CONF-800802--24

PAPER PRESENTED AT SESSION ON
CONVERSION OF BIOMASS TO ENERGY
AND HIGH VALUE PRODUCTS
AIChE Meeting, Portland, Oregon, August 17-20, 1980

AN INDIRECT THERMAL LIQUEFACTION PROCESS FOR PRODUCING LIQUID FUELS FROM BIOMASS

by

James L. Kuester
Dept. of Chemical Engineering
College of Engineering & Applied Sciences
Arizona State University
Tempe, Arizona 85281

INTRODUCTION

A process to convert biomass materials to quality liquid hydrocarbon fuels has been under development at Arizona State University since 1975. An indirect liquefaction approach is utilized, i.e., gasification followed by catalytic liquid fuels synthesis. The advantage of indirect liquefaction (vs. direct) is minimization of oxygenated compounds in the liquid hydrocarbon fuel product. The use of catalysts in the liquid fuels synthesis results in very mild processing conditions, i.e., low pressures, temperatures and residence times.

The potential products from the system are indicated on Figure 1. The medium Btu pyrolysis gas (500 + Btu/SCF) conceivably could be used as a fuel gas. The project objective however has always been to tailor the gas composition with respect to carbon monoxide, hydrogen and olefins for use as a synthesis gas for the liquid fuels system. The first reactor in the liquid fuels system contains a Fischer-Tropsch type catalyst. The condensible hydrocarbon phase is a narrow range light paraffinic fuel (C_5 - C_{17}) which can be readily tailored to match diesel, kerosene or jet fuels. If a high octane gasoline is desired, a conventional catalytic reforming step is used to achieve the desired effect.

A secondary condensible phase from the Fischer-Tropsch step is essentially a binary of normal-propanol and water. The off gases from the liquid fuels reactors are heavy in the low molecular weight paraffins (C_1 - C_5) and thus are of high heating value. It is anticipated that these would be recycled back to the gasification system.

The research scale process has a capacity of about 25 lbs/hr of feedstock. A fluidized bed with separate regenerator is employed for the pyrolysis step.

The heat transfer medium can either be catalytic or inert. The system (both functionally and operationally) is a direct analogy to a catalytic cracker in a petroleum refinery which has been successfully employed since the 1940's. A fluidized bed is also used for the Fischer-Tropsch step (to control the temperature). The reformer is a fixed catalytic bed. Equipment and procedure development have accompanied factor studies for the chemical reactor systems. Previous experimental results for the process have been reported in several publications (1-5). These include a 2^2 factorial design (temperature, feed rate) for pyrolysis, a 2^3 central composite design (CO, H_2, C_2H_4 feed composition) and temperature, pressure, catalyst loading studies for the Fischer-Tropsch system and a 2^3 central composite design (temperature, pressure, feed rate) for the catalytic reformer. In each case, the responses were the product yields and composition. Additional physical properties were reported (octane number, cetane number, heating values, specific gravity, etc). In this paper the following additional studies will be presented:

1) gasification data for alternative feedstocks,
2) steam effects on gasification performance,
3) water gas shift catalyst effects,
4) temperature effects on gasification performance, and
5) temperature effects on Fischer-Tropsch reactor performance.

ALTERNATIVE FEEDSTOCK STUDY

Fourteen alternative feedstocks were processed through the gasification system. A listing along with some feedstock analysis information is shown in Table 1. Many of the materials represent industrial wastes (e.g., guayule cork, bagasse; jojoba meal; almond hulls, shells; sawdust). The Eco-Fuel II material is a preprocessed municipal refuse (Combustion Equipment Associates). The ash content varies among the feedstocks, ranging from negligible for the synthetic polymers to over 15% for Eco-Fuel II, Russian thistle and water hyacinth. The maximum sulfur content was for Eco-Fuel II (0.75 wt %).

Pyrolysis gas composition data is listed in Table 2. Run conditions were as follows:

temperature, °F:	1150-1450
pressure, psig:	1.0
residence time, sec:	3-6
solids feed rate, lbs/hr:	2.5-11.5
solids media:	70-90 mesh sand

The biomass, refuse and peat feedstocks yield a gas with a heating value of about 500 Btu/SCF. The gas from the synthetic polymers has a much higher heating value due to the absence of oxygenated compounds. The gas composition results are masked somewhat by the variation in temperature settings for the runs. However, several conclusions can be drawn:

1) The more cellulosic type feedstocks yield the lowest total olefin content (generally in the 5-10 mole % range).

2) materials containing hydrocarbon materials (e.g., oils, latex, synthetic polymers) result in total olefin yields in the 10-25% mole % range.

3) pure synthetic carbon chain polymers result in total olefin yields of over 30 mole %.

4) hydrogen/carbon monoxide mole ratios of 0.25 to 0.80 are encountered for dry feedstocks without steam addition (excluding the synthetic

polymers).

5) an autocatalytic effect is encountered for some feedstocks with respect to the water gas shift reaction with steam addition to the pyrolysis reactor.

6) H_2S was not detected for any feedstock. This is of significance with regard to potential effects on catalyst activity downstream.

Previous studies (1,2) on the system have indicated that an optimal pyrolysis gas composition for maximizing liquid hydrocarbon fuel yields is 20 mole % + olefins and a H_2/CO mole ratio of 1 - 1.5. Selected feedstocks are capable of producing the desired amounts of olefins (e.g., guayule cork). Withoutsteam addition, all the materials (except the synthetic polymers) result in a suboptimal H_2/CO mole ratio.

STEAM USAGE AND WATER GAS SHIFT REACTION EFFECTS

A study was conducted with the objective of altering the H_2/CO ratio for various candidate feedstock materials. Two materials capable of producing a large amount of olefins were selected for study: Eco-Fuel II and guayule cork. The goal was to implement the water gas shift reaction: $CO + H_2O \rightleftarrows H_2 + CO_2$. As indicated in Table 3, steam addition appeared to have a slight effect on the H_2/CO ratio (.31 to .44) for Eco-Fuel II feedstock without the use of a shift catalyst. Use of a commercial shift catalyst (packed section of the reactor overhead gas line) achieved a major shift in the ratio (2.48). Thus control of the H_2/CO ratio appears possible for Eco-Fuel II but only with the aid of a water gas shift catalyst.

