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Concepts of Fundamental Processes Related to Gasification of Coal

Quarterly Progress Report
for the Period July - Sept 1981

MASTER

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Mining and Fuels Engineering
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Published - December 1981

Prepared for the United States
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Project A-1

Single Stage Catalytic Coal Gasification

Faculty Advisor: W.H. Wiser
Graduate Student: Ted Ajax

Introduction

Single stage catalytic coal gasification is an attractive concept as a direct method of producing high BTU gas from coal. This process involves the introduction of a coal-solvent slurry and hydrogen gas into a fixed bed catalytic reactor, which employs a catalyst high in hydrogenation and cracking activity. Steam may also be added to the system. The gas produced will be principally methane. Thermodynamic calculations indicate that this process is essentially autothermal. Since this process utilizes the heat of methanation to a maximum extent, significant overall energy savings can be achieved over the more conventional multi-stage gasification systems.

The primary objective of this research is to optimize the process variables to maximize methane yields. The -200 mesh coal will be slurried in a hydrogen donor solvent, tetralin, in a ratio of 2 parts solvent to 1 part coal by weight. Previous work in this laboratory utilized a solvent to coal ratio of 4 to 1.

The process variables have been set as

Temperature	450 - 550°C
Pressure	1200 - 1500 pis
Residence Time	10 - 30 min

Initially, a sulfided Ni-W/SiO_2-Al_2O_3 catalyst will be used.

Project Status

The gasification system is in place and has been pressure tested. The electrical system has been completed and is functional. The thermocouples and the slurry feed system have been installed. The system is undergoing final shakedown and leak testing. It is now operational.

Future Work

Experimental runs will commence immediately.

Project A-3

Reaction of Aromatic Compounds with Steam

Faculty Advisors: F.V. Hanson
A.G. Oblad
Graduate Student: I.E. Chen

Introduction

The demand for molecular hydrogen and for synthesis gas is rapidly increasing. To meet these demands, steam reforming of natural gas (CH_4) and of naptha is being carried out on a large scale at pressures up to 500 psi, steam to methane (methane equivalent of naphtha) mol ratios of two to four and temperature of 850°C. Supplies of CH_4 and naphtha for use for this purpose are diminishing. Therefore, an extensive program on steam reforming of aromatic compounds such as benzene, substituted benzenes, naphthalene and other aromatics found in coal and coal-derived liquids (CDL) is being carried out. The objectives are (1) to develop a catalyst of suitable activity and sufficient life for these reactions; (2) to determine the conversion and approach to equilibrium as a function of the main variables of the reaction: temperature, pressure, contact time and steam/carbon ratio; (3) to determine reaction mechanisms and (4) to determine the kinetics of the reforming reactions.

The combination of coal liquefaction-steam reforming of CDL could prove to be an important alternative to coal gasification for the production of SNG and hydrogen. An objective of this project is to assess the feasibility of this alternative. Potentially, coal liquids could be reformed directly in a single step to high BTU gas.

Project Status

For the safety and convenience of operation, the apparatus (Figure 1) is composed of two zones; (I) zone is the preheated and reaction zone; (II) zone is the control and product analysis zone. Steam is generated by pumping deionized water through the steam generator. The benzene is pumped into the preheater and combined with the super heated steam at 500°C. The reactor is made of 316 s.s., 30 inch long, 1 inch I.D. The catalyst is placed between 17 and 20 inches from the top and is surrounded by inert, low surface area α-Al_2O_3 1/8 inch cylindrical pellets. A 1/8 inch tube in the center of the reactor is used as a thermocouple well. The thermocouple can be moved up and down to measure the centerline temperature in the reactor. Its heating rate and temperature are controlled by a temperature programmer. A conventional condenser, separator, and liquid collector are attached to the reactor. The gas products pass through a wet test meter. A test sample is taken once the system has reached a steady state, which is about one hour after the benzene has been introduced. The steady state is checked by measuring the flow rate of products and analyzing the product gases.

To achieve uniform packing in the reactor, the α-Al_2O_3 1/8 inch cylindrical pellets and catalyst of 1/8 inch sperical pellets were poured freely into the reactor.[1] The catalyst bed is composed of a mixture of 15 grams catalyst and 30 grams α-Al_2O_3 pellets for better heat transfer, which keeps the temperature drop across the catalyst bed to less than 10°C.

