

HEAVY OIL PROCESSING IN STEAM
AND HYDROGEN PLASMAS

A
THESIS
BY

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AND HYDROGEN PLASMAS

ABSTRACT

Heavy oil in the form of a finely-divided spray was reacted with simulated steam (oxygen added in the anode of a DC torch in which hydrogen was generated) and pure hydrogen plasmas to determine the products produced under varying operating conditions. Heavy oil was preheated to 200°C, under a pressure of 2000 kPa, fed through a pressure atomizer, at flowrates from 0.002 to 0.08 m³/h, into a DC plasma jet contained in a stainless steel reactor twenty cm in diameter and 1.5 m high. The hydrogen and steam plasmas had respective maximum temperatures of 6000 K and 3450 K. The effects of the following operating conditions were studied:

- i) the steam to oil mass ratio, from 0.5 to 2.0
- ii) the energy per kilogram oil from 0.5 to 12.0 kWh/kg
- iii) the flow of atomized quench water, from 0 to 0.2 m³/h

The results have shown that the heavy oil reacts to form light olefins, soot and pitches. Light liquid hydrocarbons were not in evidence. The major gaseous products were methane, acetylene, and ethylene. Soot was also produced, and the unconverted oil residue became more viscous. Only with a steam plasma did gaseous products include carbon monoxide and carbon dioxide. Higher steam-to-oil mass ratios, and the energy-per-kg-oil increased the conversion to oil to gas in both plasmas. Olefin concentrations decreased at higher energy inputs with the steam plasma because the oxygen from the plasma preferentially reacted with the carbon to form carbon monoxide. In hydrogen plasmas, the olefin concentration continued to increase with higher energies.

RÉSUMÉ

Une huile lourde a réagi avec des plasmas de vapeur d'eau et d'hydrogène dans des conditions variées pour obtenir différents produits. L'huile lourde a été préchauffagée à 200°C, sous une pression de 2000 kPa, puis injectée par l'entremise d'un atomiseur à un débit allant de 0.002 à 0.06 m³/h, dans un jet de plasma contenu dans un réacteur de 20 cm de diamètre. Le plasma était composé d'hydrogène pur ou d'hydrogène additionné d'oxygène dans l'anode (la vapeur simulée), ayant respectivement une température maximum de 6000 et 3400 K. Les variables du procédé étaient: le rapport de la vapeur à l'huile, de 0.5 à 2.0, l'énergie électrique de 0.5 à 12.0 kWh/kg/h, et le flux de l'eau de trempe, de 0.0 à 0.2 m³/h.

Les résultats ont démontré que la gazéification et la pyrolyse de l'huile conduisent aux oléfines légères, plutôt qu'à l'amélioration au niveau des proportions de liquides, et constituent les réactions majeures. Les produits gazeux majeurs étaient du méthane, de l'acétylène, et de l'éthylène. Du charbon a aussi été produit et l'huile qui n'a pas réagi est devenue plus visqueuse. Avec un plasma de vapeur d'eau, le monoxyde de carbone et le gaz carbonique constituent une grande proportion des produits gazeux. Quant on utilise des proportions plus élevées, on constate une plus grande concentration d'oléfines et une plus grande conversion de l'huile au gaz.

ABSTRAKT

Schweröl wurde mit simuliertem Dampf und Wasserstoffplasma versetzt, um zu bestimmen, welche Produkte unter verschiedenen Betriebsbedingungen entstehen. Das Schweröl wurde unter einem Druck von 2000 kPa auf eine Temperatur von 200°C erhitzt, durch einen Zerstäubungsapparat mit einer Durchflussleistung von 0,002 bis 0.06 m³/h, in einen Reaktor mit 20 cm Durchmesser geführt und in die Flamme des Plasmas gespritzt. Das Plasma bestand entweder aus Wasserstoff (maximale Temperatur von 6000 K) oder Wasserstoff mit Sauerstoffzusatz (maximale Temperatur von 3400 K) und wurde der Anode (positive Elektrode) des Brenners zugeführt ('simulierter Dampf'). Die Betriebsbedingungen des Verfahrens wurden geändert:

Dampf zu Ölgewicht von 0,5 - 2,0;

Leistung zu Öl von 0,5 - 12,0 kWh/kg/h;

und der Wasserdampf wurde zugeschaltet oder nicht.

Die Versuchsergebnisse haben gezeigt, dass Gaserzeugung und die thermische Zersetzung des Öles in leichte Olefine die Hauptreaktionsformen sind, eher als die Umwandlung in Flüssigkeiten. Mit einem Wasserdampfplasma wurde ein grosser Teil des Gases auch von Kohlenmonoxyd aufgenommen. Steigert man das Verhältnis von Dampf zu Öl, oder Leistung zu Öl dann vergrössert sich die Umwandlung von Öl in Gas., und die Konzentration der Olefine im Gas erhöht sich ebenfalls. Die Hauptprodukte des Gases waren Methan, Azetylen, Äthylen und Russ, und der umgewandelte Ölanteil besass eine höhere Viskosität.

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Mike Harris, whose practical know-how and perseverance through 'those difficult moments' was invaluable.

All the staff of the Chemical Engineering Workshop - especially Alain Gagnon - who were always ready to give a helping hand and whose work was of the highest caliber.

Dorle

Was ist das schwerst von allem?
Was dir das leichtest dünkt:
Mit den Augen zu sehen,
Was vor den Augen dir liegt.

What is the most difficult of all?
To do that which you had thought the easiest:
To see,
That which lies before
Your eyes.

~JOHANN WOLFGANG VON GOETHE

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GENERAL INTRODUCTION

GENERAL INTRODUCTION

Hydrogen plasmas have been successfully used to crack light hydrocarbons to acetylene for over 40 years. However the economic and technical challenges presented by heavy oil cracking have yet to be overcome. This situation may be changed by the use of a novel steam plasma torch which could greatly reduce the cost of the processing. This research project therefore focuses on the potential advantages that steam may offer over hydrogen as a plasma gas. Furthermore, the changed product composition resulting from the changed reacting atmosphere must also be characterized before further work in this potentially new method of heavy oil upgrading is to be justified.

The Huels Chemical Company of West Germany has been economically cracking refinery gases to acetylene in a specially designed DC arc hydrogen plasma reactor since 1940. In 1970 the reactor was used to crack crude and heavy oils. The project was technically successful. But reduced acetylene and ethylene yields, increased soot yields, and a high fraction of unconverted oil that had to be burnt because of soot build up, prevented economic operation. (Muller, 1981)

The present work therefore examined the differences in product distribution with varying operating conditions in steam and hydrogen plasmas. This information could then be used by others to study the changed economic picture brought about by the reduced operating costs and changed product distribution of the steam plasma. The great complexity of the reaction process and constraints imposed by the use of equipment not specifically designed for the purpose necessarily made these results of a preliminary nature. The main process variables studied were:

- a) the use of either hydrogen or steam plasma
- b) the energy used per kilogram of oil (specific energy)
- c) the steam-to-oil mass ratio
- d) the quench rate.

They were varied in an attempt to understand their influence upon the product distribution. The results would be useful for further research aimed at optimizing oil conversion.

The first section of the thesis will review the following:

- 1) heavy oil properties,
- 2) the unique chemistry of the asphaltene molecules
- 3) the chemistry of heavy oil and hydrogen
- 4) current heavy oil processing methods
- 5) high temperature steam properties and reactions
- 6) hydrocarbon-plasma system species
- 7) the plasma work done by Huels with hydrocarbons
- 8) petrochemical feedstocks.

The experimental study will be described in the second section. An evaluation of the merits of this novel approach will then be attempted.

LITERATURE REVIEW

INTRODUCTION

The published literature on the treatment and upgrading of heavy oil is very extensive. This survey was therefore limited to that information directly related to the present study. The first section will review the properties of heavy oil and the basic chemistry of the heavy oil, steam, and hydrogen. This will be followed by a description of the main methods of heavy oil conversion. Two key technologies now in use will be described in depth in order to illustrate the challenges and goals that such processes encounter and strive for.

The second part will describe specifically the previous work and research done in hydrocarbon-plasma systems. The high temperature chemistry of steam and carbon-black will be described. Then the pioneering experimental work and the resulting large-scale operations of Huels Chemical Company of West Germany will be examined. They have spent considerable effort in the practical utilization of DC hydrogen arcs for the cracking of hydrocarbons, ranging from methane to heavy oil, for the production of acetylene. Lastly, the future place for this plasma technology in the changing oil refining and petrochemical feedstock world market will be studied.

HEAVY OIL PROPERTIES

In the past ten years, since the Arab oil embargo, great advances have been made in heavy oil conversion processes. These developments are a direct result of dramatically increased conventional oil prices and of the realization that light or conventional oil reserves are gradually being depleted, requiring replacement by another hydrocarbon source. World heavy oil reserves are estimated to be 760 billion barrels. Canada has proven reserves of 215 billion barrels, or 28 % of the world reserves.

Heavy Oil Properties

Heavy oil is significantly different from conventional oil in that it has a very low hydrogen-to-carbon ratio (Figure 1) and high levels of contaminants, comprising various amounts of nitrogen; sulphur, and metals, which all concentrate in the heavy asphaltic fraction. This asphaltic fraction of the heavy oil gives it unique characteristics and also is the major source of upgrading difficulties. The asphaltene molecules, to be described in a subsequent section, have a complex aromatic ring structure containing nitrogen and sulphur atoms within the structure. Typical properties of heavy and conventional oil are shown in Table I.

FIGURE 1HEAVY OIL CARBON-TO-HYDROGEN RATIO

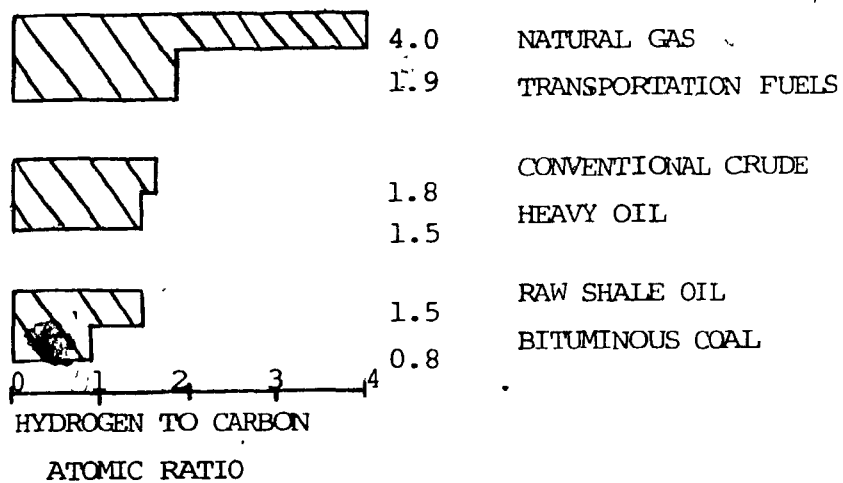


TABLE I : COLD LAKE AND CONVENTIONAL OIL PROPERTIES

Property (1)	Alberta	Cold
	Conventional	Lake
API gravity (2)	38.1	10.2
density - kg/m ³	834	998
viscosity -mm ² /s at 40°C	39	5300
sulphur - wt. %	0.21	4.4
nitrogen - wt. %	0.5	0.3
carbon - wt. %	-	82.28
hydrogen - wt. %	-	12.59
CCR - Conradson Carbon Residue(3)	-	13.1
metals - ppm : nickel	3.5	77
: vanadium	3.0	190
Boiling Point Fractions		Volume Percents
naphtha - 191°C	32	1
mid-distillate - 191-343 °C	28	18
vacuum gasoil - 343-566 °C	30	36
vacuum resid - 566°C +	8	45

(1) - All data are from a memorandum sent by O. Biceroglu of the Imperial Oil Research Centre, Sarnia, Ont.

(2) - °API gravity is the measure of the gravity of liquid petroleum products derived from the specific gravity of water; defined as:

$$\text{API gravity} = 141.5/\text{s.g.} - 131.5$$

where s.g. of 1 is 10°API

(3) - This is a traditional test which is used to predict the amount of coke production in a coking process.

HYDROCARBON CHEMISTRY CONSIDERATIONS

Chemistry of the Asphaltene Molecule

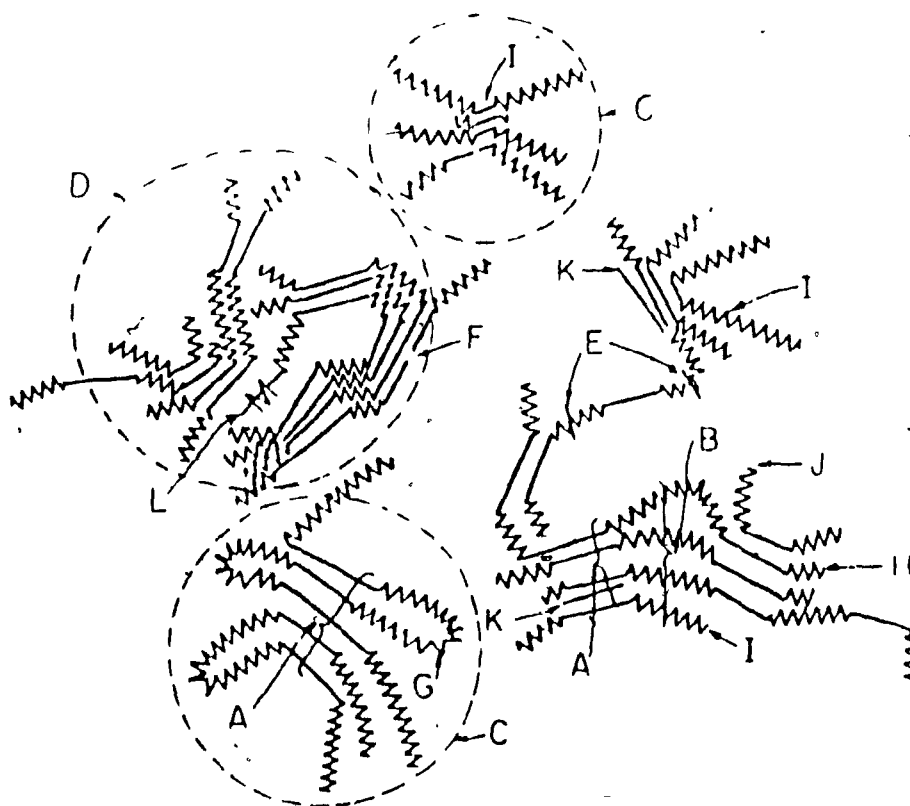
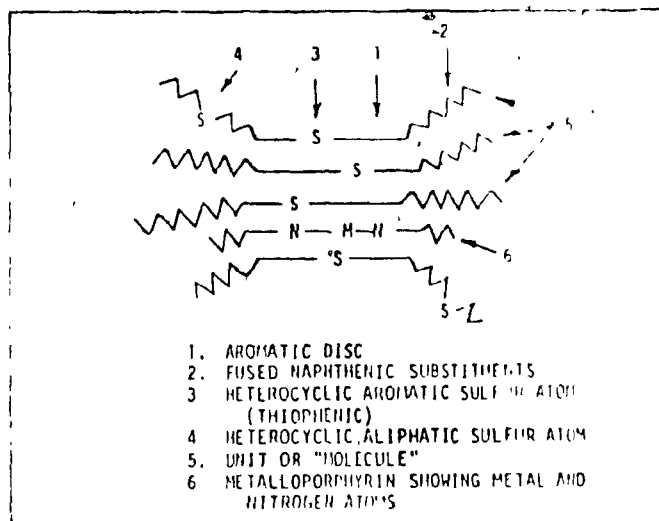
Asphaltene is that fraction of the oil insoluble in pentane at ambient temperature and soluble in benzene. Resin is that fraction soluble in pentane but insoluble in propane. Together they are known as the asphaltic fraction of oil. While all oils contain some asphaltics conventional crudes contain only 10%, while heavy oil contains 35% of this difficult-to-upgrade component.

The large asphaltene molecule has a molecular weight ranging from 1000 to 500000. A structural model has been proposed by Drushnel (1970) and is shown in Figure 2 (modified model of Kickie and Yen, 1967). An average giant molecule consists of 5 or 6 units held together by their central aromatic discs. Statistically, a molecule has one or two nitrogen atoms and five or six sulphur atoms. In the model it is assumed that one-half to two-thirds of each molecule within the particle consists of aliphatic constituents, probably in the form of fused naphthenic rings. Metals found include vanadium, nickel and iron. Metal ions can directly bond to the 'defect' centres where holes of an imperfect aromatic sheet exist. Sulphur is found in the sulphide form and is difficult to cleave from the molecule because it is located in a well protected position.

FIGURE 2

HYPOTHETICAL ASPHALTENE STRUCTURES

(Drushnel, 1970)



Macrostructure of Asphaltics

- | | |
|-------------------|-----------------|
| A. Crystallite | B. Chain Bundle |
| C. Particle | D. Micelle |
| E. Weak Link | F. Gap and Hole |
| G. Intracuster | H. Intercluster |
| I. Resin | J. Single Layer |
| K. Petroporphyrin | L. Metal |

Chemically speaking, the conversion of asphaltenes to lighter molecules will involve a combination of the following processes: hydrogenation of the aromatics, transalkylation, thermal cracking, and hydrogen transfer or hydrogenolysis. The steam cracking of high molecular weight hydrocarbons at lower temperatures is discussed by Blouri et al. (1981). With the use of thermal energy or catalysts the asphaltic stacks can be separated as the aromatic disk bonding is weakened. These lower molecular weight compounds can then be desulphurized, hydrogenated and cracked to light liquid hydrocarbons or gases. (Laimi and Trimm, 1982)

Steam and Hydrogen

A complete understanding of the reaction pathways in the steam/hydrogen plasma - heavy oil reaction is not within the scope of this thesis paper. But a comparison of results obtained here with those of other researchers can give valuable insights into the prime influences on, and routes of, the reaction complex.

Previous work with high temperature water vapour and hydrocarbon systems are extremely limited. However early research done in the U.S.S.R. (Il'in & Eremin, 1963) with the pyrolysis of gasoline vapour in a water-water vapour plasma gave product yields of acetylene and olefins which were higher than those from a hydrogen plasma.

Both experiments were carried out in the same reactor, with respective yields of 7 and 11 vol.% acetylene, and 11 and 19 vol.% total olefins. Further changes brought about by the use of steam in the plasma were the appearances of carbon dioxide, 5 vol.%, and carbon monoxide, 5 vol.%. Later work done in Japan, with conventional technology, (Gomi & Takahushi, 1975) used 2,000°C steam as a heat carrier to pyrolyze crude and heavy oil. Splits between olefinic and heavy aromatic products were approximately equal. There was a large change on the product splits when heavier oil feed was used. For example, the pitch fraction increased from 13 to 35 wt.%, and the methane and acetylene fractions decreased from about 20 to less than 4 wt.%. No carbon monoxide/dioxide was produced.

Kinetic studies of steam cracking of naphtha (Bajus and Leclercq, 1980) have shown that the formation rate of ethylene is at first higher than that of methane and acetylene, whose rates gradually increase with time. Tar and pitch formation does not begin until after a lag time of about 4 microseconds. This should be contrasted with the results of Huels (Gehrmann & Schmidt, 1971), which, in a hydrogen plasma, have indicated that the rate of acetylene formation decreases after an initial maximum, and that of ethylene gradually increases.

In current technology the use of steam to upgrade hydrocarbons usually entails the production of synthesis gas. On the other hand hydrogen acts as a homogeneous catalyst of moderate activity. A large excess is required to accelerate the rates of reaction. It also has a marked effect on the product distribution. The secondary reactions become more predominant with increasing hydrogen present, especially at higher conversion and temperatures. (Baddoux and Iwasyk, 1962) For instance, hydrogen participates in the following reactions:

1. hydrogenolysis of olefins and aromatics;
2. hydrodecyclization of polycyclic compounds;
3. retards reversible reactions, such as;
dehydrocondensation of aromatics;
4. acceleration of pyrolysis, so ethylene yields are increased and coke yields decreased.

A study into the free radical reactions of hydrocarbons at higher temperatures was done by Thomas and McNelis (1962).

HEAVY OIL PROCESSES

Survey

The optimum heavy oil conversion process should have the following characteristics:

- 1) low capital and operating costs
- 2) high liquid yields
- 3) great feed and product flexibility
- 4) no catalyst to be poisoned by the metals
- 5) high metal, nitrogen and sulphur removal
- 6) no pre- or post-treatment of the oil

Unfortunately, all these criteria cannot be met by a single process. It is only through compromise and optimization that the best process for the specific need of the refiner can be developed. The list below shows the major processes in use today in order from the simplest (lowest cost, lowest conversion, lowest contaminant removal) to those more recently developed which although yielding high quality liquid and gas products do so at a very high cost. For a complete list and study of the most recent technologies the recently published review by Schumacher (1982) should be consulted.

Heavy or Residual Oil processes can be divided into four basic groups (see Figure 4), as follows:

i) Separation Processes

Vacuum Distillation

Solvent Deasphalting

ii) Carbon Rejection Processes

Thermal: Gasification

Fluid- and Flexicoking

Combined Visbreaking/Thermal Cracking

Catalytic: Residue Catalytic Cracking

iii) Hydrogen Addition

Residue Hydrocracking

iv) Combined Carbon Rejection/Hydrogen Addition

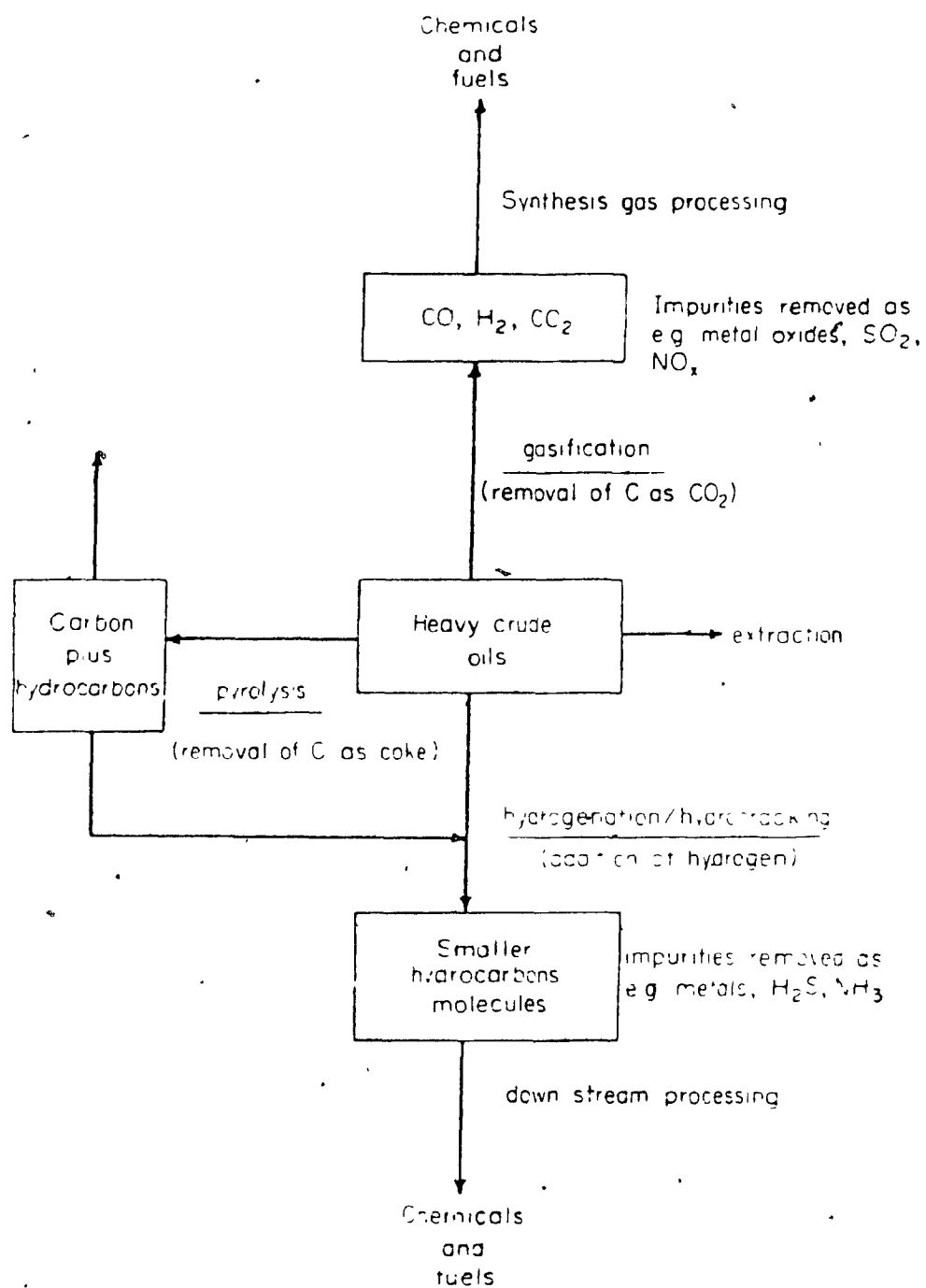
Thermal/Hydrocracking

The choice of a suitable process always depends upon the unique cost and market situation of the producer; for while the processes in categories (iii) and (iv) have a much higher conversion they also have a much higher capital and operating cost. Examples of two processing methods will now be given.

FIGURE 3

HEAVY OIL TREATMENT ROUTES

(Laimi and Trimm, 1982)



CANMET Hydrocracking

The CANMET process is a hydrocracking process for the upgrading of heavy oil recently developed by the Energy Research Laboratory in Ottawa and licensed exclusively to Petro-Canada in 1980. (Marcies and Silva, 1981) A demonstration plant of 5000 barrels per day is now under construction in Montreal.

The process uses an additive of pulverized coal impregnated with iron sulphate, representing 0.5 - 5.0 mass % of the feed. (It functions as a catalyst.) Conversions of 90% were achieved with oils such as that from Cold Lake. The following process details are revealing:

- i) the products are close to 100% liquids
- ii) the products have less than 5 ppm metals
- iii) desulphurization is better than 60%
- iv) the hydrogen consumption is less than 2 mass% of feed
- v) operating pressures are low due to the additive

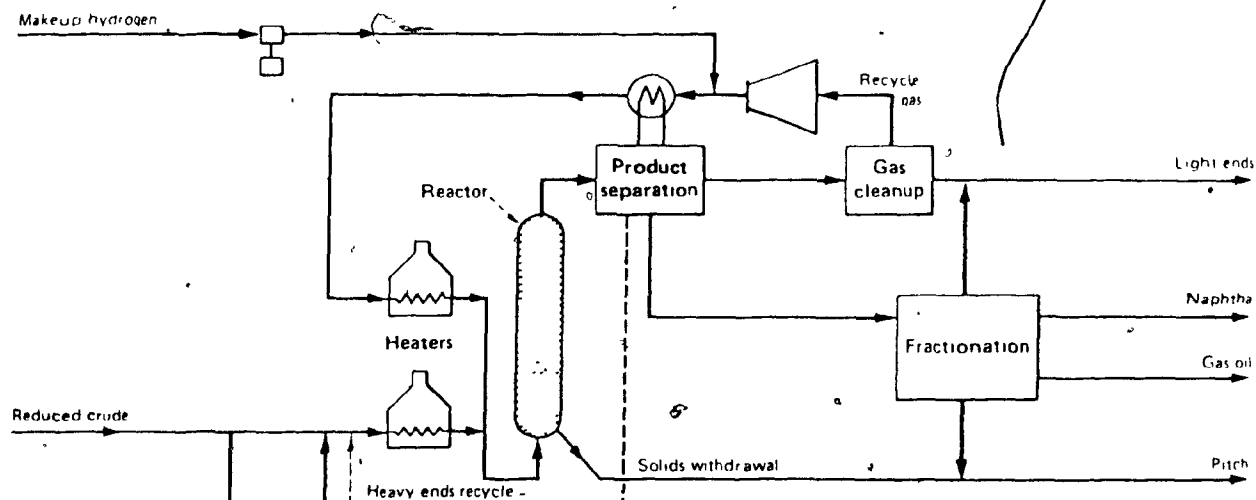
Process details are given in Figure 4, together with feed and product properties. Heavier components are separated by atmospheric and vacuum distillation ahead of the CANMET unit to produce a blended synthetic oil product of 31.6°API and 0.21 mass % sulphur.

The economics of such an operation based on the first-quarter of 1980 shows a discounted cash flow rate of return of 21.8 %, with a payout time of 3.8 years for a stand alone operation. Direct costs for the entire upgrading would be \$345 million. (Marcies and Silva, 1981)

FIGURE 4

CANMET PROCESS FLOWSHEET AND PRODUCTS

(Marcies and Silva, 1981)



Basis Cold Lake Crude with boiling point greater than 404°C, 6.3 API, 350 ppm metals

Feed	Composition	Sulfur	Products	Composition	Sulfur
Oil	99 wt %	5.2 wt %	H ₂ S	3.59	
Additive	1		CH ₄	2.07	
Hydrogen	1.97		C ₂ H ₆	1.62	
			C ₃ H ₈	1.75	
			C ₄ H ₁₀	1.35	
Conversion (524°C+)	90.5 vol %		C ₆ -204°C	19.39	0.57
Desulfurization	65.5 wt %		204 - 343°C	37.21	2.06
H ₂ consumption	1,355 scf/bbl		343 - 524°C*	27.02	2.30
			524°C+ (pitch)	7.98	3.59
			Total	101.97	

*Has less than 3 ppm metals

Oil Pyrolysis with Superheated Steam

A process was developed to produce acetylene, ethylene and aromatics from crude oil. (Gomi & Araki, 1971.) A semi-commercial plant went into operation in Oct. 1970 in Nakoso Japan, with a capacity of 100000 ton/yr. crude. Steam at 2000°C was generated in regenerative furnaces, which burn the off gases of methane and hydrogen from the reactor.

Process details include the following. The cracked bottoms consisted almost entirely of aromatics and condensed six-ring hydrocarbons. Coking is minimized by operating at maximum temperatures and minimum residence times. The oil is preheated to 300°C and injected by atomizing nozzles into the middle of the reactor; with a weight ratio of steam to oil ranging from 2:1 to 4:1. The operating temperature was from 900-1200°C, and the residence time was from 1-5 microseconds. Much of the tar and pitch produced was sent to storage and used as the base for new products.

The liquid products made up from 30-50 wt.% of the feed. The highly aromatic tars were observed to appear first late in the reaction. A process schematic is shown in Figure 5 and feed and products yields in Table II. With a change from a conventional crude feed to bottoms the methane and acetylene yields decreased from about 20 wt.% to less than 4 wt.%, while the ethylene yield stayed almost constant at about 20 wt.%.