Steam addition with guayule cork feedstock (without a water gas shift catalyst) had a dramatic effect on the H_2/CO ratio (Table 4) with an increase from 0.64 to 2.45. Similar behavior was observed for other feedstocks (e.g., guayule bagasse, peat) where steam addition was used. Other feedstocks however, (e.g., paper chips) exhibit behavior similar to Eco-Fuel II with steam addition, i.e., little if any shifting of the H_2/CO ratio occurs without the aid of a water gas shift catalyst. The phenomena is not totally understood but perhaps is related to a catalytic effect of the ash obtained for certain feedstocks. It is expected that many additional feedstocks will behave in a similar manner.

PYROLYSIS TEMPERATURE EFFECT

A study to ascertain the effect of pyrolysis reactor temperatures between 1300 - 1700 °F on gas phase composition was conducted. Paper chip feedstock was used with analysis only for the major components (H_2, CO, C_2H_4, C_2H_6, CH_4, CO_2). Recycle pyrolysis gas was used for fluidization. The feedstock was dry and steam was not fed to the system. However, some moisture is undoubtedly generated in the pyrolyzer. Also the recycle pyrolysis gas is saturated with water after passing through the wet scrubbing system. Results are shown on Figure 2. A water gas shift effect is apparent with increasing temperature. Thus conceivably a control algorithm could be developed for a feedstock to control the H_2/CO ratio via adjustments in reactor temperature and steam flow rates.

FISCHER-TROPSCH REACTOR TEMPERATURE STUDY

An isolated study of the effect of reaction temperature on the material balance for the Fischer-Tropsch system was performed. The constant reactor operating conditions were as follows:

pressure, psig:	110	
feed composition, mole%:	H_2	31.71
	CO	22.06
	C_2H_4	29.90
	CH_4	5.00
	CO_2	11.33
residence time, sec:	16	
WHSV (g feed/hr-g catalyst):	0.27	

A synthetic feed gas was used for the study. Summary results are shown in Figures 3-7. In Figure 3 grouped compound analysis effects for the liquid hydrocarbon phase are shown. Low molecular weight alcohols (C_3 - C_6) maximize at about 210°C but disappear at temperatures above 240°C. Olefins decrease and isoparaffins increase with increase in temperature. Normal paraffin production exhibits a bimodal behavior with a minimum at about 210°C and a maximum at about 260°C.

A composition-temperature plot for the water-alcohol phase is shown in Figure 4. As indicated, normal propanol composition peaks at about 210°C with a wt.% composition of about 39%. Specific gravity and yield curves for the two phases as a function of temperature are shown in Figures 5 and 6. Peak yields for the organic phase occurs at about 260°C while the water-alcohol phase peaks at about 230°C. Reactant conversion curves are shown in Figure 7. Conversion increases with temperature for all reactants as expected. The hydrogen and ethylene are depleted at the higher temperatures whereas about half the carbon monoxide is reacted.

The objective for the project has been to maximize the liquid hydrocarbon product yields. The above study indicates that the process conceivably could also be optimized to maximize for normal propanol production (1979 price: $2.22/gal.).

CONTINUING RESEARCH

A list of studies in progress and projected for the near term are listed in Table 5. A number of alternative feedstock candidates are under consideration. Of particular interest is to establish the relationship between feedstock composition and gasification system performance. Further work with water gas shift catalysts would involve optimizing performance with respect to steam addition, residence time and fixed bed temperature. Also, the catalyst activity history has not been established.

Several paths are being explored to develop the capability to manipulate pyrolysis gas composition for any commercially attractive feedstock. The gasification system is ideally setup to handle fluidized catalysts with continuous regeneration. Among the candidates are standard petroleum refinery cracking catalysts. A multi factor study to explore the effect of pyrolysis temperature, residence time, steam usage and pyrolysis recycle gas continues. The following ranges are being explored:

residence time: 0.1 to 5 seconds
temperature: 1100-1700°F
fluidization gas: 100% pyrolysis to 100% steam

Additional studies in the gasification system include a survey of alternative non catalytic heat transfer media (improved thermal properties), optimization of the scrubbing system, characterization of the ash, char and tar materials and development of techniques for feeding wet feedstocks.

Fischer-Tropsch studies are centered on improved material balances (more detailed composition analysis) and alternative catalyst screening studies. Also remaining is a characterization of catalyst activity for various feedstocks. No further work on the reforming step is planned at this time. The concept of producing high octane materials has been demonstrated. One pass liquid yield losses are about 20% but this manifests itself in the form of an extremely high quality off gas (hydrocracking effects) and thus some of the yield loss could be recovered with off gas recycle to the gasification system in an integrated system operating mode. It should be noted, however, that most industrial interest in the process to date has been aimed at the diesel fuel type product (Fischer-Tropsch hydrocarbon phase). This is consistent with fuel requirements for such equipment as farm machinery, trucks, etc. plus the projected decline in consumption of high octane fuels in the near future (in favor of paraffinic fuels). (6).

Separation of the gasification system scrubber effluent and the Fischer-Tropsch water-alcohol phase are not currently implemented on the research scale system. Techniques for accomplishing desired separations are being investigated.

The major remaining task for the research scale is an assessment of performance for the integrated system for selected feedstocks. This will include recycle of liquid fuels system off gases to the gasification system (probably a split to the pyrolyzer and regenerator). Integration of steps for separation and recycle of the scrubber effluent, Fischer-Tropsch water phase and pyrolysis char streams will remain for a larger scale facility.