The catalysts were made by impregnation of $Ni(NO_3)_2 \cdot 6H_2O$ and Na_2CO_3 solution on 1/8 inch spherical active alumina pellets and reduced at 700°C with a heating rate of 7.5°C per minute in flowing hydrogen at 85 cc per gram per minute. The nickel surface area of the catalyst is 7.17 m^2/g cat. The composition of the catalyst is 71.4% Al_2O_3, 21.9% Ni and 6.7% Na_2O.

The product gases were analyzed by gas chromatography with a thermal conductivity detector, and the hydrocarbons were double-checked with a flame ionization detector. Liquid products were measured by separating the two phases.[2]

The parameters listed in the tables and figures were calculated in the following manner:

Steam ratio = (moles of H_2O per min)/(moles of benzene per min) x 6.

W/F (contact time) = wt of cat min/cc of feed.

C_6H_6 Reacted (or conversion) (moles reacted per mole of benzene in the feed) = (moles of benzene input-moles of benzene output)/ moles of benzene input.

CO formed (moles formed per mole of benzene in the feed) = (the composition of CO in product gases x the flow rate of product gases)/ (molar volume of CO x moles feeding rate of benzene).

CH_4 formed (moles formed per mole of benzene in the feed) = (the composition of CH_4 in product gases x the flow rate of product gases)/ (molar volume of CH_4 x moles feeding rate of benzene).

CO_2 formed (moles formed per mole of benzene in the feed) = (the composition of CO_2 in product gases x the flow rate of product gases)/ (molar volume of CO_2 x moles feeding rate of benzene).

The experimental results are shown in Figures 2-5. These figures show the conversion of benzene in terms of moles reacted per mole of benzene in the feed and the production of carbon monoxide, methane and carbon dioxide in terms of moles formed per mole of benzene in the feed. The formation of methane at 0 psig is equal to or less than 0.01 mole per mole of benzene in feed. The data were collected at 700°C with a steam to carbon ratio of 3:1.

These data were fitted to a third degree polynomial by regression analysis. These regression coefficients are shown in Table 1.

By application of a simple continuity balance, the rate of reaction can be shown to be the slope of these conversion and production curves. Therefore, the first derivative of these cubic equations indicates the rate of reaction.

Yang and Hougen[3] have shown that the effect of total pressure would be important in determining the mechanism of a solid-gas reaction. The initial rate of reaction is expressed as the coefficient C_1 in Table 1. From Table 1, it shows that the initial rate is similar with respect to the change of total pressure. This indicates that the overall rate is controlled by a step involving desorption of products. Allen[4] got a similar result in the steam-methane reaction. A possible reaction mechanims of steam-benzene reaction has been proposed.

In the proposed mechanism, the absorbed benzene is assumed to be rapidly hydrocracked to methane at the top of the catalyst bed. The above assumption is supported by Rase.[5] Rostrup-Nielsen[6] and Hyman[7] also observed that no intermediates were identified in the steam-naphtha reaction, and Rostrup-Nielsen demonstrated that the rapid methane formation and breakdown of the naphtha occur in the initial part of the reactor.

The stepwise breakdown of the benzene to methane is another possible mechanism proposed by Schnell.[8] This reaction is then followed by the steam-methane reaction and water shift reaction. It is generally accepted that the last two reactions tend to effect complete equilibrium among all the components of the product gases.[6,8,9]

Future Work

The steam reforming of more complex aromatic species and of coal-derived will be conducted.