FIGURE 5

SCHEMATIC OF THE SUPERHEATED STEAM PROCESS

(Gomi and Araki, 1971)

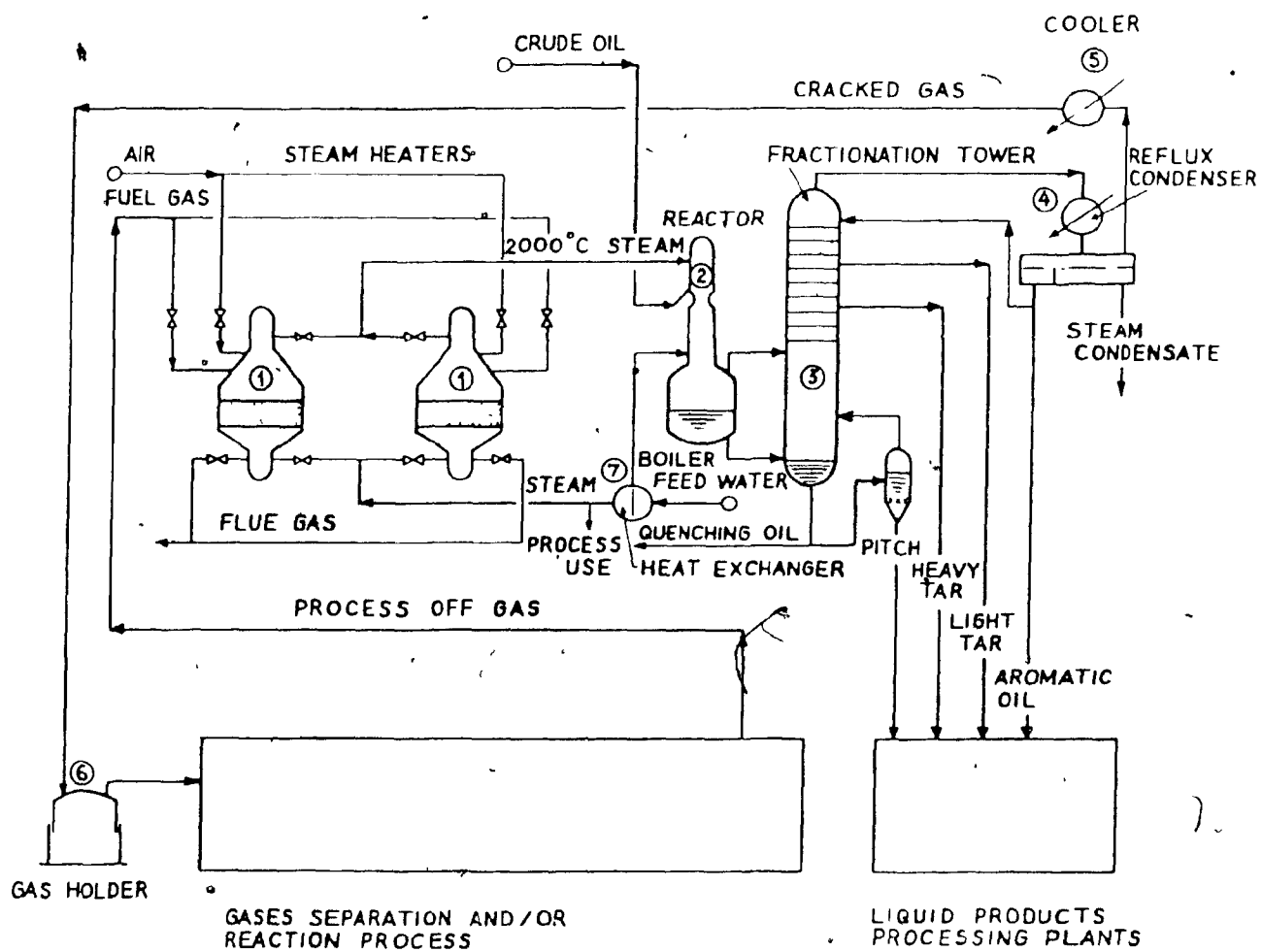




TABLE II

YIELDS FROM OIL PYROLYSIS IN STEAM

(Gomi and Araki, 1971)

Wt ratio of ethylene to acetylene		Case 1	Case 2
H ₂	[% vol]	50	10
CH ₄	[% vol]	15	30
C ₂ H ₂	[% vol]	13	3
C ₂ H ₄	[% vol]	12	30
C ₃ H ₆	[% vol]	2	7
C ₄ H ₆	[% vol]	<1	2
Others (C ₃ +)	[% vol]	<1	7
CO, CO ₂	[% vol]	8	4

Feedstock	Seria crude	Minas crude	Aramco crude	Kafuji crude	Kafuji bottom
<i>Cracking conditions</i>					
Temperature of steam (°C)	2000	1650	1450	2000	1650
Weight ratio of steam to feedstock	2.9	2.6	3.2	2.8	2.6
Reaction to temperature (°C)*	1150	1000	950	1150	1000
Reaction time (sec)†	0.005	0.010	0.010	0.005	0.010
<i>Products</i>					
(% wt to feedstock)‡					
CH ₄	15.7	7.7	5.1	13.7	7.8
C ₂ H ₂	21.5	1.4	1.1	17.7	1.6
C ₂ H ₄	20.4	26.2	29.4	18.6	25.2
C ₃ H ₆	0.8	9.5	11.2	0.7	8.7
C ₄ H ₆	0.5	3.4	3.7	0.5	2.8
Benzene fraction (BP -200°C)	6	2	1	5	1
Naphthalene fraction (BP 200-250°C)	5	12	11	4	10
Tar fraction (BP 250-450°C)	7	15	20	6	15
Pitch fraction (BP -450°C)	13	10	12	25	20

* Measured at the outlet of the reactor before quenching.

† Approximate calculated figure.

‡ Balances to 100% are H₂, C₃ and C₄ fractions

STEAM PLASMA CONSIDERATIONS

Introduction

A thermal plasma is defined as "an electrically conducting but neutral gas at a high temperature consisting of electrons, atoms, excited atoms and small concentrations of ions". (Howatson, 1976) The production of a plasma of superheated vapour and its applications to chemical processing has been under study in these laboratories for about three years. (Gauvin, W.H., Can. Patent No. 1160593 (1984), U.S.A. Patent No. 4376010 (1983).) Also patent applications on the torch design have been submitted. (Gauvin, patent March 30, 1983.) Development of a special torch design capable of handling the aggressive atmosphere of high temperature steam is currently underway and applications to spray drying (Amelot, 1983) and synthesis gas production from peat (Grosdidier, 1983 and Stuart, 1984) have been studied. A steam plasma has several unique potential advantages in the heavy oil processing field.

Firstly, steam itself:

- a) acts both as a heat source and as a reactant
- b) lowers the hydrocarbon partial pressure and thereby encourages higher selectivity to the desired olefinic products
- c) reduces the partial pressure of higher boiling aromatics in the zone of high conversion, lessening the tendency to form coke and tar.

d) also reduces the coking tendency of the reaction by the presence of oxygen which reacts with carbon to form CO & CO₂ gases, thereby effectivley increasing the reactant hydrogen-to-carbon ratio

e) is much cheaper than hydrogen

f) the enthalpy of the steam in the effluent gas can be recovered.

Secondly, a water plasma reactor:

i) is a simple, non-catalytic, one-step process with no moving parts

ii) combines heating and reacting systems with a very high throughput requiring less materials; reducing capital costs

iii) creates an intensive high temperature reaction zone which results in increased rates of heat and mass transfer, and of reaction.

Reactions, Reactive Constituents and Energies

Reactions at 3400 K, the calculated plasma jet temperature at the anode base, (See Appendix II for calculations) include :

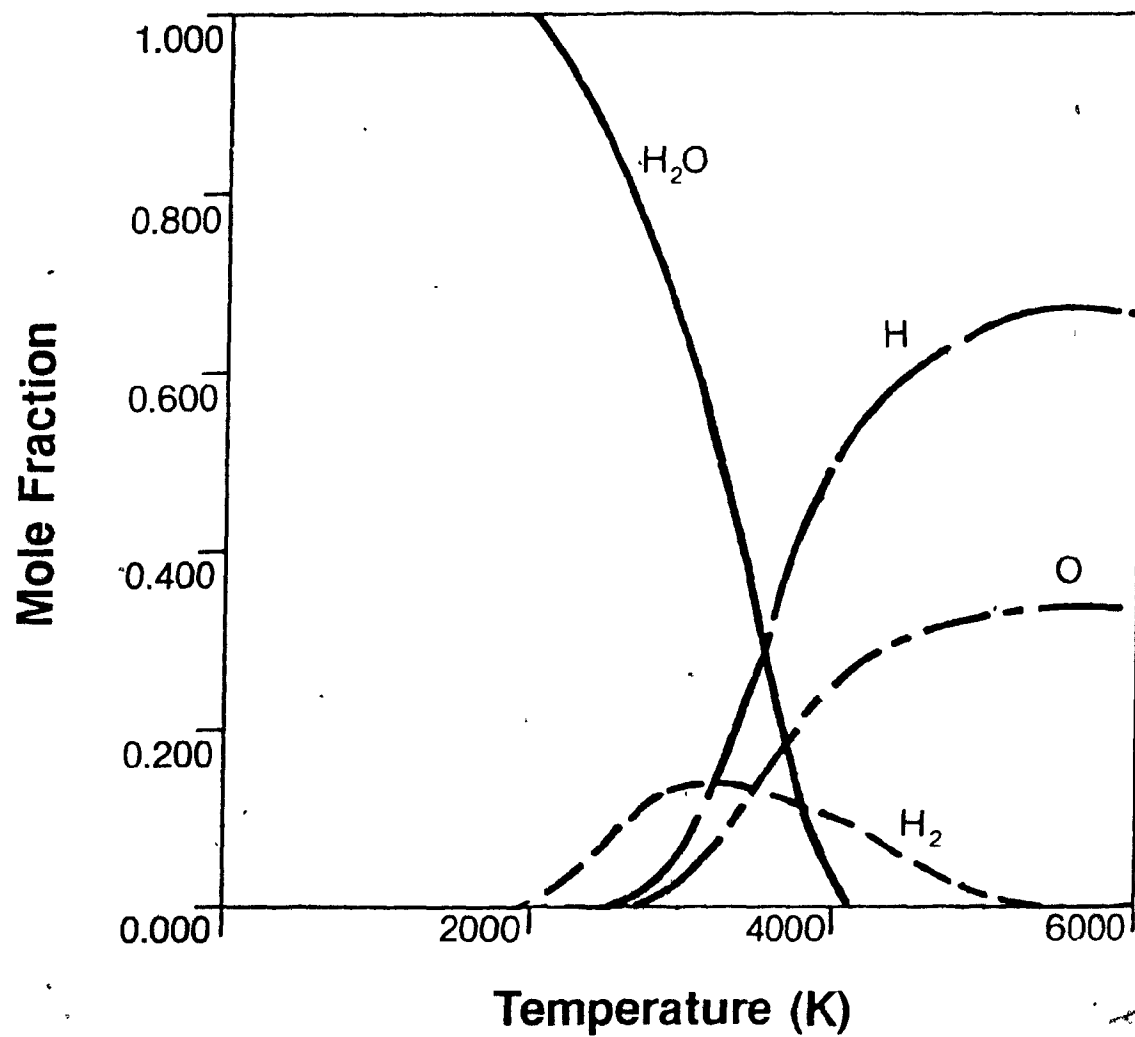


Mole fractions are given as a function of temperature in

Figure 6.

FIGURE 6

STEAM PLASMA SPECIES MOLE FRACTION AS
A FUNCTION OF TEMPERATURE

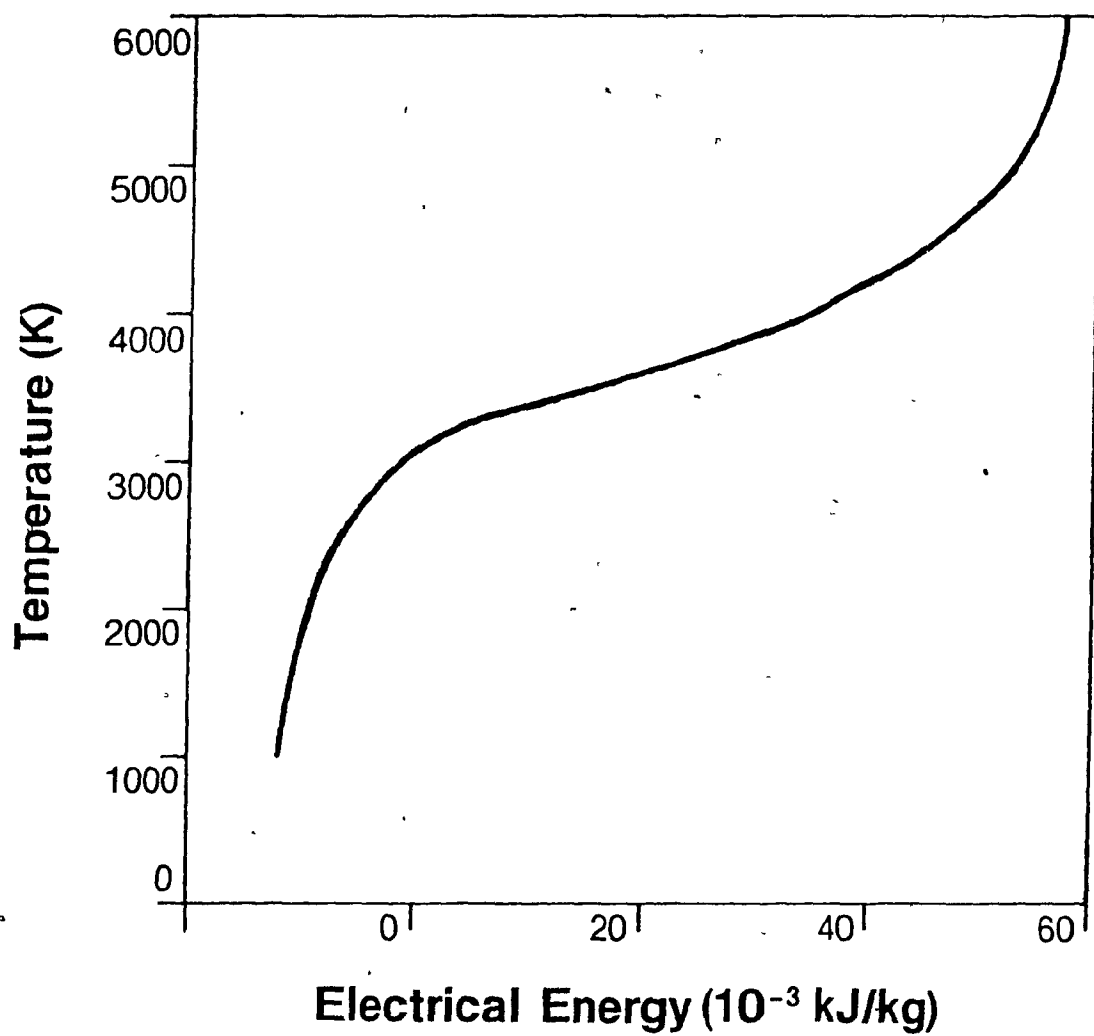


These compositions were calculated using a free energy minimization program, assuming ideal gases at equilibrium and one atmosphere. The values are in good agreement with those published by Ihara (1977). These high temperature constituents, plus some H^+ and O^{--} , should give steam plasma a unique ability to react with heavy oil in ways different from those of other upgrading processes. The steam plasma should serve the dual functions of:

- 1) thermally cracking the carbon-to-carbon bonds of the large molecules to reduce their molecular weights
- 2) allowing hydrogen to increase the saturation of the aromatic ring and asphaltenes by hydrogenation.

Of special interest are the high energies required for dissociation of the water molecules. As can be seen in Figure 7, (as calculated in Appendix II) to achieve temperatures beyond 3500 K demands vast increases in electrical energy input. This is a result of the molecular dissociation which increases the enthalpy of the steam, but not the temperature. So although the steam plasma temperatures are not very high (that is, by plasma standards) their enthalpies are high. Finally, the properties of steam at high temperatures are summarized in Table I of Appendix II.

FIGURE 7STEAM TEMPERATURE VS. ELECTRICAL INPUT



Carbon Black Formation

Because of its importance industrially carbon black has been a subject for much research. Characterization of its formation by hydrocarbon cracking in hydrogen plasma reactors, done in France (Bolouri & Amouroux, 1983), gives some interesting insights into hydrocarbon reactions and equilibrium species existing at high temperatures. The results suggest that carbon black formation is a function of temperature, pressure, and hydrogen to carbon ratio, which is in opposition to the findings of other authors (Abrahamson, 1977 and Gaydon, 1960) who have suggested that a certain number of radical species primarily effect the formation mechanisms.

The study has been able to reconcile these different schools of thought by the recognition that three different "zones" exist, in which the primary reaction route differs. (See Figure 8.) At temperatures less than 1700 K, the "aromatic" route dominates, in which methane, ethylene, and benzene are the main species. At temperatures from 1700 to 3000 K (the "acetylene" route) acetylene and hydrogen being the dominant species. At temperatures above 3000 K (the "molecular" carbon route) H, C, C₂, C₃, and C₂H radicals dominate.

In the conditions of a plasma reactor carbon-black is a favoured final reaction product whose yield can be reduced by the use of a quench, but not completely eliminated.

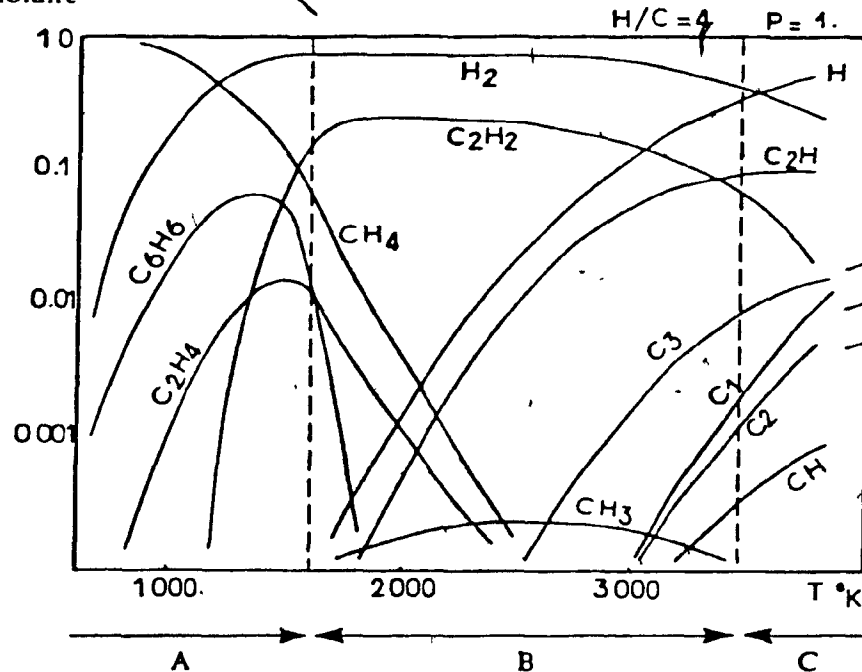
FIGURE 8EQUILIBRIUM HYDROCARBON SPECIES IN A HYDROGEN PLASMA

(Bolouri and Amouroux, 1983)

Théorie de formation
des cycles aromatiques
Abrahamson (19)

Théorie de Hudson
et Porter (20, 3)

Fraction molaire



PLASMA PROCESSES

Introduction

Due to the lack of an industrially proven steam plasma torch no processes now exist utilizing the technology. However research was carried out at McGill (Stuart, 1984) using a simulated steam plasma to gasify peat to synthesis gas. Furthermore a report describing the economics (Gauvin et Costin, 1981) of a steam drying process was most encouraging.

However the processing of light refinery gases to acetylene and ethylene in a hydrogen plasma has been successfully and economically done at Huels (Gladisch, 1962) since 1940. This process is a useful yardstick for comparison with the proposed processing of heavy oil in a simulated steam plasma. Other hydrocarbon-plasma processes are also examined in papers by Eckert (1974), Fauchais (1980), Kovener (1983), Babcock (1975), and Christofides (1983).

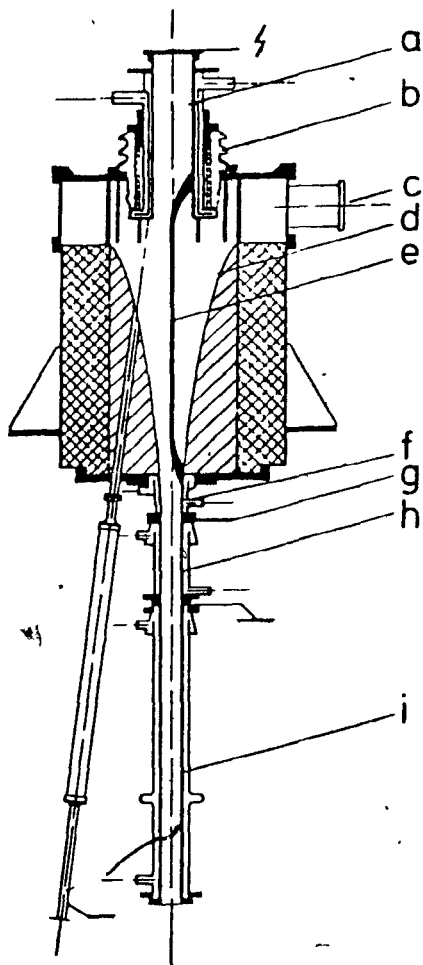
Hydrocarbon Cracking in Hydrogen Plasma by Huels

Huels Chemical Company of Marl, West Germany, has been producing acetylene and ethylene from refinery gases and naphthas since 1940. Hydrocarbon cracking in plasmas began in 1925 and the first operational plant in the Second World War met the high demand for synthetic rubber by converting motor fuel by-products to acetylene in a hydrogen plasma.

FIGURE 9

THE HUELS ARC FURNACE

(Muller, 1983)



DC

- (a) cathode
- (b) insulator
- (c) vortex chamber
- (d) graphite lined chamber
- (e) electric arc
- (f) anode nozzle
- (g) hydrocarbon injection
- (h), (i) reactor

In the Huels process, hydrocarbon gas enters the reactor tangentially just after the 100-mm long arc strikes the anode, as shown in Figure 9. There is a two-stage quench, the first using liquid hydrocarbons, which increases the acetylene yield, and the second of water, from which steam is formed and used to generate power. Radially stratified temperature gradients and large recirculation rates in the reactor result in a heterogeneous product. Of the energy input, 45% is used for chemical reaction, 5% is lost by radiation, and 50% leaves with the product gases. The mean hydrogen jet temperature is 3300 K, with reaction residence times of 1-4 milliseconds.

Although the plant now in operation uses refinery gases and naphthas as feedstock, research was carried out in 1970 to see if crude and heavy oil stocks could be used as feed. At this time the reactor was slightly modified to allow for liquid oil injection behind the anode nozzle, to provide an oil quench to wash out the soot and to recycle the unconverted feed. The yields achieved were highly dependent upon the oil characteristics, with a typical example of feed and product results given in Table III. Less ethylene and acetylene were produced with an oil feed. With heavier crudes this trend was accelerated, together with increased carbon-black yields. The last was an insurmountable problem, because carbon black was absorbed by the oil during the quench. A bleed stream had to be burnt to maintain the carbon-black in 20 mass % suspension in the oil. This drastically reduced the economic viability of the process. (Muller, 1983)

2

TABLE IIIPRODUCTS FROM THE HUELS PLASMA REACTOR WITH
CRUDE OIL FEEDSTOCK

(Muller, 1983)

Power Input 8500 kW Feedstock Crude Oil

Properties of Feedstock

Spec gravity [kg/l]	Analysis by boiling (ASTM)				Sulphur cont. [% wt]
	Gasoline [% wt] < 180°C	Kerosene [% wt] 180-260°C	Gas oil [% wt] 260-360°C	Residue oil [% wt] > 360°C	
0.838	14	19	24	43	0.32

Feed per 100 kg C_2H_2 [kg] 367

Products per 100 kg C_2H_2

Ethylene [kg] 48

C_1-C_6 Hydrocarbons [kg] 82

Hydrogen [Nm³] 112

Waste oil (20% carbon black) [kg] 127

Energy consumption per 100 kg C_2H_2
(without gas separation) [kWhr] 980

Selectivity $C_2H_2 + C_2H_4$ [% wt] 56

Cracked gas analysis [% vol]

C_2H_2	14.5	C_4H_6	0.20
C_3H_4	0.31	C_6H_6	0.38
C_4H_2	0.30	CH_4	6.04
C_4H_4	0.38	C_2H_6	0.26
C_2H_4	6.51	C_3H_8	0.12
C_3H_6	1.12	$i-C_4H_{10}$	0.05
Allen	0.17	$n-C_4H_{10}$	0.17
$i- + n-C_4H_{10}$	0.20	$i-C_5H_{12}$	0.10
$trans-C_4H_8$	0.03	$n-C_5H_{12}$	0.16
$cis-C_4H_8$	0.02	H_2	68.5
$1-3-C_4H_6$	0.33	CO	0.15

PETROCHEMICAL FEEDSTOCKSIntroduction

The conversion of heavy oil to liquid hydrocarbons is the preferred upgrading route; as exemplified by the CANMET hydrocracking process results. Other existing processes, such as Flexi-Cracking (Allan et al. 1981) also seek to maximize liquid yields while others, such as visbreaking, produce useable hydrocarbons at a minimum cost. (Allad and Martinez, 1983) However another viable alternative is to crack the oil to olefins; with a tar and pitch residual. This route was illustrated by the Japanese Steam Cracking Process. Because of its short residence times and high temperatures plasma used for hydrocarbon pyrolysis or cracking produces light olefins; specifically acetylene, as its most valuable product. It is not presently a widely-used chemical feedstock. However this situation may change, as described in the paper by Babcock (1975), in which the plasma-acetylene process was described as being one of the technologies of tomorrow. Compounding this hurdle is the present oil glut which has made the large capital investment needed for a heavy oil upgrading plants unattractive. (Green, 1981) But what about future possibilities?

2

Ethylene or Acetylene ?

Acetylene once was, and ethylene now is, the building block for the petrochemical industry in the production of synthetic materials such as vinyl chloride, vinyl acetate, and neoprene. While ethylene production has doubled in the past ten years, acetylene production has decreased by over 50%. (Morris, 1983) This has been due in large part to the present costs of hydrocarbon feeds, which although expensive, are still relatively lower than that of electricity. For the major cost directly affecting ethylene processing cost is the hydrocarbons feed price, and for acetylene it is the price of electricity; assuming a hydrocarbon feed is used rather than the old calcium carbide.

However during the 1970's this price advantage offered by cheap hydrocarbons was slowly offset by increased OPEC oil prices. This change is as yet insufficient to cause major changes this moment. In processing strategy, perhaps in the not so distant future, when cheap electricity offered by nuclear, or other new means, is available, will acetylene be a competitive petrochemical feedstock.

Hydrocarbon Upgrading: Processing Trends

Interest is high in the world's vast bitumen deposits and heavy oil fields, despite falling oil prices: first because there is a perception that oil prices will rise again as world economies gain strength, and that new discoveries of light crude fields are not keeping pace with demand, so heavy crudes (Ondish and Suchanek, 1979) must soon supply the shortfall. However extra care must be taken when processing such an energy intensive (one third of the oil is used in processing) and environmentally expensive (ie. sulphur removal) hydrocarbon. More of the 'bottom end of the barrel' must be used; but how to do it most effectively?

There are a host of alternatives - almost as many as there are companies interested. (Shah, 1983) However all of these new processes have a single theme: the use of higher temperatures, shorter residence times, smaller scale, no catalyst, and flexible feed. The plasma process offers all these advantages.

But although the production of light liquid hydrocarbons does not seem suited to use of plasmas, the production of olefins is a very viable option. This 'slice of the future' may yet see the use of plasmas.

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EXPERIMENTAL SECTION

INTRODUCTION

The interest in the application of plasma technology to the processing of hydrocarbons has grown significantly in recent years. Trends in oil upgrading have begun to emphasize the need for flexible and low capital cost processing units which operate at higher operating temperatures and shorter residence times. Plasma processing meets these new demands. However, there are still severe cost constraints to be overcome. Although Huels of W. Germany has economically cracked methane to acetylene in a hydrogen plasma reactor (Gehrmann, 1971) high electricity costs have led to the preponderance of ethylene as a petrochemical feedstock. This high cost of electricity is not an obstacle in Québec since its electricity cost is among the world's lowest. Another high cost associated with the plasma process is the necessity of using hydrogen as a plasma gas. The use of a steam plasma would significantly reduce this cost.

The experimental work done here has sought to demonstrate the viability of heavy oil processing in steam plasmas. The objectives of the experimental study were:

- 1) to react heavy oil with both steam and hydrogen plasmas and compare the reaction products
- 2) to examine the effect of steam-to-oil mass ratio on the reaction products
- 3) to examine the effect of specific energy consumption on the reaction products

- 4) to examine the influence of quench on the reaction products.

It was decided to use the particle contacting methodology developed in this laboratory many years ago, whereby a spray of finely divided droplets, issuing from an atomizing nozzle, is entrained by the reacting gas, in this case water vapour or hydrogen, and allowed to react in a finite contacting time. This technique, called "the atomized suspension technique" (AST) permits very high rates of heat transfer because of the small size of the particles (Gauvin, 1981). The author was assisted by the existence in the laboratory of the reactor and plasma generating equipment used by P. Stuart in a previous plasma project (Stuart, 1984). However, since the equipment was not specifically designed to handle heavy oils considerable modifications had to be made to it, which put some severe limitations on the range of operating conditions which could be used.

APPARATUS

The apparatus used in the experimental work consisted of plasma generator, heavy oil feeding, reacting and sampling units. The general layout of the laboratory is shown in Figure 1.

The system can be broken down into four sections for further examination:

1. steam plasma generating equipment with torch
2. heavy oil preheater and atomizer
3. reactor and auxiliaries
4. sampling and collection train
5. effluent system.

Steam Plasma Generating Equipment

The DC power supply (Figure 1; #1) was manufactured by Miller Electrical Manufacturing (model SR-1500F7) and was a 1500-ampere model wired to a 575 volt, 60 Hz, three phase power source. The control console (Figure 1: #2) was made by Metco Inc. (model 2MC). The plasma torch (Figure 1; #3) was manufactured by the Thermal Dynamics Corp. (model U51-T55) of New Hampshire. It is shown in Figure 2. A steam plasma flame ^{is shown} in Figure 3. A hydrogen plasma flame is shown in Figure 1, Appendix I. Although the hydrogen flame looks much longer this was not the case in the reactor. In the open, where the photograph was taken, the hydrogen reacted with the oxygen in the air. In the reactor, the hydrogen gas would only react with the heavy oil droplets. The steam plasma flame was split; because of the two oxygen entry ports which disturbed the evenly distributed hydrogen gas flow. Both flames are of sufficient length and breadth to fully cover the area covered by the oil spray.