SUMMARY AND CONCLUSIONS

A progress report on a process to convert biomass type materials to quality liquid hydrocarbon fuels has been presented. The particular experiments emphasized in this paper lead to the following conclusions:

1) A wide variety of feedstocks can be processed through the gasification system to a gas with a heating value of 500 + Btu/SCF.
2) Some feedstocks are more attractive than others with regard to producing a high olefin content. This appears to be related to hydrocarbon content of the material.
3) The H_2/CO ratio can be manipulated over a wide range in the gasification system with steam addition. Some feedstocks require the aid of a water-gas shift catalyst while others appear to exhibit an auto-catalytic effect to achieve the conversion.
4) H_2S content (beyond the gasification system wet scrubber) is negligible for the feedstocks surveyed.

5) The water gas shift reaction appears to be enhanced with an increase in pyrolysis reactor temperature over the range of 1300 - 1700°F.

6) Reactor temperature in the Fischer-Tropsch step is a significant factor with regard to manipulating product composition analysis. The optimum temperature however will probably correspond to maximum conversion to liquid hydrocarbons in the C_5 - C_{17} range.

Continuing research includes integrated system performance assessment, alternative feedstock characterization (through gasification) and factor studies for gasification (e.g., catalyst usage, alternate heat transfer media, steam usage, recycle effects, residence time study) and liquefaction (e.g., improved catalysts, catalyst activity characterization).

ACKNOWLEDGEMENTS

The work in progress is supported by the U. S. Department of Energy (Contract No. EY-76-S-02-2982, Alternate Materials Utilization Branch, Branch Chief: Dr. Jerome Collins) and the Arizona Solar Energy Commission (Project No. 104-79, Dr. Frank Mancini, Associate Director). The following graduate students have participated on the experiments reported in this paper: Mark Wallington, Lee Scott, Mike Hunter and Michael Wang. The following undergraduate students have also contributed: Kevin Jackson and Gary Heath. The feedstock materials were supplied by several institutions and companies: Golden Byproducts (Turlock, CA), Centro de Investigacion en Quimica Aplicada (Saltillo, Coahuila, Mexico), The University of Arizona (Office of Arid Land Studies, Environmental Research Laboratory), Colby Farms (Crosswell, NC), Phillips Petroleum Co., San Carlos Apache Reservation, and Combustion Equipment Associates.

LITERATURE CITED

1. Kuester, J. L., "Conversion of Cellulosic and Waste Polymer Material to Gasoline," presented at the American Chemical Society Symposium on Thermal Conversion of Solid Wastes, Residues and Energy Crops, Washington, D. C., September, 1979 (published in Preprints and Symposium Series).

2. Kuester, J. L., "Conversion of Cellulosic Wastes to Liquid Fuels" presented at Engineering Foundation Conference on Municipal Solid Waste as a Resource: The Problems and the Promise, Henniker, New Hampshire, July, 1979 (published by Ann Arbor Press).

3. Kuester, J. L., "Liquid Hydrocarbon Fuels from Biomass," presented at The Biomass as a Non-Fossil Fuel Source Symposium, American Chemical Society, Honolulu, April, 1979 (published in Preprints and Symposium Series).

4. Kuester, J. L., "Liquid Fuels from Biomass," presented at the AIAA/ASERC Conference on Solar Energy, Phoenix, November, 1978 (published in Proceedings).

5. Kuester, J. L., "Conversion of Waste Organic Materials to Gasoline," Proceedings of the Fourth National Conference on Energy and the Environment, Cincinnati, October, 1976.

6. Wall Street Journal, CII (46), March 6, 1980.

Table 1

FEEDSTOCK ANALYSIS (wt. %)

Feedstock	% Nitrogen	% Sulfur	% Ash	% Loss on Ignition
Almond Hulls	0.88	0.08	5.91	94.09
Almond Shells	0.68	0.03	8.75	91.25
Raw Guayule	0.81	0.18	5.14	94.86
Guayule Bagasse	0.66	0.11	3.27	96.73
Guayule Cork	0.91	0.34	3.53	96.47
Russian Thistle	1.33	0.19	15.45	84.55
Peat	0.97	0.15	7.63	92.37
Water Hyacinth	1.87	0.53	18.97	81.03
Polyethylene	0.09	0.17	0.04	99.96
Polypropylene	0.13	0.03	0.03	99.97
Paper Chips	0.13	0.08	0.58	99.42
Sawdust	0.28	0.12	7.03	92.97
Jojoba Meal	3.94	0.36	3.04	96.96
Eco-Fuel II	0.40	0.75	14.68	85.32

Table 2

Pyrolysis Gas Composition (mole%)[1]

Feedstock	Almond Hulls	Almond Shells	Raw Guayule	Guayule Bagasse[2]	Guayule Cork	Russian Thistle	Peat[2]	Water Hyacinth	Poly-ethylene	Polypro-pylene	Paper Chips	Sawdust	Jojoba Meal	Eco-Fuel I
H_2	28.08	26.03	17.28	41.40	14.37	26.37	45.05	23.00	14.19	13.57	14.77	15.13	11.96	15.74
O_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.23	0.42	0.41	0.05
CO	35.44	38.06	34.98	25.29	51.11	36.08	18.48	42.43	0.96	0.69	58.86	55.57	37.56	50.40
CO_2	13.92	12.15	8.51	12.10	4.30	14.62	16.29	13.94	0.23	0.00	3.27	5.31	10.32	3.20
H_2S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH_4	14.96	17.21	26.17	13.81	18.50	16.23	10.69	14.34	43.56	42.43	14.76	16.37	23.21	15.03
C_2H_2	0.05	0.06	0.04	0.13	0.09	---	0.12	0.00	0.61	1.18	0.10	0.10	0.00	0.00
C_2H_4	4.01	3.09	5.57	4.93	6.34	3.21	4.15	3.52	19.29	13.34	3.70	2.63	9.15	6.04
C_2H_6	1.29	1.72	2.31	0.85	2.63	1.69	1.88	1.62	6.78	6.13	2.26	2.36	3.44	3.60
C_3 olefins	1.23	0.54	1.50	0.31	1.24	0.61	1.21	0.57	5.30	9.77	1.21	1.13	2.01	2.03
C_3H_8	0.03	0.06	0.05	---	0.02	0.02	0.09	0.02	0.00	0.00	0.08	0.09	0.03	0.10
C_4 olefins	0.12	0.10	0.56	0.04	0.27	0.14	0.19	0.13	0.59	3.64	0.18	0.20	0.45	0.51
C_4H_{10}	0.00	0.00	0.01	0.01	0.02	0.01	0.01	0.00	0.02	0.06	0.00	0.01	0.01	0.11
C_5H_{12}	0.01	0.01	0.04	0.00	0.02	0.01	0.02	0.08	0.00	0.00	0.00	0.00	0.08	0.00
C_5 + olefins	0.86	0.97	2.97	1.10	1.20	1.02	1.83	0.35	7.49	9.20	0.57	0.67	1.78	3.13

