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CONVERSION OF CELLULOSIC WASTES TO LIQUID FUELS

by

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DISCLAIMER

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SUMMARY

The current status and future plans for a project to convert waste cellulosic (biomass) materials to quality liquid hydrocarbon fuels is described. This report will update a previous Interim Report (COO-2982-38, March 28, 1979).

The Statement of Work for the contract period (June 1, 1979 to May 31, 1980) was as follows:

(1) Feedstock studies - The study will be limited to industrial cellulosic wastes with emphasis on wood wastes. Other feedstocks to be considered include cotton gin trash and guayule bagasse. Paper chip feed will be used as appropriate to establish base conditions. An additional study will be to study the effect of degree of moisture in the feed on the process performance. It is anticipated that the main difficulty here will be feed control reliability problems with increasing amount of moisture. Finally, an attempt will be made to correlate the characteristics of the feedstock (chemical analysis, etc) with gasifier yields and composition.

(2) Gasification system optimization - New 10" fluidized beds (currently being installed) will be tested with the objective of allowing for investigation of higher reactor temperatures (1500-2000°F) and increased feed rates. From prior studies, the indication is that gas phase yields and composition will be improved in the new ranges of these two factors. In

addition, studies on the use of catalysts in the pyrolysis step will be continued. This will include both water gas shift catalysts (with steam addition) and tar cracking catalyst. Both fixed bed (at the reactor overhead discharge) and fluidized bed (replacing inert heat transfer medium) modes will be explored. The objective is to reduce carbon monoxide in favor of hydrogen (water gas shift) and reduce tar formation in favor of gas phase yield improvement (tar cracking).

(3) Waste stream characterization - A characterization and environmental assessment of potential waste streams will be conducted. The candidates are combustor off gas, scrubber liquid discharge and modified Fischer-Tropsch water phase trap discharge. The primary stream of concern is the pyrolysis reactor scrubber liquid discharge (tars, aldelydes, furfural, etc). The thrust here will be to minimize the formation of potential wastes in the gasification step (via catalyst usage for example).

(4) Liquid fuels synthesis and tailoring - Three subtasks will be addressed: 1) catalyst activity, 2) diesel fuel production capability, and 3) high octane gasoline yield improvement. Catalyst activity is difficult to study without continuous, around the clock operation. Nevertheless, an attempt will be made to characterize the catalyst life and the effect of alternate feedstocks for both the

modified Fischer-Tropsch and reforming steps. Of particular concern is the effect of possible trace poisons in the feedstock (from pesticides, etc). A major emphasis will also be placed on producing a diesel type fuel product from the modified Fischer-Tropsch reactor. This will involve achieving control of both product structure and molecular weight. Past studies have shown that the product is very paraffinic in nature like diesel fuel but insensitive to changes in process conditions. Thus tailoring of the product may require some physical separation development work. Some analytical development work is also anticipated here (cetane number etc). Finally, an effort will be made to improve catalytic reformer yields. Past studies have shown that a volumetric yield drop of about 20% occurs to achieve commercial octane rating. Isomerization and prehydrogenation studies in progress will be continued in this regard.

All tasks were completed as posed. Some additional studies were also implemented. Gasification data was obtained on twenty-seven feedstocks. New 10" fluidized beds were installed in the gasification system. Additional equipment modifications included feeder, scrubber and burner revisions, control systems improvement (including a separate control room), installation of new chromatographs, computer-integrator, compressor and obtainment of additional size reduction equipment. Wet feedstock development work was implemented. Elemental and ash analysis was obtained on a number of feedstocks. Temperature, catalyst, steam, recycle and residence time effects were studied in the gasification system. A limited amount of scrubber effluent characterization was accomplished. Liquid fuels system work included a continuation of factor studies for the modified Fischer-Tropsch reactor and catalytic reformer, alternative catalyst screening initiation and isomerization and prehydrogenation studies. Some separation work on the Fischer-Tropsch liquid product phases was also accomplished as well as development work on analytical procedures (eg, cetane number etc). A limited amount of catalyst activity assessment was accomplished.

The unique features of the process continue to be the ability to process a wide variety of feedstocks to diesel type fuels or high octane gasoline at mild operating conditions with commercially viable equipment. The major effort remaining at the research scale is to demonstrate that economically attractive product yields can be achieved for various feedstocks with an integrated unit. Additional future tasks fall into the categories of factor studies and alternative feedstocks.

INTRODUCTION

The project has been under development since 1975. The basic approach is indirect liquefaction, ie, thermal gasification followed by catalytic liquefaction. The indirect approach results in separation of the oxygen in the biomass feedstock, ie, oxygenated compounds do not appear in the liquid hydrocarbon fuel product. The general conversion scheme is shown in Figure 1. The process is capable of accepting a wide variety of feedstocks. Potential products include medium quality gas, normal propanol, paraffinic fuel and/or high octane gasoline. Conceivably, the process could be optimized for different products at different locations, depending on local marketing conditions and needs. To date, most industrial interest has been in diesel type fuels for transportation vehicles (trucks, farm machinery, etc.).

A flow diagram is shown in Figure 2 with laboratory photos in Figure 3. A fluidized bed pyrolysis system is used for gasification. The pyrolyzer can be fluidized with recycle pyrolysis gas, steam or recycle liquefaction system off gas or some combination thereof. Tars are removed in a wet scrubber. Unseparated pyrolysis gases are utilized as feed to a modified Fischer-Tropsch reactor. The liquid condensate from the reactor consists of a normal propanol-water phase and a paraffinic hydrocarbon phase. The reactor can be operated to optimize for either product. If a high octane gasoline is desired, the paraffinic fuel is passed through a conventional catalytic reformer. The normal propanol could be used as a fuel extender

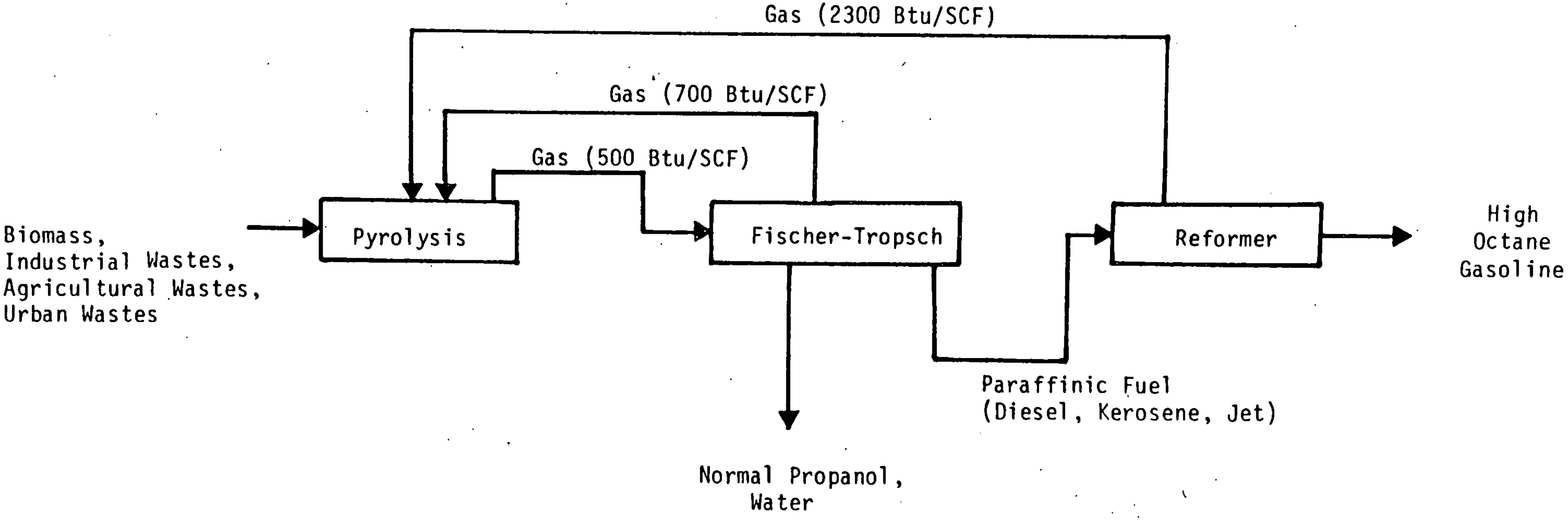
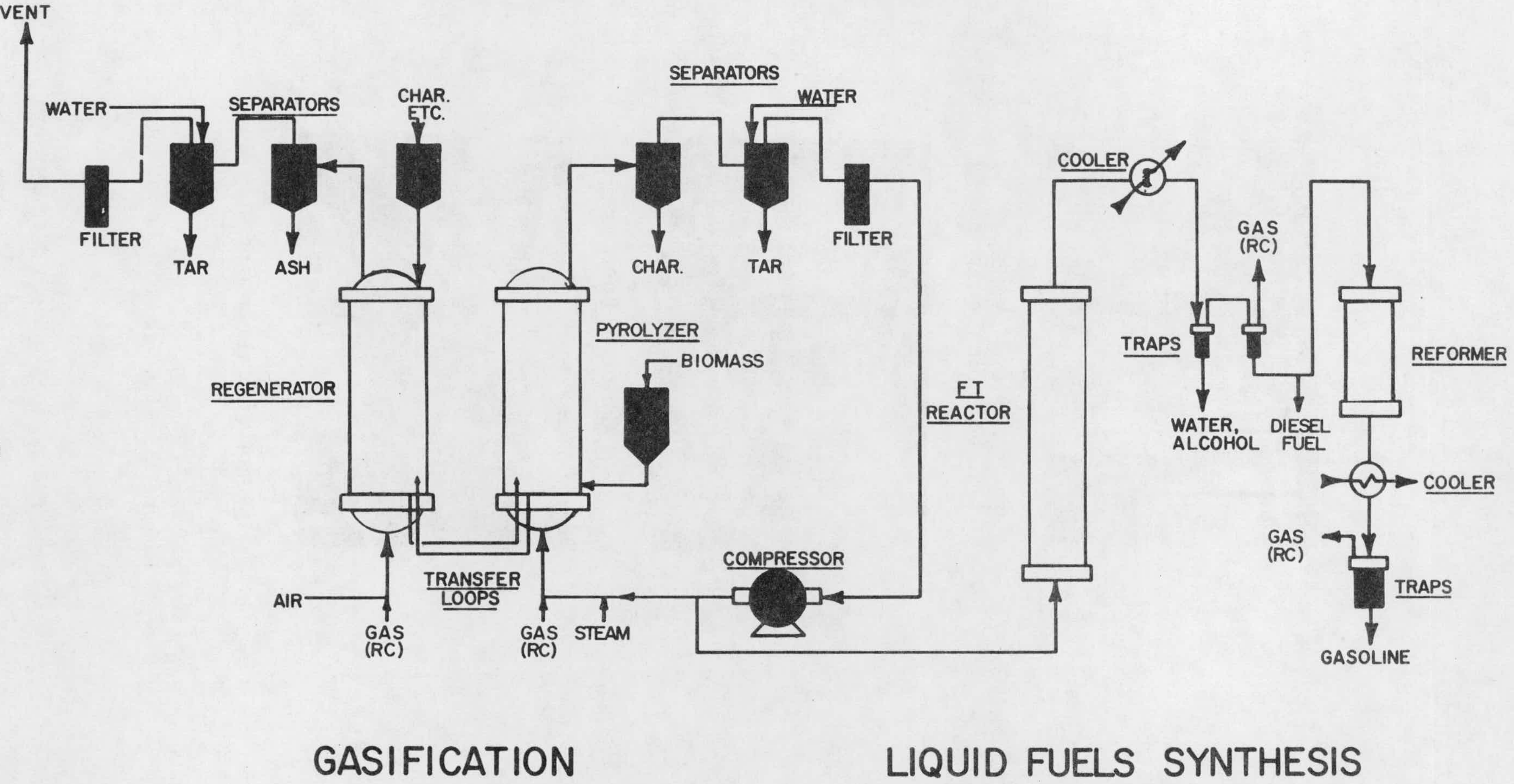


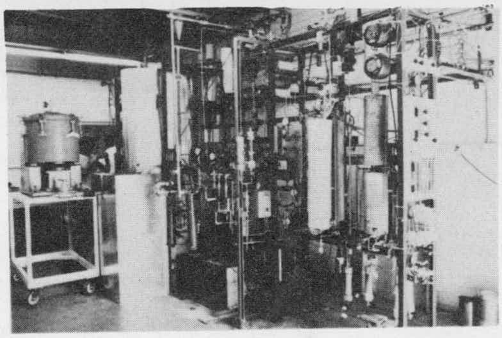
Figure 1.

Basic Chemical Conversion Scheme

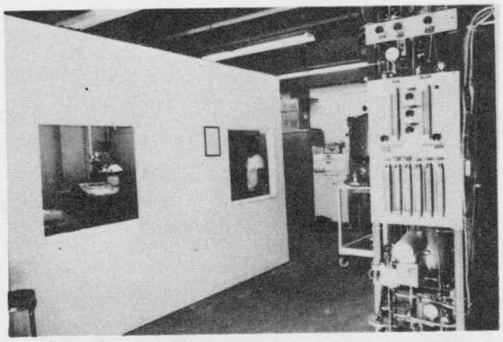
Figure 2.

CONVERSION SYSTEM SCHEMATIC





Conversion Equipment



Control Room

Analytical Equipment

Figure 3. Conversion Laboratory

if blended with the hydrocarbon fuel products. It has superior heating value and miscibility properties than methanol or ethanol. Blending the alcohol with the hydrocarbon fuel would result in a "gasohol" product where both the alcohol and gasoline components are derived by the same process from the same feedstocks. The tax advantages could be unique. Off gases from the downstream reactors are of very high quality due to the accumulation of low molecular weight paraffins.

CURRENT STATUS

The following tasks were specified in the statement of work for the contract period: (1) feedstock studies, (2) gasification system optimization, (3) waste stream characterization and (4) liquid fuels synthesis. In addition, several equipment improvements were implemented. (see APPENDIX).

