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THE UNIVERSITY OF ALBERTA

THERMAL HYDROPROCESSING OF HEAVY GAS OILS

by

Ⓒ SAMUEL Y.K. CHUNG

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE
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ABSTRACT

The thermal hydroprocessing of heavy gas oils was studied in continuous flow laboratory reactors. The primary objective of the study was to measure intrinsic rate data for the conversion of a high boiling fraction (343 - 524 °C) called the pitch fraction, and of sulphur compounds in the gas oil in a stirred reactor. The rate data along with a mixing model can be used to predict the performance of thermal hydroprocessing reactors.

Rate data for Lloydminster Vacuum Gas Oil (LLVGO) were derived from thermal hydroprocessing runs made in a 0.3 L stirred reactor at 13.9 MPa, temperatures of 400 to 440 °C and nominal LHSV of 0.75 to 1.5 h^{-1}. Pitch conversions ranged from 11 to 65 percent while sulphur conversion ranged from 4 to 30 percent. A method of sampling reactor contents under reaction conditions was developed and thus true concentrations of reactive constituents in the reacting liquid phase were used to correlate the rate data. Hydrogen solubility and consumption were measured for all runs.

The rate of conversion of the pitch fraction was correlated with two kinetic models. Model 1 assumes that conversion is first order in pitch concentration and Model 2 assumes that conversion is first order in both concentration of pitch and dissolved hydrogen. Model 1 provides a better fit of the rate data. The rate of hydrodesulphurization was correlated with sulphur concentration. A pseudo-first order

equation provided a good fit of the sulphur removal rate data. The rate expressions obtained for LLVGO are presented below with the gas constant expressed in kJ mol⁻¹ K⁻¹.

$$-r_p = 6.165 \times 10^{10} \exp\left(-\frac{170.6}{RT}\right) C_{RL} \qquad \text{(MODEL 1)}$$

$$-r_p = 4.674 \times 10^{13} \exp\left(-\frac{167.1}{RT}\right) C_{RL}\, C_H \qquad \text{(MODEL 2)}$$

$$-r_S = 1.816 \times 10^{6} \exp\left(-\frac{115.7}{RT}\right) C_S$$

Coke formation is significant when processing LLVGO above 440 °C. Blending LLVGO with a lighter CANMET gas oil (EMRGO) greatly reduced coke formation and allowed processing at 450 °C. Five different gas oils, ranging from lighter hydrotreated Athabasca gas oils to heavier Cold Lake gas oils, were hydroprocessed at 13.9 MPa, nominal LHSV of 1.0 h⁻¹, and temperatures up to 460 °C. The relative coking tendencies for these feedstocks were examined. Measured rate data were correlated based on models developed from correlation of LLVGO data.

The thermal hydroprocessing of LLVGO was also studied in a 2.34 I.D. 0.3 L tubular reactor at 13.9 MPa. Measured pitch conversions ranging from 17 to 60 percent agree with values predicted by a plug-flow model. A preliminary study of catalytic hydroprocessing in the stirred reactor was made with EMRGO feedstock and a commercial nickel-molybdenum catalyst. Experimental conditions used were 13.9 MPa, nominal LHSV of 0.28 h^{-1} and temperatures of 400 to 440 °C. Pitch conversion approached 95 percent at 440 °C. Near complete hydrodesulphurization was achieved but extensive coke deposition occurred on the catalyst.

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NOMENCLATURE

A_t	cumulative area response at retention time t
BP	boiling point
C_F	pitch concentration in liquid feed at 23°C, mol mL^{-1}
C_H	hydrogen concentration in reactor liquid phase at reaction conditions, mol mL^{-1}
C_p	pitch concentration in liquid product at 23°C, mol mL^{-1}
C_{RL}	pitch concentration in reactor liquid phase at reaction conditions, mol mL^{-1}
C_S	sulphur concentration in reactor liquid phase at reaction conditions, mol mL^{-1}
C/C_o	ratio of concentrations of tracer in sample to that in feed for RTD run
CSTR	constant stirred tank reactor
d/dt	rate of change
F_1	volumetric flowrate of liquid feed at 23°C, mL min^{-1}
F_2	volumetric flowrate of liquid product at 23°C, mL min^{-1}
k	reaction rate constant
$\bar{k}$	coefficient used to correct liquid density for thermal expansion, g^2 m^{-6} $^oC^{-1}$
K_d	instrument constant for densimeter
LHSV	liquid hourly space velocity, h^{-1}
m	kinetic model parameter
m_{H_2S}	molar flowrate of H_2S in product gas stream, mol min^{-1}

$\dot{m}_{H_2}$	mass flowrate of feed H_2, g min^{-1}
$\dot{m}_{PG}$	mass flowrate of product gas, g min^{-1}
MW_F	average molecular weight of pitch fraction in liquid feed, g mol^{-1}
MW_p	average molecular weight of pitch fraction in liquid product, g mol^{-1}
MW_{RL}	average molecular weight of pitch fraction in reactor liquid phase, g mol^{-1}
MW_S	molecular weight of sulphur, g mol^{-1}
M_{RL}	mass of reactor liquid phase sample, g
n	kinetic model parameter
N_G	moles of gas dissolved in reactor liquid phase sample, mol
P	reactor pressure, psia
P_S	partial pressure of single sulphur compound, psia
P_H	partial pressure of hydrogen, psia
R	gas constant
$-r_p$	rate of pitch conversion, mol mL^{-1} min^{-1}
$-r_S$	rate of sulphur conversion, mol mL^{-1} min^{-1}
RT	retention time
RTD	residence time distribution
T	reaction temperature, ^{o}C
T_1	frequency reading for reference fluid in density analysis
T_2	frequency reading for liquid sample in density analysis

V_t	cumulative volume of sample eluted at retention time t
V_i	volume fraction of component i
W_F	weight fraction of pitch in liquid feed
W_p	weight fraction of pitch in liquid product
W_{RL}	weight fraction of pitch in reactor liquid phase
W_S	weight fraction sulphur in sample
W_{SF}	weight fraction sulphur in liquid feed
W_{SP}	weight fraction sulphur in liquid product
W_{SR}	weight fraction sulphur in reactor liquid phase
x_H	mole fraction hydrogen in dissolved gas in reactor liquid phase sample
x_g	weight fraction gas oil in liquid product
x_S	weight fraction sulphur in liquid product
x_N	weight fraction nitrogen in liquid product
X_p	fractional pitch conversion
X_S	fractional sulphur conversion
α_1	fraction reactive sulphur compounds in liquid product
α_2	fraction less reactive sulphur compounds in liquid product
ψ	term used to account for changing axial volumetric flowrate of liquid phase in tubular reactor
ψ_{av}	estimate of ψ based on CSTR data at similar conversion level
$\frac{\Delta S.G.}{\Delta \theta}$	rate of change of liquid product specific gravity, h^{-1}

ρ_F	liquid feed density, g mL^{-1}
ρ_P	liquid product density, g mL^{-1}
ρ_{RL}	reactor liquid phase density, g mL^{-1}

SUPERSCRIPT

$'$	denotes term evaluated at reaction conditions

SUBSCRIPT

i	denotes term representing component or fraction i
T	denotes term evaluated at temperature T

I. INTRODUCTION

Residuum upgrading has become more attractive in recent years. Rising conventional crude oil prices and the availability of heavier and more sour feedstocks are contributing factors. There are various upgrading processes available commercially(31). A group of upgrading processes known as hydrogen addition or hydrocracking processes are particularly attractive because of high distillate yields thus providing for the efficient use of a non-renewable resource. These processes convert the high boiling fractions by thermally cracking the heavy molecules in a hydrogen-rich atmosphere at high temperature and pressure, with or without the presence of a catalyst.

A hydrocracking process known as the CANMET Thermal Hydrocracking Process has been developed by the Energy Research Laboratories of the Department of Energy, Mines and Resources in Ottawa. The process was developed mainly to upgrade heavy oil or bitumen at moderate pressure and high temperature in the presence of an inexpensive additive. The additive prevents coke deposition in the reactor to allow for operation at low pressure and high conversion of the 524°C$^+$ fraction(14). In the first stage of the process, the feedstock is thermally hydrocracked to remove most of the metals and the worst of the coke forming compounds and concentrate them in a heavy fraction. The distillate product stream then enters a second stage catalytic hydrocracking reactor where near complete sulphur, nitrogen and oxygen removal is achieved together with the production of lighter liquid fractions and gas.

It has been recognized that the design and scale-up of reactors used for the thermal hydroprocessing of bitumens and heavy oils as in the CANMET Hydrocracking Process would be assisted if definitive information were available on the dependence of rates of hydrocracking and hydrodesulphurization on the concentrations of reactive constituents in the oil at reaction conditions. For example, having intrinsic rate data would make it possible to account for differences in mixing patterns when scaling up from pilot plant work to commercial reactors.

The present project was undertaken to obtain such information, and thus to determine the effect of reactor configuration on hydroconversion and desulphurization in a hydroprocessing reactor. The continuous thermal hydroprocessing of a Lloydminster Vacuum Gas Oil (LLVGO) was studied at 13.9 MPa in two different laboratory reactors; (i) a stirred autoclave reactor (CSTR), and (ii) a 2.34 cm I.D. tubular reactor. Both reactors have a volume of 0.3 L and comprise part of a laboratory scale hydroprocessing unit that has been constructed in the Department of Chemical Engineering at the University of Alberta.

Some additional work was done on obtaining thermal hydroprocessing results for different heavy gas oil feedstocks from CSTR runs. The primary objectives of the study can be briefly summarized as follows :

1. Operation of the CSTR to obtain information to relate the rates of hydroconversion of a high boiling fraction defined as pitch and of sulphur conversion to the concentration of pitch, sulphur and hydrogen in the reacting liquid phase at temperatures between 400 and 475°C for different heavy gas oils. For this study, pitch conversion is defined as the conversion of the 343 to 524°C boiling point fraction into lower boiling liquids, gases and coke.
2. To study the relative coking tendencies of the heavy gas oils.
3. Attempt to develop kinetic equations to represent the intrinsic rate data measured from CSTR runs.
4. Measurement of the degree of pitch conversion and hydrodesulphurization in the tubular reactor at temperatures between 400 and 475°C. Liquid flow in this reactor is assumed to approximate "plug flow".
5. To compare the measured conversions of pitch in the tubular reactor with the performance predicted by using a plug flow model and intrinsic rate data derived from the CSTR study.
6. To undertake preliminary experiments to evaluate the CSTR unit for catalytic hydroprocessing.

II. LITERATURE SURVEY

There are extensive published literature on the hydroprocessing of petroleum oils. Only those publications directly related to this work will be discussed. The fundamental aspects of hydroprocessing of petroleum or coal-based oils are not well understood. Most of the published information on petroleum hydroprocessing centre on the following areas:

1. Distillate Yields
2. Product Distributions
3. Effect of Process Variables on Yields
4. Catalyst Performance
5. Mechanism of Hydrocracking of some pure hydrocarbons

The distillate yields are dependent on catalyst activity and reaction conditions. At the more severe operating conditions, conversion levels are high. At these conditions, equipment operation is often hampered by rapid catalyst deactivation due to solid deposition on catalyst surface and also by coke formation on the walls in the reactor and downstream separators. A brief summary of the groups of reactions encountered under normal hydroprocessing conditions were prepared by Man(15).

A. Thermal Hydroprocessing

Thermal Hydroprocessing or thermal hydrocracking is a process which could be used as the primary (or first) step in the upgrading of bitumen or heavy oil as an alternate process to thermal coking. Much literature information on thermal hydrocracking originates from the Canada Centre for Mineral and Energy Technology (CANMET) of the Department of Energy Mines and Resources in Ottawa(25).

Development work on a upgrading process using thermal hydrocracking started in the 1960's at CANMET. Much of the operating difficulties arising from using the technology to upgrade heavy residuum materials like bitumen and heavy oil such as coke formation have been investigated in detail. Khulbe and co-workers(10-12) in 1976 reported the effect of heavy oil recycle on pilot plant operation, product quality and reactor fouling. The work was done using a conventional flow apparatus with a 4.5 L, 3.81 cm I.D. tubular reactor(17). They found that recycling of heavy oil increased the ash content in the reactor liquid which greatly suppressed coke and sludge formation in the reactor. However the conversion of the $524^{\circ}C^{+}$ fraction was decreased.

Other investigators have studied the thermal hydrocracking of Athabasca bitumen and their findings were generally in agreement with the results obtained at CANMET. Chervenak and Wolk(4) investigated the thermal hydrocracking of bitumen and found that for bitumen samples containing 4.0 to 10.0 weight percent ash, there was no coke deposition in the reactor. Layng(13) investigated the effect of quenching the reactor effluents by introducing a part of the fresh feed or heavy ends between the reactor and separator. McColgan and co-workers(16) observed that a feed containing a high concentration of mineral matter could be hydrocracked at higher temperatures with no coking or reactor fouling problems.

The effect of adding sub-bituminous or lower rank coal particles to a reaction mixture of hydrogen and Athabasca bitumen at 13.9 MPa and 723 K was studied by Ternan and co-workers(33) in a bench-scale, fixed bed, 2.54 cm I.D. tubular reactor with a volume of 155 mL. It was observed that coke from hydrocracking the bitumen deposits on the coal particles and not on reactor walls thus improving process operations. Nandi and co-workers(19) presented evidence that the deposits of coke formed on the coal particle surfaces originated primarily from the bitumen rather than from the coal itself.

Pruden(24-25) reviewed the research activity on the hydrocracking of bitumen and heavy oils at CANMET. The effects of process variables like temperature, hydrogen partial pressure, liquid hourly space velocity (LHSV) and gas recycle rate on hydroconversion of a high boiling (524°C+) fraction, hydrodesulphurization and hydrodenitrogenation were discussed. Operating pressure was found to have little effect on product yields but higher pressure reduced greatly reactor fouling problems at high conversion levels. Over 90 percent of the 524°C⁺ fraction is converted at 13.9 MPa, 460°C and LHSV of 1.0 h^{-1}. Sulphur removal approached 25 percent at the more severe operating conditions(3).

George and co-workers(8) studied the distribution of compound types in the thermal hydrocracking of Athabasca bitumen. Gross composition analysis showed an increase in the amounts of light oil at the expense of heavy oil and the asphaltene contents. Compound type analysis showed that saturates and mononuclear aromatics increase with operating severity.

There is very limited published information on the kinetics of the thermal hydrocracking of residuum fractions. Man(15) studied the thermal hydrocracking of a heavy gas oil in a constant stirred tank reactor (CSTR). His results showed that a simple first order kinetic model represents the rate data quite well for the conversion of a high boiling fraction (343°C⁺). His data also indicated that the total pressure has negligible effect on the conversion level. A second order kinetic equation was found to fit the sulphur conversion rate data.

B. Catalytic Hydroprocessing

Catalytic hydrocracking is usually used in secondary upgrading processes in the production of lower boiling distillates or naphtha and in the removal of most of the sulphur and nitrogen compounds in the feedstock. It can be used as a second stage upgrading to further improve the quality of the distillate product from a first stage thermal hydrocracking unit for heavy oil or bitumen. The performance of a two-stage thermal and catalytic hydrocracking process pilot unit for Athabasca bitumen was evaluated by Ranganathan and co-workers(30). The first thermal hydrocracking stage converts most of the 524°C$^+$ fraction into lighter distillates, and removes most of the inorganic matter, coke precursors and metals. Partial desulphurization and denitrogenation also occur. Hence longer catalyst life can be expected for the second-stage catalytic hydrocracking unit.

A major concern in catalytic hydrocracking is in maintaining catalyst life and activity. The catalyst used in commercial hydrorefining reactors is often presulphided with carbon disulphide (CS_2) or some other appropriate sulphur compound before being put on stream. This presulphiding step converts the catalyst from its oxidized form to a sulphided form which in most cases increases catalyst life and activity(35). Ternan and Whalley(34) investigated the effect of presulphiding conditions on a nickel molybdenum catalyst performance in the hydroprocessing of a heavy gas oil derived from Athabasca bitumen. It was found that presulphiding with the heavy gas oil containing 3.64 weight percent sulphur, with CS_2, or with hydrogen sulphide (H_2S), produced essentially the same results in terms of catalyst sulphur content and the amount of coke deposition on catalyst surfaces.

Aitken and co-workers(1) studied the catalytic hydrogenation of a heavy coker distillate derived from Athabasca bitumen over a fixed bed of cobalt molybdate on alumina catalyst at various operating conditions. From their results, they obtained an empirical equation describing the effect of pressure on catalyst deactivation:

$$\frac{\Delta\ S.G.}{\Delta\ \theta} = \frac{1.24 \times 10^{6}}{P^{3.1}} \qquad (2.1)$$

where,

Δ S.G./Δ θ = rate of change of product sp. gravity, h^{-1}

P = operating pressure, psia

The rate of change of product specific gravity was used to indicate catalyst deactivation since that characteristic is easily and accurately determined. Their results showed that increasing the operating pressure reduces the rate of catalyst deactivation.

The hydrocracking of a gas oil boiling in the range 300°C to 430°C over nickel-tungsten catalyst in a fixed bed tubular reactor was investigated by Qader and Hill(26). Their results indicated that the conversion to gasoline, middle distillate and gas increased with temperature but decreased with increasing space velocity. A simple first order kinetic equation was used to model their rate data and the following kinetic equations for the rate of hydrocracking, desulphurization and denitrogenation were obtained, respectively:

$$-dx_g/dt = 1.0 \times 10^7 \exp\left(-\frac{88.3}{RT}\right) x_g \tag{2.2}$$

$$-dx_S/dt = 6.814 \times 10^4 \exp\left(-\frac{70.3}{RT}\right) x_S \tag{2.3}$$

$$-dx_N/dt = 8.253 \times 10^4 \exp\left(-\frac{72.8}{RT}\right) x_N \tag{2.4}$$

where,

dx_i/dt = reaction rate, h^{-1}
x_i = weight fraction of component i
R = gas constant, kJ mol^{-1} K^{-1}
T = reaction temperature, K

The equations were obtained based on reactant concentrations expressed as the initial and final weight percent of gas oil, sulphur and nitrogen. The activation energies were expressed in kJ/mol. Hydrogen concentration was found not to affect the rates of hydrocracking and sulphur and nitrogen removal for the range of operating conditions of 7.0 - 15.3 MPa and 300 - 430°C. Similar first order kinetics was observed in their studies on the catalytic hydrocracking of low temperature coal tar(28).

In a follow-up work(27), they studied the hydrocracking of petroleum and coal oil fractions over nickel-tungsten catalyst in a fixed bed reactor. They found that naphtha yields from hydrocracking the petroleum fractions increased linearly with temperature but did not change appreciably with pressure. The yields from the coal oil fractions however increased with pressure and temperature indicating that higher pressure is required for hydrogenating the relatively greater amounts of aromatic and heterocyclic hydrocarbon compounds present in coal based oils.

Eqbal and Sarkar(6) studied the hydrocracking of a vacuum gas oil in a continuous bench scale flow reactor over a commercial nickel-molybdenum catalyst. Studies were also made over a uranium oxide impregnated commercial cobalt molybdate catalyst. Results showed that conversion to gas and gasoline increases with temperature and decreasing space velocity. Yields of diesel fuel follow the same trend but pass through a maximum value.

In studying the catalytic hydrodesulphurization of a light catalytic cycle oil, Frye and Mosby(7) found that the first order equation for the disappearance of any single compound fits their data quite well.

$$dx_S/dt = k\ P_S\ P_H \qquad (2.5)$$

where,

dx_S/dt = rate of sulphur removal, h^{-1}

k = reaction rate constant, h^{-1} $psia^{-2}$

P_S = partial pressure of single sulphur cpd., psia

P_H = partial pressure of hydrogen, psia

El-Kady(5) studied the hydrocracking of a vacuum distillate fraction boiling in the range 380°C - 550°C over a bifunctional nickel-molybdenum on silica-alumina catalyst in a fixed bed tubular reactor. The conversion to gasoline, middle distillate and gas oils was found to increase with temperature and decreasing LHSV. A vacuum distillate conversion of 97 percent was obtained at 450°C and LHSV of 0.5 h^{-1}. Their data showed that overall kinetics indicate the hydrocracking, desulphurization and denitrogenation reactions to be first order. The kinetic equations presented are of the same form as those presented by Qader and Hill (Equations (2.2) to (2.4)).

Other researchers like Hoog(9), Schuit and Gates(32), Paraskos and co-workers(23), and Yitzhaki and Aharoni(37) obtained similar results in that a first order kinetic equation fit their catalytic hydrodesulphurization rate data for petroleum fractions quite well. Schuit and Gates(32) proposed a kinetic equation of the form:

$$-dx_S/dt = k_1 \alpha_1 x_S + k_2 \alpha_2 x_S \qquad (2.6)$$

where,

$-dx_S/dt$ = rate of sulphur removal, h^{-1}

α_1 = fraction reactive sulphur cpd.

α_2 = fraction less reactive sulphur cpd.

x_S = weight fraction sulphur

k_1, k_2 = reaction rate constants, h^{-1}

The equation takes the sulphur compounds in the feedstock to be composed of two hypothetical sulphur containing groups; a reactive group and a less reactive group of sulphur compounds. Hence at practical hydrodesulphurization conditions, the reactive portion is rapidly converted and the rate of conversion of the less reactive group becomes controlling. The results of Hoog(⁹) seem to support equation (2.6) with data showing that the rate of sulphur removal is faster for a lighter fraction than for a heavier fraction.

Yitzhaki and Aharoni(³⁷) extended this idea by splitting the gas oil feed into narrow boiling fractions. The diversity of sulphur compounds in narrow boiling range fractions is less than in wide boiling range fractions thus allowing for the accurate application of simple kinetic equations. They treated hydrodesulphurization of the gas oil as the sum of processes taking place in individual narrow boiling range fractions. The rate equation for each fraction was found to approach first order.

$$dx_S/dt = \sum k_i \, x_{S_i} \tag{2.7}$$

where,

dx_S/dt = rate of sulphur removal, h^{-1}

x_{S_i} = weight fraction sulphur in fraction i

A study on the catalytic hydrodesulphurization of Middle Eastern crudes by Beuther and Schmid(2) showed that the rate of sulphur removal can be represented by a simple second order model:

$$-dx_S/dt = k \, x_S^{2} \tag{2.8}$$

The reason for the second-order behaviour under rather mild reaction conditions was proposed to be due to the wide variation of sulphur compounds with different reactivities present in the petroleum fractions. If each type of sulphur compound were removed by a first order reaction with respect to sulphur concentration, the apparent first order reaction rate constant would continually decrease as the more reactive sulphur compounds are depleted, the more stable sulphur compounds remaining in the residue. This sequence will lead to an apparent second-order behaviour.

Ranganathan and co-workers(29) studied the catalytic hydrocracking of coker distillates derived from Athabasca bitumen. Their results indicated that a second order kinetic equation fits the desulphurization data while denitrogenation is adequately represented by a first order kinetic equation. Wakabayashi and co-workers(36) investigated the hydrocracking of Cold Lake bitumen over cobalt-molybdenum supported on alumina catalyst in a batch reactor. Operating pressures range from about 6.8 - 19.4 MPa while operating temperatures are from 375 - 435°C. A second order kinetic equation is also found to fit the hydrodesulphurization rate data well with an estimated activation energy of 109 kJ/mol.

Ozaki and co-worker(22) studied the hydrodesulphurization of residual oils in a conventional high-pressure flow unit over a catalyst containing a mixture of nickel, cobalt and molybdenum oxides on alumina support. Their results indicated that the apparent order of hydrodesulphurization reactions of residual oils vary with temperature. They showed that a n th order kinetic equation fits the rate data quite well.

$$-dx_S/dt = k\, x_S^n \tag{2.9}$$

Their experimental results also showed that the rate of sulphur removal is higher for lighter fractions than for heavier fractions supporting the results of previous investigators.

Metzger and co-workers(1[illegible]) studied the data from a process based on the Gulf Distillate Desulphurization Process on the desulphurization of various gas oils. A single pseudo-component approach was used to represent the kinetics of hydrogenation of a sulphur containing hydrocarbon. Their rate data on the hydrodesulphurization of Kuwait Virgin distillates was well represented by a kinetic equation of the form:

$$-dx_S/dt = k\ x_S^{1.7} \qquad (2.10)$$

The effect of hydrogen partial pressure on the rate of hydrodesulphurization was found to be negligible for hydrogen partial pressures above 4.1 MPa.

The literature survey showed that simple equations can be used to model the kinetics of hydroconversion, hydrodesulphurization and hydrodenitrogenation. However due to the simplicity of these equations, each of which are based on data for individual feedstock and range of operating conditions, their use is limited to the individual feedstock and range of operating conditions.

III. EQUIPMENT

The hydroprocessing process unit used in this study can be described as a system comprised of three zones: (A) a feeding zone, (B) a reactor zone, and (C) a pressure reduction and separation zone. Figure III.1 shows a schematic diagram of the whole process unit set-up. Detailed diagrams of individual sections are given in Figures III.2 to III.5. Figure III.2 shows a schematic diagram of the feeding zone. The reactor zone consists of two high-pressure flow reactors connected in parallel: (a) a stirred reactor and (b) a tubular reactor. The reactors share a common feeding and pressure reduction and separation zones but only one of them may be on stream at a time. Schematic diagrams of the reactors are given in Figures III.3 and III.4. Figure III.5 shows a schematic diagram of the pressure reduction and separation zone.

The process unit is automated through the incorporation of two flow control loops and three pressure control loops. Figures III.2 to III.5 show the location of the various control loops. Table III.5 lists the control loop components. By implementing these control loops, the process unit can be operated for extended runs of up to several days with minimal supervision.

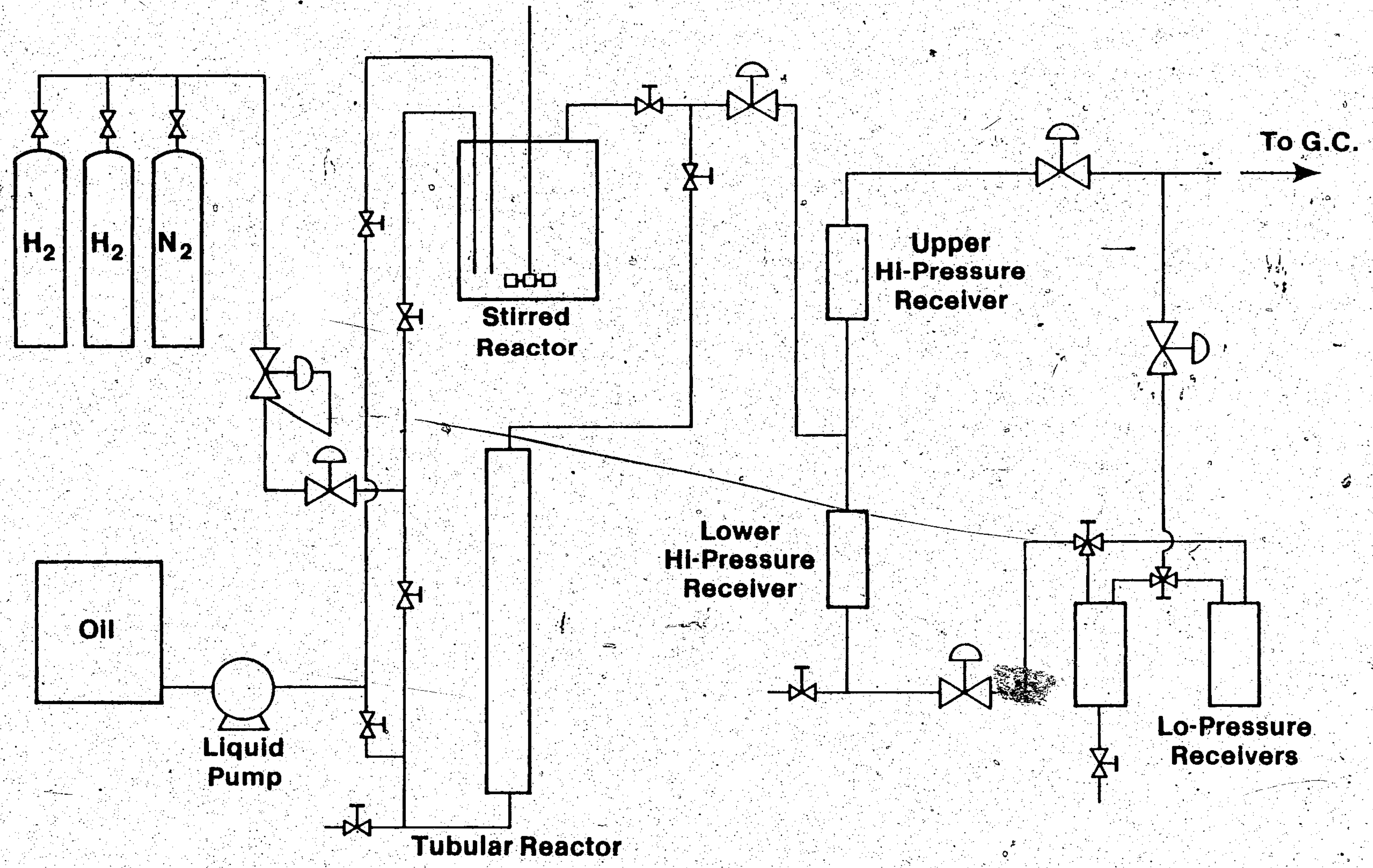


Figure III.1 Hydroprocessing Process Unit Set-Up

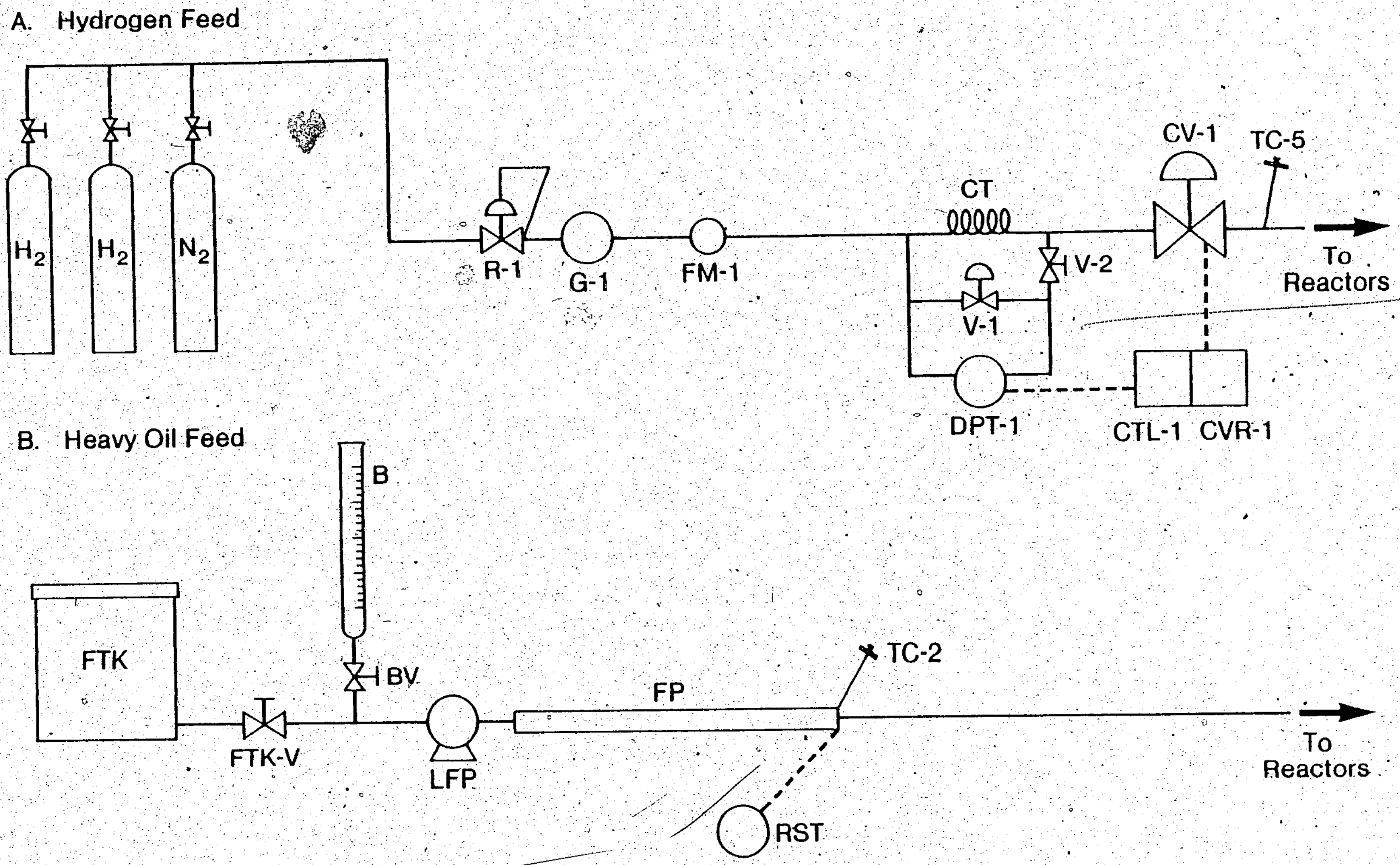


Figure III.2 Feeding Zone

Table III.1. Symbols for Figure III.2

B	burette for oil feedrate measurements
BV	burette valve
CT	capillary tubing
CV-1	hydrogen feedrate control valve
CTL-1	hydrogen feedrate controller
CVR-1	converter for CTL-1
DPT-1	differential pressure transmitter for hydrogen flow control
FM-1	mass flowmeter sensor
FP	feed oil preheater
FTK	oil feed tank
FTK-V	feed tank valve
G-1	pressure gauge
LFP	liquid feed pump
R-1	high pressure regulator for H2 supply
RST	power control rheostat for preheater
TC-2	oil preheater outlet thermocouple
TC-5	feed hydrogen thermocouple
V-1	hydrogen flow control loop by-pass valve
V-2	hydrogen flow control loop isolation valve

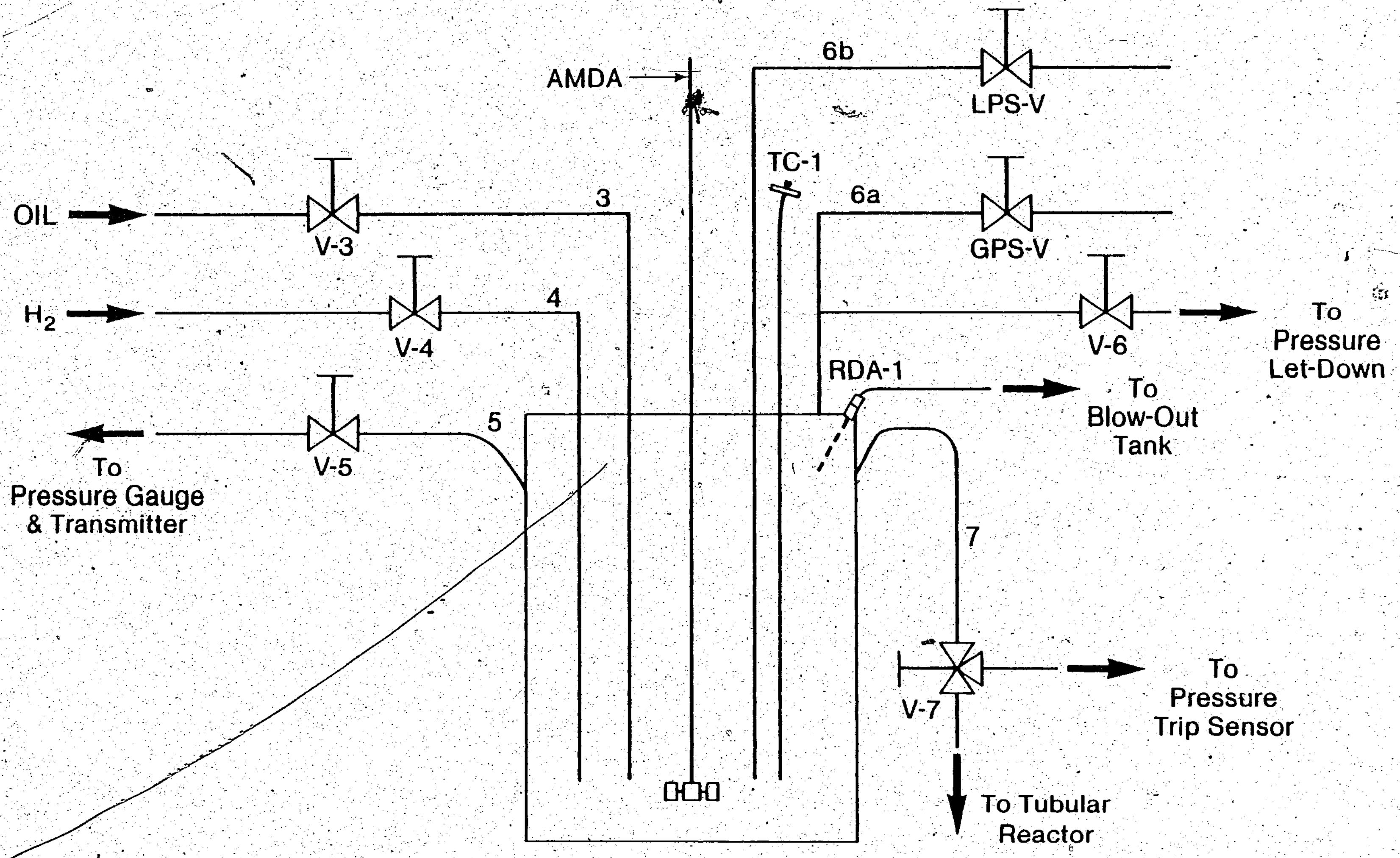


Figure III.3 Stirred Reactor

Table III.2. Symbols for Figure III.3

AMDA	agitator magnetic-drive assembly
GPS-V	reactor gas phase sampling valve
LPS-V	reactor liquid phase sampling valve
RDA-1	rupture disc assembly for stirred reactor
TC-1	stirred reactor thermocouple
V-3	oil feed shutoff valve
V-4	hydrogen feed shutoff valve
V-5	shutoff valve to pressure sensors
V-6	reactor isolation valve
V-7	three way valve connected to safety pressure trip circuit

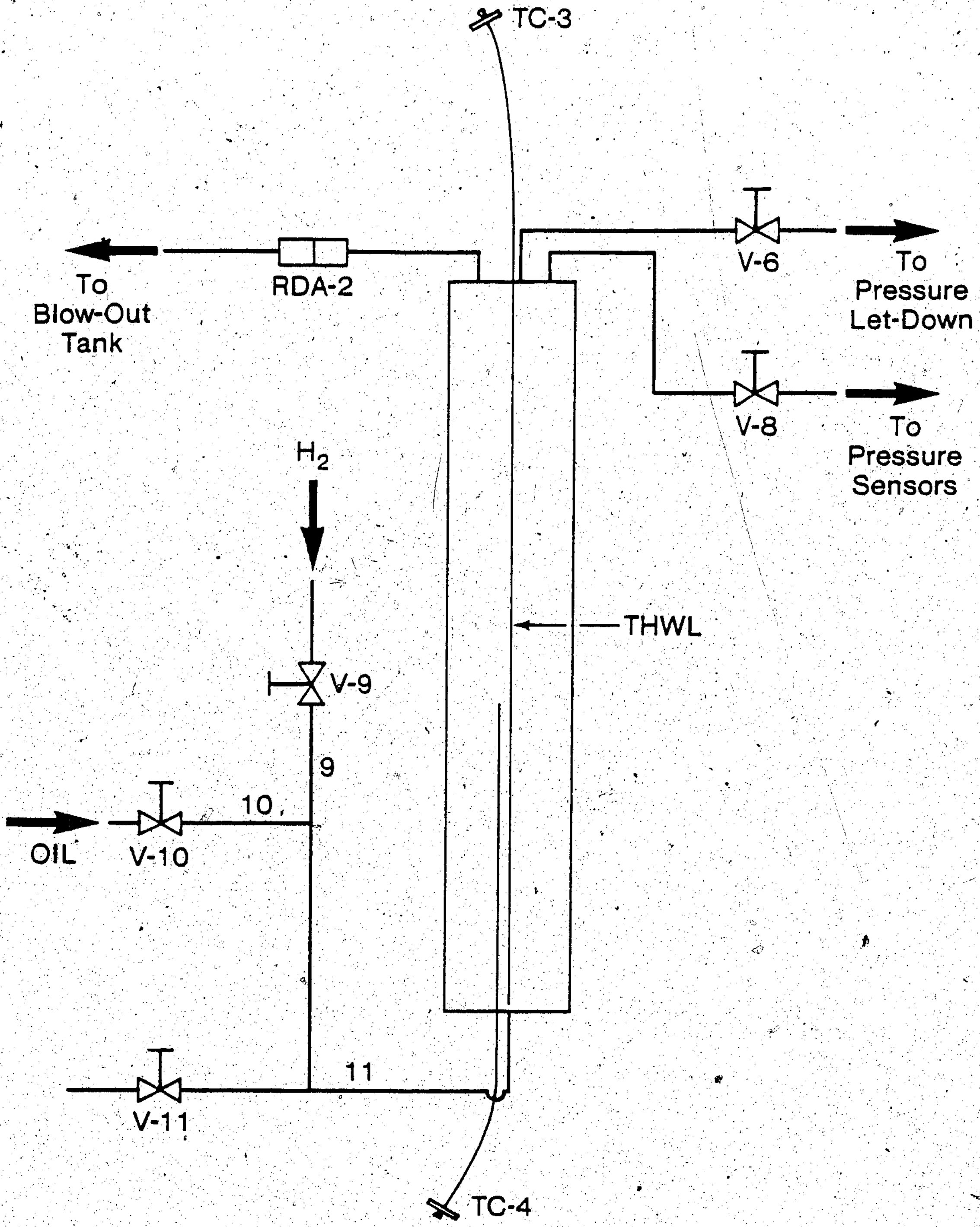


Figure III.4 Tubular Reactor

Table III.3. Symbols for Figure III.4

RDA-2	rupture disc assembly for tubular reactor
THWL	thermowell for travelling thermocouple TC-3
TC-3	travelling thermocouple along tubular reactor length
TC-4	fixed thermocouple in reactor
V-6	reactor isolation valve
V-8	shutoff valve to pressure sensors
V-9	hydrogen feed shutoff valve
V-10	oil feed shutoff valve
V-11	purge line shutoff valve
9, 10	hydrogen and oil feed lines
11	combined feed line

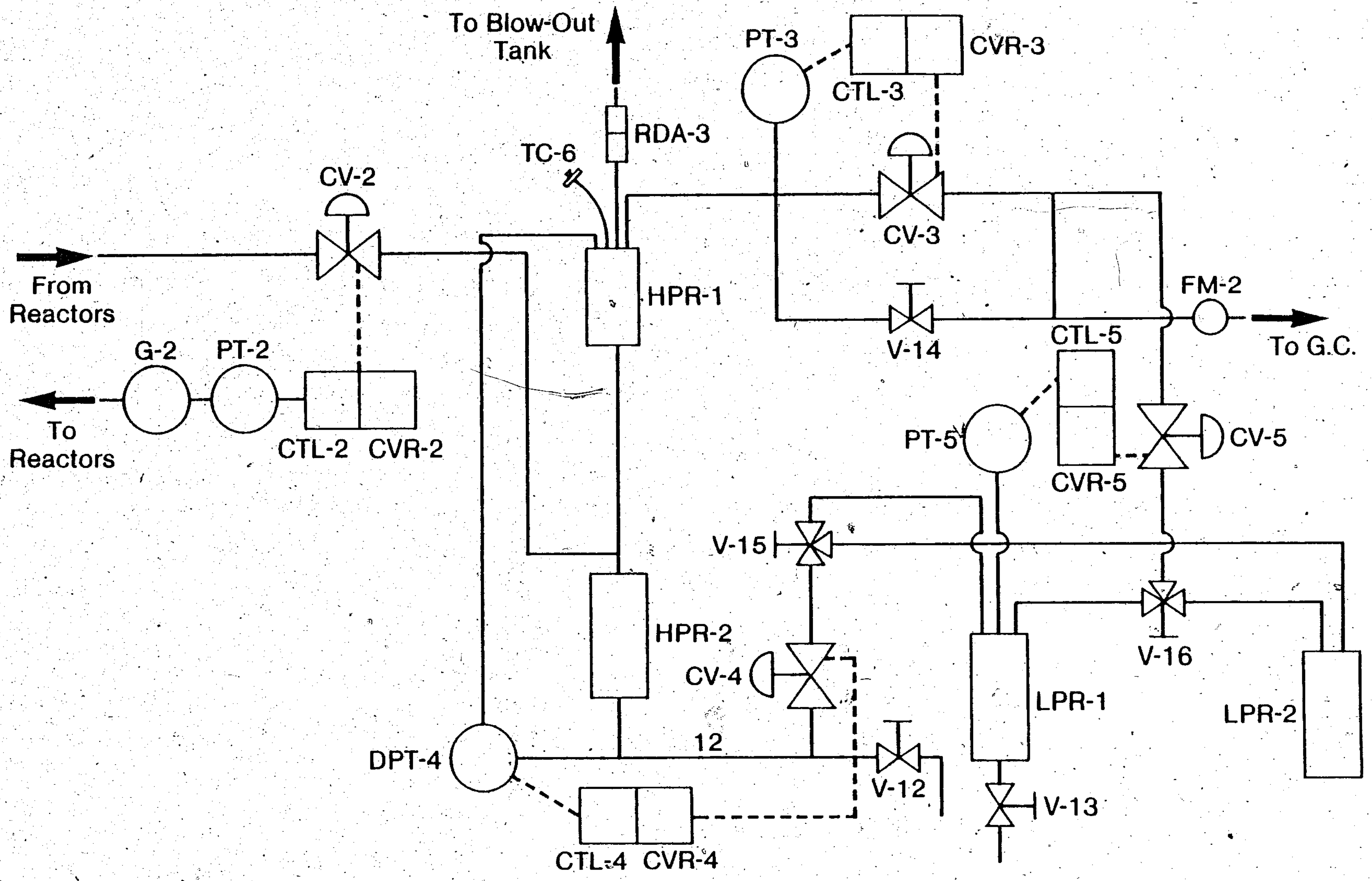


Figure III.5 Pressure Reduction and Separation Zone

Table III.4. Symbols for Figure III.5

CV-2	control valve for reactor pressure control
CTL-2	reactor pressure controller
CVR-2	converter for CTL-2
CV-3	control valve for pressure control in high pressure receivers
CTL-3	high pressure receivers pressure controller
CVR-3	converter for CTL-3
CV-4	control valve for liquid level control in HPR-2
CTL-4	HPR-2 liquid level controller
CVR-4	converter for CTL-4
CV-5	control valve for pressure control in LPR-1
CTL-5	LPR-1 pressure controller
CVR-5	converter for CTL-5
DPT-4	differential pressure transmitter for liquid level control in HPR-2
FM-2	mass flowmeter sensor
G-2	pressure gauge
HPR-1	upper high pressure receiver
HPR-2	lower high pressure receiver
LPR-1	low pressure liquid holding tank
LPR-2	auxiliary low pressure liquid holding tank
PT-2	pressure transmitter for reactor pressure

	measurements
PT-3	pressure transmitter for pressure measurement in the high pressure receivers
PT-5	pressure transmitter for LPR-1
RDA-3	rupture disc assembly for HPR-1 and HPR-2
TC-6	thermocouple for HPR-1
V-12	liquid product sampling valve
V-13	drain valve for LPR-1
V-14	regulating valve on bypass line on control loop no. 3
V-15	three way valve connected to LPR-1 and LPR-2
V-16	three way valve connected to LPR-1 and LPR-2

Table III.5 Hydroprocessing Unit Control Loops Makeup

CONTROL LOOP	COMPONENTS			
	Measurement Device	Controller	Converter	Control Valve
1. Hydrogen flow control loop no. 1	Beckman model 864 differential pressure transmitter, DPT-1	Beckman model 8830 controller, CTL-1	Foxoboro I/P model 69TA-II converter,CVR-1	Annin model 5061 control valve with size "AA" trim,CV-1
2. Reactor pressure control loop no. 2	Beckman model 864 pressure transmitter, PT-2	Beckman model 8830 controller, CTL-2	Foxoboro I/P model 69TA-II converter,CVR-2	Annin model 5061 control valve with size "AA" trim,CV-2
3. High pressure receivers pressure control loop no. 3	Beckman model 864 pressure transmitter, PT-3	Beckman model 8830 controller, CTL-3	Foxoboro I/P model 69TA-II converter,CVR-3	Badger model P786 research control valve, type TLDA positioner,CV-3
4. Liquid level/flow control loop no. 4	Beckman model 864 differential pressure transmitter, DPT-4	Beckman model 8830 controller, CTL-4	Foxoboro I/P model 69TA-II converter,CVR-4	Badger model P785 research control valve, type BLRA positioner,CV-4
5. Low pressure receiver pressure control loop no. 5	Beckman model 864 pressure transmitter, PT-5	Beckman model 8830 controller, CTL-5	Foxoboro I/P model 69TA-II converter,CVR-5	Badger model P786 research control valve, type TLDA positioner,CV-5

A. Feeding Zone

The hydrogen gas used for the hydroprocessing studies is supplied from two high pressure (41.4 MPa) commercial cylinders (manufactured by Linde Division of Union Carbide Corporation) connected in parallel. In the feeding zone of the process unit, the supply hydrogen from the cylinders, passes through a Matheson Model 3062B high pressure regulator, R-1, which reduces the gas pressure to about 700 kPa above the desired reactor pressure. The downstream pressure from R-1 is measured by pressure gauge G-1. The hydrogen gas flowrate is then measured by a high pressure Tylan Model FM 360 mass flowmeter, FM-1. In FM-1, two resistance thermometers are wound adjacent to each other on the outside of a sensor tube as part of a bridge circuit. When there is flow in the tube, the upstream sensor is cooled while the downstream sensor is heated. This produces a signal from the bridge proportional to the flow. The mass flowmeter was acquired and used during the latter part of the study.