[1] Water, nitrogen free basis

[2] Steam fluidization with recycle pyrolysis gas to sparges (other runs with total recycle gas)

Table 3

STEAM EFFECT - ECO-FUEL II FEEDSTOCK[1]

	No Steam	Steam	Steam + Water Gas Shift Catalyst
H_2	15.74	21.96	42.59
O_2	0.05	0.08	0.00
CO	50.40	49.66	17.18
CO_2	3.20	3.79	12.52
H_2S	0.00	0.00	0.00
CH_4	15.03	8.68	16.45
C_2H_2	0.00	0.08	0.11
C_2H_4	6.04	9.23	5.03
C_2H_6	3.60	3.02	3.67
C_3 olefins	2.03	0.09	1.03
C_3H_8	0.10	0.09	0.03
C_4 olefins	0.51	0.56	0.30
C_4H_{10}	0.11	0.13	0.02
C_5H_{12}	0.00	0.00	0.02
C_5 + olefins	3.13	2.61	1.05
total olefins	11.71	12.49	9.84
H_2/CO	0.31	0.44	2.48

---

[1] results in mole % (water, nitrogen free basis)

Table 4

STEAM EFFECT - GUAYULE CORK FEEDSTOCK[1]

	No Steam	Steam
H_2	14.32	35.24
O_2	0.04	0.00
CO	22.23	14.40
CO_2	8.21	12.95
H_2S	0.00	0.00
CH_4	29.75	19.83
C_2H_2	0.00	0.06
C_2H_4	11.03	10.83
C_2H_6	4.62	3.34
C_3 olefins	4.16	1.19
C_3H_8	0.19	0.03
C_4 olefins	1.45	0.15
C_4H_{10}	0.02	0.01
C_5H_{12}	0.00	0.02
C_5 + olefins	3.96	1.95
total olefins	20.60	14.12
H_2/CO	0.64	2.45

[1] results in mole % (water, nitrogen free basis)

Table 5

STUDIES IN PROGRESS/PROJECTED

1. ALTERNATE FEEDSTOCKS
2. WATER GAS SHIFT CATALYST ASSESSMENT
3. GASIFICATION SYSTEM CATALYST ASSESSMENT/ALTERNATE HEAT TRANSFER MEDIA
4. STEAM/RESIDENCE TIME/RECYCLE/TEMPERATURE EFFECTS
5. SCRUBBER OPTIMIZATION
6. ASH/CHAR/TAR CHARACTERIZATION
7. WET FEEDSTOCK ASSESSMENT
8. ALTERNATE FISCHER-TROPSCH CATALYSTS
9. SCRUBBER EFFLUENT/FISCHER-TROPSCH WATER PHASE PROCESSING
10. INTEGRATED SYSTEM YIELD/OPERATIONAL RELIABILITY DEMONSTRATION