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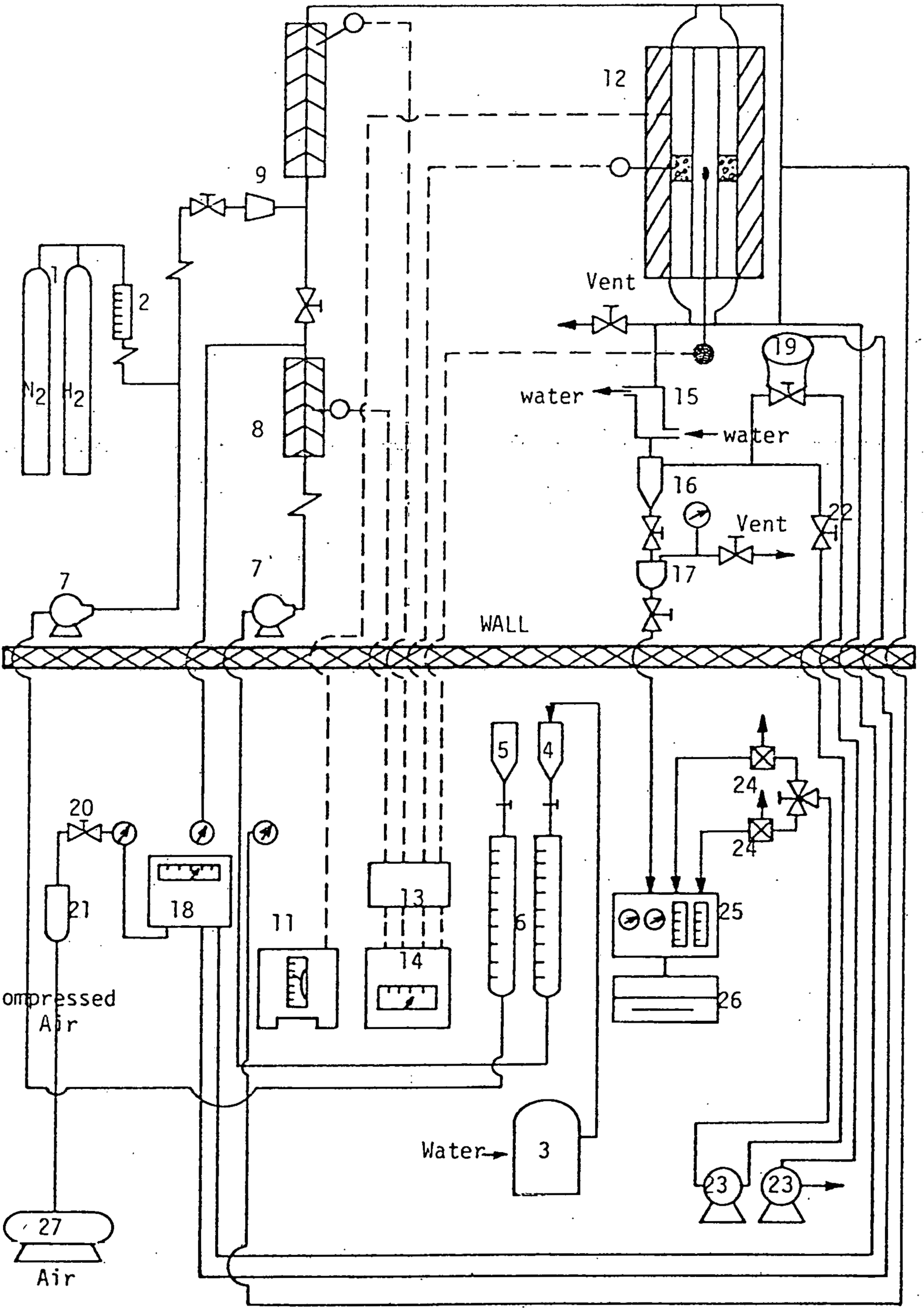
Preheating and Reaction Zone



Control and Product Analyzed Zone

Figure 1. Reactor System

Figure 1. Nomenclature for Reactor System.

1. Gas Cylinder
2. Gas Flow Meter
3. Deionized and Deimpurity System
4. Water Stock
5. Hydrocarbon Stock
6. Burette
7. Controlled Volume Pump
8. Steam Generator
9. Atomizer
10. Preheater
11. Temperature Programmer
12. Reactor
13. Thermocouple Selector
14. Temperature Recorder
15. Condensor
16. Separator
17. Collector
18. Pressure Controller
19. Pressure Controlled Valve
20. Air Pressure Regulator
21. Air Filter
22. Micro-Metering Valve
23. Wet Test Meter
24. Automatic Sampling Loop
25. Gas Chromatograph
26. Autolab Minigrator
27. Air Compressor