FIGURE 1EXPERIMENTAL SYSTEM

1. Rectifier
2. Control Console
3. Plasma Torch
4. Oil Supply
5. Steam Boiler
6. Reactor
7. Liquid Collector
8. Gas Condensor
9. One-Way Gas Flow Control
10. Sample Bottles

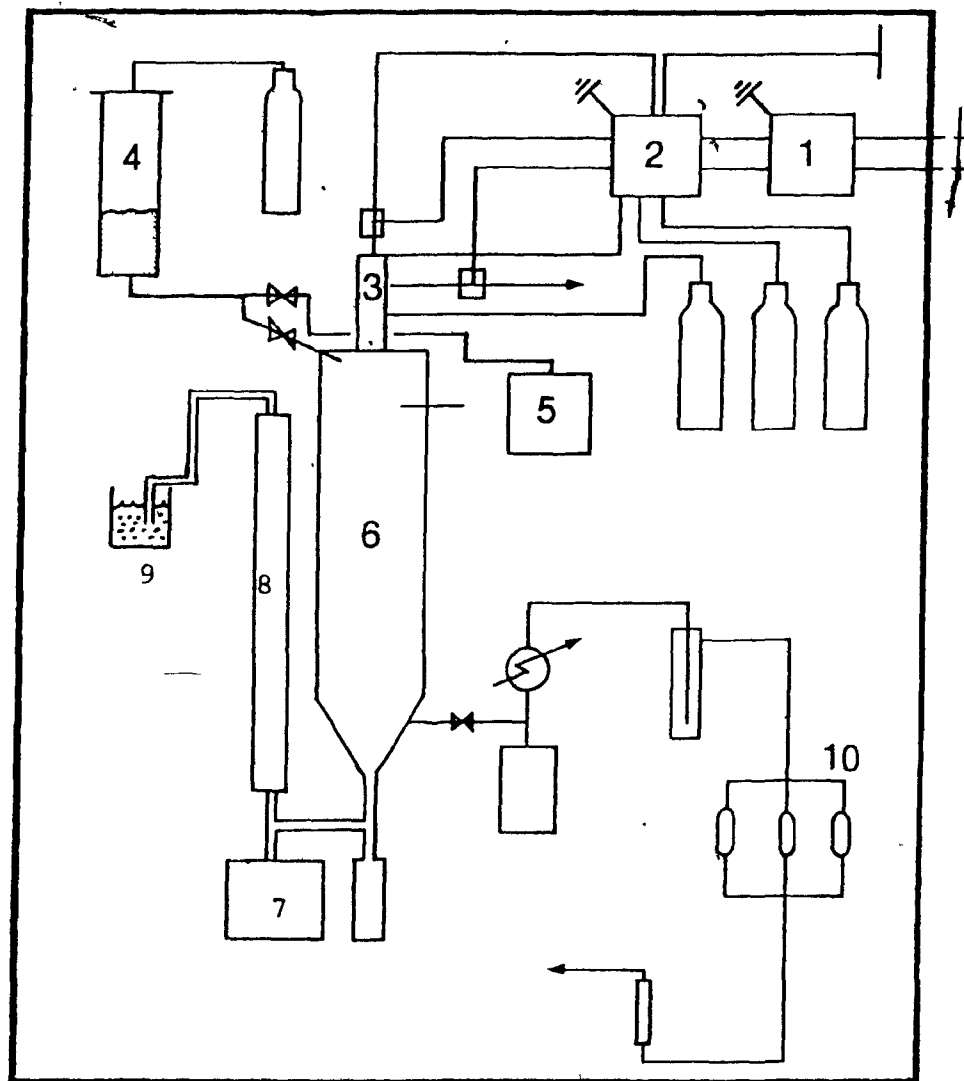
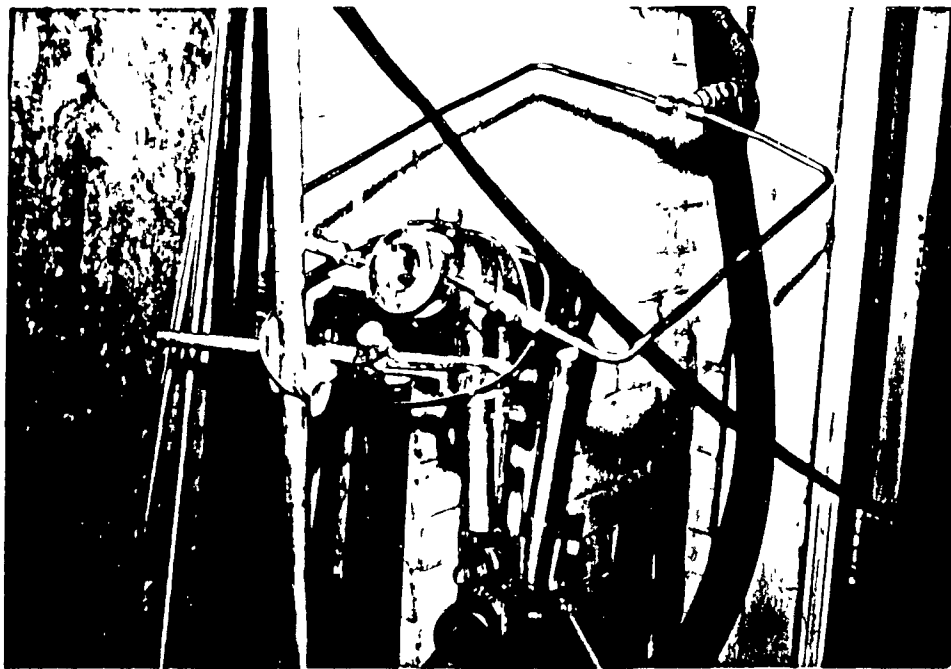


FIGURE 2

THE PLASMA TORCH

FIGURE 3

A STEAM PLASMA FLAME



The steam plasma generating equipment consisted of a power source which sent a 400-volt open circuit DC voltage to the control console and hence to the torch. The controls on the console regulated the current and gas flows to the torch. The cooling water flowrate to the torch was set using a calibrated rotameter. The electrical power entered the torch through the brass connections on the water lines. Argon and hydrogen flow through the control console, regulated by calibrated rotameters, and into the torch. Oxygen enters the torch anode to generate the simulated steam plasma. See Figure 2 in Appendix I for details of the torch cathode and anode configuration with its gas streams.

It is appropriate to emphasize here that 'simulated' steam plasma was used, in that the gas passing through the arc was hydrogen which reacted with oxygen in the lower section of the anode to produce a steam plasma. A plasma torch whose electrodes can tolerate the injection of pure steam into the arc was not available in these laboratories, but one is currently being developed in association with the Hydro-Québec Research Institute. Studies have shown that hydrogen and oxygen react to form steam in a very small fraction of a second (Aiken, 1982). The dramatic shortening of the hydrogen plasma flame, as photographed, was due to oxygen addition. This showed that a true steam plasma existed at the level of oil injection.

Heavy Oil Preheater and Atomizer

The heavy oil was preheated to 200°C in a steel pipe of twelve cm in diameter and fifty-five cm in length (Figure 1; #4). An electrical heating tape on the outside, wrapped about with fiberglass insulation, together with two immersion coils within the preheater, heated the oil. A diagram of the preheater is given in Appendix I, Figure 3. A pressure of 2000 kPa (nitrogen gas) was maintained in the vessel to reduce evaporation of the lighter fractions of the oil and to drive the oil through the pressure atomizer. The heavy oil flowed through 0.635 cm stainless steel tubing to the atomizer which is located in the reactor top: two cm from base of the plasma jet. The atomizer was at an angle of 15° from the axis of the plasma jet, as shown in Figure 4. The atomizers used were the common oil burner nozzles, full cone design, supplied by Delevan Corp. of South Carolina. The heavy oil used in this research project was supplied by Imperial Oil from its Cold Lake reserves. Typical properties are shown in Table I, following.

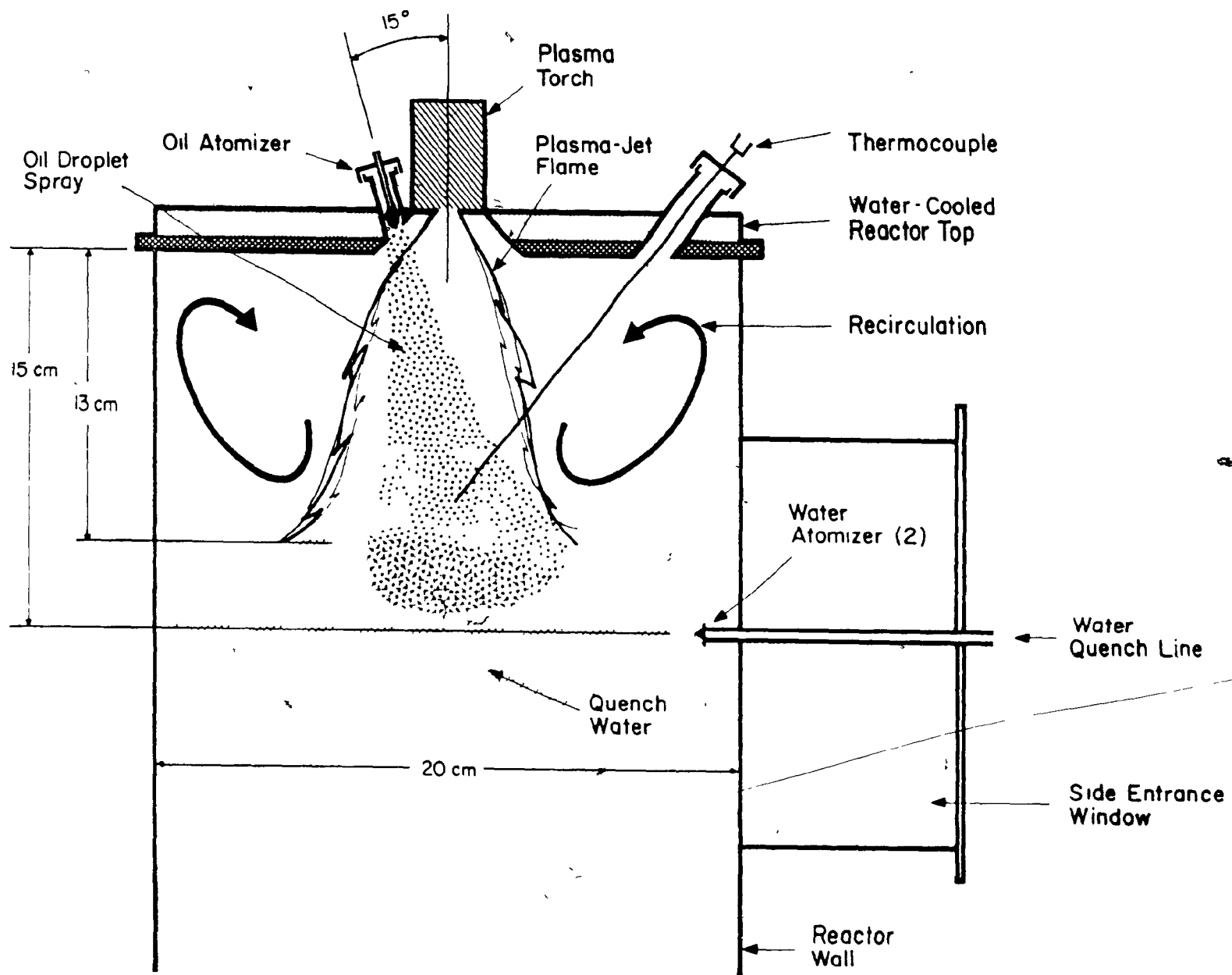
TABLE I : COLD LAKE HEAVY OIL PROPERTIES

<u>Property</u>	<u>Value</u>
API gravity	10.2
density - kg/m ³	998
viscosity -mm ² /s at 40°C	5300
sulphur - wt.%	4.4
nitrogen - wt.%	0.3
carbon - wt.%	82.28
hydrogen - wt.%	19.59
CCR - Conradson Carbon Residue	13.1
metals - ppm : nickel	77
: vanadium	190

<u>Volume Percent</u>	<u>Distillation °C</u>
initial boiling point	165
5	249
10	290
20	354
30	415
40	475
45	510

FIGURE 4

THE REACTION ZONE



Reactor and Auxiliaries

The reactor (Figure 1; #6), which was 120 cm long and 20 cm in diameter, was constructed of 316 stainless steel, as shown in Figure 5. A small boiler (Figure 1; #5) was used to generate steam to keep the oil entry lines warm and hence the oil flowing and the atomizer unplugged. The reactor top was water-cooled, as was the side observation window, from which the quench line and safety nitrogen purge line entered. Shielded thermocouples provided information on gas and wall temperatures. This information was gathered with a digital voltmeter and voltages converted to temperatures.

Sampling and Collection Train

The collection and sampling train consisted of two major parts; that for gas sampling and that for solid and liquid collection. The gases taken at the reactor exit were passed through two water-cooled condensers and a drying column to lower the temperature and remove water vapour which would have disturbed the gas chromatograph analysis. Glass sampling bottles (Figure 1; #10) were used to transport the gas samples to the gas chromatograph. (See Figure 6.) These gases were then vented to the atmosphere. The liquids were collected in three metal containers located below the reactor, and below the condensor (Figure 1; #7). Solids were scraped from the reactor wall.



FIGURE 5

THE REACTOR

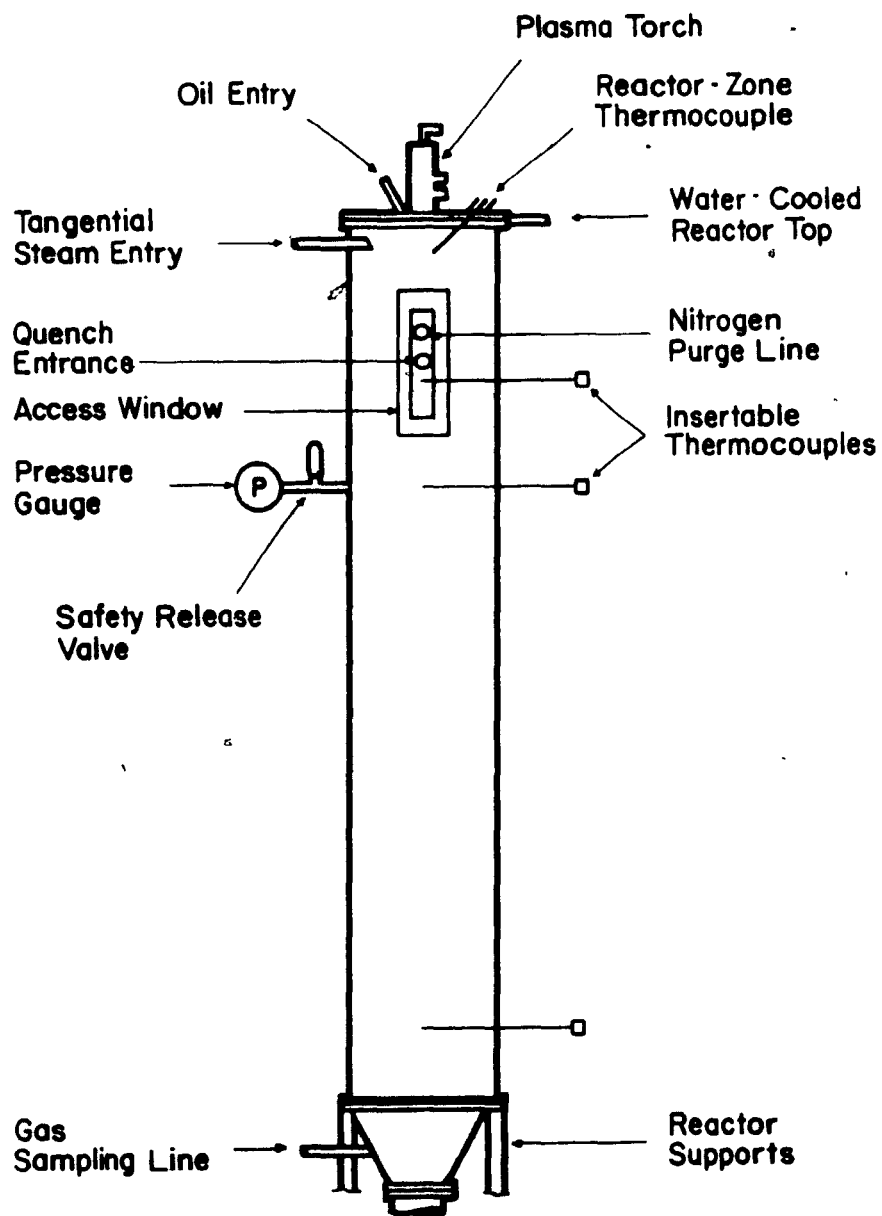
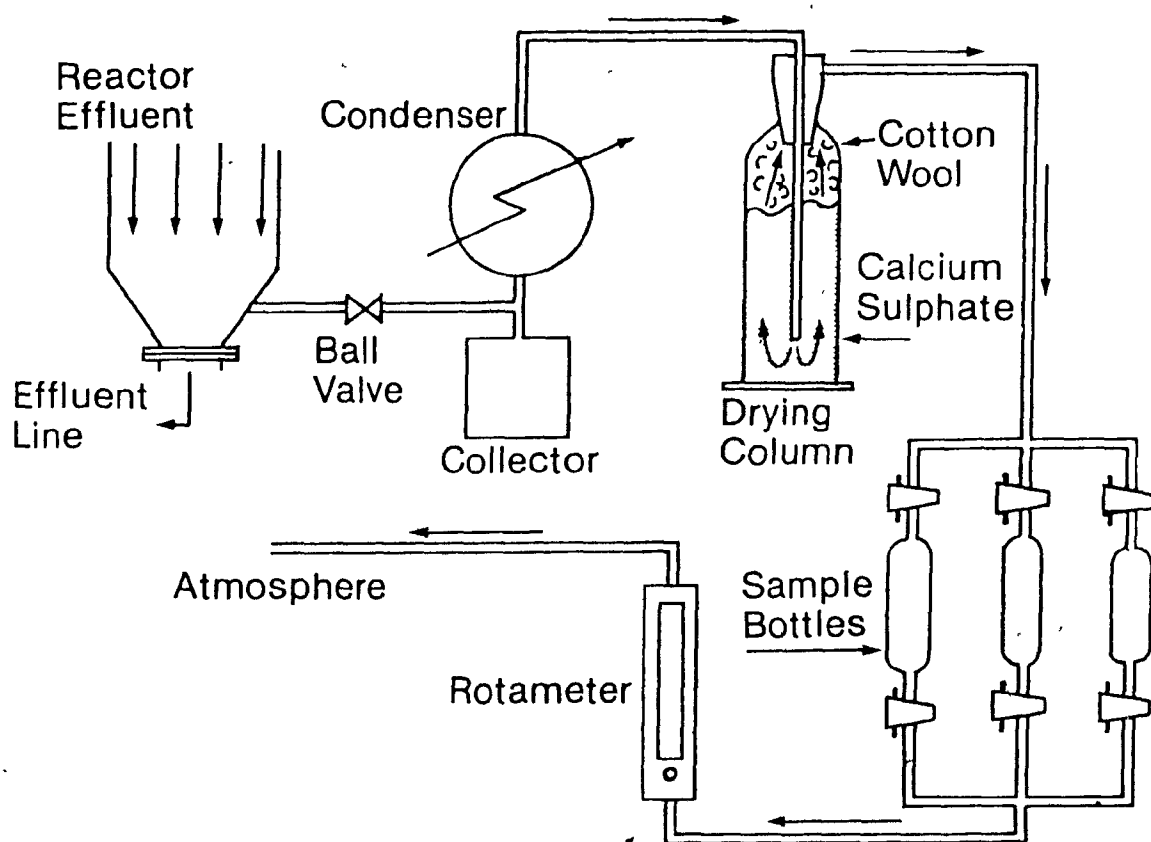


FIGURE 6

THE SAMPLING SYSTEM



Effluent System

The effluent system was designed to allow safe exit of the reactor gases. It consisted of:

- a) a large condensor (Figure 1; #8),
which drained into a collector;
- b) exit piping with a minimum number of bends (to minimize the pressure drop);
- c) an orifice plate to measure exit gas flowrate;
- d) a bucket (Figure 1; #9);
in which the end of the exit pipe was
placed to prevent entrainment of air upon shutdown;
- e) a purge line near the exit to flood the line with
nitrogen at shutdown.

These last two precautions would allow gases to exit the reactor system, but allow none to enter. This would be the case with an emergency shutdown, when the sudden drop in flow and temperature in the reactor would form a vacuum and suck in outside gases and possibly cause an explosion. The effluent exit system, although designed for a minimum pressure drop, built up reactor pressure to unacceptable levels (100 kPa) when high oil and/or plasma flows were used. See Appendix I, Figure 4, for a diagram of the system. The calibration curves for the orifice plate are given in Appendix IV.

Constraints

One of the main objectives of the project was to observe the change in product composition with operating variable settings. Therefore it was of the utmost importance to determine the limits within which the equipment could be used to achieve these changes. The whole experimental program could only be planned within these constraints.

There were five limitations:

- a) comparison between hydrogen and steam plasmas at the same specific energy and mass ratio settings was not possible;
- b) completely independent variation of the specific energy consumption (S.E.C.) and the steam-to-oil mass ratio with steam plasmas was not possible;
- c) the oil flow could only be varied by a factor of three - from 0.008 to 0.02 m³/h;
- d) hydrogen gas flows in the torch could only be varied by a factor of two - from 8.5 to 17 m³/h;
- e) electrical power could be changed by varying the amperage by a factor of two - from 100 to 200 A.

Comparative Hydrogen and Steam Plasma Conditions

Energy input into the system was controlled by variation of the current from 100 to 200 A. With the hydrogen plasma this was the sole source of energy. However, because the energy of combustion ($H_2 + 1/2 O_2 = H_2O$) of the simulated steam plasma was so high - almost three times that possible from electrical sources - the specific energy consumption was always much higher for the steam plasma (about 1.5 vs. 6 kWh/kg oil for hydrogen and steam plasmas respectively). Also, because hydrogen is so much lighter than steam, steam-to-oil mass ratios were always an order of magnitude larger than the hydrogen-to-oil mass ratios (about 0.08 vs. 0.8 kg/kg oil respectively). It should be noted that at steam-to-oil mass ratio settings nine times larger than the hydrogen-to-oil mass ratio the amount of hydrogen available for reaction in each case was equal, since the difference was made up by the oxygen alone.

Independent Variation of Specific Energy Consumption and the Steam-to-Oil Mass Ratio

For hydrogen plasmas the specific energy consumption could be varied completely independently of the hydrogen-to-oil mass ratio by simply increasing the current. With steam plasmas it was required to change the plasma gas flow to give meaningful variation in specific energy consumption, because the energy of combustion constituted 70-80% of the total energy input to the system.

For instance, to reduce the S.E.C. by 50% (at a fixed oil flow) the current could be at most, cut in half, from 200 to 100 A. This would only bring about a change of 10% in the total energy, so that the remaining 40% energy reduction had to be accomplished by a corresponding 40% reduction in plasma gas flow. Changes to the gas flowrates, then, change the stoichiometry of the system and of the reaction.

Oil Flow Variation

The pressure nozzles used had been designed for the atomization of water or light oils. With the use of heavy oil, even preheated to 200°C, the high viscosity prevented atomization at low oil flows. This lower flow limit was found by commissioning experiments. In the same set of experiments it was found that at excessive oil flows there was insufficient hydrogen plasma gas available for reaction, or high enough reaction temperatures, so that most of the oil left the reactor unchanged. The oil flow limits were:

- 1) low oil flow limit: 0.008 m³/h
- 2) high oil flow limit: 0.02 m³/h.

Plasma Gas Flow Variation

The plasma torch had been designed for operation within a relatively narrow range of gas flows. These limits were found by commissioning experiments to be 8.5 to 17 m³/h. At high hydrogen gas flows the arc either blew right out of the anode or increased the voltage so much that the arc failed. This was a result of lower gas temperatures and low gas electrical conductivity. At low gas flows the increased gas temperatures resulted in a very high anode erosion rate and short anode life.

Electrical Power Variation

Power limits were set by arc stability and anode erosion - at low powers there was insufficient power to maintain the arc. At high powers high anode erosion did not allow the experiments to run for the necessary ten minutes.

EXPERIMENTAL PROCEDUREGeneral

A very detailed eight page long procedure stating every step and precaution to be taken was used during each experiment. While it will not be included here its major points have been outlined in Appendix III.

To carry out an experiment two people were needed; one at the control console to maintain gas flows, current settings, and a stable arc, and one other to switch oil and quench flows on/off, take the gas samples, and gather all the flow, temperature, and pressure data needed. The sequence of events during the actual running of the experiment were as follows:

- 1) the argon plasma started and transfer to a hydrogen or steam plasma was done after two minutes of stable operation;

- 2) the quench water immediately started (if any) and the oil flow begun after the system had reached a stable temperature (three minutes); pressures and temperatures were recorded;

- 3) samples were taken two and four minutes after oil flow had begun (negligable change in gas samples were found with these times) and pressure and temperature readings taken to ensure that equilibrium had been reached.

Pressures measured indicated exit gas flow (orifice plate) and reactor pressure (for safety). Temperatures were taken with thermocouples in the reaction zone, after the quench, and at the orifice plate. Plasma gas flows, currents, and voltages were noted. Afterwards the reactor, collectors, and all piping were cleaned. All water, residue and soot found were weighed.

The quench water entered the reactor from the side 15 cm down from the torch. Flat spray atomizers which covered the entire reactor areas were used. For hydrogen and steam plasma respectively the flowrates were 0.1 and 0.2 m³/h. Because of the higher energy input from the steam plasma higher quench flows were used for it.

Sample and Data Treatment

The gas analysis was done with a Hewlett-Packard gas chromatograph (model 5700A) with a Spherocarb carbon molecular sieve made by Chromatographic Co. The column was calibrated for each of the gases present in the gas mixture, using a carrier of helium with nine percent hydrogen, a mixture which would detect both hydrogen and the other gases. This special carrier was necessary because a normal helium carrier gas has a thermal conductivity so close to that of hydrogen that the hydrogen would not be detected. The solids (carbon-black) and liquids (tars) were analyzed in Sarnia by the Imperial Oil Research Laboratories. Viscosity tests were done on some liquid samples, with one total metal and sulphur analysis.

The data collected, listed below, were all entered into the mass balance program, attached in Appendix V :

1. All oil, plasma, and quench water flows were measured. The mass balance was carried out, using these flows, on the following atomic species: carbon, hydrogen, and oxygen.
2. The experimentally determined flow and power settings, were used to calculate the steam-to-oil mass ratio, specific energy consumption, and the oil-to-gas/soot/residue conversion.

Conditions

By varying the three system parameters listed below the total range of experimental conditions (as listed in Table II and shown in Figure 7) were set :

- a) the current : 100 - 200 A
- b) the plasma gas flow : 8.5 - 17 m³/h
- c) the oil flowrate : 0.008 - 0.02 m³/h.

Figure 7 illustrates well the strong proportionality between the mass ratios and the specific energy consumption.

The temperature in the reaction zone was measured for the last half of the experiments with a digital voltmeter after it was found that the strip chart recorder was giving spurious readings due to a stripped printing wheel and faulty relay switch. Therefore there are no results for the first experiments. The temperatures of the steam plasma alone and with oil injection respectively, 10 cm from the torch exit, were approximately 2300 K and 2100 K. With quench the temperatures were only 900 K at this point. After the quench line, 22 cm from the torch exit, temperatures were , respectively for steam plasmas with and without quench, 1400 K and 300 K. The measurements made 13 cm from the torch exit were made with a bare rhodium-platinum (type S) thermocouple and those after the quench with a shielded chromel-alumel (type K) thermocouple.

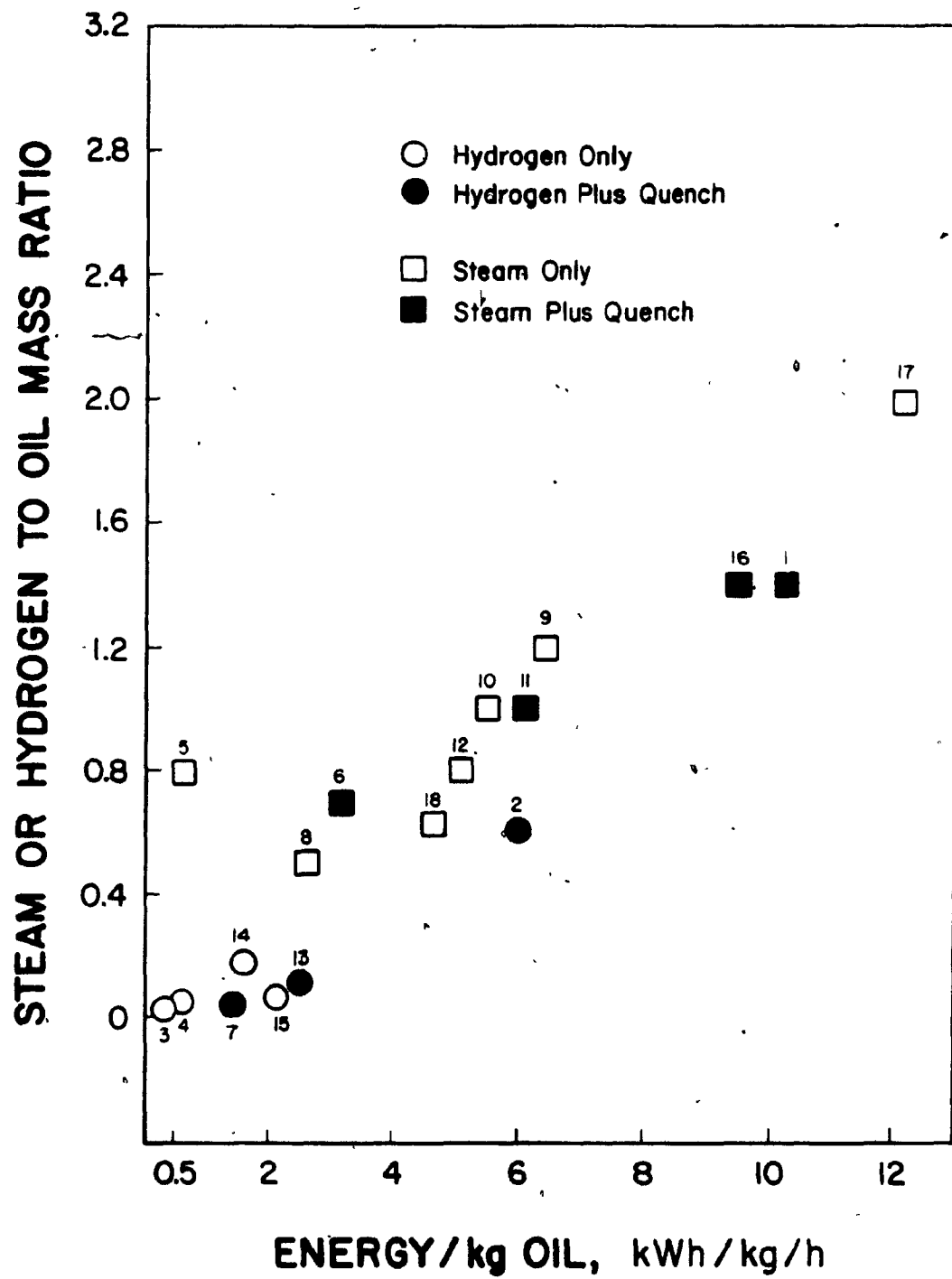
TABLE II : EXPERIMENTAL CONDITIONS

- (1) - A: hydrogen plasma only B: hydrogen with quench
 C: steam plasma only D: steam with quench
- (2) - reaction zone only

EX. #	TYPE (1)	ENERGY/ KG OIL	STEAM/HYDROGEN TO OIL MASS RATIO	OIL KG/H	PLASMA M ³ /H	CURRENT AMPS	POWER KW
1	D	10.4	1.5	3.0	6.3	100	32
2	B	6.0	0.5	2.4	13.8	130	14
3	A	0.4	0.05	25.0	15.3	100	11
4	A	0.5	0.06	21.7	15.3	100	11
5	C	0.6	0.09	60.0	7.5	100	35
6	D	3.1	0.54	21.5	15.7	100	66
7	B	1.5	0.06	14.1	10.6	200	21
8	C	2.6	0.46	22.8	14.2	100	60
9	C	6.5	1.2	8.9	14.2	100	58
10	C	5.5	1.0	10.4	14.2	110	58
11	D	6.2	0.9	8.9	10.6	200	55
12	C	5.1	0.81	13.2	14.5	200	67
13	B	1.7	0.07	11.8	9.8	200	20
14	A	1.7	0.17	7.4	15.3	100	13
15	A	2.2	0.08	9.9	9.9	200	21
16	D	9.6	1.5	7.6	15.3	200	73
17	C	12.6	2.0	3.3	8.7	120	41
18	C	4.7	0.65	11.2	9.9	190	52
19	A	0.6	0.07	18.2	15.3	100	11

FIGURE 7EXPERIMENTAL CONDITIONS

- hydrogen plasma only (all with the expt.# attached)
- hydrogen plasma plus quench
- steam plasma only
- steam plasma plus quench



Droplet Size Distribution

Pressure atomizers manufactured by Delevan Corporation were used to atomize the heavy oil. A pressure of 2000 kPa and a temperature of 200°C was needed to sufficiently atomize the heavy oil, for the viscosity had to be reduced to a level that allowed droplet breakup to occur. (See Sakai et al. for report on pressure atomization.) Atomizer flowrates generally ranged from 0.008 to 0.02 m³/h; where at each individual flowrate a different atomizer was used. Representative pictures of the oil droplets are shown in Figure 8.

