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HYDROPROCESSING OF HEAVY OILS FOR THE PRODUCTION OF FUEL-CELL QUALITY FUELS

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Project 9102 Final Technical Report

For the Period September 30, 1977, Through September 30, 1978

Prepared by
Institute of Gas Technology
IIT Center, 3424 S. State Street
Chicago, Illinois 60616

Prepared for the
UNITED STATES DEPARTMENT OF ENERGY

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For the Period September 30, 1977, Through September 30, 1978

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UNITED STATES DEPARTMENT OF ENERGY

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ABSTRACT

"Hydroprocessing of Heavy Oils for the Production of Fuel Cell Quality Fuels" is a Department of Energy program to establish whether heavy oils such as No. 4 or No. 6 fuel oil can be hydrogasified or hydrotreated to produce a steam-reforming feed suitable for use in an integrated fuel cell power generation facility.

During fiscal year 1978, we purchased equipment and conducted experiments on both No. 4 and No. 6 fuel oil. Hydrogasification data show that methane is the major gas product, along with a certain amount of coke formation. The liquid product was similar to the feed oil indicating that the oil did not fully enter the reaction. The hydrotreating apparatus was fully tested and proved to be operational. A trial run on No. 4 fuel oil using a Ni/MoO₃ hydrodesulfurization finishing catalyst showed very good sulfur removal to the gas phase, along with substantial reduction of specific gravity in the liquid product over the feed oil.

Whereas the coke formation during hydrogasification is a clear disadvantage, further testing is required of the hydrotreating catalysts to determine quantitatively how efficient the sulfur removal can be and how amenable to steam reforming the hydrotreated oil will be.

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INTRODUCTION

A fuel cell power plant uses commercially available fuels and produces a-c power. A complete fuel cell generator system (Figure 1) has three sections: a fuel processor-gas cleanup, to convert a utility fuel to a clean, hydrogen-rich gas; the fuel cell stacks, to produce d-c power; and a power conditioner or inverter, to convert d-c power to a-c power compatible with the utility bus.

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Figure 1. COMPLETE FUEL CELL POWER PLANT

The use of fuel cells for base-load, peak, and intermediate electric power generation (cogeneration = electricity + heat) is under active development by the electric and gas industries and by other private and government organizations because of the high fuel-to-electricity efficiencies attainable. An extensive research and development effort in this area is currently being sponsored by the Electric Power Research Institute (EPRI), the Department of Energy (DOE), and the Gas Research Institute (GRI); and commercialization of a number of first-generation (phosphoric acid technology) fuel cell power plants is expected in the early 1980's, using naphtha as the feed. Second-generation molten carbonate fuel cell power plants will reach the commercialization stage in the late 1980's. Two of the important concerns for the commercialization of these power plants are 1) fuel availability and 2) the ability to process hydrocarbons ranging from No. 2 fuel oil to coal.

Naphtha is the indicated fuel cell fuel for the 1980's for peak and intermediate power generation. Technology to process naphtha to fuel cell fuels is state-of-the-art. However, because of the uncertainty in the energy supply and demand scenario, to ensure the successful introduction and penetration of fuel

cells in the power generation market, flexibility should be built into the design of fuel cell systems to allow the use of alternative fuels, with special emphasis on the use of distillate fuel oils, residual oils, and coal.^{1,2}

The choice of fuel processing technology itself involves decisions concerning cost, availability, and efficiency. The various components of the integrated power system each have various efficiencies, depending on the particular fuel choice. Because the total efficiency is a product of the fuel treatment, fuel cell and power conditioning efficiencies, a system containing a process such as thermal cracking may well be faced with a critical system efficiency in the fuel processing section alone. For this reason, a study of the most efficient means to process each of the available feedstocks for fuel cell power generation should be undertaken.

This study has been undertaken to determine whether heavy fuel oils such as No. 4 or No. 6 fuel oil can successfully and efficiently be used as a fuel cell feedstock. Among the choices for the production of hydrogen-rich gas from heavy fuel oil are partial oxidation, thermal and cyclic cracking, hydrogasification, hydrotreating, and adiabatic reforming. These processes produce fuels much more manageable than heavy fuel, but must be further processed to produce the hydrogen required for the fuel cell.

Partial oxidation is a means of supplying less than the stoichiometric requirement of oxygen to a hydrocarbon and producing carbon monoxide, hydrogen, and some water as a result. Given the proper downstream conditions, the carbon monoxide and added water can shift to hydrogen and carbon dioxide. The exothermic process liberates a great deal of heat that must be utilized, if the process is even to be competitive in thermal efficiency. The mechanical details of supplying either air or oxygen to the process and the thermal inertia required to manage the heat transfer are not amenable to the fast load cycling envisioned for fuel cell power systems.

Thermal cracking is a means of heating hydrocarbons so hot and at such pressures that methane and solid carbon are the only products. In cyclic cracking, two or more vessels are used so that one vessel can be taken off line in turn for removal of carbon deposits via steam or air burn-off. The product gas from thermal cracking can be steam reformed using proven technology, but the thermal inertia and waste heat recovery requirements pose serious obstacles for the suitability of the process for fuel cell power generation.

Hydrogasification involves the addition of hydrogen gas to the hydrocarbon molecule at temperatures and pressures suitable for methane production. The carbon deposition problem is greatly reduced, as is the need to manage the heat from carbon burn-off. The main disadvantage has been the supply economics for hydrogen. In the fuel cell application, however, hydrogen is available. Therefore, hydrogasification should be seriously considered as a means of treating heavy fuel oil.

Hydrotreating, as a broad description, includes hydrodesulfurization, hydrodenitrification, hydrocracking and olefin saturation. These processes use catalysts, including nickel or cobalt in molybdenum or tungsten sulfide, to accelerate hydrogenation at lower temperatures and pressures than those proposed for hydrogasification. Because these processes operate at lower temperatures and pressures than hydrogasification or thermal cracking, the coke formation problems are significantly lessened. The product from hydrotreating is liquid, more saturated than the feed oil, and easier to steam reform than methane gas would be. The hydrotreating processes introduce the problems of catalyst life, activity, and maintenance, not associated with the other processes.

Steam reforming, whether combined with partial oxidation to provide the heat of reaction or provided with an external source of heat, is being considered as a means of using No. 4 and No. 6 fuel oils. At this time, much work is being performed to adapt the steam-reforming process to use No. 2 diesel fuel oil for the phosphoric acid fuel cell. Before increasing the range of steam reforming to include No. 4 through 6, however, serious questions must be answered that are beyond the scope of this work. For instance, can heavy fuel oil be mixed with a steam and air stream in such a manner as to preclude localized conditions of carbon deposition or of explosive mixtures? The answer to this question is even now being considered for No. 2 fuel oil.

Therefore, we have undertaken in this study to identify the potential thermal efficiencies of the currently available processes for heavy oil treatment, and to determine the thermal efficiency of both hydrogasification and hydrotreating. We have determined these efficiencies from literature and industry sources, according to a plausible set of operating assumptions. Laboratory apparatus has been constructed and used to estimate the performance of the hydroprocesses. The results of hydrogasification experiments are available,

which indicate that a reasonable level of performance can be expected from hydrogasification if the mechanical details of vaporization and the problems associated with the level of carbon actually produced can be successfully controlled.

The organization of this report will follow in a task-by-task manner. The discussion of Task I includes a description of the literature and calculations used to arrive at the various thermal efficiencies. Task II follows with an introduction to hydrogasification, a description of the experimental approach, and a discussion of the results obtained in FY 1978. The hydrotreating processes are discussed under Task III, along with a description of the experimental apparatus and method to be used to examine these processes. Finally, the overall progress of the program is discussed under Task IV, along with suggestions for the future continuation of this project.

TASK I. PRELIMINARY CALCULATIONS AND LITERATURE SURVEY

On the basis of previous work at IGT and elsewhere, preliminary calculations have been made to estimate the relative efficiencies of hydrogasification (HG) and of hydrodesulfurization (HDS)/hydrocracking (HC) and to compare these processes with partial oxidation, catalytic and thermal cracking, and auto-thermal reforming. The data summarized in Table 1 represent the relative efficiencies of the various heavy oil pretreatment schemes.

The literature has been surveyed for hydroprocessing citations. This survey concentrated mostly on the hydrogasification work conducted by IGT and the British Gas Council; the hydrocracking work of Gulf Research and Development Co., Houdry Division of Air Products and Chemicals, Inc., Exxon Research and Engineering Co., Shell Oil Co., Institut Francais du Petrole, British Petroleum Trading Ltd., Chevron Research Co., Standard Oil Co., and Union Oil Co. of California; and the hydrotreating work of C-E Lummus, Atlantic Richfield Co., British Petroleum Trading Ltd., Institut Francais du Petrole, Exxon Research and Engineering Co., Gulf Research and Development Co., UOP Process Division of UOP Inc., Hydrocarbon Research, Inc., Texaco Development Corp., Shell Development Co., and others. In addition, we have discussed the program with Shell Oil Co., Aramak, and American Cyanamid and have obtained their catalysts for the hydro-desulfurizing and hydrocracking experimental programs.

Based on the results of the literature survey and on the preliminary efficiency calculations conducted, hydrogasification and HDS/HC are potentially efficient approaches for the production of fuel cell fuels from heavy oils. Thermal efficiencies as high as 80% can be achieved when integrated with a molten carbonate fuel cell power plant. Their efficiencies are as good or better than those of other candidate approaches, such as partial oxidation, and catalytic and pyrolytic cracking. A bibliography of process literature is given in Appendix A relative to hydrogasification and HDS/HC.

The calculations were conducted using a heavy oil feed which can be classified as No. 6 fuel oil. Its composition is shown in Table 2, along with "average" compositions of other fuel oils. The calculations were made using the following bases and the simplified block diagram shown in Figure 1:

Table 1. SUMMARY OF THERMAL EFFICIENCY CALCULATIONS

<u>Parameter</u>	<u>Partial Oxidation, O₂-Blown</u>	<u>Cyclic Catalytic Cracking</u>	<u>Thermal Catalytic Cracking</u>	<u>HG/Steam Reforming</u>	<u>HDS/HC/Steam Reforming</u>	<u>Auto-Thermal Reforming*</u>
Fuel Processing Efficiency, including credit of 60% of MC	52-65	52-61	52-67	64-90 (85% Conv.)	61-79 (85% Conv.)	79
Fuel Cell Heat, %				60-86 (70% Conv.)	51-67 (70% Conv.)	
Oil Power Efficiency, %	30-37	30-35	30-38	37-51 34-49	35-45 29-38	45
Heat Rate, Btu/kWhr	10,860-9715	10,995-9360	10,860-8480	8715-6700 10,000-6965	9360-7585 11,770-8980	7380

* Catalytica Associates, Inc., EPRI EM-570.

Table 2. TYPICAL ANALYSES OF PETROLEUM FUELS*
(HHV = 18,720 Btu/lb)

	No. 1 Fuel Oil	No. 2 Fuel Oil	No. 4 Fuel Oil	No. 6 Fuel Oil (Low Sulfur)	No. 6 Fuel Oil (High Sulfur)	Program Efficiency Evaluation
Component, %	41.5° API	33° API	23.2° API	12.6° API	15.5° API	14.5° API
Carbon	86.4	87.3	86.47	87.26	84.67	84.60
Hydrogen	13.6	12.6	11.65	10.49	11.02	11.30
Oxygen	0.01	0.04	0.27	0.64	0.38	0.13
Nitrogen	0.003	0.006	0.24	0.28	0.18	0.40
Sulfur	0.09	0.22	1.35	0.84	3.97	3.50
Ash	<0.01	<0.01	0.02	0.04	0.02	0.07
Ni + V Comp.	10 to 500 ppm					
C/H Ratio	6.35	6.93	7.42	8.31	7.62	7.49
Specific Gravity	0.82	0.86	0.91	0.98	0.96	0.97

* Perry, R.H. and Chilton, C.H., Chemical Engineers' Handbook, 5th Edition, New York: McGraw-Hill.

1. Basis: 2000 bbl/day process feed (heavy oil listed in Table 1).
2. Efficiency of the cell (η_{FC}) assumed to be 60% [high heating value (HHV) of gaseous fuel input converted to d-c power].
3. Efficiency of d-c to a-c inverter (η_I) assumed to be 95%.
4. Efficiency of gas cleanup system (η_{GC}) determined and included with fuel processor efficiency. A basic Stretford process was used, requiring 640 kW or 860 hp for pumping/miscellaneous and 2700 lb/hr of 100 psi steam.
5. Fuel cell heat of reaction + IR heat + others, contained mostly in gaseous effluents, is recoverable at 60% efficiency, becoming a credit to the fuel processor equal to 24% ($0.60 \times 0.40 \times 100$) of the HHV of the input gaseous fuel.

Therefore, the total system efficiency (oil to a-c power) is -

$$\eta_T = (\eta_{FP} \times \eta_{GC}) \times 0.60 \times 0.95 \quad (1)$$

or

$$\eta_T = 0.57 (\eta_{FP} \times \eta_{GC}) \quad (2)$$

where -

η_T = total system efficiency, oil to a-c power

$\eta_{FP} \times \eta_{GC}$ = combined efficiency of fuel processor and gas cleanup systems.

Table 1 presents the results of these calculations. They show that the potential efficiencies (combined fuel processor and gas cleanup of the HG/Steam-reforming and HDS/HC/Steam-reforming schemes, at 85% heavy oil feed conversion and no by-product recycle, are higher than the efficiencies of partial oxidation and of both of the cracking approaches. Only autothermal reforming has the potential of equal or better efficiency. If the feed conversion is lowered to 70%, the hydrogasification scheme still shows a remarkably high potential efficiency (~80%); HDS/HC efficiency drops to the 60% range, but still, it is equal to or higher than three of the other candidate approaches considered.

Therefore, the HG/Steam-reforming and the HDS/HC/Steam-reforming hybrid processes appear to be efficient candidates to convert heavy fuel oils to fuel cell fuels.