The hydrogen stream then enters the hydrogen flow control loop. A Beckman Model 861 differential pressure cell measures pressure drop of the gas after passing through a 1.59 mm length of stainless steel capillary tubing. The signal is transmitted to a Beckman Model 8830 controller, CTL-1, which then adjusts control valve CV-1 via a converter, CVR-1. The temperature of the hydrogen leaving the flow control loop is measured by a 0.10 m long Thermo

Electric thermocouple. All thermocouples used in the process unit are of the same type: 1.59 mm 316 ss sheathed type J Ceramo thermocouples of various immersion lengths.

The liquid feed is stored in a cubical stainless steel feedtank with a capacity of about 1.7 L. Liquid feed is pumped to either of the two reactors by a Milton Roy Instrument Model 2396-57 Duplex Mini Pump, LFP. The Mini Pump is a precision positive displacement pump with rated capacities in the range from 29 mL/h to 580 mL/h. It can accurately deliver liquid at high pressures of up to 34.6 MPa (5000 psig). From the pump, the liquid enters a preheater, FP, which consists of a 2.4 m length of 0.635 cm 316 ss tubing wrapped with 1.27 cm Electrothermal HT345 heating tape. Power to the preheater is controlled via a rheostat, RST. The liquid temperature at the outlet from the preheater is measured by a 0.10 m Thermo Electric Thermocouple, TC-2.

The outputs from all thermocouples are registered on a Honeywell Electronik 16-point recorder. Similarly, the input signals from the flow and pressure control loops are registered on a Honeywell Electronik Model 16 24-point recorder.

B. Reactor Zone

This part of the process unit is made up of two flow reactors connected in parallel: (a) a stirred reactor, and (b) a tubular reactor. The reactors are both high pressure vessels constructed using series 316 and 304 stainless steels, respectively. These reactors were designed to withstand the severe operating conditions encountered in hydroprocessing studies.

Stirred Reactor

The stirred reactor is a modified MagneDrive Packless High Pressure Autoclave manufactured by Autoclave Engineers Inc. The rated capacity of the vessel is 0.30 L. The autoclave was modified from its original batch design to a flow reactor by using sampling outlets as inlet and outlet ports. A schematic diagram of the interior and exterior piping for the stirred reactor is shown in Figure III.3.

The reactor consists of a thick-walled vessel with a bolted flanged top closure. The MagneDrive Agitator assembly forms part of the top closure and is belt-driven by an Inpak V-S Drive motor unit. A pressure tight seal for high temperature hydroprocessing applications is achieved by using a 316 ss closure gasket. The maximum working pressure for the vessel is about 37.2 MPa at 343°C. The rotation speed of the agitator is measured by an Autoclave Engineers Inc. tachometer. An Autoclave Engineers Inc. high temperature furnace with a capacity of about 1.2 kW is used to heat the reactor to operating temperatures. A detailed assembly diagram of the stirred reactor may be found in the Autoclave Engineers, Inc. operating manual for the 0.30 L MagneDrive Packless autoclave.

The pressure in the reactor is monitored by a Weiss pressure gauge, G-2, and by a Beckman Model 864 pressure transmitter, PT-2. The reactor pressure is maintained at the desired level by pressure control loop no. 2. The pressure measured by PT-2 is transmitted to controller CTL-2 which adjusts control valve CV-2 via converter CVR-2. The furnace temperature is controlled by a Thermo Electric Selectrol Series 800 Controller. This temperature controller operates on a time based proportional control with automatic reset mode. A 0.20 m Thermo Electric Ceramo thermocouple, inserted in a thermowell in the reactor, is used to measure reactor temperatures.

The inlet, outlet, and thermowell openings are located on the top closure or on the side walls of the reactor (refer to Figure III.3). The liquid feed enters the reactor via line 3 while the hydrogen feed enters via line 4. Both feed lines 3 and 4 enter at the bottom of the reactor to ensure that the incoming feed gas and liquid becomes well mixed with the reactor contents. The gas and liquid products exit via line 6 to the pressure reduction and separation zone.

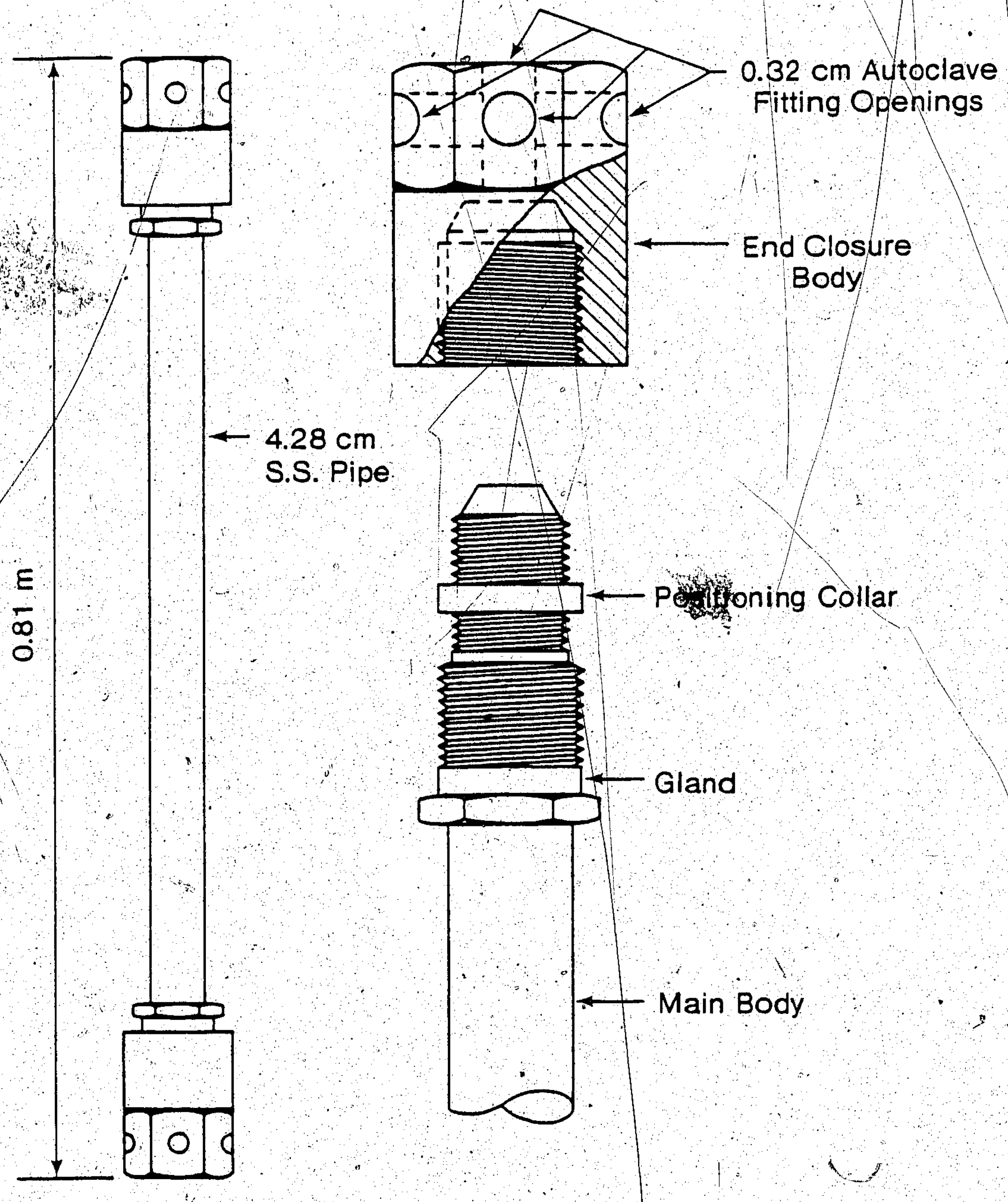
A safety head assembly, RDA-1, is threaded into the wall of the autoclave. It consists of a threaded disc housing body, gasket, rupture disc, hold-down ring and nut. The rupture disc used is made from Inconel and has a rated burst pressure of about 39.5 MPa at 23°C. The safety head assembly is connected to a blowout tank via 0.635 cm stainless steel tubing.

The reactor is also equipped with a high pressure safety trip circuit. Line no. 5 connects the reactor to a Murphy Switch Gauge which will send a signal to a magnetic trip circuit cutting off the power supplied to the reactor furnace and the liquid feed pump when the reactor pressure reaches the upper limit setting on the Switch Gauge.

Tubular Reactor

The tubular reactor used was constructed by the machine shop staff of the Department of Chemical Engineering at the University of Alberta. The main body of the reactor is made from a 4.28 cm series 304 ss pipe with a wall thickness of 0.97 cm. The ends of the main reactor body were threaded and coned. High pressure seals for both open ends of gland and collar type fittings were machined from series 316 stainless steel. The total length of the reaction zone in the reactor is 0.70 m which corresponds to a gross interior volume of 0.30 L. A detailed assembly diagram of the tubular reactor can be found in Figure III.6.

The tubular reactor is mounted vertically in a Lindberg 54000 Series Three-Zone Tube Furnace. The reactor is suspended in a centre location in the furnace by a suspended tube clamp assembly. Similarly, the furnace is vertically mounted on a support stand. Heating in the furnace is achieved by three separate heating zones. To offset higher heat losses at the ends, the two end zones are short and



Top and Bottom End Closures Identical

Figure III.6 Tubular Reactor Assembly Diagram have a much higher heating capacity than the longer and better insulated central heating zone. The temperature of each of the zones is monitored and controlled by separate temperature controllers. The maximum temperature rating for the furnace is 1000°C.

With this furnace design, the reactor can be operated at close to isothermal conditions since end heat losses can be compensated for by supplying a higher rate of heating at the end zones. Furthermore, to minimize heat losses, the end zones were insulated with high temperature fibreglass insulation.

The tubular reactor shares a common pressure measurement and control loop with the stirred reactor. With the appropriate switching of valves on the system piping, the reactor pressure measurement and control loop can be switched from the stirred reactor to the tubular reactor, or vice versa. A schematic diagram showing the tubular reactor piping is given in Figure III.4.

Hydrogen and liquid oil feed enter via lines no. 9 and 10, respectively, to form a single combined stream at line no. 11 which then enters the reactor at the bottom of the reactor. The axial temperature profile is measured by a 1.10 m Thermo Electric thermocouple, TC-3, positioned in a 0.32 cm thermowell which extends for the entire length of the reactor's interior. Another thermocouple, a 0.80 m Thermo Electric thermocouple, TC-4, is located at a fixed point about 0.20 m from the bottom of the reactor interior.

Thermocouple TC-4 is in direct contact with the reacting mixture.

A safety head assembly, RDA-2, is connected to the tubular reactor via a 0.32 cm 316 ss line at the top of the reactor. This safety head assembly was constructed of series 316 stainless steel and consists of a two-piece screw-on body, an Inconel rupture disc and a hold-down ring. The low pressure side of RDA-2 is connected to the blow out tank. Similarly, as in the stirred reactor set-up, the tubular reactor is connected to a common safety pressure trip circuit. By switching the three-way valve V-7, either of the reactors can be on-line to the safety pressure trip circuit.

C. Pressure Reduction and Separation Zone

The gaseous and liquid products leave the reactor zone via line no. 6, through the reactor zone isolation valve, V-6, and through the reactor pressure control valve, CV-2, before entering the high pressure receivers. On entering the high pressure receivers, the pressure is reduced to about 2.0 MPa. The high pressure receivers consist of an upper high pressure receiver, HPR-1, a lower high pressure receiver, HPR-2. HPR-2 is made up of an 0.15 m Jerguson high pressure sight glass to allow for visual inspection of the liquid level in the receiver. The holdup volume of HPR-2 is small (about 20 mL) which minimizes the liquid product retention time. HPR-1 is made up of a high pressure vessel with a holdup volume of about 120 mL. This vessel provides additional disengaging volume for gas-liquid separation.

The high pressure receivers are maintained at a constant pressure level by pressure control loop no. 3. A pressure transmitter measures the pressure in HPR-1. Pressure controller, CTL-3, coupled with converter, CVR-3, controls the pressure in the receivers via control valve CV-3. A schematic diagram of the pressure reduction and separation zone showing the location of various vessels and associated system piping is shown in Figure III.5.

A safety head assembly, RDA-3, is connected to the top of the upper high pressure receiver. The Inconel rupture disc used is rated at a burst pressure of 6.9 MPa at 25°C. A 0.10 m Thermo Electric thermocouple, TC-6, measures the temperature in HPR-1.

The liquid product collects in the lower high pressure receiver HPR-2. The liquid level in HPR-2 is maintained by liquid level control loop no. 4. Liquid product exits via control valve CV-4 which is controlled by controller CTL-4. The gaseous products leave HPR-1 via control valve CV-3. A sampling valve, V-12, is located on line no. 12 just downstream from HPR-2. V-12 is used to sample the liquid product.

The liquid product exits HPR-2 via CV-4 and enters the low pressure receivers where the pressure is further reduced to nearly ambient pressure. The low pressure receivers are made up of a main low pressure receiver, LPR-1, and an auxiliary low pressure receiver, LPR-2. Further gas-liquid separation occur in these receivers. Pressure control loop no. 5 maintains a constant pressure of about 109 kPa in LPR-1. Gas exits via CV-5 while liquid product accumulates in the receiver. To facilitate measurement of the cumulative liquid product flowrate, the liquid stream can be switched to auxiliary receiver LPR-2 by appropriate switching of 3-way valves, V-15 and V-16.

D. Modifications to the Stirred Reactor for Catalytic Hydroprocessing Studies

For catalytic hydroprocessing studies conducted using the stirred reactor, catalyst pellets are packed into cylindrical shaped wire-mesh baskets held in place at the wall of the reactor. Schematic diagrams of a catalyst basket and the positioning of the baskets in the reactor are shown in Figures III.7 and III.8, respectively.

Up to four catalyst baskets can be placed in the reactor depending on the catalyst loading required. The shape of the baskets and their location at the reactor wall aids mixing in the reactor as they serve as baffles which help to provide good contact between the agitated liquid phase reacting species and the catalyst surface.

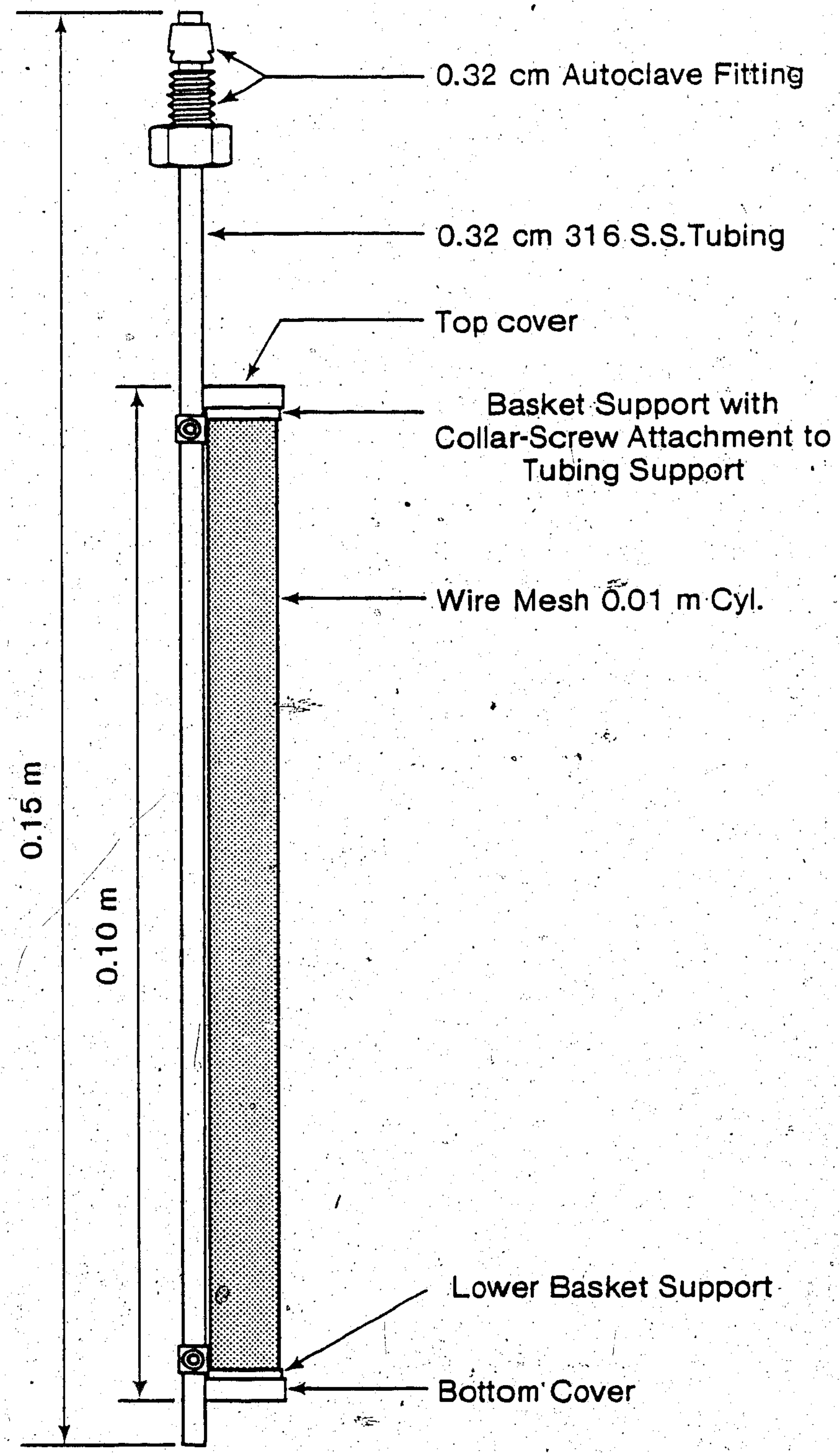


Figure III.7 Catalyst Basket Set-Up

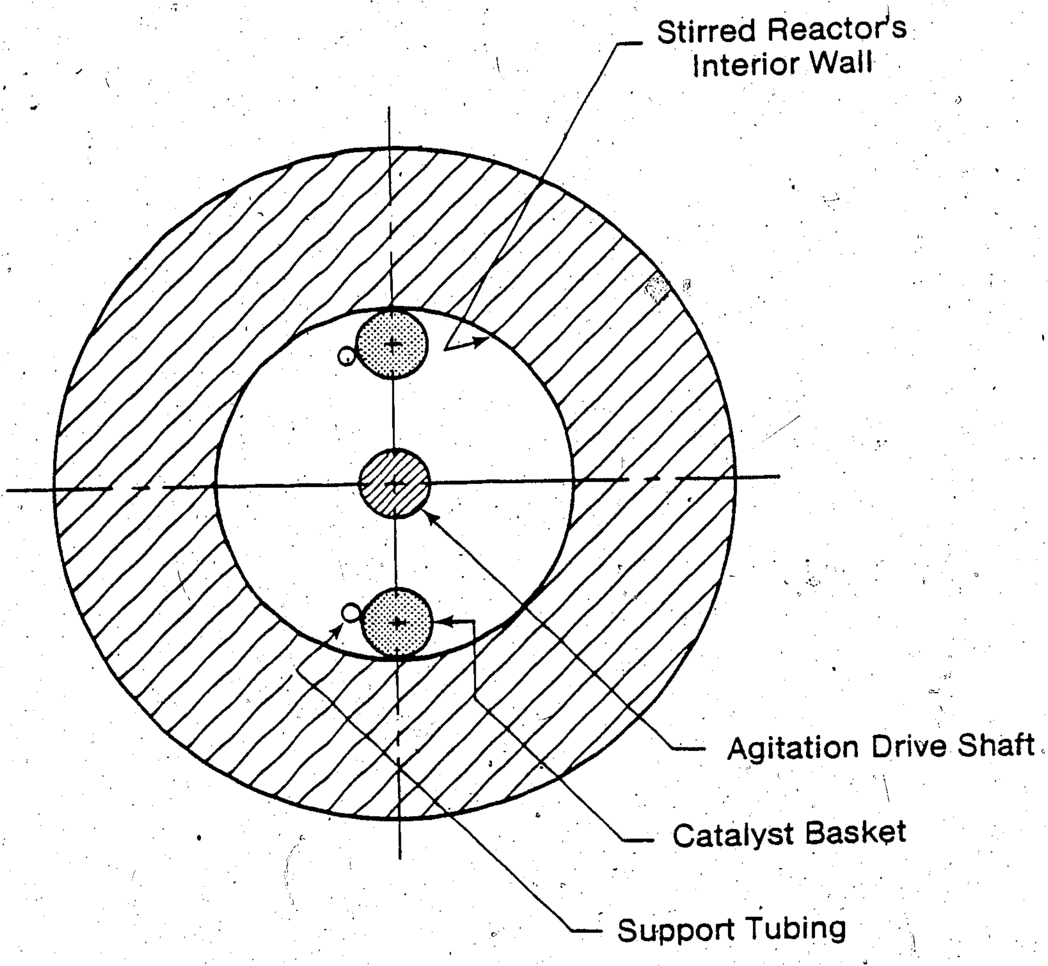


Figure III.8 Position of Catalyst Baskets in the Stirred Reactor

IV. OPERATING PROCEDURES

A. Thermal Hydroprocessing

Experiments in thermal hydroprocessing were conducted with the stirred reactor and the tubular reactor at high pressure and high temperatures. The liquid feeds used were heavy gas oils.

Stirred Reactor

The reactor was prepared for a run on the day prior to the day of the actual run. About 0.20 L of a heavy gas oil feed was placed in the reactor. The top closure and agitation assembly was then positioned and bolted to the main body of the reactor. After connecting and tightening all fittings on the reactor piping, the reactor was pressurized with hydrogen to the desired operating pressure, usually 13.9 MPa, and isolated from the rest of the system. If the pressure in the reactor dropped by less than 400 kPa in half an hour, the reactor was considered leak-free.

For the actual run, hydrogen and gas oil feed flows to the reactor were established and the flow rates adjusted to the desired values. Agitation of the reactor contents was initiated and maintained at about 800 rpm. The reactor was then heated and brought up to operating conditions at a rate of about 150°C per hour.

The volumetric flows of the liquid feed and the liquid product were determined during the run. The liquid feed rate was determined by timing the decrease of liquid level in a burette connected to the input liquid feed line over a period of 2-5 minutes. The liquid product rate was determined by diverting the product flow to the auxiliary liquid product holding tank and measuring the volume collected for a known time period.

The sampling of the gaseous and liquid products was initiated after the system had been running at the desired operating conditions for over two hours. Gaseous products exit continuously from the system as a combined stream from the high pressure receivers and the low pressure receiver. Part of the gas product stream was diverted to the gas chromatograph for analysis. Steady state operation was assumed when gas analysis showed that the product gas composition is approaching a constant level. Liquid samples were withdrawn periodically via a sampling valve located on the liquid line after the lower high pressure receiver. The samples, approximately 7 mL , were stored in capped sample vials and refrigerated until analyses could be carried out. A larger liquid product sample of about 14 mL was taken at the end of the run to be used for determining the density and the sulphur content.

Immediately after shutdown, with the reactor isolated from the rest of the system, samples of both the liquid phase and the gas phase in the reactor were taken into two high pressure sampling cylinders which were connected to the reactor liquid phase and vapour phase sampling lines. The liquid phase sample was flashed down to atmospheric pressure and the volume of dissolved gases measured using a burette system with mercury as the displacement fluid. Schematic diagrams of the sampling cylinder set-ups and the burette system are given in Appendix A.

The gases flashed from the reactor liquid phase were stored in a glass gas receiver where a saturated salt solution was displaced to accommodate the gas. This sample and the reactor gas phase sample were analyzed by gas chromatography, The weight of the reactor liquid sample was measured and then the sample was transferred to a sample bottle, capped, refrigerated and later analyzed.

The reactor was shut down by turning off the electrical power supplied to both the reactor furnace and feed preheater. The hydrogen and liquid feed supply to the reactor were then switched off and the valve on the product line leaving the reactor closed. Then the agitation rate was decreased to about 200 rpm and sampling of the reactor contents initiated. The reactor was allowed to cool-down before depressurizing and disassembling. The liquid holdup in the reactor was measured after cool-down.

Tubular Reactor

About 0.20 L of heavy gas oil feed was pumped into the reactor through the feed line. Following this, the reactor was isolated from the rest of the system and pressured with hydrogen to the desired operating pressure. Then the flowrates of the hydrogen and gas oil and the reactor and receiver pressures were set to desired values. The reactor was brought up to operating temperatures at a rate of about 150 °C per hour. The procedures used to measure feed and product rates and to sample the gaseous and liquid products obtained from the pressure reduction and separation zone were identical to those described for operation of the stirred reactor. Reactor contents were not sampled.

The shutting down of the tubular reactor was essentially the same as for the stirred reactor, except that the end fittings were left on and the reactor cleaned by flushing with solvents.

B. Catalytic Hydroprocessing

The catalytic hydroprocessing of a heavy gas oil was studied only with the stirred reactor. The catalyst was calcined at 430°C for one hour prior to loading into the reactor. The catalyst was packed into two of the specially designed baskets and suspended in the reactor. The catalyst was presulphided by gas oil mixed with carbon disulphide containing about 4.2 weight percent sulphur at 400°C and 13.9 MPa (2000 psig) hydrogen pressure for about 2 hours. The carbon disulphide contribution to the sulphur content of the presulphiding oil feed was about 1.6 weight percent.

The operation of the stirred reactor for catalytic hydroprocessing was similar to that for pure thermal hydroprocessing runs. To maintain constant catalyst activity, a new batch of catalyst was used for every two consecutive catalytic hydroprocessing runs. A typical catalytic hydroprocessing run represented about eight hours of on-stream time. The catalyst loading used in the studies was about 9 g Oil h^{-1} g Cat^{-1}.

V. RESIDENCE TIME DISTRIBUTION STUDY

A residence time distribution (RTD) study was made to determine the level of mixing that exists in the stirred reactor. A test run was made using Lloydminster Vacuum Gas Oil as liquid feed. Hydrogen was fed in at a rate of 200 m^3API/m^3Oil. The reactor was operated at a pressure of 13.9 MPa (2000 psig) and 290°C. The actual liquid hourly space velocity (LHSV) was 0.97 h^{-1}. Agitation of the reactor contents was maintained at 800 rpm.

When reactor operating conditions stabilized, the liquid feed stream was switched from a pure gas oil feed to a gas oil feed containing a tracer. Dodecane ($CH_3(CH_2)_{10}CH_3$) was used as the tracer. The amount of tracer used was 6.0 volume percent of the gas oil tracer mixture. The response from the reactor was measured as the change in concentration of the tracer in the liquid product samples collected. The samples were taken at 20 minute intervals from the liquid sampling valve on the liquid line after the lower high pressure receiver. Analysis of the gas and liquid product samples showed that at the reactor conditions for the test RTD run, no significant reaction occurred.

The results were plotted on a F-plot which is a plot of the relative concentration of the tracer in the liquid samples versus time. The experimental data are shown as points on the F-plot in Figure V.1. An F-curve generated for an ideal constant stirred tank reactor (CSTR) with an identical holdup volume as the actual reactor is shown as the solid curve on the same figure. The initial portion of the F-curve was due to a time lag of about 20 minutes required for the tracer containing gas oil to travel in a plug-flow fashion from the burette to the reactor through about 0.96 m of 0.635 cm plastic tubing. It can be seen from the plot that the experimental points agree very closely with those predicted for a CSTR. This experiment established that the level of mixing in the stirred reactor approximates that found in an ideal CSTR.

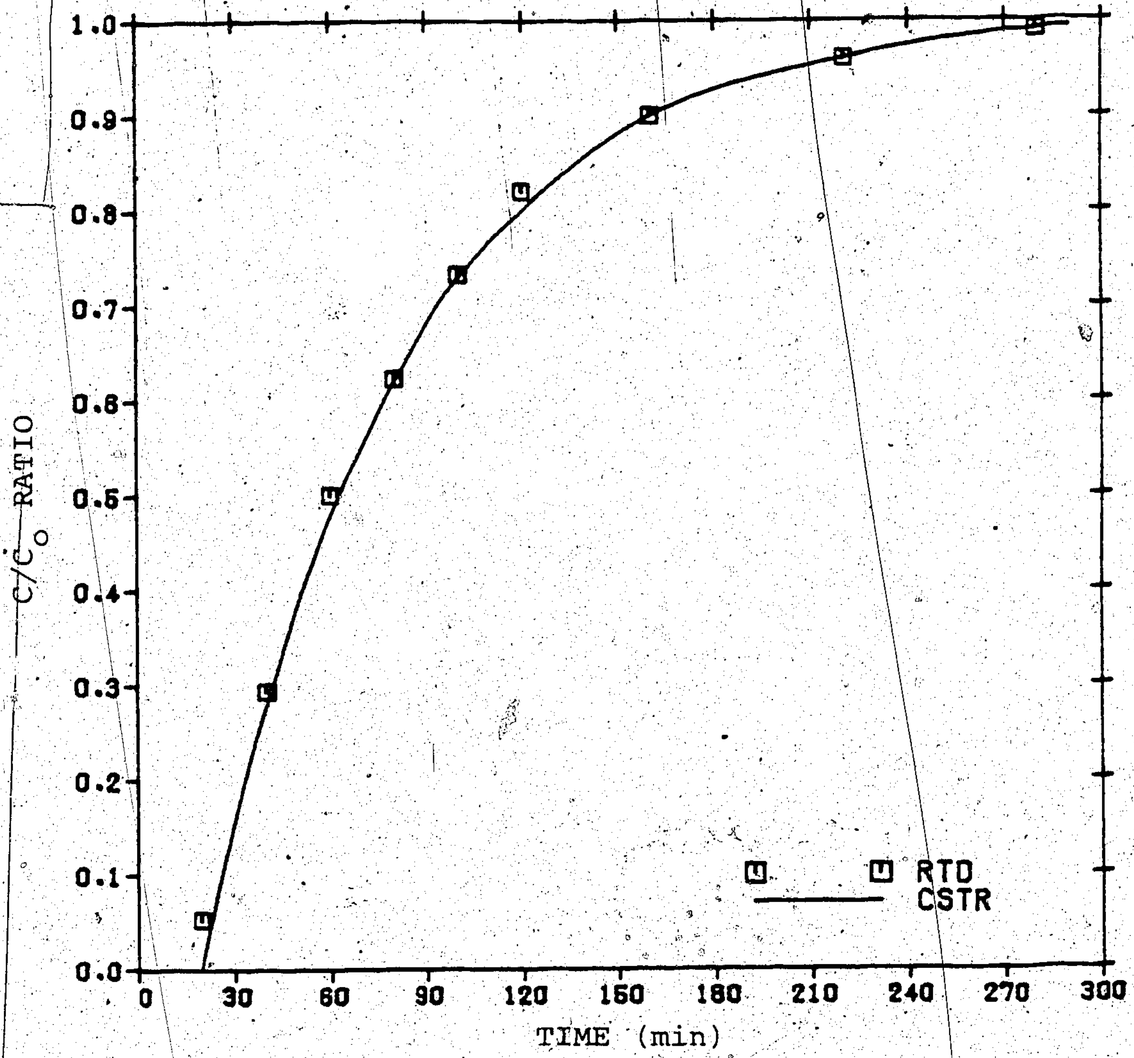


Figure V.1 F Plot for Stirred Reactor RTD Data

VI. ANALYTICAL METHODS

Advanced analytical methods were used to analyze the gaseous and liquid samples from the hydroprocessing runs. The methods used for this study included boiling point range distribution analysis by gas chromatography (simulated distillation) for liquid samples, refinery gas composition analysis by gas chromatography for gas samples, x-ray fluorescence to determine the sulphur content in liquids, and density measurements by using a precision densimeter. Bromine number determinations based on the standard method ASTM-D1159, were used to obtain a measure of the unsaturates content of liquid samples. A spinning band distillation analysis was used to determine the true boiling point (TBP) distribution of the liquid samples. The TBP data were used to check the simulated distillation analysis. A description of the analytical methods follows:

A. Simulated Distillation Analysis

The boiling range distribution of the liquid samples was determined by a simulated distillation analysis (SDA). The method used is similar to the ASTM Method D2887. In this method, the sample is injected into a gas chromatographic column of limited efficiency which separates the hydrocarbons with respect to their boiling points. A gas chromatograph (GC) with time programming capabilities, the Hewlett-Packard Model 5830A GC, was used.

In a typical analytical run, the column temperature is raised at a constant rate and the area response measured simultaneously as a function of time. The resulting data are expressed as a cumulative area (total area up to a given time) versus time relationship. Here the assumption that the volumetric response factor is unity for the individual fractions is made. This is justified since volumetric response factors for gaseous and liquid hydrocarbons determined experimentally with TCD have values close to unity. A table listing TCD volumetric response factors for various hydrocarbon compounds is given in Table VI.1.

The area axis is normalized to 100% to obtain the percent distilled off at a given time. Then, the time axis is converted to a boiling point axis by using a calibration curve based on an external standard, which contains 25 hydrocarbon compounds with boiling points across the temperature range of interest. A boiling point distribution curve or distillation curve is obtained expressed as cumulated volume percent distilled versus boiling point.

A differential thermal conductivity detector is used. The analytical and the reference GC columns are two identical 0.32 cm columns packed with 3 % Dexsil 300 GC on 80/100 mesh Chromosorb W and 0.45 m in length. The carrier gas used is pure helium. The external calibration mixture is a mixture of paraffins ranging from C9 to C40. A computer program, SIMU5, was written for data reduction. The program is listed in Appendix E. The data reduction procedure is

Table VI.1 Volumetric Response Factors for Various Hydrocarbon Compounds

Compound Name	Boiling Point (°C)	Volumetric Response Factor (TCD)
n-Hexane	69	1.0500
2,4-Dimethylpentane	81	1.1113
n-Heptane	98	0.9944
Toluene	111	0.9175
n-Octane	126	1.0000
p-Xylene	138	0.9410
n-Propylbenzene	159	0.9501
n-Decane	174	0.9844
n-Butylbenzene	183	0.9499
n-Dodecane	216	0.9780
n-Tridecane	235	0.9703
n-Tetradecane	253	0.9693
n-Pentadecane	271	0.9612

presented in Appendix B. For each liquid sample, two analyses on the GC are required; a baseline or blank run and a sample run with the GC conditions kept constant. The baseline run was required to correct for differences in characteristics between the reference and the analytical conditions. The actual GC response due to the sample was obtained by subtracting the area response for the baseline run from the corresponding area response for the sample run.

A typical chromatogram of the calibration standard mixture is given in Figure VI.1. The corresponding boiling point versus retention time is superimposed on the same diagram. A chromatogram for a typical liquid feed sample is given in Figure VI.2. The baseline run for that sample is superimposed on the diagram. A similar diagram for a typical liquid product sample is given in Figure VI.3.

B. Sulphur Determination

The sulphur content in the liquid samples was determined by X-ray fluorescence using a Panalyzer 4000 manufactured by Panametrics Inc. The radioactive source used was Fe_{55} isotope. Samples are irradiated and emit X-rays of an energy characteristic of the emitting sulphur atoms. A detector detects the X-rays and converts them into voltage pulses. The number of pulses arriving over a preset length of time is a measure of the weight percent of sulphur in the sample. Sample calculations are given in Appendix C.

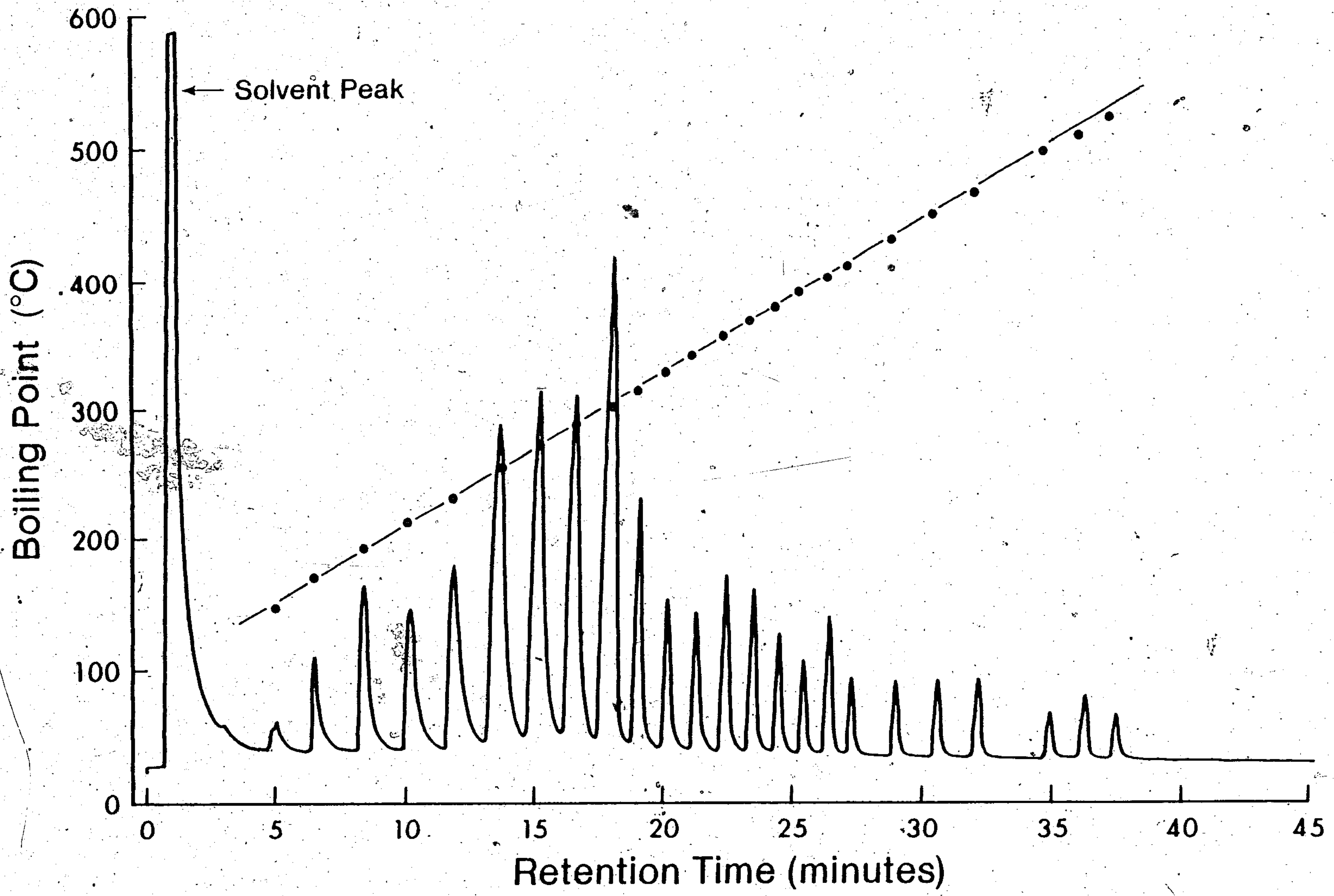


Figure VI.1 SDA Chromatogram of Calibration Standard

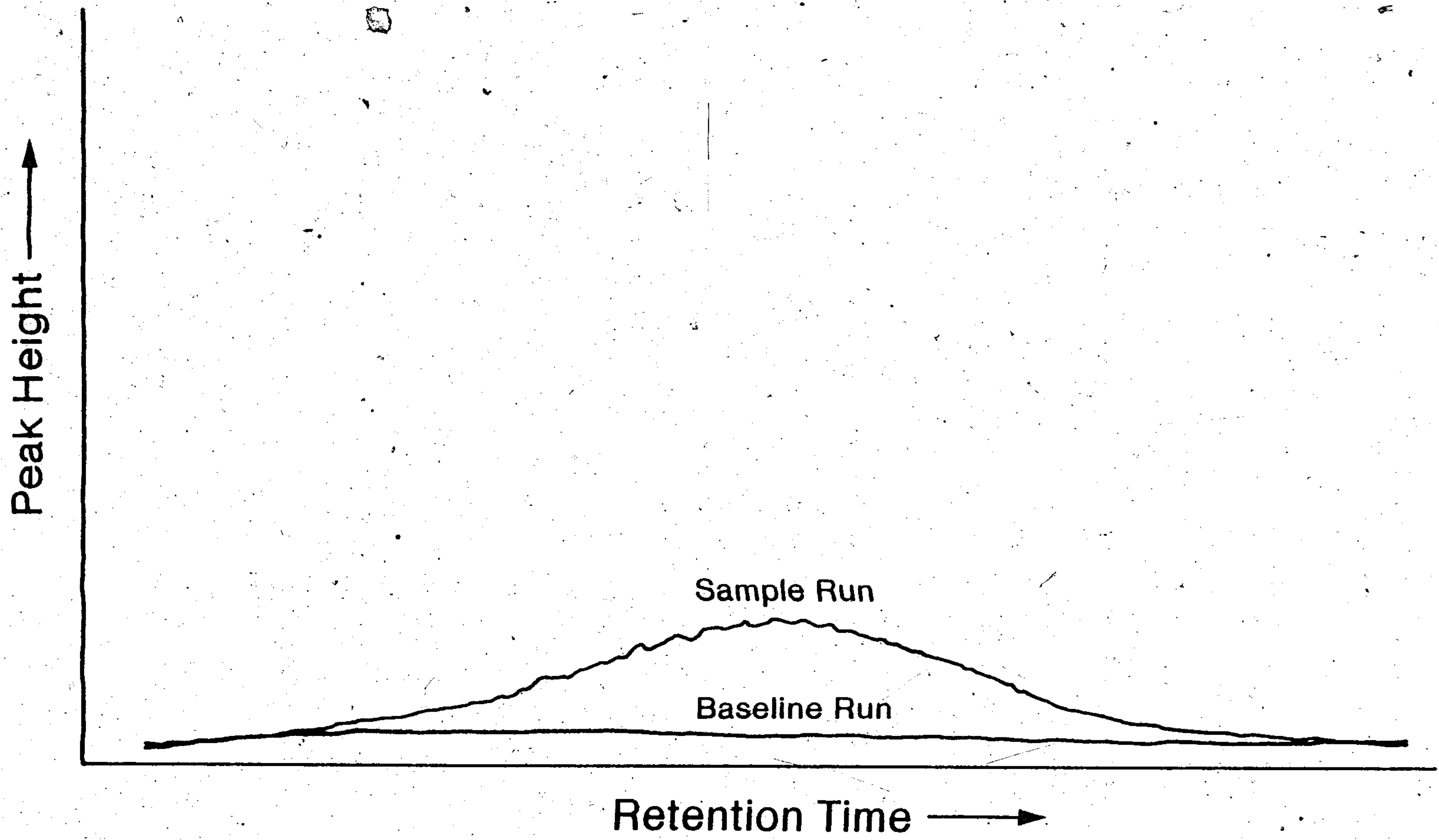


Figure VI.2 SDA Chromatogram for a Typical Feedstock Sample (LLVGO)

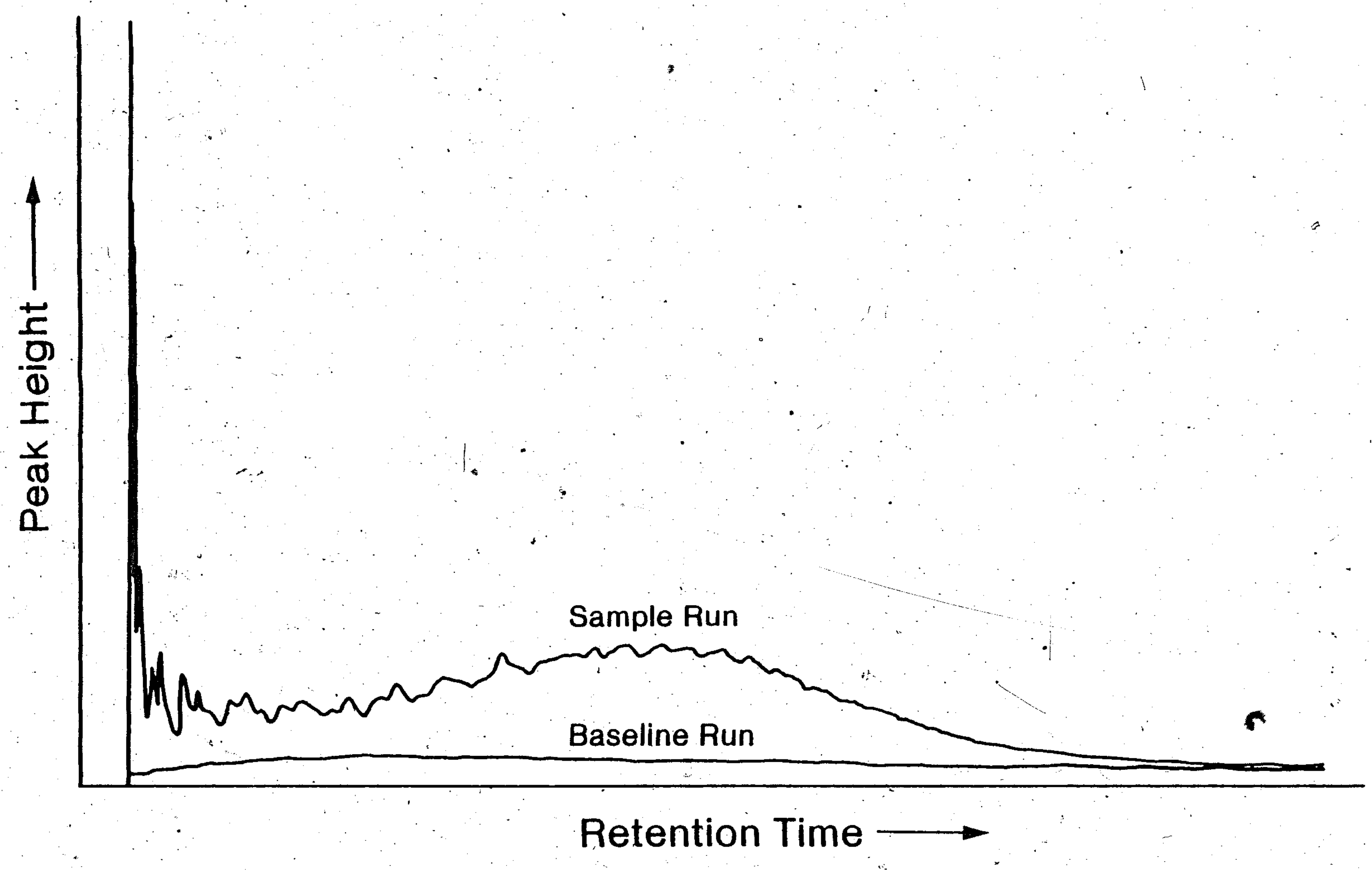


Figure VI.3 SDA Chromatogram for a Typical Liquid Product Sample

C. Density Determination

Accurate determination of the density for each of the liquid samples was obtained by using a Digital Precision Density Meter, Model DMA 02C, manufactured by the Anton Paar Company in Austria. The density meter measures the natural frequency of a hollow oscillator cell which is filled with the fluid sample. The frequency reading is directly related to the sample's density. The hollow oscillator cell is maintained at a constant temperature by a recycle flow of water from an "ultrathermostat" controlled constant temperature bath. The data reduction procedures and sample calculations are given in Appendix B and C.