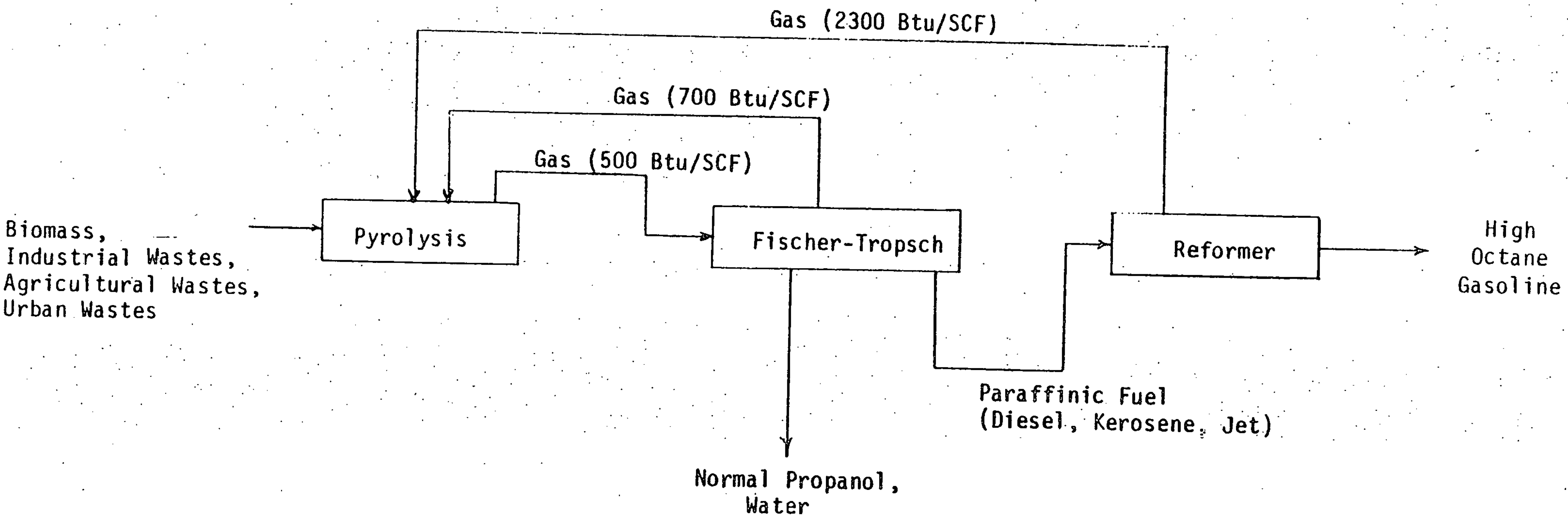

Figure 1. Basic Chemical Conversion Scheme

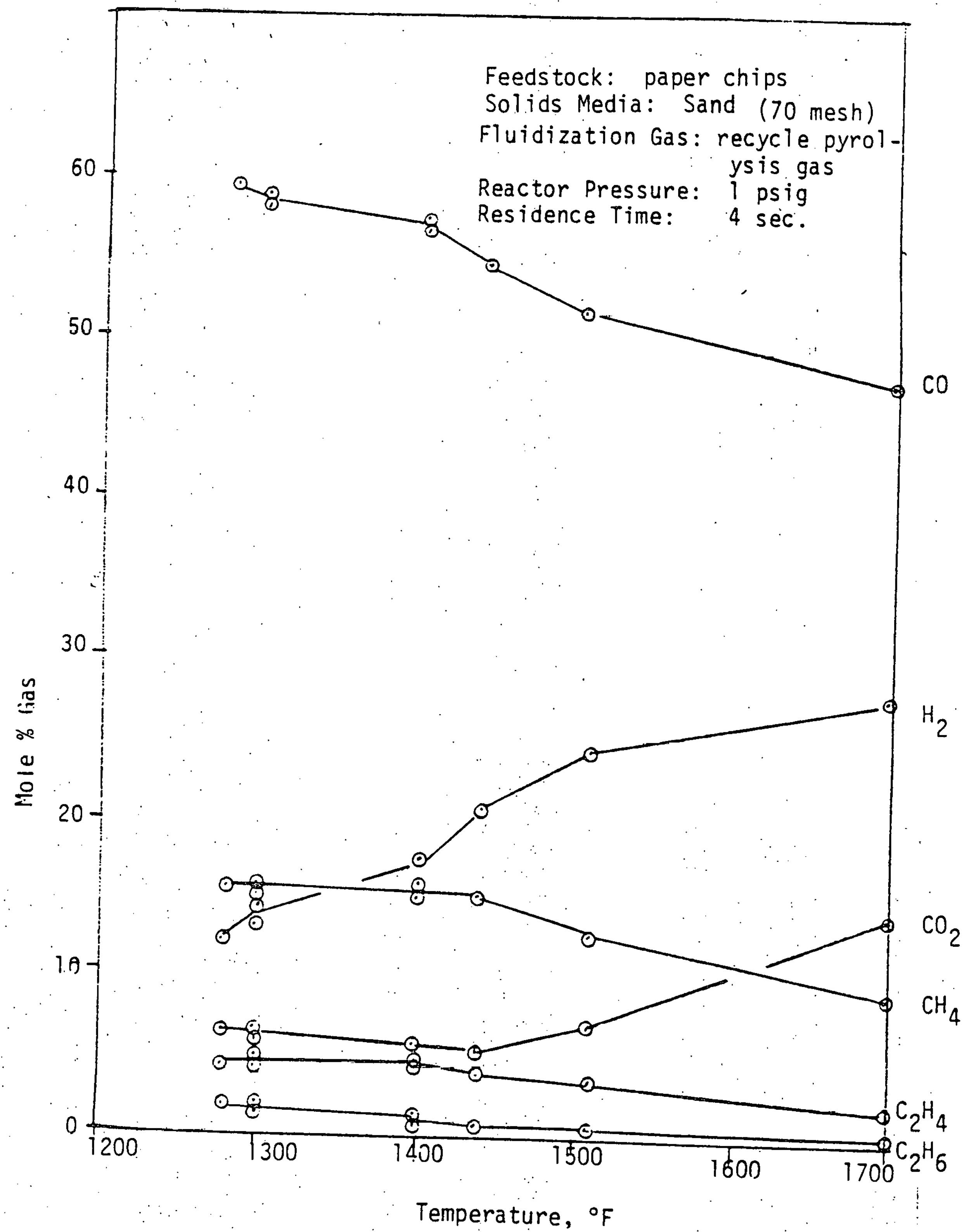

Figure 2. Pyrolysis Gas Composition vs. Temperature