Thermocouple

Check Valve

Shut Off Valve

Pressure Gauge

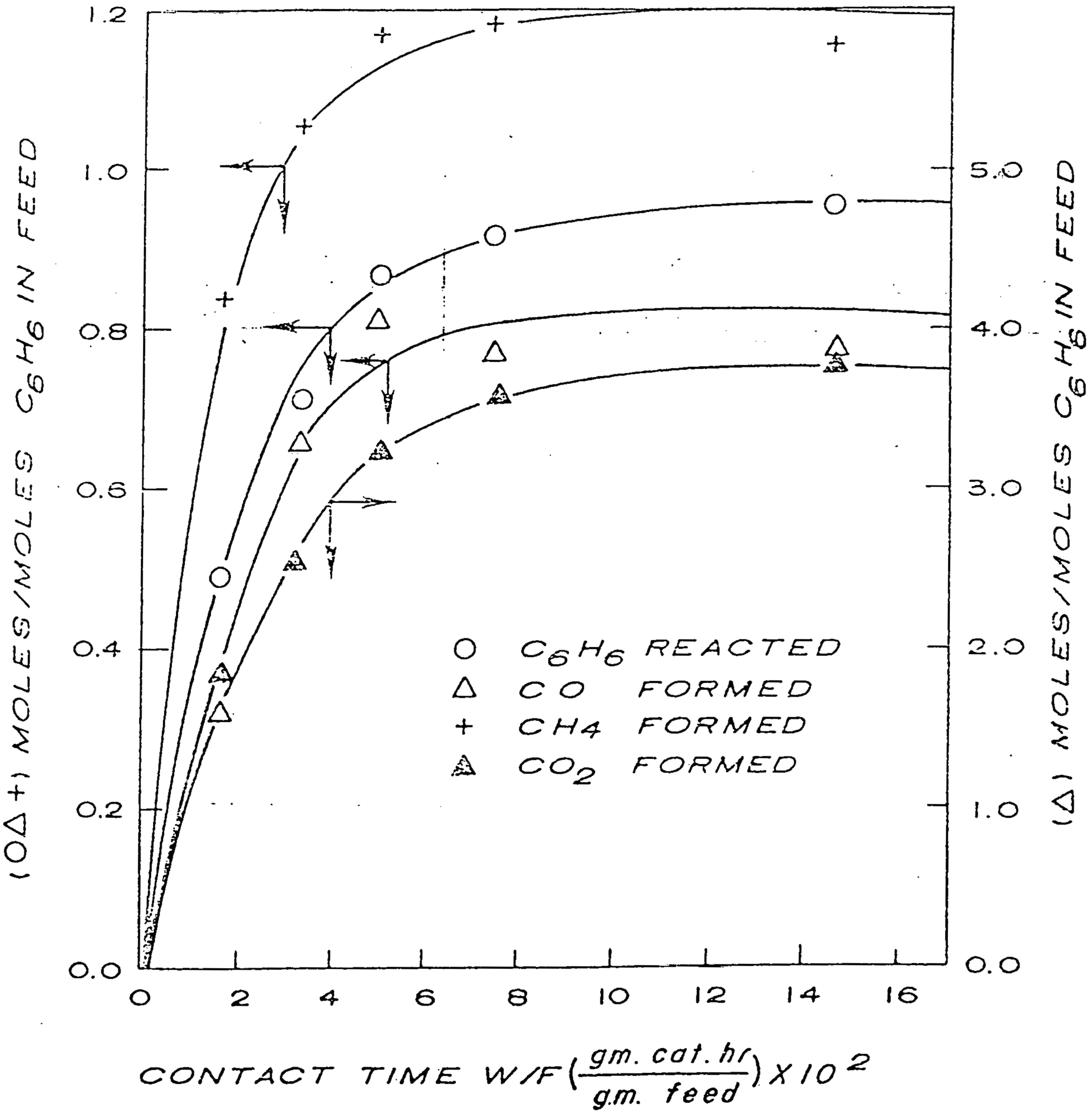


Figure 2. Effect of Contact Time on Conversion and Yield at 300 psig.