D. Bromine Number Determination

The method used is based on the ASTM Method D1159. The magnitude of the bromine number provides a rough indication of the quantity of constituents that react with bromine and hence a measure of olefinic unsaturation in the sample. An electrometric titration apparatus was used. A detailed description of the method and equipment requirements can be found in the 1977 Annual Book of ASTM Standards for Petroleum Products and Lubricants. Data reduction procedures and sample calculations to determine the bromine number for the liquid gas oil samples are in Appendix B and C.

E. Spinning Band Distillation

A Nester-Faust spinning band distillation column was used to obtain the boiling range distribution of the gas oil feed. With the large number of theoretical plates available for the column, the spinning band distillation curve obtained closely approximates the true boiling point (TBP) distillation curve. The TBP distillation curve obtained was compared with the SDA distillation curve to show that the SDA distillation curve is a good approximation of the TBP distillation curve.

In the study, the spinning band was operated using an initial charge of 100 mL of gas oil feed. The column was operated under a vacuum of less than 1.3 kPa and at high reflux ratio. Figures VI.4 and VI.5 show comparisons of the SDA and the TBP distillation curves for a CANMET heavy gas oil and the Lloydminster heavy gas oil, respectively.

F. Refinery Gas Analysis

The gaseous product samples were analyzed by a gas chromatograph specially set up for the analysis of hydrocarbon gases. A Hewlett-Packard Model 5840A gas chromatograph was used. The chromatograph system is equipped with a series of three automatic switching valves for column isolation or backflushing. This enables the separation of a large number of hydrocarbon compounds over a short analysis time. This analysis is commonly referred to as a Refinery Gas Analysis (RGA).

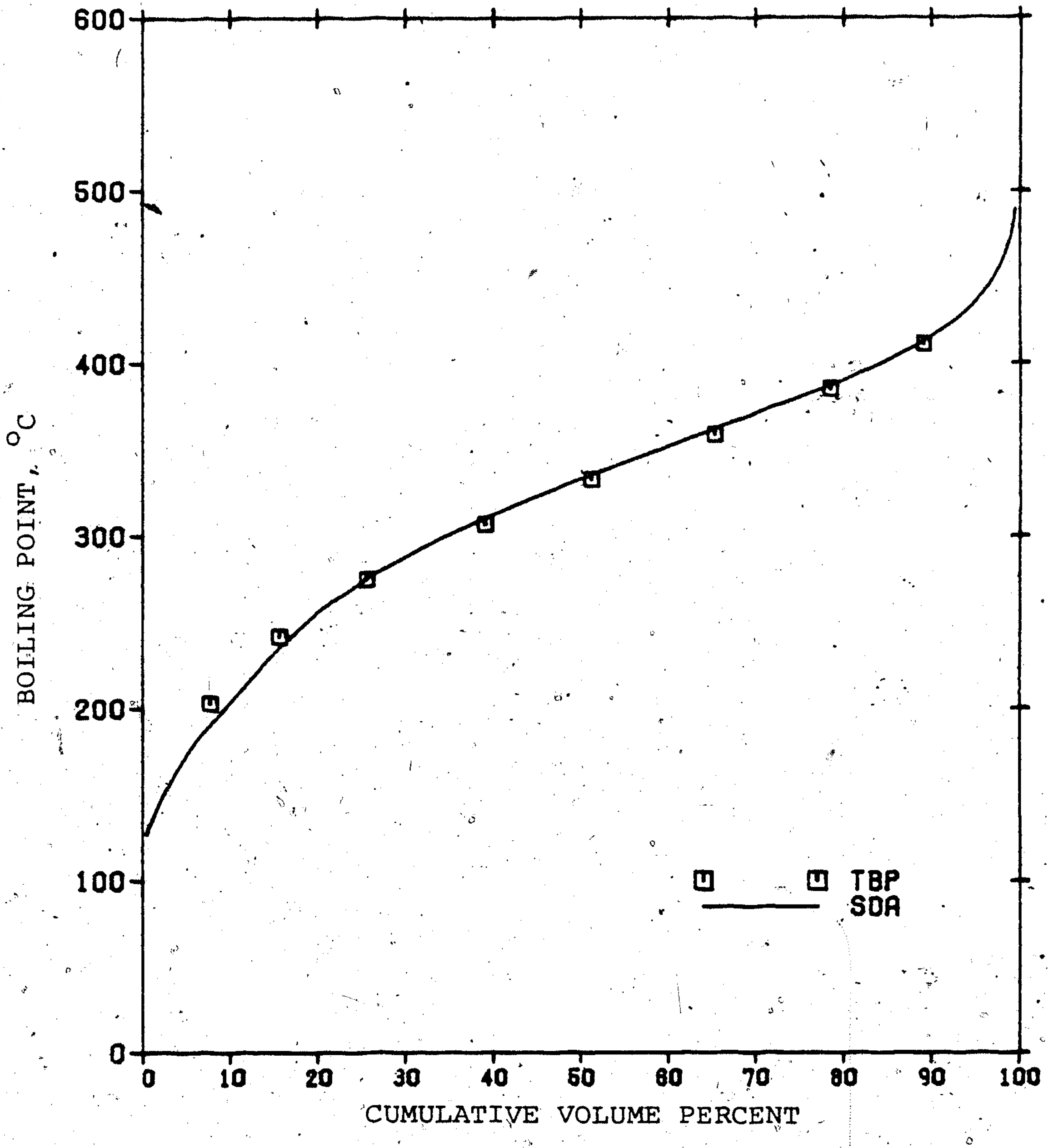


Figure VI.4 Comparison of TBP and SDA Distillation Curves for CANMET Gas Oil (EMRGO)

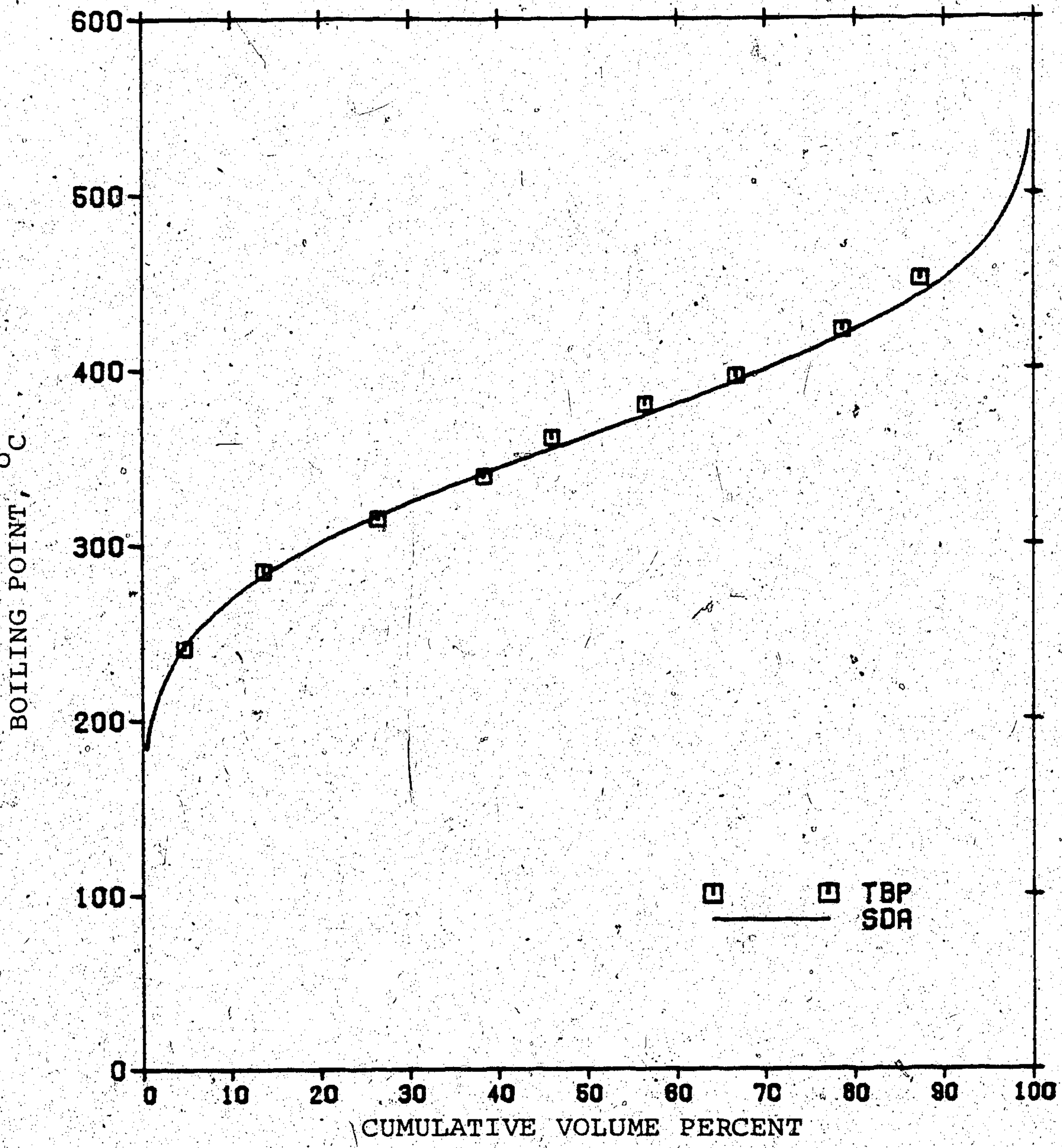


Figure VI.5 Comparison of TBP and SDA Distillation Curves for Lloydminster Gas Oil (LLVGO)

The analytical column is made up of three sub-columns connected in series. The first sub-column can be switched to a reversed flow direction (backflushing) while the latter two can be isolated individually. A single reference column was used. The columns used are listed below:

I. Analytical Columns

(1) 7.32 m of 16% bis-2-methoxyethyl adipate on 80/100 P-AW followed by 1.52 m of 30% DC 200 Silicone oil on 80/100 Chromsorb P-AW

(2) 1.83 m of Porapak Q, 80/100 mesh

(3) 3.04 m of Molecular Sieve 5A, 60/80 mesh

II. Reference Column

(1) 0.51 m of 10% UCW-892 Silicone on 80/100 Chromosorb W-HP

A mixture of 91.5 percent helium and 8.5 percent hydrogen was used as the carrier gas. This carrier gas blend was required to eliminate dual peak phenomenon. Two adjacent peaks for hydrogen will appear on the chromatogram if pure helium carrier gas is used which results in significant error in the peak area integration. With the carrier gas blend, a single hydrogen peak appears thus eliminating that source of error.

A schematic diagram of the plumbing in the RGA system is given in Appendix A. Figure VI.6 shows the sequence used in routing flow through the analytical column during a typical analytical run. Both the thermal conductivity detector (TCD) and the flame ionization detector (FID) were

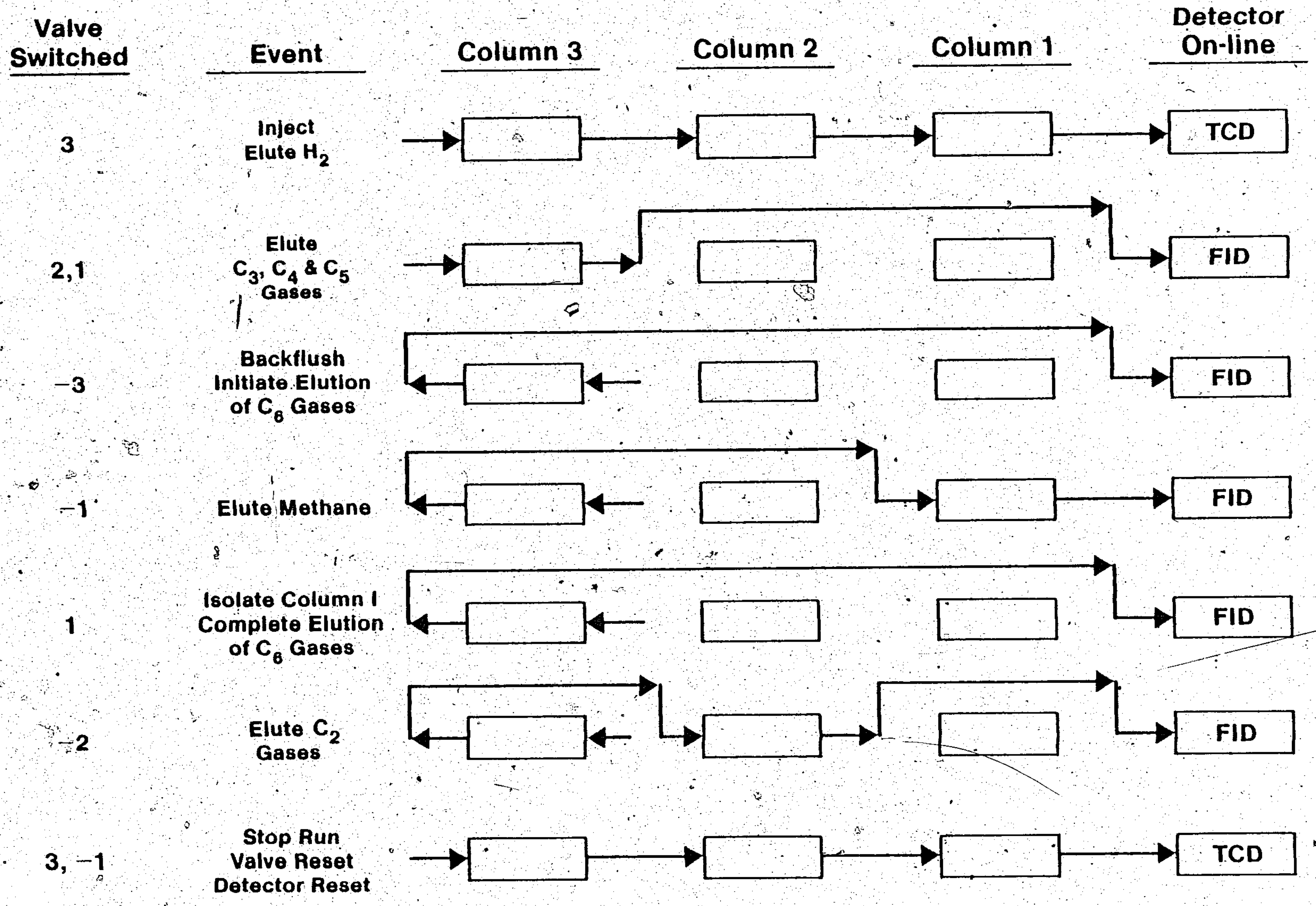


Figure VI.6 Valve Switching Sequence to Route Flow in a Typical RGA Run used. The TCD was used to detect hydrogen in the product gas stream while the FID was used to detect the rest of the hydrocarbon gases.

This set-up was required since for typical gas samples only small amounts of hydrocarbon gases were present. Hence FID being the more sensitive detector was used to determine the relative amounts of these gases. The RGA set-up however was unable to measure the hydrogen sulphide content in the gas samples. Hydrogen sulphide has the same column elution time as isobutane but passes through the column undetected s[illegible] FID does not respond to hydrogen sulphide.

A standard gas mixture prepared by Matheson Gas Products Inc. was used to calibrate the GC system. The composition of the standard gas mixture is shown in Table VI.2. The corresponding standard gas chromatogram is given in Figure VI.7, while a typical gas chromatogram for a gas product sample is given in Figure VI.8.

A computer program, &PGA, was written to combine gas composition data from RGA with hydrogen sulphide content data from absorption-iodimetric titration data. Program &PGA is listed in Appendix E.

G. Determination of the Hydrogen Sulphide Content in Gas Samples

The absorption-iodimetric method was used to determine the hydrogen sulphide content in the gas product stream. The effluent gas stream from the pressure reduction and

Table VI.2. Composition of Standard Gas Mixture for Refinery Gas Analysis

Component	Volume %
Hydrogen	88.50
Methane	1.02
Ethane	0.96
Ethylene	1.01
Propane	0.99
n-Butane	0.99
iso-Butane	1.05
1-Butene	1.01
cis-2-Butene	0.63
trans-2-Butene	0.98
Pentane	0.94
2-methyl-Pentane	0.96
Hexane	0.96

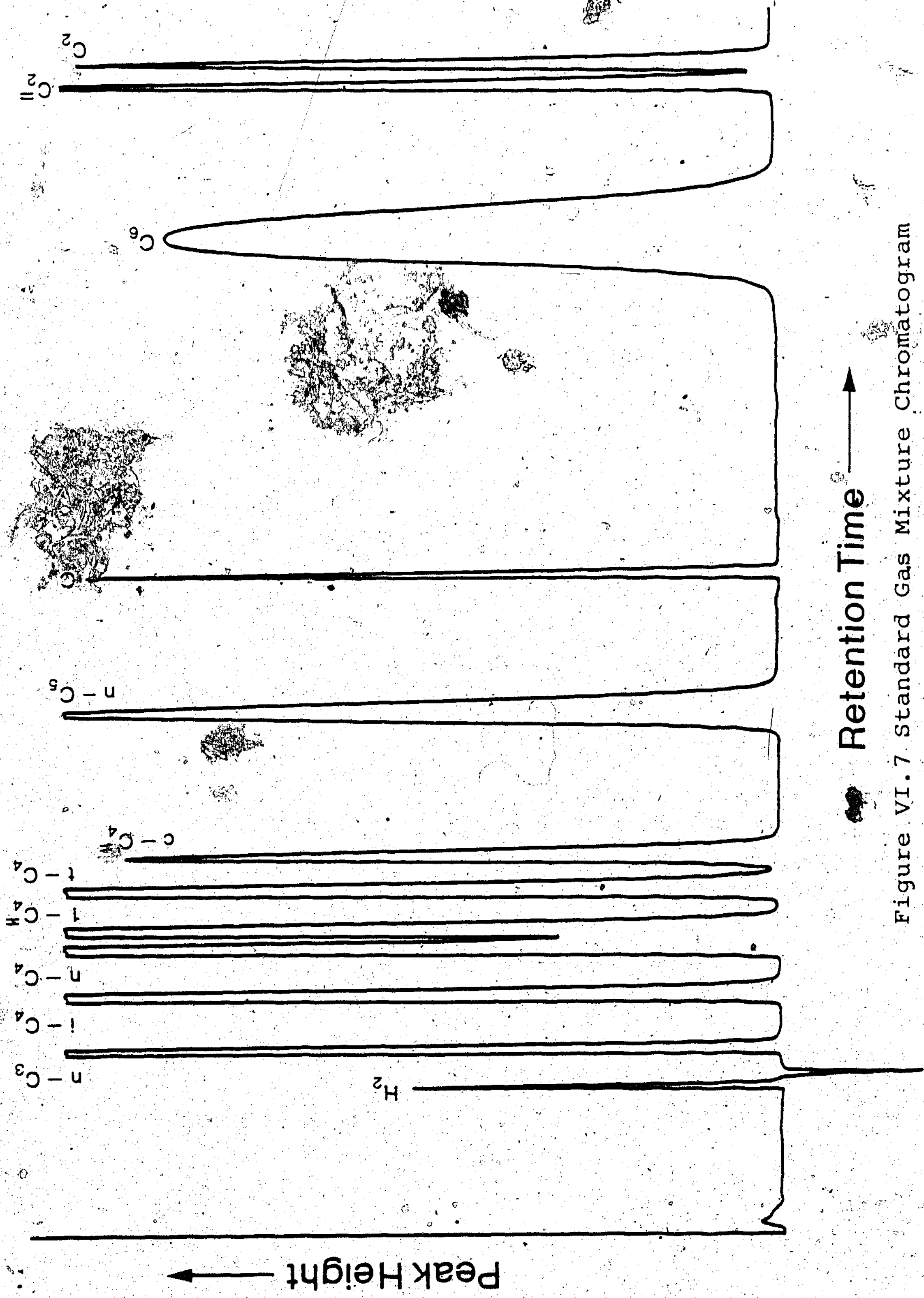


Figure VI.7 Standard Gas Mixture Chromatogram

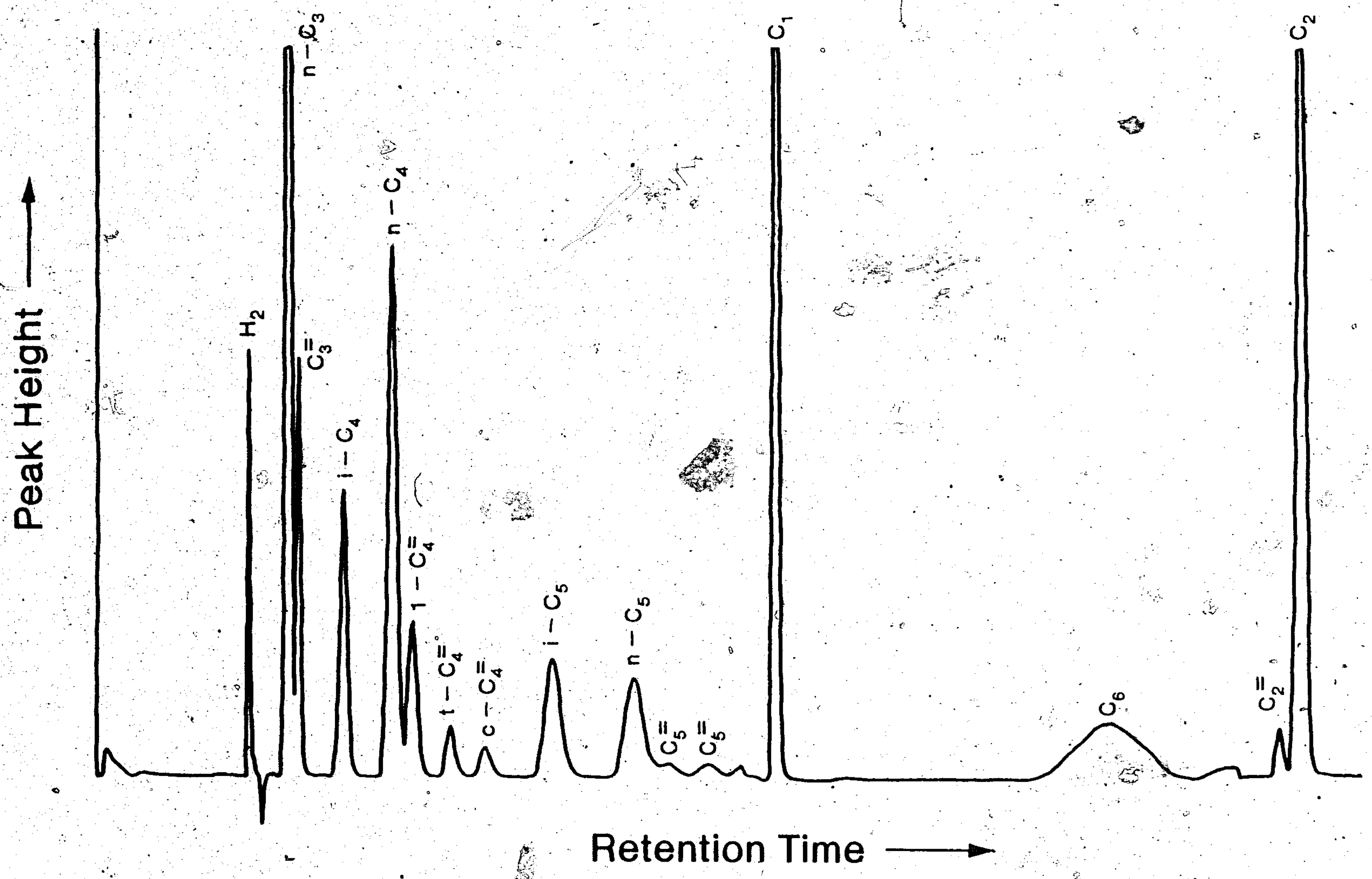


Figure VI.8 Typical Product Gas Chromatogram separation zone was allowed to bubble through a scrubbing solution of 50 mL 1.0 N caustic solution for fifteen minutes. The hydrogen sulphide in the bubbling gas would be converted into sodium sulphide as follows:

$$2NaOH + H_2S \dashrightarrow Na_2S + 2H_2O$$

The resulting absorption solution was then acidified with excess sulphuric acid and a known amount of iodine solution added. Then a fresh starch indicator was added and the excess iodine was back titrated with sodium thiosulphate. The method is based on the following reactions:

$$Na_2S + I_2 \dashrightarrow 2Na^+ + 2I^- + S$$

$$2S_2O_3^{2-} + I_2 \dashrightarrow S_4O_6^{2-} + 2I^-$$

The hydrogen sulphide content of the gas sample could then be calculated from the amount of sodium thiosulphate required for the titration. Detailed calculation procedures for this method is given in Appendix C.

VII. RESULTS

The properties of Lloydminster vacuum gas oil, including the results of a simulated distillation analysis, are given in Table VII.1. The operating conditions, liquid and gaseous product analysis, and flowrates are presented in Table VII.2 for 16 hydroprocessing runs made for this gas oil using the stirred reactor system. The results are for temperatures of 400, 420 and 440 °C, a reactor pressure of 13.9 MPa, and nominal LHSV of 0.75, 1.00 and 1.50 h^{-1}. The nominal LHSV is the liquid volumetric flowrate divided by the reactor volume of 0.30 L. The actual LHSV is based on the liquid hold-up and ranged from 0.99 to 2.36 h^{-1}. Both the liquid hold-up and liquid volumetric feedrate were measured at room temperature and corrected to reactor conditions to determine the actual LHSV. The correlation for thermal expansion of hydrocarbon feedstocks given in Table VII.3(20) was used to correct the density to reactor temperatures. The effect of pressure on density is small and was neglected. Hydrogen was supplied at rates varying between 199 and 588 m^3API per m^3 of gas oil feed. API refers to conditions of 15.0 °C and 101.3 kPa.

The results of sampling the liquid phase in the reactor are presented in Table VII.4. The dissolved gases in the reactor liquid phase were analyzed by RGA to obtain the amounts of hydrogen and hydrocarbons in the sample. The hydrogen sulphide content in the dissolved gases was taken to be that predicted by an equilibrium flash calculation. The flash calculation was done for reaction conditions on a feed consisting of the components present in the gas and liquid products from the reactor system and gave an estimate of the composition of both the gas and liquid phases in the reactor. The absorption-iodimetric method for hydrogen sulphide determination could not be used due to the small size of the gas sample.

Several attempts were made to process the Lloydminster gas oil at 450 °C and 460 °C. Runs at these temperatures had to be terminated because of excessive coking which caused the product line and control valves to block. However processing of this gas oil at 450 °C was studied by blending it with a lighter gas oil supplied by CANMET. The results of processing the CANMET gas oil and blends containing 50 and 25 percent by volume of the gas oil with Lloydminster gas oil are presented in Table VII.5. No operating difficulties were encountered but a small amount of coke deposition occured in the reactor for the blend containing 75 volume percent Lloydminster gas oil. The properties of the CANMET gas oil and of the blends are given in Table VII.6. The results of sampling the liquid and gas phases for these runs are presented in Table VII.7.

Six thermal hydrocracking runs were made using the tubular reactor. Heavy Lloydminster gas oil was used as feedstock and the reactor pressure was 13.9 MPa. Three reaction temperature levels were examined with the nominal

LHSV maintained at 1.00 h^{-1}. The temperature levels were 400, 420 and 440°C. The effect of changing LHSV was studied at 440°C for nominal LHSV of 0.75, 1.00 and 1.50 h^{-1}. The results are presented in Table VII.8.

The stirred reactor was also used to study the catalytic hydrocracking of the lighter CANMET gas oil. A nickel molybdenum (Ni-Mo) hydrodesulphurization catalyst manufactured by the NALCO Chemical Company was used. The chemical analysis and physical properties for the 1/16 inch extruded catalyst are given in Appendix G. In these runs temperature levels of 400, 420 and 440 °C were examined. The runs were made at a constant nominal LHSV of 0.28 h^{-1}. The actual measured LHSV wa[illegible]he range of 0.45 - 0.70 h^{-1}. Hydrogen feed was supplied at a rate in the range 725 - 935 m^3 API per m^3 of oil. The results for these catalytic runs are presented in Tables VII.9 and VII.10.

The results of mass balance calculations for the thermal hydroprocessing runs in both the stirred reactor and tubular reactor are given in Appendix F. The results show errors of less than 5.0 percent in the mass balance. Similar mass balance results for the catalytic hydroprocessing runs with errors of less than 4.0 percent are given in Appendix F. Sulphur balance results presented in Appendix F for thermal hydroprocessing runs show an average error of about 10.0 percent. The catalytic hydroprocessing run results show a larger error of around 30.0 percent in the sulphur balance.

Table VII.1 Properties of Lloydminster
Heavy Vacuum Gas Oil

Boiling Range, °C	192 - 566
Specific Gravity (15°C)	0.9239
Sulphur, wt.%	2.41
Nitrogen, wt.%	-
Bromine Number	7
Fractions, Vol.%	
Naphtha(C7 - 177 C)	0.0
Distillate(177 - 343 C)	37.2
Fuel Oil(343 C+)	62.8
Pitch (343 - 524°C Cut)	
Vol.%	60.7
Wt.%	61.5
Av. MW	373.5

Table VII.2 Thermal Hydrocracking Results (Stirred Reactor)
Feedstock : Lloydminster Vacuum Gas Oil

Run No.	LL-10	LL-11	[illegible]	LL-19
<u>Operating Conditions:</u>				
Reactor Pressure, MPa	13.9	13.9	13.9	13.9
Reactor Temp., °C	400	400	400	400
Nominal LHSV, h^{-1}	0.75	1.00	1.50	0.75
Actual LHSV, h^{-1}	0.99	1.55	2.25	1.15
H2/OIL, m3API/m3	304	255	187	344
Agitation Speed, rpm	800	800	800	850
Liquid Feedrate, mL/h	225	300	450	225
<u>Liquid Products</u>				
Product flowrate, mL/h	225	300	450	224
S. G. (15°C)	0.9142	0.9155	0.9200	0.9159
Sulphur, wt.%	2.12	2.13	2.37	2.24
Nitrogen, wt.%	-	-	-	-
Bromine Number	11	12	11	12
Cuts, Vol.%				
Naphtha(C7-177°C)	5.5	4.7	3.7	4.9
Distillate(177-343°C)	43.2	43.1	42.3	43.1
Fuel Oil(343°C+)	51.3	52.2	54.0	52.0
Pitch (343 - 524°C Cut)				
Vol.%	50.70	51.89	53.30	50.53
Wt.%	51.73	52.88	54.24	51.54
Av. MW	365.83	366.24	367.98	366.80
<u>Gas Products</u>, m3API/m3OIL				
C1	1.57	1.36	0.81	1.43
C2	1.04	0.79	0.48	0.94
C3	0.91	0.79	0.41	0.93
C4	0.48	0.39	0.17	0.52
C5	0.16	0.10	0.04	0.20
C6	0.11	0.08	0.04	0.16
H2S	2.19	1.95	1.19	2.35

Table VII.2 Thermal Hydrocracking Results (Stirred Reactor)
(cont'd) Feedstock : Lloydminster Vacuum Gas Oil

Run No.	LL-22	LL-05	LL-07	LL-12
Operating Conditions:				
Reactor Pressure, MPa	13.9	13.9	13.9	13.9
Reactor Temp., °C	400	420	420	420
Nominal LHSV, h^{-1}	1.00	0.75	0.75	1.00
Actual LHSV, h^{-1}	1.54	1.10	1.19	1.55
H2/OIL, m3API/m3	271	226	211	240
Agitation Speed, rpm	850	800	800	800
Liquid Feedrate, mL/h	300	225	225	300
Liquid Products				
Product Flowrate, mL/h	300	225	225	300
S. G. (15°C)	0.9188	0.9019	0.9017	0.9136
Sulphur, wt.%	2.14	2.07	2.07	2.18
Nitrogen, wt.%	-	-	-	-
Bromine Number	11	16	18	19
Cuts, Vol.%				
Naphtha(C7-177°C)	4.36	12.5	13.9	11.5
Distillate(177-343°C)	43.01	47.1	42.6	45.9
Fuel Oil(343°C+)	52.63	40.4	43.5	42.6
Pitch (343 - 524°C Cut)				
Vol.%	51.29	39.47	41.66	41.95
Wt.%	52.25	41.00	43.01	43.18
Av. MW	364.77	361.81	371.17	364.52
Gas Products, m3API/m3OIL				
C1	1.50	3.01	4.91	3.64
C2	0.98	1.71	2.69	2.16
C3	1.03	1.57	2.39	1.92
C4	0.69	0.83	1.13	0.90
C5	0.36	0.29	0.26	0.32
C6	0.31	0.19	0.17	0.16
H2S	1.14	2.93	2.82	3.36

Table VII.2 Thermal Hydrocracking Results (Stirred Reactor) (cont'd) Feedstock :- Lloydminster Vacuum Gas Oil

Run No.	LL-16	LL-20	LL-06	LL-08
<u>Operating Conditions:</u>				
Reactor Pressure, MPa	13.9	13.9	13.9	13.9
Reactor Temp., °C	420	420	440	440
Nominal LHSV, h^{-1}	1.50	1.00	0.75	0.75
Actual LHSV, h^{-1}	2.20	1.53	1.18	1.27
H2/OIL, m3API/m3	310	368	199	216
Agitation Speed, rpm	800	850	800	800
Liquid Feedrate, mL/h	450	300	225	225
<u>Liquid Products</u>				
Product Flowrate, mL/h	443	300	225	225
S. G. (15°C)	0.9130	0.9087	0.8738	0.8837
Sulphur, wt.%	2.17	2.08	1.84	1.92
Nitrogen, wt.%	–	–	–	–
Bromine Number	14	16	17	20
Cuts, Vol.%				
Naphtha(C7-177°C)	8.2	9.6	32.5	27.0
Distillate(177-343°C)	44.7	45.1	46.9	47.4
Fuel Oil(343°C+)	47.1	45.3	20.6	25.6
Pitch (343 - 524°C Cut)				
Vol.%	45.66	43.52	20.07	24.97
Wt.%	46.80	44.69	21.24	26.24
Av. MW	365.63	365.36	355.78	360.44
<u>Gas Products</u>, m3API/m3OIL				
C1	1.73	3.15	17.73	16.25
C2	1.15	1.94	8.27	7.50
C3	1.21	2.17	5.57	5.29
C4	0.75	1.51	2.45	2.28
C5	0.31	0.97	0.69	0.64
C6	0.20	0.76	0.32	0.30
H2S	3.13	3.36	4.53	4.24

Table VII.2 Thermal Hydrocracking Results (Stirred Reactor)
(cont'd) Feedstock : Lloydminster Vacuum Gas Oil

Run No.	LL-13	LL-17	LL-18	LL-21
Operating Conditions:				
Reactor Pressure, MPa	13.9	13.9	13.9	13.9
Reactor Temp., °C	440	440	440	440
Nominal LHSV, h^{-1}	1.00	1.50	0.75	1.00
Actual LHSV, h^{-1}	1.71	2.36	1.15	1.66
H2/OIL, m3API/m3	299	348	526	588
Agitation Speed, rpm	800	800	850	850
Liquid Feedrate, mL/h	300	450	225	300
Liquid Products				
Product Flowrate, mL/h	300	443	216	290
S. G. (15°C)	0.9011	0.9088	0.8948	0.8998
Sulphur, wt.%	2.05	2.05	1.87	1.90
Nitrogen, wt.%	-	-	-	-
Bromine Number	23	19	18	20
Cuts, Vol.%				
Naphtha(C7-177°C)	24.9	19.5	25.7	21.8
Distillate(177-343°C)	48.0	48.5	50.7	51.9
Fuel Oil(343°C+)	27.1	32.0	23.6	26.3
Pitch (343 - 524°C Cut)				
Vol.%	26.28	30.79	22.62	24.70
Wt.%	27.56	32.06	23.75	25.80
Av. MW	359.46	360.67	355.72	352.94
Gas Products, m3API/m3OIL				
C1	15.38	8.52	26.43	9.69
C2	8.80	4.99	13.90	5.75
C3	7.26	4.80	10.72	6.00
C4	3.62	2.99	4.97	4.59
C5	1.14	1.17	1.61	2.46
C6	0.64	0.73	0.63	2.29
H2S	5.70	4.79	7.13	6.15

Table VII.3 Correlation Used to Correct Liquid Density for Thermal Expansion

$$\rho_t = \sqrt{\rho^2_{23.0} + \bar{k}(t - 23.0)} \qquad (7.1)$$

where,

$\rho_{23.0}$ = liquid density measured at 23.0°C, g mL^{-1}

$\bar{k}$ = thermal volumetric slope

= - 0.0011 g^2 m^{-6} °C^{-1}

t = temperature of reaction mixture, °C

ρ_t = liquid density corrected to reaction temperature, g mL^{-1}

Table VII.4 Thermal Hydrocracking Results (Stirred Reactor)
Feedstock : Lloydminster Vacuum Gas Oil
Reactor Liquid Phase Sampling Results

Run No.	LL-10	LL-11	LL-14	LL-19
Reactor Liquid				
S.G. (15°C)	0.9214	0.9223	0.9212	0.9201
Sulphur, wt.%	2.17	2.13	2.31	2.28
Nitrogen, wt.%	-	-	-	-
Bromine Number	10	12	10	9
Cuts, Vol.%				
Naphtha(C7-177°C)	3.7	2.3	3.2	3.3
Distillate(177-343°C)	40.1	40.6	40.1	37.4
Fuel Oil(343°C+)	56.2	57.1	56.7	59.3
Pitch (343 - 524°C Cut)				
Vol.%	53.98	55.97	54.91	54.93
Wt.%	54.90	56.84	55.82	55.81
Av. MW	368.48	366.77	368.17	378.57
Dissolved Gases				
Mole % H_2	90.8	96.6	95.7	95.3
Solubility of H_2 (mg H_2/g Oil)	2.343	2.250	1.947	2.407

Table VII.4 Thermal Hydrocracking Results (Stirred Reactor)
(cont'd) Feedstock : Lloydminster Vacuum Gas Oil
Reactor Liquid Phase Sampling Results

Run No.	LL-22	LL-05	LL-07	LL-12
Reactor Liquid				
S.G. (15°C)	0.9235	0.9188	0.9146	0.9201
Sulphur, wt.%	2.17	2.19	2.22	2.28
Nitrogen, wt.%	-	-	-	-
Bromine Number	10	13	17	14
Cuts, Vol.%				
Naphtha(C7-177°C)	1.9	6.6	9.8	6.8
Distillate(177-343°C)	39.7	43.1	41.6	43.0
Fuel Oil(343°C+)	58.4	50.3	48.6	50.2
Pitch (343 - 524°C Cut)				
Vol.%	56.24	48.68	46.24	48.58
Wt.%	57.05	50.00	47.46	49.67
Av. MW	367.56	365.93	372.14	366.10
Dissolved Gases				
Mole % H_2	96.3	-	86.0	91.2
Solubility of H_2 (mg H_2/ g Oil)	2.203	-	2.173	2.175

Table VII.4 Thermal Hydrocracking Results (Stirred Reactor)
(cont'd) Feedstock : Lloydminster Vacuum Gas Oil
Reactor Liquid Phase Sampling Results

Run No.	LL-16	LL-20	LL-06	LL-08
Reactor Liquid				
S.G. (15°C)	0.9207	0.9206	0.9449	0.9258
Sulphur, wt.%	2.26	2.22	2.42	2.23
Nitrogen, wt.%	-	-	-	-
Bromine Number	13	9	14	18
Cuts, Vol.%				
Naphtha (C7-177°C)	6.2	5.1	15.8	16.8
Distillate (177-343°C)	41.8	42.4	46.6	46.2
Fuel Oil (343°C+)	52.0	52.5	37.6	37.0
Pitch (343 - 524°C Cut)				
Vol.%	50.16	50.36	36.33	35.04
Wt.%	51.23	51.36	37.65	36.35
Av. MW	367.32	366.62	363.51	365.93
Dissolved Gases				
Mole % H_2	91.6	90.4	66.5	64.6
Solubility of H_2 ($mg\ H_2/g$ Oil)	1.879	2.370	2.204	2.420