Feedstock Studies. A large number of feedstocks were investigated through the gasification step. (Table 1). Sources of the feedstocks are listed in Table 2. The industrial wastes refer to by-products of industrial processes. The forest residues tested are all cut by the U.S. Forest Service in the southwest United States for water conservation purposes and burned in the field. Environmental pressures will preclude burning in the future. Eco-Fuel II is a preprocessed municipal refuse. Almond prunings are cut and burned in the almond orchards and thus represent an environmental problem. Russian thistle (tumbleweeds), raw guayule, water hyacinth and peat represent materials that might be harvested deliberately for energy production purposes. Some of the feedstocks were tested at the initiative of the Principal Investigator while others were at the request of the industrial concerns, government agencies and other University laboratories. Elemental and ash analysis for some of the feedstocks are listed in Tables 3 and 4. As indicated, the carbon, hydrogen, oxygen and nitrogen compositions are similar for the biomass materials. The sulfur content is very low except for preprocessed municipal refuse (Eco-Fuel II). The ash content does vary significantly for the materials, ranging from negligable for the synthetic polymers to over 15% for a few materials (eg., Eco-

Table 1

FEEDSTOCKS

Industrial Wastes

- Sawdust
- firbark
- guayule bagasse
- guayule cork
- jojoba meal
- almond hulls
- almond shells
- paper chips
- polyethylene
- polypropylene

Forest Residues

- creosote bush
- sugar sumac
- Arizona cypress
- pringle manzanita
- Wright silktassel
- pointleaf manzanita
- shrub live oak
- hairy mountain mahogany
- Utah juniper
- pinion pine
- mesquite

Urban Wastes

- Eco-Fuel II

Agricultural Wastes

- almond prunings

Energy Crops

- Russian thistle
- raw guayule
- water hyacinth
- peat

Table 2

FEEDSTOCK SUPPLIERS

Material	Suppliers
Almond hulls, shells, prunings	Golden Byproducts, Inc. Turlock, California
Polyethylene, polypropylene	Phillips Petroleum Bartlesville, Oklahoma
Paper chips, sawdust	Local supply
Peat	Colony Farms Crosswell, North Carolina
Arizona cypress, pringle manzanita, creosote bush, pinion pine, Wright silktassel, Utah juniper, pointleaf manzanita, shrub live oak, hairy mountain mahogany, mesquite, sugar sumac	U.S. Forest Service, Rocky Mountain Forest and Range Experiment Station
Raw guayule, guayule bagasse, guayule cork	Centro de Investigacion en Quimica Aplicada, Saltillo, Coahuila, Mexico
Russian thistle	Office of Arid Land Studies University of Arizona Tucson, Arizona
Water hyacinth	Environmental Research Laboratory, University of Arizona, Tucson, Arizona
Eco-Fuel II	Combustion Equipment Assoc., Brockton, Massachusetts
Jojoba meal	San Carlos Apache Indian Reservation, San Carlos, Arizona
Fir bark	Weyerhaeuser Corp., Tacoma, Washington

Table 3

FEEDSTOCK ANALYSIS

Sample Marking	% Nitrogen	% Sulfur	% Ash	% Loss On Ignition
Guayule - Cork	0.91	0.34	3.53	96.47
Guayule - Bagasse	0.66	0.11	3.27	96.73
Guayule - Raw	0.81	0.18	5.14	94.86
Jojoba Meal	3.94	0.36	3.04	96.96
Water Hyacinth	1.87	0.53	18.97	81.03
Almond - Hulls	0.88	0.08	5.91	94.09
Almond - Shells	0.68	0.03	8.75	91.25
Almond - Cured Prunings	1.01	0.21	25.44	75.46
Eco II - Brockton	0.50	1.44	24.41	75.59
Sawdust	0.28	0.12	7.03	92.97
Paper Chips	0.13	0.08	0.58	99.42
Russian Thistle	1.33	0.19	15.45	84.55
Peat	0.97	0.15	7.63	92.37
Polyethylene	0.09	0.17	0.04	99.96
Polypropylene	0.13	0.03	0.03	99.97

Table 4

FEEDSTOCK ANALYSIS
(WT%)

	Eco Fuel II (Brockton)	Paper Chips	Guayule Bagasse
C	38.0	41.7	40.2
H	4.9	5.7	4.7
O	31.4	52.1	48.4

Fuel II, Russian thistle, water hyacinth).

Gasification operating conditions for the feedstock survey runs are listed in Table 5. The runs were performed over a period of several months and some equipment modifications were implemented (eg., feeder modification). Pyrolysis gas composition data is shown in Tables 6-8. Gas phase yield measurements varied from 50-97% but were subject to some experimental error due to lack of a continuous feedback measurement from the solids feeder and occasional coating of the venturi gas flow meter.

The operating conditions for the gasification data should not be considered optimal but are representative of the state-of-the art of the system at the time the runs were performed. Thus for a given feedstock, improvements in performance are anticipated.

All the cellulosic 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 operating conditions for the different runs. However, several conclusions can be drawn:

(1) The more cellulosic type feedstocks yield the lowest total olefin content (generally in the 5-15 mole% range).

(2) Materials containing hydrocarbon materials (eg., 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%.

Table 5

PYROLYSIS OPERATING CONDITIONS

Temperature, °F	1200-1700
Pressure, psig	0-1
Residence Time, Sec	3-6
Feed Rate, lbs/hr	2-15
Heat Transfer Media	sand

Table 6

PYROLYSIS GAS COMPOSITION (mole %)[1]

Feedstock:	Almond Hulls	Almond Shells	Almond Prunings	Poly-ethylene	Polypro-pylene	Paper Chips	Peat[2]
H_2	28.08	26.03	25.70	14.19	13.57	14.77	45.05
O_2	0.00	0.00	0.16	0.00	0.00	0.23	0.00
CO	35.44	38.06	42.68	0.96	0.69	58.86	18.48
CO_2	13.92	12.15	5.97	0.23	0.00	3.27	16.29
H_2S	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH_4	14.96	17.21	14.88	43.56	42.43	14.76	10.69
C_2H_2	0.05	0.06	0.17	0.61	1.18	0.10	0.12
C_2H_4	4.01	3.09	5.68	19.29	13.34	3.70	4.15
C_2H_6	1.29	1.72	1.05	6.78	6.13	2.26	1.88
C_3 olefins	1.23	0.54	0.21	5.30	9.77	1.21	1.21
C_3H_8	0.03	0.06	0.00	0.00	0.00	0.08	0.09
C_4 olefins	0.12	0.10	0.08	0.59	3.64	0.18	0.19
C_4H_{10}	0.00	0.00	0.01	0.02	0.06	0.00	0.01
C_5H_{12}	0.01	0.01	0.00	0.00	0.00	0.00	0.02
C_5 + olefins	0.86	0.97	3.41	7.49	9.20	0.57	1.83
total unsaturated	6.27	4.76	9.55	33.28	37.13	5.76	7.38
H_2/CO ratio	0.79	0.68	0.60	14.78	19.67	0.25	2.44

[1] - water, nitrogen free basis
[2] - Steam fluidization with recycle pyrolysis gas to sparges (other runs with total recycle gas)

Table 7

PYROLYSIS GAS COMPOSITION (mole %)[1]

Feedstock:	Fir Bark	Sugar Sumac	Raw Guayule	Guayule Bagasse	Guayule Cork	Russian Thistle	Water Hyacinth	Sawdust	Jojoba Meal	Eco-Fuel II
H_2	16.58	28.89	17.28	25.02	20.57	26.37	23.00	15.13	11.96	15.74
O_2	0.10	0.00	0.00	0.07	0.17	0.00	0.00	0.42	0.41	0.05
CO	53.42	31.88	34.98	39.61	22.14	36.08	42.43	55.57	37.56	50.40
CO_2	2.99	10.57	8.51	6.11	3.77	14.62	13.94	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
CH_4	18.07	15.16	26.17	15.36	26.03	16.23	14.34	16.37	23.21	15.03
C_2H_2	0.05	0.01	0.04	0.21	0.05	---	0.00	0.10	0.00	0.00
C_2H_4	5.71	5.75	5.57	7.14	14.80	3.21	3.52	2.63	9.15	6.04
C_2H_6	1.60	2.85	2.31	0.63	4.79	1.69	1.62	2.36	3.44	3.60
C_3 olefins	0.37	1.81	1.50	0.00	3.04	0.61	0.57	1.13	2.01	2.03
C_3H_8	0.01	0.41	0.05	0.13	0.16	0.02	0.02	0.09	0.03	0.10
C_4 olefins	0.18	0.65	0.56	0.06	0.83	0.14	0.13	0.20	0.45	0.51
C_4H_{10}	0.02	0.08	0.01	0.00	0.08	0.01	0.00	0.01	0.01	0.11
C_5H_{12}	0.00	0.00	0.04	0.00	0.00	0.01	0.08	0.00	0.80	0.00
C_5 + olefins	0.91	2.20	2.97	5.64	3.58	1.02	0.35	0.67	1.78	3.13
total unsaturated	7.22	10.42	10.64	13.05	22.30	4.98	4.57	4.73	13.39	11.71
H_2/CO ratio	0.31	0.91	0.49	0.63	0.93	0.73	0.54	0.27	0.32	0.31

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1 - water, nitrogen free basis

Table 8

PYROLYSIS GAS COMPOSITION (mole %)[1]

Feedstock:	Arizona Cypress	Pringle Manzanita	Creosote Bush	Pinion Pine	Wright Silktassel	Utah Juniper	Pointleaf Manzanita	Shrub Live Oak	Hairy Mountain Mahogany	Mesquite
H_2	26.64	24.99	25.99	25.82	25.64	28.83	24.46	27.99	27.61	33.01
O_2	0.07	0.04	0.03	0.44	0.04	0.05	0.34	0.07	0.04	0.06
CO	38.40	40.68	39.43	41.78	38.69	39.54	35.50	41.28	37.84	44.35
CO_2	7.04	6.76	7.70	4.39	5.43	6.41	10.58	4.53	4.76	5.10
H_2S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH_4	15.82	15.10	15.61	15.68	16.56	16.20	14.08	16.86	15.32	12.11
C_2H_2	0.01	0.11	0.02	0.14	0.17	0.11	0.15	0.11	0.30	0.03
C_2H_4	6.40	6.29	6.48	6.33	7.30	6.56	5.64	5.56	10.26	2.61
C_2H_6	1.65	1.29	0.93	1.87	1.68	1.60	2.00	1.12	1.53	0.18
C_3 olefins	0.65	0.44	0.45	0.28	0.53	0.43	1.21	0.15	0.67	0.00
C_3H_8	0.02	0.01	0.05	0.01	0.05	0.02	0.08	0.01	0.04	0.17
C_4 olefins	0.21	0.10	0.18	0.08	0.15	0.12	0.29	0.09	0.16	0.01
C_4H_{10}	0.03	0.02	0.02	0.01	0.03	0.04	0.12	0.01	0.02	0.00
C_5H_{12}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_5 + olefins	3.07	4.17	3.11	3.17	3.74	0.11	5.56	2.22	1.44	2.36
total unsaturated	10.34	11.11	10.24	10.00	11.89	7.33	12.85	8.13	12.83	5.01
H_2/CO ratio	0.69	0.61	0.66	0.62	0.66	0.73	0.69	0.68	0.73	0.74

1 - water, nitrogen free basis

(4) Hydrogen/carbon monoxide mole ratios of 0.25 to 0.95 are encountered for dry feedstocks without steam addition (excluding the synthetic polymers).

(5) H_2S was not detected for any feedstock. This includes high sulfur materials such as Eco-Fuel II. This is of significance with regard to potential effects on catalyst activity downstream.

Previous studies (see PUBLICATIONS) 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 ratio of 1-1.5. Selected feedstocks are capable of producing the desired amounts of olefins (eg., guayule cork). Without steam addition, all the materials (except the synthetic polymers) result in a suboptimal H_2/CO mole ratio.

The feeder system was modified during the contract period for the purpose of studying the effect of degree of moisture in the feed on the process performance. The modification consisted of a two stage screw device where the existing vibra screw feeder fed a screw projecting into the side of the reactor (as opposed to the final stage sparge blown mechanism formerly used). Feedstocks up to about 15 wt% moisture were successfully fed. Moisture contents beyond this point were not explored during the contract period. A limited range of feedstock geometry was utilized during the period. However, a formal study of feedstock size for specified feedstocks was not conducted. The limiting conditions here were availability of size reduction devices and feeder capabilities. A limited amount of feedstock analysis was performed (Tables 3 and 4) but the information is inadequate to predict reactor system performance. A breakdown of compound types via extraction studies should prove more meaningful then elemental analysis.

Gasification System Optimization. Gasification system factors for a specified feedstock type and geometry can be grouped as follows:

(1) temperature, pressure, residence time
(2) recycle effects
(3) steam or inert gas usage
(4) catalyst usage.

For maximum olefin production, a minimum reactor pressure is indicated. The rest of the factors were addressed during the contract period.

At the beginning of the new contract period, the 4" fluidized beds (carbon steel shells, refractory lining) were replaced with 10" beds (310 stainless shells, no refractory lining). The purpose was to decrease the temperature differential between the two beds via use of a smaller particle heat transfer media (increased transfer rates) and still prevent excessive blowover of solids from the reactor (smaller particle velocity). This would then allow for investigation of higher pyrolysis operating temperatures. The effect was achieved, ie, 70-100 mesh particles resulted in a temperature differential of approximately 100°F thus allowing for pyrolysis reactor experimentation in the 1500-1700°F range. Gas phase composition results for paper chip feedstock are shown in Figure 4. Only the major components were included in the analysis (H_2, CO

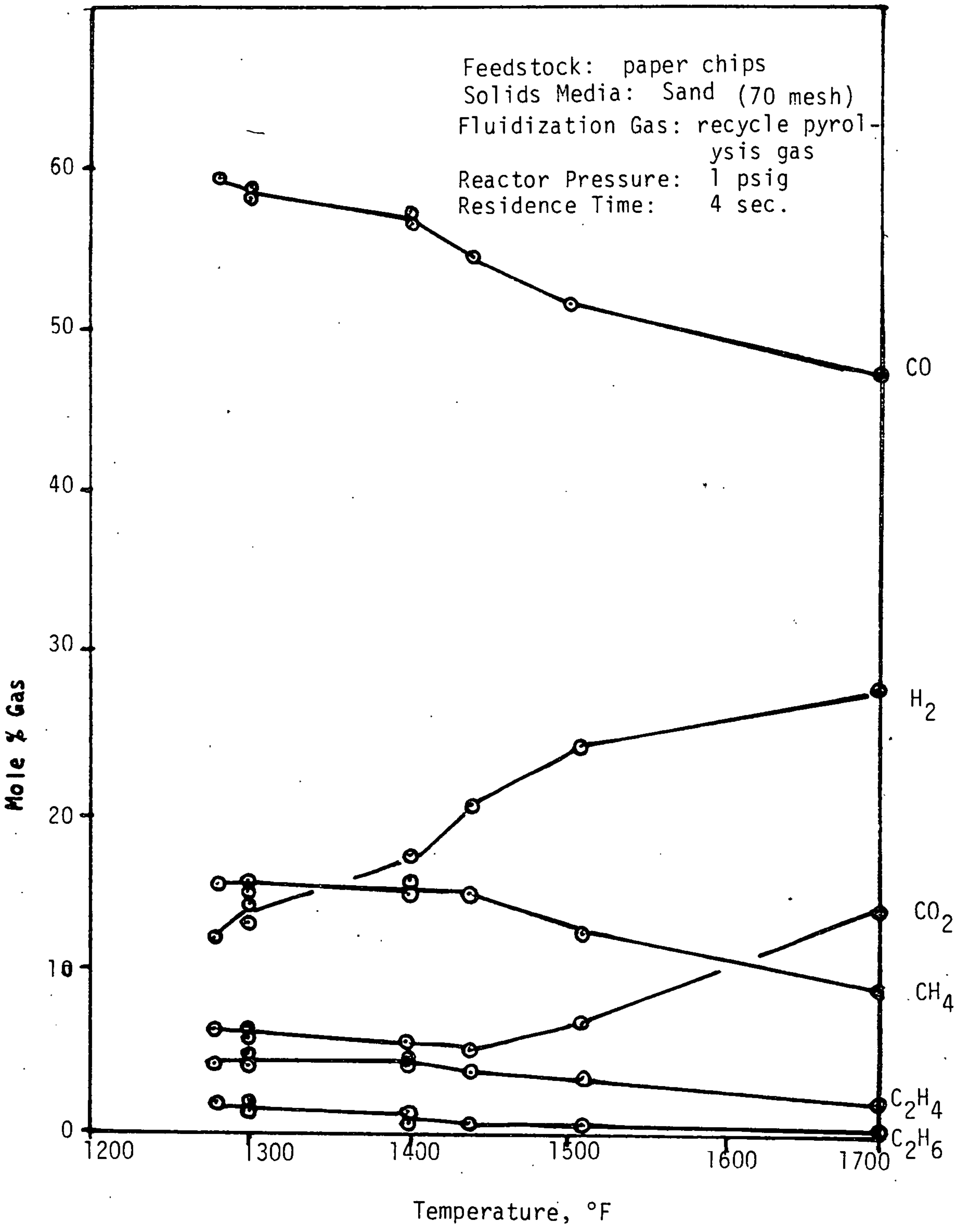

Figure 4.

Pyrolysis Gas Composition vs. Temperature

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, the recycle gas is saturated with water after passing through the wet scrubbing system. The results shown in Figure 4 indicate an apparent water gas shift effect with increasing temperature with a corresponding decline in paraffin and olefin production. When considering that gas phase yields increase with increasing temperature and that an optimal balance of carbon monoxide, hydrogen and olefin production is desired, it is apparent that temperature alone is insufficient as a control variable in the gasification system.