A brief description of each of the processes considered, some of their advantages and disadvantages, and the details of the efficiency calculations conducted are presented in Appendixes B-F.

TASK II. HYDROGASIFICATION OF HEAVY OILS

Introduction

Hydrogasification is the noncatalytic addition of hydrogen to a hydrocarbon feedstock at high temperature and pressure. Typical reactions that may occur during the process include -

Other reactions, such as thermal cracking, may also occur:

In studies previously conducted at IGT, hydrogasification feedstocks have consisted of oil shale,³ coal,⁴ petroleum oils,⁵ and hydrotreated residua.⁶ The results of these studies indicate that given the correct operating conditions, residuum oils could be gasified into methane, ethane, and other light hydrocarbons, if coke-forming tendencies could be reduced or eliminated. However, those previous studies view hydrogen consumption as an expense, whereas in the fuel cell application, hydrogen is a recyclable product. Therefore, it is the object of this study to determine whether optimum or practical conditions exist under which heavy oils, such as No. 4 and No. 6 fuel oils, can be directly hydrogasified, even if hydrogen-to-oil ratios are higher than those of previous studies.

It will be helpful at this point to briefly refer to the steam-reforming process, for which the hydrogasification and HDS/HC processes are being developed. Steam reforming is an established catalytic process involving the transfer of oxygen from water to the carbon in a hydrocarbon feed:

This reaction is endothermic over a nickel catalyst. Much work has been done to develop the process and catalysts for the process.⁷ Natural gas, light paraffins, and gasolines boiling below 375°F are suitable steam-reforming

feeds. These light fuels, which are ideal for steam reforming, are not expected to be available for electric power generation over the coming decades.⁸ Heavy fuel oils that could be available are not suitable for the process because of three problems: 1) they contain large amounts of coke-forming materials that solidify at the temperatures necessary for steam reforming, 2) the heavy oils almost always contain at least one percent sulfur by weight, which is a nickel catalyst poison, and 3) organically bound metals, such as nickel and vanadium, can reduce catalyst surface area.

Hydroprocessing is a means to produce feeds suitable for steam reforming, but it is not particularly a selective process. An equilibrium mix of many different hydrocarbons and β -graphite is likely to result from hydrogasification, rather than the more selective results that can be obtained from catalytic processes. If large amounts of benzene and other aromatic compounds remain in the product, then problems in steam reforming may result. The six-member aromatic ring has a tendency to adsorb to catalytic surfaces, blocking them for further steam-reforming activity. Conditions that minimize benzene formation without decreasing the overall rate of gasification will be advantageous.

At high hydrogasification temperatures, the formation of methane to the exclusion of other gaseous hydrocarbons is favored by equilibrium. However, the increase in methane formation does not represent an increase in the total amount of steam-reforming feed produced. Unless methane is significantly easier to reform than ethane and propane, high gasification temperatures to increase methane formation is not a distinct advantage.

Nearly all hydrocarbon feedstocks to hydrogasification will cause some degree of carbon formation. Equilibrium studies of mixtures of carbon, hydrogen, and oxygen have shown that the formation of a solid carbon at the conditions of interest is favored by thermodynamic considerations.⁹ It is unlikely that the reaction mechanism is kinetically fast enough for large amounts of solid carbon formation, but heavy fuel oils with a relatively high aromatic content have enough condensed ring structures to form a sticky carbonaceous mass that solidifies upon cooling to room temperature. The tendency toward solids formation could be lessened by the addition of water and by excess hydrogen.⁹ The hydrogasification experiments conducted to date in this study have demonstrated that indeed solids are formed during reaction over 700°C and 1500 psig. If the formation of solid matter can be kept to a minimum, and if

the molecular weight can be reduced sufficiently, hydrogasification of heavy fuel oils will produce a feedstock suitable for steam reforming.

Experimental Approach

Fuel oil for use in this program has been obtained from the Whiting, Indiana Amoco refinery. The analysis of these oils as received, together with the range of parameters as defined for No. 4 and No. 6 fuel oils, is given in Table 3.

The variable nature of fuel oil presents certain problems in conducting an experimental program. No. 6 oil is heavy, viscous, and in practice varies considerably in composition from season to season and from one supplier to the next. The ASTM specifications for No. 6 oil are defined across a necessarily broad range to include many of the heavy refinery cuts, which in the past have not been attractive for use other than for industrial fuel. Regardless, an evaluation of the candidate processes must be made on the basis of representative and available fuels. Both the No. 4 and No. 6 oils were obtained from the same refinery and were analyzed for carbon/hydrogen ratio; weight percent carbon, hydrogen, nitrogen, and sulfur; Conradson Carbon Residue content; and gas chromatograph-simulated boiling point. It is apparent that the No. 6 oil is much less volatile than the No. 4 sample, even though the carbon/hydrogen ratios are similar. The ash content of No. 6 oil is twice that of No. 4 oil. The No. 6 oil is more opaque and viscous than the No. 4 oil, which will make it difficult to analyze for aromaticity by other than gas chromatograph/mass spectrometer methods.

Laboratory equipment, as described in Table 4, was installed for use in hydrogasification. The laboratory module is a manually controlled system with provisions for remote shutoff and automatic alarm shutdown. A schematic diagram of the process is shown in Figure 2. A photograph of the mainframe is shown in Figure 3 (top photograph).

The liquid feed is measured through a metering displacement pump, while the hydrogen feed is measured by a differential pressure meter. All feed lines are steam-traced because of the high viscosity of No. 6 oil. The feed preheater is a 12-inch tube furnace with analog temperature control. The reactor is 1-1/2 inch schedule, 160 stainless steel pipe in a 36-inch tube furnace, which also has analog temperature control. Reaction temperatures are measured in a

Table 3. RANGE OF PROPERTIES FOR NO. 4 AND NO. 6 FUEL OILS

Property	No. 4 Fuel Oil			No. 6 Fuel Oil		
	Light	Under Testing in This Program	Heavy	Light	Under Testing in This Program	Heavy
Gravity, °API	28.2	22.6	17.6	24.2	16.5	-1.9
Flash Point, °F	156	--	216	16	--	400
Viscosity						
SFS at 122°F				19	150	346
CS at 100°F	9.6	59	30.1			
Pour Point, °F	-50	-45	75	0	55	130
Sulfur Content, wt %	0.46	0.84	1.44	0.32	0.89	4.00
CCR, wt %	0.52	4.3	7.60	0.2	7.9	16.0
Ash, wt %	0.00	0.008	0.03	0.001	0.015	0.16
Water and Sediment, wt %	0.00		0.20	0.00	--	0.97
Gas Chromatograph Simulated Distillation Fractions, °F						
Initial B. P.		340			460	
5%		414			586	
10		438			650	
15		455			707	
20		470			758	
30		495			878	
40		518			1012	
50		548			>1018	
60		575			"	
70		608			"	
80		663			"	
90		813			"	
95		976			"	
97		1018			"	
Final B. P.		>1018			"	
Ultimate Analysis, wt %						
Carbon		87.27			86.50	
Hydrogen		11.41			11.89	
Sulfur		0.84			0.89	
Nitrogen		0.13			0.27	
Ash		0.008			0.015	
C/H Weight Ratio		7.65			7.28	
Metal Content, ppm						
Nickel		2.2			3.5	
Vanadium		8.8			23	

Table 4. SPECIFICATIONS FOR THE HG SYSTEM

The purpose is to study the reaction of hydrogen and oils at a predetermined temperature range and to investigate the product yield as a function of flow rates, feed compositions, and pressures. It is anticipated that the reactor will be operated at temperatures up to 1450°F and pressures up to 2000 psig. A schematic diagram is attached to illustrate the minimum requirement of this reactor system.

The specifications of the instrument needed are listed below. The instrument supplied by the vendor need not be the ones specified here but must be of equivalent precision or better:

1. Pressure. Supply pressure may be as high as 4000 psig and all supply lines must have gages. The reactor pressure will be indicated by a 2000 psig Heise precision gage. The sampling lines must have gages which will indicate pressures to 30 psig and vacuum pressures to -30 psig. All regulators must have both up-stream and down-stream gages.
2. Temperature. A two or three-zone furnace for the reactor will be controlled by a multimode controller such as Barber Colman 520 and recorded. All temperatures will be recorded by Esterline Augus Speed Servo II. The temperatures of all heated lines and vessels will be controlled and recorded continually.
3. Feed gas flow rate. The flow rate of hydrogen will be in the range of 1 to 20 SCF/hr. It is required that the feed flow rate is recorded and controlled continuously by using a delt-P transducer or a mass flow control, and that the precision of measurement is independent of the flow region. The flow rates of other gases such as nitrogen and helium need not be recorded but must be controlled.
4. Liquid flow. The liquids will be heavy oils such as fuel oil No. 4 and/or No. 6. The flow rates will be from 0 to 300 cu cm/hr. To flow this type of liquid readily, the liquid vessels and lines must be heated, and a high pressure liquid pump is needed. Means of assuring constant flow rate will be provided. Provisions for vaporizing the oil prior to the reactor is needed.
5. Reactor. The reactor material must be able to operate at 2000 psig, 1450°F and hydrogen and hydrogen sulfide atmosphere. It is desired to have at least 5 thermocouples inside the reactor to give a temperature profile. The approximate size of the reactor may be 36" long x 2" ID.
6. Control unit. The reactor assembly will be behind a barricade. Therefore, remote control is necessary. Lighted switches are desired to indicate on/off operation. Digital display of temperatures and pressures are also desired. Safety alarms are needed for pressure and temperature over runs. Rupture disks and/or relief valves are to be installed on all high-pressure lines and reactors.
7. Sampling. Both the gas and liquid samples will be collected for analysis. The liquid product may require heated lines to avoid "plugging".

Figure 2. SCHEMATIC DIAGRAM OF THE HG TESTING FACILITY

Figure 3. HG APPARATUS

concentric thermowell through the length of the reactor. The reactor is followed by a condenser to separate liquid and gaseous products. Liquid products are trapped for analysis, while gaseous products are measured in a dry test meter, then sampled via gas chromatography. Alarm conditions that can cause a system shutdown include high vessel pressure, high furnace temperature, and high pump pressure. Temperature control and monitoring are completely remote from the reaction apparatus. This high-temperature, high-pressure equipment is located behind a barricade for safety. Figure 3 also shows the control and monitoring module (bottom photograph). A multichannel temperature recorder provides a hard copy record of the reaction temperature profiles, as well as the other process temperatures.

The system was thoroughly checked at high pressure and temperature, temperature controllers were adjusted to provide optimum response, and the start-up procedure refined to provide safety and efficiency. Calibration techniques were developed to provide an accurate indication of oil and hydrogen flow rates at changing reaction conditions. Pressure vessels in the system were hydrostatically tested at 3000 psig.

The system was also checked, at temperature and pressure, with diesel oil in place of heavy fuel oil for feed. This operation provided an indication of how the controllers and alarm sequences interact under actual conditions. Although the gas chromatograph had not been installed at the time of these tests, considerable gaseous products, including hydrogen sulfide (odor), and most likely methane and ethane, were evolved.

The preheater supplied with the system was found to promote severe blockages when operated at high temperature and pressure. In addition, the heat transferred to this process was easily lost.

It is possible that by simple mechanical means the hydrogasification efficiencies can be improved, as well as ensuring that the space velocity of the oil as it passes through the hot zone of the reactor is equal to that of the hydrogen. Three schemes are under consideration as means of increasing the fraction of oil vaporized and thereafter gasified. These are shown in Figure 4. Part A of Figure 4 shows the reactor in cutaway view showing the seal, the thermowell, and the reaction zone. Part A also shows the 1.04- ℓ reaction zone mostly filled with packing material. Another means is given in Part B; a shallow bed of packing material is supported over a grid. The third approach

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Figure 4. LIQUID HOLDUP SCHEMES FOR ENHANCING OIL VAPORIZATION

shown in Part C is similar to that in Part B, but with a ceramic honeycomb monolith replacing the packing material. Each of these schemes provides a surface for cool oil to gather on, rather than allowing poorly preheated oil to fall through unreacted.

Results of Hydrogasification of No. 4 and No. 6 Fuel Oils

According to previous hydrogasification work at IGT using relatively light fuels such as diesel oil,^{3,4,5} one may expect the production of methane at temperatures greater than 4000°C and at pressures in excess of 750 psig. These conditions were the baseline for this experimental program.

The thermochemical equilibrium concentration of products resulting from hydrogasification of carbon in a 4:1 hydrogen/carbon atomic ratio is given in Figure 5. At the ratio of 5:1, the graphite fraction is decreased considerably. Before taking the data in these figures as representative of fuel oil gasification, one must note that the computer program by which they were computed does not take into account the thermodynamics of the very heavy components, nor the kinetics of any reaction step in arriving at its solution of minimizing the free energy of the system. The reason is that the thermodynamics of heavy hydrocarbons is not well known. Therefore, the data in Figure 5 can serve only as a baseline for predicting the trends one might expect in actual practice.

The trends observed from the thermochemical equilibrium data alone are as follows:

- Increased pressure, at least as high as 1000 psig, is advantageous in reducing solids formation.
- Increased temperature is deleterious in that it leads to greater solids formation.
- In Figure 5, we can see that increased hydrogen availability leads to lesser solids formation.

Twenty-six experiments were conducted to hydrogasify No. 4 fuel oil at a variety of conditions. The conditions, the product gas and liquid compositions, and the product distributions are tabulated in Appendix G. The various products of reaction are listed as fractions of the total amount of carbon fed to the process. These fractions are plotted against the system pressure in Figures 6, 7, 8, and 9. The total fraction of feed carbon converted to gaseous, liquid, and solid products plotted against hydrogen-to-oil feed stoichiometry

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Figure 5. THERMOCHEMICAL EQUILIBRIUM FOR CARBON AND HYDROGEN IN 4:1 MOLE RATIO AT THE CONDITIONS CLOSE TO THAT OF THE HG EXPERIMENTS

Figure 6. NO. 4 FUEL OIL HG AT 480°C

Figure 7. NO. 4 FUEL OIL HG AT 530°C

Figure 8. NO. 4 FUEL OIL HG AT 575°C

Figure 9. NO. 4 FUEL OIL AT 620°C

is given in Figure 10. A hydrogen feed stoichiometry of 100% is defined as the condition in which the sum of the hydrogen gas feed and the hydrogen in the feed oil are sufficient to convert all of the carbon in the oil feed to methane.