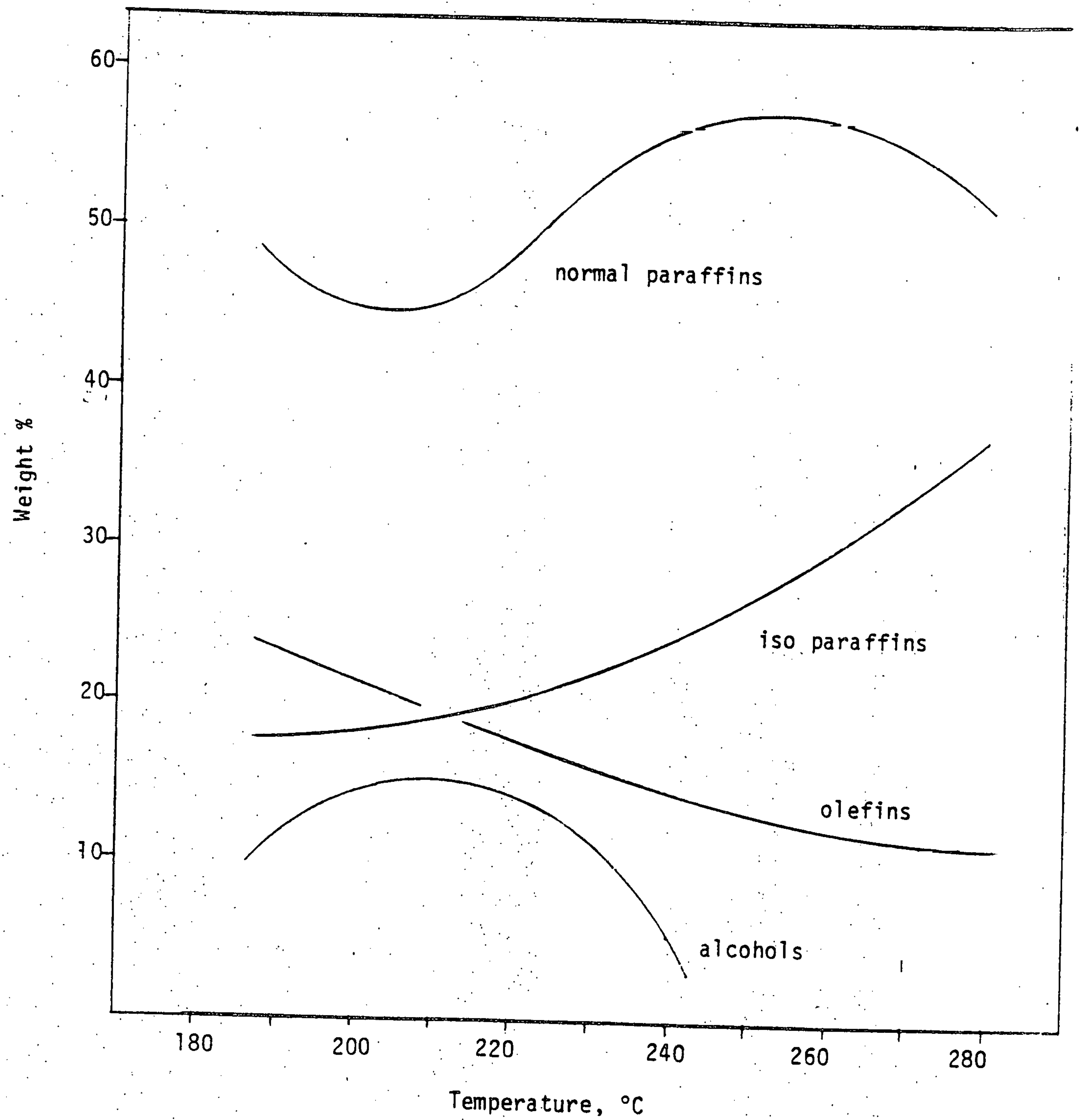

Figure 3. Fischer-Tropsch Reactor Organic Phase Composition

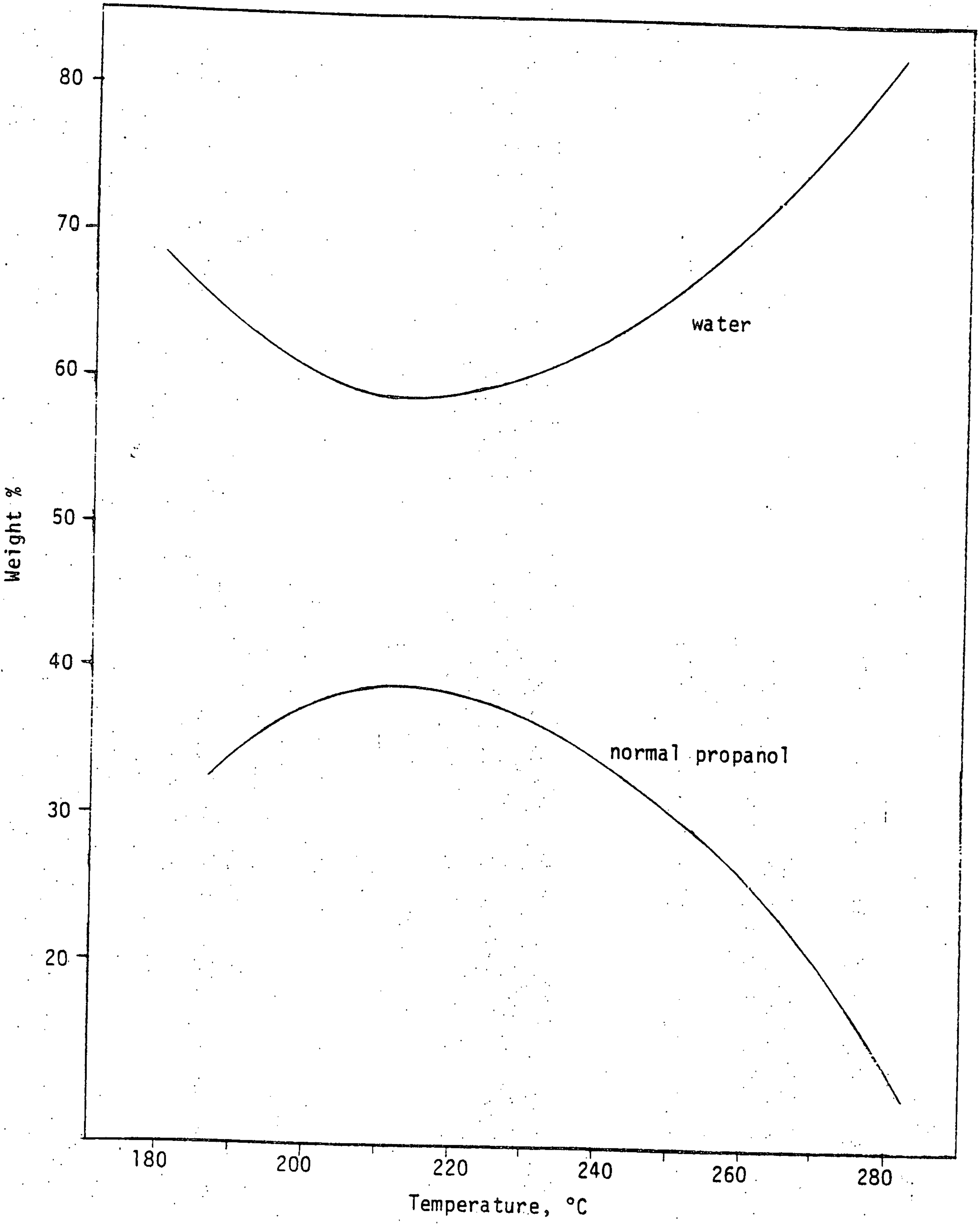