Table VII.4 Thermal Hydrocracking Results (Stirred Reactor)
(cont'd) Feedstock: Lloydminster Vacuum Gas Oil
Reactor Liquid Phase Sampling Results

Run No.	LL-13	LL-17	LL-18	LL-21
Reactor Liquid				
S.G. (15°C)	0.9469	0.9295	0.9581	0.9538
Sulphur, wt.%	2.56	2.34	2.52	2.500
Nitrogen, wt.%	-	-	-	-
Bromine Number	17	15	14	15
Cuts, Vol.%				
Naphtha(C7-177°C)	10.8	11.1	8.3	8.9
Distillate(177-343°C)	44.7	43.9	44.2	42.5
Fuel Oil(343°C+)	44.5	45.0	47.5	48.6
Pitch (343 - 524°C Cut)				
Vol.%	42.23	43.03	44.28	45.86
Wt.%	43.43	44.26	45.37	47.00
Av. MW	367.23	366.45	367.08	366.69
Dissolved Gases				
Mole % H_2	83.9	77.8	86.1	81.8
Solubility of H_2 (mg H_2/g Oil)	2.164	2.274	2.317	2.408

Table VII.5 Thermal Hydrocracking Results (Stirred Reactor)
Feedstock : Blends of Lloydminster Gas Oil with
a lighter CANMET Gas Oil (EMRGO)

Run No.	LL-23	LL-24	LL-25
Feedstock Blend No.	1	2	EMRGO
<u>Operating Conditions:</u>			
Reactor Pressure, MPa	13.9	13.9	13.9
Reactor Temp., °C	450	450	450
Nominal LHSV, h^{-1}	1.00	1.00	1.00
Actual LHSV, h^{-1}	1.69	1.60	1.79
H2/OIL, m3API/m3	702	850	507
Agitation Speed, rpm	850	850	850
Liquid Feedrate, mL/h	300	300	300
<u>Liquid Products</u>			
Product Feedrate, mL/h	290	298	295
S. G. (15°C)	0.8980	0.9036	0.9020
Sulphur, wt.%	1.58	1.55	1.68
Nitrogen, wt.%	-	-	-
Bromine Number	30	17	20
Cuts, Vol.%			
Naphtha(C7-177°C)	29.13	26.98	30.10
Distillate(177-343°C)	57.07	58.18	55.79
Fuel Oil(343°C+)	13.80	14.84	14.11
Pitch (343 - 524°C Cut)			
Vol.%	13.34	15.23	13.40
Wt.%	14.09	16.03	14.18
Av. MW	338.68	342.49	345.61
<u>Gas Products</u>, m3API/m3OIL			
C1	11.37	11.87	16.20
C2	6.95	6.59	9.72
C3	6.85	6.72	8.10
C4	5.24	5.30	4.75
C5	2.64	2.95	1.82
C6	2.56	2.80	1.59
H2S	7.10	7.81	6.86

Table VII.6 Properties of the Lloydminster Gas Oil (LLVGO) /CANMET Gas Oil Blends used for Runs No. LL-23, LL-24, and LL-25

Blend No.	EMRGO	Blend 1.	Blend 2.
Vol.% LLVGO in Blend	0.0	50.0	75.0
Boiling Range, °C	132-543	132-592	132-592
Specific Gravity (15°C)	0.9172	0.9208	0.9213
Sulphur, wt.%	2.19	2.30	2.32
Nitrogen, wt.%	-	-	-
Bromine Number	10	9	7
Fractions, Vol.%			
Naphtha(C7-177°C)	5.2	2.5	0.6
Distillate(177-343°C)	47.6	44.9	43.7
Fuel Oil(343°C+)	47.2	52.6	55.7
Pitch (324 - 524°C Cut)			
Vol.%	43.11	51.01	56.18
Wt.%	44.05	51.90	56.96
Av. MW	351.95	360.77	358.95

Table VII.7 Thermal Hydrocracking Results (Stirred Reactor)
Feedstock : Blends of Lloydminster Gas Oil with
a lighter CANMET Gas Oil
Reactor liquid phase sampling results

Run No.	LL-23	LL-24	LL-25
<u>Liquid Products</u>			
S.G. (15°C)	0.9849	0.9938	0.9674
Sulphur, wt.%	2.57	2.55	2.34
Nitrogen, wt.%	-	-	-
Bromine Number	15	14	15
Cuts, Vol.%			
Naphtha(C7-177°C)	5.8	4.3	6.4
Distillate(177-343°C)	42.7	38.5	48.5
Fuel Oil(343°C+)	51.5	57.2	45.1
Pitch (343 - 524°C Cut)			
Vol.%	48.47	54.02	43.08
Wt.%	49.47	54.95	44.10
Av. MW	365.04	369.06	358.05
<u>Dissolved Gases</u>			
Mole % H_2	88.1	89.1	86.2
Solubility of H_2 (mg H_2/g Oil)	2.344	2.020	2.260

Table VII.8 Thermal Hydrocracking Results (Tubular Reactor)
Feedstock : Lloydminster Vacuum Gas Oil

Run No.	LL-26	LL-29	LL-27	LL-32
Operating Conditions:				
Reactor Pressure, MPa	13.9	13.9	13.9	13.9
Reactor Temp., °C	400	400	420	440
Nominal LHSV, h^{-1}	1.00	1.00	1.00	0.75
Actual LHSV, h^{-1}	1.46	1.43	1.47	3.04
H2/OIL, m3API/m3	322	283	355	1055
Liquid Feedrate, mL/h	300	300	300	225
Liquid Products				
Product Flowrate, mL/h	298	302	300	222
S. G. (15°C)	0.9169	0.9204	0.9149	0.9123
Sulphur, wt.%	1.84	1.86	1.79	1.63
Nitrogen, wt.%	-	-	-	-
Bromine Number	12	10	16	17
Cuts, Vol.%				
Naphtha(C7-177°C)	6.27	4.27	12.79	13.69
Distillate(177-343°C)	42.71	43.14	46.45	50.97
Fuel Oil(343°C+)	51.02	52.59	40.76	35.34
Pitch (343 - 524°C Cut)				
Vol.%	49.07	50.29	38.33	33.21
Wt.%	50.13	51.24	39.55	34.36
Av. MW	368.03	365.10	364.77	351.84
Gas Products, m3API/m3OIL				
C1	2.05	1.47	5.82	10.13
C2	1.25	0.92	3.39	5.27
C3	1.31	0.89	3.32	5.01
C4	0.75	0.58	1.89	3.69
C5	0.20	0.20	0.62	1.57
C6	0.24	0.55	0.49	1.83
H2S	2.08	1.99	3.31	5.49

Table VII.8 Thermal Hydrocracking Results (Tubular Reactor)
(cont'd) Feedstock : Lloydminster Vacuum Gas Oil

Run No.	LL-31	LL-30
Operating Conditions:		
Reactor Pressure, MPa	13.9	13.9
Reactor Temp., °C	440	440
Nominal LHSV, h^{-1}	1.50	1.00
Actual LHSV, h^{-1}	2.51	1.66
H2/OIL, m3API/m3	540	745
Liquid Feedrate, mL/h	450	300
Liquid Products		
Product Flowrate, mL/h	447	296
S. G. 15 C	0.9175	0.9086
Sulphur, wt.%	1.70	1.58
Nitrogen, wt.%	-	-
Bromine Number	18	16
Cuts, Vol.%		
Naphtha(C7-177°C)	19.37	20.91
Distillate(177-343°C)	53.31	54.45
Fuel Oil(343°C+)	27.32	24.64
Pitch (343 - 524°C Cut)		
Vol.%	25.68	24.00
Wt.%	26.78	25.05
Av. MW	352.33	349.50
Gas Products, m3API/m3OIL		
C1	11.61	9.92
C2	6.04	4.54
C3	5.52	3.92
C4	3.34	2.78
C5	1.16	1.50
C6	1.30	4.10
H2S	4.39	6.11

Table VII.9 Catalytic Hydrocracking Results (Stirred Reactor)
Feedstock : CANMET Gas Oil
Test Catalyst : NALCO NM-502

Run No.	EC1-2	EC1-3	EC1-5	EC1-7	EC1-6
Operating Conditions:					
Reactor Press., MPa	13.9	13.9	13.9	13.9	13.9
Reactor Temp., °C	400	400	420	420	440
Nominal LHSV, h^{-1}	0.28	0.28	0.28	0.28	0.28
Actual LHSV, h^{-1}	0.45	0.48	0.51	0.51	0.70
LHSV, g/h gCat.	9.45	9.25	8.89	8.89	8.89
H2/OIL, m3API/m3	780	725	935	813	935
Agitation Speed, rpm	850	850	850	850	850
Cumulative hours on catalyst	15	23	13	29	21
H2 Consumption (m3API/m3OIL)	264	274	310	294	392
Liquid Feedrate, mL/h	84	84	84	84	84
Liquid Products					
Product Rate, mL/h	84	84	84	84	84
S. G. (15°C)	0.8745	0.8740	0.8549	0.8611	0.8460
Sulphur, wt.%	0.144	0.258	0.0	0.069	0.0
Nitrogen, wt.%	-	-	-	-	-
Bromine Number	3	3	3	5	3
Cuts, Vol.%					
Naphtha(C7-177°C)	15.0	15.2	27.2	23.1	37.4
Distill(177-342°C)	60.1	61.4	63.2	62.6	58.5
Fuel Oil(343°C)	24.9	23.4	9.6	14.3	4.1
Pitch (343 - 524°C Cut)					
Vol.%	25.86	24.97	11.36	13.72	2.50
Wt.%	26.84	25.92	11.95	14.43	2.68
Av. MW	342.84	339.63	329.07	332.69	318.01
Gas Products, m3API/m3OIL					
C1	2.13	2.54	6.61	5.78	12.81
C2	1.42	1.74	4.64	4.06	9.09
C3	1.56	1.81	4.84	4.18	9.02
C4	0.92	1.01	2.92	2.39	5.46
C5	0.35	0.36	1.05	0.91	2.30
C6	0.35	0.29	0.85	0.62	1.70
H2S	21.63	21.16	25.21	24.06	24.17

Table VII.10 Catalytic Hydrocracking Results
(Stirred Reactor)
Feedstock : CANMET Gas Oil
Test Catalyst : NALCO NM-502
Reactor liquid phase sampling results

Run No.	EC1-2	EC1-3	EC1-5	EC1-7	EC1-6
<u>Reactor Liquid</u>					
S.G. (15°C)	0.8911	0.8901	0.8893	0.8914	0.9004
Sulphur, wt.%	0.30	0.29	0.08	0.21	0.09
Nitrogen, wt.%	–	–	–	–	–
Bromine Number	3	3	3	4	4
Cuts, Vol.%					
Naphtha (C7-177°C)	6.6	6.7	7.8	8.2	10.7
Distill (177-343°C)	55.6	53.2	60.5	60.0	64.2
Fuel Oil (343°C+)	37.8	40.1	31.7	31.8	25.1
Pitch (343 - 524°C Cut)					
Vol.%	37.33	39.50	31.50	31.55	24.69
Wt.%	38.28	40.51	32.40	32.47	25.54
Av. MW	345.36	351.83	340.18	341.58	340.19
<u>Dissolved Gases</u>					
Mole % H_2	90.6	89.5	92.0	89.0	89.0
Solubility of H_2 (mg H_2/g Oil)	2.825	3.068	3.440	2.980	4.065

The thermal hydrocracking of various other feedstocks was evaluated with the stirred reactor in the later part of the study. Five different heavy gas oil feedstocks were used. They are listed as follows :

1. Suncor Hydrotreated Gas Oil (AHGO1)
2. Syncrude Hydrotreated Gas Oil (AHGO2)
3. Athabasca Virgin Gas Oil (AVGO)
4. Cold Lake Heavy Gas Oil (CLGO1)
5. Canmet Heavy Vacuum Gas Oil (CVGO)

For each feedstock, four runs were made at three temperature levels and one level of LHSV. The temperature levels were selected so as to define the temperature where coke formation causes operation problems. This temperature which gives a rough indication of the coking envelope was obtained for each of the feedstocks. The LHSV used in the runs was at a nominal level of 1.00 h^{-1}. The same equipment operating procedures and data analysis was used for these runs as in the CSTR runs with Lloydminster gas oil. The properties of the gas oils and the results of the hydroprocessing runs are given in Tables VII.11 to VII.25. Pitch conversions for these feedstocks ranged from 27.0 to 72.3 percent.

Table VII.11. Properties of Suncor Athabasca Hydrotreated Gas Oil

Boiling Range, °C	186 - 582
Specific Gravity (15°C)	0.9076
Sulphur, Wt.%	0.21
Nitrogen, Wt.%	–
Bromine Number	3
Fractions, Vol.%	
Naphtha(C7 - 177°C)	0.3
Distillate(177 - 343°C)	45.4
Fuel Oil(343°C+)	54.3
Pitch (343 - 524°C Cut)	
Vol.%	52.6
Wt.%	53.4
Av. MW	374.6

Table VII.12. Thermal Hydrocracking Results (Stirred Reactor) Feedstock : Suncor Athabasca Hydrotreated Gas Oil

Run No.	AHGO1-1	AHGO1-2	AHGO1-4	AHGO1-5
<u>Operating Conditions:</u>				
Reactor Pressure, MPa	13.9	13.9	13.9	13.9
Reactor Temp., °C	450	460	450	440
Nominal LHSV, h^{-1}	1.00	1.00	1.00	1.00
Actual LHSV, h^{-1}	1.56	1.62	1.69	1.55
H2/OIL,m3API/m3	460	478	469	463
Agitation Speed,rpm	850	850	850	850
Liquid Feedrate, mL/h	300	300	300	300
<u>Liquid Products</u>				
Product Flowrate, mL/h	304	299	301	301
S. G. (15°C)	0.9084	0.9054	0.9149	0.9040
Sulphur, Wt.%	0.21	0.19	0.16	0.17
Nitrogen, wt.%	-	-	-	-
Bromine Number	12	12	12	12
Cuts, Vol.%				
Naphtha(C7-177°C)	14.8	22.8	19.7	10.6
Distillate(177-343°C)	55.3	57.3	54.5	56.9
Fuel Oil(343°C+)	29.9	19.9	25.8	32.5
Pitch (343 - 524°C Cut)				
Vol.%	28.77	19.38	24.94	31.36
Wt.%	29.88	20.34	26.02	32.38
Av. MW	362.14	353.67	356.25	356.14
<u>Gas Products</u>, m3API/m3OIL				
C1	7.84	15.97	10.36	4.95
C2	4.92	9.10	5.84	3.27
C3	4.71	8.17	5.53	3.25
C4	2.97	5.20	3.79	2.17
C5	0.89	1.57	1.35	0.64
C6	0.76	1.38	1.24	0.58
H2S	0.22	0.42	0.20	0.16

Table VII.13. Thermal Hydrocracking Results (Stirred Reactor) Feedstock : Suncor Athabasca Hydrotreated Gas Oil, Reactor Liquid Phase Sampling Results

Run No.	AHGO1-1	AHGO1-2	AHGO1-4	AHGO1-5
Reactor Liquid				
S.G. (15°C)	0.9409	0.9869	0.9520	0.9294
Sulphur, Wt.%	0.37	0.38	0.33	0.31
Nitrogen, wt.%	-	-	-	-
Bromine Number	11	14	12	10
Cuts, Vol.%				
Naphtha(C7-177°C)	4.5	3.8	4.8	3.8
Distillate(177-343°C)	47.0	39.7	56.5	44.5
Fuel Oil(343°C+)	48.5	56.5	38.7	51.7
Pitch (343 - 524°C Cut)				
Vol.%	46.67	53.83	37.40	50.61
Wt.%	47.72	54.80	38.27	51.57
Av. MW	369.07	378.03	353.85	364.50
Dissolved Gases				
Mole % H_2	88.5	77.0	89.6	92.2
Solubility of H_2 (mg H_2/g Oil)	2.850	2.237	2.822	2.958

Table VII.14. Properties of Syncrude Athabasca Hydrotreated Gas Oil

Boiling Range, °C	222 - 581
Specific Gravity (15°C)	0.9279
Sulphur, Wt.%	0.42
Nitrogen, Wt.%	–
Bromine Number	3
Fractions, Vol.%	
Naphtha (C7 - 177°C)	0.1
Distillate (177 - 343°C)	42.1
Fuel Oil (343°C+)	57.8
Pitch (343 - 524°C Cut)	
Vol.%	53.9
Wt.%	54.6
Av. MW	387.0

Table VII.15. Thermal Hydrocracking Results (Stirred Reactor) Feedstock : Syncrude Athabasca Hydrotreated Gas Oil

Run No.	AHGO2-1	AHGO2-2	AHGO2-3	AHGO2-4
Operating Conditions:				
Reactor Pressure, MPa	13.9	13.9	13.9	13.9
Reactor Temp., °C	450	460	440	450
Nominal LHSV, h^{-1}	1.00	1.00	1.00	1.00
Actual LHSV, h^{-1}	1.61	1.71	1.60	1.62
H2/OIL,m3API/m3	472	489	465	476
Agitation Speed,rpm	850	850	850	850
Liquid Feedrate, mL/h	300	300	300	300
Liquid Products				
Product Flowrate, mL/h	292.2	294.6	299.4	295.2
S. G. (15°C)	0.9250	0.9154	0.9243	0.9293
Sulphur, Wt.%	0.32	0.34	0.37	0.37
Nitrogen, wt.%	-	-	-	-
Bromine Number	14	13	13	13
Cuts, Vol.%				
Naphtha (C7-177°C)	21.4	30.1	14.6	20.3
Distillate (177-343°C)	54.8	54.4	52.8	53.6
Fuel Oil(343°C+)	23.8	15.5	32.6	26.1
Pitch (343 - 524°C Cut)				
Vol.%	22.89	14.40	30.80	24.45
Wt.%	23.98	15.27	31.97	25.57
Av. MW	364.02	355.70	371.74	367.79
Gas Products, m3API/m3OIL				
C1	15.98	35.91	7.93	18.14
C2	8.20	15.25	4.50	8.88
C3	7.01	11.55	4.22	7.51
C4	4.25	7.03	2.58	4.50
C5	1.39	2.96	0.86	1.51
C6	1.21	2.75	0.77	1.31
H2S	0.52	0.91	0.37	0.62

Table VII.16. Thermal Hydrocracking Results (Stirred Reactor) Feedstock : Syncrude Athabasca Hydrotreated Gas Oil, Reactor Liquid Phase Sampling Results

Run No.	AHGO2-1	AHGO2-2	AHGO2-3	AHGO2-4
<u>Reactor Liquid</u>				
S.G. (15°C)	0.9890	1.0902	0.9578	0.9930
Sulphur, Wt.%	0.65	0.83	0.54	0.62
Nitrogen, wt.%	-	-	-	-
Bromine Number	15	17	11	14
Cuts, Vol.%				
Naphtha(C7-177°C)	6.0	4.8	3.9	6.3
Distillate(177-343°C)	39.8	36.8	41.8	39.6
Fuel Oil(343°C+)	54.2	58.4	54.3	54.1
Pitch (343 - 524°C Cut)				
Vol.%	49.51	53.62	50.48	48.95
Wt.%	50.57	54.63	51.45	50.02
Av. MW	386.53	386.64	382.68	385.98
<u>Dissolved Gases</u>				
Mole % H_2	77.6	54.2	89.5	75.6
Solubility of H_2 (mg H_2/g Oil)	2.152	1.138	2.460	2.193

Table VII.17. Properties of Athabasca Virgin Gas Oil

Boiling Range, °C	186 - 598
Specific Gravity (15°C)	0.9462
Sulphur, Wt.%	1.80
Nitrogen, Wt.%	-
Bromine Number	10
Fractions, Vol.%	
Naphtha(C7 - 177°C)	0.2
Distillate(177 - 343°C)	26.0
Fuel Oil(343°C+)	73.8
Pitch (343[illegible] 524°C Cut)	
Vol.%	67.2
Wt.%	67.8
Av. MW	404.7

Table VII.18. Thermal Hydrocracking Results (Stirred Reactor) Feedstock : Athabasca Virgin

Run No.	AVGO-1	AVGO-2	AVGO-3	AVGO-4
<u>Operating Conditions:</u>				
Reactor Pressure, MPa	13.9	13.9	13.9	13.9
Reactor Temp., °C	440	420	440	450
Nominal LHSV, h^{-1}	1.00	1.00	1.00	1.00
Actual LHSV, h^{-1}	1.60	1.50	1.57	1.78
H2/OIL,m3API/m3	486	487	480	489
Agitation Speed,rpm	850	850	850	850
Liquid Feedrate, mL/h	300	300	300	300
<u>Liquid Products</u>				
Product Flowrate, mL/h	298	302	298	298
S. G. (15°C)	0.9393	0.9438	0.9429	0.9724
Sulphur, Wt.%	1.46	1.60	1.50	1.64
Nitrogen, wt.%	-	-	-	-
Bromine Number	22	20	21	22
Cuts, Vol.%				
Naphtha(C7-177°C)	25.8	12.6	22.5	29.4
Distillate(177-343°C)	48.0	40.3	45.1	48.1
Fuel Oil(343°C+)	26.2	47.1	32.4	22.5
Pitch (343 - 524°C Cut)				
Vol.%	24.61	43.99	29.56	20.88
Wt.%	25.88	45.36	30.93	22.06
Av. MW	370.01	385.80	377.31	368.70
<u>Gas Products</u>, m3API/m3OIL				
C1	19.82	6.45	19.18	25.14
C2	9.29	3.51	8.97	11.08
C3	7.97	3.64	7.75	9.12
C4	4.85	2.24	4.66	5.26
C5	1.85	0.71	1.70	1.86
C6	1.82	0.78	1.57	1.61
H2S	5.68	3.55	5.68	10.42

Table VII.19. Thermal Hydrocracking Results (Stirred Reactor) Feedstock : Athabasca Virgin Gas Oil, Reactor Liquid Phase Sampling Results

Run No.	AVGO-1	AVGO-2	AVGO-3	AVGO-4
<u>Reactor Liquid</u>				
S.G. (15°C)	1.0148	0.9634	0.9972	1.0385
Sulphur, Wt.%	1.89	1.74	1.89	1.96
Nitrogen, wt.%	-	-	-	-
Bromine Number	20	18	18	20
Cuts, Vol.%				
Naphtha(C7-177°C)	7.2	4.5	6.5	7.4
Distillate(177-343°C)	35.8	33.6	34.5	33.9
Fuel Oil(343°C+)	57.0	61.9	59.0	58.7
Pitch (343 - 524°C Cut)				
Vol.%	51.33	60.39	53.38	52.48
Wt.%	52.43	61.47	54.46	53.38
Av. MW	388.30	386.35	390.27	389.78
<u>Dissolved Gases</u>				
Mole % H_2	73.1	88.7	80.4	62.8
Solubility of H_2 (mg H_2/g Oil)	1.736	2.007	1.840	1.369

Table VII.20. Properties of Cold Lake Gas Oil

Boiling Range, °C	186 - 557
Specific Gravity (15°C)	0.9347
Sulphur, Wt.%	2.94
Nitrogen, Wt.%	-
Bromine Number	8
Fractions, Vol.%	
Naphtha(C7 - 177°C)	0.1
Distillate(177 - 343°C)	32.5
Fuel Oil(343°C+)	67.4
Pitch (343 - 524°C Cut)	
Vol.%	64.2
Wt.%	65.0
Av. MW	401.2

Table VII.21. Thermal Hydrocracking Results (Stirred Reactor) Feedstock : Cold Lake Gas Oil

Run No.	CLGO1-1	CLGO1-2	CLGO1-3	CLGO1-4
Operating Conditions:				
Reactor Pressure, MPa	13.9	13.9	13.9	13.9
Reactor Temp., °C	440	450	440	420
Nominal LHSV, h^{-1}	1.00	1.00	1.00	1.00
Actual LHSV, h^{-1}	1.64	1.84	1.62	1.51
H2/OIL, m3API/m3	494	511	525	495
Agitation Speed, rpm	850	850	850	850
Liquid Feedrate, mL/h	300	300	300	300
Liquid Products				
Product Flowrate, mL/h	280	283	287	250
S. G. (15°C)	0.8953	0.8619	0.8994	0.9139
Sulphur, Wt.%	2.57	2.27	2.59	2.71
Nitrogen, wt.%	–	–	–	–
Bromine Number	21	22	21	20
Cuts; Vol.%				
Naphtha(C7-188°C)	26.2	25.7	24.4	8.1
Distillate(177-343°C)	50.2	56.0	50.1	44.9
Fuel Oil(343°C+)	23.6	18.3	25.5	47.0
Pitch (343 - 524°C Cut)				
Vol.%	23.24	17.63	23.66	44.33
Wt.%	24.47	18.54	24.85	45.51
Av. MW	367.29	359.17	370.73	387.36
Gas Products, m3API/m3OIL				
C1	16.58	21.09	15.12	4.03
C2	8.84	9.89	7.74	2.33
C3	7.96	8.20	6.75	2.55
C4	5.68	5.26	4.47	1.77
C5	2.63	2.19	1.79	0.69
C6	1.13	0.86	1.64	0.80
H2S	4.93	5.39	4.67	2.49

Table VII.22. Thermal Hydrocracking Results (Stirred Reactor) Feedstock : Cold Lake Gas Oil Reactor Liquid Phase Sampling Results

Run No.	CLGO1-1	CLGO1-2	CLGO1-3	CLGO1-4
Reactor Liquid				
S.G. (15°C)	0.9899	1.0364	0.9877	0.9428
Sulphur, Wt.%	3.25	3.40	3.25	2.95
Nitrogen, wt.%	-	-	-	-
Bromine Number	19	20	18	16
Cuts, Vol.%				
Naphtha(C7-177°C)	6.9	6.1	6.9	1.3
Distillate(177-343°C)	38.3	36.8	37.1	37.9
Fuel Oil(343°C+)	54.8	57.1	56.0	60.8
Pitch (343 - 524°C Cut)				
Vol.%	49.80	52.14	52.04	57.62
Wt.%	50.90	53.18	53.13	58.49
Av. MW	390.36	388.16	386.80	389.32
Dissolved Gases				
Mole % H_2	80.3	62.2	93.5	91.2
Solubility of H_2 ($mg\ H_2/g$ Oil)	1.994	1.386	1.731	2.125

Table VII.23. Properties of CANMET Vacuum Gas Oil

Boiling Range,°C	204 - 556
Specific Gravity (15°C)	0.9314
Sulphur, Wt.%	2.31
Nitrogen, Wt.%	[illegible]
Bromine Number	14
Fractions, Vol.%	
Naphtha(C7 - 177°C)	0.1
Distillate(177 - 343°C)	37.5
Fuel Oil(343°C+)	62.4
Pitch (343 - 524°C Cut)	
Vol.%	61.1
Wt.%	61.8
Av. MW	360.2

Table VII.24. Thermal Hydrocracking Results (Stirred Reactor) Feedstock : CANMET Vacuum Gas Oil

Run No.	CVGO-1	CVGO-2	CVGO-3	CVGO-5
<u>Operating Conditions</u>:				
Reactor Pressure, MPa	13.9	13.9	13.9	13.9
Reactor Temp., °C	440	450	440	430
Nominal LHSV, h^{-1}	1.00	1.00	1.00	1.00
Actual LHSV, h^{-1}	1.78	1.52	1.61	1.61
H2/OIL, m3API/m3	485	480	490	486
Agitation Speed, rpm	850	850	850	850
Liquid Feedrate, mL/h	300	300	300	300
<u>Liquid Products</u>				
Product Flowrate, mL/h	300	284	305	300
S. G. (15°C)	0.9321	0.9421	0.9297	0.9319
Sulphur, Wt.%	2.23	2.29	2.24	2.21
Nitrogen, wt.%	-	-	-	-
Bromine Number	18	18	18	16
Cuts, Vol.%				
Naphtha (C7 177°C)	13.3	15.8	9.0	6.8
Distillate (177-343°C)	51.4	50.9	50.0	50.0
Fuel Oil (343°C+)	35.4	33.3	41.0	43.2
Pitch (343 - 524°C Cut)				
Vol.%	33.97	31.75	39.63	42.15
Wt.%	35.13	32.94	40.73	43.21
Av. MW	355.77	357.51	356.46	356.37
<u>Gas Products</u>, m3API/m3OIL				
C1	5.32	12.10	5.57	3.36
C2	3.14	6.20	3.31	2.21
C3	3.10	5.22	3.23	2.21
C4	2.21	3.21	2.35	2.00
C5	0.86	1.04	0.89	0.69
C6	1.00	0.93	1.10	1.12
H2S	1.07	1.66	0.95	0.57

Table VII.25. Thermal Hydrocracking Results (Stirred Reactor) Feedstock : CANMET Vacuum Gas Oil, Reactor Liquid Phase Sampling Results

Run No.	CVGO-1	CVGO-2	CVGO-3	CVGO-5
<u>Reactor Liquid</u>				
S.G. (15°C)	0.9581	0.9922	0.9555	0.9512
Sulphur, Wt.%	2.43	2.66	2.39	2.40
Nitrogen, wt.%	-	-	-	-
Bromine Number	15	17	16	15
Cuts, Vol.%				
Naphtha(C7-177°C)	1.5	3.5	1.0	0.6
Distillate(177-343°C)	36.2	39.2	36.4	30.8
Fuel Oil(343°C+)	62.3	57.3	62.6	68.6
Pitch (343 - 524°C Cut)				
Vol.%	60.12	54.81	60.83	64.99
Wt.%	60.94	55.72	61.59	65.60
Av. MW	368.94	365.44	363.34	371.37
<u>Dissolved Gases</u>				
Mole % H_2	87.8	69.9	91.1	94.7
Solubility of H_2 (mg H_2/gOil)	2.154	1.582	2.155	2.280

VIII. TREATMENT OF RESULTS

To develop kinetic models for pitch and sulphur conversion, knowledge of the pitch, sulphur and hydrogen concentrations in the reactor liquid phase is required. This section explains how this information is obtained.

A. Pitch Conversion

Pitch was defined as the liquid fraction boiling between 343°C to 524°C. When the liquid feed stock is hydrocracked, part of this pitch fraction will be converted to lighter products and coke. The rate of pitch converted divided by the rate of pitch entering the reactor in moles pitch per minute, gives the fractional pitch conversion for any particular hydrocracking run.

In order to determine the molar rate of pitch entering and leaving the reactor, the weight fraction and the average molecular weight of the pitch fraction in the liquid samples are required. These were estimated from the simulated distillation curve data and data for the physical properties of paraffinic hydrocarbons by mass averaging of the simulated distillation data. The equations used are given in Table VIII.1. The computer program written to reduce simulation data results, SIMU5, calculates these two quantities for every sample. RATE1, a program written to process kinetic data, calculates the pitch conversion using data from SIMU5. The computer program listings and sample

Table VIII.1 Equations Used to Estimate the Average Molecular Weight and Weight Fraction of Pitch

$$\text{Average Pitch Molecular Weight} = \frac{\sum^{\text{pitch}} V_i \rho_i MW_i}{\sum^{\text{pitch}} V_i \rho_i} \tag{8.1}$$

$$\text{Pitch Weight Fraction} = \frac{\sum^{\text{pitch}} V_i \rho_i}{\sum^{\text{sample}} V_i \rho_i} \tag{8.2}$$

where,

V_i = volume fraction of component i

ρ_i = density of component i

MW_i = molecular weight of component i computer program outputs are presented in Appendix E and Appendix C, respectively.

The equations used to calculate pitch conversion are given in Tables VIII.2 and VIII.3. Pitch concentration data and pitch conversion values calculated for all the runs are presented in Appendix F.

B. Sulphur Conversion

The sulphur content of liquid samples was measured as weight percent sulphur in the sample. The level of sulphur conversion for any run is defined as the molar rate of sulphur converted divided by the molar rate of sulphur in the liquid feed entering the reactor. The equation used in determining the fractional sulphur conversion for a given hydrocracking run is presented in Table VIII.4. Sample calculations are shown in Appendix C.

C. Determination of Pitch, Sulphur, and Hydrogen Concentrations in the Reactor Liquid Phase Under Reaction Conditions

In modelling the kinetics of thermal hydroprocessing, the rate of pitch and sulphur conversion was taken to have some dependence on the concentration of pitch, sulphur, and hydrogen in the reactor liquid phase at reaction conditions. For the study, the concentrations of pitch and sulphur in the reactor liquid were obtained based on a mass averaging technique where weight fractions and average molecular

Table VIII.2 Equation Used to Determine Pitch Conversion

$$X_p = \frac{F_1 C_F - F_2 C_p}{F_1 C_F} \qquad (8.3)$$

where,

F_1 = volumetric flowrate of liquid feed at 23.0°C, mL min^{-1}

F_2 = volumetric flowrate of liquid product at 23.0°C, mL min^{-1}

C_F = concentration of pitch in liquid feed at 23.0°C, mol mL^{-1}

C_p = concentration of pitch in liquid product at 23.0°C, mol mL^{-1}

X_p = fractional pitch conversion

Table VIII.3 Equations Used to Determine the Pitch Concentration in the Liquid Feed and Liquid Product at 23.0 °C

$$C_F = \frac{W_F \, \rho_F}{MW_F} \tag{8.4}$$

$$C_p = \frac{W_p \, \rho_p}{MW_p} \tag{8.5}$$

where,

W_F = weight fraction of pitch in liquid feed sample

W_p = weight fraction of pitch in liquid product sample

ρ_F = density of liquid feed at 23.0°C, g mL^{-1}

ρ_p = density of liquid product at 23.0°C, g mL^{-1}

MW_F = average molecular weight of the pitch fraction in the liquid feed sample, g mol^{-1}

MW_p = average molecular weight of the pitch fraction in the liquid product sample, g mol^{-1}

C_F = concentration of pitch in the liquid feed sample at 23.0°C, mol mL^{-1}

C_p = concentration of pitch in the l [illegible] sample at 23.0°C, mol mL^{-1}

Table VIII.4 Equation Used to Determine Sulphur Conversion

$$X_S = \frac{W_{SF}\ \rho_F\ F_1 - W_{SP}\ \rho_P\ F_2}{W_{SF}\ \rho_F\ F_1} \qquad (8.6)$$

where,

W_{SF} = weight fraction sulphur in liquid feed
W_{SP} = weight fraction sulphur in liquid product
ρ_F = density of liquid feed at 23.0 °C, g mL^{-1}
ρ_P = density of liquid product at 23.0 °C, g mL^{-1}
F_1 = volumetric flowrate of liquid feed at 23.0 °C, mL min^{-1}
F_2 = volumetric flowrate of liquid product at 23.0 °C, mL min^{-1}
X_S = fractional sulphur conversion

weights of the pitch or sulphur in the reactor liquid were used in the calculations. The equations used to determine pitch and sulphur concentrations in the reactor liquid are given in Tables VIII.5 and VIII.6. Hydrogen concentration in the reactor liquid is determined from the measured mole fraction hydrogen in the dissolved gases and the mass and density of the reactor liquid sample. The equation used to determine this quantity is given in Table VIII.7.

Reactor liquid phase concentration results for pitch, sulphur, and hydrogen calculated at reaction conditions are presented in Appendix F for the stirred reactor runs.

Table VIII.5 Equation Used to Determine Pitch Concentration in the Reactor Liquid Phase at Reaction Conditions

$$C_{RL} = \frac{W_{RL}\ \rho_{RL}}{MW_{RL}} \tag{8.7}$$

where,

W_{RL} = weight fraction of pitch in the reactor liquid phase

ρ_{RL} = density of the reactor liquid phase corrected to reaction conditions, g mL^{-1}

MW_{RL} = average molecular weight of the pitch fraction in the reactor liquid phase sample, g mol^{-1}

C_{RL} = pitch concentration in the reactor liquid phase at reaction conditions, mol mL^{-1}

Table VIII.6 Equation Used to Determine Sulphur Concentration in the Reactor Liquid Phase at Reaction Conditions

$$C_S = \frac{W_{SR}\,\rho_{RL}}{MW_S} \tag{8.8}$$

where,

W_{SR} = weight fraction sulphur in the reactor liquid phase

ρ_{RL} = density of the reactor liquid phase corrected to reaction conditions, g mL^{-1}

MW_S = molecular weight of sulphur, g mol^{-1}

C_S = sulphur concentration in the reactor liquid phase at reaction conditions, mol mL^{-1}

Table VIII.7 Equation Used to Determine Hydrogen Concentration in the Reactor Liquid Phase at Reaction Conditions

$$C_H = \frac{x_H \cdot N_G \, \rho_{RL}}{M_{RL}} \qquad (8.9)$$

where,

x_H = mole fraction hydrogen in gas dissolved in reactor liquid phase sample

N_G = moles of gas dissolved in reactor liquid phase sample, mol

ρ_{RL} = density of reactor liquid phase sample corrected to reaction conditions, g mL^{-1}

M_{RL} = mass of reactor liquid phase sample, g

C_H = concentration of hydrogen in the reactor liquid phase at reaction conditions, mol mL^{-1}

IX. INTERPRETATION AND DISCUSSION

A. Stirred Reactor Results for LLVGO

Product Distributions and Coking Envelope

The experimental results from thermal hydroprocessing of LLVGO summarized in Table VII.2 have been plotted for easier interpretation. The effect of actual LHSV upon liquid product distribution at three temperature levels are presented in Figures IX.1 to IX.3. The corresponding plots of actual LHSV upon gas product distributions are shown in Figures IX.4 to IX.6. The plots show that increasing reactor residence time or increasing the reaction temperature results in gradually increasing yields of lighter liquid fractions and correspondingly, greater amounts of hydrocarbon gases. At temperatures greater than about 440 °C and at actual LHSV below 1.0 h^{-1}, the increased yield of gases indicated a rapid increase in reaction rates and greater yield of lighter fractions, a regime where the formation of coke is favoured.

The formation of coke was observed in significant amounts during the thermal hydroprocessing of LLVGO for those experiments conducted at the more severe operating conditions. Visual inspection of the interior of the stirred reactor after cool-down provided a measure of the extent of coke formation for any given run. Temperature and actual LHSV were used to chart the coking envelope. Figure IX.7