Figures 6, 7, 8, and 9 each compare results obtained between 500 and 1500 psig system pressure. However, each figure displays the data obtained near a given average temperature, namely, 480°, 530°, 575°, and 620°C, respectively. Average temperature is defined here as the average temperature of the reaction zone. The reaction zone is that portion of the reactor heated to over 400°C.

The general trends that are observed from these figures are the following:

1. Increased temperature shifts gas product distribution away from propane and heavier gases towards methane.
2. Increased temperature increases gas production.
3. Increased pressure generally has a positive effect on gas production.
4. At conditions of over 150% of the stoichiometric requirement of hydrogen, less than 5% solids formation was observed. However, generally 10% to 15% of the feed carbon is unaccounted for, other than as solid product.

At this point, it is premature to state that the trend of increasing solids formation with increasing gas product fraction, as seen in Figures 6 and 8, is general, or that the opposite trend seen in Figure 7 applies. It is likely that other factors are predominant, such as preheat efficiency, residual solids in reactor prior to experiment, or even the method of calculation for the amount of solids deposited.

The trend of increasing gas product fraction on a hydrogen-free basis with increasing hydrogen-to-oil ratio as seen in Figure 8, is especially encouraging. Even though at hydrogen-to-oil ratios close to that required for 100% methane formation, the data are widely scattered due to wide differences in operating conditions. At higher hydrogen-to-oil ratios, the gas product fraction is noticeably larger, notwithstanding variations in temperature and pressure. This finding is in accord with the justification for undertaking this study. Even though hydrogasification has been widely discussed for hydrogen intensive

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Figure 10. HG PRODUCT DISTRIBUTION AS A FUNCTION OF FEED STOICHIOMETRY
FOR NO. 4 FUEL OIL*

* Reaction conditions are specified in Appendix B per run number.

refinery applications, conditions should be sought for economic hydrogasification in the hydrogen-extensive fuel cell application. The results of Runs 119 through 122 are encouraging in this regard. Future experiments will involve conditions between two and four times the amount of reactant hydrogen for complete conversion to methane, because the integrated fuel cell system can allow for considerable hydrogen recycle from either the steam reformer, fuel cell effluent, or hydrogasification product stream.

Seven hydrogasification experiments using No. 6 fuel oil were performed during the report period. The data observed during these tests are tabulated in Appendix H. In addition, the product distribution as a function of pressure at 500° and 600°C is given in Figures 11 and 12. Figure 13 shows the product distribution for No. 6 fuel oil as a function of the hydrogen-to-oil ratio. Figure 14 compares the temperature profiles in Table H-1 (which appears in Appendix H), for No. 6 fuel oil, with the profiles in Table G-1 (which appears in Appendix G), for No. 4 fuel oil. Certain preliminary observations can be made from these data:

1. The trend toward increased methane production at increased temperature along with decreased production of propane is apparent. In addition, the total gas fraction is enhanced by increased temperature from 50% at 500°C to 75% at 600°C.
2. From 750 to 1000 psig, increasing pressure increases the gas product fraction and decreases the solids formation.
3. For each of the conditions studied so far, the formation of solid matter accounted for about 10% to 15% of the feed carbon.
4. Below a stoichiometry of 110% of the hydrogen necessary for complete methane formation, the effects of pressure and temperature predominate over the effect of hydrogen-to-oil ratio. However, at conditions of over 115% theoretical hydrogen, a slight trend is discernable relating increased gas production fraction with increased hydrogen-to-oil ratio. As in the case of No. 4 fuel oil, experiments at conditions of between 200% and 400% theoretical hydrogen will be carried out for No. 6 fuel oil to more fully demonstrate this trend.

Hydrogasification of oils such as No. 4 and No. 6 fuel oils can be used to produce methane, ethane, propane, and a small amount of a large number of other hydrocarbons. The experimentation performed so far in this study has shown that increasing system pressure from 500 to 1500 psi has in some cases improved the hydrogasification product, while in other cases, the effect of

Figure 11. NO. 6 FUEL OIL HG AT 500°C

Figure 12. NO. 6 FUEL OIL HG AT 600°C

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Figure 13. HG PRODUCT DISTRIBUTION AS A FUNCTION OF FEED STOICHIOMETRY FOR NO. 6 FUEL OIL*

* Reaction conditions are specified in Appendix C per run number.

Figure 14. TYPICAL TEMPERATURE PROFILES FOR EXPERIMENTS INVOLVING NO. 4 AND NO. 6 FUEL OIL

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pressure was not significant. System temperature, on the other hand, appears to be a very important variable for this process. Figures 6, 7, 8, and 9 bear out these trends for No. 4 fuel oil.

The suitability of the hydrogasification product must be interpreted in light of the fully integrated fuel cell power generation scheme. Table 5 shows the effect of temperature and pressure on methane formation and also on the gas product fraction.

Table 5. METHANE AND TOTAL GAS FORMATION AT
SELECTED TEMPERATURES AND PRESSURES

Pressure, psi	Temperature, °C	Feed Carbon Converted	
		to Methane, %	to Gaseous Products, %
750	530	35	54
	575	45	58
	620	56	68
1250	530	40	69
	575	50	78
	620	70	75

Higher temperature and higher pressure increase the production of methane and, in most cases, increase the total gas product fraction. There is no advantage to raising temperature and pressure solely to increase methane production, unless the total gas fraction increases, because propane is just as suitable for steam reforming as methane. Among the conditions listed in Table 5, operation at 575°C and 1250 psig pressure leads to the greatest system efficiency. At the highest temperature and pressure listed, the total gas product fraction actually decreased.

This finding is in agreement with studies in related areas. It is reasonable to expect that methane production will be favored at higher temperatures from the consideration of thermochemical equilibrium. It is also true that steam reforming has been developed for C_2H_6 and higher hydrocarbons as well as for methane. Furthermore, the stoichiometry of hydrogasification combined with that of steam reforming lead to equivalent results via either methane or propane.

The equations for hydrogasification are -

Taking the products of these reactions for comparisons via steam reforming gives -

Of course, the actual product distribution is a matter of thermochemical equilibrium, but if taken to completion without methanation interference, the net hydrogen production from the pairs of reactions (9, 12; 10, 13; and 11, 14) is equivalent:

As noted from Table 5, increased temperature does have a positive effect on the fraction of oil gasified. The fact that this trend is not uniformly borne out by all the data indicates that other factors may exert influence equal to or greater than the effect of temperature. The most significant factor, other than temperature, pressure, and oil-to-hydrogen ratio is the actual degree of oil vaporization. It is reasonable to expect that the rate of gas-phase noncatalytic reaction will increase with the rate of vaporization. Furthermore, it is reasonable to expect a higher rate of vaporization at 600°C than at 500°C. Note from Table 3 that the No. 4 fuel oil received for use in this study¹⁰ is 94% vaporized at 500°C and completely vaporized at 600°C; the No. 6 fuel oil is only 34% vaporized at 500°C and more than 50% vaporized at 600°C. Therefore,

it should be possible to vaporize No. 4 fuel oil and to vaporize at least 50% of No. 6 fuel oil.

However, we have reason to expect that the conditions and equipment arrangement so far have not been sufficient to vaporize more than about 75% of the No. 4 fuel oil. Rather, the feed oil passed through a section of tubing between the preheater and reactor, cooling to about 200°C as it did so. The relatively cool oil proceeded to drip through the hydrogasification tube reactor at much less than the stated residence time. Circumstantial evidence of this condition is given by the fact that the liquid product is similar to the feed oil in many respects, e.g., specific gravity, viscosity, optical density, and composition. According to the conversion figures, as much as 30% to 50% of the feed oil may be involved.

It will be helpful to recall data from earlier studies to compare the conversion figures. In one study,¹¹ Bunker C oil was hydrotreated to remove some coke-forming constituents and then hydrogasified in a reactor with internal provisions for oil vaporization. Specifically, the upper portion of the reactor had a large steel insert of large thermal mass through which the feed oil had to pass. This provision is not practical at present for the current study, and may well be impractical on an industrial scale also. However, the data from those previous experiments show that 90% of the feed carbon could be hydrogasified at 760°C and 80% at 610°C, with the remainder falling out as liquid products.

The results of superimposing the data obtained in this study over that obtained in the previous work^{11,12} is shown in Figure 15. It can be seen that the same order of conversions are obtained, as limited by the nature of heavy feeds. However, the residence times for the other studies are approximately in the range of 2 to 5 minutes. In the current study, hydrogen residence times of about 20 minutes were employed to obtain equivalent data. Therefore, even though the gas fraction is relatively the same, either an improvement in the system design is indicated, or operation at greatly increased hydrogen-to-oil ratios.

It is possible that the hydrogasification efficiencies can be improved. Even though we may expect better results using a form of internal packing, the improvement would not be due to catalytic activity. Heterogeneous catalysis, such as in hydrocracking and hydrodesulfurization, involves the mass transport

Figure 15. COMPARISON OF VARIOUS HG STUDIES

of gas and liquid material to finely dispersed catalytic material in porous media. The ceramic column packing is more than 100 times less porous than silica or alumina catalyst support, not to mention the fact there are no catalyst sites. These differences are displayed in Figure 16.

The reaction zone in a trickle-bed reactor is not in either the gas or liquid phase, but on the active surface of the catalyst crystallites. However, for hydrogasification in the presence of oil vaporization surfaces, the reaction zone is remote from the bead, and is in the gas phase. It can be seen that hydrogasification is not a catalytic process, because reaction proceeds even without beads or monolith surfaces for oil vaporization.

Among temperature, pressure, and oil vaporization rate, the other critical factor in hydrogasification efficiency is the hydrogen-to-oil ratio. Several different ways are used in literature to describe this ratio. Because the major product for hydrogasification is methane, the ratio is given in terms of a theoretical stoichiometric requirement of hydrogen to convert the feed completely to methane. The definition is analogous to that of theoretical oxygen in combustion stoichiometry.¹³ The theoretical hydrogen requirement is calculated according to Table 6.

Table 6. THEORETICAL HYDROGEN CALCULATION

<u>Feed Streams</u>	<u>g-atom/hr</u>
<u>H₂ Feed Stream</u>	
Hydrogen, 2.51 g-mol/hr	5.02 (as H)
<u>Oil Feed Stream, 48.1 g/hr</u>	
Carbon, 87.27 wt %, 42.0 g/hr	3.49 (as C)
Hydrogen, 11.41 wt %, 5.5 g/hr	5.44 (as H)
H/C Atom Ratio = (5.02 + 5.44)/3.49 = 2.99	
% Theoretical H/C Methane Ratio = $\frac{2.99}{4} \times 100\% = 74.9\%$	

The hypothetical case in Table 6 outlines feed conditions where 74.9% of the hydrogen necessary to fully convert all the carbon in the oil stream to methane is present, both as hydrogen feed and as the hydrogen fraction in the oil.

Figure 16. COMPARISON OF TRICKLE-BED CATALYST PELLET AND INERT OIL VAPORIZATION SURFACE

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Figures 10 and 13 detail the relation between hydrogen-to-oil ratio and gas product fraction. Figure 15 also gives similar information, but the basis is not the same, nor are the points from the current study, plotted in Figure 15, any more than generally indicative of the many conditions studied. In Figure 10, we see that at over 120% theoretical hydrogen, the fraction of carbon gasified is inversely related to the hydrogen ratio. At ratios close to 100%, no trend is apparent. That is not unusual because these points were obtained at widely varying temperatures and pressures. It is significant that at the higher hydrogen-to-oil ratios (above 120%) a trend is observable. This is not an effect of increased partial pressure of hydrogen, because the experiments were performed at varying pressures. However, an increase of hydrogen could result in an increase in fraction oil converted, if equilibrium conditions are achieved. If, on the other hand, the fraction of oil converted is controlled solely by the rate of oil vaporization, then no amount of excess hydrogen will influence the outcome of the reaction. The data support the idea that a vapor equilibrium condition exists, at least for the experiments conducted at high hydrogen-to-oil ratio. Furthermore, the same argument may hold for solids formation. Given the integrated fuel cell system, where excess hydrogen requirement is not a critical problem, the reduction in coke formation via increased hydrogen feed could help make the process practical.

In addition, comparison of the results of hydrogasifying No. 4 and No. 6 fuel oils yield the following observations:

- Nearly the same fraction of carbon feed as No. 6 fuel oil to the process was gasified as for No. 4 fuel oil.
- The fraction of carbon feed going to solid or unaccounted products was similar to and in certain cases less than that of the No. 4 fuel oil experiments.
- The composition of the product gases was not very different between No. 4 and No. 6 fuel oil experiments, considering the effect of temperature.

It is true that fewer runs were made with No. 6 fuel oil, but sufficient data are available to compare results at two temperatures, 500° and 600°C. Figure 11 shows the results from experiments conducted at 500°C and various pressures. There does not seem to be any significant effect of pressure among these three runs. Figure 12 shows the results of the three usable experiments conducted at 600°C. Note the absence of appreciable levels of propane in the product gas, as was the case for No. 4 fuel oil and also the greater overall

gas product fraction. Figure 13 shows that the hydrogen-to-oil ratio is not the controlling factor at ratios less than 120% theoretical hydrogen. No data are available yet for more than 126% theoretical hydrogen.

The similarity in product distribution is welcome, if this indicates that No. 6 fuel oil can be gasified as easily as No. 4 fuel oil. According to the oil properties listed in Table 3, the major differences between the No. 6 and No. 4 fuel oils are density, viscosity, and fractionation range, which in each case were greater for No. 6 fuel oil. Because these oils were obtained from the same refinery, one might expect that the type of hydrocarbons present might be similar. However, the two oils do represent a range within and beyond which oil delivered to a fuel cell processor might fall. It is encouraging that the performance was not significantly less in the case of the heavier oil, because the feed, therefore, can be changed from No. 4 to No. 6 fuel oil without interrupting the plant operation.