Figure 4. Fischer-Tropsch Reactor Alcohol-Water Phase Composition

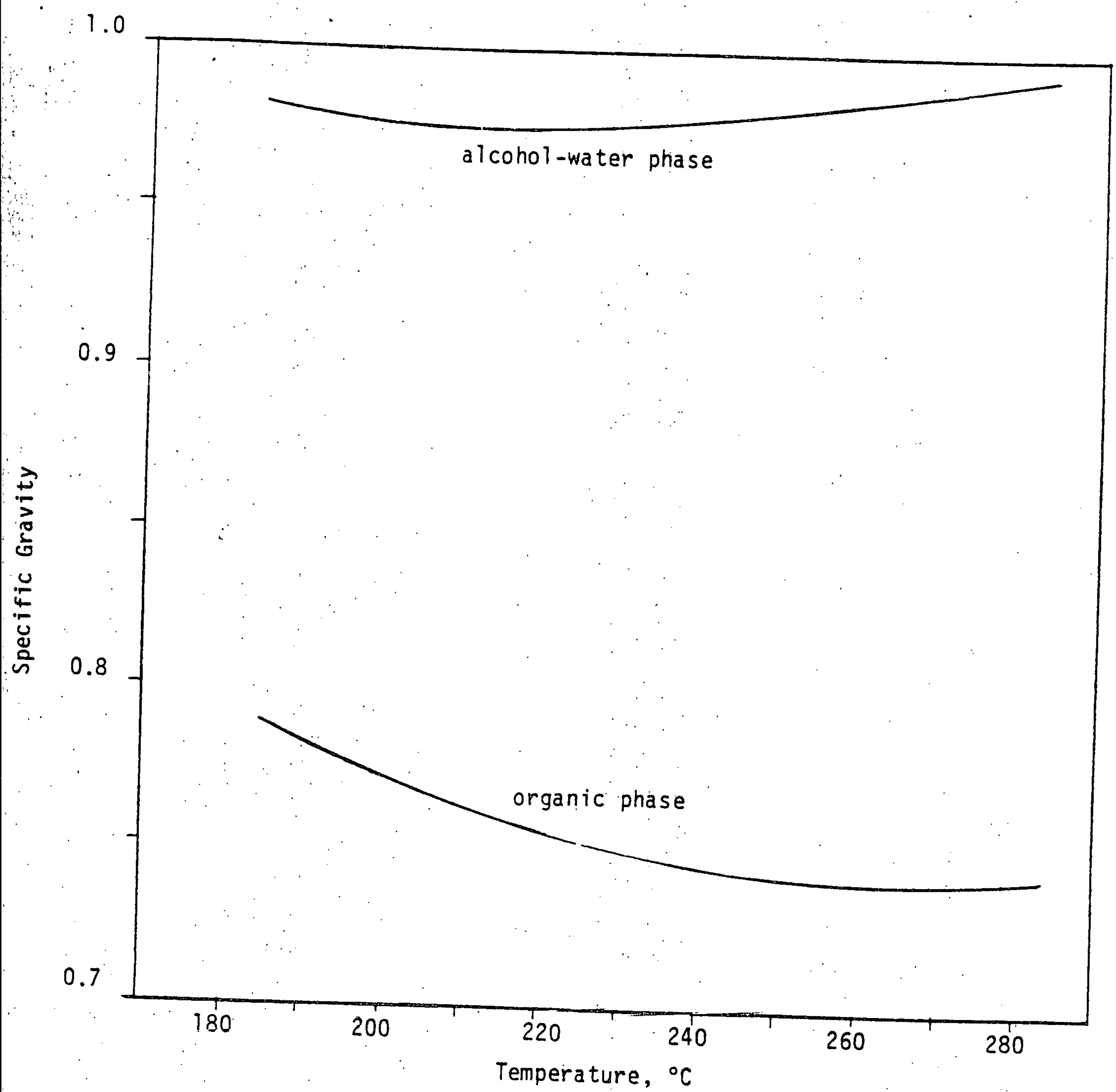

Figure 5. Fischer-Tropsch Reactor Product Specific Gravity