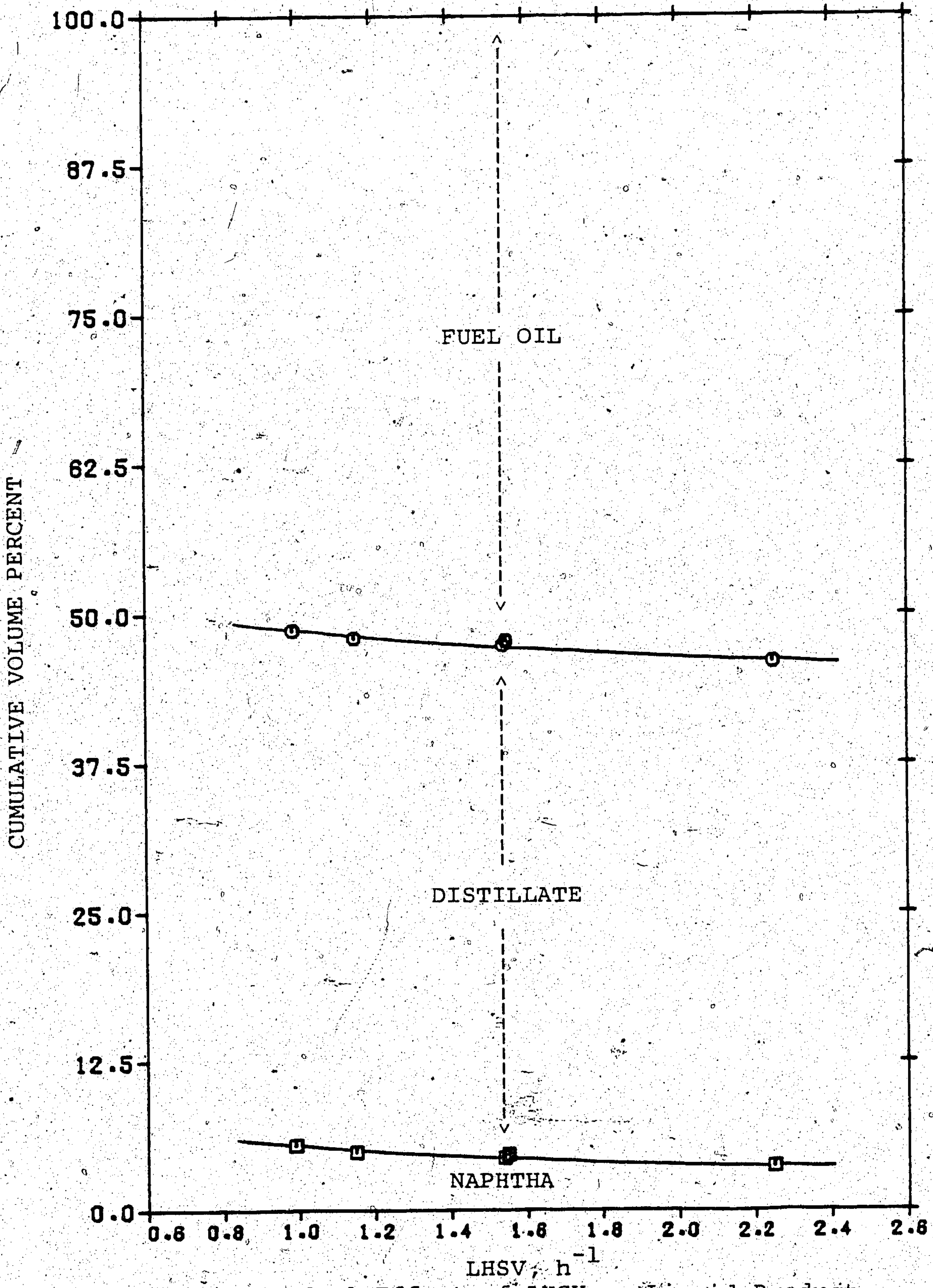


Figure IX.1 Effect of LHSV on Liquid Product Distribution at 400 C

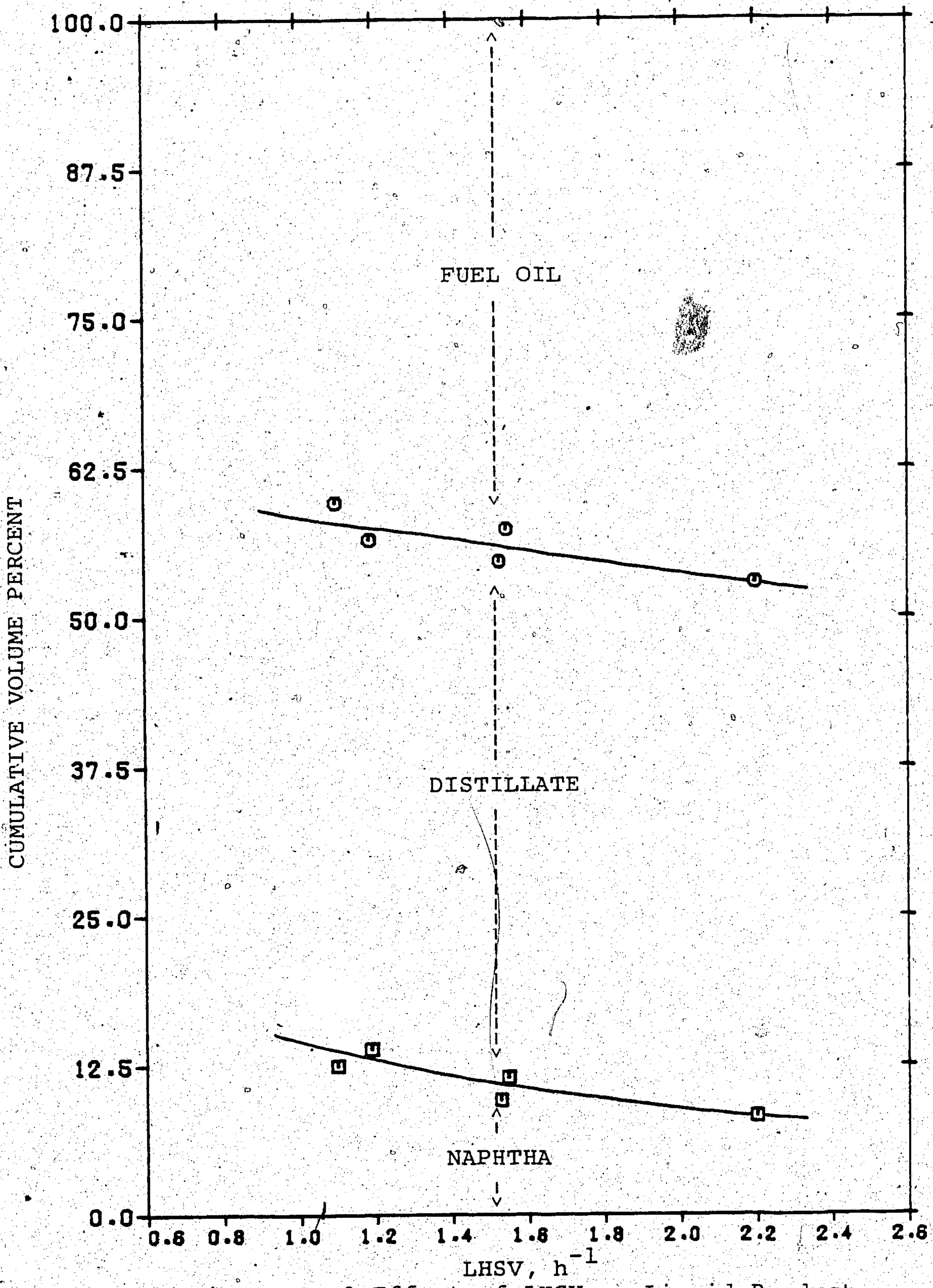


Figure IX.2 Effect of LHSV on Liquid Product Distribution at 420 C

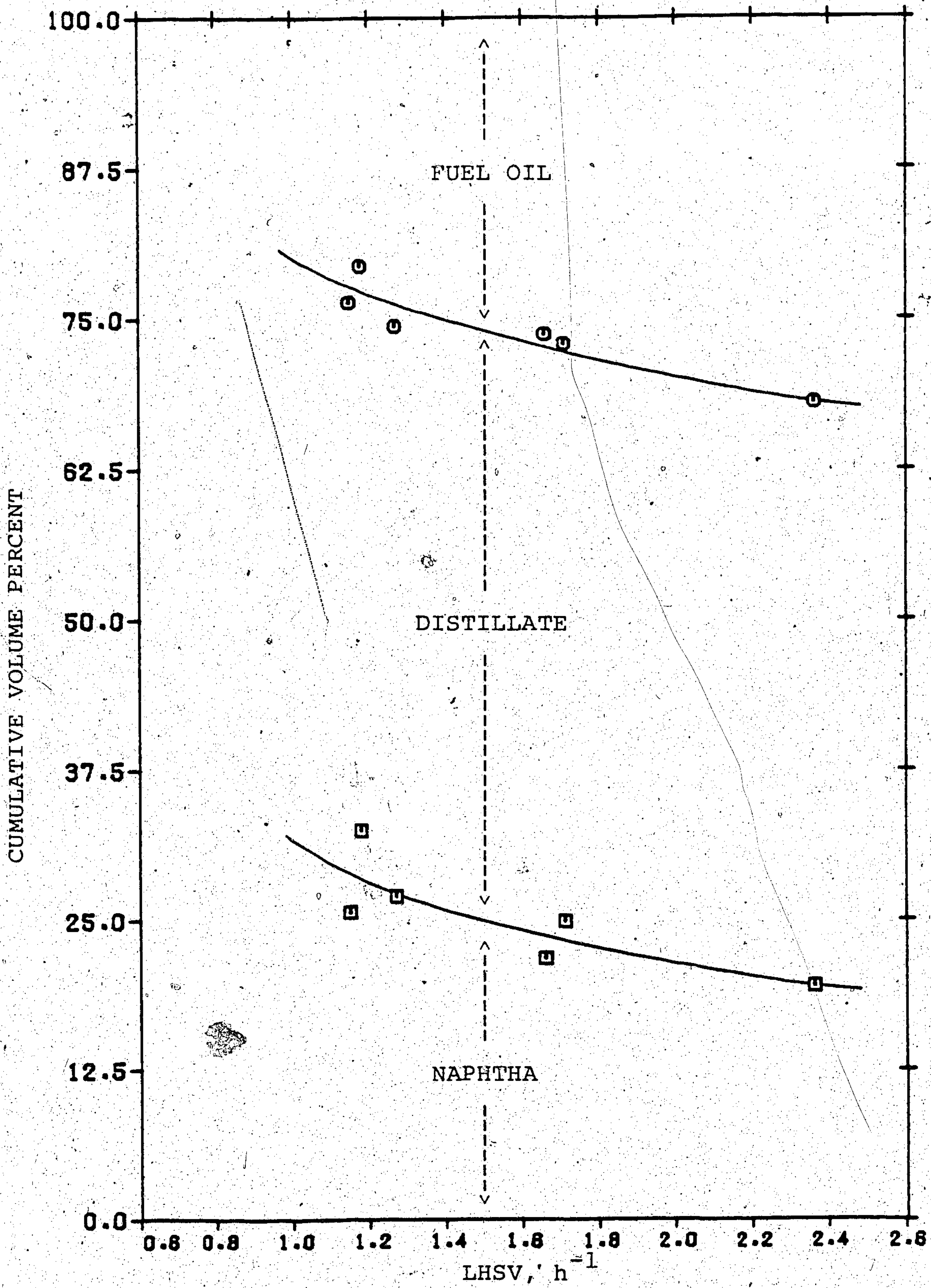


Figure IX.3 Effect of LHSV on Liquid Product Distribution at 440 C

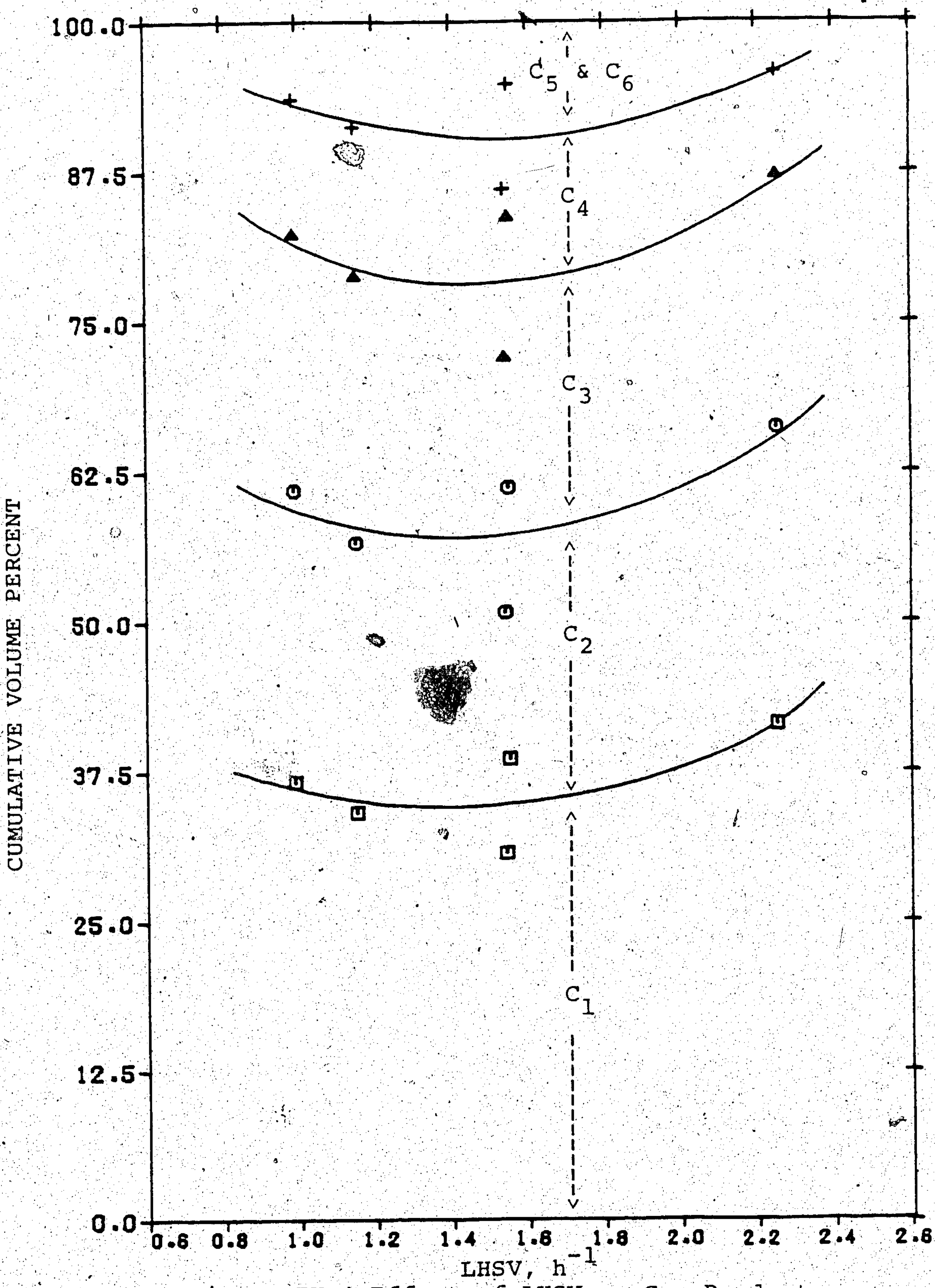


Figure IX.4 Effect of LHSV on Gas Product Distribution at 400 C

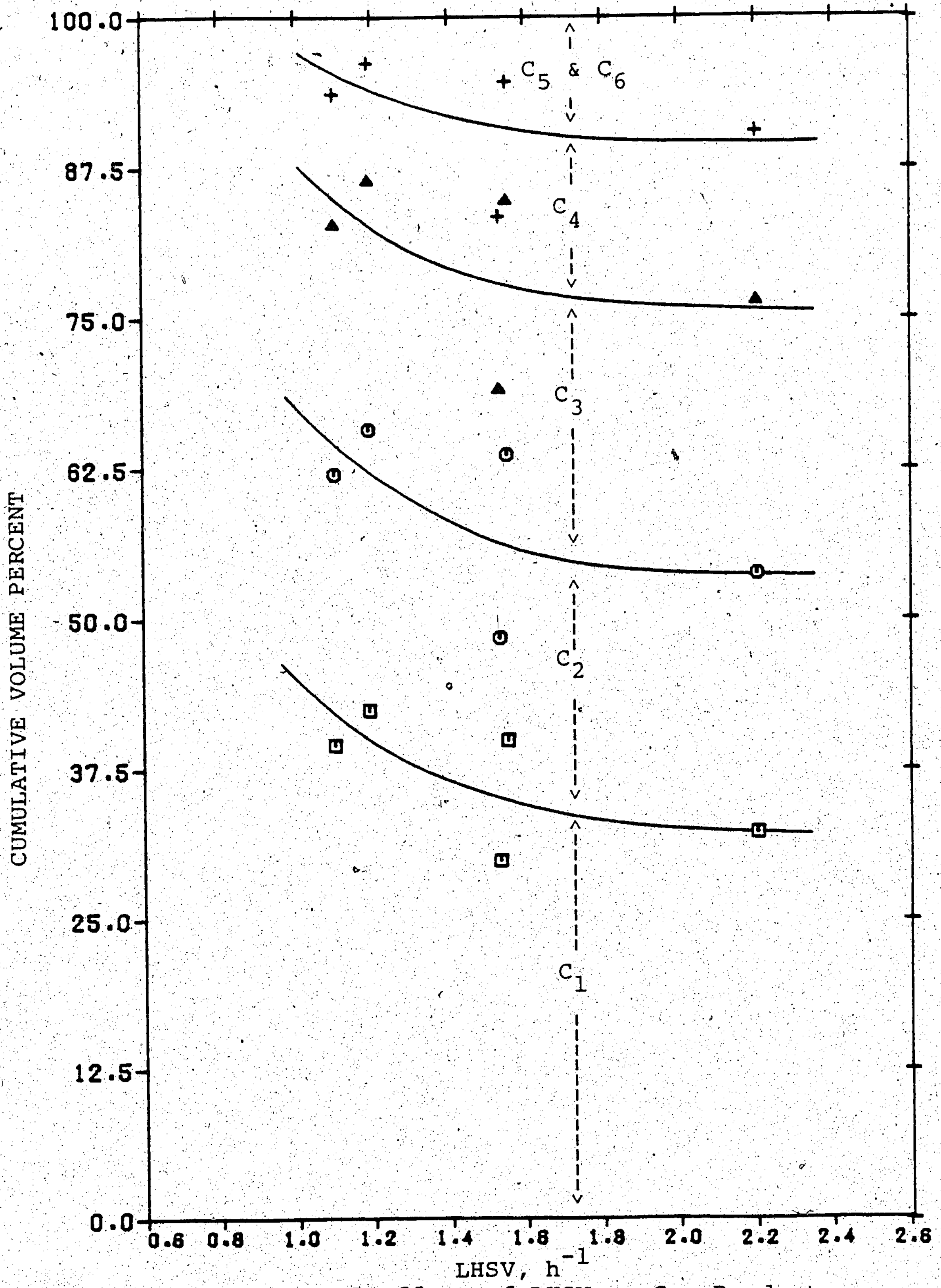


Figure IX.5 Effect of LHSV on Gas Product Distribution at 420 C

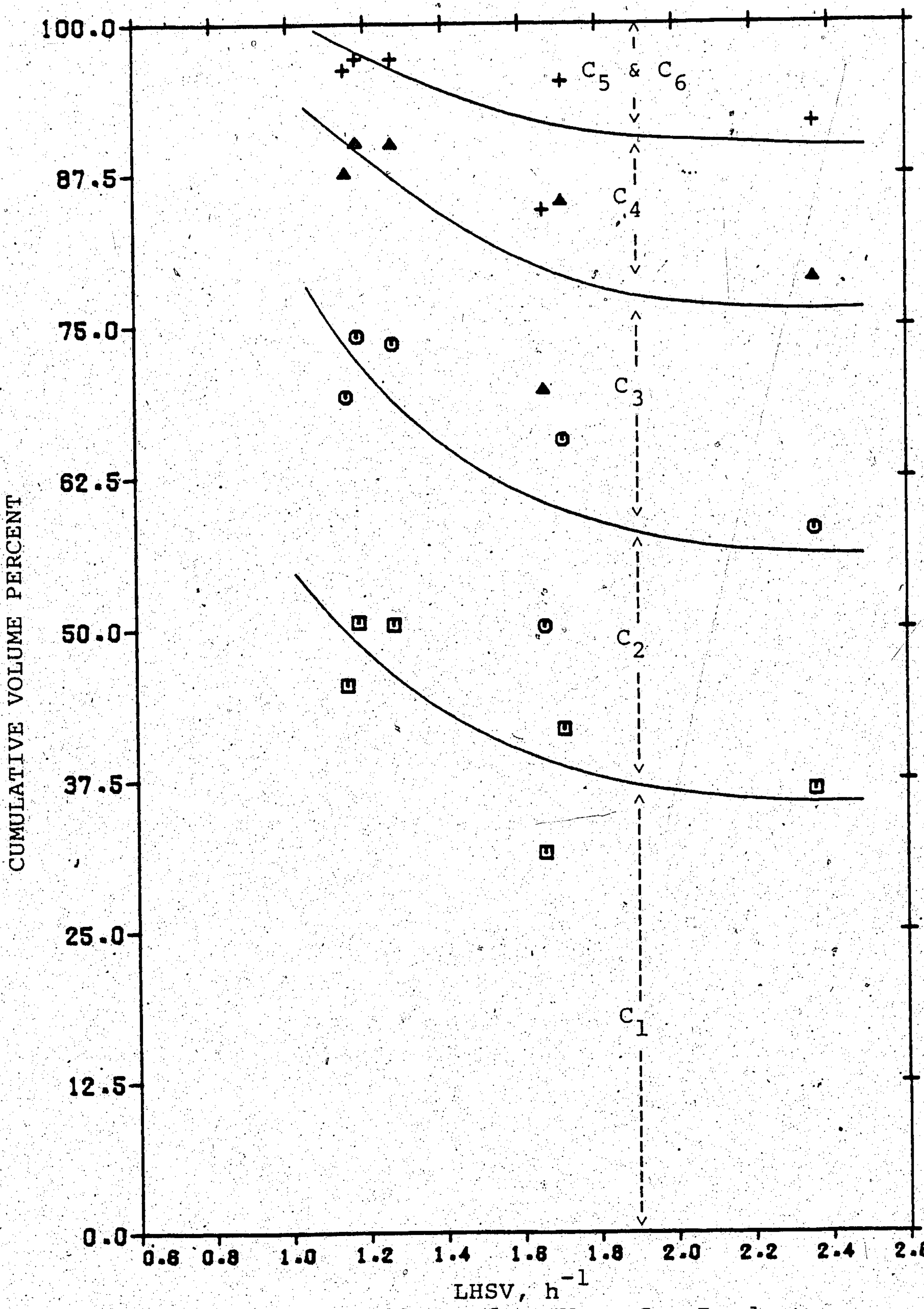


Figure IX.6 Effect of LHSV on Gas Product Distribution at 440 C

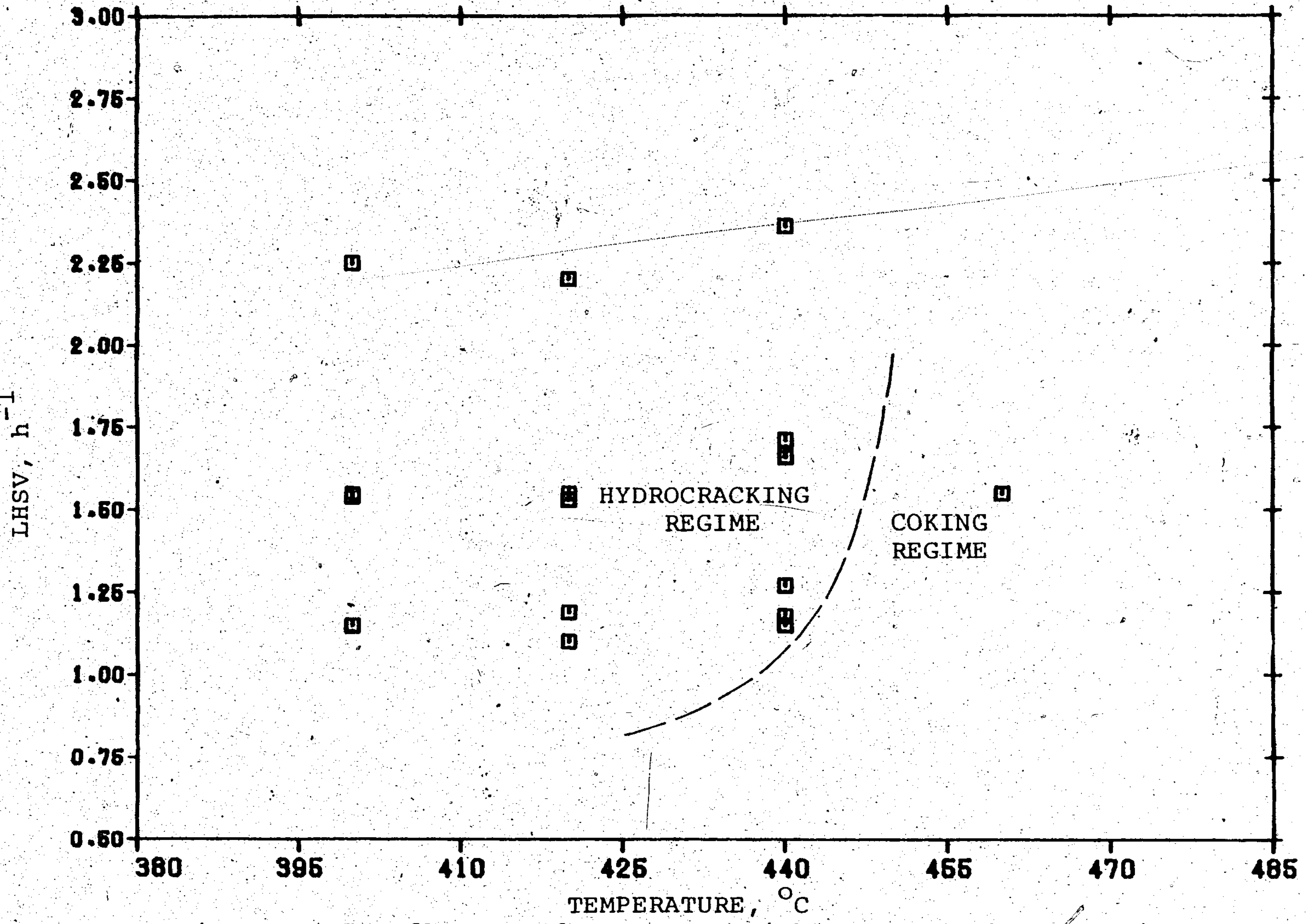


Figure IX.7 Influence of Process Variables Upon Coke Formation Thermal Hydroprocessing of LLVGO summarizes the influence upon coking of the process variables used for all the experiments. The dashed curve roughly outlines the boundary between the hydrocracking regime, where coke formation is insignificant, and the coking regime. The precise position of this boundary is not distinct and was determined from experimental observations for all the runs.

From Figure IX.7, it was observed that coke formation is significant for reaction temperatures in excess of 440°C and actual LHSV of less than about 1.0 h^{-1}. The hydrogen-to-liquid feed ratio exhibited no significant effect upon the formation of coke for ratios in excess of about 180 m^3API per m^3. This suggests that at conditions where coke formation is significant, the limiting step may be the transfer rate of hydrogen to the liquid phase. At these conditions, the rate of pitch conversion is so rapid that dissolved hydrogen in the reactor liquid phase becomes depleted well below the saturation level. For this situation where high reaction rates and conversion levels prevail, thermal cracking with insufficient hydrogenation occurs, resulting in severe coke formation.

Effect of Process Variables on Pitch Conversion

Effect of Temperature on Pitch Conversion

The effect of temperature on the conversion of the pitch fraction to lighter components is presented in Figure IX.8 to IX.10 as plots of pitch conversion

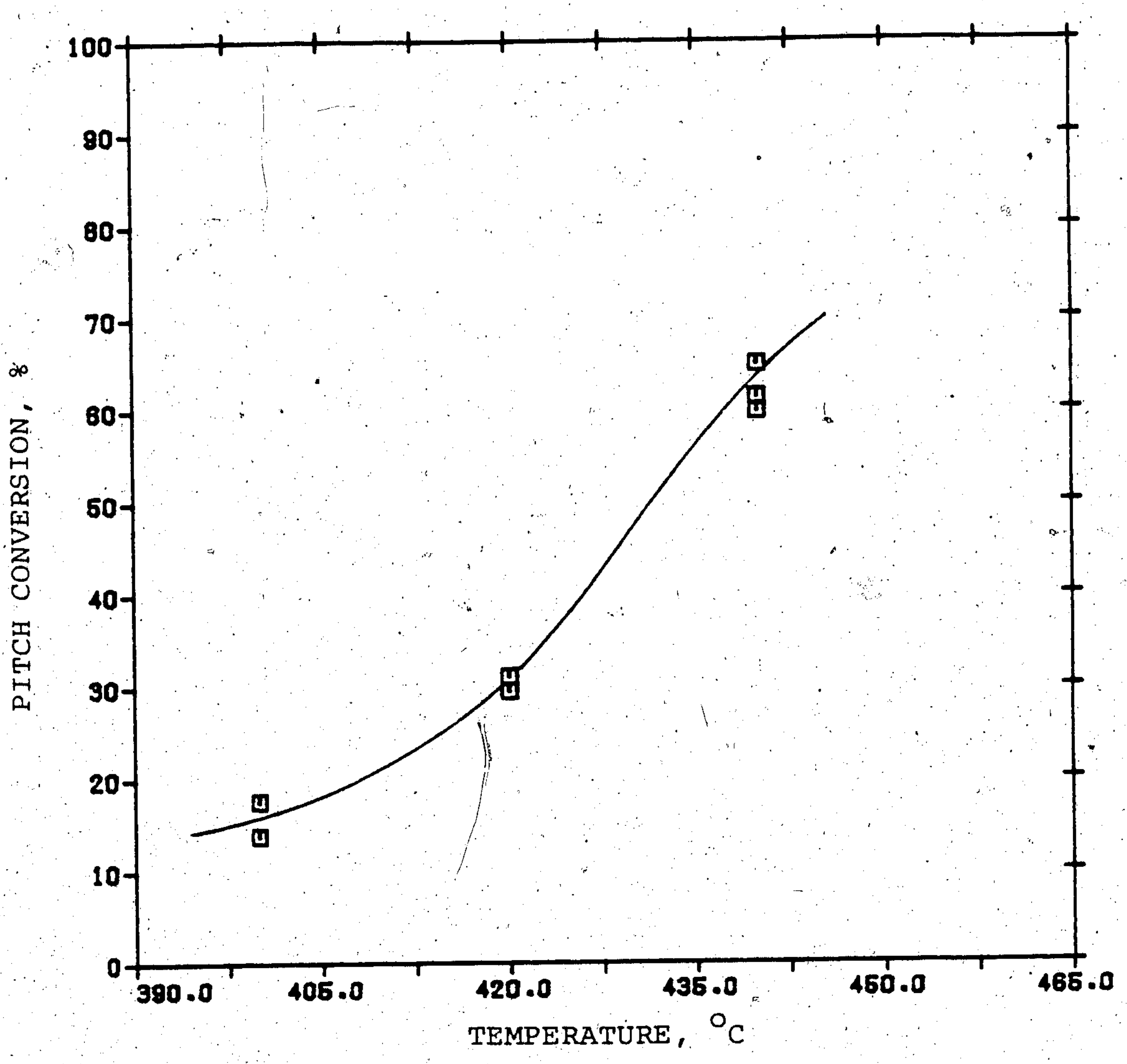


Figure IX.8 Effect of Temperature on Pitch Conversion, Nom.LHSV = 0.75, Actual Av.LHSV = 1.17

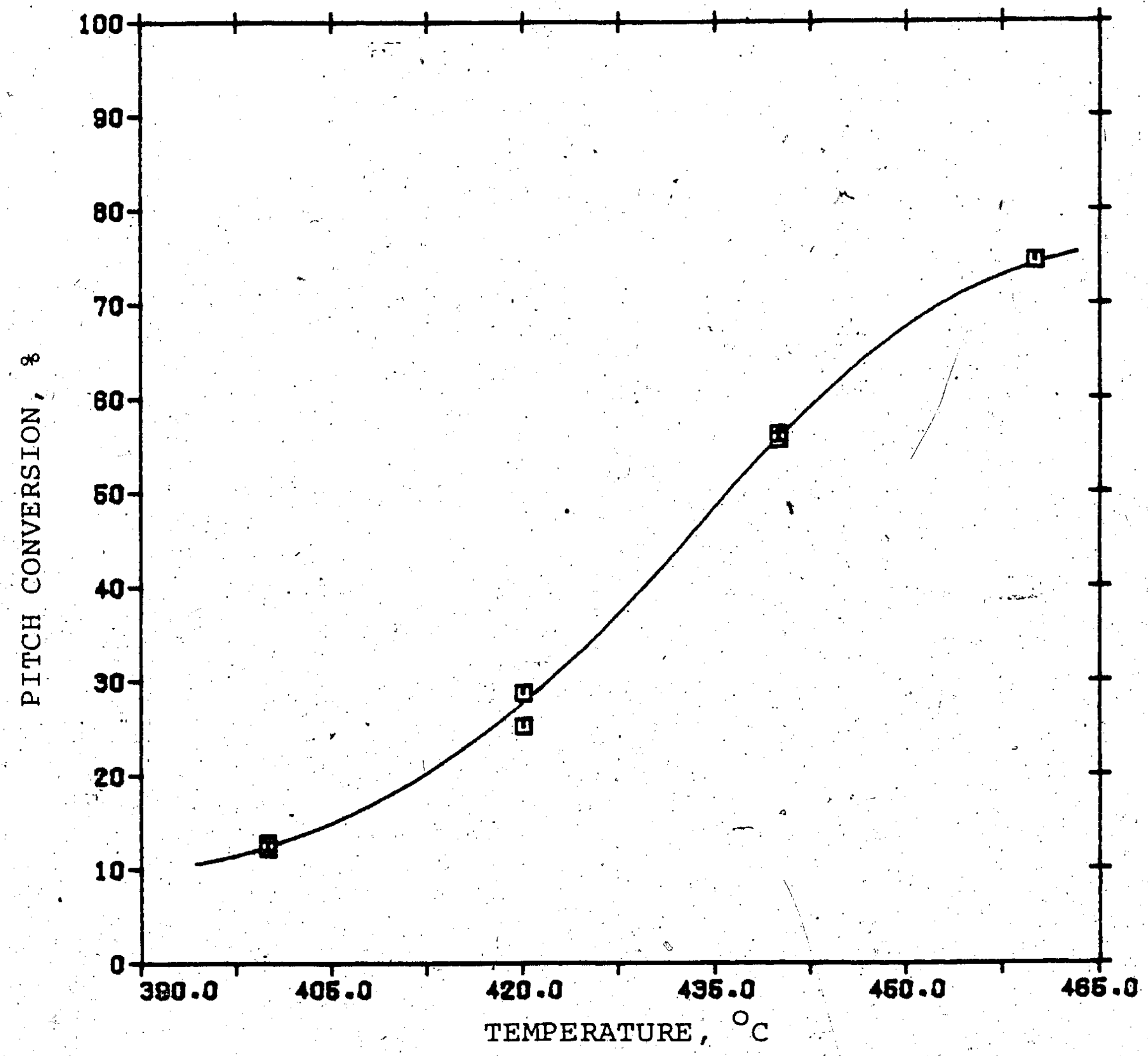


Figure IX.9 Effect of Temperature on Pitch Conversion, Nom.LHSV = 1.00, Actual Av.LHSV = 1.59

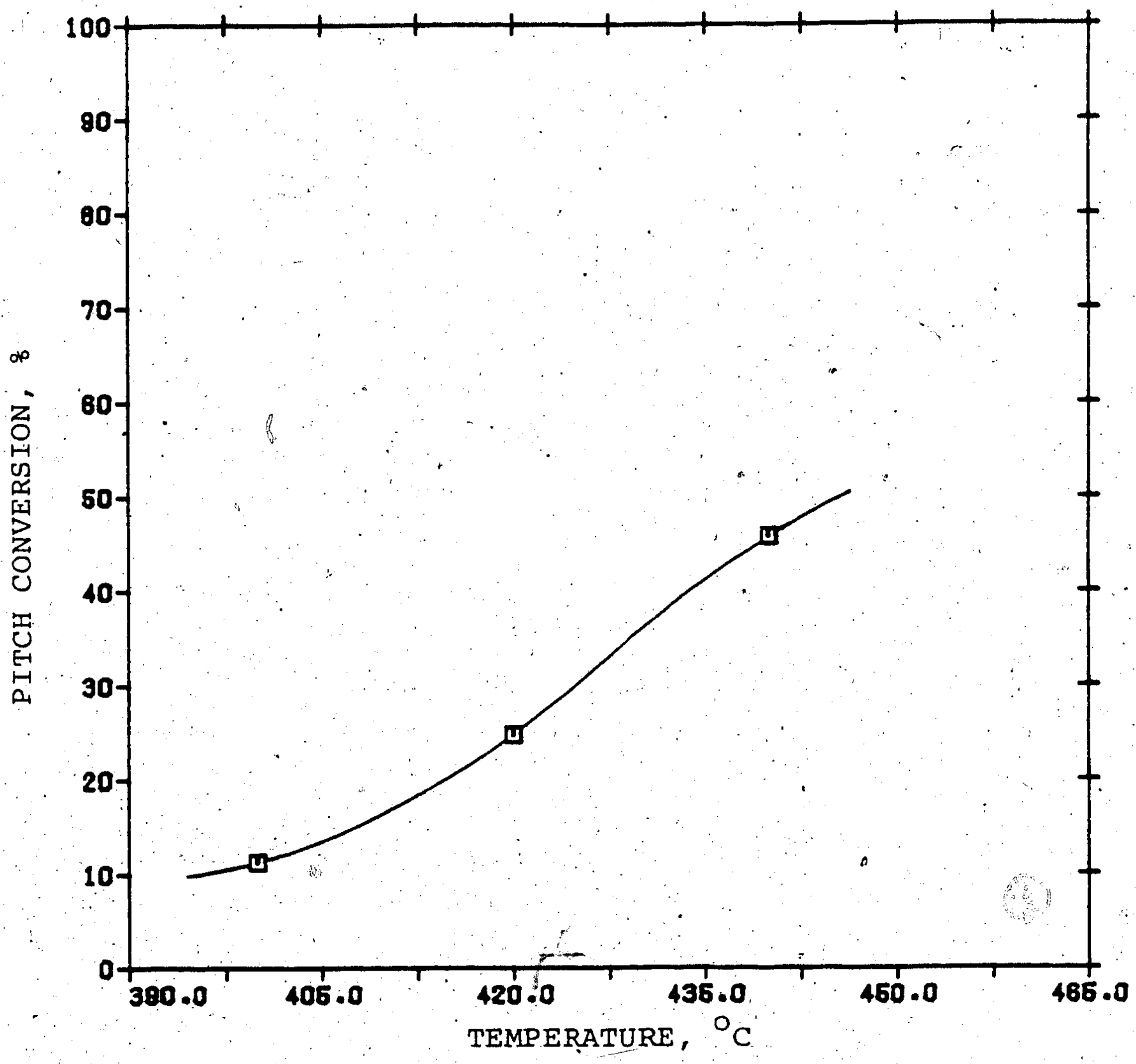


Figure IX.10 Effect of Temperature on Pitch Conversion, Nom.LHSV = 1.50, Actual Av.LHSV = 2.27

versus temperature at three levels of nominal LHSV. The corresponding actual LHSV vary less than ±8 percent about an average value. From these plots, pitch conversion was observed to increase with temperature at all three levels of nominal LHSV. One data point at 460 °C, where severe amount of coke formation resulted in plugged control valves during the latter part of the run, was included in Figure IX.9 to obtain the general shape of the curve. The curves fitted to the data points in Figures IX.8 and IX.10 were based on the shape of the fitted curve in Figure IX.9.

Figures IX.8 and IX.9 show that the point of inflection of these curves occur at a temperature of about 430 °C. This suggests that the maximum rate of pitch conversion with respect to temperature occurs at about 430 °C. Figure IX.10 is more arbitrary concerning this maximum rate of pitch conversion since the curve was fitted using only the three data points available.

Effect of LHSV on Pitch Conversion

The effect of LHSV on pitch conversion was observed as pitch conversion increasing with decreasing LHSV. Plots showing pitch conversion versus LHSV relationships are given later so that the predicted values, via kinetic models yet to be discussed, can be presented for comparison purposes on the same plots.

Effect of Hydrogen Feedrate on Pitch Conversion

Based on reactor liquid sampling, the results indicated that hydrogen feedrate has no visible effect on pitch conversion. For runs where coke formation is not significant, the dissolved gases in the reactor liquid phase have hydrogen content in excess of 70 mole percent. Doubling the hydrogen feedrate did not affect the hydrogen content and the amount of the dissolved gases in the reactor liquid phase.

Changes in hydrogen feedrate however do indirectly affect pitch conversion by causing changes in the hydrodynamics within the reactor. Increasing the hydrogen feedrate has a tendency to decrease the liquid hold-up and hence alter the residence time of liquid in the reactor.

Effect of Feedstock Pitch Content on Pitch Conversion

Some useful information on the effect of feedstock pitch content on pitch conversion was extracted from results for the runs at 450 °C in which LLVGO was blended with a lighter CANMET gas oil. Figure IX.11 shows the relation between pitch conversion versus feedstock pitch concentration. A data point obtained for hydroprocessing pure LLVGO at 460 °C is also used in this plot as an indication of the region where coke formation is significant. Although the data are limited, Figure IX.11 seems to suggest that pitch conversion increases with pitch

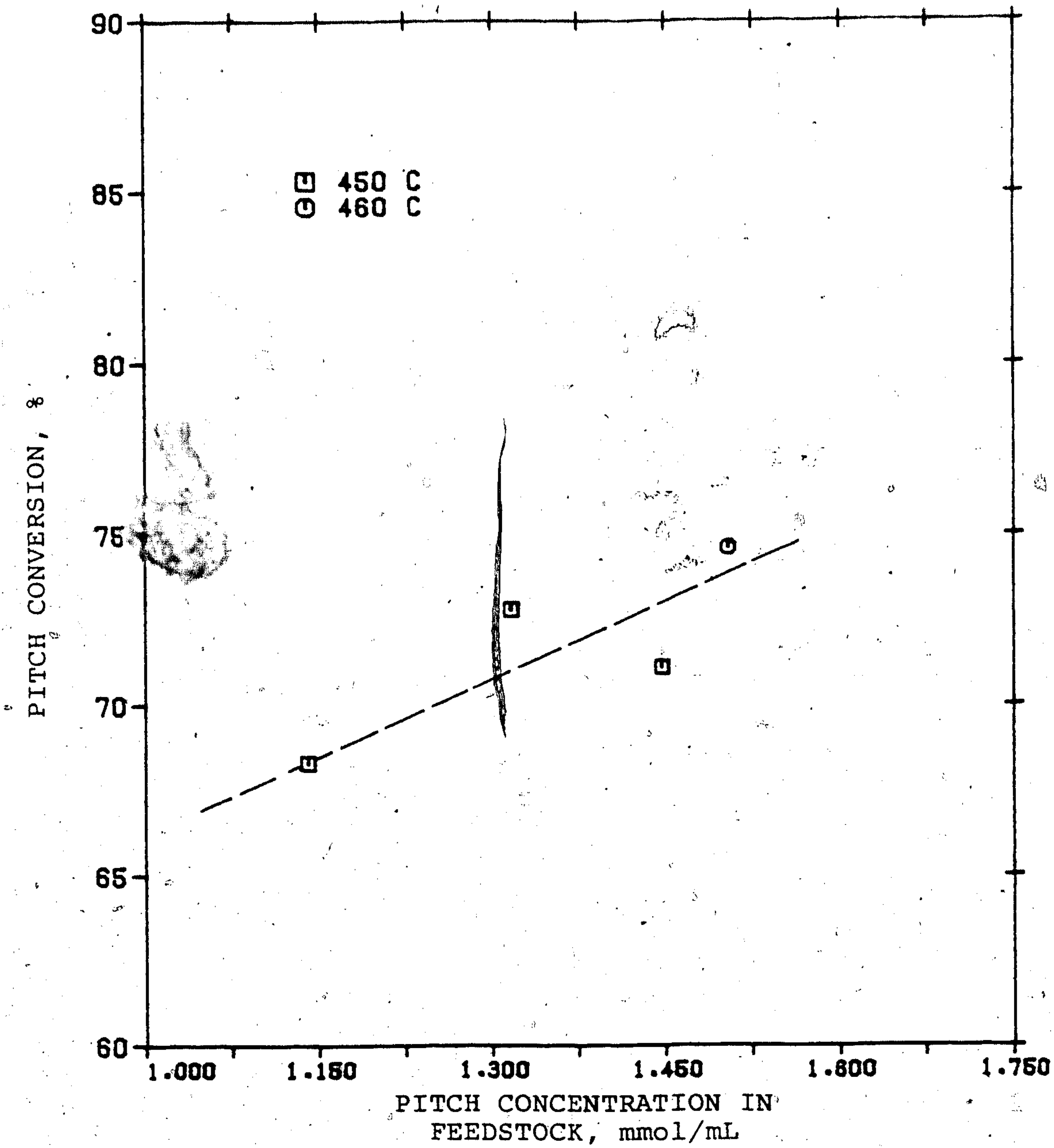


Figure IX.11 Effect of Feedstock Pitch Content on Pitch Conversion content in the feedstock and that at temperatures of 450 °C and above, coke formation becomes significant when pitch concentration in the feedstock exceeds roughly 1.4 mmol/mL (measured at 23.0°C).

Because of the considerable scatter and the small number of points, additional runs are needed to define more clearly the relationship between pitch conversion and feedstock pitch content.

Effect of Process Variables on Sulphur Conversion

The effect of temperature on conversion of sulphur compounds to hydrogen sulphide is presented in Figures IX.12 to IX.14 as plots of sulphur conversion versus temperature at three levels of nominal LHSV. The corresponding actual LHSV for each of these plots vary less than ±8 percent. From these plots, sulphur conversion is observed to increase with temperature at all three nominal LHSV, from 3.8 to 29.5 percent conversion. The plots also seem to indicate that thermal hydroprocessing is not able to hydrogenate fully the sulphur-containing compounds at practical conditions. Further hydrodesulphurization in a catalytic hydrotreater is necessary to complete the sulphur removal to acceptable levels.