The effects of steam, recycle, inert gas and residence time are difficult to isolate in a fluidized bed system. Thus for a given reactor size, lower residence times are achieved by increasing the gas throughput. This is constrained by proper particle size to prevent excessive solids carryover. Experimentation in this area during the contract period consisted of steam addition to the system with fixed reactor dimensions and particle size. Results for various feedstocks are shown in Tables 9-11. The steam was superheated to approximately 600°F via a coil in the gasification system combustor. With this system, the reactor temperature was lowered with a significant amount of steam addition to the pyrolyzer. For fir bark and guayule cork feedstock (Tables 9, 10), an increase in unsaturated compounds and H_2/CO ratio were observed with steam addition. An autocatalytic water gas shift reaction

Table 9

STEAM EFFECT - FIR BARK FEEDSTOCK

	No Steam	Partial Steam
Operating Conditions:		
temperature, °F	1400	1250
pressure, psig	0.9	0.9
residence time, sec.	4	3.2
feed rate, lbs/hr	5	5
heat transfer media	sand	sand
fluidizing gas	pyrolysis gas	pyrolysis gas + steam
Pyrolysis Gas Composition (mole %)[1]:		
H_2	16.58	29.24
O_2	0.10	0.14
CO	53.42	44.41
CO_2	2.99	3.33
H_2S	0.00	0.00
CH_4	18.07	10.60
C_2H_2	0.05	0.03
C_2H_4	5.71	7.30
C_2H_6	1.60	0.54
C_3 olefins	0.37	1.93
C_3H_8	0.01	0.06
C_4 olefins	0.18	0.46
C_4H_{10}	0.00	0.00
C_5H_{12}	0.00	0.00
C_5 + olefins	0.91	1.89
total unsaturated	7.13	11.58
H_2/CO ratio	0.31	0.66

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1 - water, nitrogen free basis

Table 10

Steam-Residence Time-Recycle Effects (Guayule Cork Feedstock)

	No Steam	Steam
Operating Conditions:		
temperature, °F	1300	1200
pressure, psig	0.9	0.9
residence time, sec	8	1
feed rate, lbs/hr.	5	5
heat transfer media	70 mesh sand	70 mesh sand
fluidizing gas	recycle pyrolysis gas	recycle pyrolysis gas + steam
Pyrolysis Gas Composition (mole %)[1]:		
H_2	20.57	24.51
O_2	0.17	0.47
CO	22.14	10.87
CO_2	3.77	10.76
H_2S	0.00	0.00
CH_4	26.03	10.95
C_2H_2	0.05	0.04
C_2H_4	14.80	16.67
C_2H_6	4.79	3.24
C_3 olefins	3.04	6.49
C_3H_8	0.16	0.25
C_4 olefins	0.83	2.65
C_4H_{10}	0.08	0.21
C_5H_{12}	0.00	0.00
C_5 + olefins	3.58	12.88
total unsaturated	22.30	38.73
H_2/CO ratio	0.93	2.25

[1] - water, nitrogen free basis

Table 11

STEAM EFFECT - ECO-FUEL II FEEDSTOCK

	No Steam	Steam	Steam + Water-Gas Shift Catalyst
Operating Conditions:			
temperature, °F	1250	1180	1260
pressure, psig	0.9	0.9	1.5
residence time, sec.	4	5	5
feed rate, lbs/hr	4	4	8
heat transfer media	sand	sand	sand
fluidizing gas	pyrolysis	pyrolysis gas + steam	pyrolysis gas + steam
Pyrolysis Gas Composition (mole %)[1]:			
H_2	16.81	23.62	42.59
O_2	0.09	0.08	0.00
CO	50.62	45.24	17.18
CO_2	2.30	3.74	12.52
H_2S	0.00	0.00	0.00
CH_4	15.92	11.34	16.45
C_2H_2	0.02	0.05	0.11
C_2H_4	7.14	7.90	5.03
C_2H_6	3.43	2.26	3.67
C_3 olefins	1.72	2.51	1.03
C_3H_8	0.11	0.17	0.03
C_4 olefins	0.25	0.78	0.30
C_4H_{10}	0.04	0.06	0.02
C_5H_{12}	0.00	0.00	0.02
C_5 + olefins	1.56	2.23	1.05
total unsaturated	10.67	13.42	7.52
H_2/CO ratio	0.33	0.52	2.48

1 - water, nitrogen free basis

effect is apparent in each case. This could be due to the presence of mixed metal oxides in the ash content of the biomass (similar to commercial water gas shift catalyst composition). Eco-Fuel II feedstock did not exhibit as significant a water gas shift effect (Table 11). However, the H_2/CO ratio was increased by a factor of 7 when a section of the reactor overhead line was packed with a commercial water gas shift catalyst. In general, it appears that the H_2/CO ratio can be manipulated with steam addition for virtually any feedstock candidate. If an autocatalytic effect is not present, a simple fixed bed shift catalyst section will achieve the desired result. Olefin production appears more complicated. The most dramatic effect occurred with guayule cork feedstock with an increase from 22 to 39% with steam addition. This however corresponded to a substantial reduction in residence time (8 to 1 seconds) and may also be feedstock dependent. Current research is aimed at lowering the residence time to less than one second via a combination of steam addition and recycle off gas from the liquefaction system. The liquefaction off gas normally would be depleted of hydrogen and olefins and thus use of this gas would avoid an effective increase in residence time with respect to these components as is the case when recycling pyrolysis gas.

In addition to experimentation with commercial water gas shift catalysts, runs were conducted with commercial silica-alumina cracking catalysts in both fixed and fluidized bed operating modes. A significant change in reactor performance was not observed for either case. The fixed bed catalyst (reactor overhead line) was well coated at the end of the operating period thus indicating that a rapid activity decline occurred. The fluidized bed demonstration (continuous generation) was hampered by the problem of obtaining material of the proper size for fluidization. The successful runs from an operational viewpoint were performed with approximately one third catalyst and two thirds sand. An increased emphasis on this area will occur in the new contract period.

Waste Stream Characterization. The waste stream of primary concern is the pyrolysis reactor scrubber effluent. Other candidates are combustor off gas, combustor scrubber effluent,gasification system ash and Fischer-Tropsch reactor water phase. With the propane-oxygen heating mode utilized for the combustor during the contract period, the combustor waste streams were not appropriate to study. On a commercial scale, the combustor would utilize recycle char, liquefaction off gas,pyrolysis gas and/or biomass as fuel. All of these materials would normally be considered to be "clean" fuels.

Scrubber effluent samples from the pyrolysis step were retained for each experimental condition. These were to be analyzed at Argonne National Laboratory. This program never developed however and thus a limited amount of on-site analysis was performed. Seven compounds were observed in the water phase. One of these was identified as furfural. The remainder were either aldehydes or ketones but specific identification was not accomplished. All compositions were less than 0.1 wt% in water. Work in this area in the new contract period will utilize more sensitive analytical equipment now available for the project.

The Fischer-Tropsch water phase normally approaches a binary of normal propanol in water. Other lower molecular weight alcohols are also present in small quantity. Normal propanol probably should be considered a marketable product stream and not a waste product. However water separation would be required. The water from this stream plus that from the gasification system scrubbers would be treated and recycled to the system on a commercial scale.

Tar and ash samples were collected during the contract period but analytical results were limited to moisture, ash, volatile matter and fixed carbon only.

Work in the new contract period will concentrate on more detailed characterization of tar, ash and scrubber effluent streams for the purpose of aiding the design of commercial scale recycle and disposal equipment.

Liquid Fuels Synthesis and Tailoring. Studies completed in the liquefaction system were as follows:

(1) Fischer-Tropsch reactor - temperature, pressure, feed rate, feed composition factor studies; liquid separation study (cobalt-alumina catalyst)

(2) Reforming - prehydrogenation, isomerization.

Catalyst activity assessment was limited by insufficient staffing to conduct extended runs. A new screening study for alternative catalysts was also begun.

A feed composition study was reported for the Fischer-Tropsch step in the previous Interim Report. Results for a temperature, pressure, feed rate and feed composition (limiting cases, real gas) are shown in Tables 12-19 and Figures 5-16. A synthetic feed gas was used for the factor studies. Significant changes in product yields and composition were observed for the temperature study. Low molecular weight alcohols (C_3-C_6) maximize at about 210°C but disappear at temperatures above 240°C in the hydrocarbon phase. (Table 13, Figure 5). 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. Chromatograms of the organic phase as a function of temperature and carbon number are shown in Figure 6. The effect of temperature on the alcohol-water phase composition is shown in Table 13 and Figure 7. As indicated, normal propanol composition peaks at about 210°C with a composition of about 39 wt%. Specific gravity and yield curves for the two phases as a function of temperature are shown in Figures 8 and 9. 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 10. Conversion increased 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 yield. The above results indicate that the process could conceivably

Table 12

LIQUID FUELS REACTOR TEMPERATURE STUDY - OPERATING CONDITIONS

pressure, psig		110
feed composition, mole%:	H_2	31.7
	CO	22.1
	C_2H_4	29.9
	CH_4	5.0
	CO_2	11.3
residence time, sec		16.3
WHSV, g feed/hr-g catalyst		0.27

Table 13

Liquid Product Analyses - Temperature Study
(Water Density: 0.9945 g/ml)

Temperature, °C	187	210	240	260	270	280
Organic phase product:						
Product flow rate, m/hr	23	51	79	89	87	84
Specific gravity	.7586	.7643	.7460	.7394	.7410	.7421
Composition, weight%:						
Paraffins	46.00	43.11	54.80	53.80	50.51	49.28
Isoparaffins	15.27	17.39	22.02	28.40	32.31	33.94
Olefins	23.61	20.40	14.41	11.78	12.61	11.11
Alcohols	10.14	15.20	5.37	-	-	-
Others	4.98	3.90	3.40	6.02	4.57	5.67
Aqueous phase product:						
Product flow rate, ml/hr	27	31	33	29	25	17
Specific gravity	.9791	.9730	.9783	.9847	.9864	.9926
Composition, weight%:						
Water	65.32	58.74	63.40	71.73	74.39	83.49
Ethanol	.17	.49	1.01	1.11	.99	.74
2-Propanol	1.24	1.11	1.09	1.12	.77	.68
1-Propanol	32.86	39.10	33.43	24.39	22.10	12.76
2-Butanol	.41	.56	1.07	1.65	1.75	2.33

Figure 5.

Grouped Compound Distribution of Organic Phase Product
Temperature Study

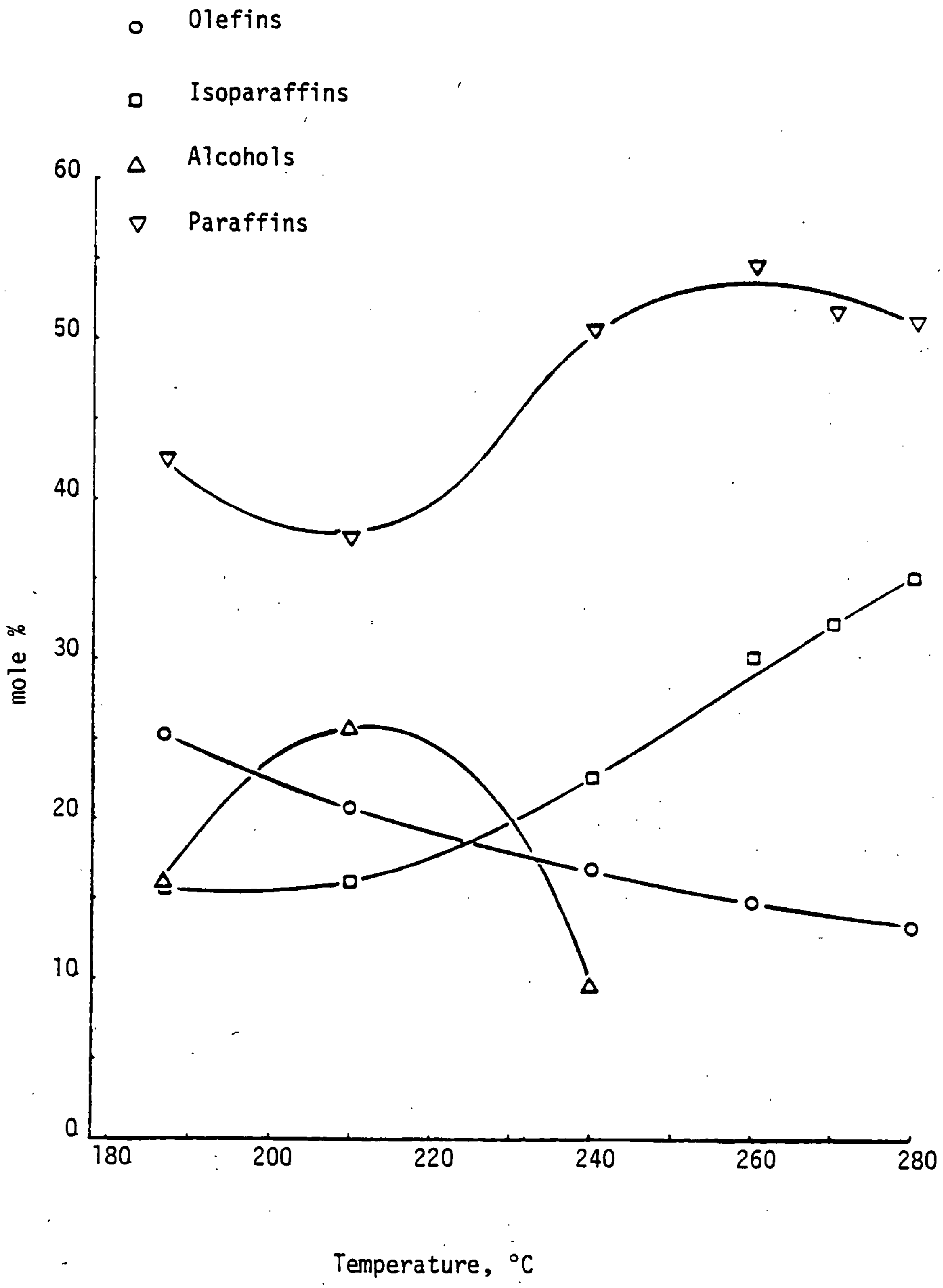


Figure 6.

