur which entered the system had already absorbed on the methanation catalyst. The DGA also got into the analytical system, destroying chromatograph columns and requiring extensive and thorough cleanup of the sampling system. It was decided to maintain the LPM Pilot Plant in a standby mode until steam-methane reformer gas could be supplied in order to study the extent of the damage done by the DGA upset on the catalyst activity.

On April 11, 1977, steam-methane reformer gas was supplied to the pilot plant for a period of 25 hours. This gas had the nominal composition: 89.0% H_2, 0.7% CH_4 and 9.4% CO. With the pressure held at 500 psig, reactor temperature was varied from 550°F to 650°F and gas space velocities ranged from 2,900 to 3,500 Hr^{-1}. The results are presented in Table IV-B-2.

The effect of temperature on the kinetic rate constant is plotted in Figure IV-B-2 for all data based upon steam-methane reformer feed gas. An activation energy of approximately 6,000 cal/gm-mole was calculated, which is considerably lower than expected for this catalyst, based upon PDU and bench scale results. The lower activation energy can be attributed to either sulfur contamination or an axial diffusion effect. This point was to be further resolved during subsequent runs. The kinetic rate constant corrected to 650°F ranged from 0.5-0.7 x 10^{-6} lb-mol/(atm-lb catalyst-sec), which is approximately 40 percent of the single value obtained before the DGA upset. Catalyst activity versus time is plotted in Figure IV-B-3 for all of Run #1.

Upon completion of the tests with reformer gas, the pilot plant was shut down. This decision was based primarily upon the scheduled shut downs of both HYGAS and the hydrogen plant for a period of two weeks. During the turnaround, required maintenance was performed and some new equipment and modifications to the unit were completed and installed. Also, the opportunity was utilized to replace the possibly deactivated catalyst with a fresh batch before starting Run #2.