The effect of actual LHSV on sulphur conversion at various temperatures is presented in Figure IX.15. Figure IX.15 shows that sulphur conversion increases with increasing average liquid residence time, i.e. decreasing

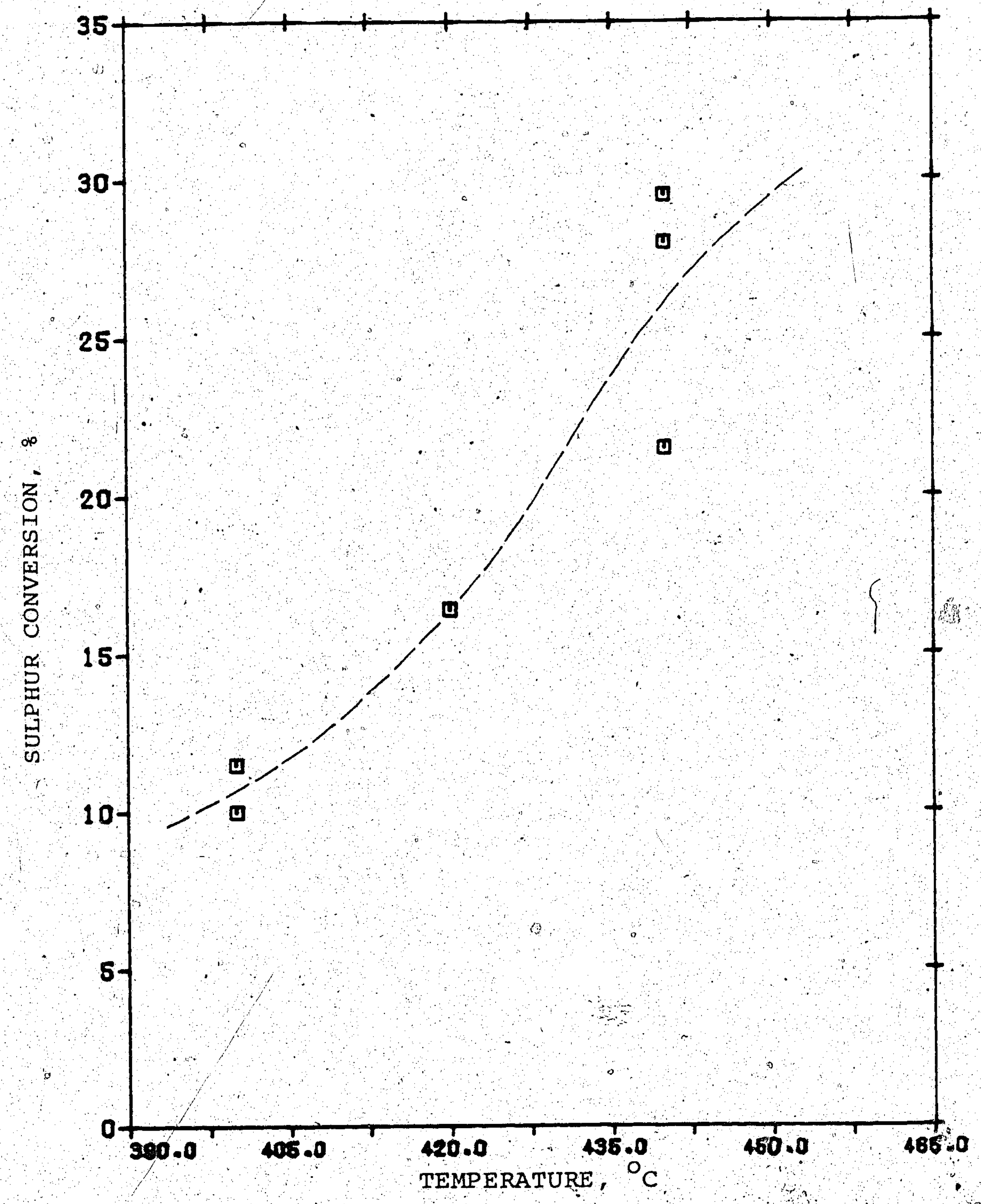


Figure IX.12 Effect of Temperature on Sulphur Conversion, Nom. LHSV = 0.75

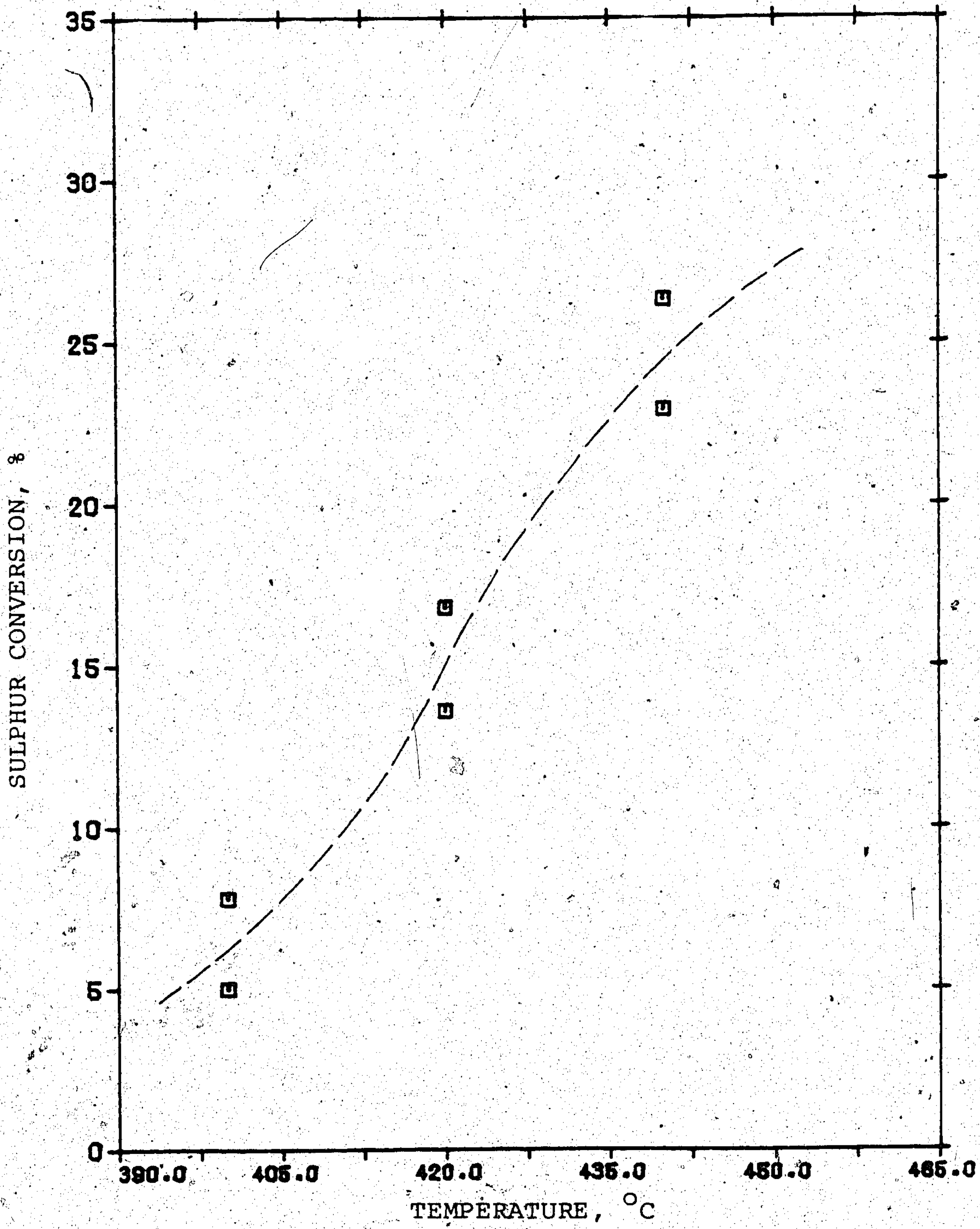


Figure IX.13 Effect of Temperature on Sulphur Conversion, Nom.LHSV = 1.00

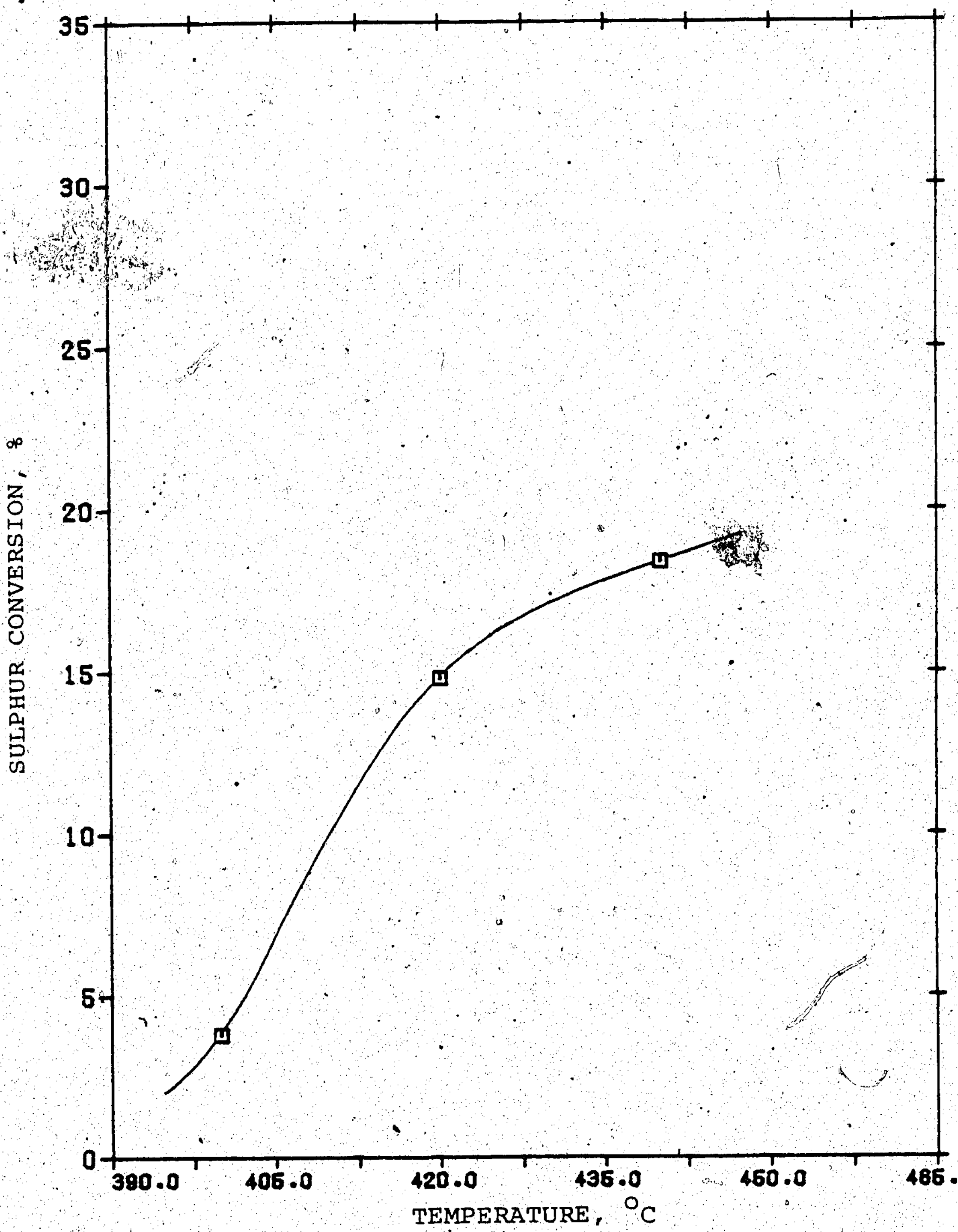


Figure IX.14 Effect of Temperature on Sulphur Conversion, Nom.LHSV = 1.50

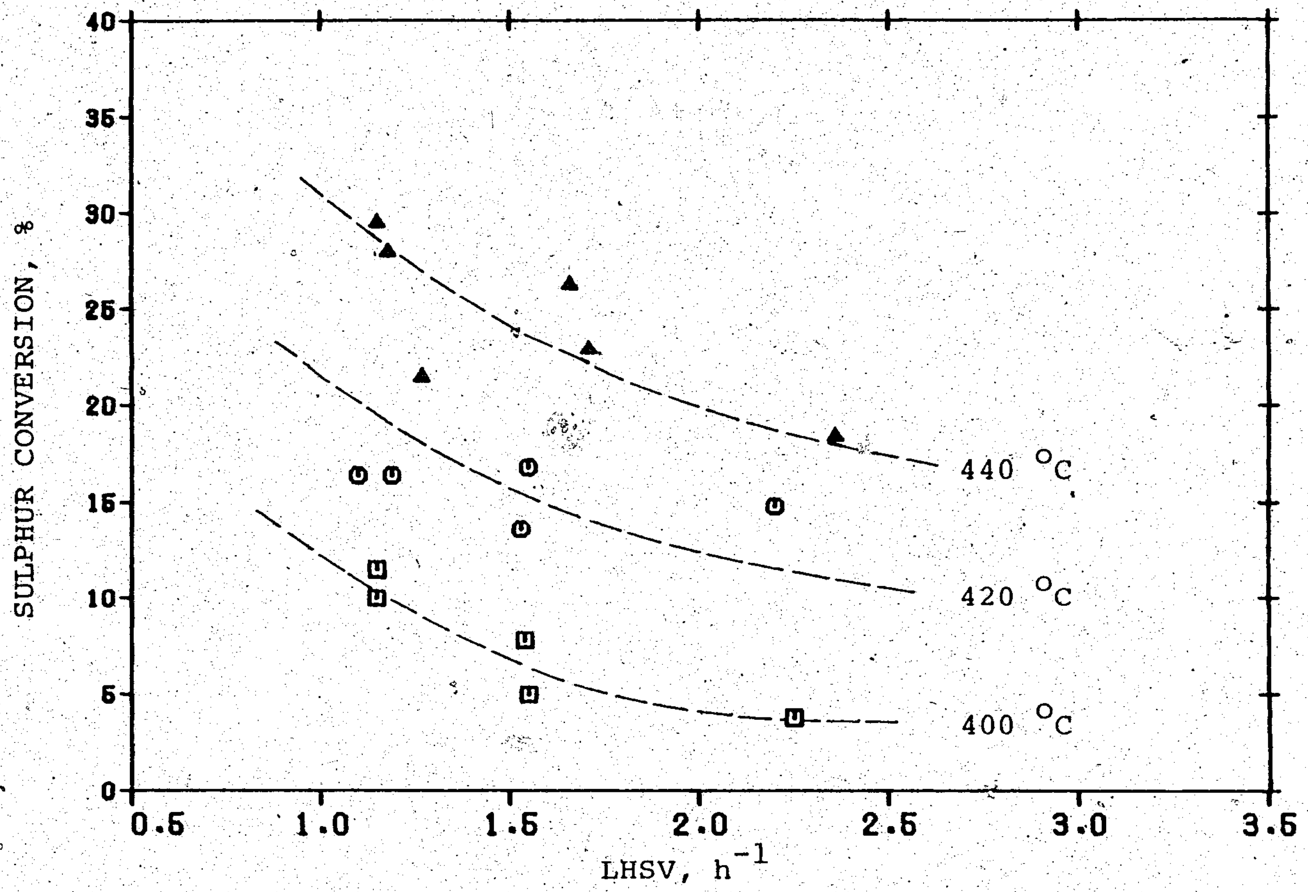


Figure IX.15 Effect of LHSV on Sulphur Conversion at the three temperature levels studied

LHSV, again up to a limiting conversion level.

Miscellaneous Observations

Sampling of Reactor Contents

Reactor liquid phase compositions are required for the correct kinetic analysis of hydroprocessing reactions in a stirred-reactor (CSTR) configuration. To determine whether the liquid product composition (collected after pressure reduction and separation from gaseous products) represents the reactor liquid phase composition at reaction conditions, a comparison was made between the two measured compositions. Figure IX.16 shows simulated distillation curves for both liquid product and reactor liquid samples of run no. LL-18. The reactor liquid is seen to be composed of higher boiling compounds compared to the liquid product.

To check the reliability of the measured compositions, an equilibrium flash program based on the Peng-Robinson equation of state was used to predict reactor contents composition at reaction conditions using the combined composition data for the liquid and gaseous products sampled after pressure reduction and separation. The predicted reactor content compositions were then compared to compositions obtained from experimental sampling of the reactor contents. Table IX.1 shows the comparison for a typical run.

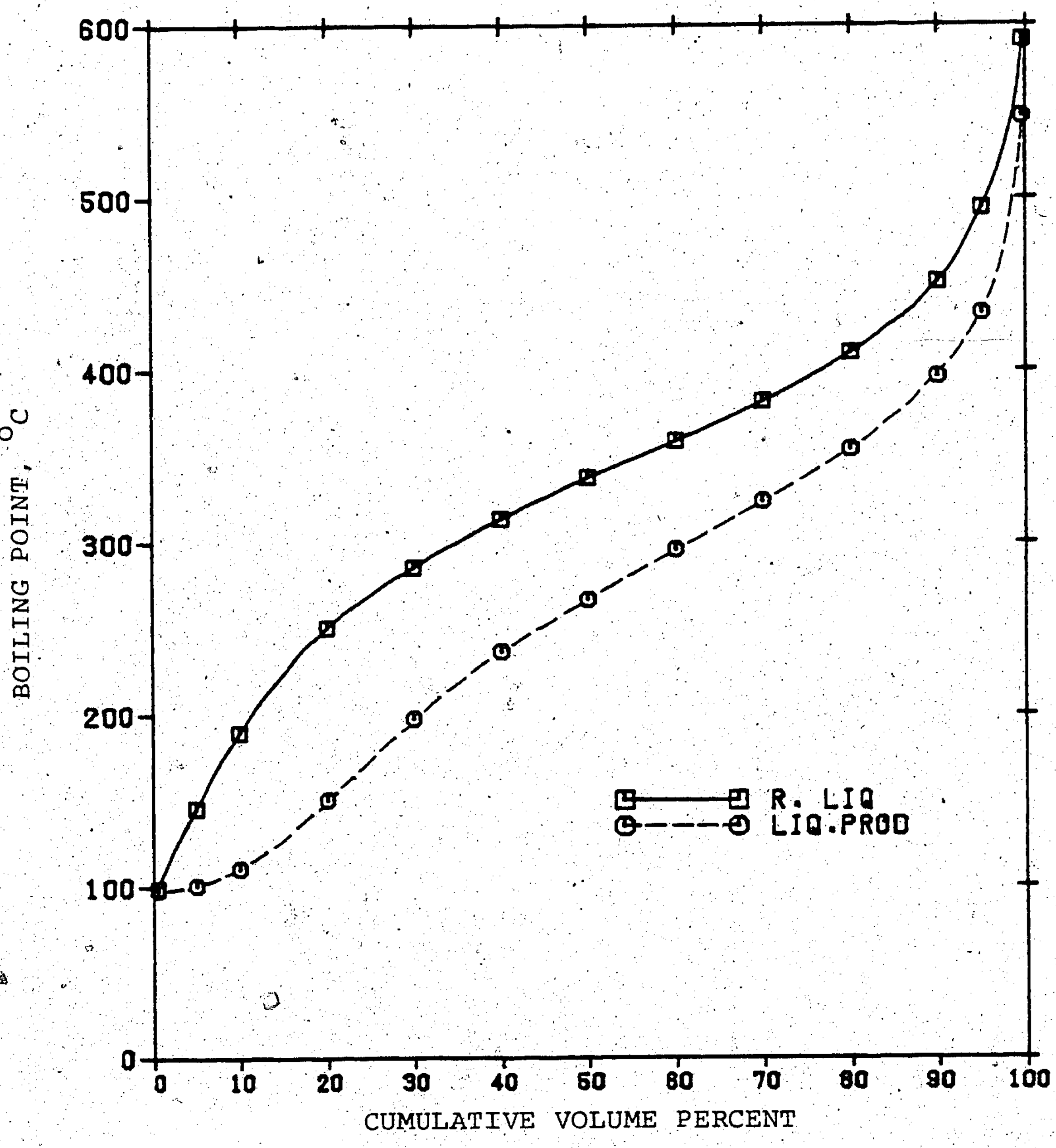


Fig IX.16 Comparison of SDA Distillation Curves for Liquid Product and Reactor Liquid Samples

Table IX.1 Comparison of the Predicted (Peng-Robinson Equilibrium Flash Program) with Measured Reactor Contents Composition Results for Run LL-18

LIQUID PHASE RESULTS

DISSOLVED GASES			REACTOR LIQUID		
Component /Fraction	Predicted Mole %	Measured Mole %	Component /Fraction	Predicted Mole %	Measured Mole %
H_2	88.01	86.13	C_8	9.68	7.67
C_1	2.88	5.22	C_9-C_{11}	11.75	12.49
C_2	1.96	2.75	C_{12}-C_{14}	13.10	12.99
C_3	2.10	2.12	C_{15}-C_{17}	16.48	16.77
C_4	1.47	0.98	C_{18}-C_{20}	15.35	16.37
C_5	0.76	0.32	C_{21}-C_{23}	12.65	13.76
C_6	0.47	0.13	C_{24}-C_{26}	8.07	8.64
H_2S	2.35	2.35*	C_{27}-C_{29}	4.92	4.89
			C_{30}-C_{32}	3.04	2.68
			C_{33}-C_{35}	1.43	1.32
			C_{36}-C_{38}	1.14	0.76
			C_{39}+	2.39	1.66
	100.00	100.00		100.00	100.00

Table IX.1 (cont'd) Comparison of the Predicted (Peng-Robinson Equilibrium Flash Program) with Measured Reactor Contents Composition Results for Run LL-18

GAS PHASE RESULTS

Component /Fraction	Predicted Mole %	Measured Mole %
H_2	92.98	91.05
C_1	2.19	3.20
C_2	1.21	1.48
C_3	1.10	1.20
C_4	0.66	0.75
C_5	0.29	0.44
C_6	0.16	0.47
H_2S	1.41	1.41*
	100.00	100.00

*Taken as value predicted by vapour-liquid flash calculations

The equilibrium flash calculations involves the use of predetermined interaction parameters for the various components in the reaction mixtures. From the results shown in Table IX.1 it can be seen that the predicted values agree quite well with measured values. On this basis, further reaction occurring in the liquid phase after leaving the reactor does not seem to be likely.

Hydrogen Solubility Results

Hydrogen solubilities in heavy gas oil were also obtained from sampling of the reactor contents and were expressed in terms of the mass of hydrogen dissolved per unit mass of reactor liquid phase. The results are presented in Figure IX.17. These results show that the solubility of hydrogen in the liquid phase at different reaction conditions varies from 1.9 to 2.5 mg H_2/g Oil.

To provide some indication on the validity of these results, the results were compared with available data from the literature on the solubility of hydrogen in Lloydminster heavy oil(21). These data were obtained at lower temperatures at non-reaction conditions, and ranged from 0.8 to 1.2 mg H_2/g Oil for temperatures of 200 to 300 °C, respectively. This shows that the hydrogen solubility results obtained for the study are of the correct order of magnitude, and thus may be

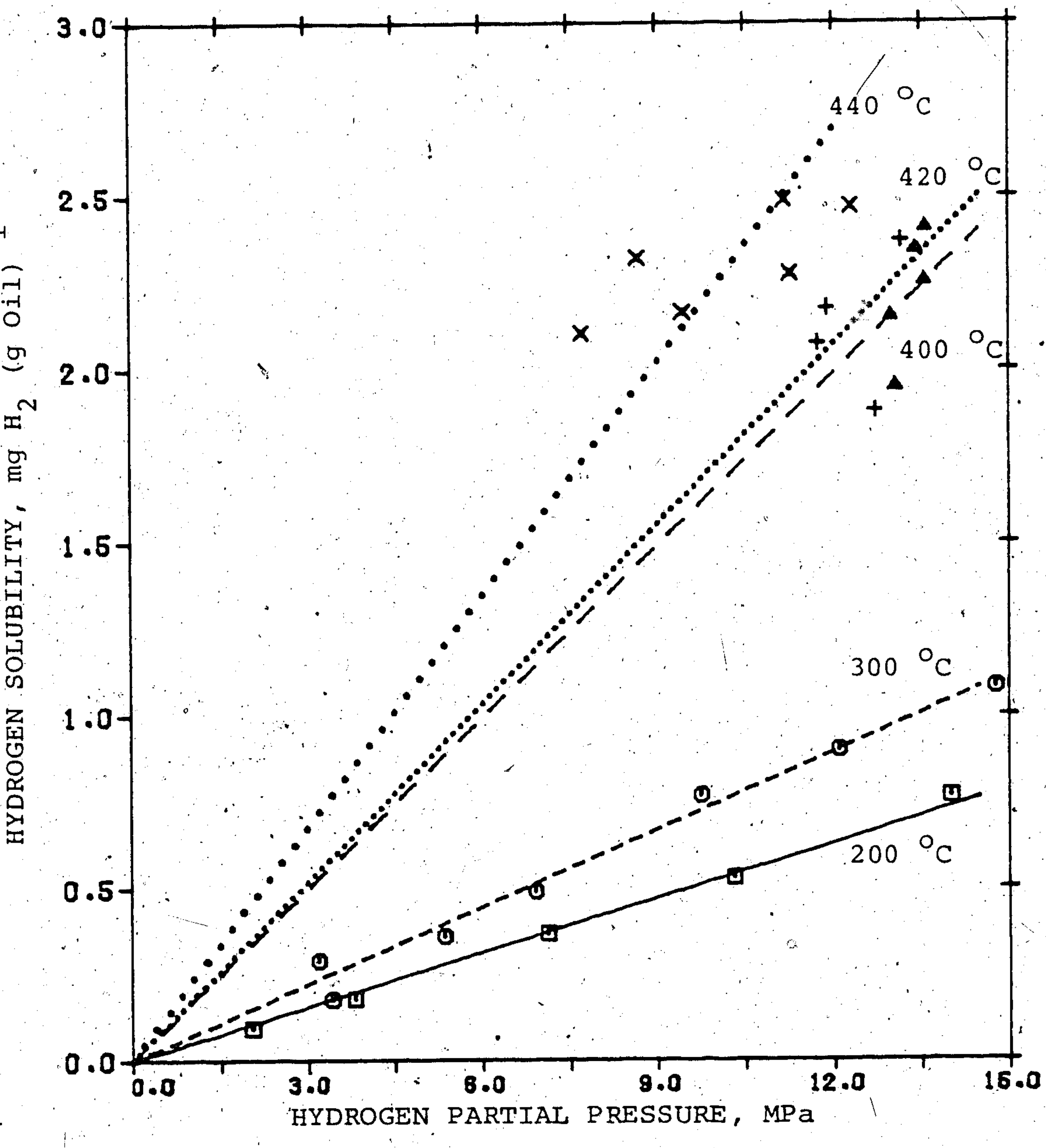


Figure IX.17 Hydrogen Solubility Results,
Thermal Hydroprocessing of LLVGO

useful in design calculations.

Hydrogen Consumption Results

Hydrogen consumption data for hydroprocessing runs were obtained by hydrogen balance calculations. The difference between the hydrogen feedrate and the effluent excess hydrogen flowrate is the hydrogen consumption. The data is expressed as volume consumed per volume of feedstock processed (m^3API H_2/m^3Oil).

Figure IX.18 shows a plot of the hydrogen consumption data versus LHSV at the three temperature levels studied. The plot shows that hydrogen consumption increases with decreasing LHSV and increases with increasing temperature. Some scatter of the data points was observed. The data showed that for practical thermal hydroprocessing conditions with Lloydminster gas oil, a hydrogen consumption of about 40 m^3API H_2/m^3Oil or 225 scf/bbl is required.

Kinetic Analysis of Conversion Results

Modelling the Kinetics of Pitch Conversion

The basic kinetic model relating the rate of pitch conversion to the concentration of pitch and the concentration of hydrogen in the reactor liquid may be expressed as:

$$-r_p = k\, C_{RL}^{\ m}\, C_H^{\ n} \qquad (9.1)$$

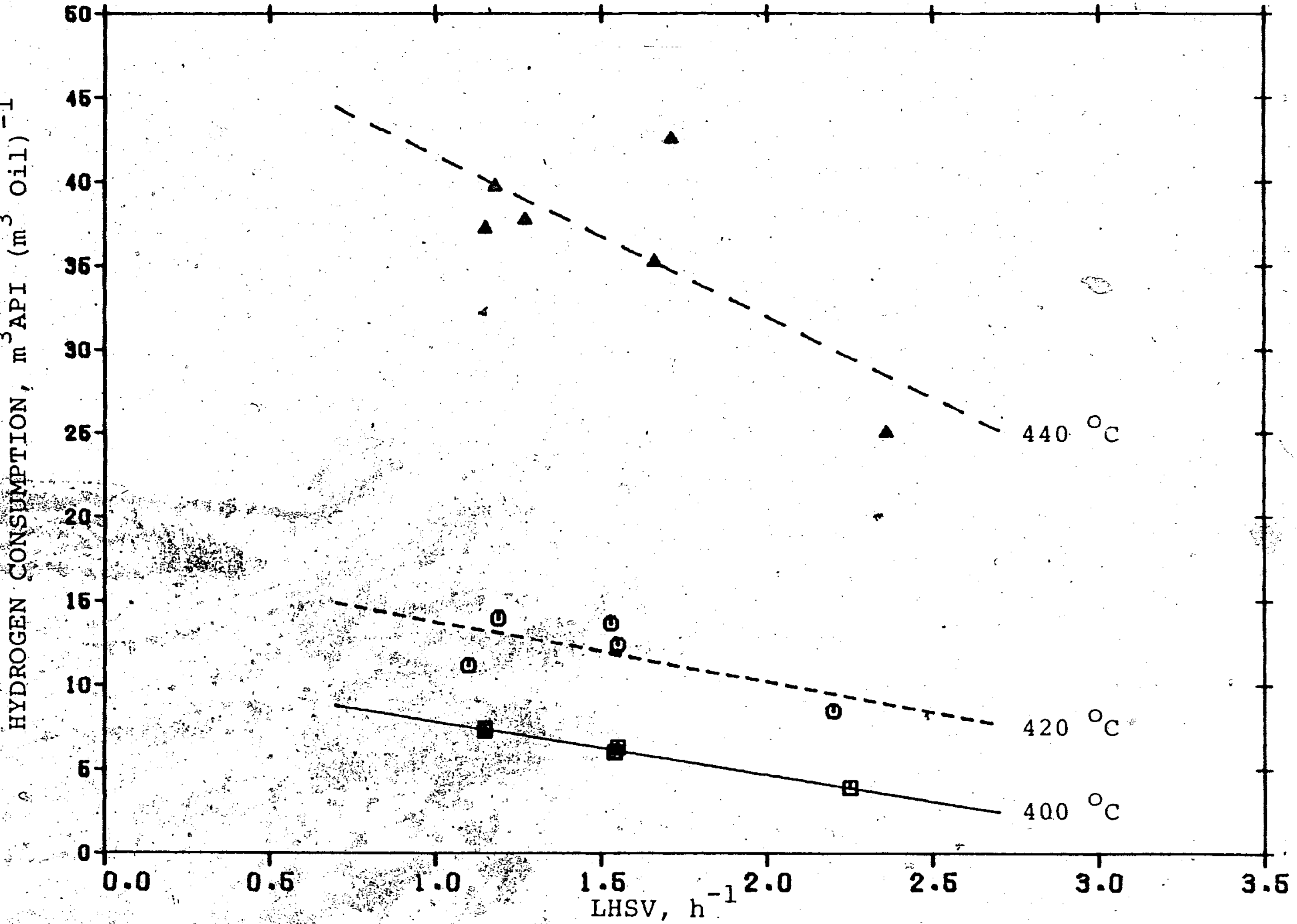


Figure IX.18 Hydrogen Consumption Results, Thermal Hydroprocessing of LLVGO where,

k = reaction rate constant, $mol^{1-m-n} mL^{m+n-1} min^{-1}$

C_{RL} = pitch concentration in reactor liquid phase at reaction conditions, $mol\ mL^{-1}$

C_H = hydrogen concentration in reactor liquid phase at reaction conditions, $mol\ mL^{-1}$

m,n = general model parameters

$-r_p$ = rate of pitch conversion, $mol\ mL^{-1}\ min^{-1}$

Preliminary studies involved fitting the calculated reaction rates to actual reactor liquid phase compositions for pitch and hydrogen based on a linearized version of equation (9.1). Due to the close proximity of the data points (concentrations and reaction rate data) multi-variable least square calculations was not able to evaluate a reliable estimate of the model parameters m and n. The input data matrix approximates a singular matrix. However the solution of equation (9.1) for an initial set of nine data points from earlier runs gave an estimate of m and n of close to unity and zero respectively. This observation of zero order dependence of reaction rate on hydrogen concentration may be a result of a nearly constant dissolved hydrogen content in the reactor liquid phase over the range of conditions studied. Hence equation (9.1) was approximated by a pseudo-first order rate equation.

Based on the preliminary findings, the rate data were analyzed using two kinetic models: Model 1 which relates the rate of pitch conversion to the concentration of pitch in the reactor liquid (m=1,n=0), and Model 2 which relates the rate of pitch conversion to pitch and hydrogen concentrations in the reactor liquid (m=1,n=1). This scheme was chosen to enable the comparison of both models to check the validity of taking n to be zero in Model 1.

Arrhenius plots of the rate constants based on both models are presented in Figures IX.19 and IX.20, respectively. It can be seen that the data agree reasonably well with their respective fitted straight lines. The activation energy estimated for Model 1 is 170.6 kJ/mol compared with 167.1 kJ/mol estimated for Model 2. The activation energies being approximately equal further indicates that the concentration of hydrogen term in the rate equation may be a constant term.

A comparison of how well the two models fit the experimental results based on some statistical tests is given in Table IX.2. The quantities in Table IX.2 are calculated based on the Arrhenius plots and tend to show that Model 1 fits the data better. The larger scatter of reactor liquid hydrogen concentration data could explain the larger scatter of data points in the Arrhenius plot based on Model 2.

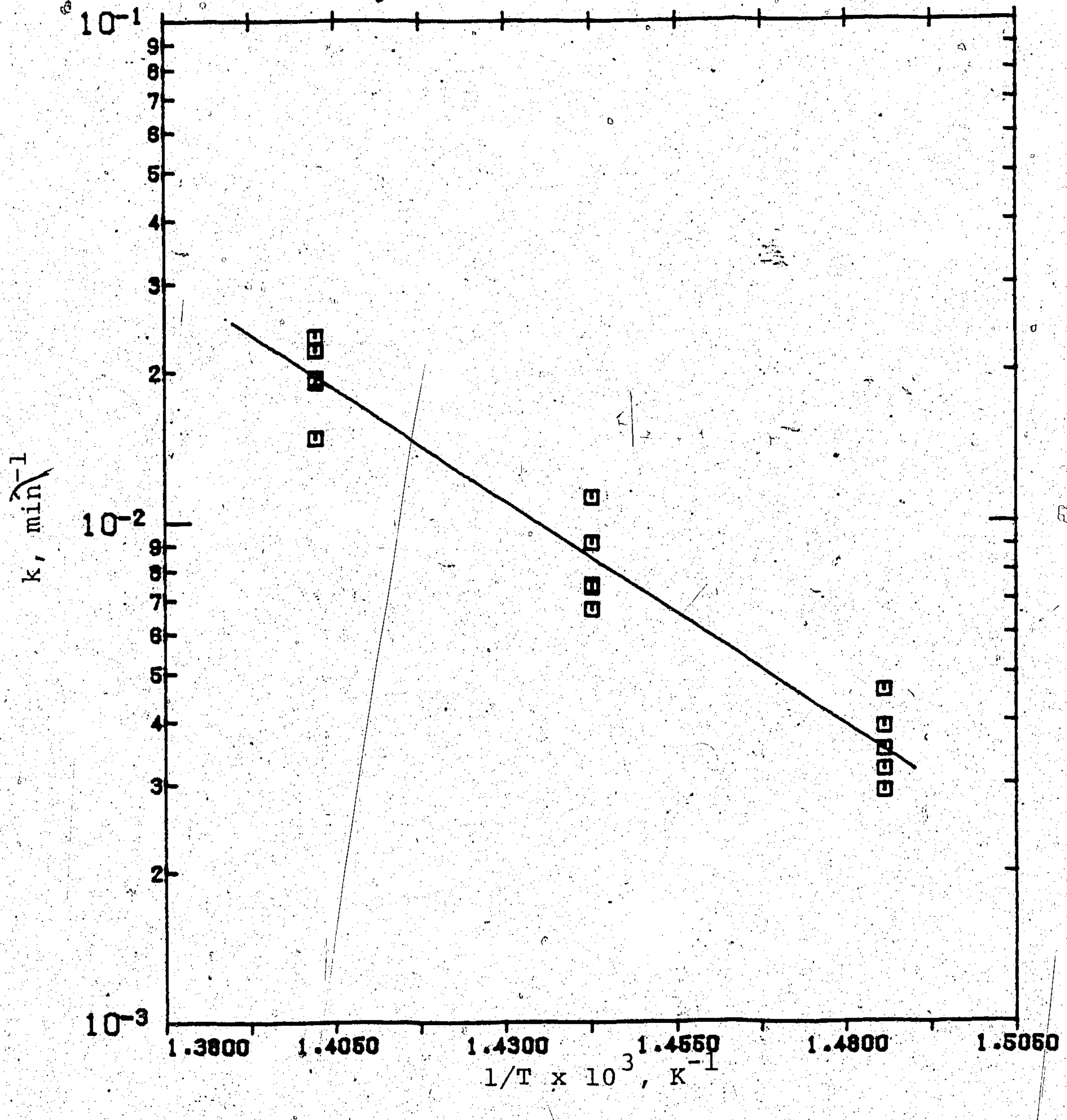


Figure IX.19 Arrhenius Plot of Pitch Conversion Rate Constants Based on Model 1

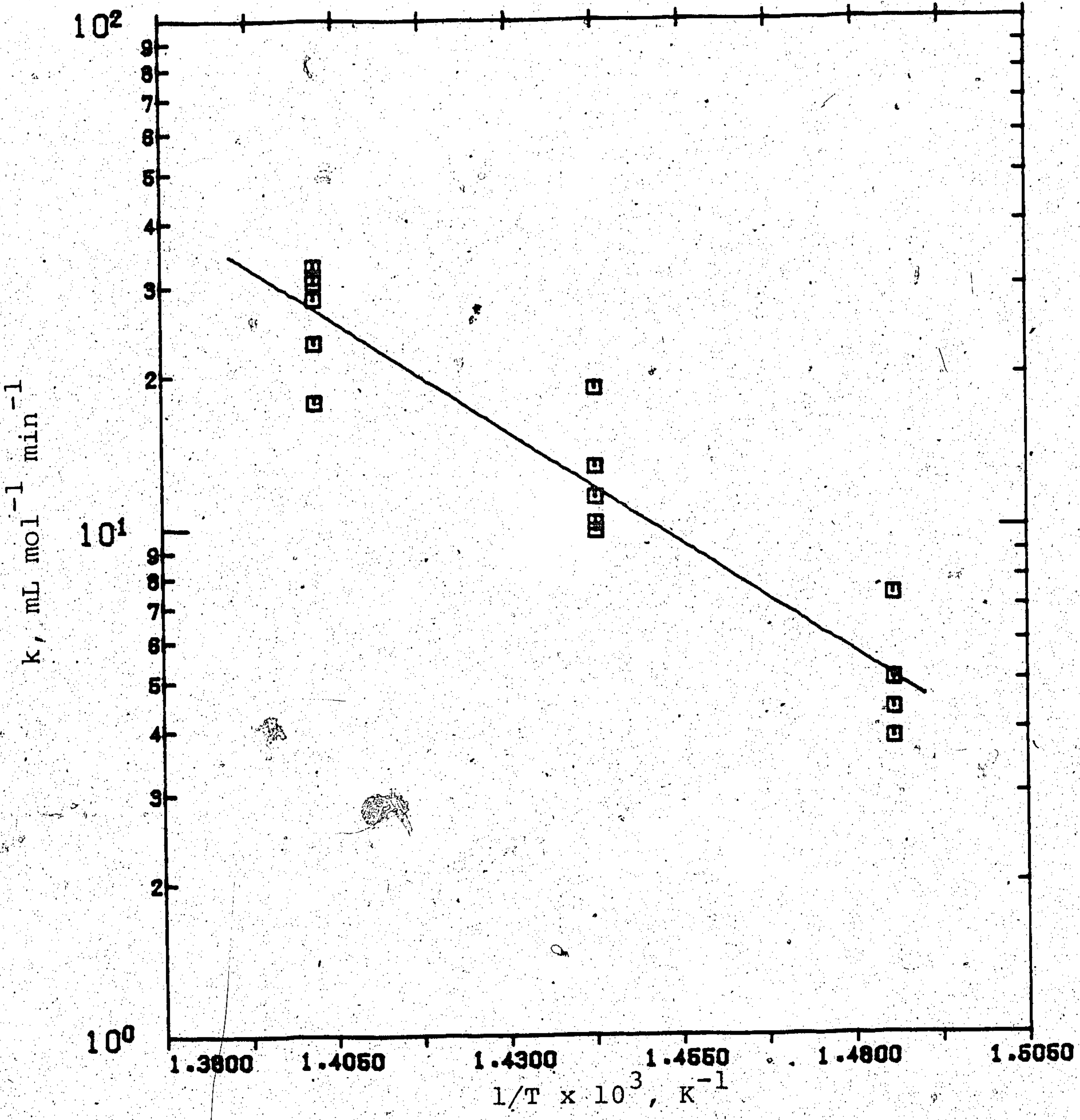


Figure IX.20 Arrhenius Plot of Pitch Conversion Rate Constants Based on Model 2

Table IX.2 Statistical Test Results for Kinetic Models Used to Correlate Pitch Conversion Rate Data in the Thermal Hydroprocessing of LLVGO

Test Coefficient	Model 1 $-r_p = k\ C_{RL}$	Model 2 $-r_p = k\ C_{RL}\ C_H$
Residual Sum of Squares	0.4377	0.7964
Coefficient of Determination	0.9480	0.9059
Correlation Coefficient	0.9737	0.9518

Modelling the Kinetics of Sulphur Removal

The general equation used to model the kinetics of sulphur removal is of the form:

$$-r_S = k\, C_S^{\,n} \tag{9.2}$$

where,

k = sulphur conversion rate constant

C_S = sulphur concentration in the reactor liquid phase at reaction conditions, mol mL^{-1}

n = model parameter

$-r_S$ = rate of sulphur conversion, mol mL^{-1} min^{-1}

In this study, two models were examined for the kinetics of hydrodesulphurization, Model 1 which relates the rate of sulphur conversion directly to concentration of sulphur in the reactor liquid ($n=1$), and Model 2 which relates the rate of sulphur conversion to the square of the concentration of sulphur in the reactor liquid ($n=2$).

The Arrhenius plots of the rate constants calculated based on these two models are presented in Figures IX.21 and IX.22. Both models fit the data reasonably well. The hydrodesulphurization activation energy estimated based on Model 1 is 115.7 kJ per mole of sulphur while that based on Model 2 is 106.6 kJ per mole of sulphur. With the available data, it was not

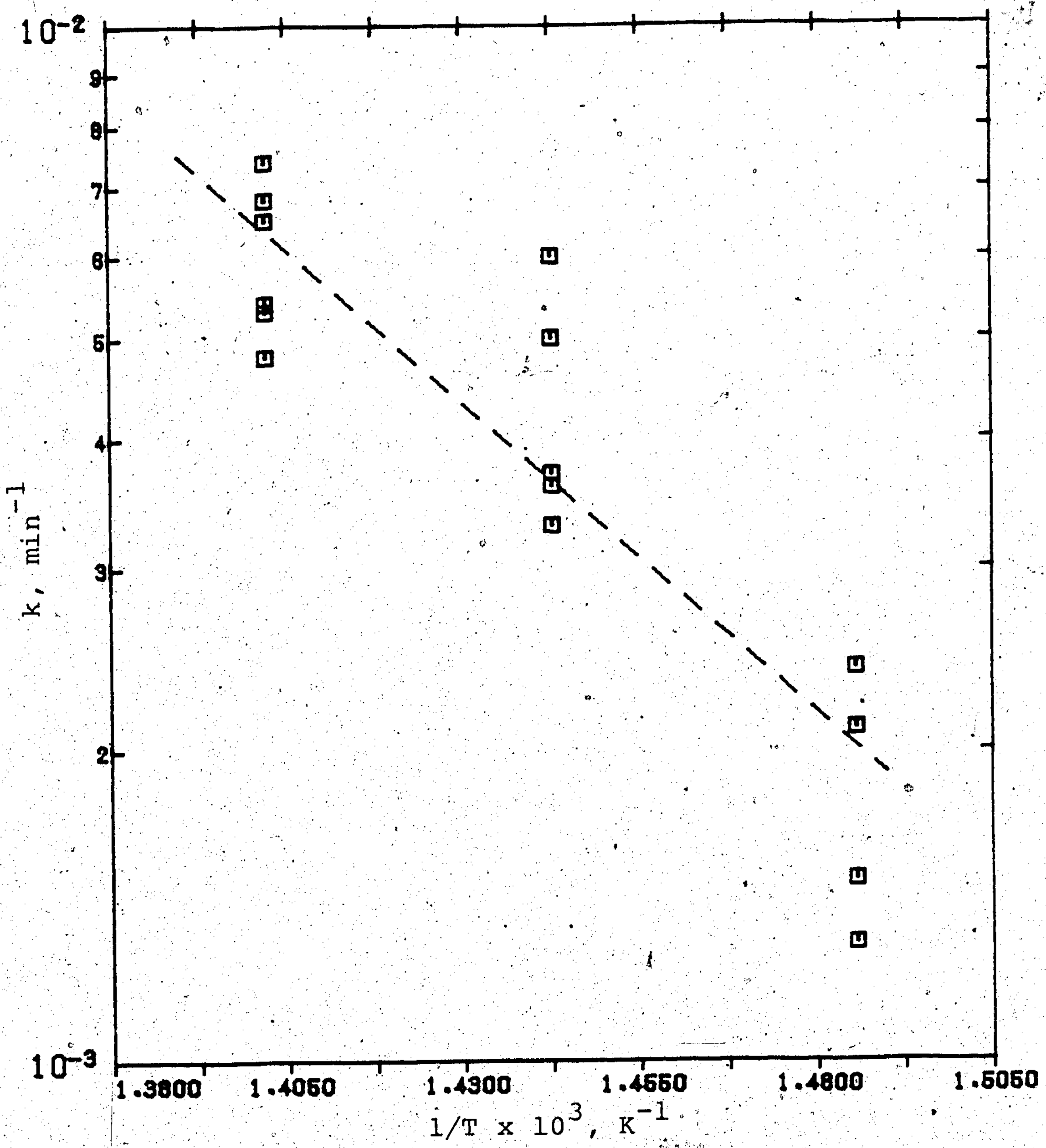


Figure IX.21 Arrhenius Plot of Hydrodesulphurization Rate Constants Based on Model 1

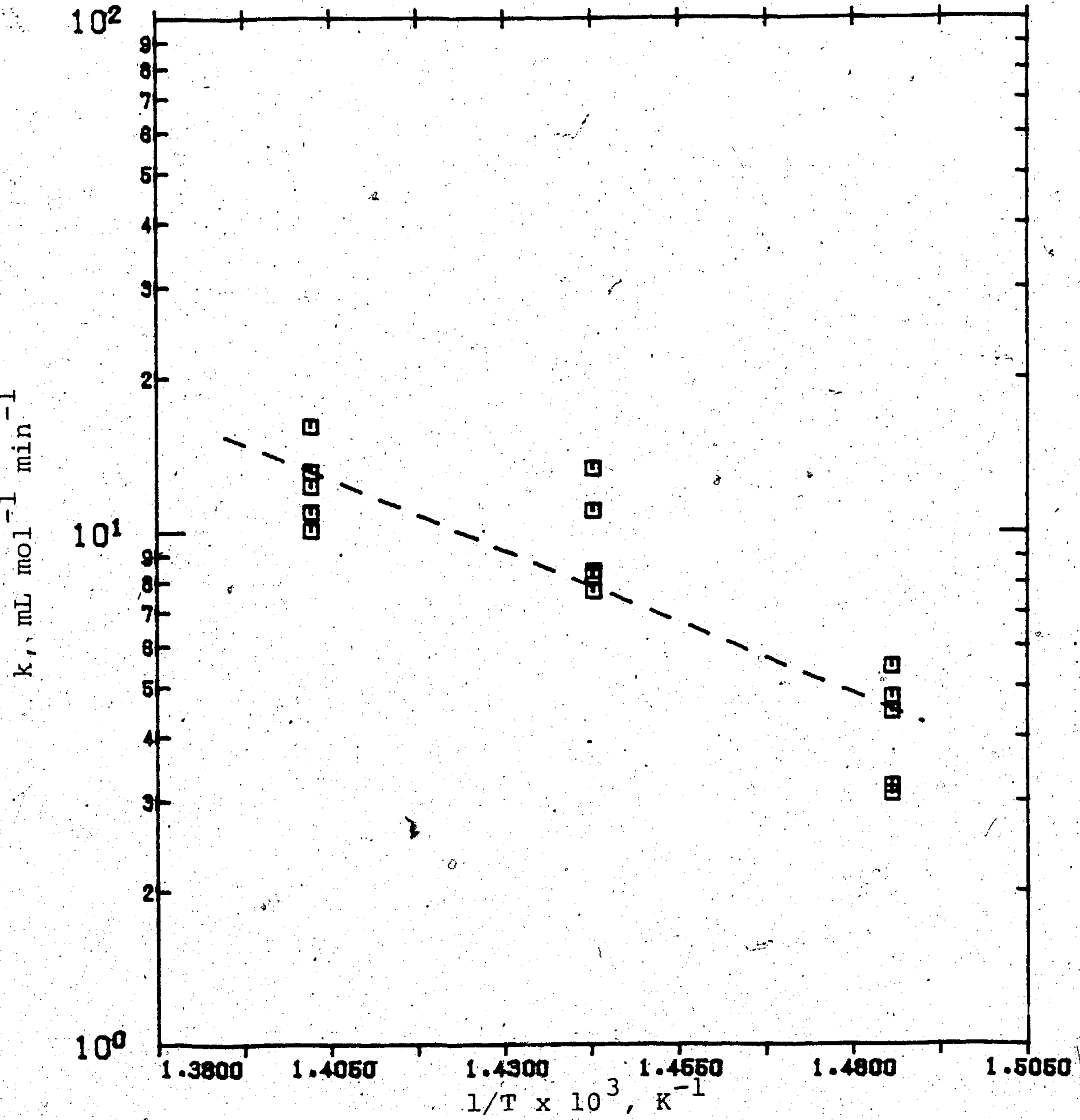


Figure IX.22 Arrhenius Plot of Hydrodesulphurization Rate Constants Based on Model 2 possible to discriminate between the two forms.

Use of Kinetic Models to Predict the Effect of LHSV on Pitch Conversion

To test the reliability of the kinetic equations for pitch conversion, the effect of LHSV on pitch conversion was predicted using the material balance equation for an isothermal CSTR. The equations used for these calculations are presented in Table IX.3 while the derivations and sample calculations are presented in Appendix D. Values of the ratio of liquid feedrate to liquid product rate (F_1'/F_2') evaluated at reaction conditions from measured run data are presented in Table IX.4. Both predicted and experimental results were plotted in Figures IX.23 to IX.25. From the plots, it can be seen that the prediction agrees quite well with experimental results.

The results indicated that a good estimate of the ratio of liquid flowrates (F_1'/F_2') is crucial to predict accurately the level of pitch conversion in the CSTR. Taking F_1'/F_2' to be unity causes equations (9.3) and (9.4) to underpredict the pitch conversion.