Organic Phase Chromatograms - Temperature Study

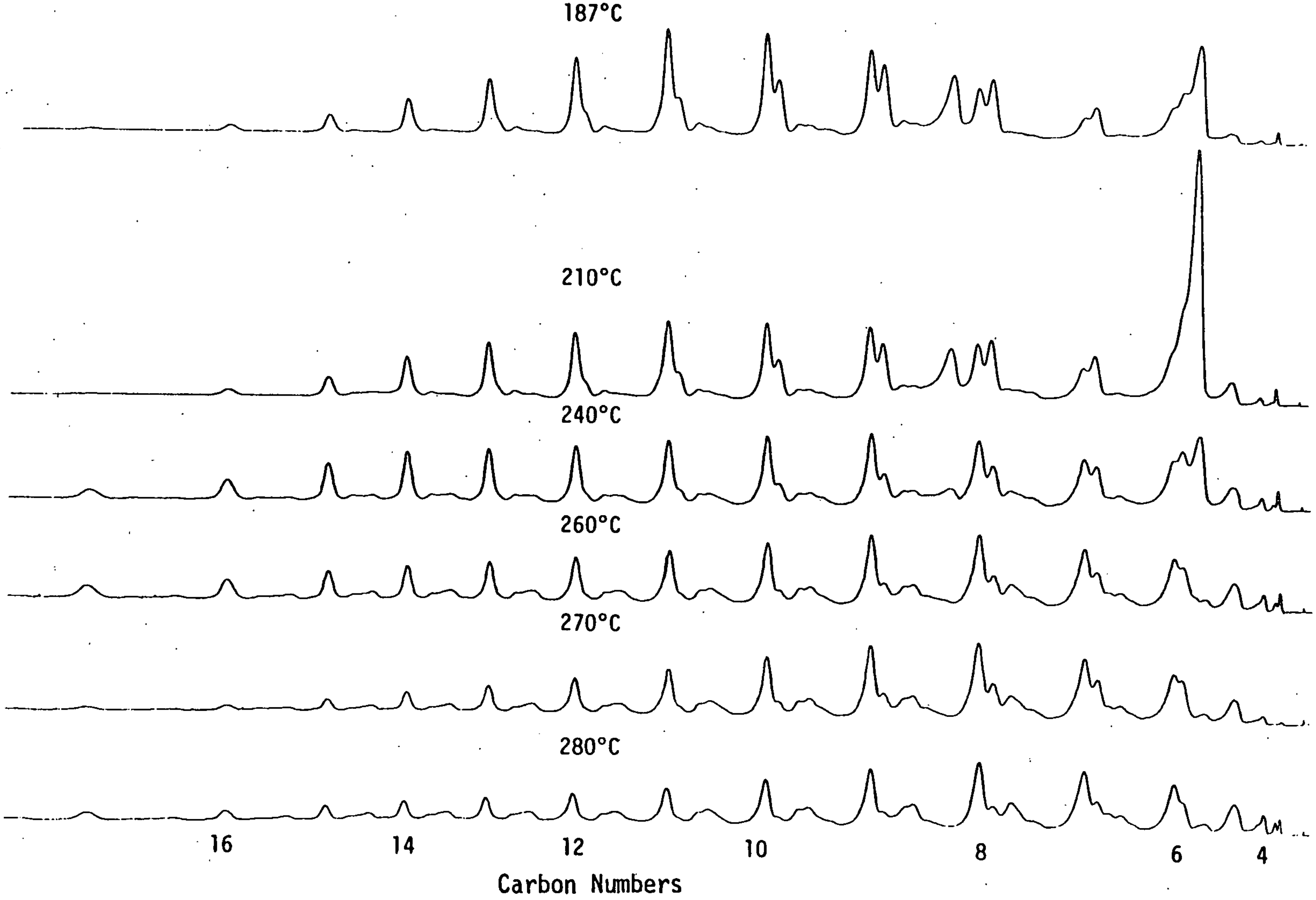


Figure 7.

Weight% Composition of Water and 1-Propanol for Aqueous Phase Product - Temperature Study

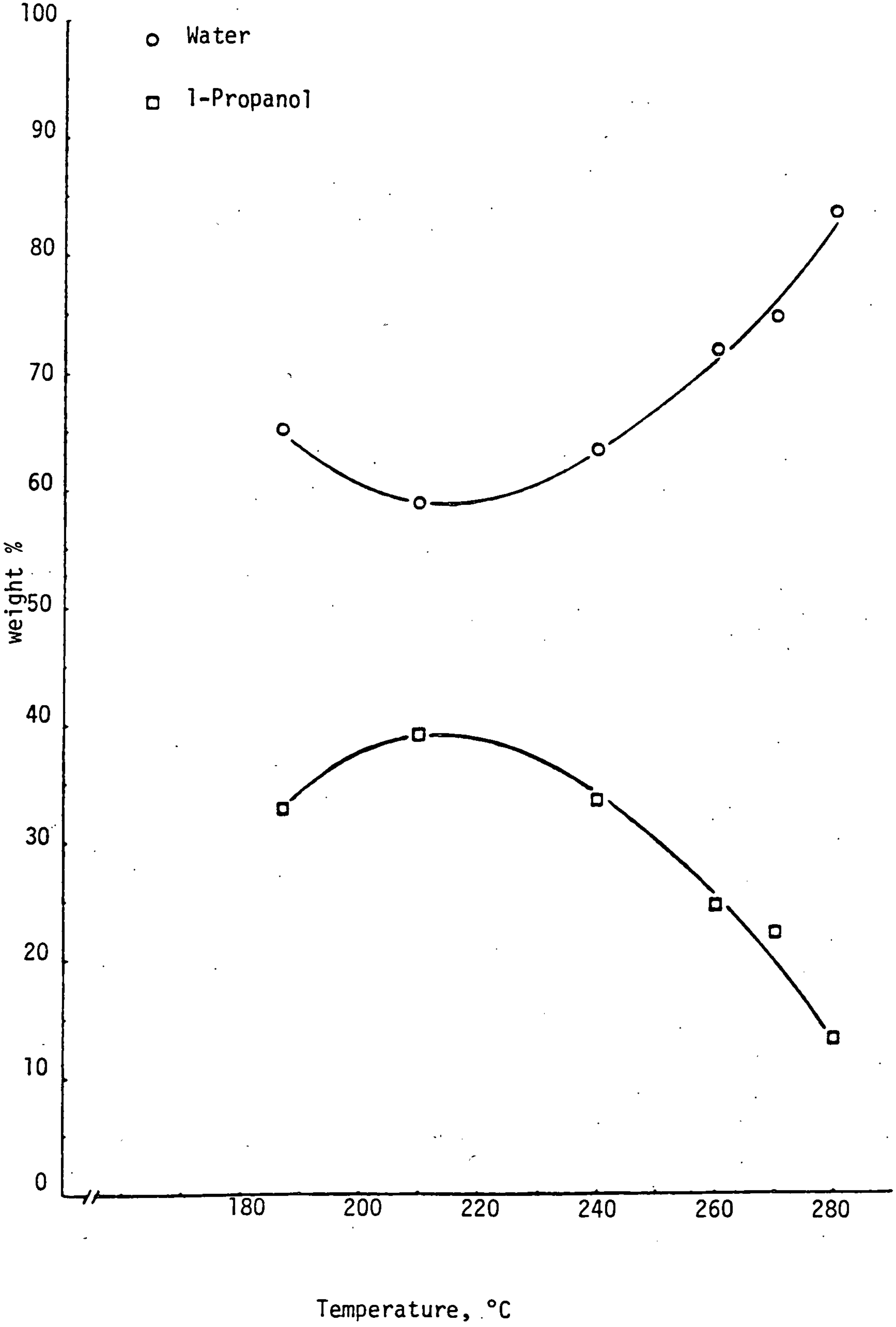


Figure 8.

Effect of Temperature on Specific Gravity of Product

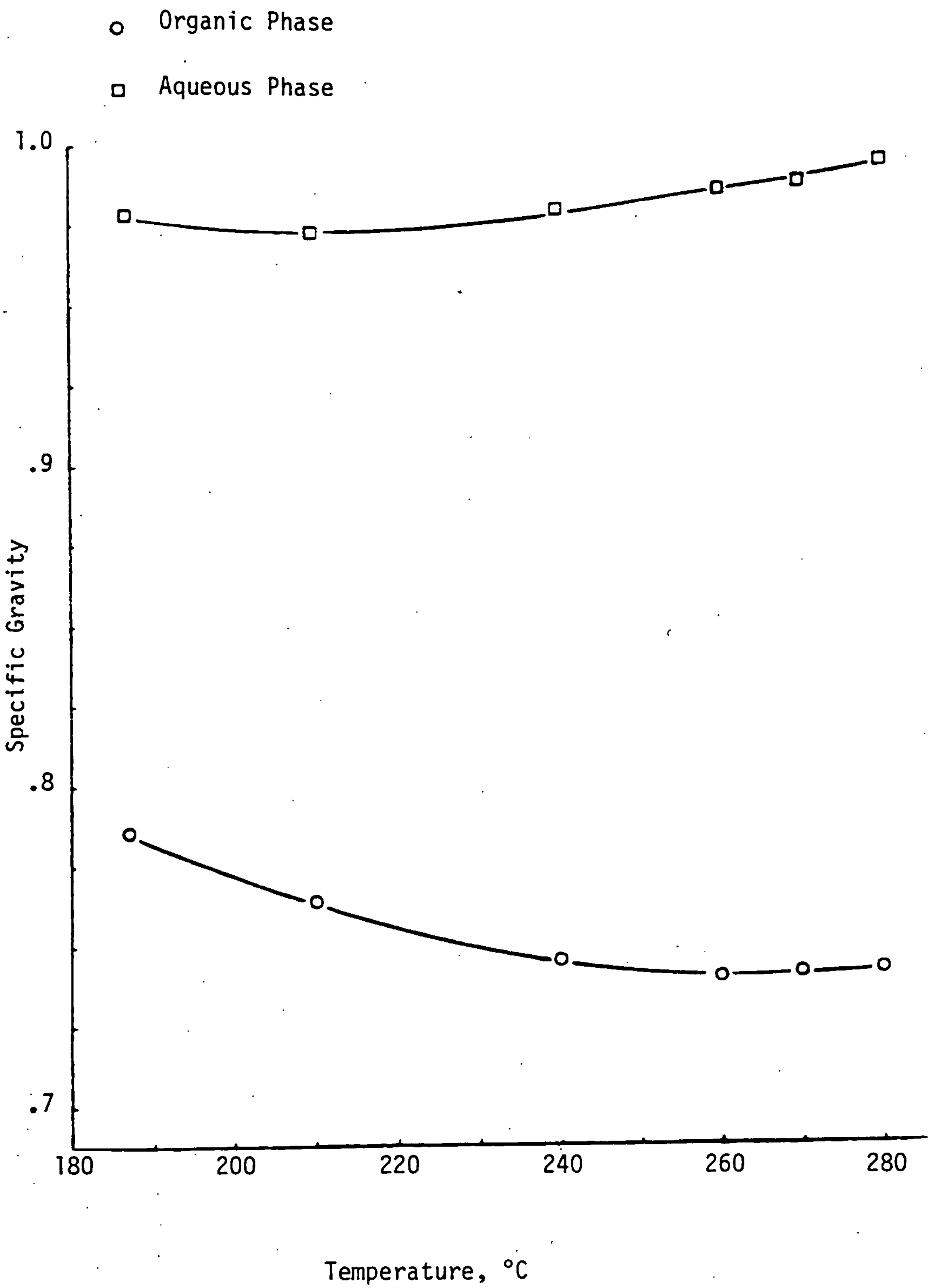


Figure 9.

Effect of Temperature on Liquid Product Flow Rate

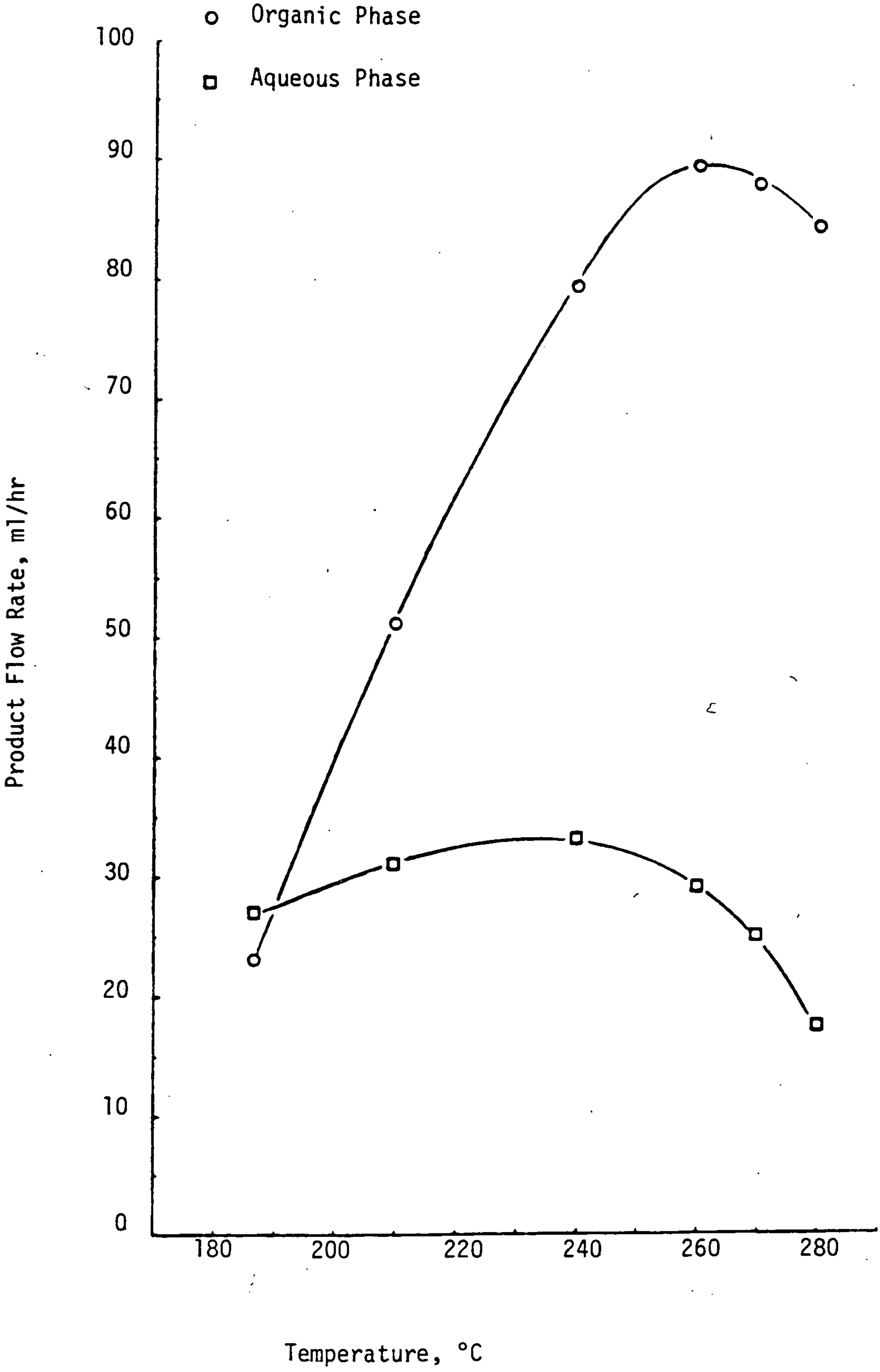


Figure 10.