Encouraging as the small differences between the oils are, both the No. 4 and the No. 6 fuel oil result in about 10% solids formation (at the conditions studied so far), which is not tolerable. Operation at 200% theoretical hydrogen will reduce the coke-forming tendency considerably. Already, experiments at various temperatures, but uniformly high-hydrogen recycle show promise in limiting coke formation.

During hydrogasification of No. 4 and No. 6 fuel oils at high-hydrogen recycle, low to moderate pressure and moderately high pressure appears to approach the optimum conditions studied so far. Even if the feedstock varies in density, viscosity, and therefore, product grade, a fairly standard product distribution can be achieved. Of the several hydrogasification experiments conducted so far, the best conditions are listed in Table 7. For the purpose of this comparison, the term "best conditions" is defined as the temperature, pressure, and hydrogen-to-oil ratio resulting in the greatest gas product fraction. For comparison, the conditions leading to the worst conversions are also listed.

There is an unmistakable trend of increasing gas product fraction with the hydrogen-to-oil ratio for No. 4 fuel oils at over 126% theoretical hydrogen. It appears that the trend may also hold true for No. 6 fuel oils. Further experimental work is required in both cases to determine the specific advantages of high-hydrogen recycle operation.

Table 7. COMPARISON OF SELECTED HG EXPERIMENTS

Run No.	Fuel Oil Type	Temperature, °C	Pressure, psi	H ₂ /Oil Ratio	Gas Product Fraction, %
122	4	538	1250	170	80
120	4	626	1250	140	75
202	6	607	1000	110	72
200	6	605	1000	113	70
119	4	618	750	133	68
203	6	614	750	122	61
112	4	574	1250	126	61
206	6	494	750	115	53
204	6	495	1500	112	51
113	4	570	1500	103	48
118	4	491	750	105	33
115	4	471	1260	105	26
116	4	469	1000	104	22

TASK III. HYDRODESULFURIZATION AND HYDROCRACKING OF HEAVY OILS

Introduction to Catalytic Hydroprocessing

Hydrodesulfurizing and hydrocracking are but two of the processes under the general heading of hydroprocessing. Intermediate in severity between hydrodesulfurizing and hydrocracking is hydrodenitrification. Hydrodemetallization occurs at even greater severity. Mildest of the hydroprocesses is hydrogenation of olefins. Each of these processes occur to some extent, based on the operating conditions and the degree of hydrogen saturation.

Through whatever source of crude petroleum, fuel oil and heavy fuel oil come from the bottom product of crude distillation. If the density is greater than 0.89 (21° API), the half of that product which does not boil at 900°F goes to asphalt. The other half is divided between gas oil that does boil below 900°F under vacuum conditions and "low-sulfur residual fuel oil." It is this residual fuel oil that we are interested in. Even though it can carry the name "low-sulfur" because the asphaltenes carry much of the sediment metals and sulfur originally in the crude petroleum, fuel oil can contain significant amounts of sulfur and heavy metals. Residual fuel oil derived from atmospheric and vacuum distillation of crude oil can account for as much as one-sixth of the crude bottoms cut.¹⁴ Therefore, effective use of residual fuel should properly occupy a niche in any petroleum energy economy.

The following reactions summarize the essence of the several hydroprocesses:

Hydrogenation (Hyd),

Hydrodesulfurization (HDS),

Hydrodenitrification (HDN),

or

Hydrocracking (HC),

and

Hydrodemetallization (HDM),

The above reactions involve R and R', representing arbitrary hydrocarbon groups. The HDM reaction (Equation 24) involves M to represent nickel, vanadium, or some other metal commonly found complexed in very heavy organic molecules.

These reactions are all catalytic in nature; that is, the reactant molecules adsorb to surfaces such as alumina, nickel, or molybdenum sulfide and pass through an activated complex in the adsorbed state. Then, products are desorbed subject to various diffusional limitations. According to experience, the most desirable catalysts for HDS and HC are molybdenum sulfide on alumina/silica support material. The fine distribution of pores through an alumina/silica bead provides support for even smaller crystals of molybdenum oxide. Nickel or cobalt is used to "promote" the molybdenum, i.e., to somewhat alter the structure to a more active state. In use, the molybdenum oxide is changed over to molybdenum sulfide because of the presence of sulfur in the feed. Fortunately for the processes intended, MoS has catalytic activity. There are other metal and metal salt crystals that also have activity, but for sulfur-containing fuel oil, experience shows that the Co/ and Ni/MoO₃/alumina/silica systems are preferred. In fact, the sparse data available indicate that the Ni/MoO₃ catalyst is even better than the Co/MoO₃.¹⁵ A typical cobalt moly catalyst as currently used in research and industry has the characteristics listed in Table 8.

Table 8. TYPICAL Co/MoO₃ CATALYST CHARACTERISTICS¹⁵

Surface Area (H ₂ chemisorption or electron micrograph)	200-300 m ² /g
Metal Crystallite Diameters, d _p	5-15 nm
Pore Volume (within catalyst bead), V _p	<0.5 cm ³ /g
Bulk Density, ρ _B	0.6-0.8 g/cm ³

The following rate equation is typical for Langmuir-Hinshelwood reaction kinetics for catalytic processes where both hydrogen and hydrogen sulfide may adsorb to the catalyst.

$$r = \frac{k\alpha p_{H_2} C_s}{(1 + K_{H_2} p_{H_2} + K_{H_2S} p_{H_2S})} \quad (25)$$

where —

r = reaction rate in units such as $\frac{\text{mols S removed}}{\text{second} - \text{cm}^3 \text{ reactor}}$

α = fraction of sulfur in feed resistant to removal

p_{H_2}, p_{H_2S} = partial pressures of H_2 and H_2S , respectively, atm

C_s = concentration of organic-bound sulfur in the reactor, mols/cm³

K_{H_2}, K_{H_2S} = adsorption coefficients for H_2 and H_2S , atm⁻¹

k = first order reaction rate coefficient, (atm⁻¹ - sec⁻¹).

According to the model, hydrogen and hydrogen sulfide compete for the available reaction sites. The effect of various trends on the reaction (Equation 25) is summarized in Table 9.

In fact, the experience in laboratory studies shows that excessive H_2S partial pressure does limit the sulfur removal rate.¹⁶

Provided that chemical equilibrium does not interfere and given fast reaction kinetics, the rate of reaction is given by the rate of mass transfer to and away from the catalytic site, regardless of the mechanism. Studies have shown that external film transport (Zones C and E in Figure 16) do not pose limitations on hydroprocessing reaction rates. Rather, intraparticle diffusion (Zones F and G in Figure 16) tends to be the critical transfer process.¹⁷ A criterion has been published to predict the significance of this transport limitation.¹⁸

Laboratory studies of the hydroprocesses routinely involve stirred-tank analysis, because reaction rate data are most simply modelled in this fashion. However, in industrial practice fluidized beds are neither the simplest to operate nor the smallest in design. Regardless, the published kinetic rate data have been obtained in high-recycle reactors modelling mixed flow. The

Table 9. THE EFFECT OF PARTIAL PRESSURE AND ADSORPTION COEFFICIENTS
ON LANGMUIR-HINSHELWOOD KINETICS

<u>Term</u>	<u>Trend</u>	<u>Significance</u>
K_1	large	The "i" species adsorbs very strongly.
$K_{H_2S} P_{H_2S}$	large	Potentially active sites are dominated by H_2S molecules. The rate becomes inversely proportional to H_2S partial pressure.
$K_{H_2} P_{H_2}$	large	The effect of H_2 partial pressure cancels out; the rate is proportional only to sulfur concentration in the feed oil.
$K_{H_2} P_{H_2}$	large	
with P_{H_2}	small	Hydrogen adsorbs so strongly that the rate is reduced to a certain limit.
$K_{H_2} P_{H_2}$	large	
with K_{H_2}	small	Rate is limited only by feed sulfur concentration.

spinning-basket Carberry reactor¹⁹ and the magnetically-driven, stirred-gas, fixed-solid Bertly reactor²⁰ are the foremost laboratory reactors for this purpose.

Considering the fact that the industrial application of hydroprocessing technology is usually a fixed-bed reactor or liquid phase ebullated beds, some research has involved the performance of these reactors. One study¹⁷ used radioactive reactant tracer to determine accurately the residence time and determined only small deviations from piston-flow through a trickle bed. Although any lab scale-up involves some degree of assumption, the data obtained in this study should be easily scaled up using the piston-flow model.

Hydrodesulfurization of Heavy Oils

Hydrodesulfurization of naphthas and distillate fuel oils has been considered well developed technology for over a decade. In 1965, the technology was available to design, construct, and operate a plant to remove sulfur from distillate fuels at 99.97% removal efficiency.²¹ This corresponds to preparing catalytic reformer feed with only 0.5 ppm sulfur. Since that time, the effort to adapt the process to high-molecular-weight sulfur-containing compounds has been proceeding.

Unfortunately, the heavier molecules also contain metal catalyst poisons and are harder to react. As the molecular weight of the feedstock rises, the reaction order shifts from first- to second-order kinetics.¹⁶ These effects combine to make hydrodesulfurization of heavy feeds more difficult than hydrodesulfurization of lighter fuels.

In any hydrodesulfurization study — whether laboratory, pilot plant, or commercial scale — care is necessary to consider the actual hydrogen requirement. Because hydrogen partial pressure can be the critical reaction variable, it is important to determine the actual hydrogen partial pressure in light of the amount dissolved in the liquid phase and that portion lost in chemical equilibrium to feed impurities, olefin saturation, aromatics saturation, and the small level of hydrocracking. Notwithstanding the care required to compare processes and process conditions according to the true hydrogen partial pressure, any extra hydrogen required above the stoichiometric amount used solely for hydrodesulfurization will be recovered later in the integrated fuel cell system.

The reaction networks for simple systems of thiophenes²² and benzothiophenes²³ have been studied. A definitive study considering all of the organic sulfur molecules typically found in heavy fuel oil would be complex indeed, as the following table of organic sulfur molecules attests.

These compounds are listed in increasing difficulty to remove via hydrodesulfurization. For the purpose of this study, given the high-performance catalysts available and the conditions of interest, the sulfides and thiols will be completely converted. Among the aromatic compounds in Table 10, thiopene is preferentially desulfurized, while the benzothiopene and higher will undergo hydrogenation before being desulfurized. This circumstance makes a priori determination of the stoichiometric requirement for sulfur removal very difficult.

Current chemical hydrogen consumption for H-Oil, Amoco, and Gulf processes²⁴ are estimated between 400 and 1350 SCF/bbl, depending on the crude source, the Conradson Carbon residue (7 to ~12%), and the amount of feedstock nitrogen (400 to 1200 in most U.S. crudes, but 4000 to 6600 ppm in California crudes).

Table 10. TYPICAL ORGANIC SULFUR MOLECULES FOUND IN FUEL OIL¹⁶

<u>Name</u>	<u>Structure</u>
Thiols (Mercaptans)	$R - SH$
Disulfides	$R - S - S - R'$
Sulfides	$R - S - R'$
Thiophenes
Benzothiophenes
Dibenzothiophenes
Benzonaphthothiophenes

Hydrodenitrification

Depending on the crude oil source, heavy fuel oil will contain a varying amount of feed nitrogen. This fact is of concern to petroleum refiners because fuel nitrogen ultimately is combusted to form NO_x , a serious pollutant in many areas of the country, such as California. In the fuel cell application of hydroprocessing, feed nitrogen levels are of concern if the nitrogen or ammonia become catalyst poisons. A third concern common to fuel cell and refinery applications is that portion of the hydrogen requirement which is not economic to recover. Ammonia is recovered from steel mill coke ovens, but only in sufficient volume to be economically attractive.

At given operating conditions where 93% of the feed sulfur is removed from a light distillate fuel, only 27% to 53% of the feed nitrogen can be removed.¹⁵ This is because ring-bound nitrogen requires hydrogenation in advance of denitrification, rather than the reverse, as in the case for desulfurization of light molecules. For the heavy molecules common in heavy fuel oil, the removal efficiency for nitrogen and sulfur might be more nearly equal, but not through an increase in nitrogen removal efficiency.

The presence of nitrogen in heavy oil feedstock is an unavoidable drain on recycle hydrogen. One might hope for feedstock low in nitrogen, yet the circumstance can be handled if necessary. Recent developments in hydrocracking and cat-reforming catalysts have increased the nitrogen tolerance of these processes.¹⁵

Hydrocracking

The common hydrocracking catalysts are said to be bifunctional, that is, hydrocracking is a hybrid of two processes, namely cracking and hydrogenation, which occur on the same catalyst bead.

The first reaction, cracking, is endothermic and can be either noncatalytic, as in thermal cracking, or catalytic, as in cat cracking. In practice, a combination of both routes are followed by long-chain hydrocarbons. The generic types of products from given reactant types is given in Table 11.

Table 11. TYPICAL HYDROCARBON CRACKING PRODUCTS*

<u>Reactant</u>	<u>Products</u>
Paraffin	Olefin and Paraffin
Olefin	Olefin and Olefin
Alkyl Aromatic	Aromatic and Olefin (dealkylation)
Alkyl Aromatic	Alkyl Aromatic and Paraffin (side chain cracking)
3 Cycloparaffin	Olefin and Olefin
Cycloparaffin	Cyclohexane, Olefin, and Paraffin

*This table was condensed from cracking studies in the absence of hydrogenation.¹⁵

The reaction networks for cracking have been studied for several fuel types. In the case of thermal cracking, it is believed that free radicals form. This cycle involves the formation of α olefins and the eventual production of a significant amount of ethylene. The catalytic cycle involves the acidic alumina sites of the hydrogenation catalyst support. According to this theory, carbonium ions are formed which rapidly convert to tertiary carbonium ions. The carbonium ion can attack any hydrocarbon to accomplish any of these secondary reactions: hydrogen transfer to a double bond, forming another, olefin isomerization, condensation, and disproportionation. In the absence

of hydrogenation, cracking over acidic alumina sites causes some degree of condensation and, ultimately, coking. However, in the presence of hydrogenation catalysts, and via either the catalytic or noncatalytic route, shorter-chain hydrocarbons are formed.