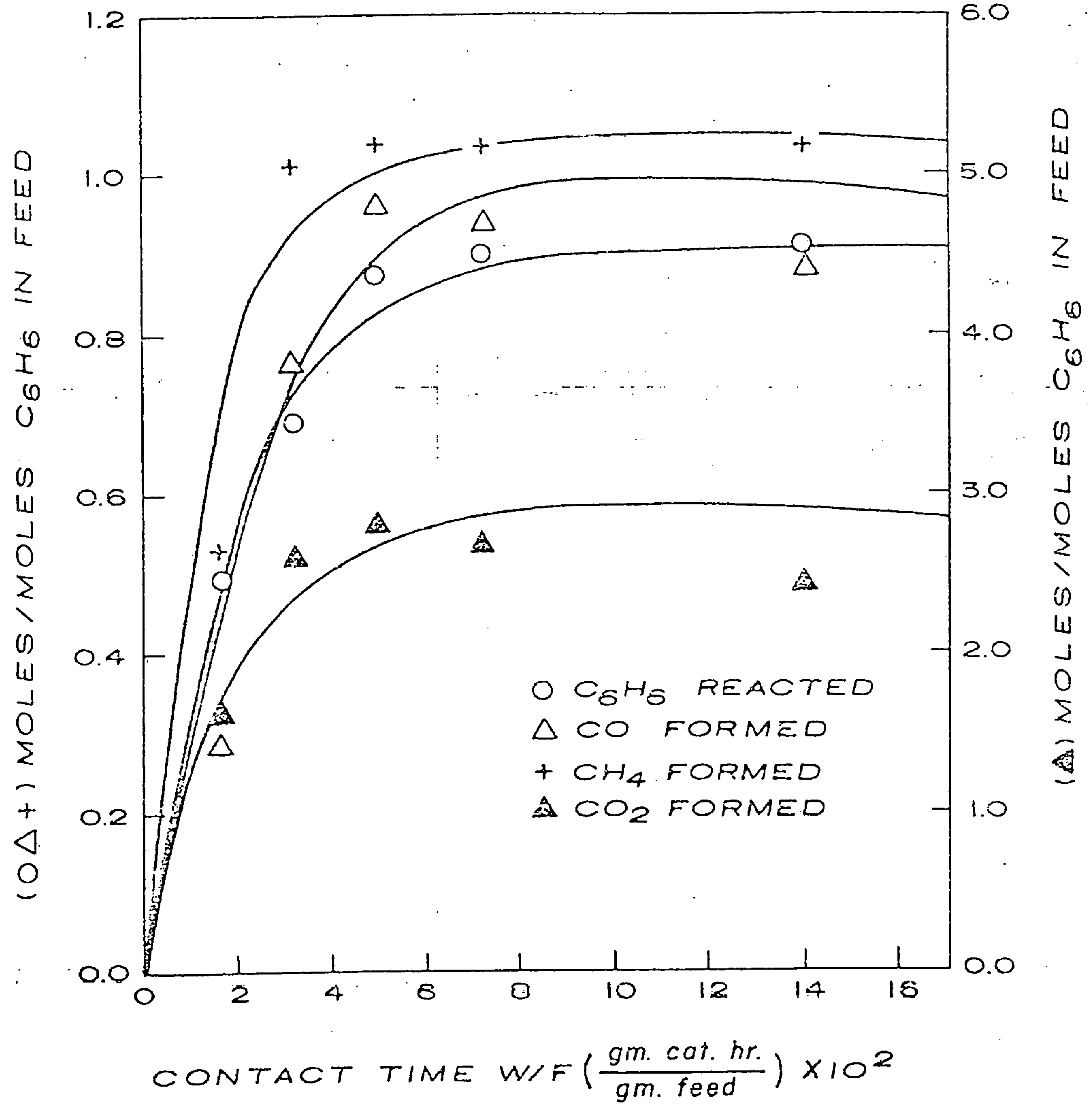


Figure 3. Effect of Contact Time on Conversion and Yield at 200 psig.