Conversion of Feed Gases - Temperature Study

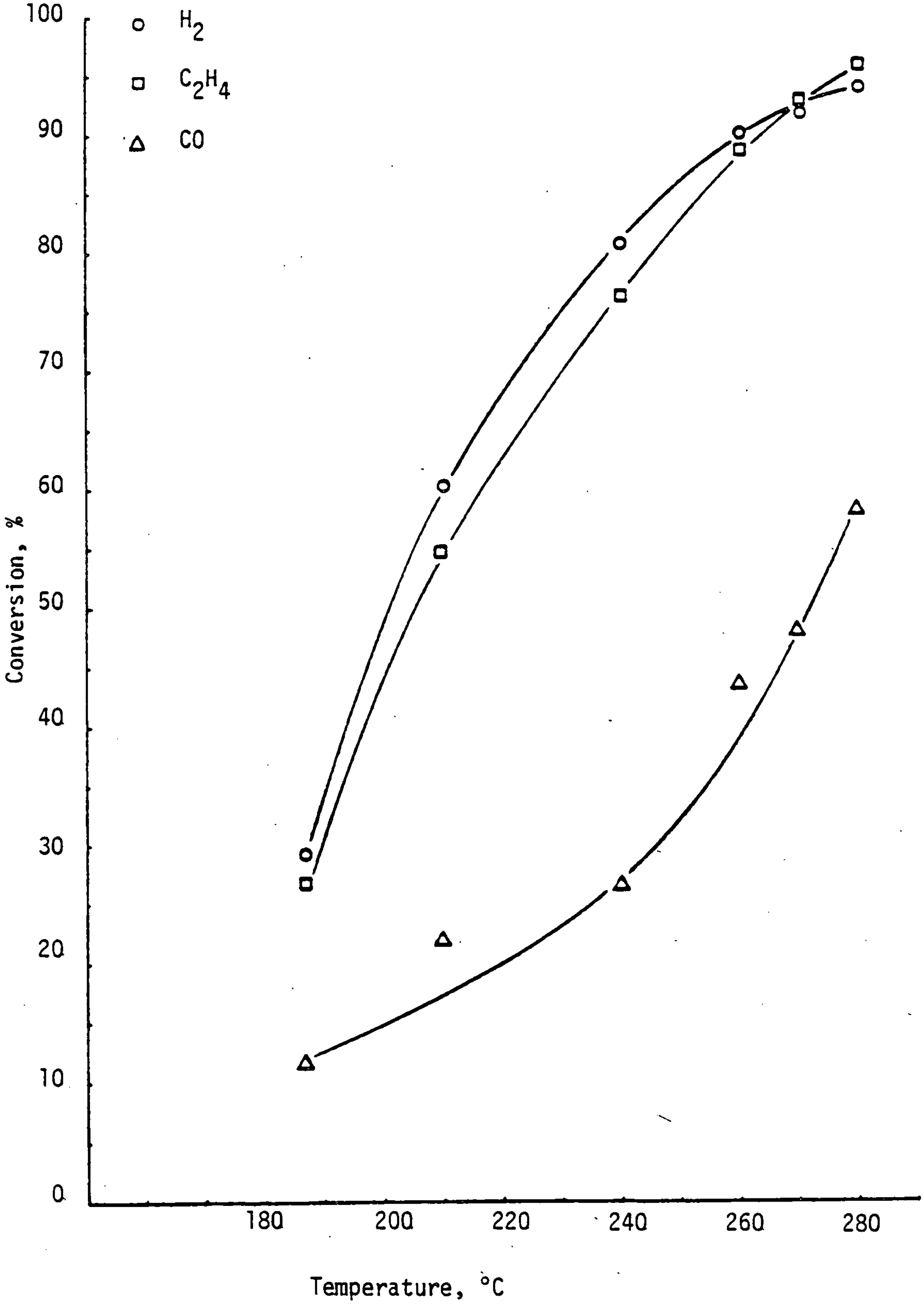


Table 14

LIQUID FUELS REACTOR PRESSURE STUDY - OPERATING CONDITIONS

temperature, °C		260
feed composition, mole%:	H_2	31.7
	CO	22.1
	C_2H_4	29.9
	CH_4	5.0
	CO_2	11.3
residence time, sec.		16.3
WHSV, g feed/hr-g catalyst		0.27

Table 15

Liquid Product Analyses - Pressure Study
(Water Density: 0.9945 g/ml)

Pressure, psig	120	131	141	150
Organic phase product:				
Product flow rate, ml/hr	50	58	62.4	61.5
Specific gravity	.7677	.7700	.7702	.7729
Composition, weight%:				
Paraffins	42.62	42.93	43.22	43.68
Isoparaffins	23.33	22.85	23.00	22.40
Olefins	18.98	18.51	18.07	18.16
Alcohols	9.95	9.98	9.69	10.24
Others	5.12	5.73	6.02	5.52
Aqueous phase product:				
Product flow rate, ml/hr	22.5	21.9	20.8	20
Specific gravity	.9798	.9780	.9783	.9778
Composition, weight%:				
Water	60.02	59.35	59.54	59.29
Ethanol	.79	.81	.77	.80
2-Propanol	2.82	3.07	3.12	3.23
1-Propanol	33.85	33.54	32.85	32.50
2-Butanol	2.52	3.23	3.72	4.18

Figure 11.

Organic Phase Chromatograms - Pressure Study

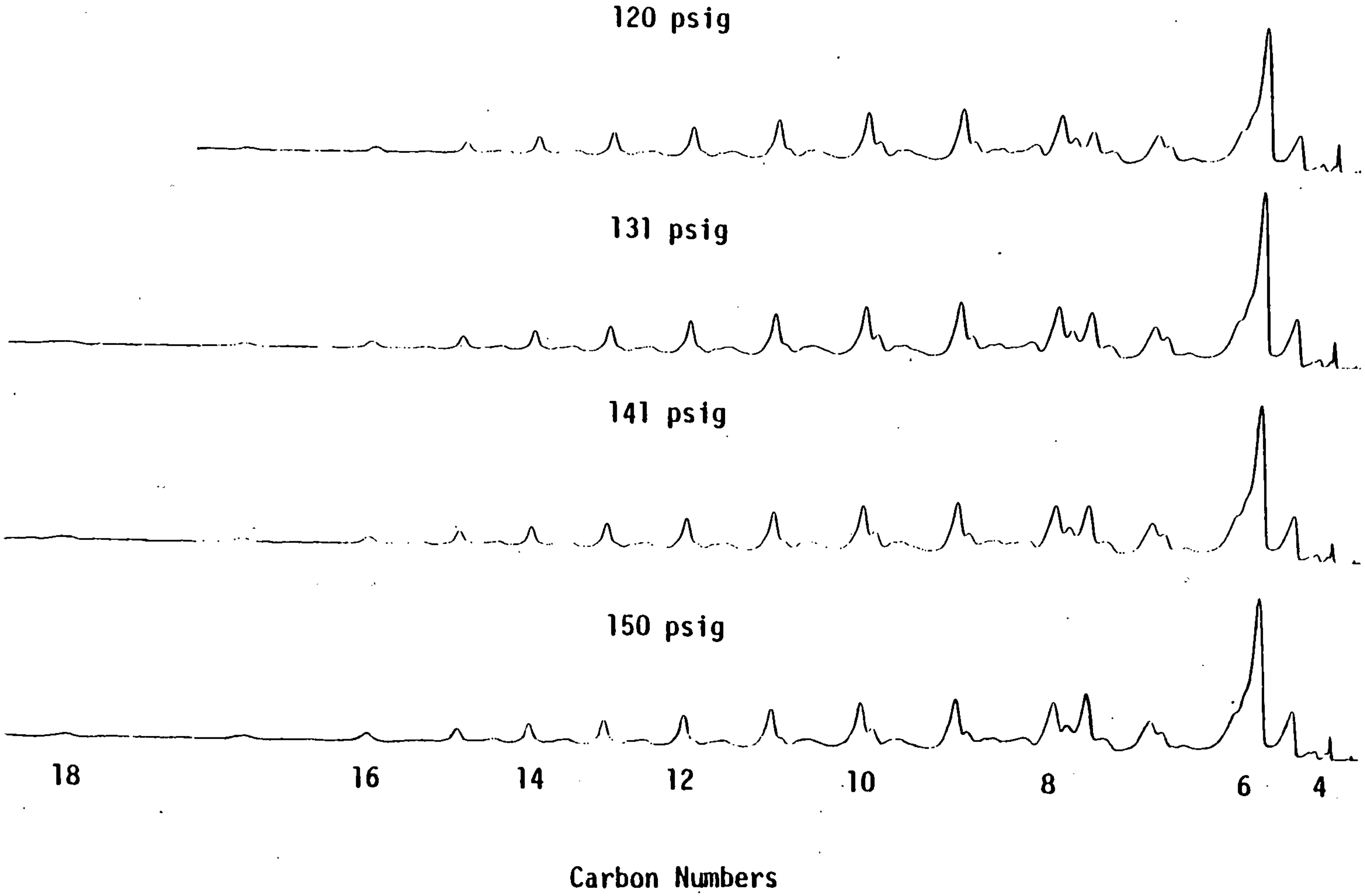


Figure 12.

Effect of Pressure on Liquid Product Flow Rate

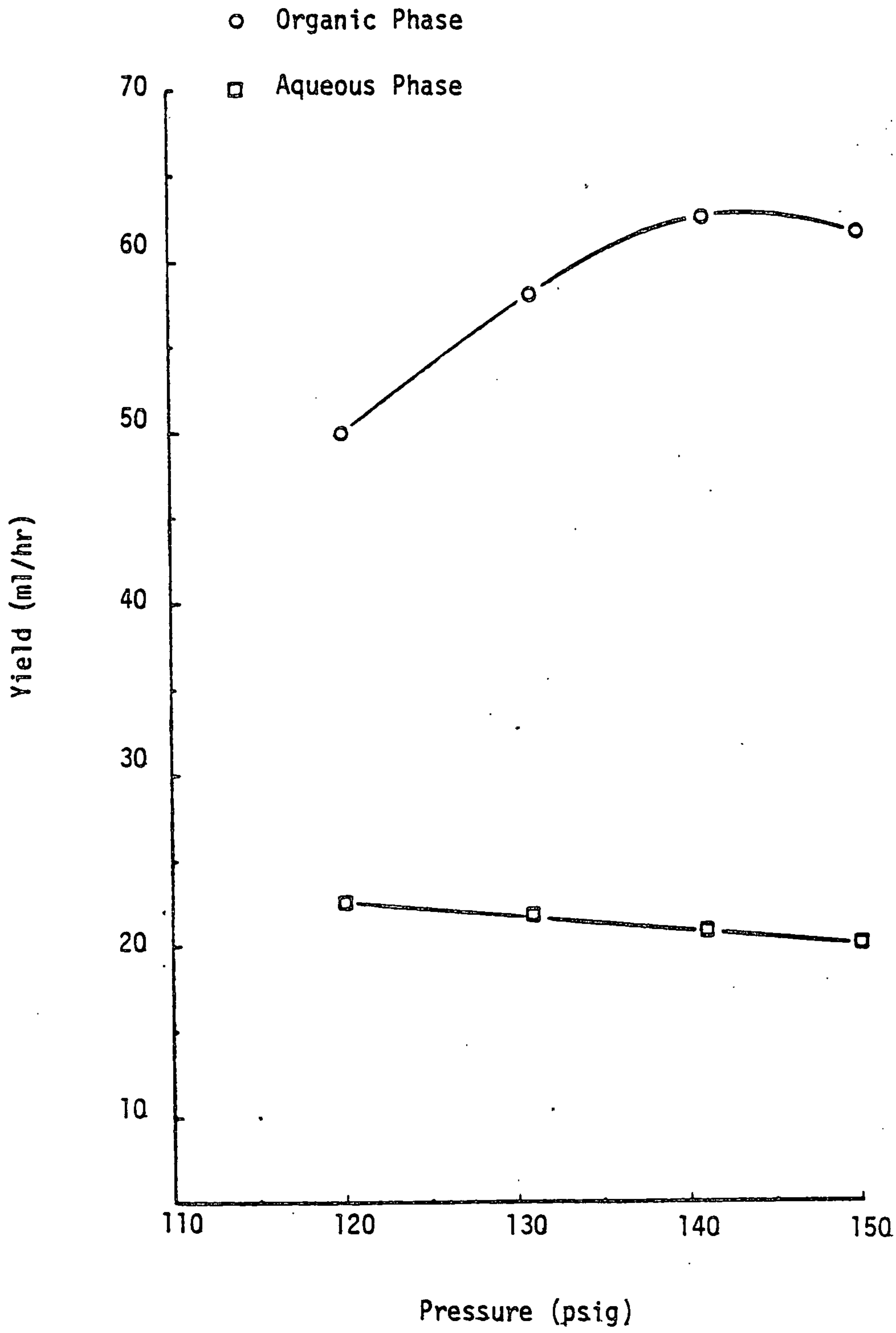


Table 16

LIQUID FUELS REACTOR FEED RATE STUDY - OPERATING CONDITIONS

temperature, °C		280
pressure, psig		120
feed composition, mole% :	H_2	31.7
	CO	22.1
	C_2H_4	29.9
	CH_4	5.0
	CO_2	11.3

Table 17

Liquid Product Analyses - Feed Rate Study
(Water Density: 0.9945 g/ml)

Feed Rate, SCFH :	20	25	30	35	40
Residence time (sec) :	25.2	20.1	16.8	14.4	12.6
WHSV (g feed/hr -g catalyst) :	.18	.22	.26	.31	.35
Organic phase product:					
Product flow rate, ml/hr	17.6	22.8	28.0	33.3	39.0
Specific gravity	.7675	.7672	.7693	.7732	.7748
Composition, weight%:					
Paraffins	47.88	48.18	47.75	47.55	47.31
Isoparaffins	29.22	29.52	29.49	27.61	27.72
Olefins	14.57	14.74	14.62	14.54	14.44
Alcohols	3.43	2.76	3.55	4.02	4.45
Others	4.90	4.80	4.59	6.28	6.08
Aqueous phase product:					
Product flow rate, ml/hr	7.7	10.2	12.6	14.2	18.0
Specific gravity	.9870	.9871	.9876	.9851	.9851
Composition, weight%:					
Water	69.51	67.74	65.70	63.10	61.78
Ethanol	.49	.53	.59	.57	.71
2-Propanol	1.43	1.34	1.36	1.93	1.89
1-Propanol	20.92	20.67	22.50	25.87	27.35
2-Butanol	7.65	9.72	9.85	8.53	8.27

Figure 13.

Organic Phase Chromatograms - Feed Rate Study

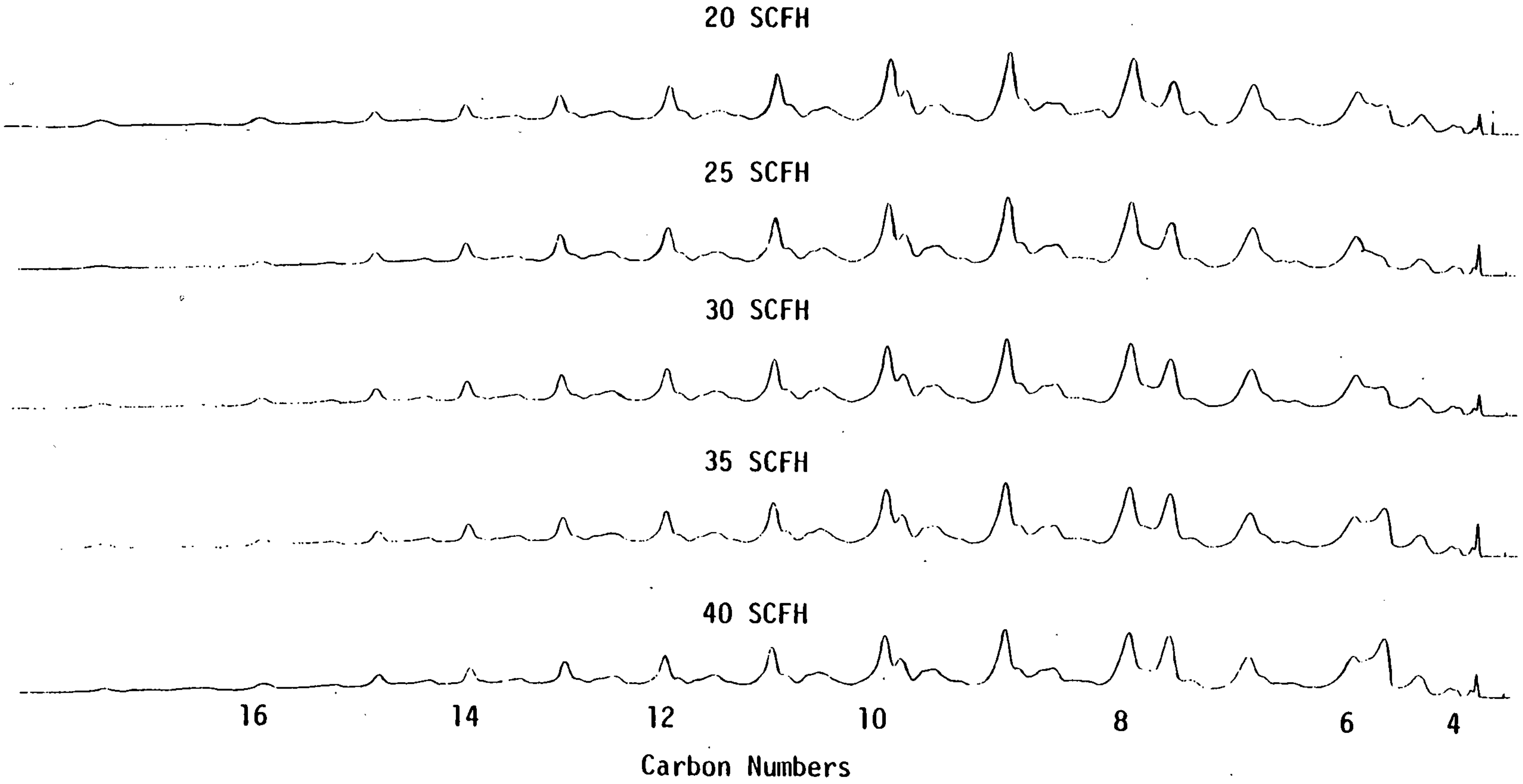


Figure 14.