Droplet sizes were measured by the placing of microscope slides under the atomizer as it sprayed oil in the open atmosphere for a small fraction of a second. Pictures were then taken of the droplets through a microscope and then measurements made of approximately 200 droplets. The results of calculations of the mean number droplet size and standard deviation for the atomizers at the lowest and highest flow extremes are:

$$\text{i) at } 0.008 \text{ m}^3/\text{h} : \bar{d} = 290 \text{ } \mu\text{m}$$

$$\sigma = 23$$

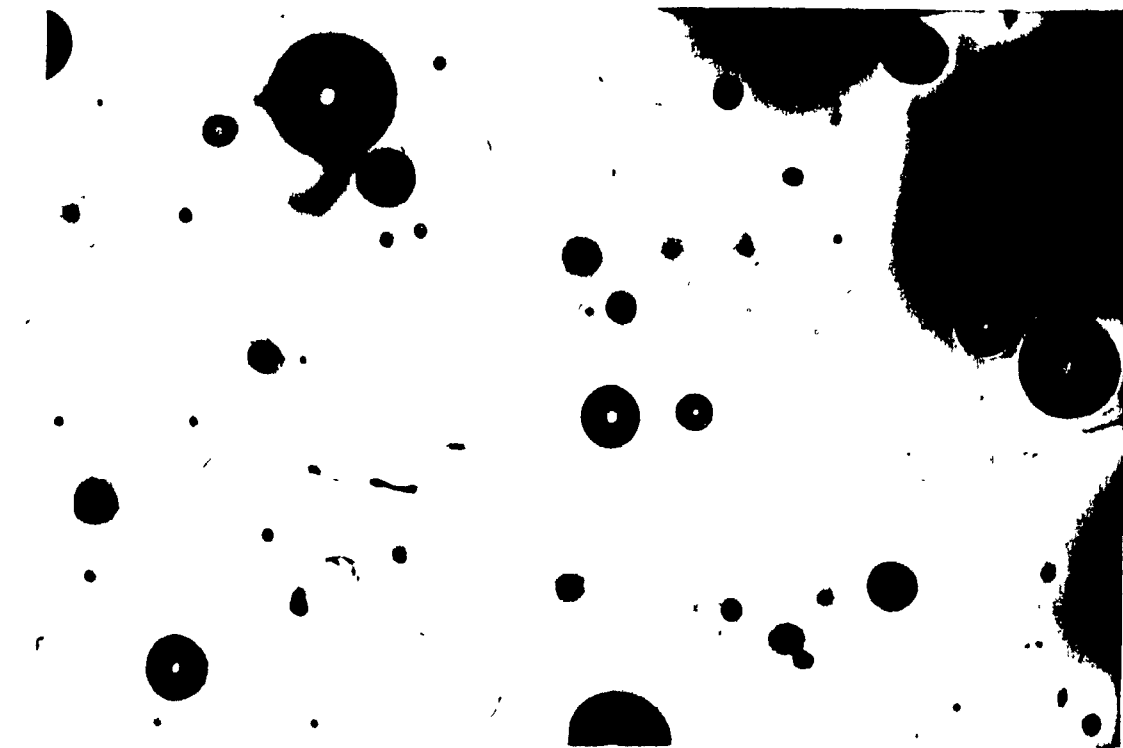
$$\text{ii) at } 0.02 \text{ m}^3/\text{h} : \bar{d} = 220 \text{ } \mu\text{m}$$

$$\sigma = 15$$

Variations in droplet size distribution will have an effect on the ease of oil gasification, the smaller drops vapourizing more quickly and hence with increased gasification and olefins in the gas. Over the entire range of conditions the mean droplet size varied by only 25%. This was felt to have a minimum influence on the experimental results. Significantly smaller particles would be expected to vapourize and react more quickly, but this could not be quantified.

For the quench water flat spray atomizers manufactured by John Brooks were used. Higher flowrates were used for the steam than the hydrogen plasma experiments. Although higher flows were provided better quenching a lower flow reduced problems during the experiment (such as pressure buildup in the reactor), and also reduced cooling of reaction zone.

FIGURE 8OIL DROPLETS



Mass Balances

A complete mass balance was carried out on all experiments. The program, included in Appendix V, had the following five major sections:

- i) experimental data entry
- ii) orifice meter gas flows
- iii) mass and energy inputs
- iv) gas and liquid output calculations
- v) oil conversions.

In the first section the powers, flows, times, and collected weights of all products were entered. In the second section measured flows and gas volume percents were entered in to the equation generated by the orifice plate calibration curves for hydrogen and steam. In the third section all oil, plasma, and quench flows and total weights were calculated, as well as the powers. In the fourth section the individual gas masses and products per 100 kg acetylene were calculated. Finally, the oil-to-gas, soot, and residue conversions were calculated. Complete mass balances were achieved about the experimental system.

RESULTS

Products and Conversions

Pyrolysis and gasification were found to be the major conversion processes in the plasma reactor. The gases found included hydrogen, methane, ethylene, acetylene, and traces of ethane for both hydrogen and steam plasmas. Only with steam plasmas were carbon monoxide/dioxide formed - as a result of reaction with oxygen contained in the steam. Soot (carbon and ash) was also formed with both types of plasmas. Partially or unreacted heavy oil was also collected from the experiments with higher oil flowrates.

There was no upgrading of the heavy oil to lighter liquid hydrocarbons in either plasma, because the high temperatures vapourized the droplets. Flash distillation of the oil occurred in the reactor. The oil droplets only reacted with the hydrogen or steam while in the gas phase. Analyses have indicated that reaction had occurred between the lighter oil fractions first, then with the heavier asphaltics, since when excess oil was fed, that residue collected was extremely viscous, very much like unreacted 'asphaltics', the heavy end of the heavy oil (called 'residue' from on). Residue was only collected at higher oil flows.

The products per 100 kg acetylene are given in Table IV, to allow comparison with the results of other workers. Minimum process values for the production of 100 kg of acetylene in a hydrogen plasma were:

- i) 233 kg of feed oil (ex.#14)
- ii) 235 kWh of energy (ex.#3)

And for a steam plasma:

- i) 543 kg of feed oil (ex.#17)
- ii) 552 kWh of energy (ex.#6)

Information in Table III shows that the maximum acetylene concentrations (dry gas) for hydrogen and steam plasmas were respectively 13 and 7 vol.%. Conversions to gas, as shown in Table V, were as high as 100%.

It should be noted that all gas volume percents given are on a dry basis. However the water vapour fractions have also been presented in Table III. Only when water quench was used, especially with the steam plasma, did the water vapour make up a substantial fraction of the gas. For instance, with steam plasma and quench (ex.#11) the water vapour made up 48 vol.% of the total gas, while without quench it made up only 4 vol.%.

TABLE III : DRY GAS VOLUME COMPOSITIONS

EX. #	ACETYLENE	ETHYLENE	METHANE	HYDROGEN	CARBON MONOXIDE	CARBON DIOXIDE	WATER
1	4.5	6.5	4.5	38	23	21	64
2	4.0	0.0	1.0	75	3	15	1
3	14.0	6.0	7.0	74	0	0	0
4	12.0	6.0	9.0	73	0	0	0
5	7.0	4.5	7	53	7	23	3
6	4.5	4.5	13	30	30	15	88
7	7.0	3.0	11	65	15	0	24
8	4.0	7.0	14	35	34	0	4
9	3.0	3.0	6	42	35	0	4
10	3.0	4.0	5	43	36	3	5
11	2.0	2.0	3	30	21	10	48
12	5.0	7.0	12	45	22	0	4
13	7.0	4.0	5	42	22	0	2
14	13	7.0	10	71	0	0	0
15	10	10.0	15	64	0	0	0
16	2.0	1.0	3	25	16	9	44
17	5.0	10.0	11	32	34	1	4
18	3.0	4.0	8	39	41	0	4
19	8.0	4.0	5	82	0	0	0

TABLE IV : PRODUCTS PER 100 KG ACETYLENE

EX. #	OIL KG	PLASMA KG	ELECTRICAL POWER-KWH	RESIDUAL OIL - KG	SOOT KG	ETHYLENE KG	METHANE KG
1	661	1287	2409	43	0	139	38
2	425	279	2563	149	0	0	9
3	533	40	235	399	0	41	19
4	497	51	252	333	0	48	28
5	4258	756	759	3948	0	62	38
6	781	894	552	290	0	96	110
7	738	69	1115	530	0	41	60
8	2490	1994	1476	1493	344	169	133
9	691	1610	932	0	88	97	76
10	803	1609	905	0	93	129	63
11	1637	2637	3818	939	0	96	57
12	703	1034	1056	25	235	134	91
13	646	110	1086	262	0	55	27
14	233	65	383	0	45	52	29
15	405	57	873	0	210	96	57
16	1638	8044	4909	933	0	49	57
17	543	1853	2143	0	0	193	84
18	1057	1471	1909	0	279	129	101
19	533	66	322	387	0	48	24

TABLE V : CONVERSIONS AND POWERS

EX. #	GAS	SOOT	RESIDUE	POWER - KW		TOTAL
	WT. %	WT. %	WT. %	ELECTRICAL	CHEMICAL	
1	94	0	6	11	21	32
2	65	0	35	14	0	14
3	28	0	72	11	0	11
4	33	0	67	11	0	11
5	7	0	93	11	24	35
6	63	0	37	15	51	66
7	28	0	72	21	0	21
8	26	13	60	14	46	60
9	87	13	0	12	46	58
10	89	12	0	12	46	58
11	43	0	57	20	35	55
12	63	33	4	20	47	67
13	59	0	41	20	0	20
14	80	20	0	13	0	13
15	48	52	0	21	0	21
16	43	0	57	23	50	73
17	100	0	0	13	28	41
18	74	26	0	20	32	52
19	27	0	73	11	0	11

Repeatability

Repeat experiments were performed for both hydrogen (ex. 3, 4 & 19) and steam plasmas (ex. #9 & 10). For most process variables and products repeatability was excellent. For instance, for the hydrogen plasma experiment heavy oil-to-gas conversion varied from 28 to 33 wt.%, acetylene concentrations were 14 and 12 vol.%, and the oil needed to produce 100 kg of acetylene changed from 553 to 497 kg (respectively from ex. #3 & 4). These differences were within 15%. Although the results from experiments 3&4 agree well the third repeat, ex. #19., had olefin gas concentrations 25-50% less than the two previous. The probable cause for this difference is a reduced flow into the sample bottles, giving concentration from early on in the experiment (ie. partially plugged line). Because all other gas concentrations from hydrogen plasma experiments are in agreement with those of ex. #3&4 the results from ex. #19 have been rejected. For the steam plasma (ex. #9 & 10 respectively) oil-to-gas conversions varied from 87 to 89 wt.%, acetylene concentrations not at all, and the oil required per 100 kg acetylene produced from 691 to 803 kg. These differences were also within 15% of each other.

Sources of experimental uncertainty, and their effects, are now listed:

- 1) gas chromatographic analysis - variation in areas of an individual gas peak could vary up to 10% of the reported value;
- 2) plasma and exit gas and oil flow measurements - were dependent upon the accuracy of the instrumentation:

for the plasma gas the rotameters, for the exit gas flow the orifice plate, and the oil flow the oil height change measurement of the preheater. Total uncertainty from these sources is estimated to be 5%;

3) collection of soot, oil residue and water - after each experiment the entire reactor, collectors and exit lines had to be scraped out; minor accumulations occurred at hard to reach places. The total uncertainty in the mass of material collected is estimated to be 5%.

Therefore the experimental uncertainty for the following experimental variables and products presented was:

- i) 20% : all values per 100 kg acetylene produced;
- ii) 10% : gas concentrations;
- iii) 5% : oil-to-gas/soot/residue conversions;
- iv) 5% : energy setting, all gas flows,

oil and water flowrates. These uncertainties accounted for the variations observed.

DISCUSSION

Introduction

Three main reactions occur simultaneously in the plasma-heavy oil system; these are: hydrogenation, coke formation, and gasification. Gases rather than liquids were the main reaction products, because the homogeneous gas forming reaction were so much faster than the multistep liquid forming reactions. This difference in rates of formation was vital since the

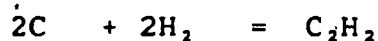
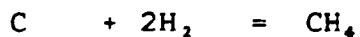
reaction time (oil droplet in the hot plasma zone) was small; being in the order of several milliseconds.

A decrease in the molecular weight is achieved by a hydrogenolysis/ hydrogenation mechanism (Blouri et al. 1981) by the addition of hydrogen. Hydrogen is also available in the steam plasma as dissociated water vapour. Coke formation is a problem in heavy oil processing because many species in the heavy oil, such as polycyclic aromatics, and naphthas, readily form coke. Acetylene is also well known as a soot precursor. Lower hydrogen excesses and higher temperatures also favour coke formation.

Many possible reactions simultaneously occur, as shown in Figure 9, in which two main types are important: the degradation of the molecule to lighter components, and polymerisation/hydrogenation reaction to produce coke. Although these reactions for oil are very complex the most important olefin forming steps are the carbon-carbon bond breakage, and free-radical combinations:



The hydrogen reacts (Figure 9) first to acetylene and ethylene and then to methane and soot. Some of the most important olefin forming reactions, of the many possible, are:



High temperatures and low pressures favour bond breakage near the end of the chain, as was the case here. The production of tars and coke does not begin until after an induction period in which olefins are produced (Taniowski et al. 1981).

A study of the hydrogen content in the exit gases has shown that 85 to 95 wt.% of the hydrogen from the plasma leaves as part of an olefin molecule.

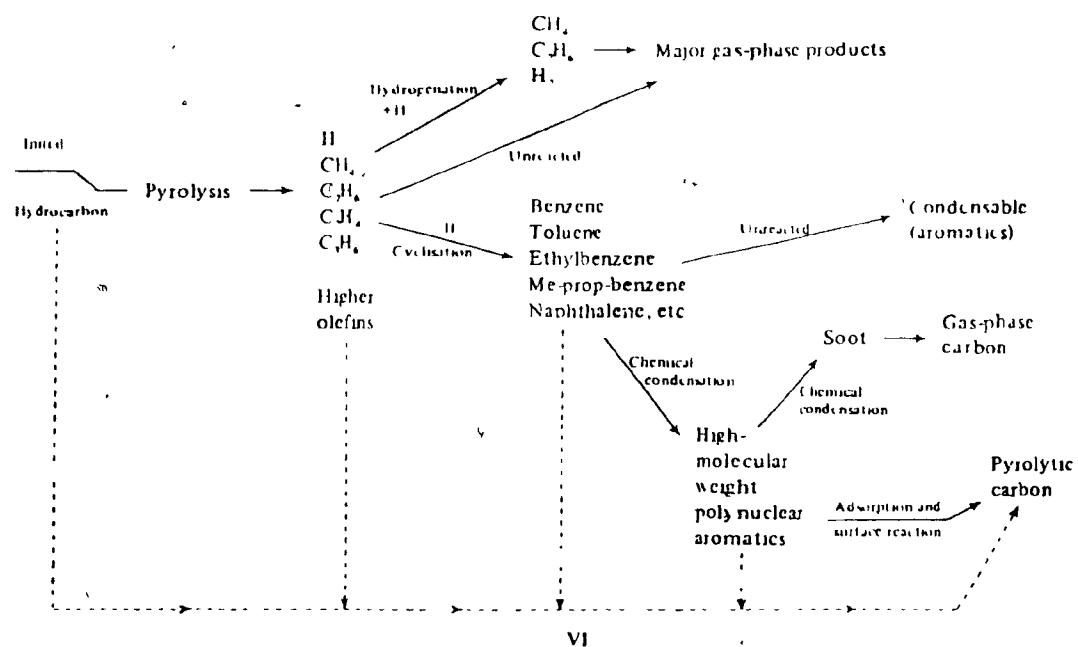
Analyses of the heavy oil residue show that although the metals concentrated in this phase the sulphur was equally split between the gas and residue phases. Metals, in one analysis (ex.#5), increased from 77 to 116 ppm nickel, and from 190 to 295 ppm vanadium. At the same time the sulphur weight fraction only increased from 4.4 to 4.9 wt.%. When all the oil reacted it was completely gasified to soot and olefins, thereby opening up the possibility for the use of this technology for the gasification/pyrolysis of heavy oil. Viscosity measured were in the order of three times that of the raw feed oil. However boiling point analyses were not done so there is a slight possibility that some of the soot entrained in the residue to increase its viscosity. This increased viscosity indicates that the lighter hydrocarbons were vapourized, leaving the heavy asphaltics unreacted.

The four variables studied in the following pages are:

- i) plasma gas used : hydrogen or steam
- ii) specific energy consumption (S.E.C.)
- iii) steam or hydrogen-to-oil mass ratio
- iv) water quench on or off

FIGURE 9HYDROCARBON PYROLYSIS REACTION SEQUENCE

(Liami and Trimm, 1981)



Differences in Hydrogen and Steam Plasma Products

The most striking differences between the hydrogen and steam plasma products were:

- i) large amounts of carbon monoxide and/or carbon dioxide with the steam plasma only
- ii) generally higher olefin concentrations with the hydrogen plasma.

The results for comparative soot (carbon plus ash) yields were inconclusive: both plasmas produced considerable soot. For both steam and hydrogen plasmas this occurred at higher S.E.C. values. For instance, for the hydrogen plasma, at 0.5 kWh/kg oil (ex.#3/4) no soot was formed and large amounts of liquid residue remained; while at 2.0 kWh/kg oil (ex.#14/15) large amounts of soot were formed and no residue remained (see Table V).

The carbon monoxide/dioxide produced in the steam plasma were a result of the following reactions (Bajus et al., 1980):



In the hydrogen plasma there was no oxygen and so neither of these gases were produced.

Lower olefin gas fractions were generally observed in the steam plasma (Figure 10). For instance, the maximum acetylene gas concentration in the hydrogen plasma was 13 vol.% and in the steam plasma the maximum was 5 vol.%. This was because the carbon or hydrocarbon available for reaction to olefins reacted preferentially with the oxygen. This would proportionally decrease the olefin yield as more carbon monoxide/dioxide were produced. Carbon dioxide was formed only when quench was used.

Comparisons between products of the two plasmas are shown in Figure 10. Oil to gas/soot/residue conversions were defined as that weight percent of the oil, fed which reacted to one of the three aforementioned products. (residue being that liquid pitch collected at the bottom of the reactor; the asphaltics)

In Figures 10 and 11 comparisons have been made between the best results for the respective hydrogen and steam plasmas. Best results have been defined as those with the highest concentrations of olefins in the gas and requiring the minimum oil feed and energy input per 100 kg acetylene product. However it should be noted that the S.E.C. and steam/hydrogen-to-oil mass ratios differ considerably between the two. The experimental settings were:

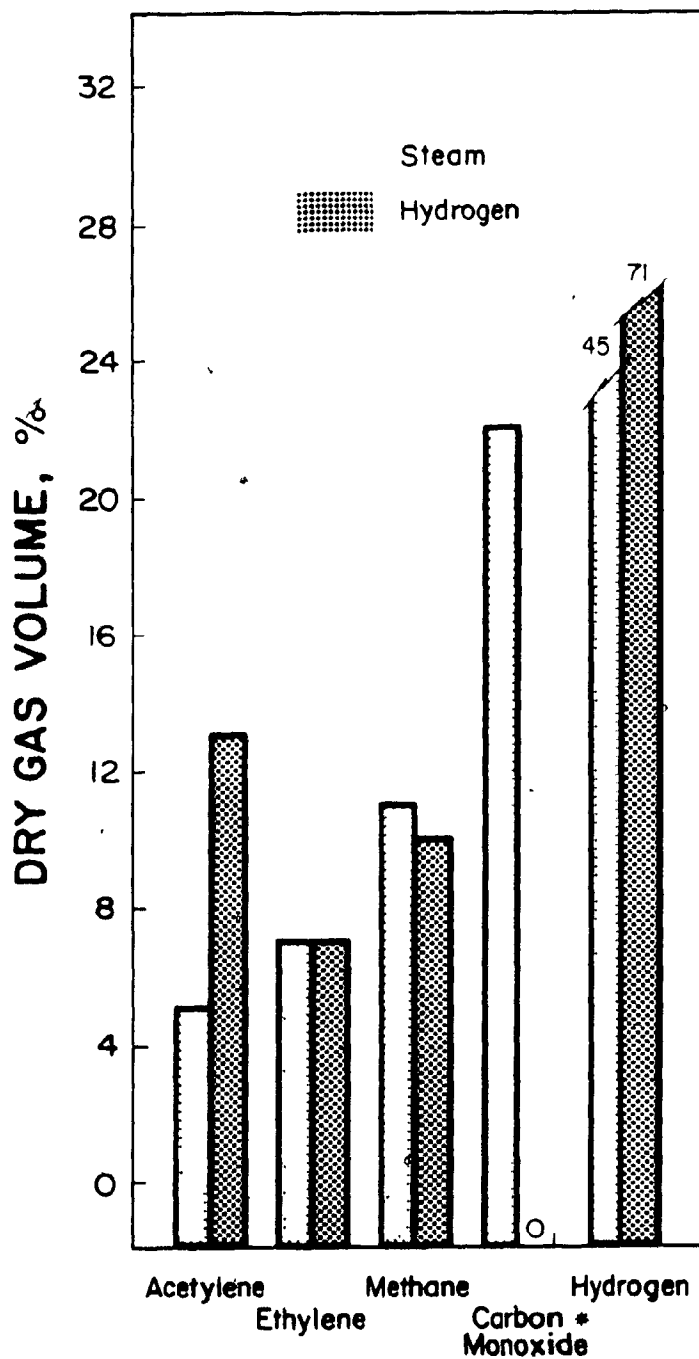
- 1) hydrogen plasma - ex.#14 : 1.7 kWh/kg oil,
0.17 kg hydrogen/kg oil;
- 2) steam plasma - ex.#12 : 5.1 kWh/kg oil,
0.81 kg steam/kg oil.

Although there was much more steam than hydrogen available for reaction, the actual weight of hydrogen available from the steam plasma was almost half that for the hydrogen plasma. Furthermore, as shown in Figure 11, the weight of hydrogen plasma gas needed to produce 100 kg of acetylene was almost identical for both types of plasma.

In spite of the higher S.E.C. of the steam plasma, oil-to-gas conversions were higher with the hydrogen plasma; 63 vs. 80 wt.%, perhaps as a result of the greater availability of hydrogen. Furthermore, as can be seen in Figure 11, all utilities needed and by-products of the production of 100 kg of acetylene were higher with the steam plasma. This indicates the reduced efficiency of conversion to acetylene via the steam plasma route. For instance, the unwanted soot by-product yield was 235 kg with the steam plasma and 45 kg with the hydrogen plasma.

FIGURE 10GAS CONCENTRATIONS WITH STEAM
AND HYDROGEN PLASMAS

○ steam plasma : 5.1 kWh/kg oil, 0.81 kg steam/kg oil
: experiment # 12
■ hydrogen plasma : 1.7 kWh/kg oil, 0.17 kg hydrogen/kg oil
: experiment # 14



PRODUCT

* No carbon dioxide.

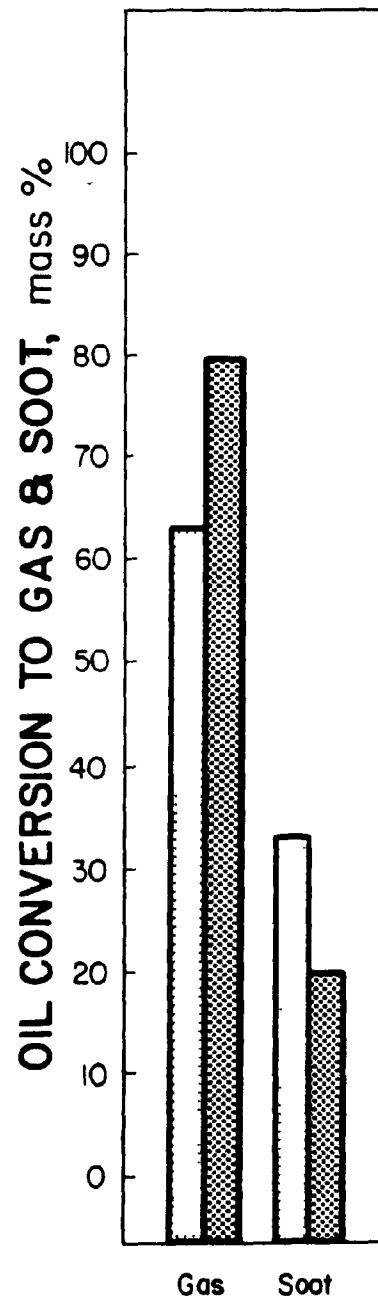
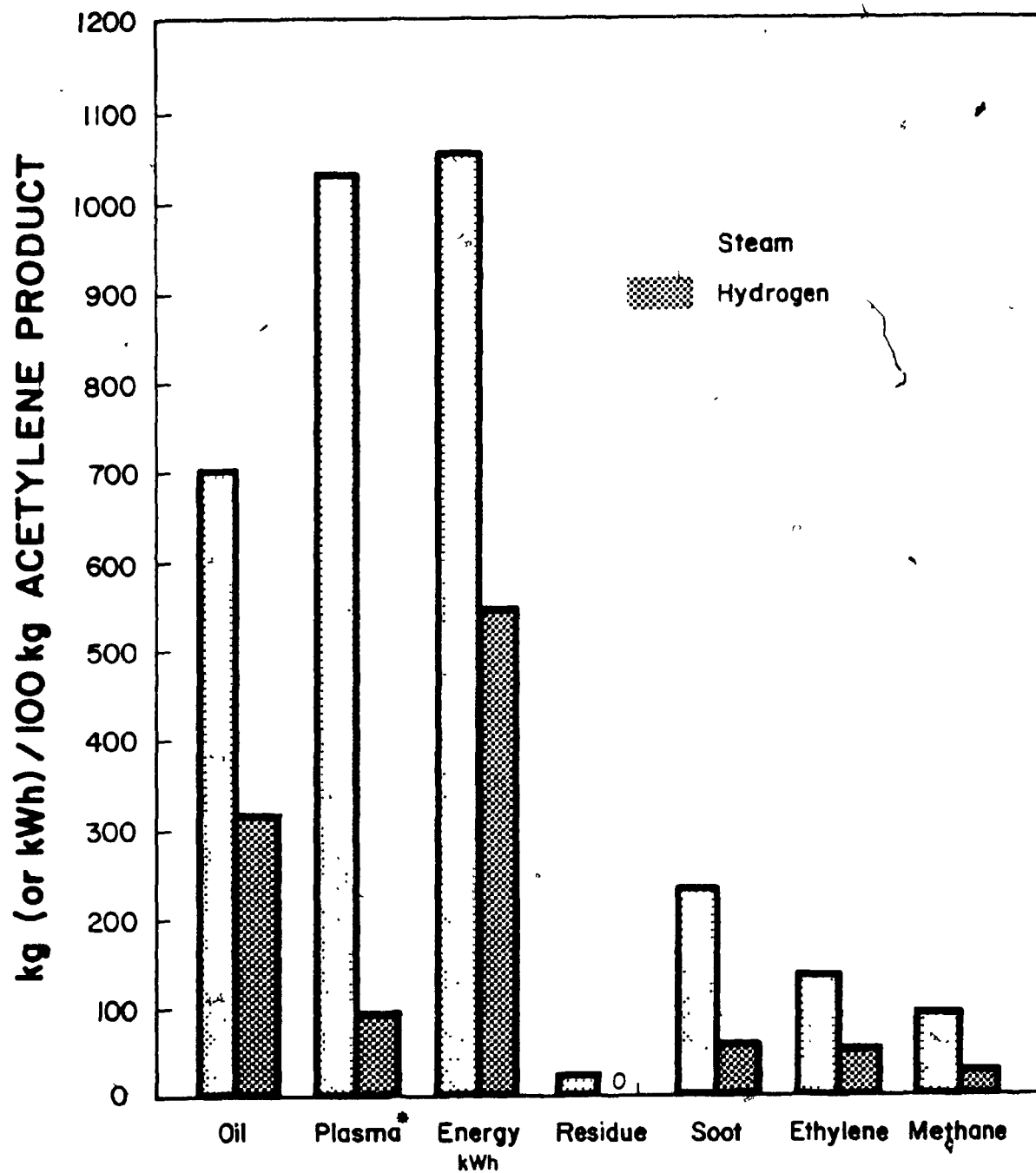


FIGURE 11

UTILITIES AND BY-PRODUCTS PER 100 KG ACETYLENE :

STEAM AND HYDROGEN PLASMAS

- steam plasma : experiment # 12
- hydrogen plasma : experiment #14



PROCESS VARIABLE AND PRODUCT

* Amount of hydrogen is approximately the same.

Effect of Specific Energy Consumption

Increasing power, for a given oil and plasma gas flow, was the equivalent of increasing the reaction temperature. Because of equipment constraints already mentioned it was difficult to vary the S.E.C. independently of the steam/hydrogen-to-oil mass ratio (as shown in Figure 8). The results given are therefore not at exactly equal mass ratios, but are close. The discussions will only be for those experiments without quench, so as to make the comparison independent of the quench effect.