FIGURE IV-B-2

TEMPERATURE EFFECT ON KINETIC RATE CONSTANT

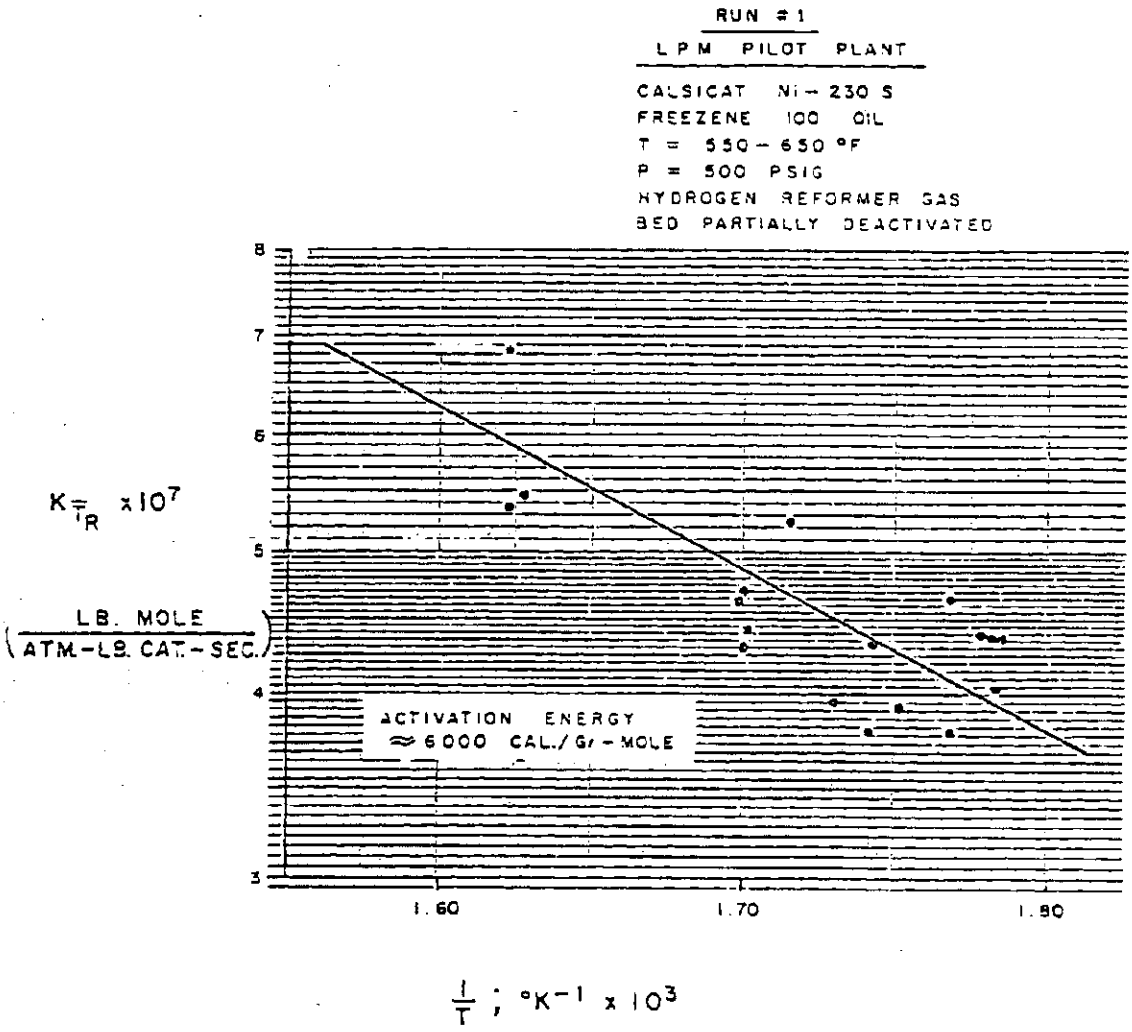


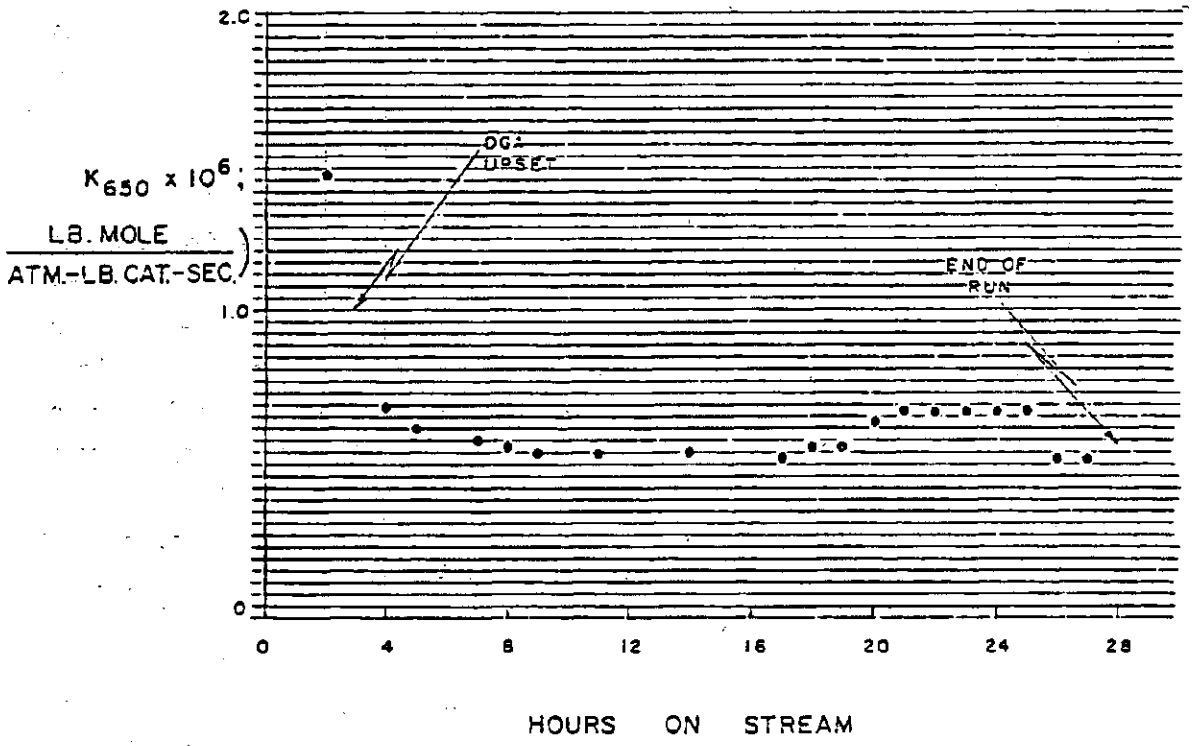
FIGURE IV-B-3

CATALYST ACTIVITY VS. TIME

L P M PILOT PLANT

RUN # 1

CALSICAT Ni 230 S
FREEZENE 100 OIL



The used catalyst from Run #1 was removed from the reactor on April 20, 1977, after first flooding the reactor with water. No problems were encountered and most of the inerts were removed at the same time. Samples of the catalyst and inerts were sent to Chem Systems' Fairfield Laboratory for analysis. The reactor was then washed thoroughly with water to eliminate residual catalyst that might have been sticking to the walls.

The circulating oil cooler by-pass valve was taken apart and a solid plug of dirt was found inside which had caused the by-pass line to be non-functional. Some dirt had also fallen into the cooler. In order to open the cooler, two lines had to be cut and flanges were welded at these cuts to facilitate opening the cooler in the future. The cooler was cleaned out and thoroughly inspected.

The remainder of the month was occupied with mechanical and maintenance work. Process oil and seal flush filters were changed. The demister was installed. The product gas sample line was relocated to a position where condensed liquids would not enter. The vapor leg to the reactor separator level transmitter was extended so that liquids would not splash into the line and accumulate. Orifice taps on the BFW line, oil make-up line and oil line to the degasser were relocated downward to prevent vapor entrapment and a weep hole was drilled in the BFW orifice. Transfer hose couplings were welded to the oil and water drains on the product gas separator. Vent connections from the analytical system in the control room were repiped.

All major leaky valves in the pilot plant were repacked and the bonnets tightened. Surface thermocouples at twelve key locations around heat exchangers were installed and limit switches were added to the reactor level detector lift mechanism. An access ladder to the reactor level was fabricated.

A new shipment of 1,500 gallons of Freezene-100 oil was received and stored in the oil make-up drum.