Effect of Feed Rate on Liquid Product Flow Rate

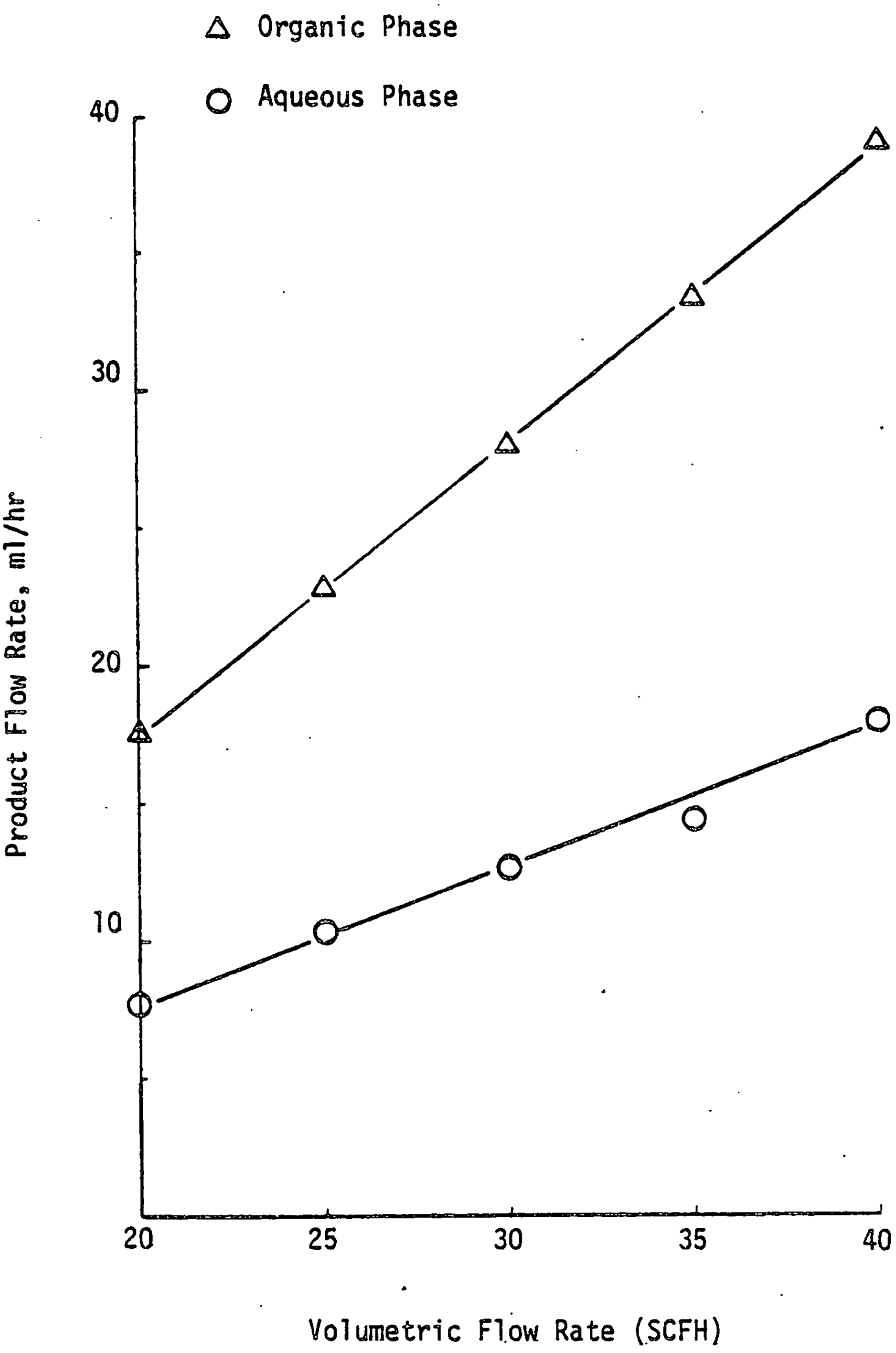


Table 18

LIQUID FUELS REACTOR LIMITING COMPOSITION STUDY - OPERATING CONDITIONS

temperature, °C	260
pressure, psig	110
residence time, sec	16.8
WHSV, g feed/hr-g catalyst	0.26

Table 19

Liquid Product Analyses - Limiting Composition Study
(Water Density: 0.9965 g/ml)

Run	H_2/CO	N_2/C_2H_4	H_2/C_2H_4
Composition, mole%	66.7/33.3	43.9/56.1	43.9/56.1
Organic phase product:			
Product flow rate, ml/hr	13	4	1.4
Specific gravity	.73	.76	.76
Composition, weight%:			
Paraffins	76.3	70.11	70.28
Isoparaffins	20.0	19.82	17.57
Others	3.7	10.07	12.15
Aqueous phase product:			
Product flow rate, ml/hr	115	-	-
Specific Gravity	.9999	-	-
Composition, weight%:			
Water	100		

Figure 15.

Organic Phase Chromatograms - Limiting Composition Study

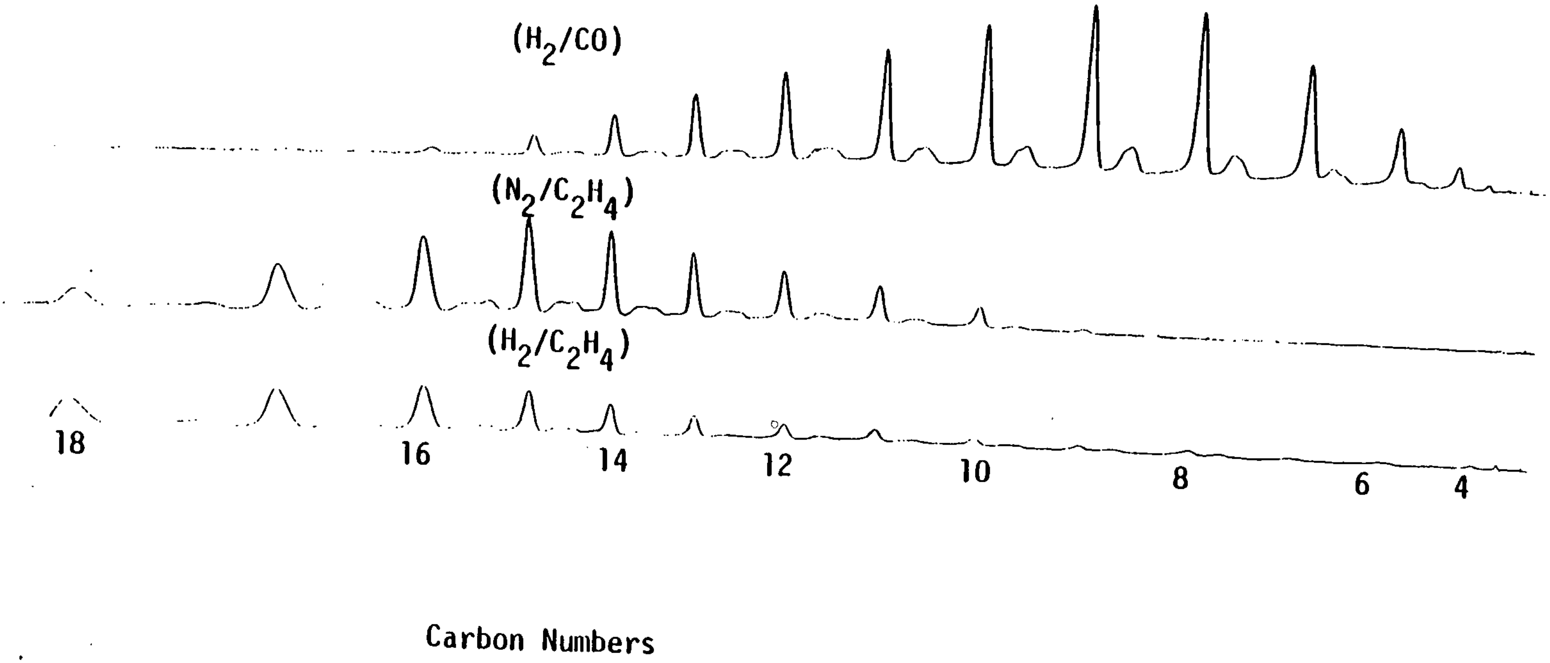
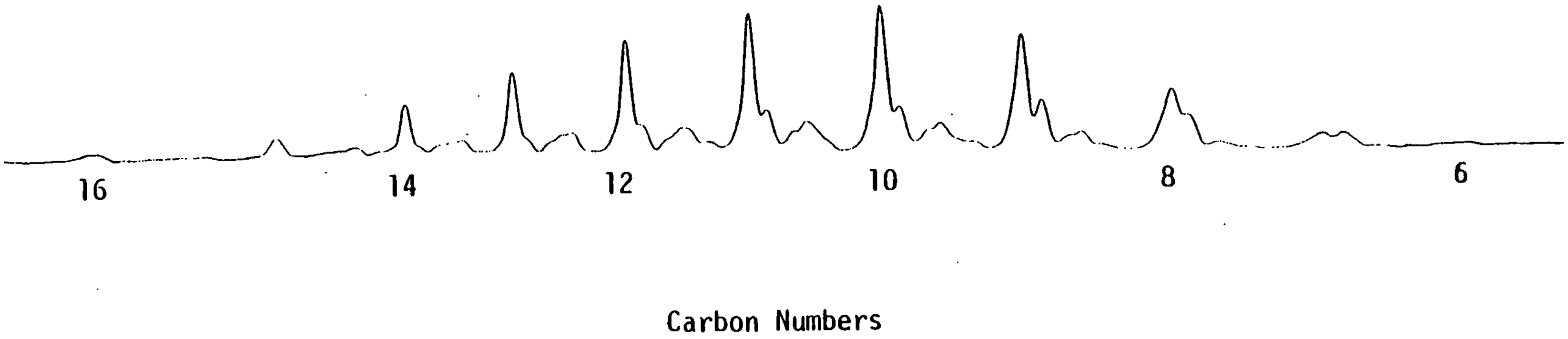


Figure 16.

Organic Phase Analysis - Pyrolysis Gas Run

Composition:	weight %
Paraffins:	50.32
Isoparaffins:	21.43
Olefins:	21.86
Others:	6.39



be optimized for normal propanol production (1979 price: $2.22/gal.).

The pressure study (Tables 14, 15; Figures 11, 12) reveal little change in composition with pressure flucuations. Liquid hydrocarbon production peaks at about 140 psig. Similarly, feed rate has no noticeable effect on product composition (Tables 16, 17; Figure 13). Liquid product flow rates do increase with increase in reactant feed as expected (Figure 14) with optimization of residence time not yet established.

A limiting feed composition study was also performed (hydrogen + carbon monoxide, nitrogen + ethylene, hydrogen + ethylene). Results are summarized in Table 18, 19 and Figure 15. Large amounts of pure water were produced for the (H_2/CO) run. No alcohols were produced in the three limiting runs. Relatively low molecular weight hydrocarbons were observed in the organic phase for the (H_2/CO) run while relatively high molecular weight hydrocarbons were detected for the (N_2/C_2H_4) and (H_2/C_2H_4) runs. Olefins were not detected in the hydrocarbon product for these three runs. The results indicate the necessity for all three reactant types to maximize liquid hydrocarbon yields.

A run with activated alumina only in the reactor (120 psig, 260°C, 30 SCFH, feed mole%= 31.71 H_2, 22.06 H_2, 29.90 C_2H_4, 5.00 CH_4, 11.33 CO_2) produced pure water only (no liquid hydrocarbons). Thus the synthesized hydrocarbons are apparently formed by catalysis with the cobalt oxides (not via alumina or by thermal reaction).

Several runs were performed using real pyrolysis gas. Compressor limitations at the time limited the Fischer-Tropsch operating pressure to atmospheric resulting in low organic product yields. Product quality remained high and similar to that obtained from a synthetic feed gas. A typical chromatogram of Fischer-Tropsch organic phase product obtained using real pyrolysis gas is shown in Figure 16.

A comparison of experimental undistilled Fischer-Tropsch hydrocarbon phase properties with that of commercial materials derived from petroleum is shown in Table 20 and Figure 17. The two experimental samples represent limits from the factor studies. As indicated, the closest similarity is with JP-4 jet fuel. A simple distillation (Table 21, Figure 18) will result in a closer match for diesel fuel or kerosene. All organic phase product (real or synthetic gas feed) has been in the C_4-C_{17} carbon range.

A brief study was conducted to assess the feasibility of separating the normal propanol from the water in the Fischer-Tropsch liquids. A combination of processes, including distillation, saltation, and extraction, was carried out to concentrate the normal propanol. A procedure to obtain pure normal propanol is shown in Figure 19. Potassium chloride was used for saltation on the basis of its zero solubility in normal propanol. Part of the water was removed by saltation. Hexane extraction was considered as a method to break the azeotropic point of the normal propanol-water mixture (87.7°C at 73.4 wt% of normal propanol). A result of 92 wt% of normal propanol was achieved. To obtain a higher purity normal propanol product, the mixture could be dried with anhydrous potassium carbonate or with anhydrous calcium sulphate, and

Table 20

Properties of Fischer-Tropsch Product and Commercial Fuel Oils

		Commercial Fuel Oils			Fischer-Tropsch Product	
		No. 2 Diesel	Kerosine	JP-4	Sample 1	Sample 2
Specific gravity		.836	.8108	.7586	.7268	.7483
Gravity, API°		37.8	43/43.4*	55/52.8*	63.1	57.6
Boiling point range, °F						
evaporated at	10%	369	336/373*	147/209*	180	140
	50%	458	410/418*	302/311*	306	279
	90%	563	479/480*	438/419*	457	475
Calculated Cetane Index		45.9	47.8/50.6*	48.3/46.6*	66.4	47.9
Heating value, Btu/lb		19383	21676	22440	20430	22113

* from "Petroleum Products Handbook", McGraw Hill, 1960

Figure 17.