For a hydrogen plasma increasing the S.E.C. from 0.6 to 2.2 kWh/kg, ex.#4 & 15 respectively, (at hydrogen-to-oil mass ratio of 0.07 kg hydrogen/kg oil) had the following effects (Figure 12):

- i) olefin gas concentrations increased slightly;
- ii) oil conversion to gas increased;
- iii) soot was formed only at higher specific energies;
- iv) residue remained only at low specific energies.

Additionally, less oil was needed to produce the same amount of acetylene at higher energies (see Figure 13). The formation of by-products (soot, ethylene, and methane), and energy requirements were significantly higher at higher specific energy consumptions.

For the steam plasma an increase from 2.6 to 4.7 kWh/kg, ex.#8 & 18 respectively, (at steam-to-oil mass ratio of 0.5 kg steam /kg oil) had the following effects (Figure 14):

- i) decreased hydrocarbon gas concentrations;
- ii) increased conversion to gas;
- iii) increased soot formation and much less residue.

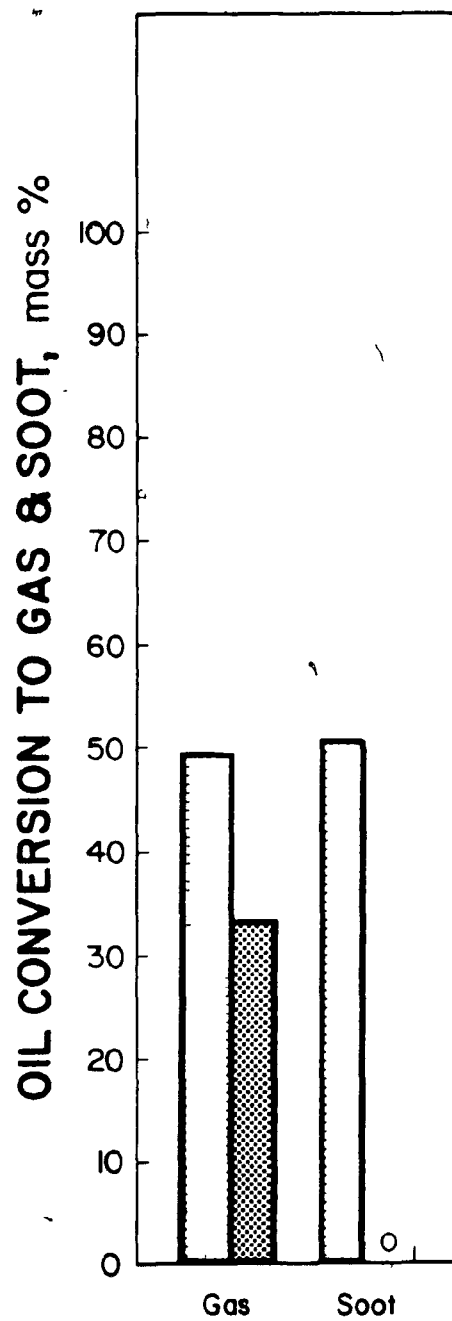
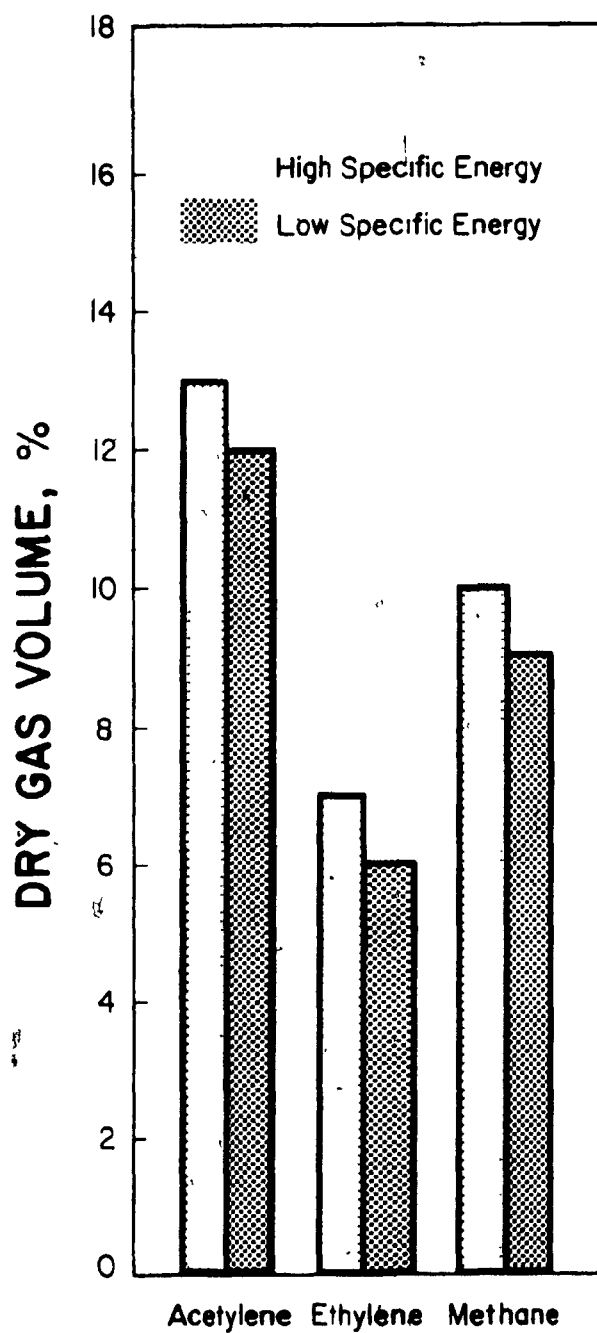
Although the energy input to produce 100 kg of acetylene at higher S.E.C.'s (Figure 15) was 23% more, 58% less oil was needed and by-product formation was reduced.

Gas conversions increased in the hydrogen plasma because at the higher S.E.C. the temperatures were higher. At the lower temperatures the heavy oil molecules were not vapourized, a prerequisite for the gas phase reactions occurring in the reactor. The soot and gases produced at these high S.E.C.'s are an indication that the heavy oil has been exposed to higher temperatures, because pyrolysis has not taken place to produce light or heavy liquid products.

However the decreased hydrocarbon gas concentrations in the steam plasma highlight the differences in this reacting atmosphere; that is, the presence of oxygen. At higher S.E.C.'s (and thus assumed higher temperatures) more carbon monoxide is formed, (increasing from 34 to 41 vol.%). At these higher temperatures there would be more free oxygen, and because the oxygen is more reactive than is the hydrogen, it reacted preferentially with the hydrocarbons and soot to reduce the hydrocarbon gas concentrations and increase the carbon monoxide concentrations. However this disadvantage (the production of more CO) is more than offset by the threefold increase in oil-to-gas conversion.

FIGURE 12ENERGY EFFECT ON COMPOSITION :HYDROGEN PLASMA

- high specific energy consumption: expt.#15 - 2.2 kWh/kg oil
- low specific energy consumption : expt.#4 - 0.6 kWh/kg oil



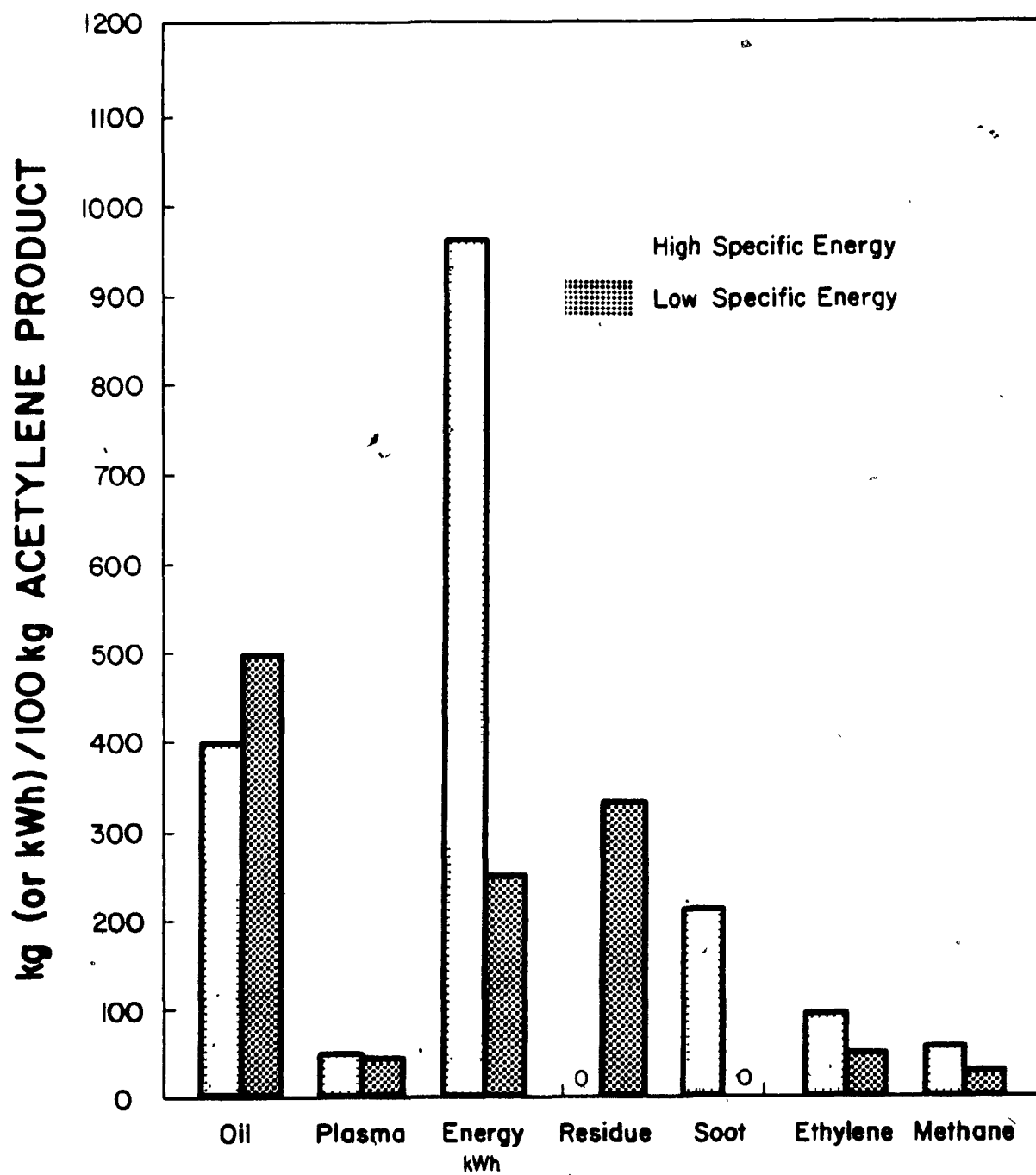
PRODUCT

FIGURE 13

UTILITIES AND BY-PRODUCTS PER 100 KG ACETYLENE :

ENERGY EFFECT ON HYDROGEN PLASMAS

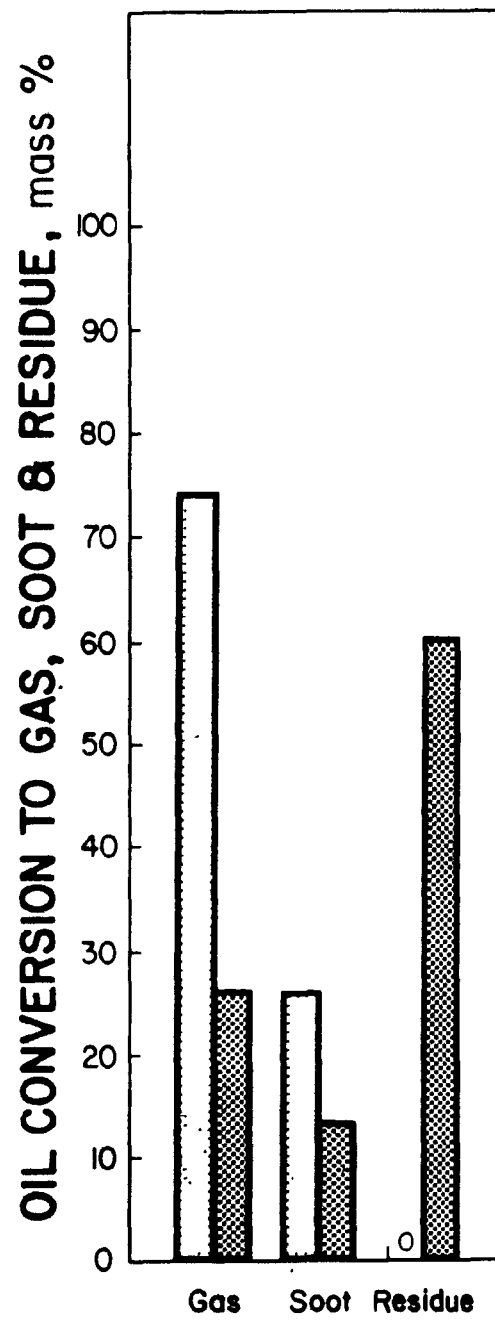
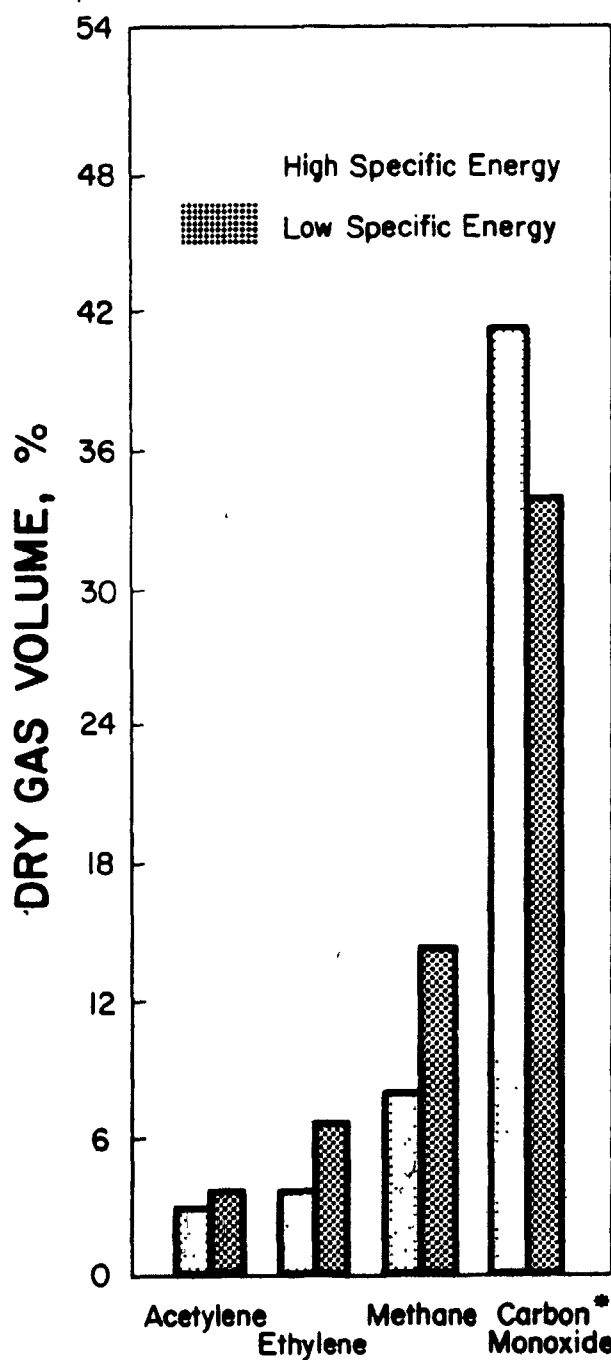
- high specific energy consumption : expt.#15 - 2.2 kWh/kg oil
- low specific energy consumption : expt.#4 - 0.6 kWh/kg oil



PROCESS VARIABLE AND PRODUCT

FIGURE 14ENERGY EFFECT ON COMPOSITION :STEAM PLASMA

- high specific energy consumption: expt.#18 - 4.7 kWh/kg oil
- low specific energy consumption : expt.#8 - 2.6 kWh/kg oil



PRODUCT

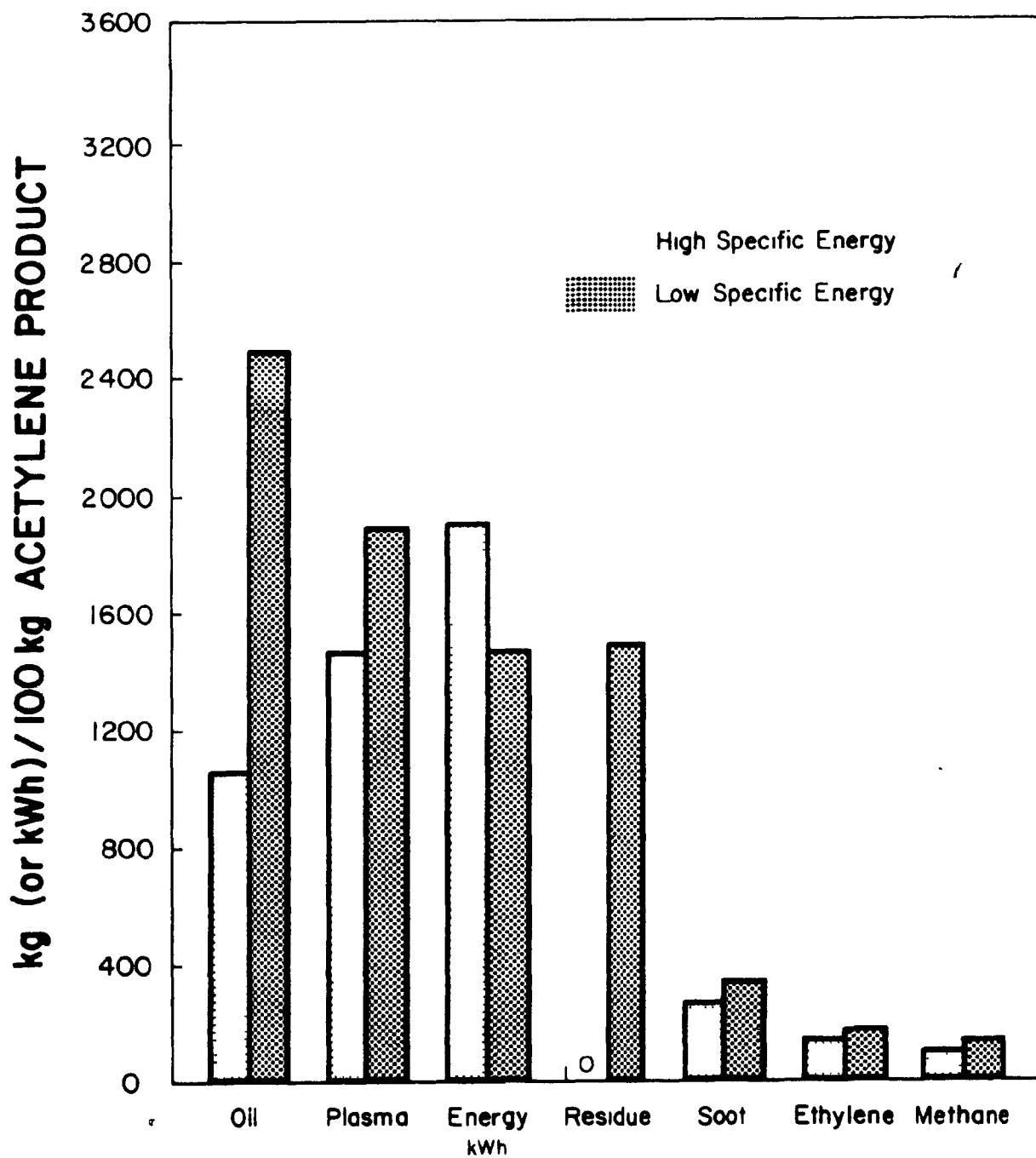
* No carbon dioxide.

FIGURE 15

UTILITIES AND BY-PRODUCTS PER 100 KG ACETYLENE :

ENERGY EFFECT ON STEAM PLASMAS

- high specific energy consumption: expt.#18 - 4.7 kWh/kg oil
- low specific energy consumption : expt.#8 - 2.6 kWh/kg oil



PROCESS VARIABLE AND PRODUCT

Effect of Stoichiometry

For the hydrogen plasma, without quench, increasing the hydrogen-to-oil mass ratio from 0.08 to 0.17, ex.#15 & 14 respectively, (at 2 kWh/kg oil) had the following effects (Figure 16):

- i) gas conversion increased from 48 to 80 wt.%
- ii) soot formation decreased by over 50 %
- iii) gas concentrations were about constant - acetylene increased while ethylene and methane decreased

As can be seen from Figure 17 the oil and energy needed per 100 kg of acetylene decreased by about 50%.

For the steam plasma, without quench, an increase from 0.65 to 1.12 kg steam/kg oil, ex.#18 & 9 respectively, (5.5 kWh/kg oil) had the following effects (Figure 18) :

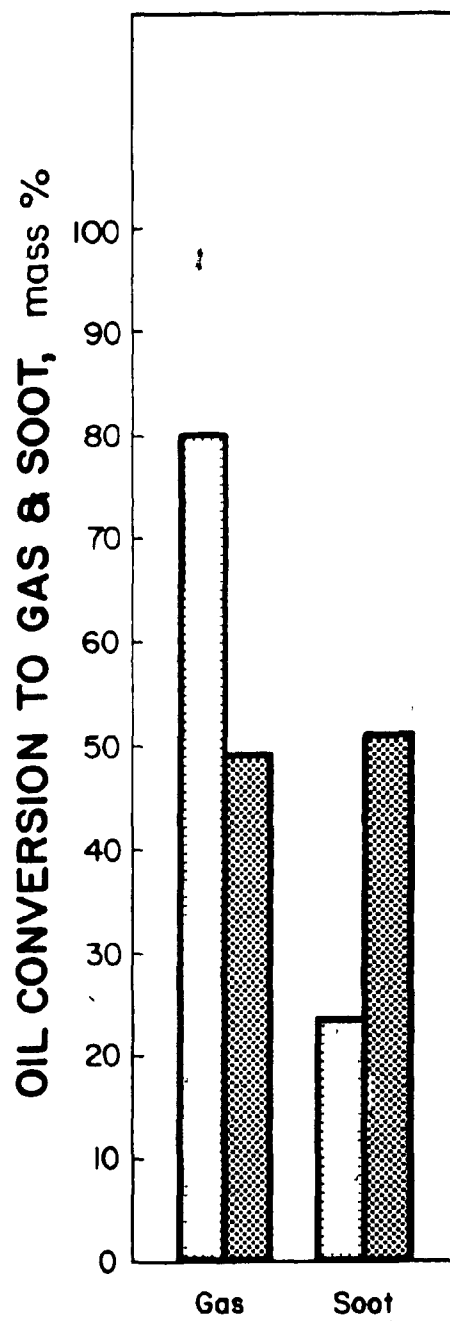
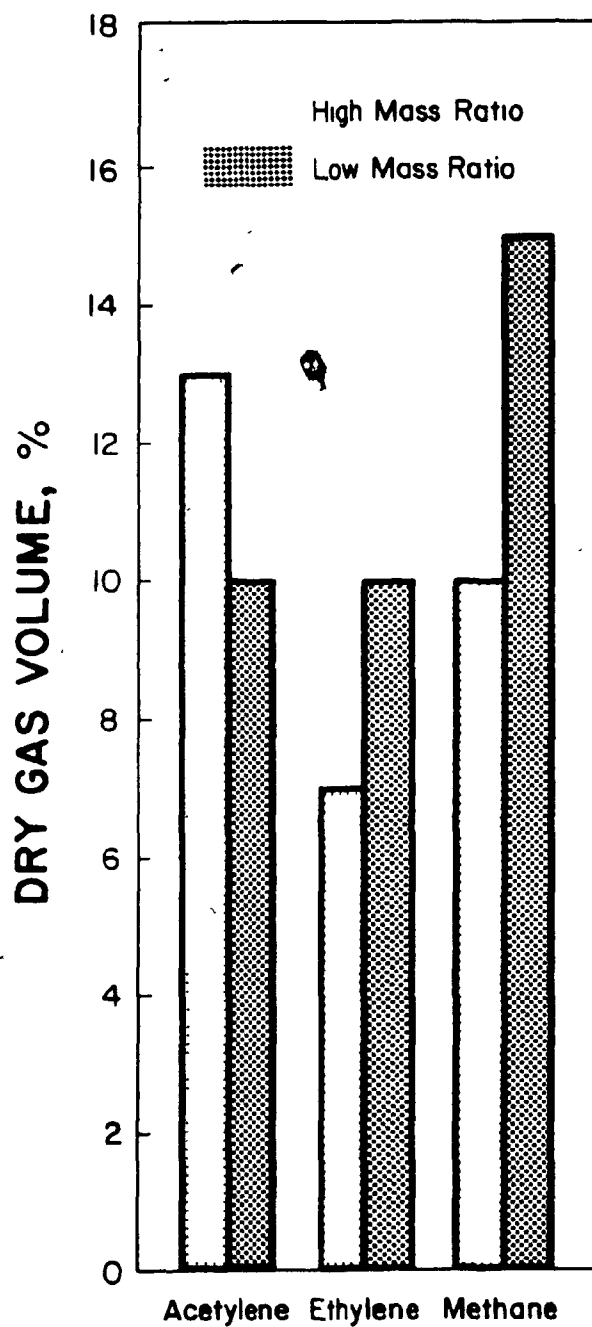
- i) increased oil to gas conversion from 74 to 87 wt.%, proportionally decreasing the soot formation
- ii) gas concentrations stayed about constant

Additionally, as shown in Figure 19, the oil and energy needed per 100 kg acetylene decreased by about 50%.

The increased gas conversions, and consequent decreased soot formation, were a result of more hydrogen being available for reaction. At the lower hydrogen/steam-to-oil mass ratios there was insufficient hydrogen for the carbon to react with, so that it remained as free carbon; that is, soot. Gas concentrations (volume percents) stayed about constant because the temperature was constant; it being the single most important influence on changing gas concentrations. Oil and energy needed per 100 kg acetylene decreased so drastically as a result of the increased gasification of the heavy oil to hydrocarbon gases.

FIGURE 16EFFECT OF STOICHIOMETRY ON COMPOSITIONHYDROGEN PLASMA

- O high mass ratio : expt.#14 - 0.17 kg hydrogen/kg oil
- low mass ratio : expt.#15 - 0.08 kg hydrogen/kg oil



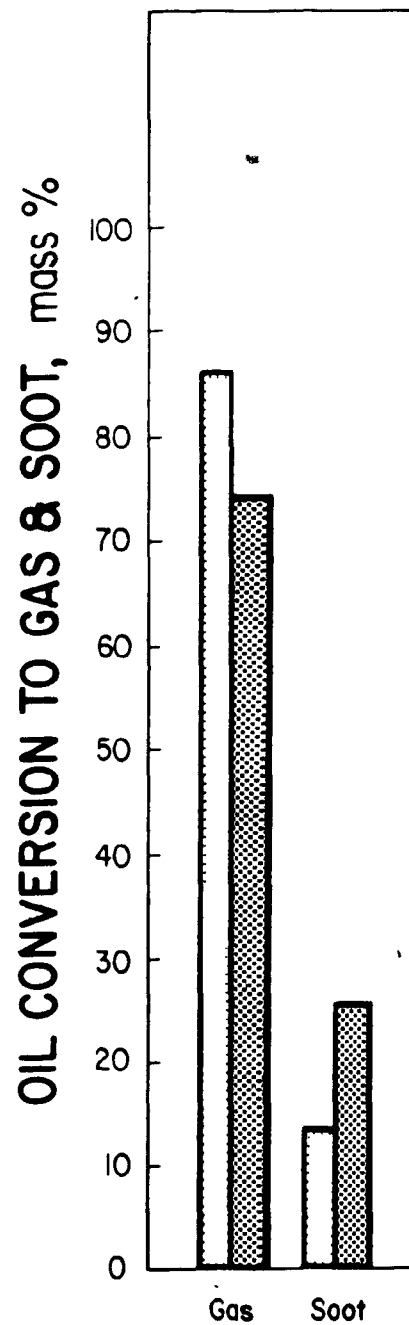
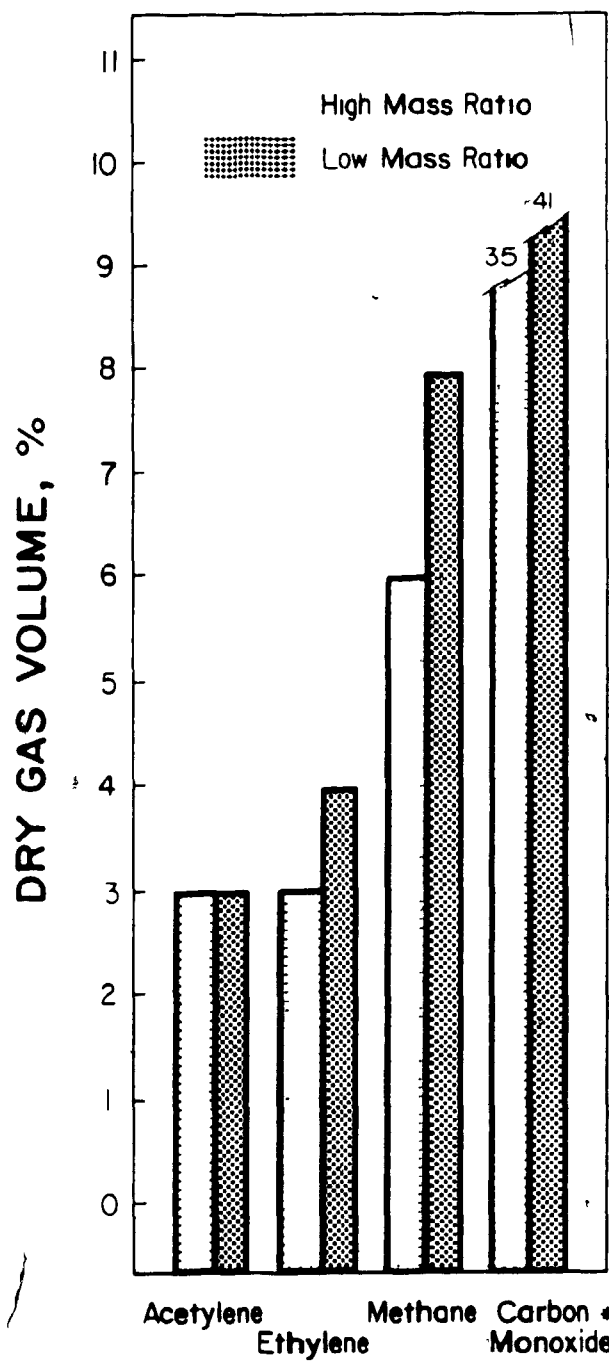
PRODUCT

FIGURE 18

EFFECT OF STOICHIOMETRY ON COMPOSITION :

STEAM PLASMA

- high mass ratio : expt.#9 - 1.12 kg steam/kg oil
- low mass ratio : expt.#18 - 0.65 kg steam/kg oil



PRODUCT

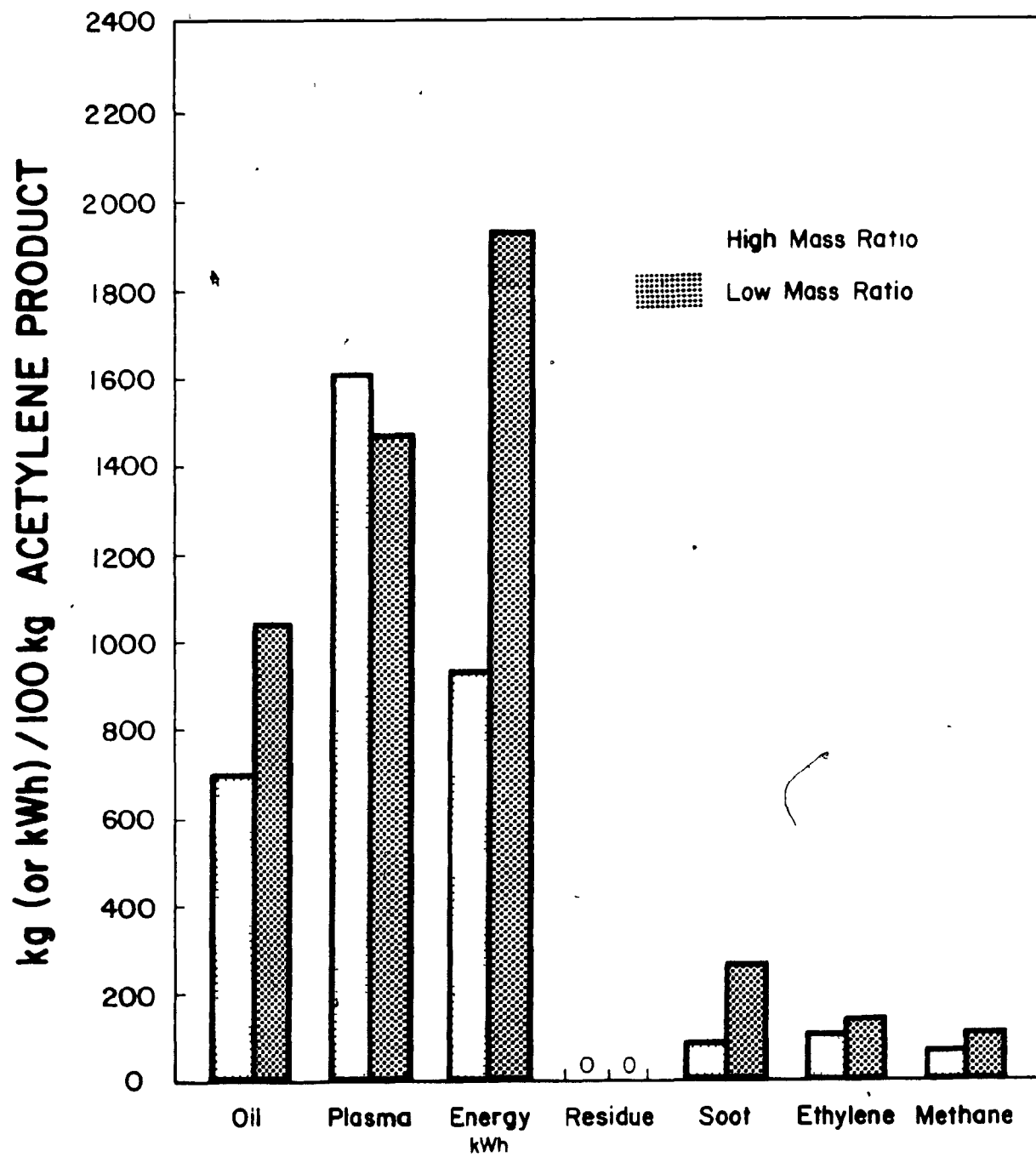
* No carbon dioxide.