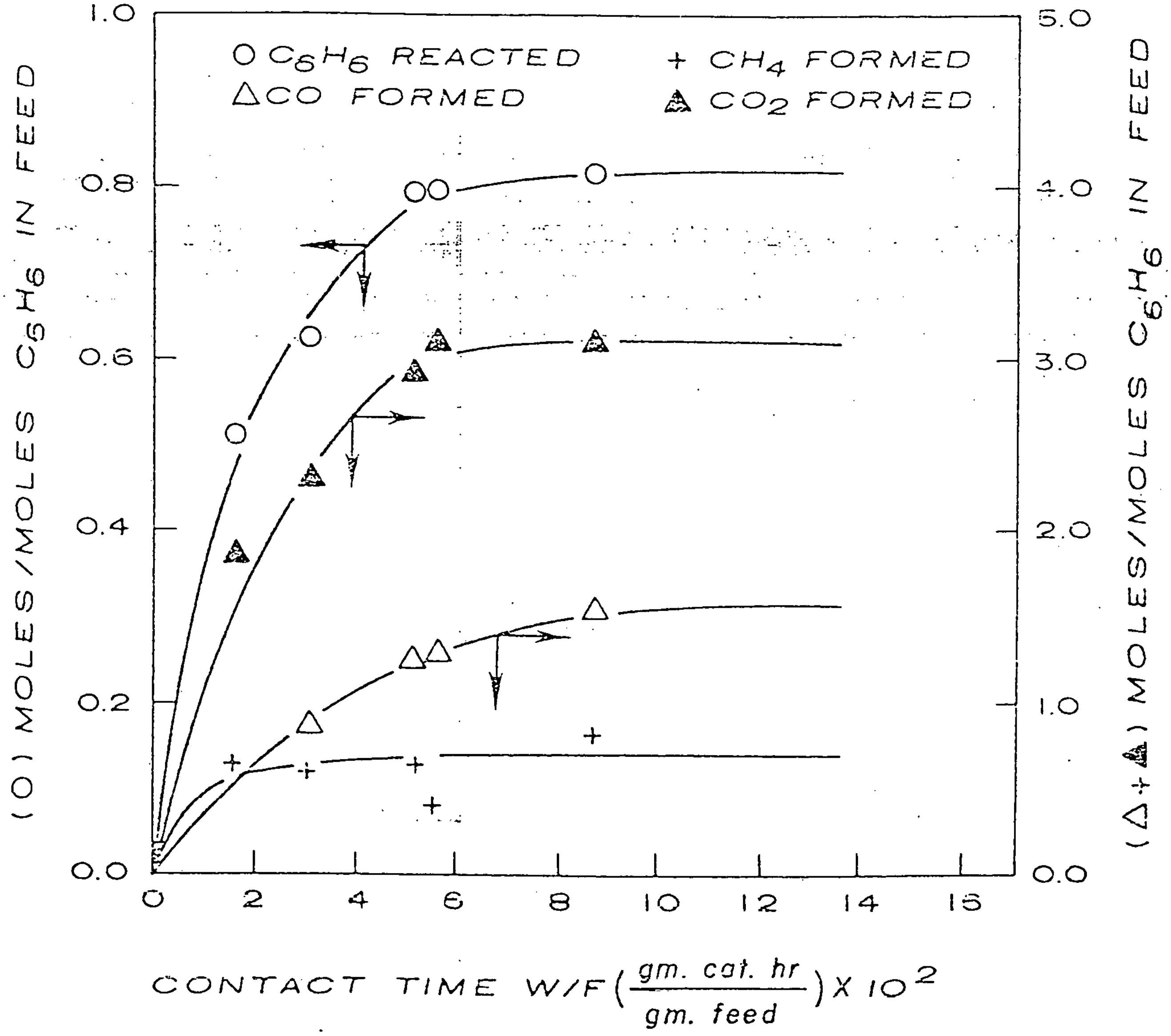


Figure 4. Effect of Contact Time on Conversion andYield at 100 psig.