Organic Phase Chromatograms of Fischer-Tropsch Products and Commercial Fuel Oils

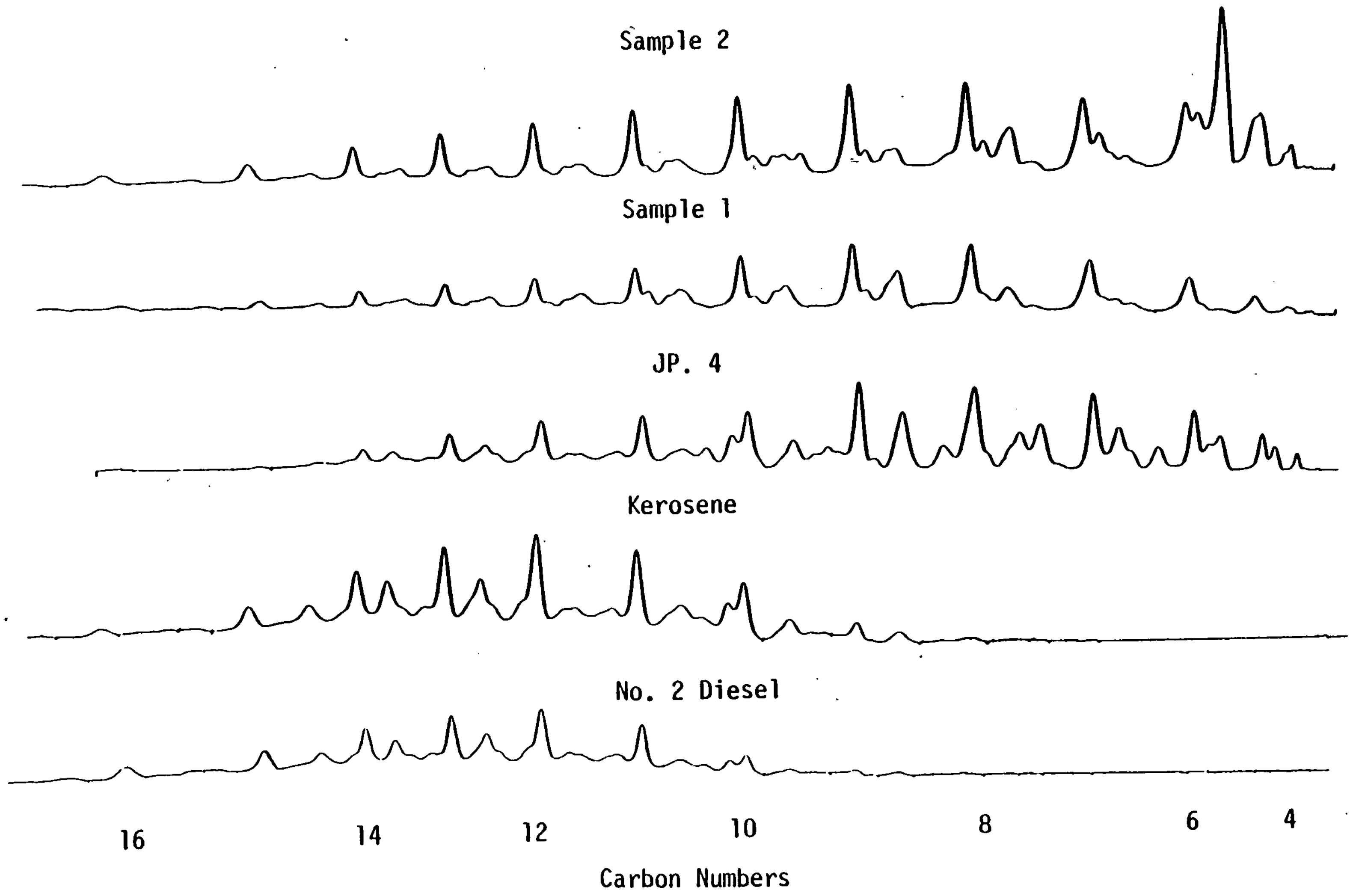


Table 21

Grouped Analysis for the Distillation of The Fischer-Tropsch Organic Phase Product

	Undistilled	Condensates (150°C$^-$)	Remainders (150°C$^+$)
Volume, ml	100	34.2	60.4
Specific Gravity	.7382	.7303	.7685
Grouped Analysis, mole%			
Paraffins			
C_4-C_9	29.81	43.55	10.01
C_{10}^+	20.37	3.19	44.88
Isoparaffins			
C_4-C_9	14.29	17.47	4.56
C_{10}^+	12.50	4.01	23.08
Olefins			
C_4-C_9	11.39	17.06	1.36
C_{10}^+	2.53	.62	3.87
Alcohols	5.15	13.99	-
Others	3.96	-	12.24

Figure 18.

Organic Phase Chromatograms - Distillation Separation

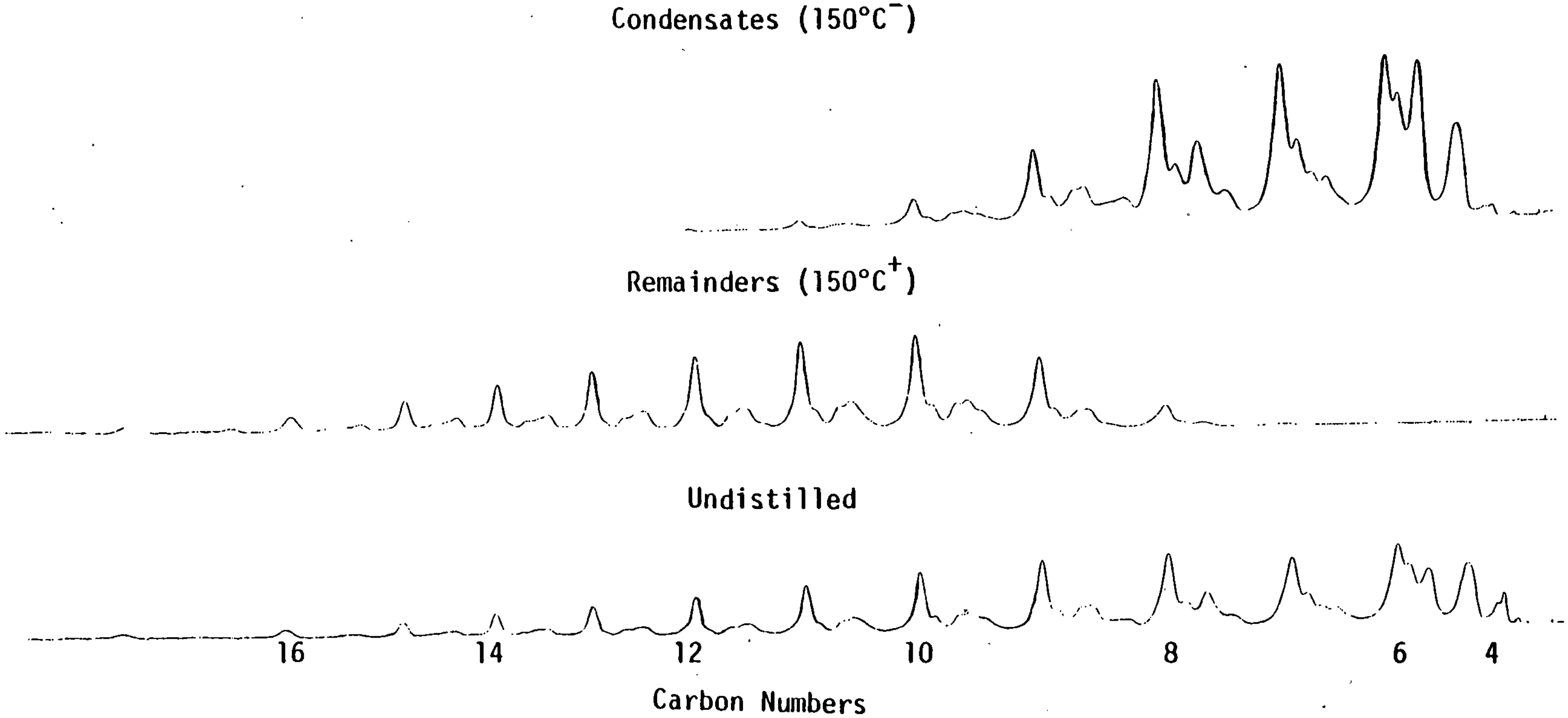
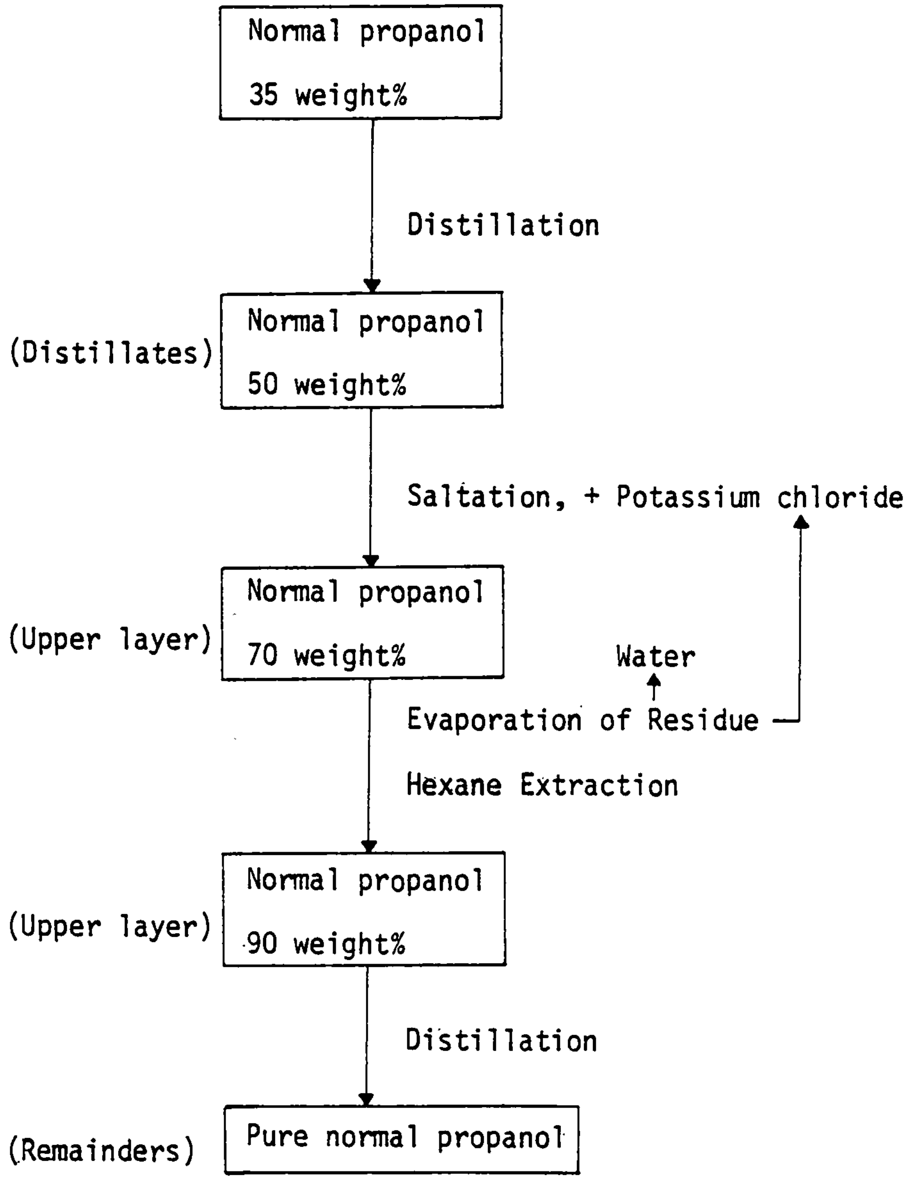


Figure 19.

Procedure for 1-Propanol Purification



distilled through an efficient fractionating column operating at atmospheric pressure and a temperature of about 97°C. The purification technology for separating normal propanol from water should be considered state-of-the-art.

Previous studies on the reforming step (see previous Interim Report) indicated that the Fischer-Tropsch hydrocarbon phase could be converted to a high octane gasoline but with a volumetric yield loss of about 20%. The loss manifests itself in the form of a high quality off gas (primarily C_1-C_5 normal paraffins). Thus some of the yield loss should be recoverable via recycle of the off gas back to the gasification system. However it was desired to assess the effect of isomerization and hydrogenation on reforming performance independent of recycle effects.

The isomerization process is generally used in a petroleum refinery to convert n-pentane and n-butane to i-pentane and i-butane, which give a higher octane rating. The i-pentane and i-butane are then blended with the gasoline for a higher octane rating. The hydrogenation process has been used in the petroleum industry for cracking low grade crudes and residues, desulfurizing gasoline and saturating olefins for a longer catalyst life and better product quality. In order to survey these processes, a Ni type isomerization catalyst and a Ni type hydrogenation catalyst were obtained from Harshaw Chemical Company.

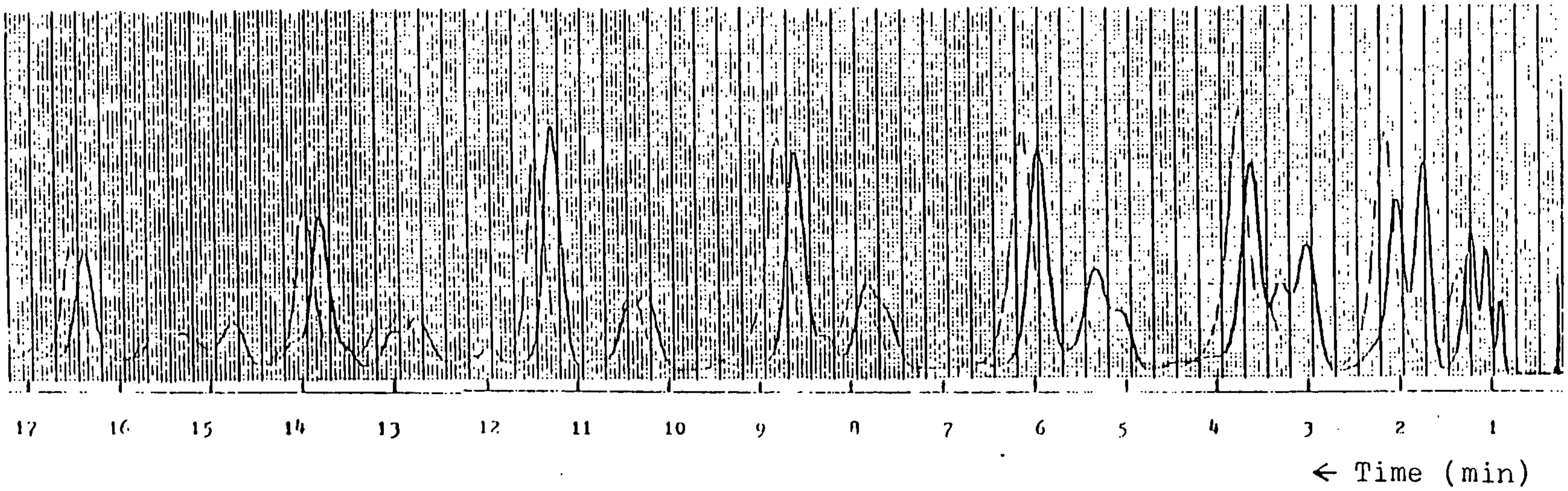
The reforming unit was used for the isomerization study where the reforming catalyst was replaced by the isomerization catalyst.

The same amounts of catalyst were used in both cases. The base point operating condition of the reforming catalyst was used for comparison purposes. The reactor operating conditions were:

Temperature:	850°F
Pressure:	500 psig
Feed Rate:	1.0 ml/min
Catalyst:	Ni-4301, Harshaw Chemical Company 298 gm, @ Virgin Activity.

The octane number of this product was 73, and 42% liquid yield was produced. Under similar operating conditions, the octane number of the reformate was 81, and 46% of liquid volume was produced, using a reforming catalyst from American Cyanamid Company. Figure 20 shows a comparison of gas chromatograms of the isomerization. Isomerization does occur in the low molecular weight portion (carbon number less than seven). For the other portions isomerization has little effect on the composition. The amount of toluene, benzene, and other aromatics was not significantly increased, which indicated that the dehydroisomerization of alkylcyclo-pentanes to aromatics was not significantly improved on the surface of this catalyst. However, it is a good isomerization catalyst for light hydrocarbons such as pentane, butane, etc. Further study on this catalyst is indicated, using fractionated feedstock.

Hydrogen was used to saturate the olefins in the Fischer-Tropsch organic phase for the hydrogenation study. A unit identical to the reforming process was used for hydrogenation. Hydrogen



* This is a multiple gas chromatogram chart. Time scale shown here is for product, while the time scale for feed is not shown on chart, which is about 12 sec. later than product.