FIGURE 19

UTILITIES AND BY-PRODUCTS PER 100 KG ACETYLENE :

STOICHIOMETRIC EFFECT ON STEAM PLASMA

- high mass ratio : expt.#9 - 1.12 kg steam/kg oil
- low mass ratio : expt.#18 - 0.65 kg steam/kg oil



PROCESS VARIABLE AND PRODUCT

Quench

The quench was meant to reduce the reaction time and thereby allow the examination of this factor. However it only served to slow the reaction by decreasing the overall temperature. For instance, measured temperatures in the steam plasma decreased from 2100°C to 900°C when the quench water was applied. (These measurements were taken above the quench entrance line.)

In the hydrogen plasma, at settings of about 2.3 kWh/kg oil and 0.09 kg hydrogen/kg oil, the change to quench (ex.#15 without and ex.#13 with) had the following effects (Figure 20):

- a) olefin gas fractions decreased by over 50%;
- b) conversion to hydrocarbon gas increased slightly from 46 to 59 wt.%;
- c) soot formation halted and the residue remaining increased from 0 to 41 wt.% of feed.

As shown in Figure 21 about 100% more oil feed was needed for an equivalent amount of acetylene produced.

In the steam plasma, at settings of about 5.5 kWh/kg oil and 0.85 kg steam/kg oil, (Figure 22) results were very similar to those mentioned above (ex.#12 & 11 respectively) :

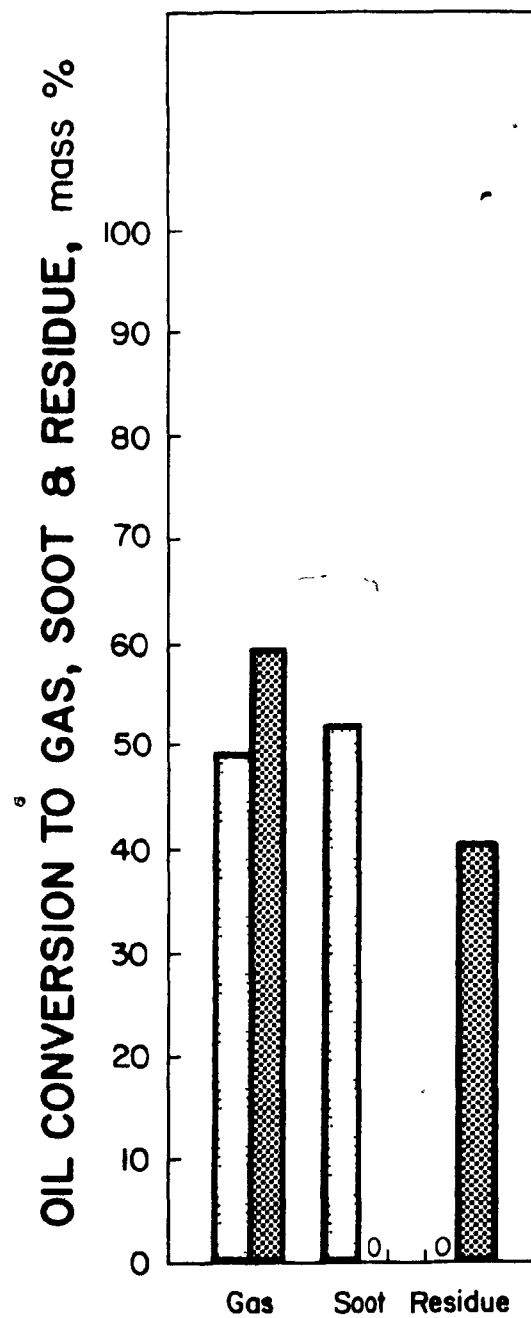
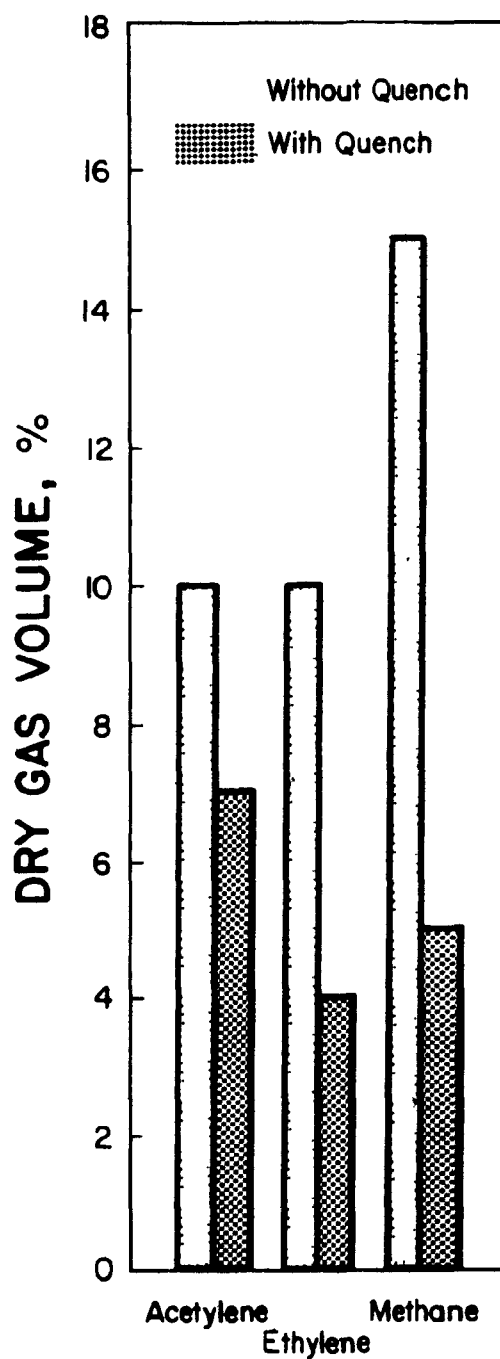
- a) acetylene concentrations decreased from 5 to 2 vol.%
- b) gas conversion decreased from 63 to 43 wt.%
- c) unconverted oil increased from 4 to 57 wt.% of feed.

The oil, plasma gas, and energy needed to produce the same amount of acetylene tripled (Figure 23).

All these results point to one thing: that the water quench did not perform its intended function of simply reducing the reaction time (with expected higher acetylene and reduced methane and ethylene gas yields). The water only cooled the reaction zone temperature to the point where less gasification occurred. This is highlighted by the vastly increased residue collected, and the halted soot production. And with the steam plasma carbon dioxide gas, which is produced only at lower temperatures, was found when the quench was used. These results were caused by the reactor design. The atomized quench water sprayed perpendicularly to the reactor walls at a high velocity. The water reflected off in all directions - including the reaction zone. The result was a temperature decrease in the reactions zone.

FIGURE 20QUENCH EFFECT ON COMPOSITION :HYDROGEN PLASMA

- without quench: expt.#15 - 2.3 kWh/kg oil, 0.09 kg H₂/kg oil
- with quench : expt.#13 - (the same)



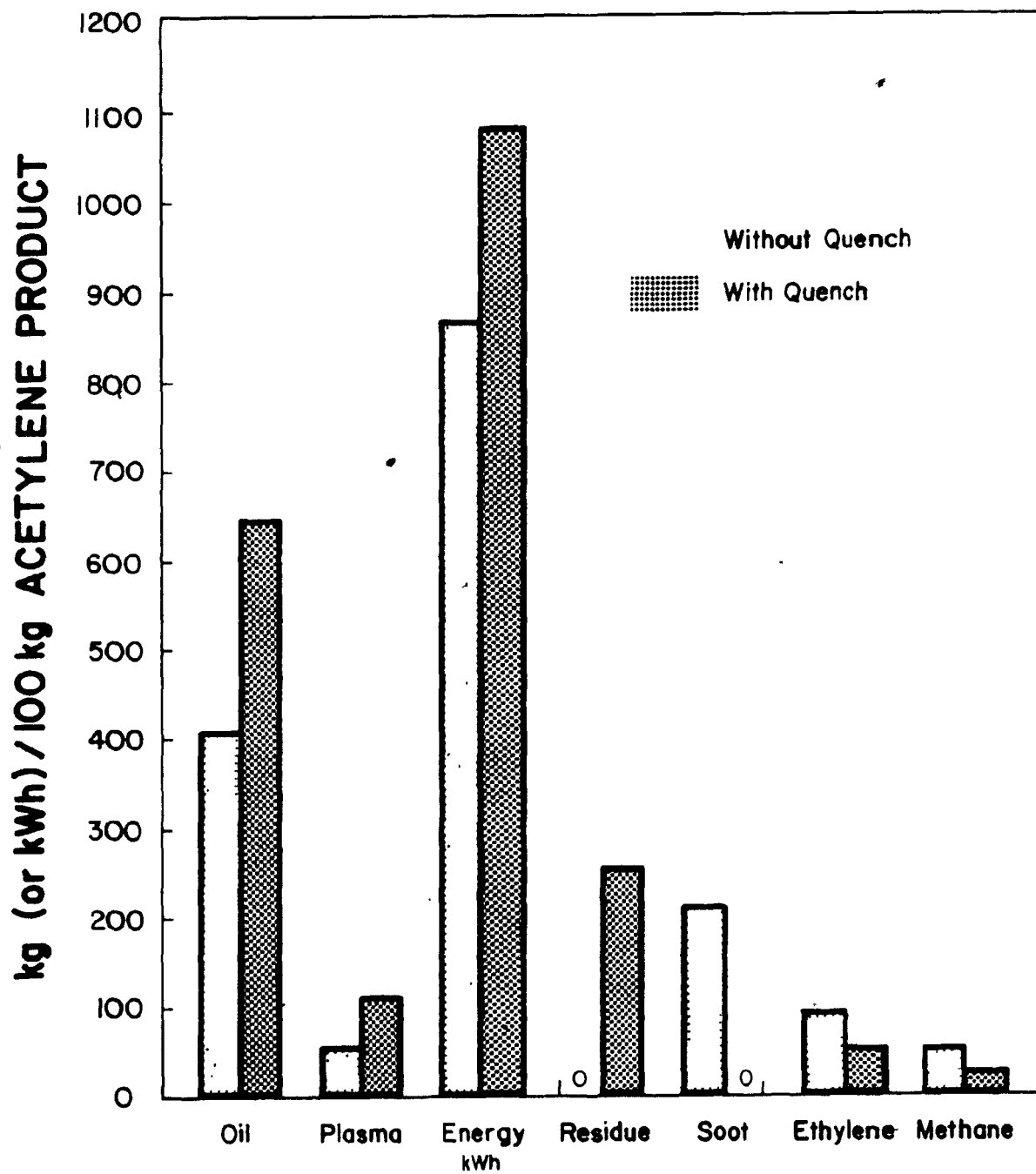
PRODUCT

FIGURE 21

UTILITIES AND BY-PRODUCTS PER 100 KG ACETYLENE :

QUENCH EFFECT ON HYDROGEN PLASMA

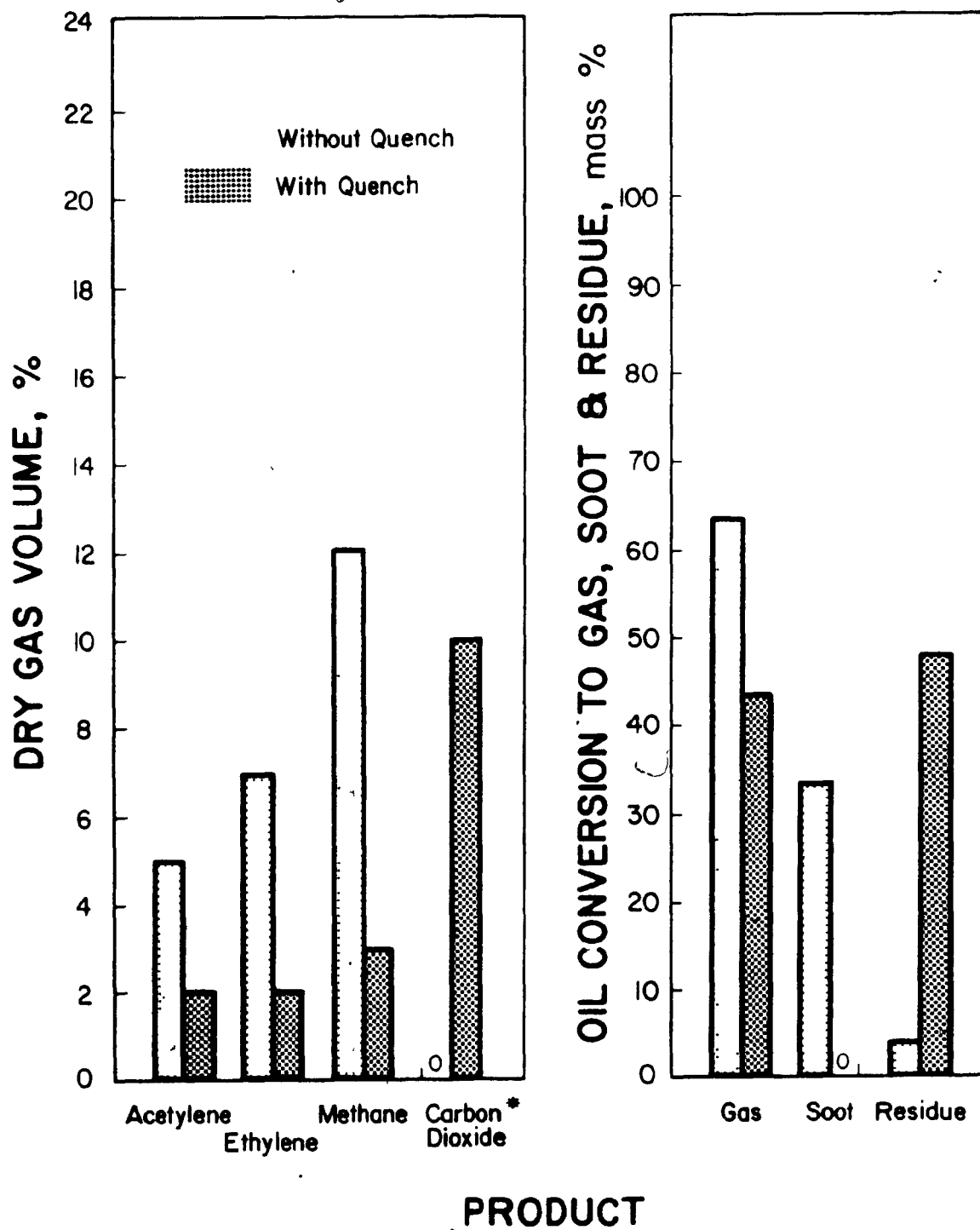
- without quench : expt.#15 - 2.3kWh/kg oil, 0.09 kg H₂/kg oil
■ with quench : expt.#13 - (the same)



PROCESS VARIABLE AND PRODUCT

FIGURE 22QUENCH EFFECT ON COMPOSITION :STEAM PLASMA

- O without quench: expt.#12- 5.5 kWh/kg oil, 0.85 kg H₂O/kg oil
- with quench : expt.#11- (the same)



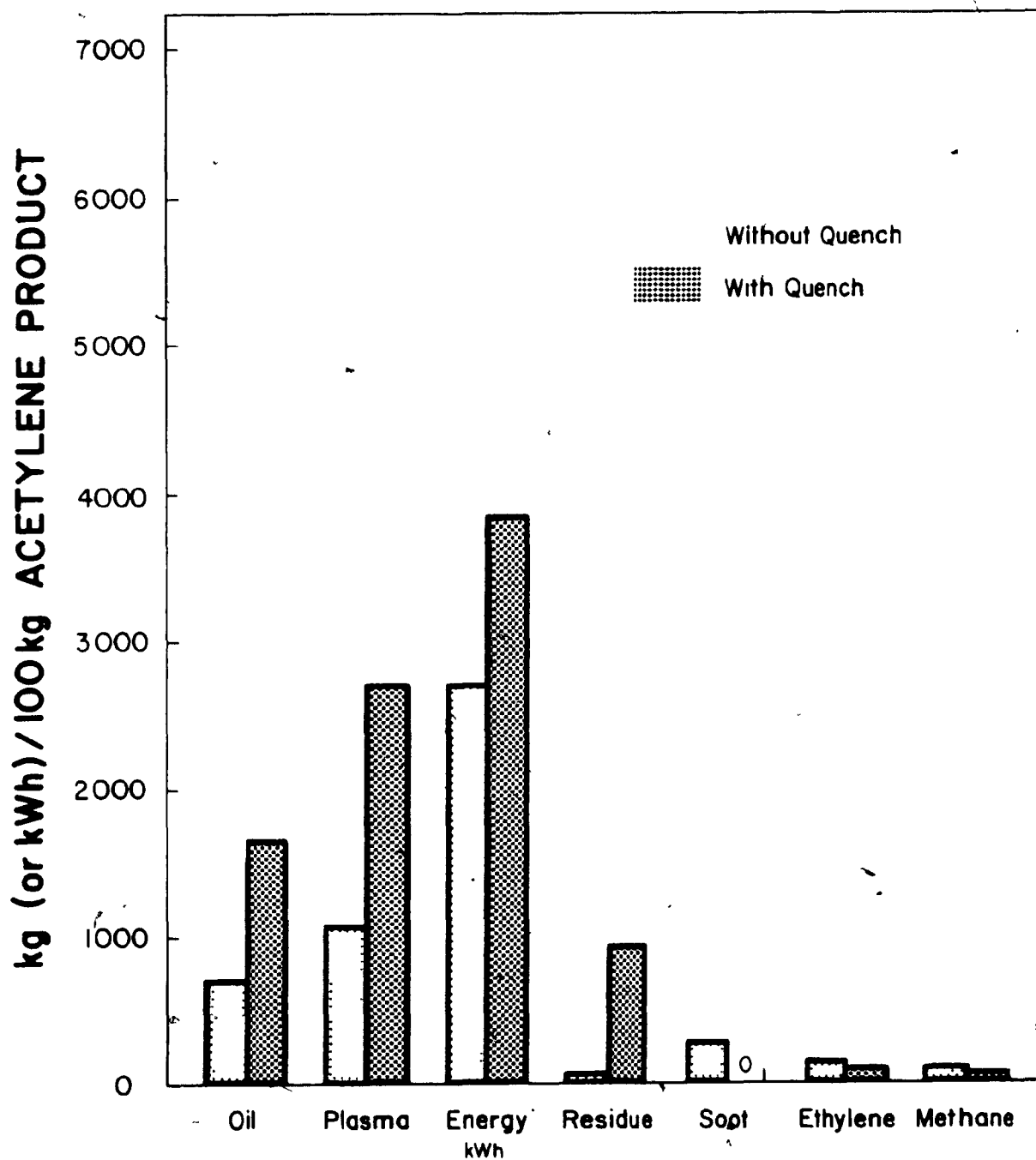
* Carbon monoxide stayed constant at 21 volume %.

FIGURE 23

UTILITIES AND BY-PRODUCTS PER 100 KG ACETYLENE :

QUENCH EFFECT ON STEAM PLASMA

- without quench: expt.#12 - 5.5kWh/kg oil, 0.85 kg H₂O/kg oil
■ with quench : expt.#11 - (the same)



PROCESS VARIABLE AND PRODUCT

Comparison With Other Processes

Comparisons of results of the steam plasma process with the other heavy oil processes discussed in this thesis are presented in the table following. First (Table VI), the lower temperature processes (CANMET and Superheated Steam) produce significant amounts of light hydrocarbons (boiling points less than approximately 500°C). They use longer residence times (in the order of a second) than the two plasma processes presented. Although the CANMET process data are unavailable similar processes have temperatures and residence times in the same region as the Japanese process. This is by design. The CANMET process is designed to produce light liquid hydrocarbons and uses a special additive to encourage conversions to liquids. The Japanese steam process is a compromise - achieving reduced liquid, and increased gas and pitch yields, with a less expensive and a less complex process.

In both the Huels and steam plasma processes the high temperatures preclude the production of liquids, rather favouring gasification. The acetylene gas fraction produced with the steam plasma was about a third of that produced by the Huels process. However the ethylene concentration was equal, and the methane was twice that of Huels. These differences result from the lack of quench for the steam plasma. As can be seen from Table VII the Huels process required less feed and energy to produce the same 100 kg of acetylene. Huels was able to recycle its unconverted oil (feed was crude oil) and thus increase the process efficiency. However the hydrogen plasma results from this research (expt.#14) gave better results than those of Huels - reduced oil feed and energy for equivalent acetylene production. This can be misleading since the anode lives of this process are only a few minutes and the Huels reactor can run continuously for hundreds of hours.

TABLE VI : COMPARISON OF HEAVY OIL PROCESSES

Process and Type	Temp. °C	Gas WT.% acetylene	ethylene	methane	Liquid Wt.% light pitch	Time millisec
------------------	----------	-----------------------	----------	---------	----------------------------	------------------

CANMET

Hydro-Cracking	-	0	0	2	90(1) 8	-
----------------	---	---	---	---	---------	---

Superheat-

ed Steam	950	21.5	20.4	15.7	18(3) 13	101
----------	-----	------	------	------	----------	-----

Pyrolysis

(2)

Huels

Hydrogen	3000	14.5 vol%	6.5 vol%	6 vol%	0	35(7) 1-4
----------	------	-----------	----------	--------	---	-----------

Arc (4)

Steam

Plasma	1800	14	19	13	0	37(6) 3-7
--------	------	----	----	----	---	-----------

(5)		5 vol.%	7 vol.%	12 vol.%		(8)
-----	--	---------	---------	----------	--	-----

- (1) - light hydrocarbons with boiling point less than 524°C
- (2) - results for Kafuji bottoms feed
- (3) - light hydrocarbons with boiling point less than 450°C
- (4) - crude oil feed
- (5) - ex. # 12
- (6) - includes 33 wt.% soot
- (7) - 20 wt.% soot
- (8) - estimated from mean jet temperature and flowrate

TABLE VII : COMPARISON OF PLASMA-HEAVY OIL PROCESSESPARAMETERS PER 100 KG OF ACETYLENE PRODUCT

Process	Feed kg	Methane kg	Ethylene kg	Waste oil-kg(1)	Soot kg	Energy kWh
---------	------------	---------------	----------------	--------------------	------------	---------------

Huels

Hydrogen	367	48	82	127	-	980
----------	-----	----	----	-----	---	-----

Arc

Hydrogen

Plasma	233	29	52	0	45	383
--------	-----	----	----	---	----	-----

(2)

Steam

Plasma	703	91	134	26	235	1056
--------	-----	----	-----	----	-----	------

(3)

(1) - 20 wt.% soot

(2) - ex.#14

(3) - ex.#12

CONCLUSION

Heavy oil was reacted in both simulated steam and hydrogen plasmas. In both cases the most significant reactions were those of gasification and pyrolysis. Comparisons of results, from the two plasmas, were made. Three other operating variables were changed, namely: the energy-per-kg-oil, the steam/hydrogen-to-oil mass ratio, and the use or not of quench. Comparisons were made with the results of other heavy oil processes described in this study. This represents a preliminary study into this area.

The major reaction products were acetylene, ethylene, methane, and soot. Gas compositions ranged from 3 to 15 vol.% and soot yields from 0 to 50 wt.%. Oil to gas conversions of 100% were achieved.

Steam plasma differed most significantly from hydrogen plasma in that carbon monoxide constituted a high fraction of the gas. This is a result of reaction with oxygen made available from the dissociated steam. This reduced the carbon available for reaction to olefins, and hence the olefin gas concentrations were less with the steam plasma.

Increased energy-per-kg-oil (and hence temperatures) increased oil-to-gas conversions, and soot formation for both plasmas. However, while olefin gas fractions increased with increasing energy for the hydrogen plasma, a decreased

hydrocarbon gas fraction was observed with the steam plasma. This was a result of increased fractions of dissociated oxygen, available at the higher temperatures, reacting to form larger fractions of carbon monoxide.

Increased steam/hydrogen-to-oil mass ratios caused increased oil-to-gas conversions, and decreased soot formation, for both plasmas. As the mass ratio increased (within the limits given) more hydrogen was made available for reaction, so that the carbon could react with it to form olefins, and not remain as free carbon (soot). Gas compositions remained constant because temperature, not mass ratio, had the biggest influence on the gas composition.

The use of water quench did not reduce the residence time. It simply sprayed into the reaction zone and slowed gasification considerably.

It can be concluded that although steam offers considerable cost advantages over hydrogen as a plasma gas the olefin production is decreased because of carbon monoxide formation. Furthermore, this process, like previous plasma processes, gasified and pyrolyzed, rather than liquefied, the heavy oil. Gases rather than liquids were the main reaction products because the homogeneous gas forming reactions were so much faster than the multistage liquid-forming reactions. However if olefins and/or synthesis gas products are desired to be obtained from heavy oil by relatively simple means this process offers great potential.

RECOMMENDATIONS FOR FURTHER WORK

The results of this work, while giving a good overall picture of the steam plasma-heavy oil reaction, have contributed little to a fundamental understanding of the reactions occurring. Additionally, the equipment used was not specifically designed for this work, so that process optimization was not possible.

Therefore the following is recommended:

- a) a kinetic study of the steam plasma-heavy oil reactions on single droplets;
- b) process optimization with a specially designed reactor and system, including recycle of the unreacted oil and consultation with Huels to discuss their experience;
- c) experiments under more severe conditions: higher temperatures and higher steam-to-oil mass ratios.

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APPENDICES

APPENDIX I

EQUIPMENT DETAILS

The following diagrams have been referred to in the main body of the thesis. They serve to better clarify the description of the equipment used.