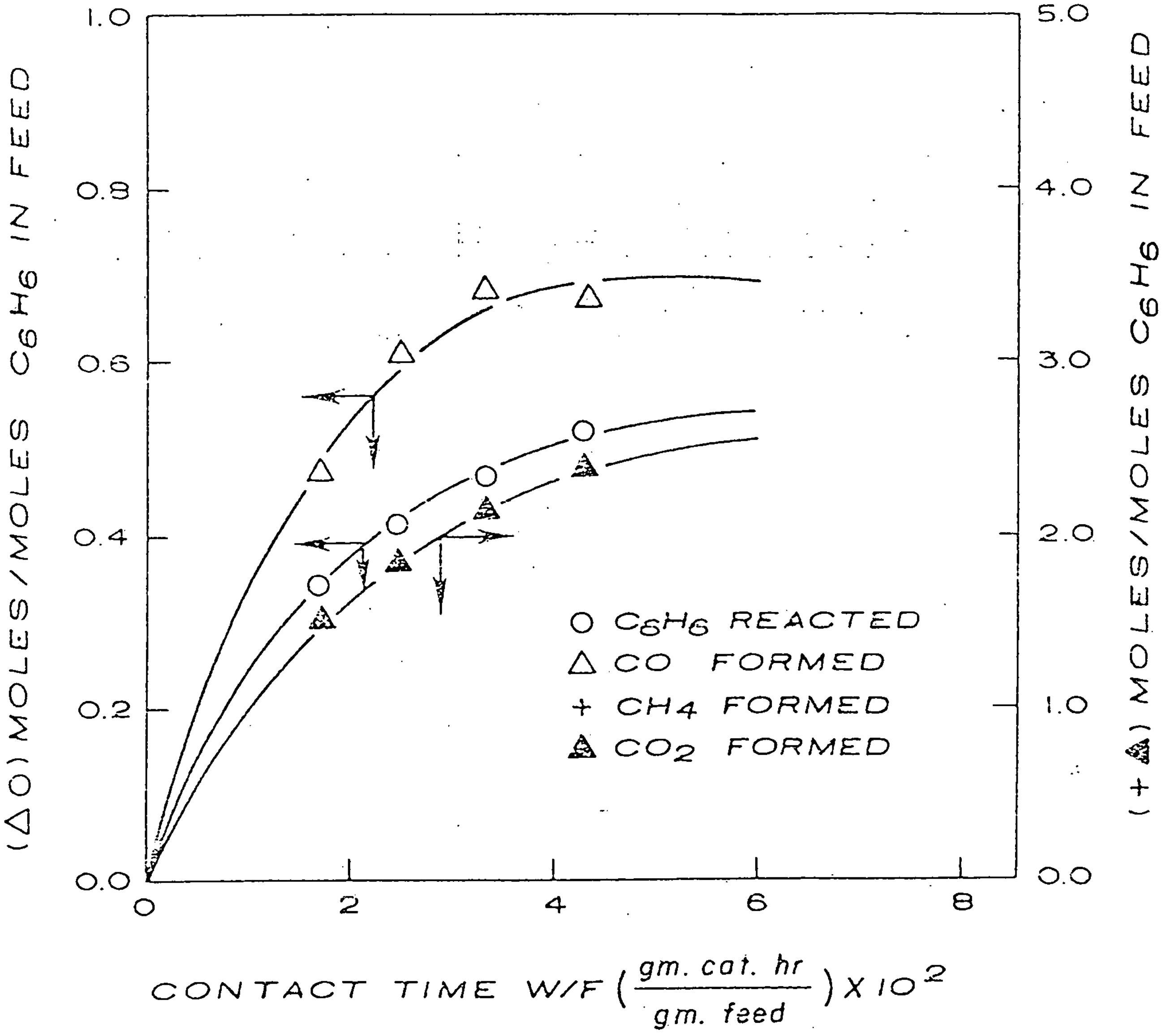


Figure 5. Effect of Contact Time on Conversion and Yield at 0 psig.

TABLE 1

CORRELATION OF CONVERSION DATA

$$X = C_o + C_1 (W/F) + C_2 (W/F)^2 + C_3 (W/F)^3$$

Pressure (psig)	Components	Coefficients			
		C_o	C_1	C_2	C_3
300	C_6H_6	0.0127	0.5700	-0.1142	0.0071
	CH_4	0.0441	0.8998	-0.2094	0.0139
	CO	-0.0380	0.5333	-0.1081	0.0066
	CO_2	0.0634	1.9611	-0.3588	0.0212
200	C_6H_6	0.0092	0.5777	-0.1187	0.0075
	CH_4	-0.0485	0.9028	-0.1758	0.0105
	CO	-0.0497	0.5752	-0.1018	0.0055
	CO_2	-0.0069	2.2169	-0.5236	0.0349
100	C_6H_6	0.0127	0.6041	-0.1554	0.0133
	CH_4	0.0188	0.9099	-0.3902	0.0477
	CO	0.0026	0.6175	-0.0806	0.0035
	CO_2	0.0533	2.1598	-0.5315	0.0441
0	C_6H_6	0.0001	0.5345	-0.2285	0.0396
	CO	0.0000	0.5900	-0.1014	-0.0109
	CO_2	0.4236	2.2584	-0.8805	0.1458