Table IX.3 Equations Used to Predict the Level of Pitch Conversion in the CSTR

Basis : First Order Kinetics (Model 1)

$$X_p = \frac{k_1 \ (F_1'/F_2') \ (LHSV^{-1})}{1 + k_1 \ (F_1'/F_2') \ (LHSV^{-1})} \qquad (9.3)$$

Basis : Overall Second Order Kinetics (Model 2)

$$X_p = \frac{k_2 \ C_H \ (F_1'/F_2') \ (LHSV^{-1})}{1 + k_2 \ C_H \ (F_1'/F_2') \ (LHSV^{-1})} \qquad (9.4)$$

where,

F_1'/F_2' = ratio of volumetric liquid feedrate to volumetric liquid product rate evaluated at reaction conditions

C_H = hydrogen concentration in the reactor liquid phase at reaction conditions, mol mL^{-1}

k_1, k_2 = reaction rate constants

X_p = fractional pitch conversion

Table IX.4 Values of F_1'/F_2', the ratio of Liquid Feedrate to Liquid Product Flowrate, evaluated at Reaction Conditions

$$\text{Basis} : F_2' = \frac{F_1'C_F'(1 - X_p)}{C_{RL}}$$

Run No.	F_1' mL min^{-1}	F_2' mL min^{-1}	F_1'/F_2'
LL-10	5.26 (400 °C)	4.96 (400 °C)	1.06
LL-11	6.91 (400 °C)	6.40 (400 °C)	1.08
LL-14	10.53 (400 °C)	10.26 (400 °C)	1.03
LL-19	5.26 (400 °C)	4.96 (400 °C)	1.06
LL-22	7.02 (400 °C)	6.39 (400 °C)	1.10
LL-05	5.41 (420 °C)	4.42 (420 °C)	1.22
LL-07	5.41 (420 °C)	4.89 (420 °C)	1.11
LL-12	7.21 (420 °C)	6.28 (420 °C)	1.15
LL-16	10.82 (420 °C)	9.74 (420 °C)	1.11
LL-20	7.21 (420 °C)	6.22 (420 °C)	1.16
LL-06	5.56 (440 °C)	2.88 (440 °C)	1.93
LL-08	5.56 (440 °C)	3.88 (440 °C)	1.43
LL-13	7.41 (440 °C)	4.45 (440 °C)	1.67
LL-17	11.12 (440 °C)	7.79 (440 °C)	1.43
LL-18	5.55 (440 °C)	2.59 (440 °C)	2.14
LL-21	7.42 (440 °C)	3.82 (440 °C)	1.94

av. F_1'/F_2' = 1.07 at 400°C
= 1.15 at 420°C
= 1.70 at 440°C

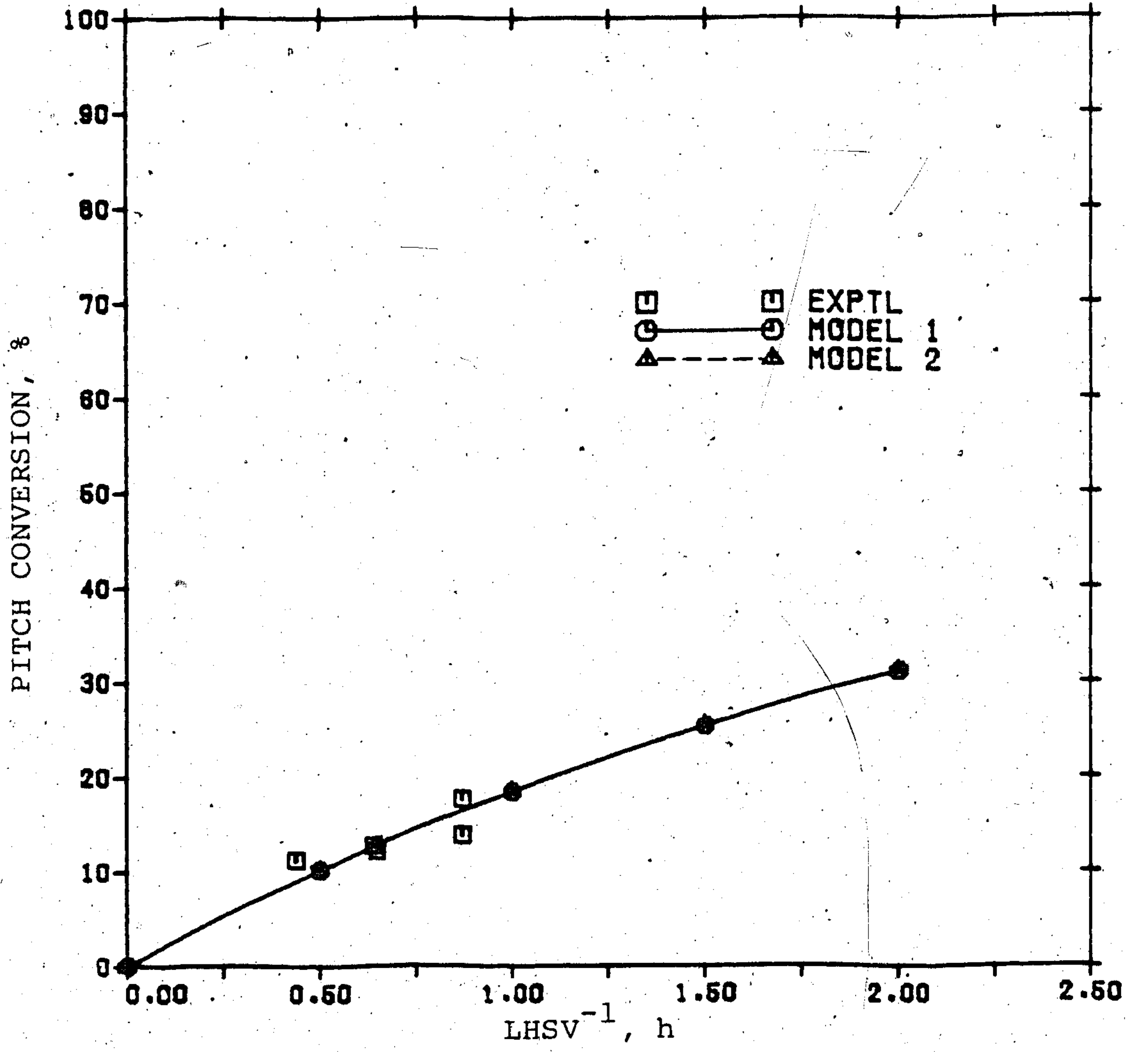


Figure IX.23 Effect of LHSV on Pitch Conversion at 400 C (CSTR)

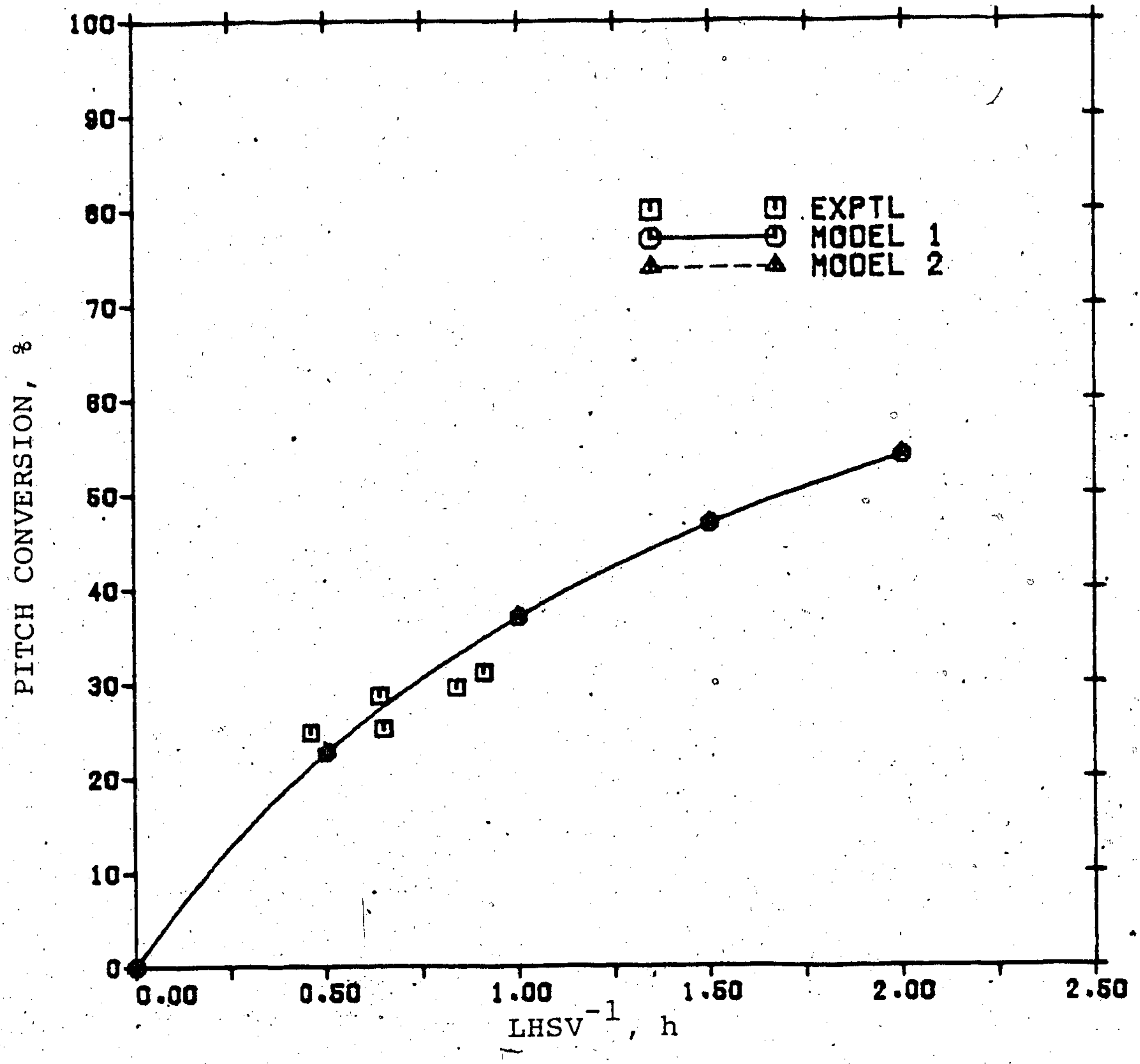


Figure IX.24 Effect of LHSV on Pitch Conversion at 420 C (CSTR)

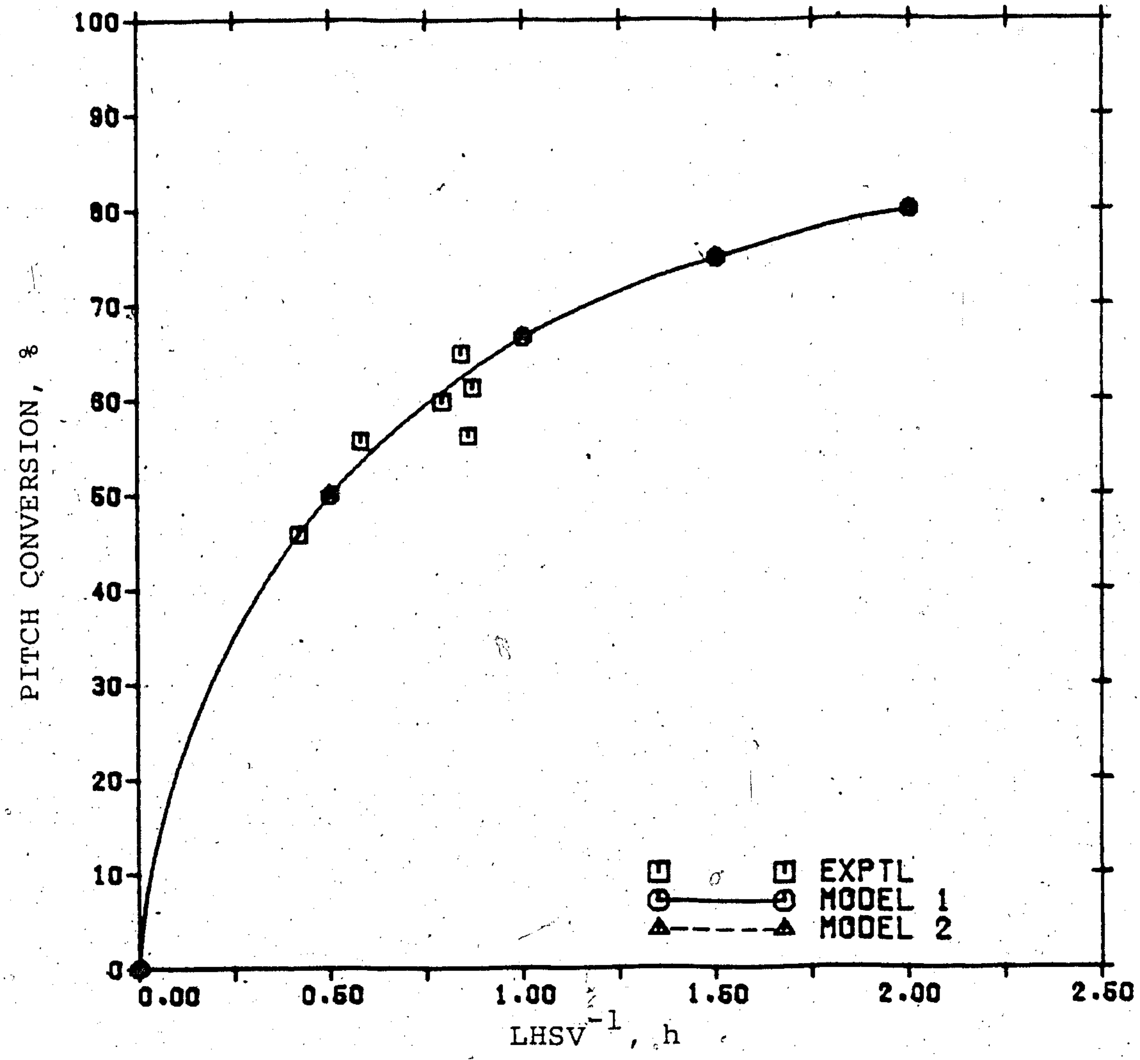


Figure IX.25 Effect of LHSV on Pitch Conversion at 440 C (CSTR)

B. Additional Stirred Reactor Results For Other Gas Oils

Product Distribution and Coking Envelope

The experimental results from the thermal hydroprocessing of five gas oil feedstocks ranging from the lighter Athabasca hydrotreated gas oils to the heavier Cold Lake gas oil are summarized in Tables VII.11 to VII.25. The product distributions for each feedstock have been plotted for easier interpretation. The effect of temperature on liquid and gaseous product distributions are plotted in Figures IX.26 to IX.35. These plots show that increasing the reaction temperatures increases the yield of lighter liquid fractions and lighter hydrocarbon gases.

These runs were used to study the relative coke formation tendencies of different feedstocks. The reaction temperature was used to locate the boundary where coke formation begins to become significant. Figure IX.36 shows a pitch conversion versus temperature plot for the five gas oils and LLVGO at a constant nominal LHSV of 1.0 h^{-1}. The observed coking envelope was superimposed on the same plot. The plot shows that for the heavier feedstocks (high pitch content), the temperature at which coke formation is significant is lower than for a lighter feedstock.

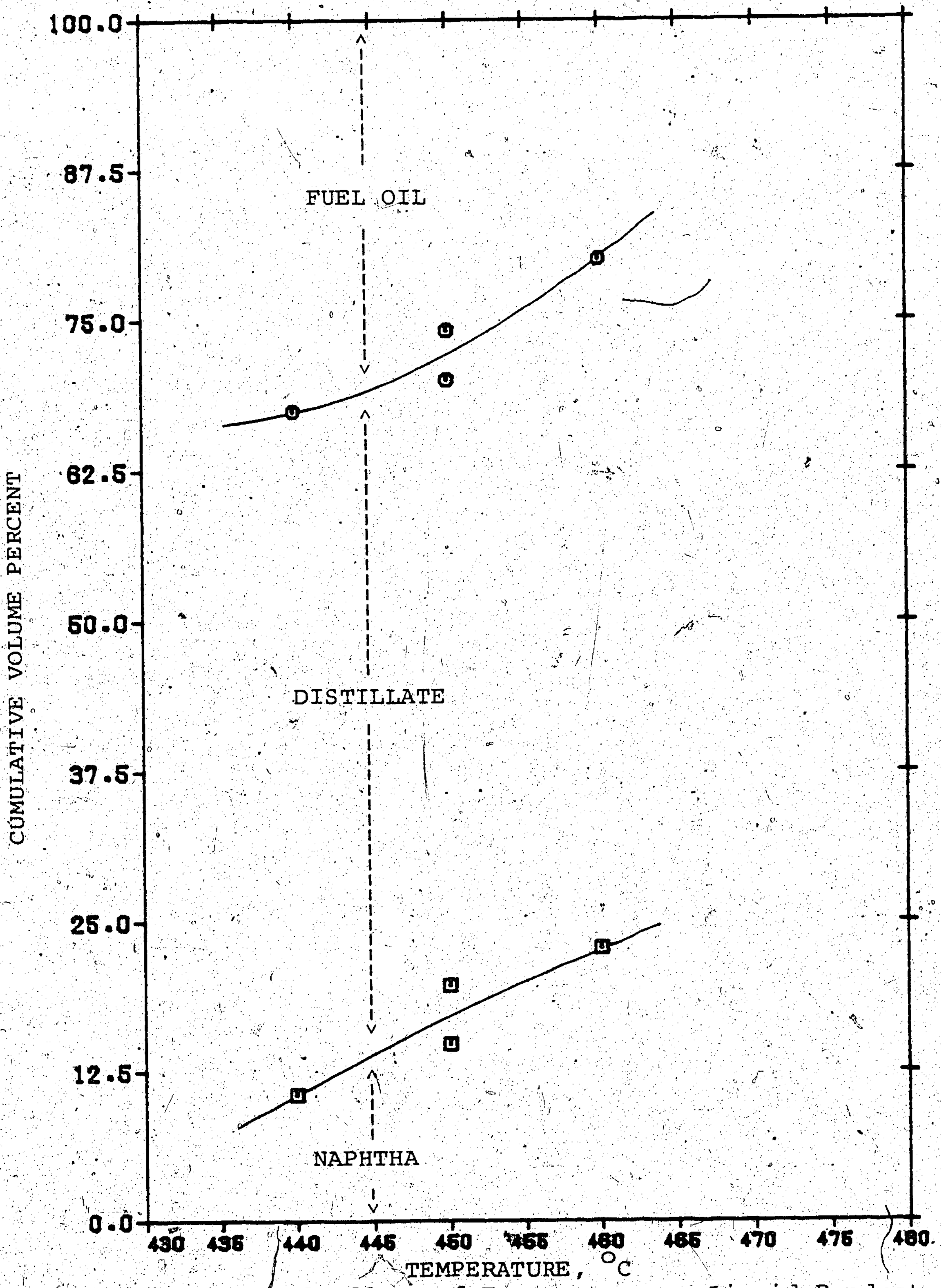


Figure IX.26 Effect of Temperature on Liquid Product Distribution, Suncor Athabasca Hydrotreated Gas Oil

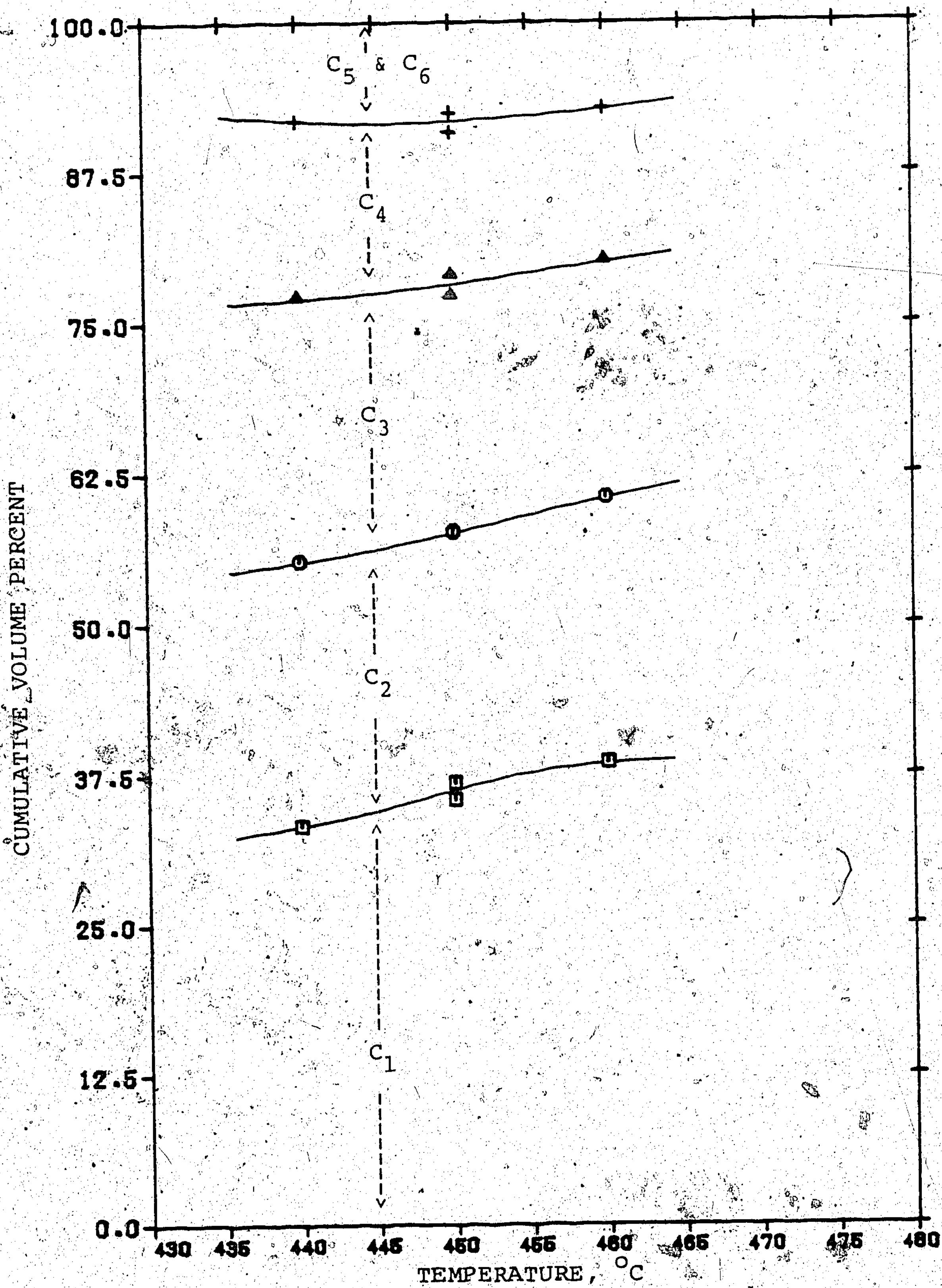


Figure IX.27 Effect of Temperature on Gas Product Distribution, Suncor Athabasca Hydrotreated Gas Oil

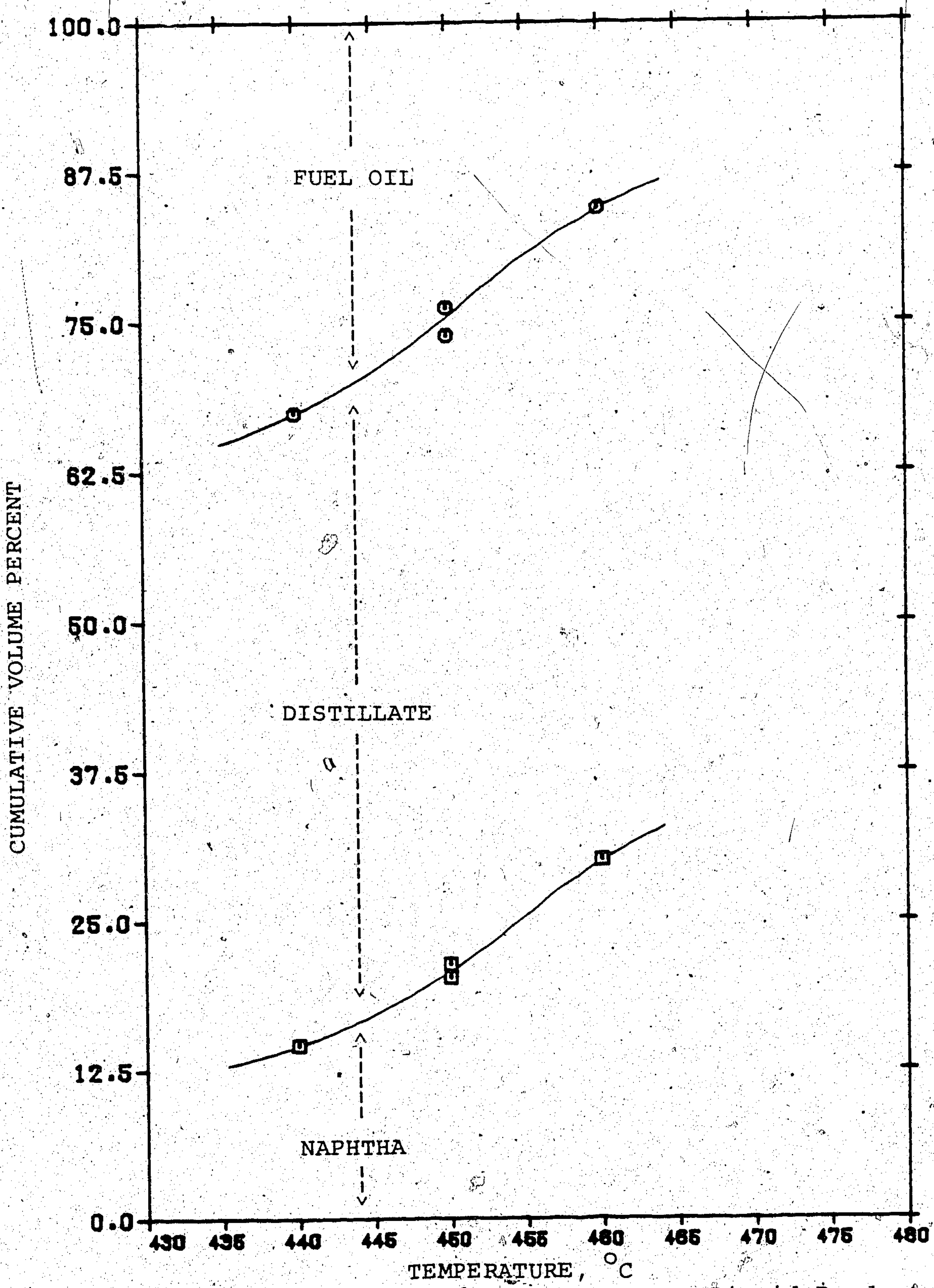


Figure IX.28 Effect of Temperature on Liquid Product Distribution, Syncrude Athabasca Hydrotreated Gas Oil

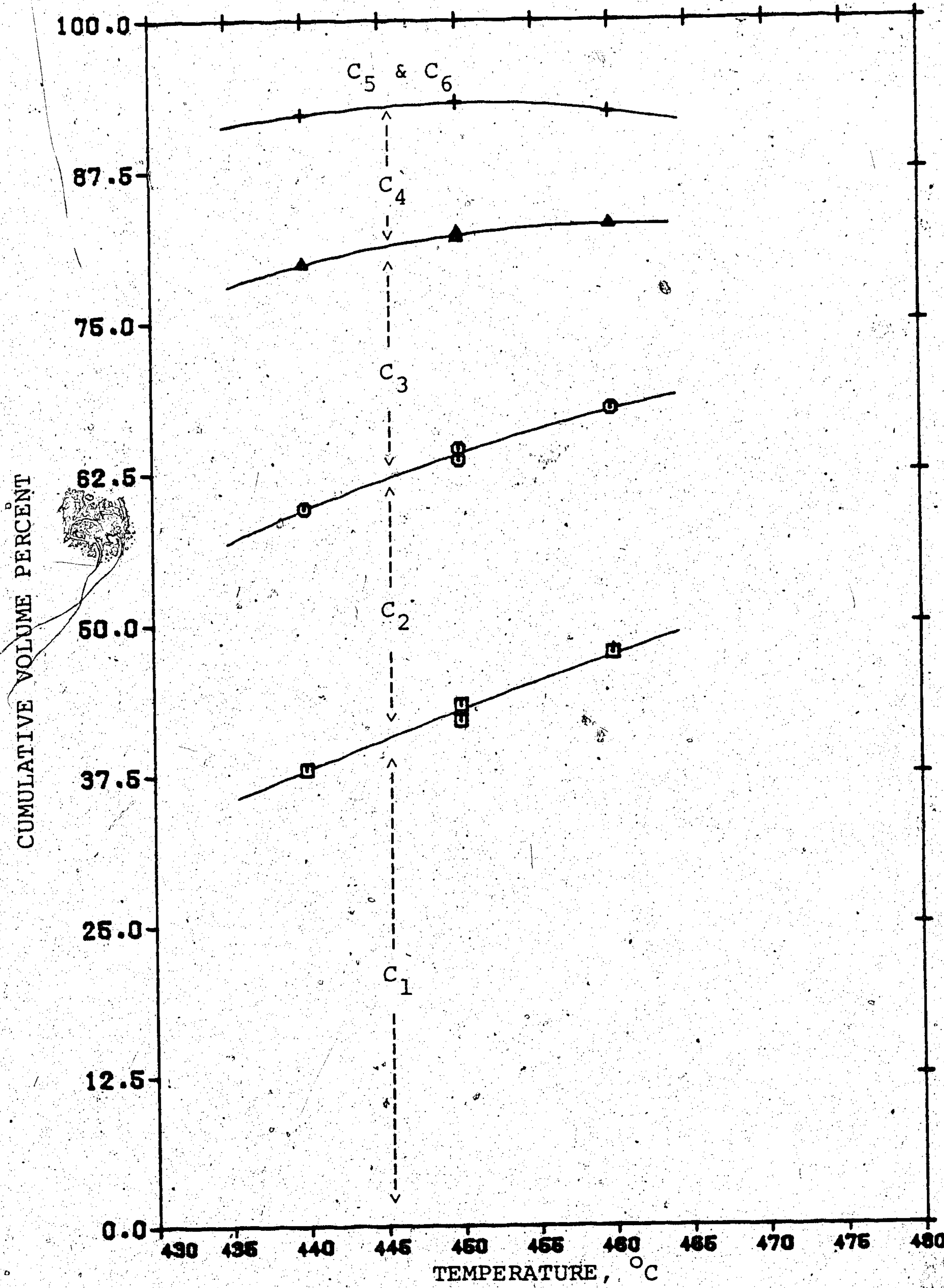


Figure IX.29 Effect of Temperature on Gas Product Distribution, Syncrude Athabasca Hydrotreated Gas Oil

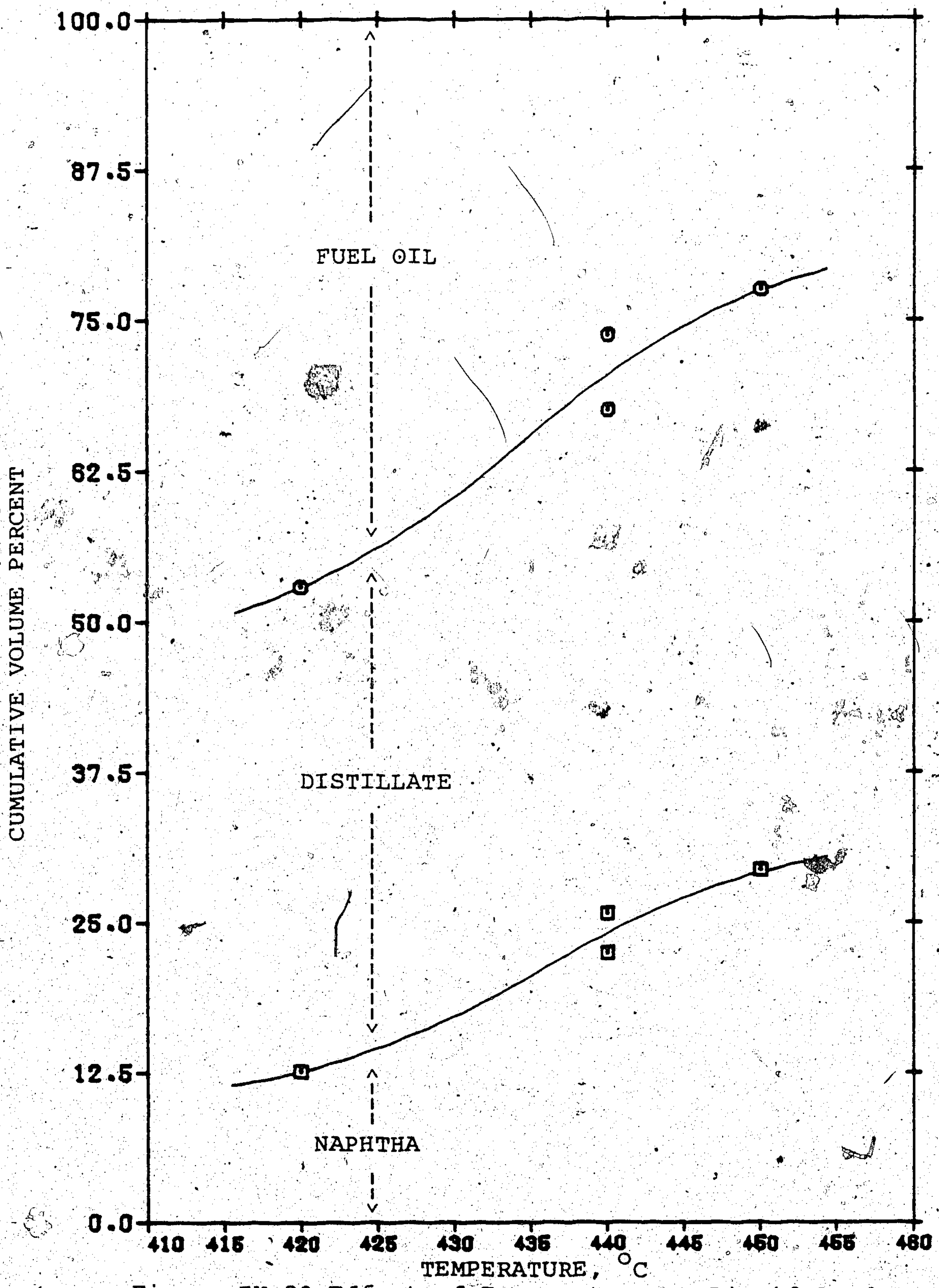


Figure IX.30 Effect of Temperature on Liquid Product Distribution, Athabasca Virgin Gas Oil

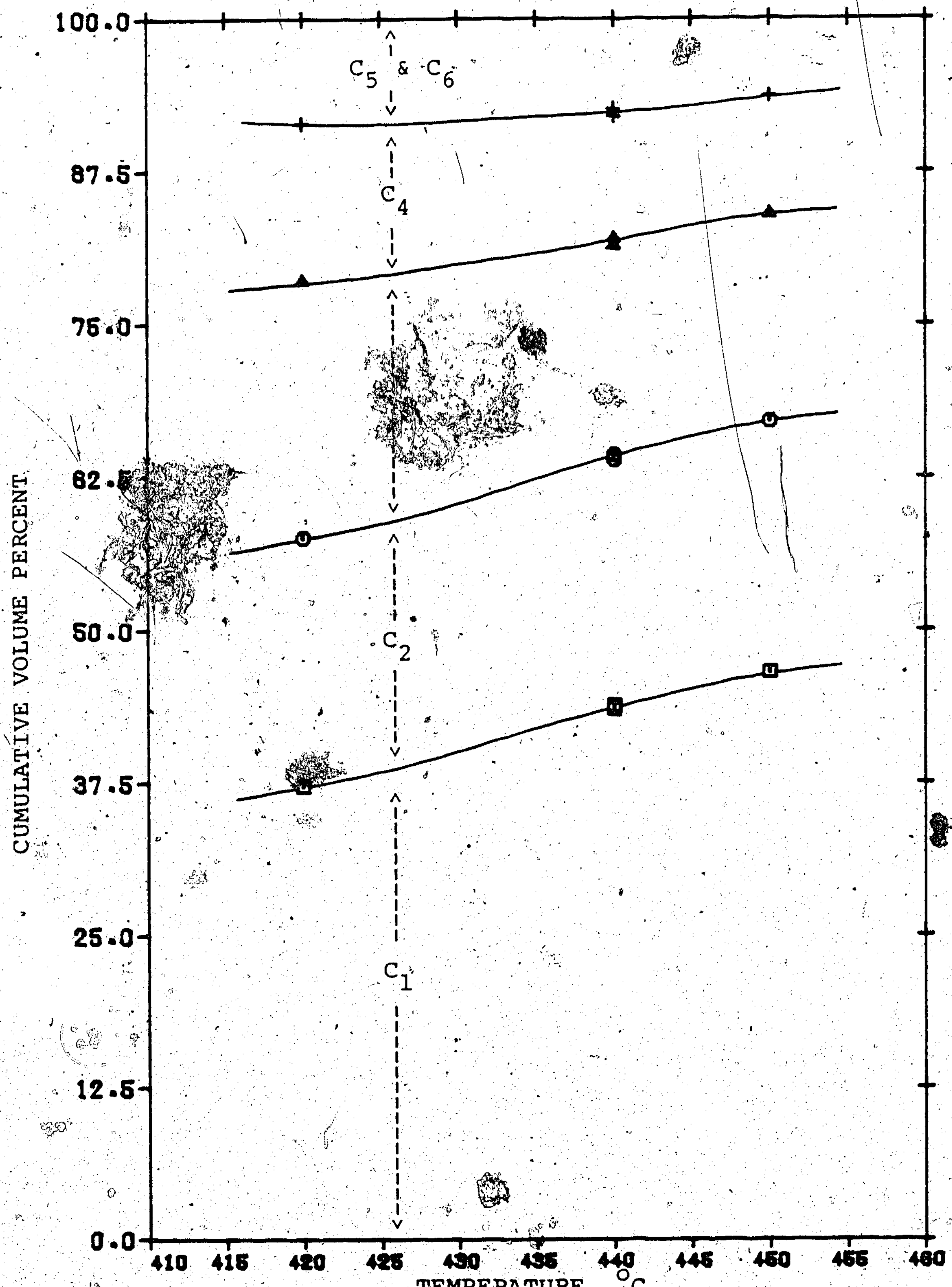


Figure IX.31 Effect of Temperature on Gas Product Distribution, Athabasca Virgin Gas Oil

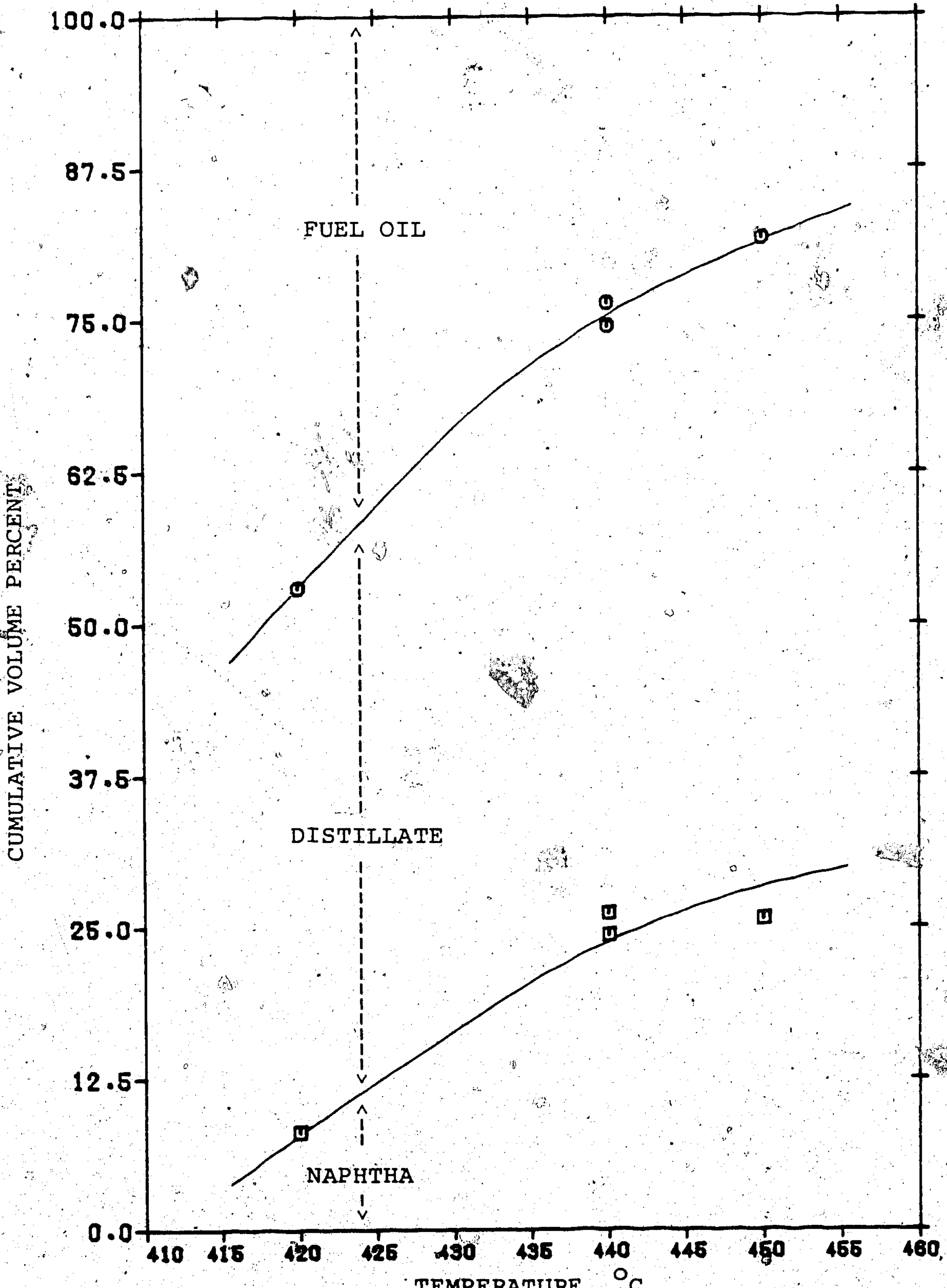


Figure IX.32 Effect of Temperature on Liquid Product Distribution, Cold Lake Gas Oil

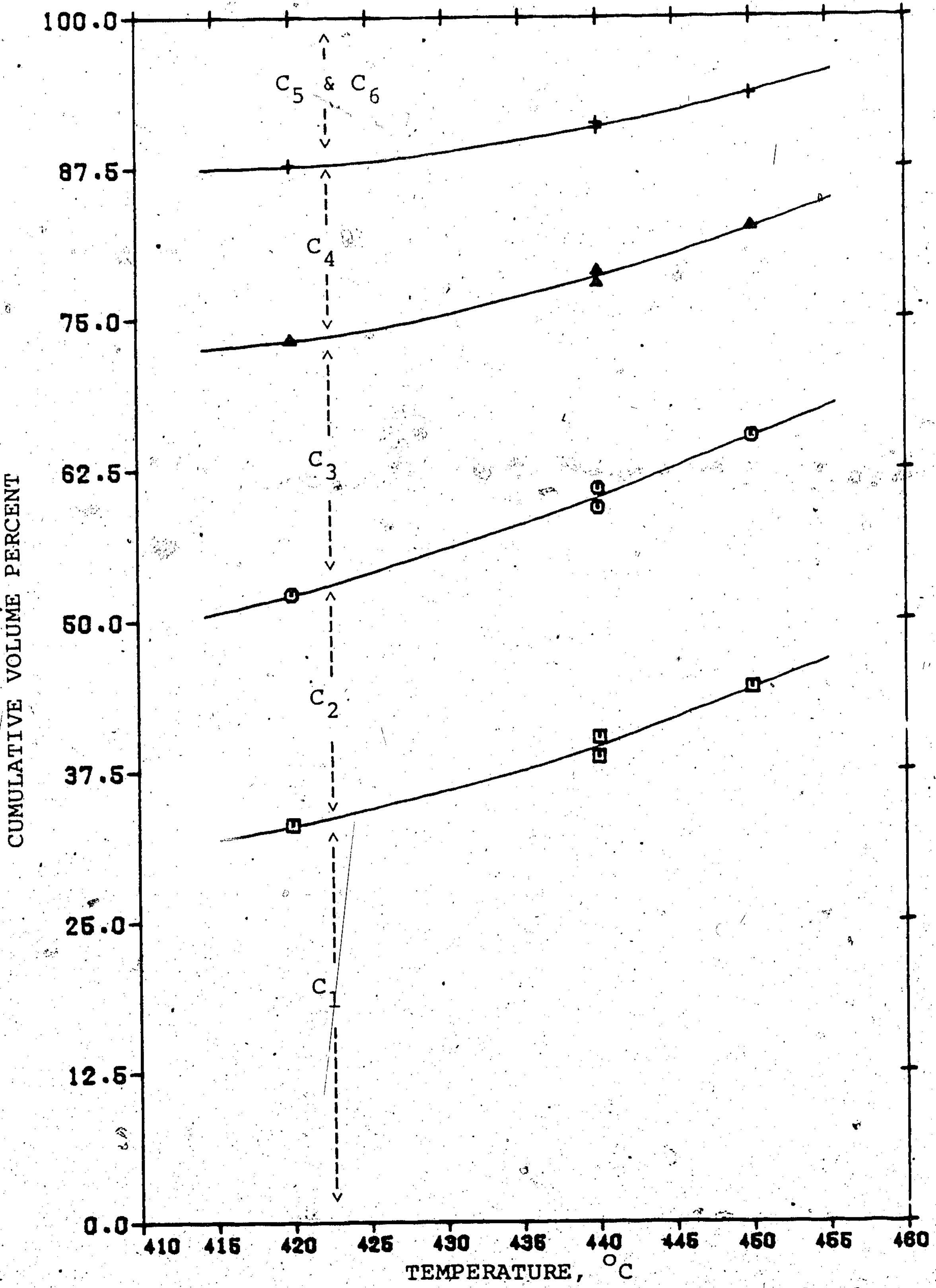


Figure IX.33 Effect of Temperature on Gas Product Distribution, Cold Lake Gas Oil