The following has been included:

- i) photograph of a hydrogen plasma
- ii) bottom of the DC-jet plasma torch
- iii) the preheater
- iv) effluent system

FIGURE 1

Photograph of Hydrogen Plasma

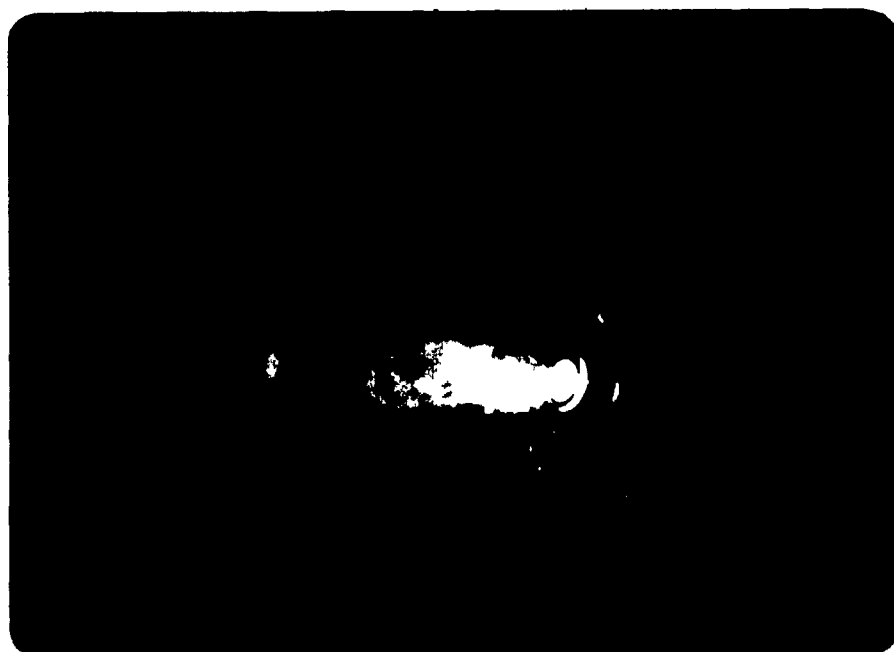
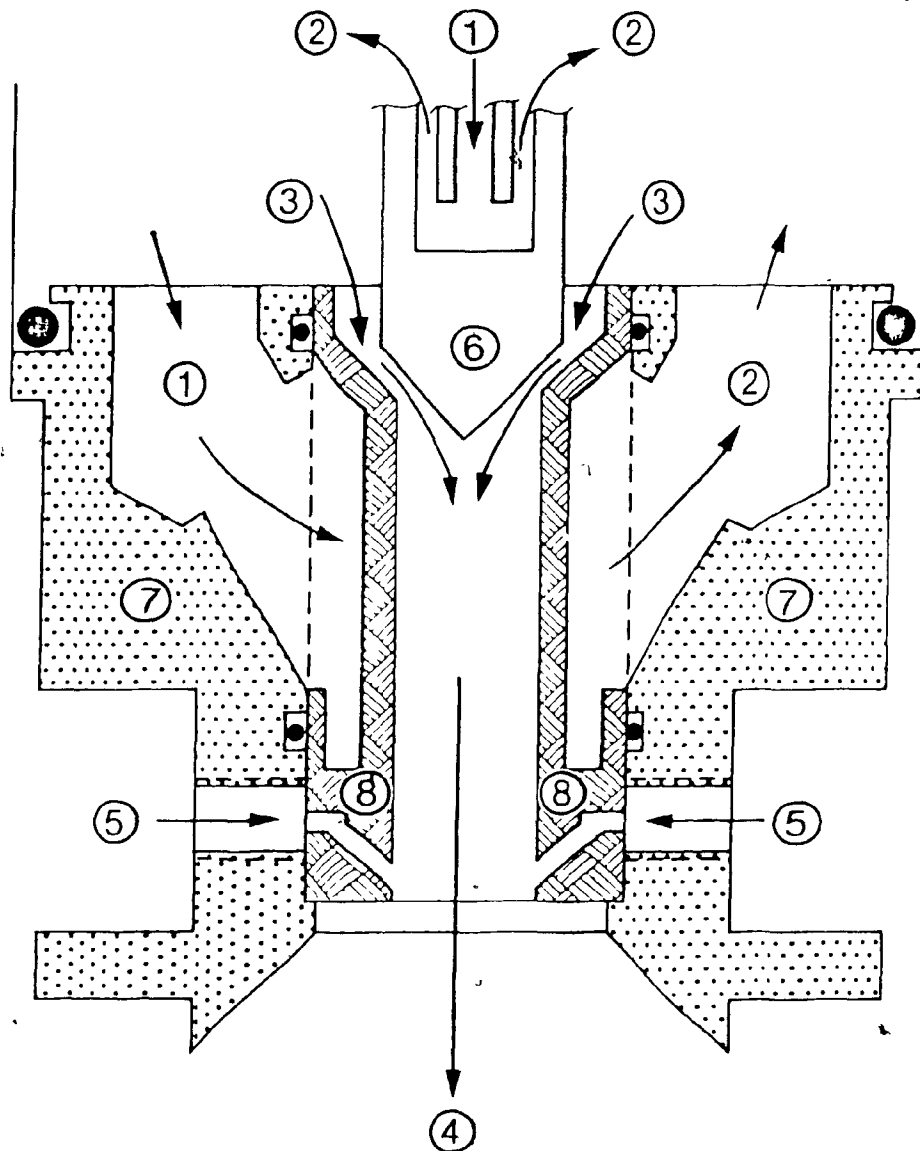


FIGURE 2Bottom of the DC-Jet Plasma Torch

length of anode holder: 4 cm diameter of inner annulus: 5 mm

outside diameter of anode holder: 2 cm



1. Cooling water in
2. Cooling water out
3. Plasma gas in
4. Plasma gas out
5. Auxiliary gas injection
6. Cathode
7. Anode holder
8. Anode

FIGURE 3

The Preheater

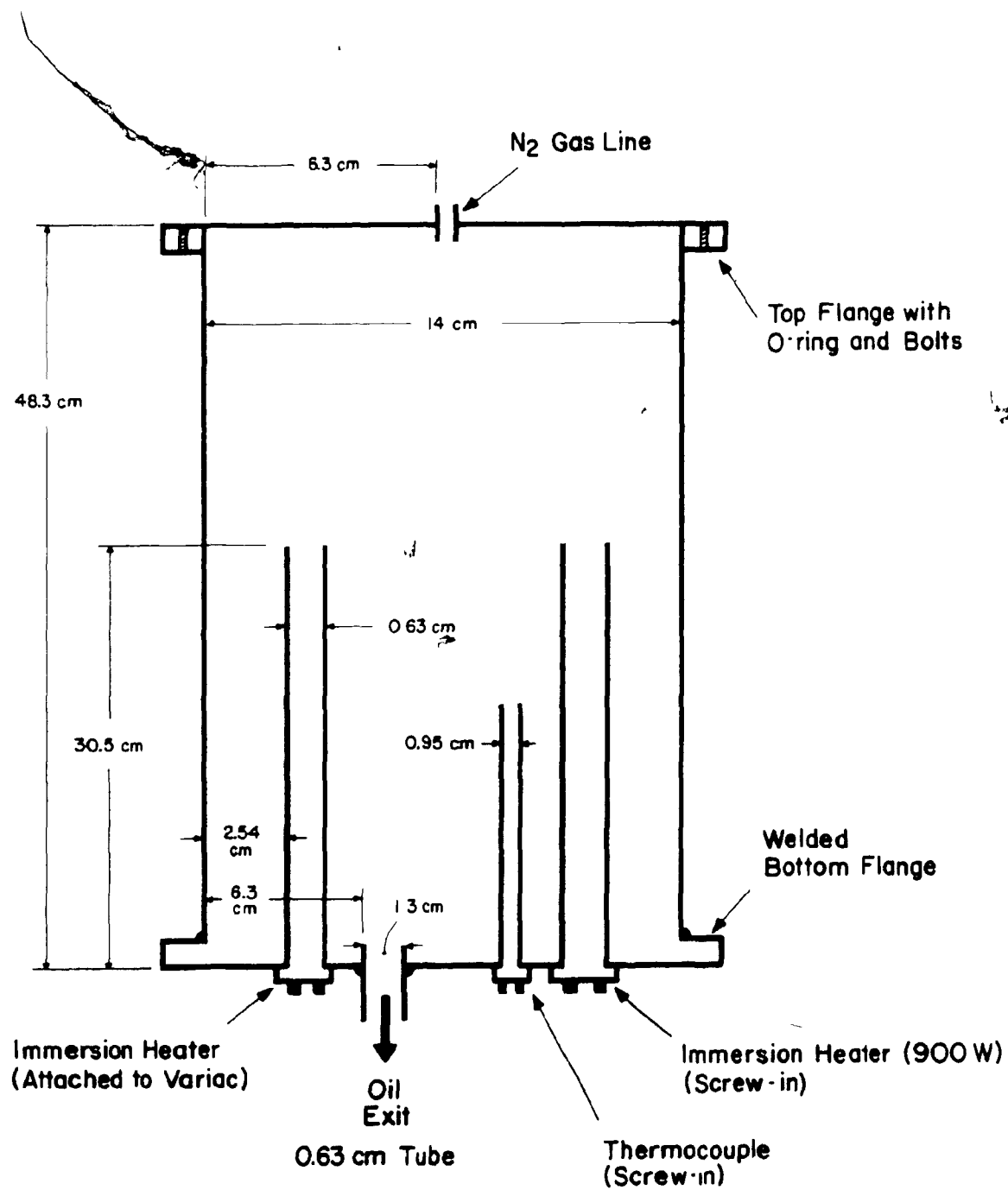
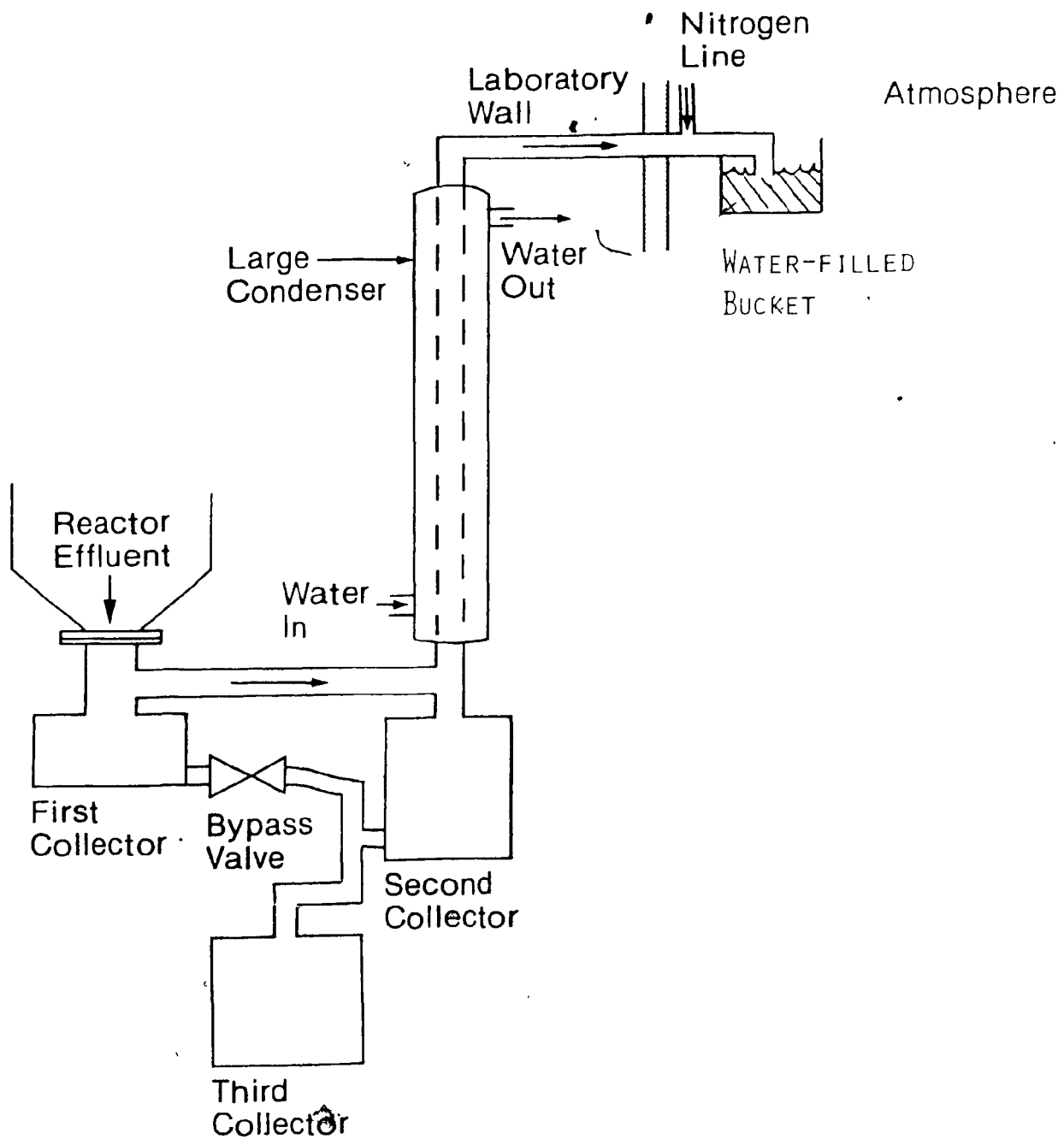


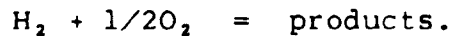
FIGURE 4

Effluent System



APPENDIX IICalculations for the Plasma Temperature

To estimate the plasma flame, torch exit, temperature and enthalpy the EQUILIB program of the McGill Music computer system was employed. Furthermore, the composition at equilibrium was calculated. For the simulated plasma the reaction was:



, where the products are those as discussed in the section on steam plasma in the literature survey.

To calculate the temperature of the simulated steam plasma, based on these equilibrium predictions, the power input into the torch was equated with the enthalpy of reaction (as calculated by EQUILIB). The power input to the torch was:

$$Q = \eta IV$$

where: Q : power, J/s

η : efficiency

I : current, amps

V : voltage, volts (characteristic for hydrogen)

(EQUILIB is a Gibb's Free Energy minimization program used at McGill for Thermodynamic analysis of reactions.)

Given that the characteristic voltage of the hydrogen is 160 V, that the normal operating efficiency of the torch is 75%, and that a stable current for the torch with hydrogen is 200 A, Q can then be calculated to be:

$$Q = 0.75 (200) (160) = 24,000 \text{ J/s}$$

To convert these units to those appropriate for enthalpy data:

$$H = Q/m \text{ where: } m = \text{mass flowrate of steam, gmol/s}$$

The known flowrate of the hydrogen in the plasma torch ranges about 630 ft³/h:

$$\begin{aligned} m &= 630 (1000/35.3) (273/298)/22.4 \\ &= 724 \text{ gmol/h (3600)} \\ &= .2025 \text{ gmol/s} \end{aligned}$$

Therefore the enthalpy of the plasma gas is, at these maximum settings, 118,889 J/gmol. This corresponds to a temperature of 3400 K, as calculated with EQUILIB.

The same procedure was carried out for hydrogen alone. The maximum plasma temperature was found to be 6000 K.

TABLE I : HIGH TEMPERATURE STEAM PROPERTIESEQUILIBRIUM THERMODYNAMIC PROPERTIES AT 1 ATMOSPHERE

T	H	S	G	C _p	M	TOTAL
K	kcal/mol	cal/mol	kcal/mol	cal/mol/K	g/mol	MOLES
1000	-51.602	55.521	-1.7.103	9.806	18.016	1.000
2000	-39.974	63.104	-166.102	14.386	17.952	1.004
3000	-5.614	65.002	-200.621	63.724	15.366	1.172
3400	25.249	60.138	-174.221	101.677	12.036	1.497

MOLE FRACTIONS AT 1 ATMOSPHERE

T(K)	H ₂ O	HO	H	O	H ₂	O ₂
1000	1.000	0.0	0.0	0.0	0.0	0.0
2000	0.9096	0.00211	0.00013	0.000033	0.0058	0.0023
3000	0.6437	0.09286	0.05932	0.024507	0.1335	0.0461
3400	0.3037	0.14701	0.28741	0.094196	0.1839	0.0599

LN(KP) : EQUILIBRIUM CONSTANT OF REACTION

T(K)	H ₂ O=H+HO	HO=H+O	2 H = H ₂	2 O = O ₂
1000	-45.0182	-39.628	39.799	45.15716
2000	-15.130	-13.15.35	12.81289	14.61841
3000	-4.76101	-4.15693	3.63954	4.34078
3400	-2.31090	-2.0816	1.45308	1.91106

APPENDIX IIIProceduresProcedures

1. The oil heater was switched on several hours before start-up.

2. A preliminary check of the utilities and safety systems by the operators.

3. The torch was checked for gas and water leaks, the argon gas flow set and the arc centered.

4. The argon plasma was started, then transferred over to a hydrogen/steam plasma, the quench water flow started, and oil flow began once the system had reached a stable temperature and pressure.

5. After about two minutes samples were taken over the next several minutes and temperatures and pressures at each sample time noted.

6. The oil, steam, and quench flows were stopped and argon plasma allowed to purge the system.

7. The gas samples were analyzed immediately, the liquids and solids collected and a portion sent to the Imperial Oil Research Lab in Sarnia for analysis, the quench water and oil preheater volumes measured, and the whole apparatus cleaned.

APPENDIX IVOrifice Plate Calibration Curves

On the following two pages are the two calibration curves used for the data analysis. The first shows the measured flowrates for air and corresponding manometer height measurements. The second shows lines corresponding to equations with density corrections made for several possible plasma gases: hydrogen, steam, and argon.

FIGURE 5

ORIFICE PLATE CALIBRATION CURVE :

MEASURED

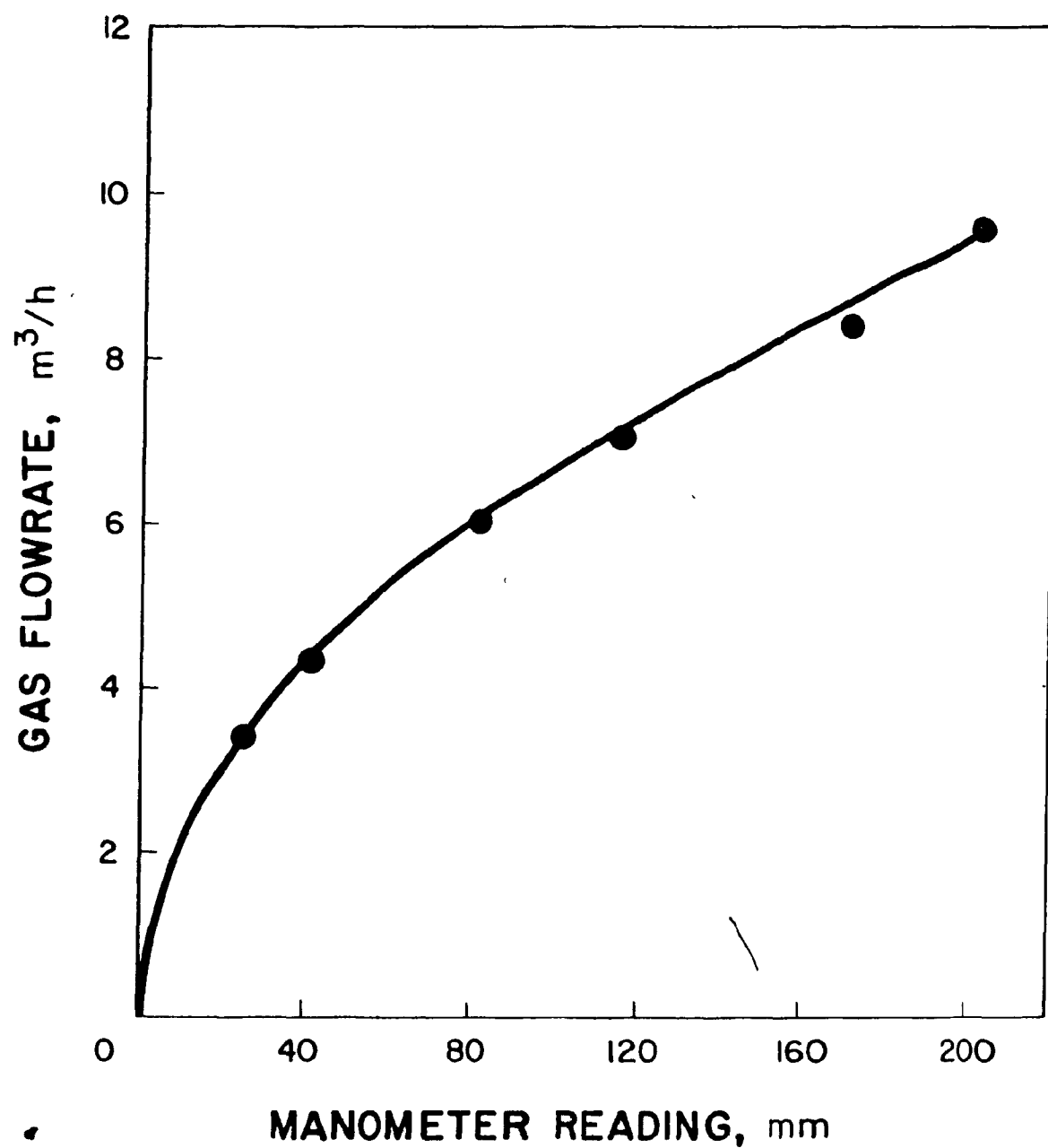
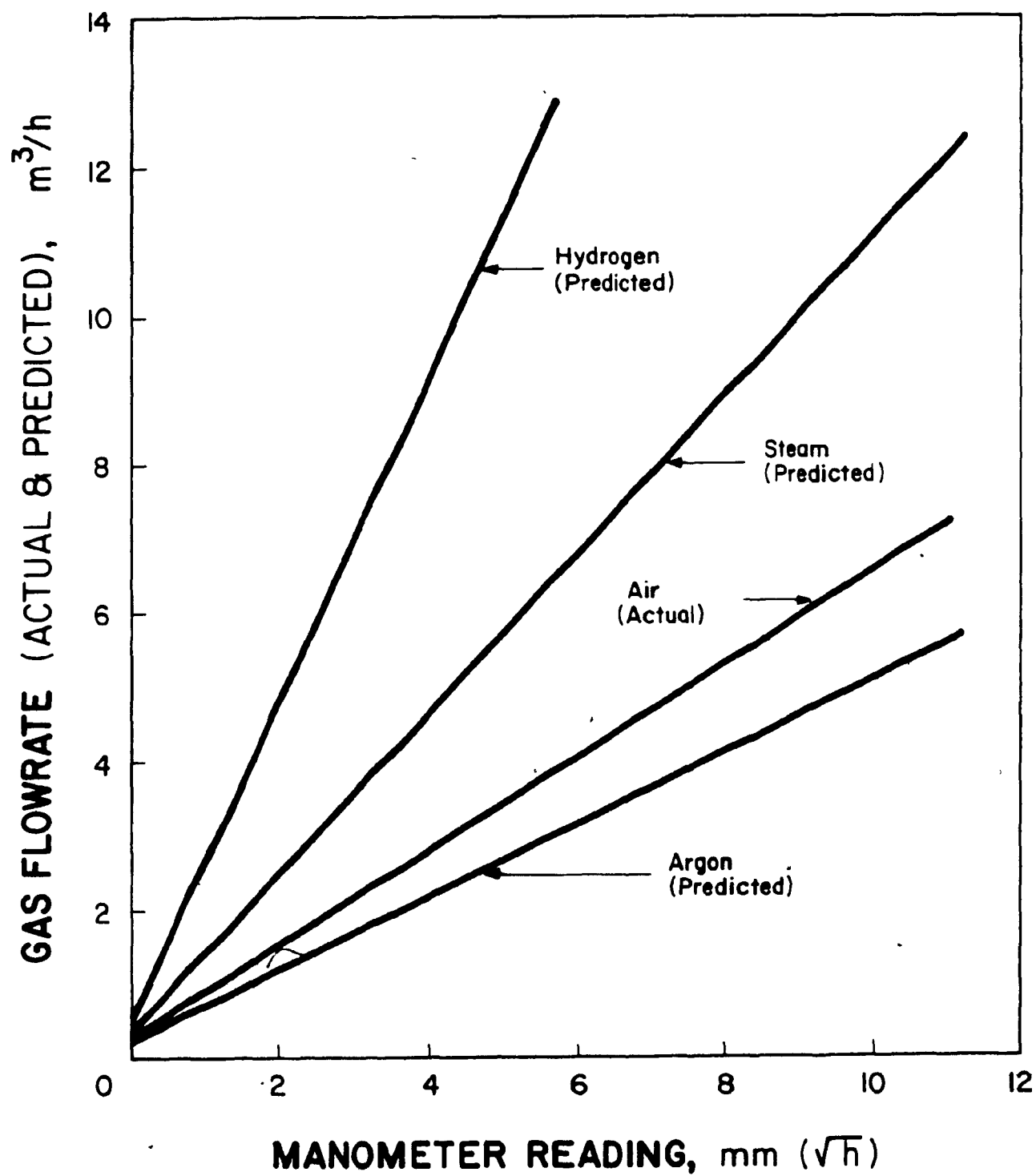


FIGURE 6

ORIFICE PLATE CALIBRATION CURVES :

CALCULATED



APPENDIX V

MASS BALANCE COMPUTER PROGRAM

*BATCH PRINTA CFM0000 CYB9 (999,9999)

/ID MUSJOB CYB9 000 010 050 000 R=BH106 C=1 F=
**EXCESSIVE TIME ESTIMATED ASSUMING 180 SERVICE UNITS
/SYS REQ=200
/LOAD WATFIV

C \$WATFIV NOLIST
C PROGRAM MASS16, HYDROGEN PLASMA - NO QUENCH
C THIS IS USING MUSIC 'A' SUBMITTING MODE
C
C THIS PROGRAM DOES A MASS BALANCE ON THE EXPERIMENTAL SYSTEM
C AND DOUBLECHECKS THE CONSISTANCY OF THE DATA
C THE VARIOUS PROCESS PARAMETERS ARE PRINTED, TOGETHER WITH THE
C CONVERSION OF THE OIL TO THE VARIOUS PRODUCTS
C THE ENERGY CONSUMED IS ALSO CALCULATED

1 REAL K1, K2, K3, K4, K5, K6, K7, K8, K9, K10, K11

C
C *****
C A EXPERIMENTAL DATA
C *****
C

2 VOLT = 150 0
3 AMP = 200 0
4 V = 150 0
5 A = 200 0
6 POWOIL = 0 67
7 STOILD = 0 0
8 H2OILD = 0 222
9 OILD = 2 6

C THE ABOVE 5 VALUES ARE THOSE ORIGINALLY DESIRED BY PLAN
10 EFF= 0 71

C VOLUME % OF THE EXIT GAS AS FROM THE GC

11 H2 = 0 64
12 O2 = 0 0
13 CO = 0 0
14 CO2 = 0 0
15 CH4 = 0 15
16 C2H2 = 0 10
17 C2H4 = 0 10
18 C2H6 = 0 02
19 H2O = 0 0

20 XX = (1 00 - H2O)
C TERM TO CONVERT GAS ANALYSIS RESULTS FROM DRY TO WET BASIS

21 AH2 = H2*XX
22 AO2 = O2*XX
23 ACO = CO*XX
24 ACH4 = CH4*XX

C DON'T KNOW WHERE THE SULPHUR GOES

25 ACO2 = CO2*XX
26 AC2H2 = C2H2*XX
27 AC2H4 = C2H4*XX
28 AC2H6 = C2H6*XX
29 H2OX = H2O*100 0
30 H2X = AH2*100 0
31 O2X = AO2*100 0
32 COX = ACO*100 0
33 CO2X = ACO2*100 0
34 CH4X = ACH4*100 0
35 C2H2X = AC2H2*100 0
36 C2H4X = AC2H4*100 0

37 C2H6X = AC2H6*100 0
 38 C NOW FOR THE GAS VOLUME ON A DRY BASIS
 39 H2Y = H2X/XX
 40 O2Y = O2X/XX
 41 COY=COX/XX
 42 CO2Y = CO2X/XX
 43 CH4Y=CH4X/XX
 44 C2H2Y = C2H2X/XX
 45 C2H4Y = C2H4X/XX
 46 C2H6Y=C2H6X/XX
 H2OY = H2OX
 C
 47 HEIGHT = 57 0/25 4
 C INCHES OF OIL HEIGHT CHANGE IN THE PREHEATER
 48 H2ROT = 24 0
 C ROTOMETER SETTING
 49 PLAST = 6 00/60
 C PLASMA TIME, HOURS
 50 OILT = 3 5/60
 C OIL FEED TIME, HOURS
 51 QUENT = 0 0/60
 C QUENCH WATER TIME, HOURS
 52 GRATE = 0 0
 C QUENCH WATER RATE, USGPH
 53 ATOMIZ = 2 6
 C OIL FLOW, USGPH
 54 COLREA = 0 00/3 785
 C WATER COLLECTED BELOW THE REACTOR, USGL
 55 COLCYC = 0 0/3 785
 C WATER FROM THE CYCLONE, GL
 56 SOOT = 0 4
 C CARBON SOOT COLLECTED FROM THE REACTOR, KG
 57 OILLIN = 0 0
 C OIL COLLECTED FROM THE FEED LINES, KG
 58 OILCOL = OILLIN
 C OIL FROM BELOW/IN THE REACTOR, KG
 59 TEXTIT = 338 0
 C TEMP, K, AT THE ORIFICE PLATE
 60 TPLAS = 1500 0
 C 'K, OF THE PLASMA, HYDROGEN ALONE
 61 PEXIT = 16 0
 C PSIG, @ ORIFICE, ABSOLUTE P= 2 ATM.
 62 HPLAS = 9 5
 C MM OF HG WITH PLASMA ONLY, DELTA P
 63 HOIL = 19 0
 C MM OF HG AT ORIFICE, WITH GASIFICATION, DELTA P
 64 VEXIT = 653 0
 C FT3/HR OF GAS WITH OIL GASIFICATION, ESTIMATED
 65 VOLPLA = 347 0
 C MEASURED PLASMA FLOW FROM ROTOMETER TO THE TORCH
 66 VEXIT1 = 347 0
 C FT3/HR OF PLASMA AS MEASURED AT THE ORIFICE PLATE
 67 VEXIT3 = 500 0
 C FT3/HR OF GAS WITH OIL, # SUCH THAT THE ATOMIC OUTPUT BALANCED
 68 AUXSTE = 0 00
 C AUXILIARY STEAM FLOW, KG
 C
 C CONVERSION FACTORS AND CONSTANTS
 C
 69 R = 42 5796

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70 C      PSIA*FT3/KGMOL/K
      PV = PEXIT*VEXIT3/(R*TEXTIT)
      WITH OIL GASIFICATION, USING EXIT FLOW SO ATOMIC BALANCE BALANCES
      = IDEAL GAS LAW USING VOLUMETRIC MEASURED EXIT GAS FLOW
71 C      PV1 = PEXIT*VEXIT1/(R*TEXTIT)
      PV/RT FOR THE PLASMA ALONE
72 C      K1 = 35 314
      = FT3/M3
73 C      K2 = 0 040872
      = 1000L/M3 *(273/298 K) / 22 414 L/GMOL/1000 GMOL/KGMOL
74 C      K3 = 2 0
      = 2 G/MOL
75 C      K4 = 16 0
76 C      K5 = 18 0
77 C      K6 = 3 777
      = 998 KG/L * 3 785 L/USGAL
78 C      K7 = 79 437
      = 68,317 CAL/GMOL*4 186J/CAL/ 3600S/HR/1000W/KW*1000GMOL/KGMOL
79 C      K8 = 13 846
      = 13 846 = SLOPE OF THE H2 ROTOMETER CURVE
80 C      K9 = 32 0
81 C      K11 = 4 329E-3
      = 7 48 GL/FT3 / 1728 IN3/FT3
82 C      AREA = 15 71
      AREA OF THE INSIDE OF THE PREHEATER, IN2
      C
      C
      C *****
      C      B      ORIFICE FLOWMETER CALCULATIONS
      C *****
      C
      C Q= VOL FLOW, M= MASS FLOW, D= DENSITY, H= MANOMETER HEIGHT
      C A= AIR, G=GAS MIXTURE OF EXPERIMENT SUBSCRIPTS USED
83 C      GAPLAS= 22 07*HPLAS**1/2 + 6 31
      FOR PLASMA ALONE
84 C      GAOIL = 22 07*HOIL**1/2 + 6 31
      FLOW WITH OIL GASIFICATION
      C MANOMETER CALIBRATION CURVE FOR AIR
85 C      DA = 0 8711
      UNITS OF DENSITY ARE KG/M3, FLOW ARE FT3/HR, HEIGHT IN MM
86 C      QHPLAS = 71 95*HPLAS**1/2 + 20 6
87 C      QHOIL = 71 95*HOIL**1/2 + 20 6
      C FLOW FOR HYDROGEN PURE, QH == 3 26*QA
      C NOW TO CALCULATE AN AVERAGE DENSITY TO CONVERT MANOMETER READING
      C TO A CORRECT VALUE OF FLOWRATE; AVG DENSITY = DAV
      C GAS DENSITIES ARE GIVEN FOR 80(1) AND 130 C(2)
88 C      DH21 = 0 0609
89 C      DH22 = 0 0696
90 C      DO21 = 0 969
91 C      DO22 = 1 105
92 C      DCO1 = 0 848
93 C      DCO3 = 0 848
94 C      DCH41 = 0 443
95 C      DCH42 = 0 492
96 C      DCO21 = 1 333
97 C      DCO22 = 1 525
98 C      DACET1 = 1 171
      C THIS ACETYLENE DENSITY IS FOR 0 C
99 C      DACET2 = 1 3
100 C      DETH1 = 1 11
101 C      DETH2 = 1 269