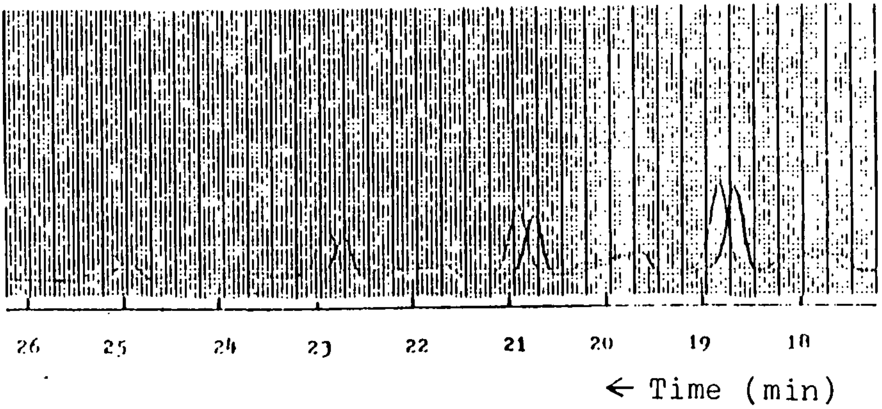


Figure 20.

Isomerization Products vs. Feed

gas was combined with liquid hydrocarbons before entering the reactor. An excess amount of hydrogen was used to complete olefin saturation. The reaction temperature used shouldn't be high enough to saturate the phenyl groups. A temperature of 500°F was suggested by Harshaw Chemical Company. A rotameter was used to control the hydrogen flow rate. The maximum system pressure of the rotameter is 350 psig. For safety considerations, the system pressure was set at 250 psig. The operating conditions are summarized as follows:

Temperature:	500°F
Pressure:	250 psig
Feed rate (H_2):	100.0 ml/min
Feed rate (HC):	2.0 ml/min
Catalyst:	Ni-3266, Harshaw Chemical Company 278 gram, @ Virgin Activity.

The octane number of the hydrogenation product was less than 10, and only 33% liquid yields were obtained in these runs. Figure 21 shows a comparison of the gas chromatograms of the hydrogenation product and feed. It indicates that the olefins have disappeared, and the concentration of saturated paraffins is increased.

The hydrogenation products were then fed to the reformer for catalytic reforming at optimum operating conditions for comparison purposes. The octane rating of this product was 73, with a volumetric yield of 43%. Figure 22 shows a comparison of the gas chromatograms of feed and the reformer product for the run at the optimum conditions. Although the olefins were eliminated, neither the octane rating nor yield was improved as compared with unhydrogenated feed.

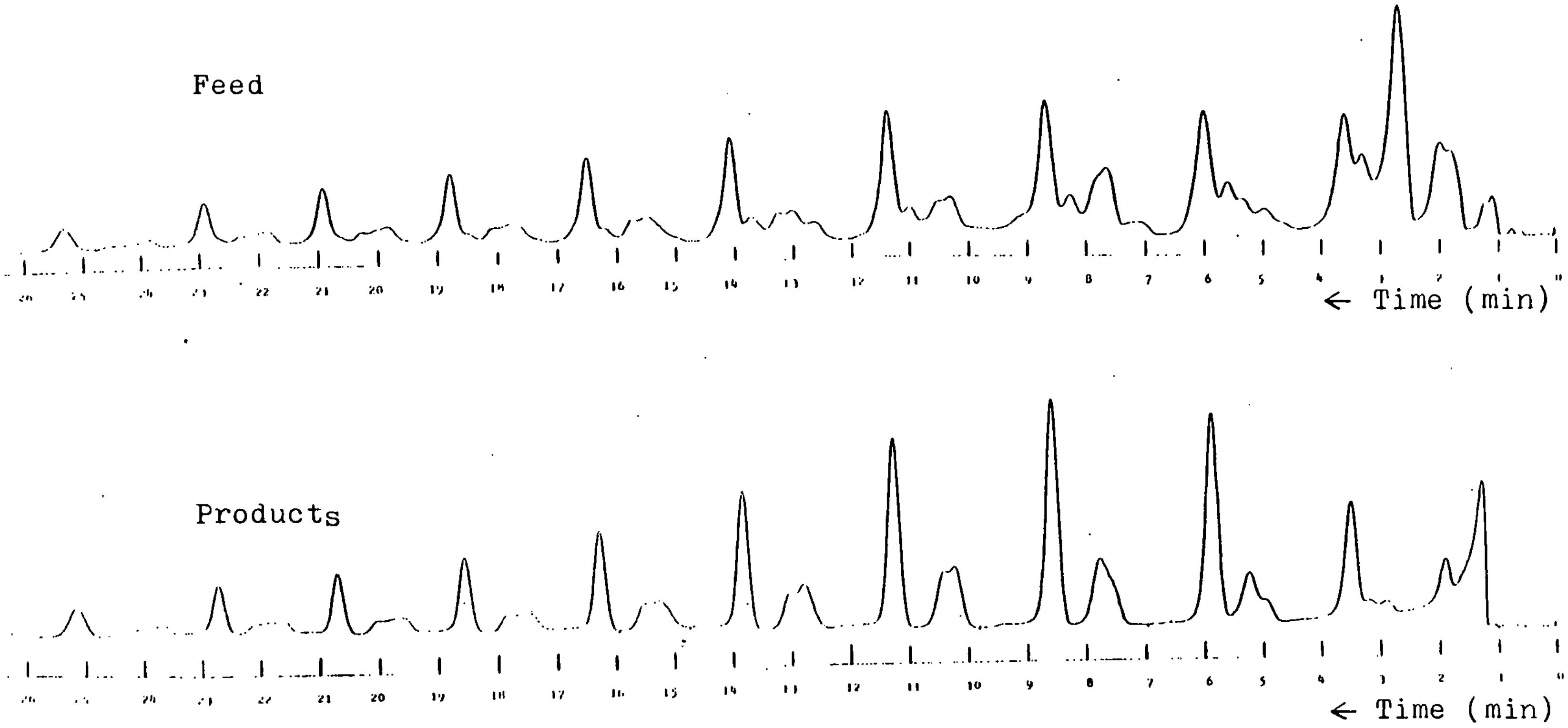


Figure 21.

Hydrogenation Products vs. Feed

Feed

Optimum Run by Using Hydrogenate

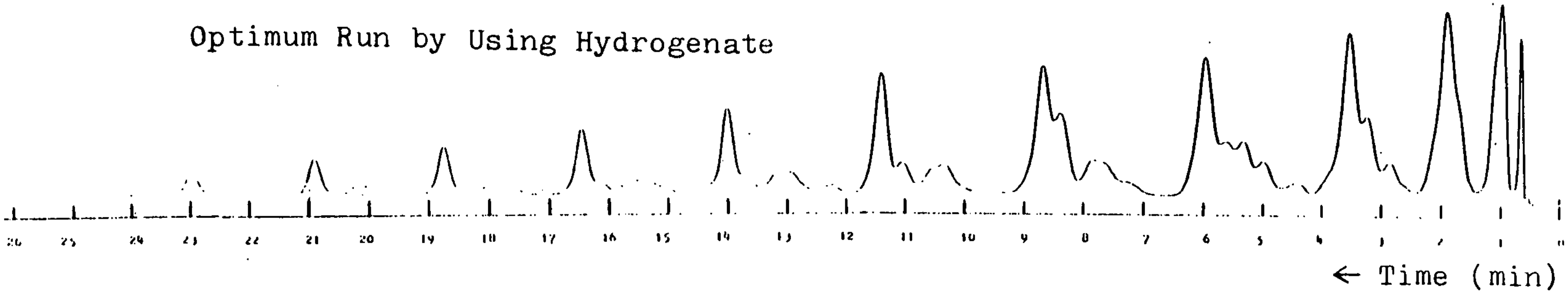


Figure 22.

Optimum Run by using Hydrogenate as Feed

Therefore, the hydrogenation process gave no overall improvement in quality and yield of product. Due to limited reactor operating time, it is difficult to tell whether the reforming catalyst life is prolonged. The decrease in octane rating can be attributed to the higher octane numbers for the unsaturated compounds as compared with their saturated counterparts. The decrease in liquid yield can be attributed to the increase of saturated paraffins in the feedstock, which enhance the selectivity of hydrocracking and produce more vapor phase hydrocarbons than the unhydrogenated feed.

Research on the reforming step was terminated during the contract period due to the advanced stage of the research in this area and the heavy industrial interest in paraffinic type transportation fuels (eg., diesel) rather than high octane gasoline. If a high octane product is desired, there is little doubt that it can be produced from the Fischer-Tropsch hydrocarbon phase. Further work should also result in a reduction in single pass yield losses for the reforming step.

A definitive assessment of catalyst activity in the Fischer-Tropsch and reforming steps was not established due to the short scheduled duration of the individual runs. In general, longer run lengths (with corresponding adequate staffing) will be required to establish the catalyst activity history.

Further work in the liquefaction section is indicated in the area of catalyst tailoring and characterization. Thus if pyrolysis gas composition is necessarily limited by feedstock type, the catalyst may have to be adjusted to be compatible with the resulting synthesis gas composition. A separate catalyst screening effort was started during the contract period toward this goal and will continue in the new contract period.

CONTINUING RESEARCH

The proposed research for the new contract period (June 1, 1980 to May 31, 1981) can be grouped into three categories: (1) integrated runs, (2) factor studies, and (3) alternative feedstocks. Equipment modifications necessary to implement the above are (1) additional size reduction equipment, (2) new compressor, (3) additional control equipment, (4) revised steam system, and (5) revised feeder system.

Integrated Runs. The major outstanding item remaining at the research scale is an assessment of performance for the integrated system, ie, continuous operation from the biomass feeder through the liquefaction step. This will include a measurement of product yields (rather than a measured-calculated hybrid) and product quality for selected feedstocks. Long run lengths will be required with appropriate staffing. It is anticipated that the Fischer-Tropsch off-gas will be recycled back to the gasification system. Use of the reforming step is not anticipated, ie, the desired product will be a paraffinic transportation fuel such as diesel. Separation and recycle of the scrubber effluent, Fischer-Tropsch water phase and pyrolysis char streams are not anticipated although these items will be addressed with regard to scale up to a commercial facility. The ultimate objective will be reliable material and energy balances for the selected feedstocks. An environmental assessment of the process will accompany the integrated run effort.

New equipment to be purchased and/or fabricated for the integrated run series includes a new compressor (to replace the Nash-Worthington sequence), new control gear (recycle streams), new solids feeder with feedback control (for more accurate yield measurements), and more efficient size reduction equipment (hammer mill, cutting mill).

Factor Studies. The system optimization problem is to maximize the liquid hydrocarbon yields subject to constraints on product quality and operating conditions. For the gasification step, the subobjective is to maximize gas phase yields subject to constraints on reactive components (hydrogen, carbon monoxide, olefins). The purpose of the liquefaction step is to achieve maximum conversion of these reactive components to quality liquid hydrocarbon products.

Factor studies anticipated for the gasification system include a continuation of studies of the effect of type of fluidizing gas (steam vs recycle pyrolysis gas vs recycle liquefaction system off gas), fluidized solid (inerts vs catalysts), residence time, temperature and wet vs dry feedstocks. New equipment to be purchased and/or fabricated for implementing the above studies include a steam generation and control system and catalyst development apparatus.

Liquefaction system factor studies will concentrate on catalyst improvements. Any new catalyst will require optimization with regard to reactor operating variables (eg, temperature, pressure, residence time, feed composition). New catalyst testing equipment will be implemented. It should be noted that development of a liquefaction catalyst that will achieve desired conversions at lower pressures will result in considerable process simplicity.

Alternate Feedstocks. Feedstocks have been selected based on industrial and/or scientific interest. Thus some feedstocks may be outstanding in performance but are not considered to be commercially viable.

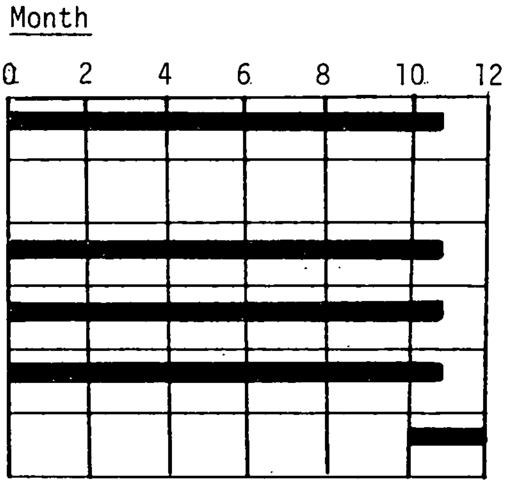
The purpose in studying these materials is to elucidate the reasons for high performance and hopefully to extrapolate this information to materials of industrial interest. In this regard, an active program is anticipated (in cooperation with other laboratories) to characterize various biomass materials with regard to compound analysis and hopefully correlate this with conversion performance.

The laboratory will continue to cooperate with external concerns interested in testing feedstocks (within the constraints of budget and staffing).

A projected task schedule for the new contract period follows:

Task

1. integrated runs
2. factor studies
    a. gasification
    b. liquefaction
3. alternate feedstocks
4. report



As indicated, the multiple tasks will be considered a parallel effort. Thus the system will be staffed to allow for 2-3 two shift runs per week. It is anticipated that this schedule will allow for multiple objectives to be addressed within an operational period, ie, integrated run + factor studies + alternate feedstock study.

COMMERCIALIZATION

The primary commercialization virtues of the process are as follows:

(1) capability to produce a high quality product readily marketable in the vicinity of a conversion facility

(2) capability of using multiple feedstocks

(3) minimal environmental problems.

The industrial interest in the project has centered on the ability to produce a diesel type material to be used as a transportation fuel (trucks, farm machinery, etc) or a storable industrial processing fuel (extraction processes etc), compatible with existing distribution systems and engine designs. Previous economic projections (see Interim Report COO-2982-38) indicated a breakeven scale of about 300 tons/day of dry, ash free feedstock with existing liquid fuel revenues. With liquid fuel revenues increasing at a faster rate than the overall rate of inflation, the breakeven scale could decrease independent of processing improvements.

The next logical step towards commercialization is the construction of a pilot facility (eg, 10 tons feedstock/day). The primary purpose would be for endurance testing (catalysts, equipment) and production of a sufficient amount of material for applications testing at operating conditions recommended from research scale studies. Process improvement studies (eg, factor studies, new catalysts) as well as initial screening of new feedstocks are more efficiently performed in the research scale facility. Thus a minimum amount of experimentation should be performed in the pilot facility. A normal pilot phase program would be about five years (starting from decision to fund) with a commercialization decision dependent on results from the pilot plant phase.

It is anticipated that revised economic projections via external entities will accompany the continued development of the process.

PUBLICATIONS

The following publications concerning this project were completed during the contract period:

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).

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).

Kuester, J.L., DOE Progress Reports. COO-2982-43,44,46,47, 49-54.

APPENDIX

Equipment Revisions

A number of improvements were implemented in the experimental facilities during the contract period. These include:

1) installation of new 10" fluidized beds in the gasification system (310 stainless steel).
2) installation of a Vibra-Screw commercial feeder and modifications.
3) acquisition of several milling devices.
4) installation of a new Nash pyrolysis gas compressor.
5) acquisition of new analytical hardware (Carle gas chromatograph with columns for extended gas phase analysis and Hewlett-Packard gas chromatograph for more accurate liquid sample analysis).
6) acquisition of new computation equipment (Spectra-Physics) for chromatograph data processing.
7) control room construction (to house analytical and control gear).
8) acquisition of several new recorders and controllers to improve the monitoring and control of the system.
9) improvements to the gasification burner and scrubber systems.

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