Hydrogenation is considered separately as one of the hydroprocesses, but is also the second step of hydrocracking. Without hydrogenation, fouling due to coke formation is fast and sure to follow. A large number of hydrogenation catalysts have been studied. Recently, in the prospect of large-scale coal gasification, synthesis gas hydrogenation (methanation) has received a great deal of attention as a means of increasing the heating value of synthesis gas.²⁵ The catalysts considered in these studies typically are Group VIII metals in a reduced, metallic state: Ni, Co, Pt, Ru, and Ir. However, these catalysts are poisoned by the sulfur unavoidably present in heavy oil hydroprocesses. Former studies of other catalysts,^{26,27} including sulfided tungsten and molybdenum, showed that sulfide catalysts retain their low-hydrogenation activity even in the presence of additional feed sulfur. Therefore, as long as active hydrogenation sites are close enough to the acidic alumina cracking sites, hydrocracking can proceed on Co/MoO₃/silica/alumina catalysts, without undue coke formation.

All crude oils contain asphaltenes that are present in varying amounts depending on the source of the crude oil. These are very high-boiling, high-molecular-weight, polycyclic compounds, which, upon distillation of the lighter oils from the crude, make up a significant portion of the residual bottoms from the distillation. The carbon residue test is the most common test utilized to provide a guide to the asphaltene concentration. Much of the sulfur, nitrogen and metals present in the crude are bound up in the asphaltenes. The compounds may be partly removed during the course of hydrotreating, but there is considerable loss of catalyst life if treating conditions are severe. Thus, residual oils may be hydrotreated for sulfur removal, but could be a source of excessive coking at elevated hydrocracking conditions.

Existing sulfur removal problems are approached by separating the asphaltenes before treating the oil, even though sulfur and nitrogen can be removed catalytically. One separation scheme involves a catalytic support material with pores too small for the asphaltenes to reach the catalytic site. The net result of this approach is to increase the catalyst life, remove most of the

non-asphaltene sulfur, and to produce a bimodal product distribution. In this case, a separation step is required downstream of the reaction; but this separation removes a smaller fraction of feed oil while removing the same amount of catalyst poisons, than in the case of upstream separation.

Experimental Approach

The laboratory facilities for hydrosulfurizing and hydrocracking were fully constructed and installed. Safety and other operating procedures have been developed for use in this aspect of the program. From our experience and the literature on similar processes, we anticipate that a suitable product for steam reforming can also be obtained from hydrosulfurizing and hydrocracking of heavy oil.

Table 12 is a list of the basic system specifications for the hydrotreating apparatus.

Figure 17 is a process and instrumentation diagram of both the hydrocracking and hydrosulfurizer units. The primary difference between the units is in the catalysts and conditions to be employed, rather than in hardware. Figures 18, 19, 20, and 21 are various views of the hydrocracker, identifying major pieces of equipment.

Procedures for the calibration of the instruments have been provided and are being adapted to our application. Procedures for routine operation, as well as alarm or emergency situations, are also being refined.

During this report period, the systems have been brought up to operating temperatures and pressures several times. Catalyst and inert material have been loaded and unloaded from the reactor vessel. The appropriate control settings for the proportional and integral control algorithms have been determined for the three oven zones and the flow control loop. At present, all systems are functional.

By searching the literature and with private communications from catalyst suppliers, preliminary operating conditions were selected. These conditions are in the range of conditions listed for heavy fuel oil in Table 13 and will serve as a starting point in our evaluation studies.

Table 12. SPECIFICATIONS FOR THE HDS SYSTEM AND HC SYSTEM

The purpose of the hydrodesulfurization unit is to study the reactions of sulfur removal from the oil. The reactor will be operated at temperatures up to 1000°F and pressures up to 2000 psig. That of the hydrocracking unit is to study the reactions of lowering the molecular weight of the feed oil. The reactor will be operated at temperatures up to 1100°F and pressures up to 2000 psig. A schematic diagram is attached. Two separate units with the following descriptions are required.

1. Pressure. Supply pressure may be as high as 4000 psig and all supply lines must have gages. The reactor pressure will be indicated by a 2000 psig Heise precision gage. The sampling lines must have -30 to +30 psi gages. All regulators must have up- and down-stream gages. Hydrogen sulfide will be used. Therefore, all pressure measuring devices must be resistant to H_2S .
2. Temperature. A two or three zone furnace for the reactor will be controlled by Barber Colman 520 controller and recorded by Esterline Angus Speed Servo II recorder. The temperatures of all heated lines and vessels will be controlled and recorded. Split tube-type furnaces are desired for reactors and liquid feed vessels.
3. Feed gas flow rate. The hydrogen flow rate will be in the range of 3 to 50 SCF/hr. This flow rate will be controlled and recorded continuously by using a delt-P or mass flow transducer. Automatic control is desired because continuous over-night operation is anticipated. The hydrogen sulfide, nitrogen, and helium flow rates will be in the range of 0 to 10 SCF/hr, and continuous recording of these flow rates is desired.
4. Liquid flow. The liquids will be heavy oils such as fuel oils No. 4 and No. 6. The flow rates will be from 0 to 450 cu cm/hr. All flow lines are to be steam traced. The liquid pump must be able to perform at operating temperatures and pressures and methods of measuring constant flow rates must be provided.
5. Reactor. The reactor material must be able to operate at above mentioned conditions and atmospheres. Catalyst will be used in this study, therefore easy access to the interior of the reactor is necessary. The approximate size of the reactor will be 30" long x 1" ID. Four thermocouples inside the reactor are desired. A three-zone, split tube type furnace with an ID of about 2" is desired.
6. Control unit. The reactor assembly will be behind a barricade. Remote controls on all feed gases, liquids, products, temperature and pressure are necessary. Light switches are desired. If the control unit is computer-based which is desired, the software must offer IGT the flexibility of manipulation to facilitate experimental conditions. Digital displays of flow, pressure, and temperature are required. Visual and audio safety alarm systems are required. Automatic shut down logic system is desired for unattended long term operations. Recorders used must be of equivalent quality such as Esterline Angus Speed Servo II.
7. Sampling. All product vessels must be heated and provisions are made for sampling, collection, and purging. Both gaseous and liquid products' flow rates must be measured.

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Figure 18. CRT TERMINAL DISPLAYING PROCESS VARIABLES

Figure 19. APPARATUS MAINFRAME

Figure 20. REAR VIEW OF PRODUCT HANDLING MODULES

Figure 21. REAR VIEW OF REACTANT DELIVERY MODULES

Table 13. TYPICAL PROCESS CONDITIONS FOR HDS OF HYDROCARBON FEEDSTOCKS¹⁵

	<u>Distillate Fuels</u>	<u>Petroleum Residua</u>	<u>Coal-Derived Liquids</u>
Temperature, °C	300-400	340-430	400-450
Pressure, psia	500-1000	800-2500	2000-4000
LHSV, vol oil/vol reactor/hour	2-10	0.2-1	0.2-0.3
Hydrogen Feed, SCF/bbl	300-1500	2000-10,000	25,000-100,000
Catalyst Lifetime, years	10 Regenerable	0.5-1 Unregenerable	Undetermined (Short)

As delivered, the oils do not contain as much sulfur as one would expect. Hence, we will increase the sulfur content of our test oils from 0.9 weight percent sulfur to 2.5 or 3.0 weight percent sulfur by adding organic sulfur as thiophene. It will be necessary to add about 320 grams of thiophene to 2 gallons of oil to reach 2.5 weight percent sulfur. Other forms of sulfur, such as dibenzothiophene, could be used — but at a much greater effort, for very little in return. However, in practice, fuel oil contains all forms of organic sulfur.

In previous catalyst studies,²⁸ the behavior of the catalyst is observed over a period of days, as it slowly loses activity. However, our current objective is primarily to observe the effect of reaction conditions on process efficiency, rather than catalyst evaluation. Accordingly, we will use aged (1 month), stable catalyst to simulate steady-state operation. Each hydrodesulfurizing and hydrocracking experiment will run for at least 48 hours so that any effect of catalyst degradation will be identified, if it is present. A list of the catalysts received for use in the program is given in Table 14.

Table 14. CATALYSTS RECEIVED FOR HDS AND HC TESTING

<u>Supplier</u>	<u>Catalyst</u>
Shell	324
Shell	444
Armak	KF-165
Armak	KF-153S
American Cyanamid	Aero-2

The process of catalyst activation has also been given attention.

Two different catalyst activation procedures were considered. On the one hand, using H_2S gas at moderately high temperature is an excellent means to fully activate a catalyst sample. On the other hand, an activation schedule closely following the operations used in full-scale industrial practice will provide more relevant results. This requires that sulfur be introduced via high-sulfur oil feedstock and that hydrogen be introduced in a manner similar to the industrial practice of recycling the product gas, even during activation, or "start-up." Our procedure will follow the industrial practice as closely as possible.

One sample of Shell 444 has been activated for use in hydrocracking. It was used over a 30-hour period to process No. 4 fuel oil. The results of that test are given in Figures 22, 23, and 24. Notwithstanding, the analytical data obtained in this manner, the test was primarily a trial run intended to demonstrate that the system functions properly. The explanation of the peaks and valleys reflect the different temperatures and pressures used. They are not to be taken as indicative of the expected start-up performance of a catalyst.

Table 15 gives the ultimate analysis of the liquid product samples taken over the test period. Note that in each case the hydrogen weight percent increased from 11.41% to as much 13.99%. Also, the weight percent of sulfur was reduced from 0.84% to 0.04% and, in one instance, to less than 0.01%. This significant sulfur removal came over a hydrocracking catalyst operating at rather severe conditions. The data from Table 15 are also given in Figure 22. The figure shows how the carbon/hydrogen ratio of the liquid products were in each case less than that of the No. 4 fuel oil feed.

Even though a significant fraction of the feed oil in this trial run was converted to gaseous products, the chromatograph was not calibrated for the wide range of low boiling products that were produced. Based on peak weight alone, approximately 10% of the feed oil was converted to CH_4 , C_2H_6 , C_3H_8 , olefins, and H_2S . If any steam had been present, we might have encountered COS as well.

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Figure 22. PRODUCT CARBON/HYDROGEN WEIGHT RATIOS
FOR NiMoO₃ HYDROTREATING TEST

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Figure 23. DISTILLATION FRACTIONS AT 260°C AS A FUNCTION OF TIME ON STREAM FOR TRIAL HYDROTREATING TEST

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Figure 24. AROMATIC FRACTIONS IN HIGHER AND LOWER BOILING PORTIONS OF TRIAL HYDROTREATING PRODUCT SAMPLES

Table 15. PRODUCT OIL COMPOSITIONS FOR TRIAL HYDROTREATING TEST

<u>Time of Sample, hr</u>	<u>C</u>	<u>H</u>	<u>S</u>
	<u>wt, %</u>		
0*	87.27	11.41	0.84
6	86.01	13.99	0.00
7	86.27	13.72	0.01
15	87.83	12.72	0.02
25	87.06	12.89	0.05
32	87.21	12.13	0.04

* Untreated No. 4 fuel oil, as delivered.

Of the product fraction sampled in the liquid state, some dissolved low-boiling hydrocarbons were undoubtedly lost due to flashing as the liquid products were dropped from high pressure to atmospheric pressure in a vented sample holding vessel. It would be possible to estimate the fraction and quantity lost in sampling by a vapor-liquid equilibrium back calculation based on the liquid product composition. However, it will be simpler and more reliable to collect and sample the gas directly.

Figure 23 gives the distillation fractions of the liquid product samples boiling above and below 260°C. Figure 24 gives the breakdown for each of these fractions of aromatic and non-aromatic composition. Because aromaticity is not desirable for most of the steam-reforming processes, conditions that lead to lesser aromatic compositions will be advantageous.

TASK IV. PROCESS SELECTION AND REVIEW OF
PROGRESS BY PROGRAM MONITOR

Sufficient data have been gathered at this time to begin to make judgments about hydrogasification of heavy oils. Previous studies have revealed process data on other feedstocks, and a comparison can be made with these results.

On the other hand, considerable effort has been devoted to bringing the hydrodesulfurizing and hydrocracking equipment into operation, although there are insufficient HDS/HC data at this time. However, there are enough data in the literature concerning other feedstocks to lay the groundwork for comparison with heavy oil processes.

In a letter dated May 16, 1978, from the Randall Corporation, a Houston-based modular process unit fabricator, we received preliminary cost estimates for the 2000-bbl/day hydroprocessing units below. In addition to these costs will be the costs associated with the generation of hydrogen, utilities, and offsite facilities.

1. No. 4 Fuel Oil (Distillate) low or high sulfur

Hydrodesulfurization	\$1,000,000-\$2,000,000
Hydrocracking	\$1,500,000-\$2,250,000
Hydrogasification	\$2,000,000-\$3,000,000

2. No. 6 Fuel Oil (Residual) low or high sulfur

Hydrodesulfurization	\$1,750,000-\$2,500,000
Hydrocracking	\$2,500,000-\$3,000,000
Hydrogasification	\$3,000,000-\$3,500,000

CONCLUSIONS

For hydrogasification —

- Hydrogen-to-oil feed ratio is more critical than other process conditions when temperature and pressure are high enough to overcome kinetic limitations.
- Hydrogen should be fed to heavy oil hydrogasification in excess of 200% of the stoichiometric requirement for complete conversion to methane. Operation at lesser ratios leads to unacceptable coke formation.
- Although isothermal operation is not practical in this case, the reaction zone temperature should be between 500° and 600°C for most effective operation.
- Pressure is not as critical a process variable as is temperature. Pressure can be limited by the materials of construction used for the reactor. Increasing pressure has the effect of increasing partial pressures and lengthening residence times. Operations at over 1000 psig, and less than 1500 psig, may be close enough to optimum for design purposes.