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102      DETHA1 = 0 810
103      DETHA2 = 0 826
104      DH201 = 0 55
105      C      USING LINEAR INTERPOLATION, TOR IS THE ORIFICE TEMP
106      TOR = 110 0
107      DH2 = (1/(130 0-80 0))*((130-TOR)*DH22-(80 0-TOR)*DH21)
108      DO2 = (1/(130 0-80 0))*((130-TOR)*DO22-(80 0-TOR)*DO21)
109      DCO = (1/(130 0-80 0))*((130-TOR)*DCO3-(80 0-TOR)*DCO1)
110      DCH4 = (1/(130 0-80 0))*((130-TOR)*DCH42-(80 0-TOR)*DCH41)
111      DCO2 = (1/(130 0-80 0))*((130-TOR)*DCO22-(80 0-TOR)*DCO21)
112      DACET = (1/(130 0-80 0))*((130-TOR)*DACET2-(80 0-TOR)*DACET1)
113      DETH = (1/(130 0-80 0))*((130-TOR)*DETH2-(80 0-TOR)*DETH1)
114      DETHA = (1/(130 0-80 0))*((130 0-TOR)*DETHA2-(80 0-TOR)*DETHA1)
115      DH20 = DH201
116      C      WEIGHT FRACTIONS FROM VOLUME %
117      H2W = H2*DH2
118      O2W = O2*DO2
119      COW = CO*DCO
120      CO2W = CO2*DCO2
121      CH4W = CH4*DCH4
122      H2OW = H2O*DH2O
123      C2H2W = C2H2*DACET
124      C2H4W = C2H4*DETH
125      C2H6W = C2H6*DETHA
126      Y = C2H6W+C2H4W+C2H2W+CH4W+H2OW+COW+CO2W+O2W+H2W
127      H2Z = H2W/Y
128      O2Z = O2W/Y
129      COZ = COW/Y
130      CO2Z = CO2W/Y
131      CH4Z = CH4W/Y
132      C2H2Z = C2H2W/Y
133      C2H4Z = C2H4W/Y
134      C2H6Z = C2H6W/Y
135      H2OZ = H2OW/Y
136      DAVG1 = H2Z*DH2+O2Z*DO2+COZ*DCO+CH4Z*DCH4+CO2Z*DCO2
137      DAVG2 = C2H2Z*DACET+C2H4Z*DETH+C2H6Z*DETHA+H2OZ*DH2O
138      DAV = DAVG1 + DAVG2
139      C      FLOW DENSITY CORRECTION EQUATION
140      QPLAS = QHPLAS*(DH2/DAV)**(1/2)
141      C      FINAL CORRECTED FOR PLASMA FLOW
142      QOIL = QHOIL*(DH2/DAV)**(1/2)
143      C      FINAL CORRECTED FOR FLOW WITH OIL
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909      C      C
910      C      C
911      C      C
912      C      C
913      C      C
914      C      C
915      C      C
916      C      C
917      C      C
918      C      C
919      C      C
920      C      C
921      C      C
922      C      C
923      C      C
924      C      C
925      C      C
926      C      C
927      C      C
928      C      C
929      C      C
930      C      C
931      C      C
932      C      C
933      C      C
934      C      C
935      C      C
936      C      C
937      C      C
938      C      C
939      C      C
940      C      C
941      C      C
942      C      C
943      C      C
944      C      C
945      C      C
946      C      C
947      C      C
948      C      C
949      C      C
950      C      C
951      C      C
952      C      C
953      C      C
954      C      C
955      C      C
956      C      C
957      C      C
958      C      C
959      C      C
960      C      C
961      C      C
962      C      C
963      C      C
964      C      C
965      C      C
966      C      C
967      C      C
968      C      C
969      C      C
970      C      C
971      C      C
972      C      C
973      C      C
974      C      C
975      C      C
976      C      C
977      C      C
978      C      C
979      C      C
980      C      C
981      C      C
982      C      C
983      C      C
984      C      C
985      C      C
986      C      C
987      C      C
988      C      C
989      C      C
990      C      C
991      C      C
992      C      C
993      C      C
994      C      C
995      C      C
996      C      C
997      C      C
998      C      C
999      C      C
1000      C      C

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145 C          KG/HR OF PLASMA
146 O2MOL1 = 0 0
147 O2KG1 = 0 0
      H2OGL = 0 0
      C          USGL/HR
      C          H2OML1 = H2MOL1
148 H2OML1=0 0
149 H2OPLA = 0 0
      C          USGAL
150 PLASKG = H2MOL1*PLAST*K3
      C          KG OF PLASMA FED
      C          PLASMA VOLUMETRIC FLOW IN FT3/HR CORRECTED FOR THE EXIT TEMP
151 VEXIT2 = PLASMA*TEXIT/TPLAS
      C -----
      C OIL FLOW
      C -----
152 ATOM1 = ATOMIZ*OILT
      C          USGAL- TOTAL
153 OILHEI = HEIGHT*K11*AREA
      C          VOLUME OF OIL CHANGED IN PREHEATER, US. GALLONS
154 OILHIE = OILHEI*K6
      C          WEIGHT, KG, OF OIL FROM THE PREHEATER, MEASURED
155 OILGL = (ATOM1 + OILHEI)/2 0
      C          AVG OF OIL USED, GL
156 OILKG1 = OILHIE/OILT
      C          MEASURED KG/HR
157 OILGLH = OILKG1/K6
      C          MEASURED USGAL/HR
158 OILKG3 = ATOMIZ*K6
      C          KG/HR
159 OILKG2 = ATOM1*K6
      C          KG OF OIL FED, CALCULATED
      C
      C          KG & GMOL OF ATOMIC SPECIES FROM THE OIL FED
      C
160 COLKG = OILHIE*0 8228
161 HOLKG = OILHIE*0 1059
162 SOLKG = OILHIE*0 044
163 COLMOL = COLKG/12 0
164 HOLMOL = HOLKG
165 SOLMOL = SOLKG/32 0
      C -----
      C QUENCH WATER
      C -----
166 QUENCH = GRATE*QUENT
      C          GAL
167 QUENKG = QUENCH*3.785
      C          KG
168 QUEKG2 = GRATE*3.785
      C          KG/HR
169 WATIN = QUENCH + H2OPLA
      C          TOTAL WATER INPUT FROM THE QUENCH & PLASMA, GAL
170 WATIN1 = QUENKG+AUXSTE
      C          KG OF TOTAL WATER IN FROM QUENCH AND PLASMA & AUX STEAM
171 HQUKG = QUENKG*2.0/18.0
      C          KG OF H IN THE QUENCH WATER
172 OQUKG = QUENKG*16.0/18 0
173 HQUML = HQUKG
      C          KG MOL OF H FROM THE WATER
174 OQUML = OQUKG/16.0

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C -----
C      POWER INPUT, KW, ELECTRICAL, CHEMICAL & TOTAL
C -----
175      ELEPOW = VOLT*AMP*EFF/1000 0
176      CHEMPO = 0 0
177      POWER = ELEPOW + CHEMPO

C
C      RATIOS
C      UNITS, KG STEAM/KGOIL, KGH2/KGOIL, KGOIL/KW POWER
C
178      STOIL = H2OKG2/OILKG1
179      H2OIL = H2KG1/OILKG1
180      POWOIL = POWER/OILKG1
C -----
C      TOTAL KGMOL OF INPUT
C -----
181      CMOLIN = COLMOL + 0 82*OILCOL/12 0
182      SMOLIN = SOLMOL
183      OMOLIN = O2MOL1*2 0*PLAST + OGUMOL
184      HMOLIN = HGUMOL + H2MOL1*2 0*PLAST + HOLMOL + 0 11*OILCOL
C
C      * TOTAL KG INPUT OF ATOMIC SPECIES, & TOTAL WEIGHT
C
185      CKGIN = COLKG
186      SKGIN = SOLKG
187      OKGIN = O2KG1*PLAST + OGUKG + AUXSTE*16 0/18 0
188      HKGIN = H2KG1*PLAST + HGUKG + HOLKG + AUXSTE*2 0/18 0
189      TOTIN1 = CKGIN + SKGIN + OKGIN + HKGIN
190      TOTIN = OILHIE + QUENKG + PLASKG + AUXSTE
C
C      *****
C      D GAS AND LIQUID OUTPUT CALCULATIONS
C      *****
C
C      WATER AND OIL RESIDUE COLLECTED
C
191      WATCOL = COLREA + COLCYC
192      WATKG = WATCOL*3 785
193      DELWAT = WATIN1 - WATKG
194      DELWAA = DELWAT/18 0
195      OILKG = OILCOL
196      DELOIL = OILHIE - OILKG-SOOT
197      TOTLIQ = WATKG + OILKG
C
C      *****
C      D ALTERNATIVE METHOD OF GAS BALANCE
C      *****
C
198      FIRST CONVERSION OF VOL. % FLOW TO WT FLOW, THEN TO TOTAL KG
199      H2DENS = H2*GOIL*DH2/K1
200      H2DENZ = GPLAS*0.082/K1
201      H2KG = H2DENS*OILT + (PLAST-OILT)*H2DENZ
202      O2DENS = O2*GOIL*DO2/K1
202      O2DENZ = 0 0

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203 C          CALCULATED TOTAL PLASMA KG
204 PLASKG = (H2DENZ+O2DENZ)*PLAST
205 O2KG = O2DENS*OILT + (PLAST-OILT)*O2DENZ
206 COKG = CO*GOIL*DCO/K1*OILT
207 CO2KG = CO2*GOIL*DCO2/K1*OILT
208 CH4KG = CH4*GOIL*DCH4/K1*OILT
209 C2H2KG = C2H2*GOIL*DACET/K1*OILT
210 C2H4KG = C2H4*GOIL*DETH/K1*OILT
211 C2H6KG = C2H6*GOIL*DETHA/K1*OILT
212 H2OKG = H2O*GOIL*DH2O/K1*OILT
213 TOTKG = H2KG+O2KG+COKG+CO2KG+CH4KG+C2H2KG+C2H4KG+H2OKG+C2H6KG
214 GASKG = TOTKG/OILT
215 C          NOW TO CONVERT TO KG OF ATOMIC SPECIES
216 HKGSUB = C2H4KG*2 0/28 0+C2H2KG*2 0/26 0+CH4KG*4 0/16 0
217 HKGGAS = HKGSUB+H2KG+H2OKG*2 0/18 0+C2H6KG*2 0/30 0
218 HKG = HKGGAS+0.1059*OILKG+WATKG*2 0/18 0
219 OKGGAS = CO2KG*32 0/44 0+COKG*16 0/28 0+O2KG+H2OKG*16 0/18 0
220 OKG = OKGGAS+WATKG*16 0/18 0
221 CKGSUB = C2H6KG*24 0/30 0+C2H4KG*24 0/28 0+COKG*12 0/28 0
222 CKGGAS = CKGSUB+C2H2KG*24/26+CO2*12 0/44 0
223 CKG = CKGGAS+0.8228*OILKG+SOOT
224 C          CALCULATED OIL TO GAS CONVERSION
225 HGAS = CKGGAS*0.106/0.823
226 GASOIL = HGAS +CKGGAS
227 TOTOUT=OILKG+WATKG+TOTKG
228 TOTOT1=HKG+OKG+CKG
229 C          CALCULATE THE PROCESS VALUES PER 100 KG ACETYLENE
230 K10 = 100 0/C2H2KG
231 SOOTZ = SOOT*K10
232 OILKGZ = OILHIE*K10
233 HYDRKG = PLASKG*K10
234 CH4KG=CH4KG*K10
235 ELETKG = ELEPOW*K10*OILT
236 C2H4KG = C2H4KG*K10
237 RESIDK = OILCOL*K10
238 H2M3 = PLASMB*QILT
239 C          *****
240 C          E GASIFIED OIL CONVERSION, WT%, AND TOTAL OUTPUT
241 C          *****
242 C          CONVE1=GASOIL/OILKG2*100 0
243 C          TO GAS - CALCULATED; USING GAS FLOWS AND ATOMIZER FEEDRATE; %
244 C          CONVE2=(OILHIE - OILKG - SOOT)/OILHIE*100 0
245 C          TO GAS; MEASURED; WITH RESIDUE COLLECTED & HEIGHT IN PREHEATER; %
246 C          CONVE3 = SOOT/OILHIE*100 0
247 C          OIL CONVERSION TO SOOT
248 C          CONVE4 = OILCOL/OILHIE*100 0
249 C          OIL CONVERSION TO RESIDUE
250 C          TOTAL OUTPUT OF ATOMIC SPECIES, KG; & TOTAL OUTPUT
251 C          NOW ASSUMING THE RESIDUE HAS THE COMPOSITION AS THE FEED
252 C          TOTOT3 = OILKG+WATKG+SOOT
253 C          TOTKG2 = TOTIN - TOTOT3
254 C          GAS OUT BY MEASURENT, DIFFERENCE; KG
255 C          TOTOT2 = TOTOT3+TOTKG2
256 C          TOTAL OUT BY MEASUREMENT ALONE; KG

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C
C      CARBON ATOM SPLIT IN PRODUCTS
242 RESIDC=0 823*OILKG
243 GASC=CKG-RESIDC-SOOT
C
C *****
C      F THE PRINTOUT
C *****
C
244 WRITE (6,1)
245 1   FORMAT('1')
246 WRITE (6,2)
247 2   FORMAT(//,72('*'))
248 WRITE (6,3)
249 3   FORMAT(//, ' EXPERIMENT NO 16, OCT 1 ,1984 - HYDROGEN PLASMA,
$ WITH NO QUENCH ')
250 WRITE (6,4)
251 4   FORMAT(//,72('*'))
252 WRITE (6,6) CONVE2
253 6   FORMAT(//, 'THE OIL-TO-GAS CONVERSION IS           ',F6 3,' WT %')
254 WRITE (6,7) H2X, O2X, COX, CH4X, CO2X
255 7   FORMAT(//, 'WET EXIT GAS VOLUME %, OF,           H2- ',
$F5 2,' O2- ',F5 3,' CO- ',F5 3,' CH4- ',F6 3,' CO2- ',F5 3)
256 WRITE (6,8) C2H2X, C2H4X, C2H6X, H2OX
257 8   FORMAT(//, 'WET EXIT GAS VOLUME %,           C2H2- ',
$F7 4,' C2H4- ',F6 2,' C2H6- ',F5 3,2X,' WATER- ',F6 2)
258 WRITE (6,9) H2Y, O2Y, COY, CH4Y, CO2Y
259 9   FORMAT(//, 'DRY EXIT GAS VOL %           H2 ',F6 3,2X,' O2 ',F6 3,2X,
$ 'CO ',F6 3,2X,' CH4 ',F6 3,2X,' CO2 ',F6 3)
260 WRITE (6,10) C2H2Y, C2H4Y, C2H6Y, H2OY
261 10  FORMAT(//, 'DRY EXIT GAS VOL %           C2H2 ',F6 3,2X,' C2H4 ',F6 3,2X,
$ 'C2H6 ',F6 3,2X,' H2O ',F6 3)
262 WRITE (6,11) CONVE3
263 11  FORMAT(//, 'THE OIL TO SOOT CONVERSION IS           ',F6 3,' WT %')
264 WRITE (6,12) CONVE4
265 12  FORMAT(//, 'THE OIL TO RESIDUE CONVERSION IS           ',F6 3,' WT %')
266 WRITE (6,14) STOIL, STOILD
267 14  FORMAT(//, 'THE STEAM-TO-OIL WEIGHT RATIO IS           ',F6 3,'
$ HOWEVER THE DESIGNED RATIO WAS           ',F6 3)
268 WRITE (6,16) H2OIL, H2OILD
269 16  FORMAT(//, 'THE HYDROGEN-TO-OIL WEIGHT RATIO IS           ',F6 3,'
$ HOWEVER THE DESIGNED RATIO WAS           ',F6 3)
270 WRITE (6,18) POWOIL, POWOID
271 18  FORMAT(//, 'THE POWER-TO-OIL RATIO IS           ',F6 3,' KW/KG/HR,
$ HOWEVER THE DESIGNED RATIO WAS           ',F6 3)
272 WRITE (6,19) OILGLH, OILD
273 19  FORMAT(//, 'THE OIL FEEDRATE IS           ',F6 3,' USGPH,
$ HOWEVER THE DESIGNED FLOW WAS           ',F6 3)
274 WRITE (6,20) PLASMA, GOIL
275 20  FORMAT(//, 'THE PLASMA FLOWRATE IS           ',F7 2,' CFH',
$ ' CALCULATED GAS FLOW WITH OIL ',F9 3)
276 WRITE (6,21) ORATE
277 21  FORMAT(//, 'THE QUENCH RATE IS           ',F6 3,' USGPH')
278 WRITE (6,22) TOTIN
279 22  FORMAT(//, 'THE TOTAL INPUT OF MASS MEASURED IS           ',F6 3,' KG')
280 WRITE (6,24) TOTOT2
281 24  FORMAT(//, 'THE TOTAL OUTPUT IS           ',F6 3,' KG')
282 WRITE (6,26) POWER
283 26  FORMAT(//, 'THE TOTAL POWER INPUT IS           ',F5 2,' KW')

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284      WRITE (6,27) AMP, VOLT
285  27    FORMAT(/, 'THE POWER SETTINGS ARE ', F7 3, ' AMPS ', F7 3, ' VOLTS')
286      WRITE (6,28) OILKGZ
287  28    FORMAT(/, 'THE PRODUCTS AND INPUTS FOR 100 KG OF ACETYLENE ARE
      $      OIL FEED ', F6 2, ' KG')
288      WRITE (6,29) HYDRKG, ELETKG
289  29    FORMAT(/, 'STEAM PLASMA SUPPLIED ', F6 2, ' KG &      THE
      $ELECTRICAL POWER IS ', F9 2, ' KWHR')
290      WRITE (6,30) C2H4KG, RESIDK
291  30    FORMAT(/, 'ETHYLENE PRODUCT ', F6 2, ' KG &      THE RESIDUAL
      $OIL ', F6 2, ' KG')
292      WRITE (6,32) H2M3, SOOTZ, CH4KG
293  32    FORMAT(/, 'CUBIC METERS OF HYDROGEN ', F8 2, ' SOOT ', F8 2,
      $', METHANE ', F7 2)
294      WRITE (6,34) H2Z, O2Z, COZ, CO2Z, CH4Z
295  34    FORMAT(/, 'THE WEIGHT % PRODUCT GASES ARE, H2 ', F5 3, ' O2 ',
      $F5 3, ' CO ', F5 3, ' CO2 ', F5 3, ' CH4 ', F5 3)
296      WRITE (6,35) C2H2Z, C2H4Z, C2H6Z, H2OZ
297  35    FORMAT(/, 'WT % ACETYLENE ', F5 3, ' C2H4 ', F5 3, ' ETHANE ',
      $F5 3, ' WATER ', F5 3)
298      WRITE (6,38)
299  38    FORMAT(/, 'COMMENTS')
300      WRITE (6,39)
301  39    FORMAT('1')
302      WRITE (6,40)
303  40    FORMAT('EXPERIMENT #16- OCT 1 , 1984    HYDROGEN WITH NO QUENCH')
304      WRITE (6,42)
305  42    FORMAT(/, 72('*'))
306      WRITE (6,43)
307  43    FORMAT(/, 'THE OIL ATOMIZER IS POINTED DOWN FROM THE REACTOR TOP
      $, NEAREST TO THE TORCH, BEING A DELEVAN 30 DEGREES, 2 5 GPH@100PSI')
308      WRITE (6,45) H2ROT, TPLAS, TEXTIT
309  45    FORMAT(/, 4X, 'H2 ROTOMETER SETTING ', F6 2, 10X, 'EST PLASMA TEMP .
      $ ', F9 2, 'K', 10X, 'EXIT GAS TEMPERATURE ', F6 2, 'K')
310      WRITE (6,46) PLAST, QUENT, OILT
311  46    FORMAT(/, 4X, 'FEED TIMES, HOURS PLASMA ', F6 4, 10X, 'QUENCH WAT
      $ER ', F6 4, 10X, 'OIL ', F6 4)
312      WRITE (6,48) H2X, O2X, COX, CH4X, CO2X, C2H2X, C2H4X
313  48    FORMAT(/, 'EXIT WET GAS OUTPUT, VOLUME % H2-', F6 2, 2X, 'O2-', F
      $7 3, 2X, 'CO-', F7 3, 2X, 'CH4-', F6 2, 2X, 'CO2-', F6 2, 2X, 'C2H2-', F6 2, 2X
      $, 'C2H4-', F6 2, 2X, 'C2H6-', F5 3)
314      WRITE (6,50) C2H6X, H2OX
315  50    FORMAT(/, 'WET EXIT GASES, VOL % ETHANE- ', F6 2, 2X, 'WATER- ', F6 2)
316      WRITE (6,52)
317  52    FORMAT(/, 20('*'))
318      WRITE (6,60) OILGLH, OILKG1, OILHIE
319  60    FORMAT(/, 5X, ' THE OIL FEEDRATE, IS, USGPH ', 7X, F6 2, 9X, 'KG/HR
      $ ', F7 4, 9X, ' TOTAL KG ', F7 4, 4X, 'AS BY MEASUREMENT')
320      WRITE (6,65) OILD
321  65    FORMAT(/, 5X, 'HOWEVER THE DESIRED OIL FEEDRATE IS ', F6 2, ' GPH')
322      WRITE (6,70) PLASKG, H2KG1, PLASKG
323  70    FORMAT(/, 5X, ' THE PLASMA FLOWRATE, IS, CFH ', 7X, F6 2, 9X, 'KG/HR
      $ ', F6 2, 11X, 'TOTAL KG: ', F7 4)
324      WRITE (6,71) PLASKG
325  71    FORMAT(/, 'THE CALCULATED TOTAL PLASMA KG , ', 40X, F7 4)
326      WRITE (6,72) GRATE, QUEKG2, QUENKG
327  72    FORMAT(/, 5X, ' THE QUENCH RATE, IS, GPH ', 8X, F6 2, 9X, 'KG/HR
      $, F6 2, 9X, ' TOTAL KG ', F6 2)
328      WRITE (6,73) TOTIN, TOTIN1
329  73    FORMAT(/, 5X, ' THE TOTAL INPUT BY ADDITION OF THE ABOVE ', 30X, F6

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330      $ 3, ' KG MEASURED', 5X, F8 4, ' KG CALCULATED' )
331      74      WRITE (6,74) WATKG, OILKG, TOTKG2, SOOT
      FORMAT(//, 5X, ' MEASURED OUTPUT WEIGHTS OF ', 6X, ' WATER - ', F6 3, 6X,
$ ' OIL RESIDUE - ', F6 3, 6X, ' GAS BY DIFF - ', F8 4, ' KG', 6X,
$ ' SOOT - ', F8 4)
332      WRITE (6,76) TOTOT2, TOTOT1
333      76      FORMAT(//, 5X, ' TOTAL BY ADD OF PREVIOUS OUTPUTS - ', 33X, F8 4, ' KG,
$ ' MEASURED', 5X, F8 4, ' KG CALCULATED ' )
334      WRITE(6,80) POWER, CHEMPO, ELEPOW
335      80      FORMAT(//, 5X, ' THE TOTAL POWER INPUT, KW, IS ', 6X, F6 2, 12X, ' CHEMICAL
$ ' ', F6 2, 12X, ' ELECTRICAL ', F6 2)
336      WRITE (6,92) H2OIL, H2OILD
337      92      FORMAT(//, 5X, ' HYDROGEN TO OIL WT FEED RATIO IS ', 12X, F6 2, 10X,
$ ' HOWEVER DESIRED IS ', F6 3)
338      WRITE (6,120) POWOIL, VOLT, AMP
339      120     FORMAT(//, 5X, ' THE POWER TO OIL RATIO, KW/KG/HR, IS ', 14X, F10 5,
$ 4X, ' WITH SETTINGS OF ', 3X, F6 2, ' VOLTS', 4X, F7 3, ' AMPS' )
340      WRITE (6,125) POWOIL, V, A
341      125     FORMAT(//, 5X, ' HOWEVER THE DESIRED POWER/OIL RATIO IS ', 15X, F6
$ 3, 4X, F6 2, ' VOLTS', 5X, F6 2, ' AMPS' )
342      WRITE (6,130) CONVE2, CONVE1
343      130     FORMAT(//, 5X, ' OIL TO GAS - CONVERSION, WEIGHT% ', 8X,
$ ' MEASURED ', F6 2, ' %', 10X, ' CALCULATED ', F8 4, ' %' )
344      WRITE (6,131) CONVE3
345      131     FORMAT(//, 5X, ' OIL TO SOOT - CONVERSION WT % ', 9X, F6 2)
346      WRITE (6,133) CONVE4
347      133     FORMAT(//, 5X, ' OIL TO RESIDUE - CONVERSION WT % ', 9X, F6 2)
348      WRITE (6,134) GOIL, GASKG
349      134     FORMAT(//, 5X, ' MEASURED EXIT FLOWRATE OF GAS ', F8 2, ' FT3/HR
$ ', 5X, ' CALCULATED EXIT FLOW TO BALANCE KG OUTPUT ', F8 2, ' KG/HR' )
350      WRITE (6,135) QPLAS, VOLPLA
351      135     FORMAT(//, 5X, ' MEASURED @ ORIFICE PLATE EXIT PLASMA FLOW ', F8 2, 5X
$ ', ' MEASURED @ GAS ROTOMETER ', F6 2, ' FT3/HR' )
352      WRITE (6,145)
353      145     FORMAT(//, 72(' '))
354      WRITE (6,150)
355      150     FORMAT(//, 5X, ' KG OF INPUT OUTPUT' )
356      WRITE (6,152)
357      152     FORMAT(//, 72(' '))
358      WRITE (6,160) HKGIN, HKG
359      160     FORMAT(//, 4X, ' HYDROGEN ATOM ', F7 4, 20X, F7 4)
360      WRITE (6,170) OKGIN, OKG
361      170     FORMAT(//, 4X, ' OXYGEN ATOM ', F7 4, 20X, F7 4)
362      WRITE (6,190) CKGIN, CKG
363      190     FORMAT(//, 4X, ' CARBON ATOM ', F7 4, 20X, F7 4)
364      WRITE (6,191) TOTIN1, TOTOT1
365      191     FORMAT(//, 2X, ' BY SUM OF ATOM WTS ', 3X, F6 3, 17X, F8 4)
366      WRITE (6,194)
367      194     FORMAT(//, 72(' '))
368      WRITE (6,196)
369      196     FORMAT(//, 25X, ' DOUBLECHECKS' )
370      WRITE (6,198)
371      198     FORMAT(//, 72(' '))
372      WRITE (6,200) WATIN1, WATKG, DELWAT
373      200     FORMAT(//, 4X, ' KG OF WATER ', F6 2, 15X, F6 2, ' ; COLLECTED',
$ 10X, ' THEREFORE WATER TO VAPOUR IS ', F6 2, ' KG' )
374      WRITE (6,210) OILHIE, OILKG, DELOIL
375      210     FORMAT(//, 4X, ' KG OF OIL ', F6 3, 15X, F6 3, ' ; COLLECTED',
$ 8X, ' THEREFORE THE OIL TO GAS IS ', F9 5, ' KG' )
376      WRITE (6,220) GASOIL, SOOT

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377 220 FORMAT(/, 'CALCULATED GAS TO OIL KG      ', F7 4, 2X, 'MEASURED SOOT ',
      $F6 2)
378 WRITE (6, 280) ATOMIZ, OILGLH
379 280 FORMAT(/, 4X, 'USGAL/HR OIL FLOW      ESTIMATED - ', F6 2, 15X, 'MEASURE
      $D - ', F6 2)
380 WRITE (6, 300) OILKG2, OILHIE
381 300 FORMAT(/, 5X, 'TOTAL OIL FEED, KG - ESTIMATED      ', F6 2, 15X, '
      $BY MEASUREMENT      ', F6 2)
382 WRITE (6, 305) OILKG3, OILKG1
383 305 FORMAT(/, 5X, 'KG/HR OF OIL FEED - ESTIMATED      ', F7 4, 15X, ' BY
      $ MEASUREMENT      ', F7 4)
384 WRITE (6, 306) H2KG, O2KG, COKG, CH4KG, CO2KG, C2H2KG, C2H4
      $KG, H2OKG
385 306 FORMAT(/, 3X, 'OUTPUT KG OF      H2-', F5 3, ' O2-', F5 3, ' CO-', F5 3,
      $ ' CH4-', F5 3, ' CO2-', F5 3, ' C2H2-', F5 3, ' C2H4-', F5 3, ' H2O '
      $, F7 4)
386 WRITE (6, 307) TOTKG, TOTKG2
387 307 FORMAT(/, 5X, 'TOTAL GAS OUTPUT ,KG .BY CALCULATION - ', F8 4, 10X,
      $ 'BY DIFFERENCE MEASUREMENT - ', F6 3)
388 WRITE (6, 314) TOTIN, TOTIN1
389 314 FORMAT(/, 'IN, SUM OF OIL&PLASMA&QUENCH BULK KG      ', F6 3, 10X,
      $ 'SUM OF ATOMIC WEIGHTS IN, KG ', F6 3)
390 WRITE (6, 316) TOTOT2, TOTOT1
391 316 FORMAT(/, 'OUT, SUM OF COLLECTED OIL&WATER&WATER VAPOUR, KG
      $, F6 3, 5X, ' SUM OF ATOMIC WEIGHTS OUT, KG      ', F6 3)
392 WRITE (6, 318) DAV
393 318 FORMAT(/, 'THE AVERAGE GAS DENSITY IS      ', F8 3, ' KG/M3')
394 WRITE (6, 319) K10
395 319 FORMAT(/, ' K10      ', F8 2)
396 WRITE (6, 322) RESIDC
397 322 FORMAT(/, 'CARBON ATOM IN RESID OIL ', F6 2)
398 WRITE (6, 324) GASC, HKGGAS, OKGGAS
399 324 FORMAT(/, 'IN THE GAS CARBON ', F6 2, 2X, 'HYDROGEN ', F6 2, 2X,
      $ 'OXYGEN ATOM ', F6 2)
400 WRITE (6, 330)
401 330 FORMAT('1')
402 STOP
403 END

```

\$DATA
 COMPILE = 1 89 SU