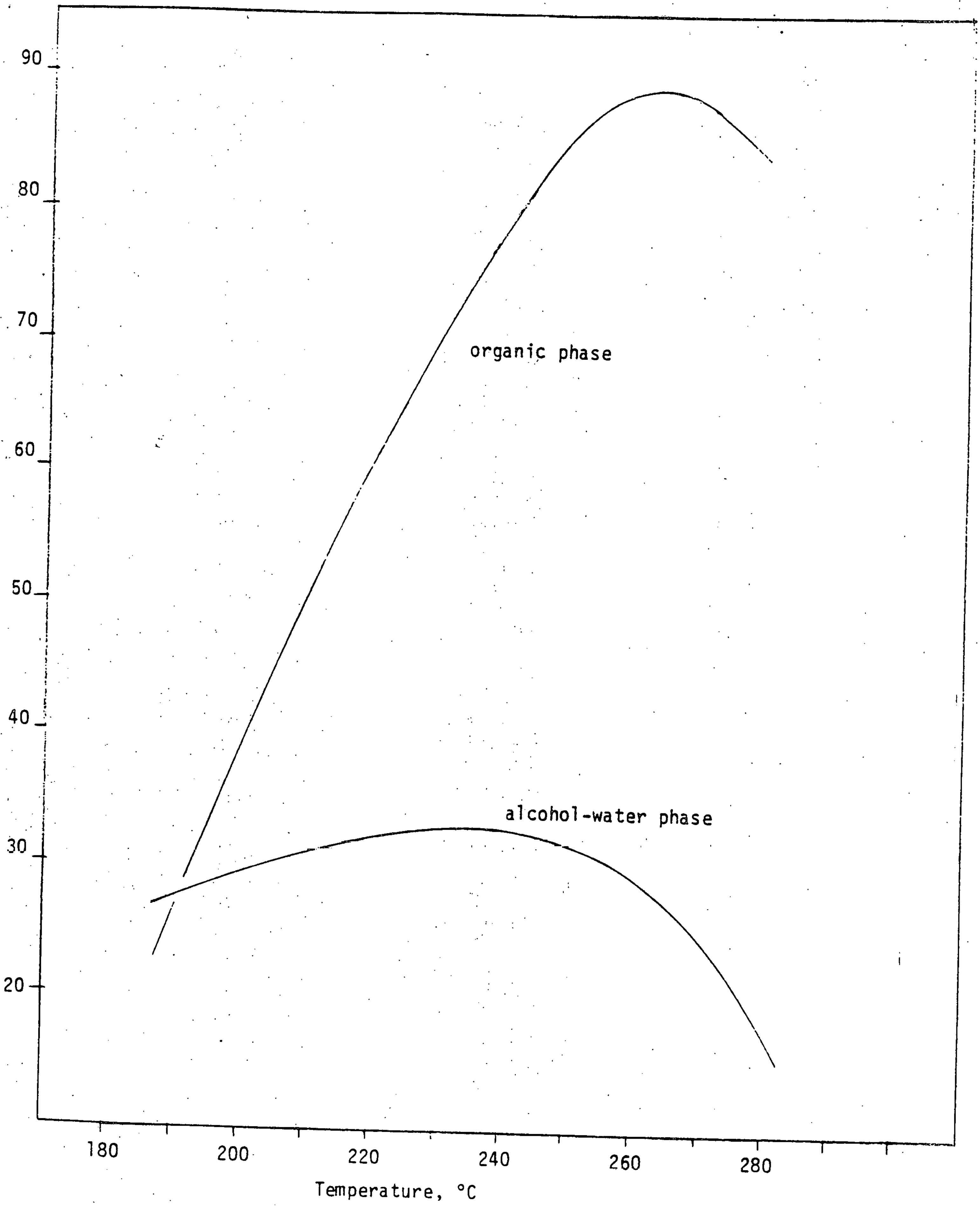

Figure 6. Fischer-Tropsch Reactor Product Yields

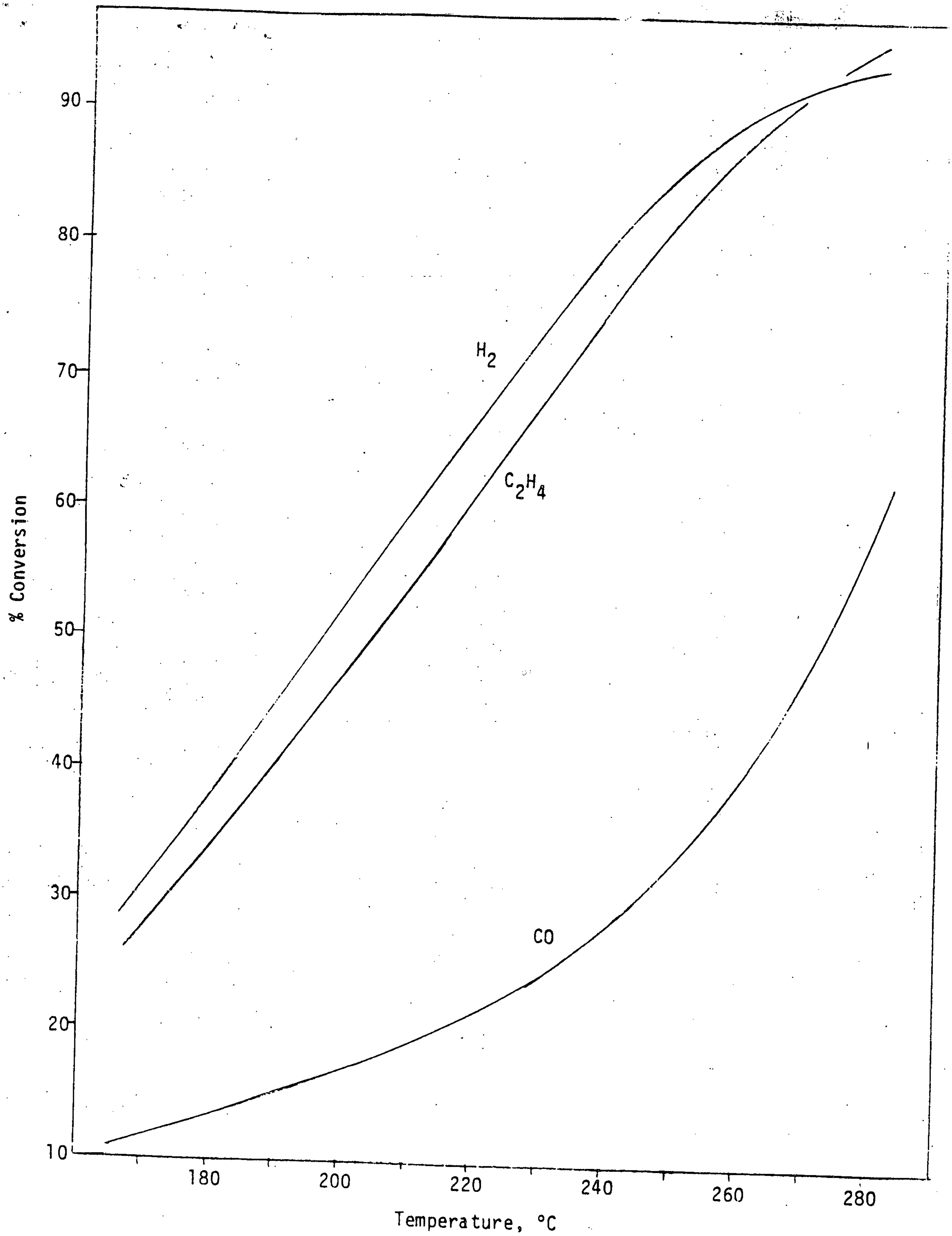

Figure 7. Fischer-Tropsch Reactant Conversions