For hydrotreating —

- The theoretical efficiency of hydrotreating is acceptable for serious consideration in a fuel cell power plant.
- The lower temperatures and pressures sufficient for catalytic processing will not lead to as severe a coke formation product.

Many items remain to be seen during the continuation of this program. For instance, is there a way to increase the participation of the oil in hydrogasification without increasing coke formation? Will the liquid product from hydrotreating contain the compounds known to be less difficult to steam reform than methane? What will the volume of the gaseous fraction from hydrotreating be? How will that volume affect H_2S separation? In order to answer these and other questions, we look forward to the continuation of this project during FY 1979.

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APPENDIX A. Bibliography

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APPENDIX B. Partial Oxidation of Heavy Oils (Oxygen-Blown) —
Preliminary Thermal Efficiency Calculations

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PARTIAL OXIDATION OF HEAVY OILS (OXYGEN-BLOWN) —
PRELIMINARY THERMAL EFFICIENCY CALCULATIONS

Basis: 2000 bbl/day processing to gaseous fuel cell fuels.

Product Gas From Partial Oxidation (Oxygen-Blown)

	<u>mol %</u>	<u>mol/hr</u>	<u>lb/hr</u>	<u>SCF/hr</u>
O ₂	--	--	--	--
N ₂	1.40	53	1498	19,027
CO	46.90	1792	50,190	643,328
CO ₂	4.30	164	7221	58,876
H ₂	46.10	1761	3650	632,199
H ₂ O	--	--	--	--
CH ₄	0.40	15	244	5385
H ₂ S	0.90	35	1179	12,565

	<u>mol %</u>	<u>mol/hr</u>	<u>lb/hr</u>	<u>SCF/hr</u>	<u>10⁶ Btu/hr</u>
O ₂	--	--	--	--	--
N ₂	1.41	53	1498	19,027	--
CO	47.33	1792	50,190	643,328	206.5
CO ₂	4.34	164	7221	58,876	--
H ₂	46.52	1761	3650	632,199	205.5
H ₂ O	--	--	--	--	--
CH ₄	0.40	15	244	5385	5.45
H ₂ S	--	--	--	--	--
				TOTAL	417.45

* HHV of CO = 321 Btu/SCF.
 HHV of H₂ = 325 Btu/SCF.
 HHV of CH₄ = 1012 Btu/SCF.

Gas Production = 32.6×10^6 SCF/day

Electric Power Generation = $417.45 \times 10^6 \times 0.6 = 250.5 \times 10^6$ Btu/hr
 = 73,375 kW

Credit to Be Applied for Fuel Cell Effluent = $417.45 \times 10^6 \times 0.4 \times 0.6$
 = 100.2×10^6 Btu/hr

Partial Oxidation Process Power Requirements

	hp	10^6 Btu/hr
Air Separation Plant	7250	18.45
Partial Oxidation Process	433	1.10
Miscellaneous	708	1.80
Desulfurizing	<u>1027</u>	<u>2.60</u>
TOTAL	9418	24.0

Process Power Requirement to be supplied by Multiple Stage Turbines.

Inlet Steam = 1500 psig and 900°F, 1430 Btu/lb

Outlet Steam = 7 psig and 180°F, 1138 Btu/lb

Steam Enthalpy Drop = 292 Btu/lb

Steam required to generate 9418 hp + $\frac{24.0 \times 10^6}{292} = 82,200$ lb/hr at 1500 psig, 900°F
 = 117.6×10^6 Btu/hr

Low-quality steam available for use in process + 82,200 lb/hr at 7 psig, 180°F
 = 93.5×10^6 Btu/hr

NOTE: No credit is given for this steam because of its low quality.

Fuel Cell Feed Gas Preheating From 100° to 1150°F

Equivalent requirement + 78,700 lb/hr of 1500 psig, 900°F, 1430 Btu/lb, steam
 = 112.5×10^6 Btu/hr

Total Requirement of 1500 psig, 900°F Steam

$82,200 + 78,700 = 160,900$ lb/hr or 230.1×10^6 Btu/hr

Partial Oxidation Plant Steam Requirements

Steam at 600 psig, 1204 Btu/lb

	<u>lb/hr</u>
Oil and O ₂ Preheating to 500°F	10,300
Partial Oxidation Process Steam	11,250
Desulfurizing Stripping Steam	<u>4300</u>
TOTAL	25,850.

Credit for Steam From Waste Heat Boiler 44,000—

Net Excess Steam, 18,150 lb/hr or 21.7×10^6 Btu/hrFinal Plant Heat Balance — Maximum

	<u>10⁶ Btu/hr</u>
Processing Oil Feedstock	531.1
Fuel Cell Credit	-100.2
Process Power Requirement and Gas Preheating	230.1
Excess Steam Credit	<u>-21.7</u>
TOTAL	639.3

Under this plant heat balance, we obtain —

$$\text{Fuel Processing Efficiency} = 417.45 \times 10^6 / 639.3 \times 10^6 = 65\%$$

$$\text{Heat Rate} = 639.3 \times 10^6 / 73,375 = 8715 \text{ Btu/kW-hr}$$

$$\text{Oil to a-c Power Efficiency} = 0.65 \times 0.60 \times 0.95 = 37\%$$

Final Plant Heat Balance — Minimum

	<u>10⁶ Btu/hr</u>
Processing Oil Feedstock	531.1
Fuel Cell Credit	-100.2
Process Power Requirement and Gas Preheating, generated and transferred at 60% total efficiency	383.5
Excess Steam Credit, transferred at 60% efficiency	<u>-17.4</u>
TOTAL	797.0

Under this plant heat balance, we obtain —

$$\text{Fuel Processing Efficiency} = 417.45 \times 10^6 / 797.0 \times 10^6 = 52\%$$

$$\text{Heat Rate} = 797.0 \times 10^6 / 73,375 = 10,860 \text{ Btu/kW-hr}$$

$$\text{Oil to a-c Power Efficiency} = 0.52 \times 0.60 \times 0.85 = 30\%$$

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Figure B-1. PARTIAL OXIDATION (Shell Oil Company)

APPENDIX C. Cyclic Catalytic Cracking of Heavy Oils —
Preliminary Thermal Efficiency Calculations

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CYCLIC CATALYTIC CRACKING OF HEAVY OILS —
PRELIMINARY THERMAL EFFICIENCY CALCULATIONS

Basis: 2000 bbl/day processing to gaseous fuel cell fuels.

Product Gas From Cyclic Catalytic Cracking

	Fuel Oil		Residue (tar)	
	wt %	lb/hr	wt %	lb/hr
C	84.8	24,060	86.4	1593
H	11.7	3320	8.8	162
S	3.5	992	4.8	89
		28,372		1844

	Combustion Air, P = 10 psig, T = 70°F			Flue Gas		
	mol %	mol/hr	lb/hr	mol %	mol/hr	lb/hr
N ₂	79.0	3792	106,190	78.5	3792	106,190
O ₂	21.0	998	31,927	3.2	155	4960
SO ₂				0.3	14	896
CO ₂				16.8	812	35,728
H ₂ O				1.2	58	1044
		4790	138,017		4831	148,818

	Raw Product Gas, P = 100 psig, T = 100°F			Reformer Feed, P = 80 psig, T = 100°F		
	mol %	mol/hr	lb/hr	mol %	mol/hr	lb/hr
CO	14.5	314	8805	16.2	314	8805
CO ₂	10.0	217	9534			
H ₂	49.0	1060	2140	54.8	1060	2140
H ₂ O	0.9	19	336	1.0	19	336
CH ₄	15.0	332	5318	17.1	332	5318
C ₂ H ₄	6.7	145	4064	7.5	145	4064
H ₂ S	0.6	14	480			
N ₂	3.3	65	1820	3.4	65	1820
		2166	32,497		1935	22,483

Reformer Product Gas, P = 60 psig, T = 1400°F

	<u>mol %</u>	<u>mol/hr</u>	<u>lb/hr</u>	<u>SCF/hr</u>	<u>10⁶ Btu/hr</u>
CO	13.5	731	20,468	262,429	84.3
CO ₂	3.0	163	7172	58,517	
H ₂	46.5	2519	5088	904,321	293.9
H ₂ O	35.0	1896	34,128	680,664	
CH ₄	0.8	43	688	15,437	15.6
C ₂ H ₄	--				
N ₂	1.2	65	1820	23,335	
		5417	69,364	1,944,703	393.8

Gas Production = 46.7×10^6 SCF/day

Electric Power Generation = $393.8 \times 10^6 \times 0.6 = 236.3 \times 10^6$ Btu/hr
 = 69,215 kW

Credit to Be Applied for Fuel Cell Effluent = $393.8 \times 10^6 \times 0.4 \times 0.6$
 = 94.5×10^6 Btu/hr

Cyclic Catalytic Cracking Process Power Requirements

Acid Gas Removal 487 hp

Raw Product Gas Compression After 1939
 Catalytic Cracking

Miscellaneous 350

2776 hp or 7.1×10^6 Btu/hr

Process Power Requirement to be supplied by Multiple Stage Turbines.

Inlet Steam = 1500 psig, 900°F, 1430 Btu/lb

Outlet Steam = 7 psig, 180°F, 1138 Btu/lb

Steam Enthalpy Drop = 292 Btu/lb

Steam required to generate 2776 hp = $\frac{7.1 \times 10^6 \text{ Btu/hr}}{292} = 24,315 \text{ lb/hr}$
 at 1500 psig, 900°F

Low-quality steam available for use in process = 24,315 lb/hr at 7 psig, 180°F

NOTE: No credit is given for this steam because of its low quality.

Cyclic Catalytic Cracking Plant Steam Requirement

Steam at 350°F, 100 psig, 1200 Btu/lb

	<u>lb/hr</u>
Cyclic Catalytic Cracking Process Steam	77,410
Steam Reforming Process Steam	43,450
Auxiliary and Acid Gas Stripping Steam	57,750
Credit for Steam From LP Waste Heat Boiler	-69,263
Credit for Steam From Product Gas Waste Heat Boiler	<u>-9800</u>
Net Requirement	99,547 lb/hr, 119.5×10^6 Btu/hr

Final Plant Heat Balance — Maximum

	<u>10^6 Btu/hr</u>
Fuel Oil Feedstock	531.1
Fuel Cell Credit	-94.5
Process Plant Steam Requirement	119.5
Process Power Requirement	34.8
Credit for Steam From HP Waste Heat Boiler	-35.5
Process Heat for Steam Reforming	<u>92.2</u>
TOTAL	647.6

Under this plant heat balance, we obtain —

$$\text{Fuel Processing Efficiency} = 393.8 \times 10^6 \text{ Btu/hr} / 647.6 \times 10^6 \text{ Btu/hr} = 61\%$$

$$\text{Heat Rate} = 647.6 \times 10^6 \text{ Btu/hr} / 69,215 = 9360 \text{ Btu/kW-hr}$$

$$\text{Oil to a-c Power Efficiency} = 0.61 \times 0.60 \times 0.95 = 35\%$$

Final Plant Heat Balance — Minimum

	<u>10⁶ Btu/hr</u>
Fuel Oil Feedstock	531.1
Fuel Cell Credit	-94.5
Process Power Requirement, generated and transferred at 60% total efficiency	199.1
Credit for Steam From HP Waste Heat Boiler, transferred at 80% efficiency	-28.4
Process Heat for Steam Reforming, generated and transferred at 60% total efficiency	<u>153.7</u>
TOTAL	761.0

Under this plant heat balance, we obtain —

Fuel Processing Efficiency = $393.0 \times 10^6 \text{ Btu/hr} / 761.0 \times 10^6 \text{ Btu/hr} = 52\%$

Heat Rate = $761.0 \times 10^6 \text{ Btu/hr} / 69,215 = 10,995 \text{ Btu/kW-hr}$

Oil to a-c Power Efficiency = $0.52 \times 0.6 \times 0.95 = 30\%$

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Figure C-1. SEGAS CYCLIC CATALYTIC CRACKING PROCESS BLOCK FLOW DIAGRAM

APPENDIX D. Thermal Cracking of Heavy Oils —
Preliminary Thermal Efficiency Calculations

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THERMAL CRACKING OF HEAVY OILS — PRELIMINARY
THERMAL EFFICIENCY CALCULATIONS

Product Gas Composition

	<u>mol %</u>	<u>SCF/hr</u>	<u>HHV, 10⁶ Btu/hr</u>
CO	13.86	262,369	84.2
CO ₂	1.36	25,745	--
H ₂	43.39	821,373	
H ₂ O	40.71	770,640	
CH ₄	0.27	5111	5.2
N ₂	0.41	7761	
			<hr/> 356.4

Final Plant Heat Balance

	<u>10⁶ Btu/hr</u>
Process Feedstock	531.1
Reformer Process Heat	102.9
Steam and Power Requirements	121.5
Regeneration	<hr/> 3.0
	227.4
Credit for Tar Heating Value	-178.7
Waste Heat Boiler Steam	-52.4
Credit for Fuel Cell Effluent	<hr/> -85.5
	-316.6
Irrecoverable Process Heat	89.2

The heat recovered as tar, in the waste heat boiler, and in the fuel cell effluent is 89.2 MM Btu/hr greater than the process utility requirements and can not be further utilized in the process. Most of the heat required for thermal cracking is supplied by combustion of the deposited carbon. The entry in the table labeled regeneration represents the additional heat required for thermal cracking which must be supplied. This leaves only process feedstock requirements, and neither fuel cell effluents nor steam is directly substitutable for process oil. Therefore, for the purpose of calculating thermal efficiency, the heat input to the process is only 531.1 MM Btu/hr.

Electric Power Generation = $356.4 \times 10^6 \text{ Btu/hr} \times 0.6 = 214.0 \times 10^6 \text{ Btu/hr}$
= 62,640 kW

Fuel Processing Efficiency = $356.4 \times 10^6 \text{ Btu/hr} / 531.1 \times 10^6 \text{ Btu/hr} = 67\%$

Heat Rate = $531.1 \times 10^6 \text{ Btu/hr} / 62,640 = 8480 \text{ Btu/kW-hr}$

Oil to a-c Power Efficiency = $.67 \times 0.6 \times 0.95 = 38\%$

Figure D-1. SIMPLIFIED BLOCK FLOW DIAGRAM OF THERMAL CRACKING (TPC) PROCESS

APPENDIX E. Hydrodesulfurizing-Hydrocracking Reforming —
Preliminary Thermal Efficiency Calculations

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HYDRODESULFURIZING-HYDROCRACKING REFORMING -
PRELIMINARY THERMAL EFFICIENCY CALCULATIONS

Process Feedstock = 2000 bbl/day = 28,372 lb/hr = 531.1×10^6 Btu/hr

Description Temperature, °F Pressure, psig	Process Feedstock		Hydrocracked Naphtha		Furnace Oil Recycle		Asphalt Residue	
	70		380		600		1000	
	550		530		530		550	
	wt %	lb/hr	wt %	lb/hr	wt %	lb/hr	wt %	lb/hr
C	84.6	24,003	85.9	20,556	86.0	13,865	85.9	853
H	11.3	3205	13.6	3260	12.8	2071	8.0	80
O	0.13	993					1.6	16
N	0.40	113					0.6	6
S	3.50	37	0.5	120	1.20	194	2.7	27
Ash	0.07	20					1.2	11
		28,372		23,936		16,130		993

Description Temperature, °F Pressure, psig	Naththa to Reformer			Product Gas From Reformer			Make-up H ₂		
	700			1700			1700		
	520			510			510		
	<u>wt %</u>	<u>lb/hr</u>		<u>mol %</u>	<u>mol/hr</u>	<u>lb/hr</u>	<u>mol %</u>	<u>mol/hr</u>	<u>lb/hr</u>
C	86.3	20,556	CO	13.7	1299	36,650	13.7	143	4005
H	13.7	3260	CO ₂	6.7	635	25,250	6.7	70	3081
S	0.005	1	H ₂	48.8	4626	9420	48.8	508	1024
			H ₂ O	30.8	<u>2920</u>	<u>52,970</u>	30.8	<u>320</u>	<u>5772</u>
		23,819			9480	124,290		1041	13,882

Feed Gas to Fuel Cell

	<u>mol %</u>	<u>mol/hr</u>	<u>lb/hr</u>	<u>SCF/hr</u>	<u>10⁶ Btu/hr</u>
CO	13.7	1156	32,368	415,004	133.2
CO ₂	6.7	565	24,860	202,835	
H ₂	48.8	4118	8236	1,478,362	480.4
H ₂ O	30.8	<u>2600</u>	<u>46,800</u>	<u>933,400</u>	
		8439	112,264	3,029,601	613.6

Electric Power Generation = $613.6 \times 10^6 \text{ Btu/hr} \times 0.6 = 368.0 \times 10^6 \text{ Btu/hr} = 107,830 \text{ kW}$

Fuel Cell Credit to Be Applied = $613.6 \times 10^6 \text{ Btu/hr} \times 0.4 \times 0.6 = 147.3 \times 10^6 \text{ Btu/hr}$

Process Power Requirements

	<u>hp</u>
H ₂ Recycle Compressors	160
Acid Gas Removal Pumping Requirement	1030
Oil and Naphtha Feed Pumps	50
Miscellaneous	<u>310</u>
	1550 ($4.0 \times 10^6 \text{ Btu/hr}$)

Process Power Requirements to be supplied by Multiple Stage Turbines.

Inlet Steam = 1500° psig, 900°F, 1430 Btu/lb

Outlet Steam = 7 psig, 180°F, 1138 Btu/lb

Steam Enthalpy Drop = 292 Btu/lb

Steam required to generate 1550 hp = $\frac{4.0 \times 10^6}{292} = 13,700 \text{ lb/hr at } 1500^\circ \text{psig, } 900^\circ \text{F}$
 $= 19.6 \times 10^6 \text{ Btu/hr}$

Low-quality steam available for use in process = 13,700 lb/hr at 7 psig, 180°F
 $= 15.6 \times 10^6 \text{ Btu/hr}$

NOTE: No credit is given for this steam because of its low quality.

Process Plant Steam Summary Requirement

Steam at 550 psig, 600°F, 1294 Btu/lb

Steam-Reformer Process Steam	105,535 lb/hr
Credit for Steam From Waste Heat Boiler	<u>-29,200 lb/hr</u>
Net Requirement	76,335 lb/hr
	or $98.8 \times 10^6 \text{ Btu/hr}$

Stripping Steam for Acid Gas Scrubbing

Steam at 20 psig, 1156 Btu/lb

Requirement = 1710 lb/hr or 2.0×10^6 Btu/hr

Final Plant Heat Balance — Maximum

	<u>10^6 Btu/hr</u>
Process Fuel	531.1
Reformer Fuel Requirement	272.7
HC/HDS Utility Fuel	16.0
Process Plant Steam	98.8
Steam for Power Generation	19.6
Fractionation	2.8
Stripping Steam	2.0
Credit for Asphalt Residue	-17.8
Credit for Fuel Cell Effluent	<u>-147.3</u>
TOTAL	777.9

Under this plant heat balance, we obtain —

$$\text{Fuel Processing Efficiency} = \frac{613.6 \times 10^6 \text{ Btu/hr}}{777.9 \times 10^6 \text{ Btu/hr}} \times 100 = 79\%$$

and,

$$\text{Heat Rate} = \frac{777.9 \times 10^6 \text{ Btu/hr}}{107,830 \text{ kW}} = 7225 \text{ Btu/kW-hr}$$

Final Plant Heat Balance — Minimum

	<u>10^6 Btu/hr</u>
Process Fuel	531.1
Reformer Fuel Requirement, at 60% efficiency	454.5
HC/HDS Utility fuel, at 60% efficiency	26.7
Process Plant Steam, transferred at 80% efficiency	123.5
Steam for Power Generation, at 60% efficiency	32.7
Fractionation and Stripping Steam	5.0
Credit for Asphalt Residue	-17.8
Credit for Fuel Cell Effluent	<u>-147.3</u>
TOTAL	1008.3

Under this plant heat balance, we obtain -

$$\text{Fuel Processing Efficiency} = \frac{613.6 \times 10^6 \text{ Btu/hr}}{1008.3 \times 10^6 \text{ Btu/hr}} = 61\%$$

and,

$$\text{Heat Rate} = \frac{1008.3 \times 10^6 \text{ Btu/hr}}{107,830 \text{ kW}} = 9350 \text{ Btu/kW-hr}$$

$$\text{Oil to a-c Power Efficiency} = 0.61 \times 0.6 \times 0.95 = 35\%$$

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Figure E-1. BLOCK FLOW DIAGRAM OF HYDROGASIFICATION-REFORMING PROCESS

APPENDIX F. Hydrogasification/Steam Reforming —
Thermal Efficiency Calculations

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HYDROGASIFICATION/STEAM REFORMING — THERMAL EFFICIENCY CALCULATIONS

Material Balance

Process Feedstock, 28,372 lb/hr

	<u>wt %</u>	<u>lb/hr</u>
C	84.6	24,003
H	11.3	3206
O	.13	37
N	.40	113
S	3.50	993
ash	.07	20

The H/C ratio must be increased to 3.17 by adding H₂ in a recycle stream.

- H present in stream 1: 3206 lb/hr
- H necessary for H/C ratio: 7583 lb/hr
- H necessary to be added: 4377 lb/hr

HG Feed, 50,847 lb/hr

	<u>wt %</u>	<u>lb/hr + (recycle)</u>	<u>wt %</u>
C	70.03	29,248	57.52
H	22.93	7200	14.16
O	4.33	13,334	26.22
N	.18	108	.21
S	2.52	<u>957</u>	1.88
		50,847	

The water in the recycle stream is dropped in a condenser.

HG Product Tar, 762 lb/hr

	<u>wt %</u>	<u>lb/hr</u>
C	85.17	649
H	10.75	82
O	.07	0.5
N	.07	0.5
S	3.94	<u>30</u>
		762

HG Gas Product, 50,085 lb/hr

	<u>wt %</u>	<u>lb/hr</u>
C	57.10	28,599
H	14.21	7118
O	26.62	13,334
N	.21	107
S	1.85	<u>927</u>
		50,085

Purification By-product Gas, 1108 lb/hr

	<u>wt %</u>	<u>lb/hr</u>
C	--	--
H	6.67	73.9
O	--	--
N, as NH ₃	9.70	107.5
S, as H ₂ S	83.63	<u>927</u>
		1108.4

Purification By-product Liquid, 3416 lb/hr

	<u>wt %</u>	<u>lb/hr</u>
C, as C ₆ H ₆	65.25	2229
H	8.75	299
O, as H ₂ O	26.00	888
N	--	--
S	--	<u>--</u>
		3416

Steam for reformer, 109,374 lb/hr

This stream provides H₂O for the material balance, but not necessarily enough enthalpy for the energy balance.

Steam-Reformer Product, 154,930 lb/hr

	<u>wt %</u>	<u>lb/hr</u>		<u>mol %</u>
C	17.02	26,370	CO	12.093
H	14.46	22,404	CO ₂	4.398
O	68.52	<u>106,162</u>	H ₂	54.549
		154,930	H ₂ O	28.960

Recycle to HC/HG (less water), 25,564 lb/hr

	<u>mol %</u>	<u>mol/hr</u>	<u>lb/hr</u>
CO	12.093	481.33	13,484
CO ₂	4.398	175.05	7703
H ₂	54.549	2171.19	4377
H ₂ O	28.960	1152.68	20,766

Feed to Fuel Cell, 108,606 lb/hr

	<u>mol %</u>	<u>wt %</u>	<u>lb/hr</u>	<u>mol/hr</u>	<u>SCF/hr</u>
CO	12.093	29.10	31,604	1128.3	405,056
CO ₂	4.398	16.63	18,061		
H ₂	54.549	9.45	10,263	5090.9	1,827,642
H ₂ O	28.960	44.82	48,677		

$$\text{HHV} = 130 \times 10^6 + 594 \times 10^6$$

$$= 724 \times 10^6 \text{ Btu/hr}$$

$$\begin{aligned} \text{To d-c Power via Fuel Cells} &= 724 \times 10^6 \times 0.6 = 434.4 \times 10^6 \text{ Btu/hr} \\ &= 127,240 \text{ kW} \end{aligned}$$

$$\begin{aligned} \text{Credit to Be Applied for Fuel Cell Effluent} &= 724 \times 10^6 \times 0.4 \times 0.6 \\ &= 174 \times 10^6 \text{ Btu/hr} \end{aligned}$$

Power Requirements

	<u>hp</u>
H ₂ Recycle Compressors	800
Acid Gas Pumps/Purification	1500
Feed Pumps	150
Miscellaneous	<u>500</u>
	2950 (7.5 X 10 ⁶ Btu/hr)

$$1500 \text{ psi, } 900^\circ\text{F steam} = 1430 \text{ Btu/lb}$$

$$\begin{aligned} \text{to 7 psi, } 180^\circ\text{F steam} &= \frac{1138 \text{ Btu/lb}}{292} \end{aligned}$$

$$\begin{aligned} \text{Steam Required to Generate Power} &= \frac{7.5 \times 10^6}{292} = 25,720 \text{ lb/hr} \\ &(\text{1500 psi, } 900^\circ\text{F}) \end{aligned}$$

$$= 36.8 \times 10^6 \text{ Btu/hr}$$

$$\begin{aligned} \text{Less Steam Produced by Gasifier} &= 19,770 \text{ lb/hr at 1500 psi, } 900^\circ\text{F} \\ &= 28.3 \times 10^6 \text{ Btu/hr} \end{aligned}$$

$$\text{Net Steam Required} = 5950 \text{ lb/hr} = 8.5 \times 10^6 \text{ Btu/hr}$$

Process Steam Requirement (550 psi, 600°F)
1294 Btu/lb

For Steam Reformer	109,374
Less Steam From WHB After Reformer	44,000
Net Requirement	65,374 = 84.6×10^6 Btu/hr

Stripping Steam (20 psi, 1156 Btu/hr)

3.0×10^6 Btu/hr

<u>Final Balance — Maximum</u>	<u>10^6 Btu/hr</u>	<u>10^6 Btu/hr</u>
Process Feedstock	531.1	531.1
Fractionation	3.5	5.8
Utility Fuel	36.8	61.0
Reforming Fuel	380.0	633.0
Steam for Power Regeneration	8.5	14.2
Process Steam	84.6	141.0
Acid Gas Scrubbing	3.0	5.0
Less Fuel Oil & Benzene HHV	-86.0	-86.0
Fuel Cell Credit	<u>-174.0</u>	<u>-174.0</u>
	787.5	1131

Maximum Efficiency = $724/788 \times 100 = 92\%$

Oil to a-c Power = 52%

Heat Rate = 6215 Btu/kW-hr

Minimum Efficiency = $724/1131 \times 100 = 64\%$

Oil to a-c Power = 36%

Heat Rate = 8933 Btu/kW-hr

F-7

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Figure F-1. BLOCK FLOW DIAGRAM FOR HYDROCRACKING-REFORMING PROCESS

APPENDIX G. No. 4 Fuel Oil Hydrogasification Data

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Table G-1. PRELIMINARY TRIAL RUNS OF NO. 4 FUEL OIL

	Run No.						
	100	101a	101b	102a	102b	102c	103
Average Temperature, °C	650	500	500	500	500	600	700
Feed Conditions							
Hydrogen, l/min (20°C, 15 psia)	2.6	2.0	2.6	2.45	3.12	4.42	3.49
H ₂ , g-mol/min	.110	.085	.110	.104	.132	.188	.146
Oil Flow Rate, ml/min	.82	.50	.50	.52	.51	.51	.52
Oil Flow Rate, g/min	.742	.453	.453	.469	.462	.462	.471
Stoichiometric Ratio, % CH ₄	141	168	207	192	236	319	253
Wt % C	87.27	87.27	87.27	87.27	87.27	87.27	87.27
Wt % H	11.41	11.41	11.41	11.41	11.41	11.41	11.41
Wt % S	.84	.84	.84	.84	.84	.84	.84
Exit Conditions							
Exit Gas Flow, l/min (20°C, 15 psia)	--*	--	--	--	--	--	--
Exit Gas Flow, g-mol/min	--	--	--	--	--	--	--
Vol% H ₂							~90%
Vol% CH ₄							~10%
Vol% C ₂ H ₆							
Vol% C ₃ H ₈							
vppm H ₂ S							Trace
Exit Pressure, psig	500	120	260	280	400	1000	520

* Coke buildup stopped flow.

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Table G-2. HG DATA FOR NO. 4 FUEL OIL

	Run No.																		
	104	105	106	107	108	109 ^c	110	111	112	113 ^c	114	115	116	117	118	119	120	121	122
Location of Thermocouple From Top, cm	-6.4	-6.4	-6.4	-6.4	-6.4	-6.4	-6.4	0	0	0	0	0	0	0	0	0	0	0	0
	3.8	3.8	3.8	3.8	3.8	3.8	3.8	16.5	16.5	16.5	16.5	16.5	16.5	16.5	16.5	16.5	16.5	16.5	16.5
	19.1	19.1	19.1	19.1	19.1	19.1	19.1	47.0	47.0	47.0	47.0	47.0	47.0	47.0	47.0	47.0	47.0	47.0	47.0
Temperature, °C	48.9	48.9	48.9	48.9	48.9	48.9	48.9	76.2	76.2	76.2	76.2	76.2	76.2	76.2	76.2	76.2	76.2	76.2	76.2
					655	677	669	685	685	689	532	539	502	540	544	660	663	536	555
				708	714	715	704	714	722	710	568	582	569	586	597	735	729	646	642
				732	608	608	598	603	606	609	494	492	499	499	507	605	635	564	561
					410	407	410	397	396	387	341	344	352	368	363	475	479	389	394
Average Temperature, °C	675	700	700	700	575	576	570	572	574	570	467	471	469	482	491	618	626	533	538
Feed Conditions																			
H ₂ , l/min (20°C, 15 psia)	2.07	1.91	2.1	1.72	2.15	---	2.11	1.90	2.29	1.93	2.15	2.0	2.03	2.10	2.02	2.86	3.23	4.40	4.01
H ₂ , g-mol/min	.088	.081	.089	.073	.093	---	.090	.081	.097	.082	.091	.085	.086	.089	.086	.121	.137	.187	.170
Oil Flow Rate, ml/min	.45	.49	.48	.445	.94	---	.894	.86	.85	.97	.98	.98	1.01	1.00	.995	.98	1.03	1.00	.99
Oil Flow Rate, g/min	.407	.443	.456	.403	.851	---	.809	.778	.769	.878	.887	.887	.914	.905	.900	.887	.932	.905	.896
Stoichiometric Ratio, %	188	165	173	164	113		115	110	126	103	110	105	104	107	105	133	140	181	170
Wt % C	87.27	87.27	87.27	87.27	87.27		87.27	87.27	87.27	87.27	87.27	87.27	87.27	87.27	87.27	87.27	87.27	87.27	87.27
Wt % H	11.41	11.41	11.41	11.41	11.41		11.41	11.41	11.41	11.41	11.41	11.41	11.41	11.41	11.41	11.41	11.41	11.41	11.41
Wt % S	.84	.84	.84	.84	.84		.84	.84	.84	.84	.84	.84	.84	.84	.84	.84	.84	.84	.84
Exit Conditions																			
Exit Gas Flow, l/min (20°C, 15 psia)					2.23		1.87	1.94	1.91	1.15	1.42	2.00	1.43	1.39	1.51	3.09	3.04	3.75	3.86
Exit Gas Flow, g-mol/min					.095		.079	.082	.081	.049	.060	.085	.061	.059	.064	.131	.129	.159	.164
Vol % H ₂	~79	~69	~51	NA	NA	NA	~69	19.48	19.42	21.35	27.53	3.77	5.07	6.29	NA	8.1	19.10	26.93	7.76
Vol % CH ₄	15	25	45	NA	NA	NA	19.48	19.42	21.35	27.53	3.77	5.07	6.29	NA	8.1	19.10	26.93	7.76	11.22
Vol % C ₂ H ₆	6	6	4	NA	NA	NA	11.55	9.44	10.21	10.98	2.40	3.50	4.53	NA	5.2	6.99	5.97	5.51	7.96
Vol % C ₃ H ₈			.043	NA	NA	NA	.24	.06	.06	.05	2.12	2.52	2.97	NA	5.0			1.26	1.48
H ₂ S, vppm	trace	trace	trace	NA	NA	NA	1190	1930	2190	3760	810		3.40	1480	1120	1570	1800	711	794
Exit Liquid Flow, g/min	.052	.138	.053	NA	NA	---	.269	.199	.133	.287	.562	.725	.62	.44	.45	.152	.120	.280	.284
Wt % C	NA ^b	NA	NA			---	90.36	90.08	83.67	86.23	86.46	83.89	86.15	87.64	87.94	91.59	92.11	91.06	91.50
Wt % H	NA	NA	NA			---	6.75	6.67	6.07	6.84	9.21	8.48	9.03	8.79	8.98	7.16	7.58	7.41	7.43
Wt % S	NA	NA	NA			---	1.41	.73	.59	.51	1.05	1.11	1.13	1.09	1.17	.57	.31	1.42	1.18
Exit Temperature, °C							385	380	380	335	340	350	360	360	300	410	410	330	340
Exit Pressure, psia	510	740	1500	1900	250	500	750	1000	1250	1500	1500	1260	1000	750	750	750	1250	750	1250
Space Time at Exit Conditions, min					3.33		12.4	16.0	20.4	43.6	35.0	20.5	22.4	17.3	17.6	7.2	12.2	6.7	10.7

a. Reactor volume = 1.04 l.

b. NA = no analysis.

c. These runs encountered severe coking problems.

d. Unstable flow measurement.

e. Argon GC carrier used for Run 118.

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Table G-3. HG PRODUCT DISTRIBUTION FOR NO. 4 FUEL OIL

	Run No.																		
	104	105	106	107	108	109††	110	111	112	113†	114	115	116	117	118	119	120	121	122
Temperature, °C	675	700	700	700	575	576	570	572	574	570	467	471	469	482	491	618	626	533	538
Pressure, psig	510	740	1500	1900	250	500	750	1000	1250	1500	1500	1260	1000	750	750	750	1250	750	1250
Stoichiometry, %	188	165	173	164	113		115	110	126	103	110	105	104	107	105	133	140	181	170
Feed Carbon, g-mol/min	.0296	.0322	.0331	.0293	.0618		.0588	.0565	.0559	.0638	.0644	.0644	.0644	.0658	.0654	.0644	.0677	.0658	.0651
Product Gas, g-mol/min					.0947		.0794	.0824	.0811	.0488	.0603	.0849	.0607	.0590	.0641	.1312	.1291	.1592	.1639
Methane, g-mol/min					NA ⁺	NA	.0155	.0160	.0173	.0134	.00227	.00431	.00382	NA	.0052	.0251	.0348	.0124	.0184
% of feed C					NA	NA	26.4	28.3	30.9	21.0	3.5	6.7	5.8	NA	8.0	39.0	51.4	18.8	28.3
Ethane, g-mol/min					NA	NA	.0092	.0078	.0083	.0054	.00145	.00297	.00275	NA	.0033	.0092	.0077	.0088	.0130
% of feed C					NA	NA	31.3	27.6	29.7	16.9	4.5	9.2	8.3	NA	10.1	28.6	22.7	26.7	39.9
Propane, g-mol/min					NA	NA	.0002	trace	.00005	.00002	.00128	.00214	.00180	NA	.0032	trace	trace	.0020	.0024
% of feed C					NA	NA	1.0	~1.0	.3	.1	6.0	10.0	8.1	NA	14.7	1.0	1.0	9.1	11.1
Total Gas % of feed C							58.7	56.9	60.9	48.0	14.0	25.9	22.2	~15	32.8	68.6	75.1	54.6	79.3
Product Liquid, g/min	.052	.138	.053				.269	.199	.133	.287	.562	.725	.62	.44	.45	.152	.120	.280	.284
Wt % C	NA	NA	NA				90.36	90.08	83.67	86.23	86.46	83.89	86.15	87.64	87.94	91.59	92.11	91.06	91.50
C, g-mol/min	~.004	~.01	~.004				.0202	.0149	.0093	.0206	.0405	.0506	.0445	.0321	.0329	.0116	.0092	.0212	.0216
% of feed carbon	-13	-30	-12			small	34.4	26.4	16.6	32.3	62.8	78.6	67.0	48.8	51.4	18.0	13.6	32.3	33.2
Unaccounted Carbon, g-mol/min							.0040	.0094	.0126	.0126	.0149		.0072	~.024	.0101	.0086	.0076	.0086	unclear
C, g/min							.048	.113	.151	.151	.179		.086	~.3	.1215	.1037	.0918	.1033	unclear
% of feed C						large	6.9	16.7	22.5	19.7	23.2		10.8	~36	15.8	13.4	11.3	13.1	

* Reactor volume = 1.04 %.

† NA = no analysis.

†† These runs encountered severe coking problems.

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APPENDIX H. No. 6 Fuel Oil Hydrogasification Data

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Table H-1. HG DATA FOR NO. 6 FUEL OIL

	Run No.						
	200	201	202	203	204	205	206
Location of Thermocouple From Top, cm	0	0	0	0	0	0	0
	16.5	16.5	16.5	16.5	16.5	16.5	16.5
	47.0	47.0	47.0	47.0	47.0	47.0	47.0
	76.2	76.2	76.2	76.2	76.2	76.2	76.2
Temperature, °C	603	603	623	618	522	509	518
	719	700	728	733	565	622	597
	669	621	646	675	508	533	500
	429	421	433	430	387	337	363
Average Temperature, °C	605	588	607	614	495	500	494
Feed Conditions							
H ₂ , l/min (20°C, 15 psia)	1.93	1.86	1.96	2.32	1.89	2.34	2.14
H ₂ , g-mol/min	.082	.079	.083	.098	.080	.099	.091
Oil Flow Rate, ml/min	.88	.92	.93	.94	.87	.90	.95
Oil Flow Rate, g/min	.792	.828	.837	.846	.783	.810	.855
Stoichiometric Ratio, %	113	107	110	122	112	126	115
Wt % C	86.50	86.50	86.50	86.50	86.50	86.50	86.50
Wt % H	11.89	11.89	11.89	11.89	11.89	11.89	11.89
Wt % S	.89	.89	.89	.89	.89	.89	.89
Exit Conditions							
Exit Gas Flow, l/min (20°C, 15 psia)	1.78	3.22 ^{††}	1.79	1.64	1.23	1.43	1.89
Exit Gas Flow, g-mol/min	.076	.137	.076	.070	.052	.061	.080
Vol % H ₂							
Vol % CH ₄	27.70	5.19	27.76	28.57	16.87	16.42	13.30
Vol % C ₂ H ₆	11.93	1.01	13.93	12.13	12.47	12.00	8.57
Vol % C ₃ H ₈		6.20			4.39	4.16	3.54
H ₂ S, vppm	2520	1500	2510	2480	2570	1910	1591
Exit Liquid Flow, g/min	.170	.020 ^{††}	.143	.188	.194	.232	.232
Wt % C	84.59	NA [†]	92.29	91.64	90.49	90.84	90.32
Wt % H	6.44	NA	6.80	7.17	8.54	8.33	8.15
Wt % S	.53	NA	.93	1.05	1.38	1.50	1.52
Exit Temperature °C	400	400	400	400	350	300	325
Exit Pressure, psia	1000	1000	1000	750	1500	1000	750
Space Time at Exit Conditions, min	17	9.4	16.9	13.8	39.8	25.9	13.8

* Reactor volume = 1.04 l.

† NA = no analysis.

†† These runs encountered severe coking problems.

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Table H-2. HG PRODUCT DISTRIBUTION FOR NO. 6 FUEL OIL *

	Run No.						
Run Number	200	201 ^{††}	202	203	204	205	206
Temperature, °C	605	588	607	614	495	500	494
Pressure, psig	1000	1000	1000	750	1500	1000	750
Stiochiometry, %	113	107	110	122	112	126	115
Feed Carbon, g-mol/min	.0570	.0596	.0603	.0609	.0564	.0583	.0616
Product Gas, g-mol/min	.0756	.1367	.0760	.0696	.0522	.0607	.0802
Methane, g-mol/min	.0209	.0071	.0211	.0199	.0088	.0100	.0107
% of feed C	36.7	11.9	35.0	32.7	15.6	17.1	17.3
Ethane, g-mol/min	.0090	.0014	.0106	.0084	.0065	.0073	.0069
% of feed C	31.6	4.6	35.1	27.7	23.1	25.0	22.3
Propane, g-mol/min	trace	.0085	trace	trace	.0023	.0025	.0028
% of feed C	1.0	42.7	1.0	1.0	12.2	13.0	13.8
Total Gas % of feed C	69.3	59.2	71.1	61.4	50.9	55.1	53.4
Product Liquid, g/min	.170	.020 ^{††}	.143	.188	.194	.232	.232
Wt % C	84.59	NA	92.29	91.64	90.49	90.84	90.32
C, g-mol/min	.0120	NA	0.0110	.0143	.0146	.0175	.0174
% of feed carbon	21.0	NA	18.2	23.6	25.9	30.1	28.3
Unaccounted Carbon, g-mol/min	0.0055	NA	.0065	.0091	.0131	.0086	.0113
C, g/min	.0664	NA	.0775	.1097	.1572	.1036	.1354
% of feed C	.97	NA	10.7	15.0	23.2	14.8	18.3

* Reactor volume = 1.04 l.

† NA= no analysis.

†† These runs encountered severe coking problems.

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