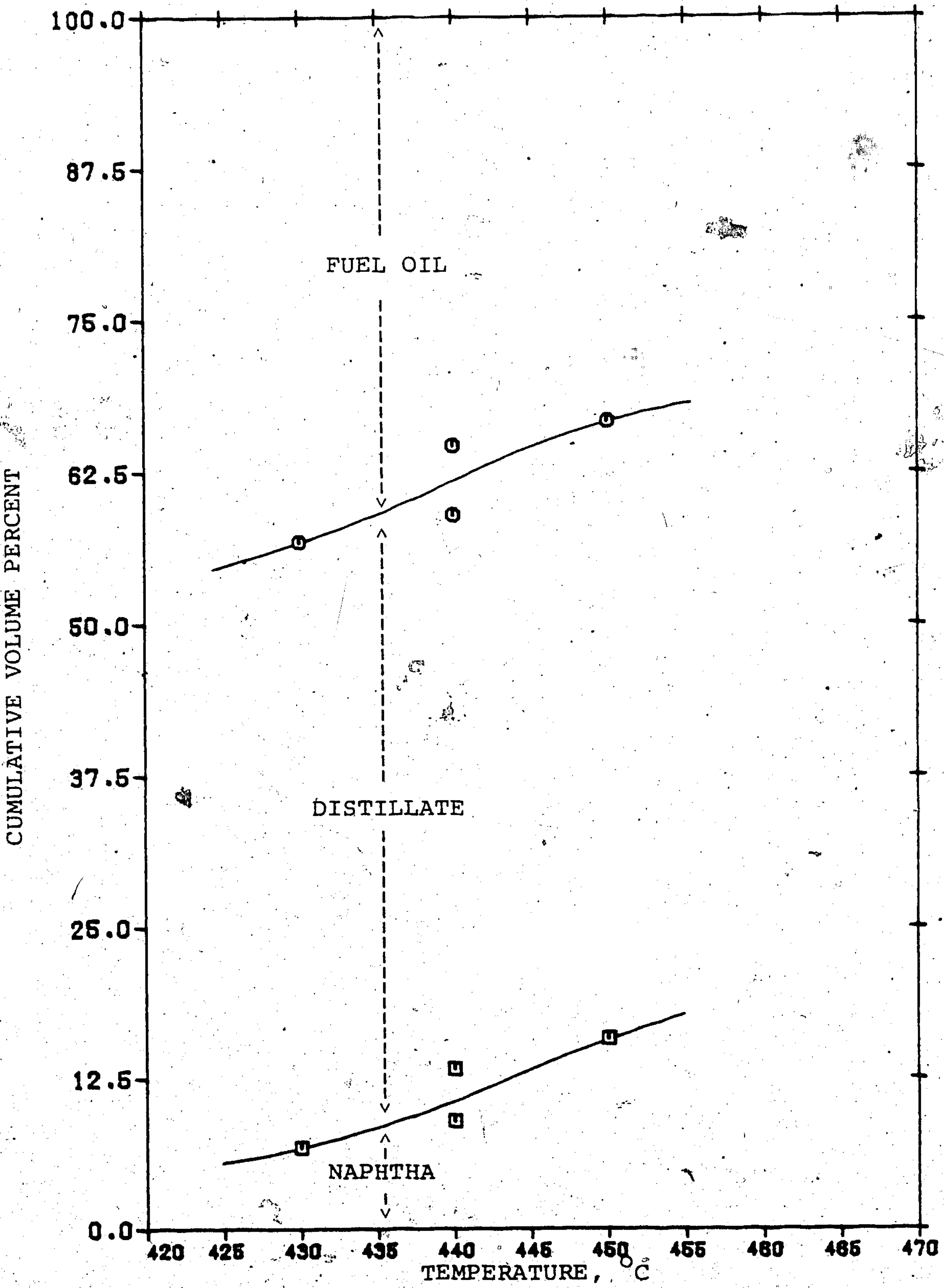


Figure IX.34 Effect of Temperature on Liquid Product Distribution, CANMET Vacuum Gas Oil

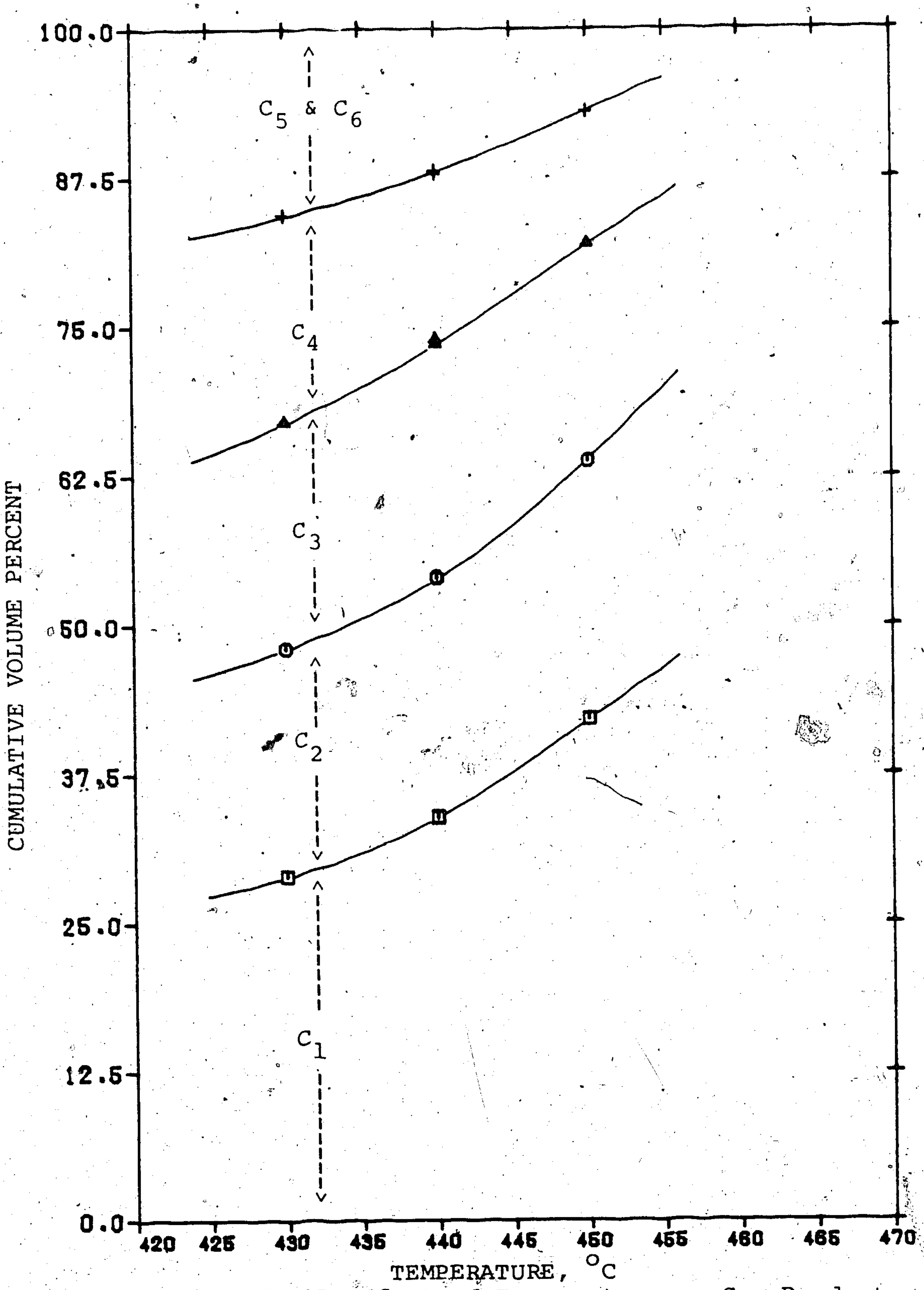


Figure IX.35 Effect of Temperature on Gas Product Distribution, CANMET Vacuum Gas Oil

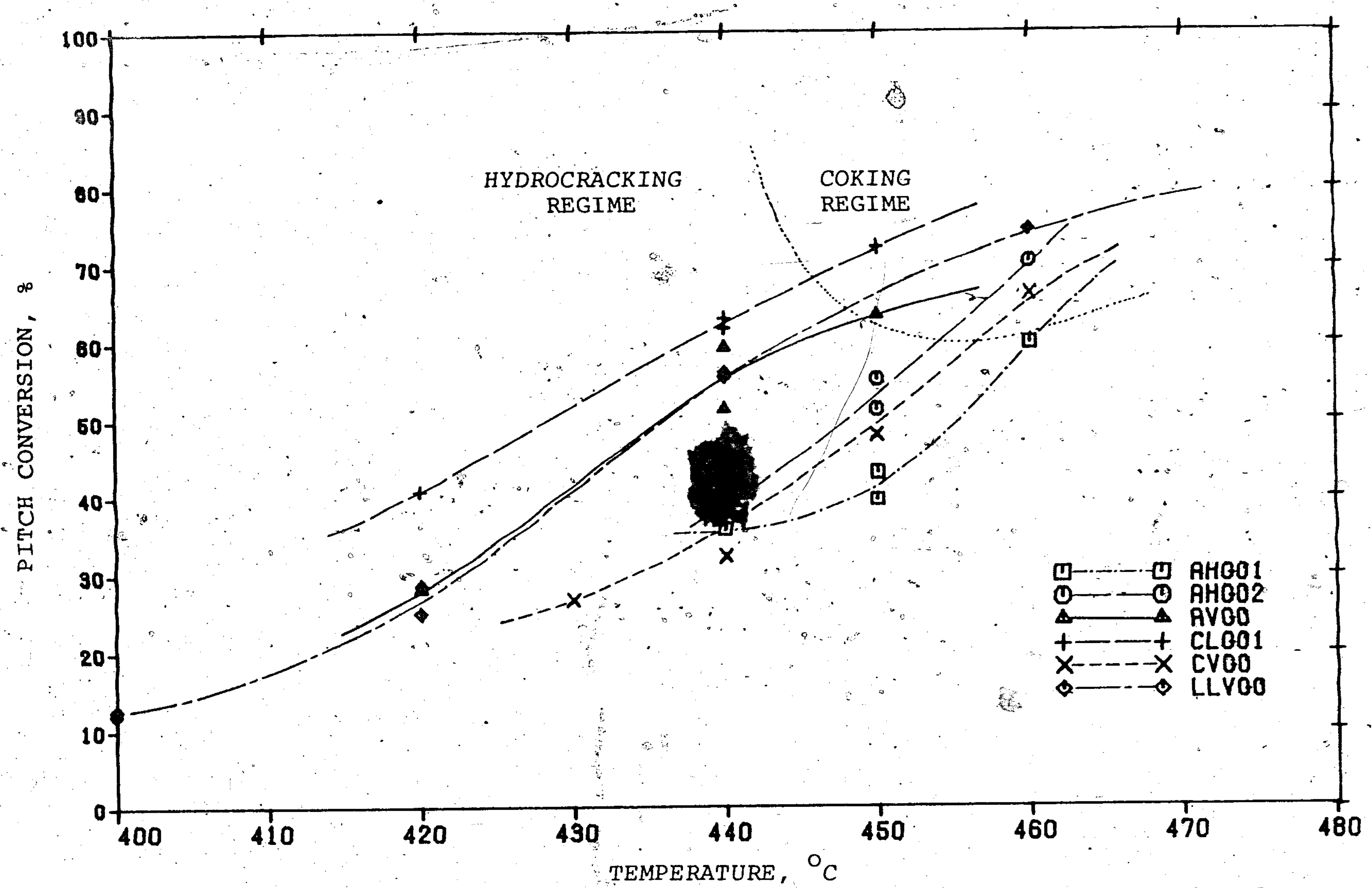


Figure IX.36 Effect of Temperature on Pitch Conversion and Coke Formation for various Heavy Gas Oils at 13.9 MPa, Nom.LHSV = 1.00

Hydrogen Solubility and Consumption Results

Hydrogen concentration results obtained from reactor liquid phase sampling for the five gas oils are presented as a plot of the apparent Henry Law constant versus the inverse of temperature in Figure IX.37. The plot shows that the concentration of hydrogen in the reactor liquid decreases with increasing temperatures. Since hydrogen solubility in the reactor liquid should increase with temperature, this observed trend strongly suggests that the reactor liquid phase is not saturated with hydrogen and that the rate of reaction is influenced by the rate of transfer of hydrogen from the gas phase to the liquid phase in the reactor. As the temperature is increased, the reaction rate becomes increasingly more rapid than the transfer rate of hydrogen to the liquid phase. Hence a diffusion controlled situation may exist.

Hydrogen consumption results were also obtained for the thermal hydroprocessing of the gas oils. Figure IX.38 presents the data as hydrogen consumption (m^3API H_2 consumed per m^3 Oil) versus temperature at a nominal LHSV of 1.0 h^{-1}. It can be observed that hydrogen consumption increases strongly with reaction temperature. At the temperatures studied, hydrogen consumption ranges from 10 to 70 m^3API/m^3Oil or 56 to 393 scf/bbl.

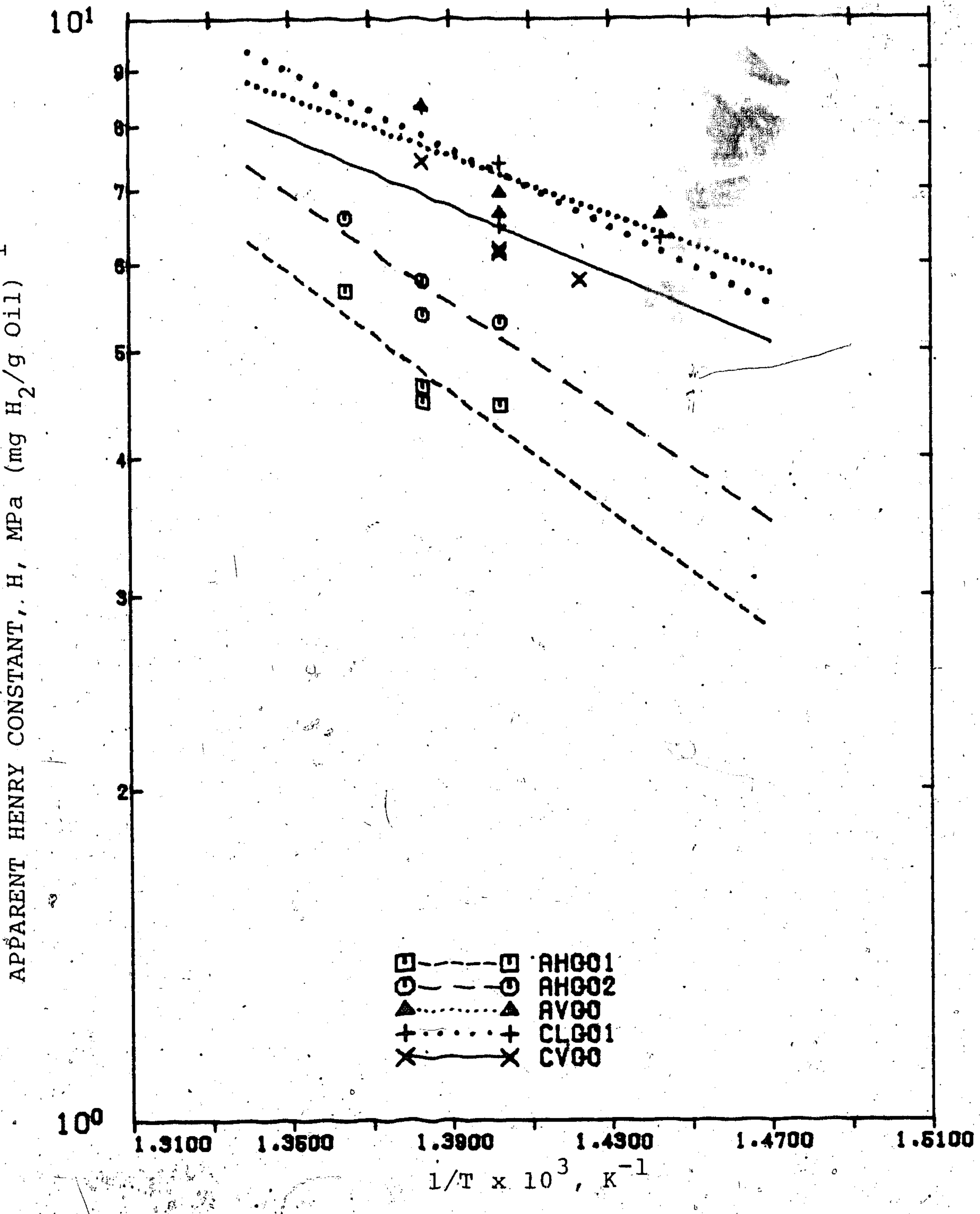


Figure IX.37 Hydrogen Concentration Results for various Heavy Gas Oils
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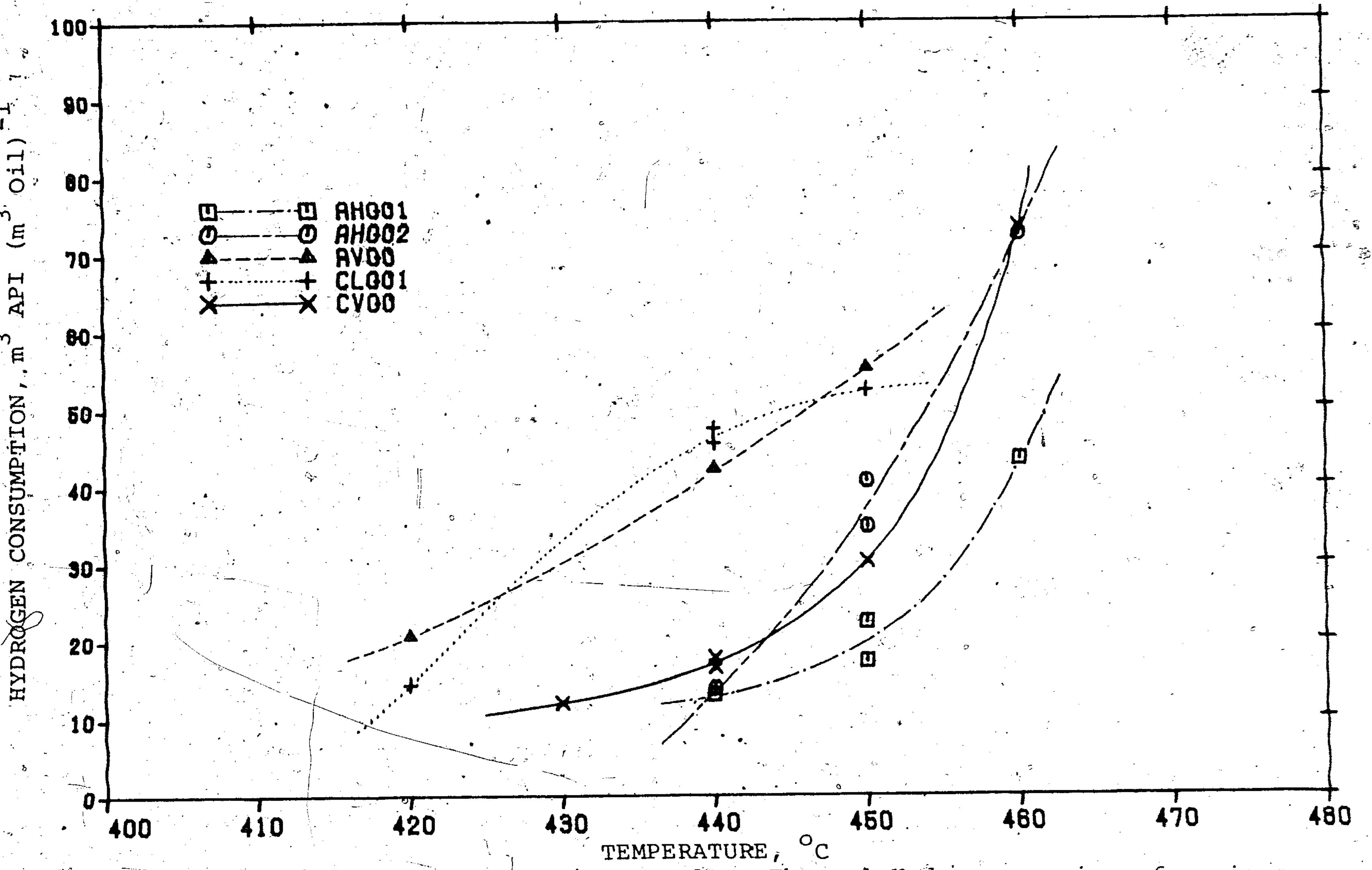

Figure IX.38 Hydrogen Consumption Results, Thermal Hydroprocessing of various Heavy Gas Oils

Kinetic Analysis Results

The rate data obtained from the runs with the five gas oils were correlated based on the two models developed in earlier work with LLVGO. A table listing the kinetic equations for each feedstock is summarized in Table IX.5. The rate data for all these feedstocks also tend to fit Model 1 or the pseudo-first order kinetic equation better.

Table IX.5 Kinetic Equations fitted to Thermal Hydrocracking Rate Data for different Heavy Gas Oils

FEEDSTOCK	MODEL 1	MODEL 2
AHGO1	$-r_p = 2.1572 \times 10^5 \exp(-\frac{101.1}{RT})\ C_{RL}$	$-r_p = 1.4015 \times 10^9 \exp(-\frac{111.7}{RT})\ C_{RL}\ C_H$
AHGO2	$-r_p = 2.0019 \times 10^5 \exp(-\frac{99.2}{RT})\ C_{RL}$	$-r_p = 8.3026 \times 10^{11} \exp(-\frac{147.5}{RT})\ C_{RL}\ C_H$
AVGO	$-r_p = 2.1353 \times 10^9 \exp(-\frac{152.2}{RT})\ C_{RL}$	$-r_p = 5.6940 \times 10^{13} \exp(-\frac{168.9}{RT})\ C_{RL}\ C_H$
CLGO1	$-r_p = 1.2051 \times 10^6 \exp(-\frac{106.7}{RT})\ C_{RL}$	$-r_p = 8.1062 \times 10^9 \exp(-\frac{115.5}{RT})\ C_{RL}\ C_H$
CVGO	$-r_p = 7.8501 \times 10^7 \exp(-\frac{135.4}{RT})\ C_{RL}$	$-r_p = 7.1987 \times 10^{15} \exp(-\frac{200.8}{RT})\ C_{RL}\ C_H$

$-r_p$ in mol mL^{-1} min^{-1}, C_{RL} & C_H in mol mL^{-1}, R = 0.008314 kJ mol^{-1} K^{-1}, T in K

C. Tubular Reactor Results for LLVGO

Product Distributions and Coking

The trends observed in the product distributions for the tubular reactor are similar to those observed in hydroprocessing with the stirred reactor. Plots of the effect of temperature on both liquid product distribution and gas product distribution are given in Figures IX.39 and IX.40. The effect of actual LHSV at 440 °C on liquid product and gas product distributions are given in Figures IX.41 and IX.42. These plots also show that additional lighter liquids and hydrocarbon gases were formed with increased temperature and average liquid residence time.

The formation of coke in significant amounts was observed to occur apparently under less severe conditions in the tubular reactor than in the stirred reactor. Higher pitch conversions were encountered in the tubular reactor compared to the stirred reactor at the same temperature and nominal LHSV due to the larger average liquid residence time in the tubular reactor. As the liquid phase moves up the tubular reactor, conversion to vapour phase occurs continuously resulting in the gradual decrease of the liquid holdup. Liquid holdup in the tubular reactor is a function of conversion along the axial direction of the reactor. There is no concentration gradients in the radial direction if complete radial backmixing prevails in the reactor.

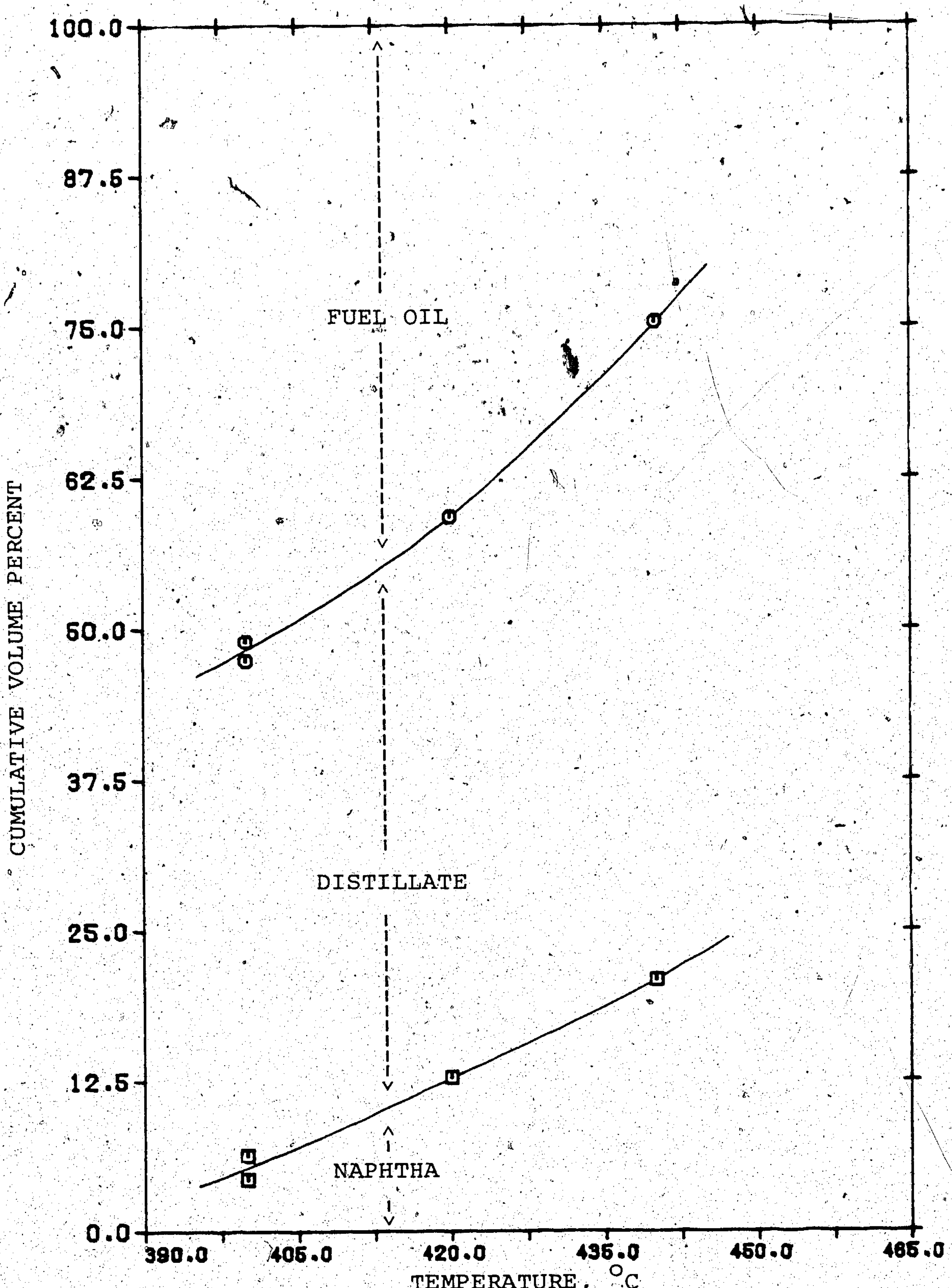

Figure IX.39 Effect of Temperature on Liquid Product Distribution in the Tubular Reactor at Nom.LHSV = 1.0

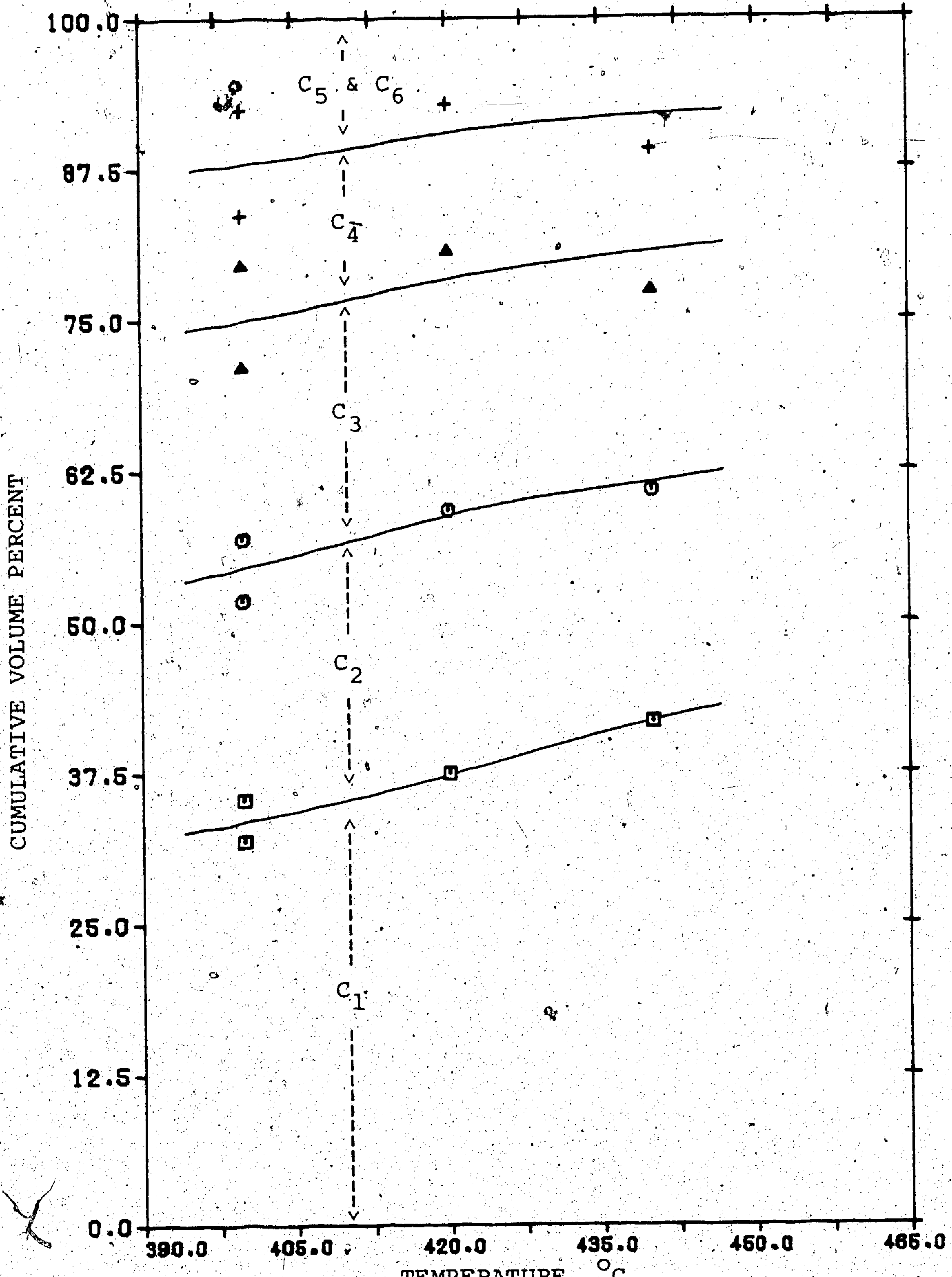

Figure IX.40 Effect of Temperature on Gas Product Distribution in the Tubular Reactor at Nom.LHSV = 1.0

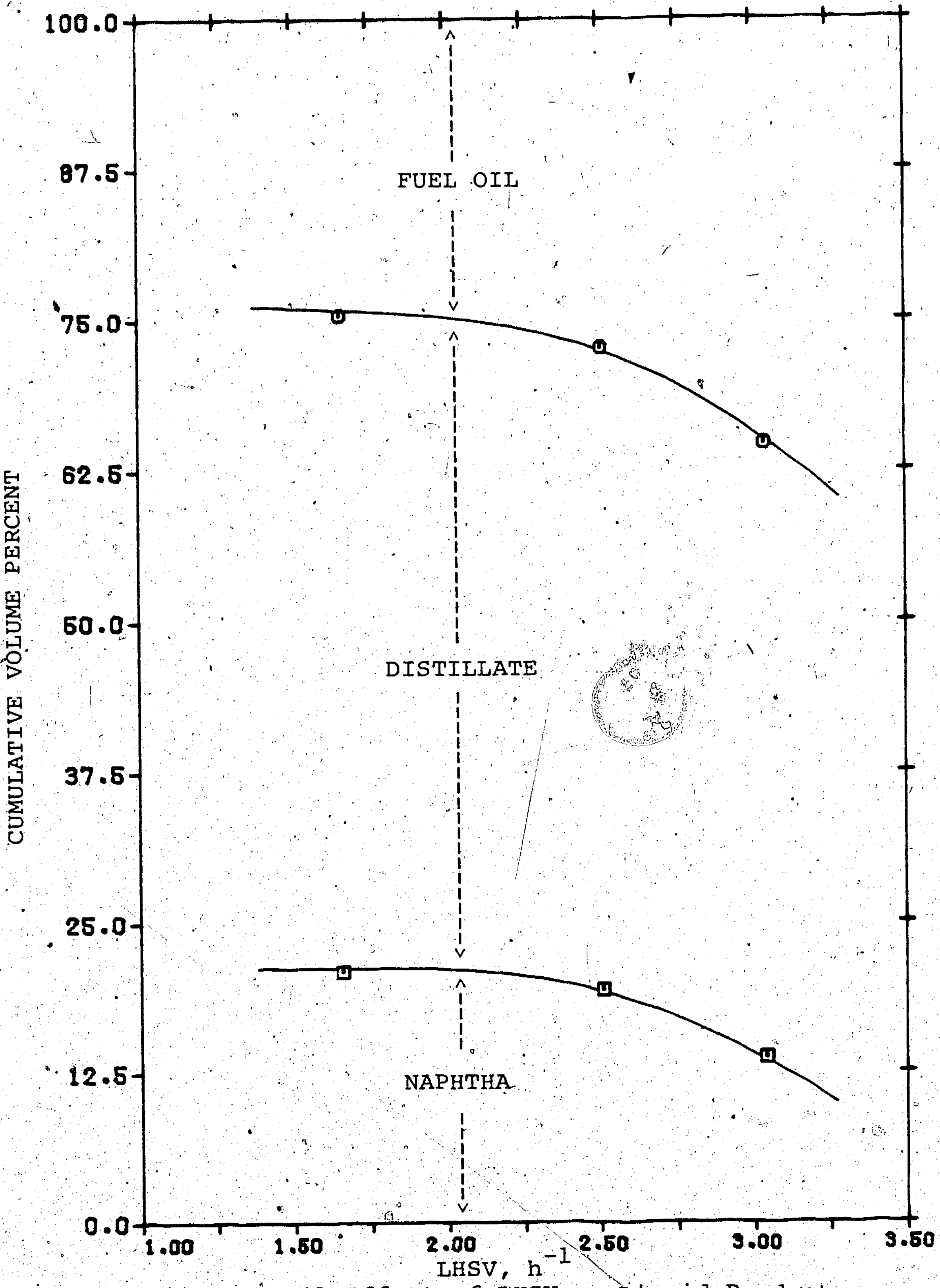

Figure IX.41 Effect of LHSV on Liquid Product Distribution in the Tubular Reactor at 440 C

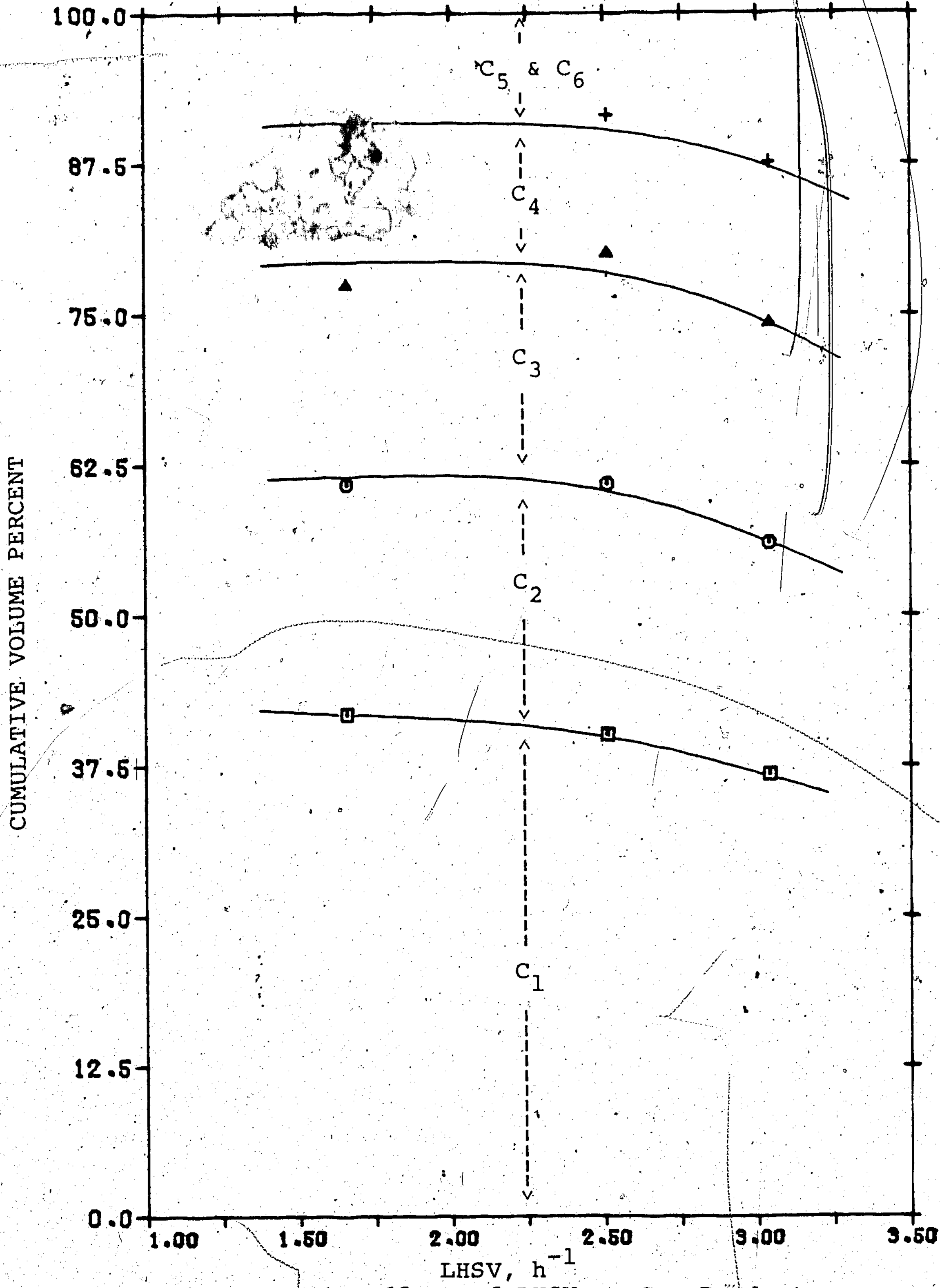

Figure IX.42 Effect of LHSV on Gas Product Distribution in the Tubular Reactor at 440 C

Performance of the Tubular Reactor

Influence of Temperature upon Observed and Predicted Pitch Conversions

Figure IX.43 shows the effect of temperature upon pitch conversion in the tubular reactor at a nominal LHSV of 1.0 h^{-1}. A model based on assuming plug flow of the liquid phase in the reactor was developed to model the rate of pitch conversion in the tubular reactor. A equation derived to obtain an estimate of pitch conversion in the tubular reactor, based on the pseudo-first order kinetic equation developed from CSTR run data, is presented in Table IX.6.

A term was incorporated into the equation to account for the decreasing volumetric flowrate of the liquid phase in the reactor due to conversion to vapour phase as the liquid proceeds up the reactor. An average value of the term (ψ) was estimated from CSTR data and assumed to be constant at each temperature level. The derivations for equation (9.5) and sample calculations are given in Appendix D.

From Figure IX.43, it can be seen that the predicted pitch conversions are lower than measured values at 400 and 420°C. At 440°C, the predicted value is slightly higher than the measured value. These discrepancies could be due to errors arising from an incorrect estimate of the term ψ which is a function of

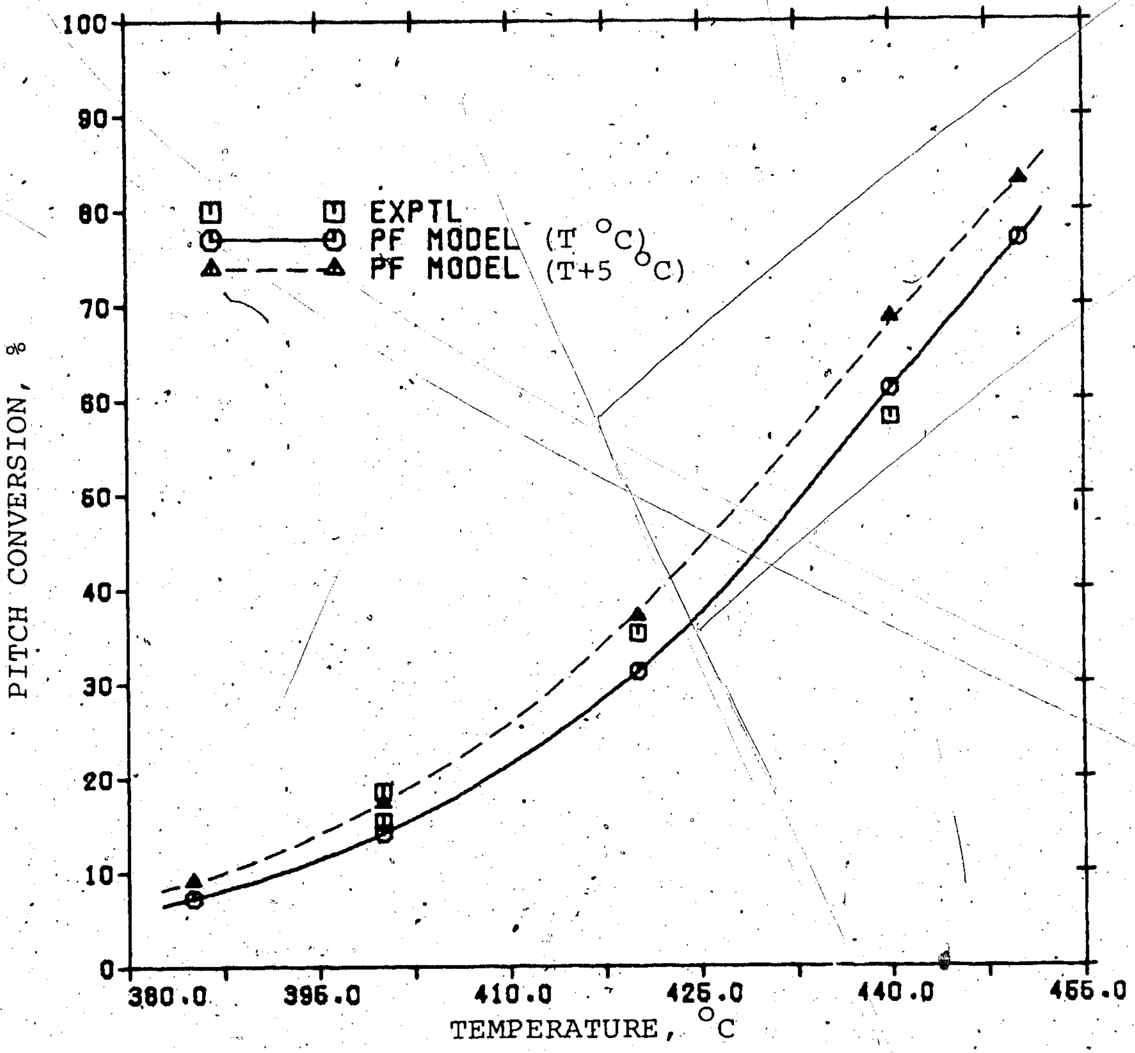

Figure IX.43 Effect of Temperature on Pitch Conversion in the Tubular Reactor, Nom.LHSV = 1.0

Table IX.6 Equation Used to Predict Pitch Conversion in the Tubular Reactor based on the Plug Flow Model and First Order Kinetics

$$X_p = 1 - \exp\left[\frac{k_1\ (\mathrm{LHSV}^{-1})}{(\psi_{av} - 1)}\right] \tag{9.5}$$

where,

k_1 = reaction rate constant based on first order kinetic equation, h^{-1}

ψ_{av} = term used to account for decreasing volumetric flowrate of liquid phase along the axial direction of the tubular reactor

X_p = fractional pitch conversion

conversion. This method of estimation is necessary since the liquid phase in the tubular reactor was not sampled at reaction conditions.

The observed differences between measured and predicted conversions in Figure IX.43 could also be due to errors in the pseudo-first order kinetic equation used in the plug flow calculations. Errors in reactor temperature measurements arising from a slight radial temperature gradient (5-10°C) in the liquid phase could also cause these observed differences. The wall temperature could be 5 - 10°C higher than the bulk liquid temperature. Tubular reactor run data showed a maximum difference of 4°C between the outside wall and bulk liquid temperatures. As shown in Figure IX.43, an error in the reactor temperature measurements of 5°C, a corresponding error in the kinetic equation or a combination of both could shift the predicted curve by a significant amount.

Influence of LHSV upon Observed and Predicted Pitch Conversions

The effect of LHSV on pitch conversion at 440 °C in the tubular reactor is given in Figure IX.44. Both the measured conversions and plug flow model predicted conversions are shown. Pitch conversions at 440°C predicted based on the CSTR model are also shown on the same plot. It can be seen that there is some

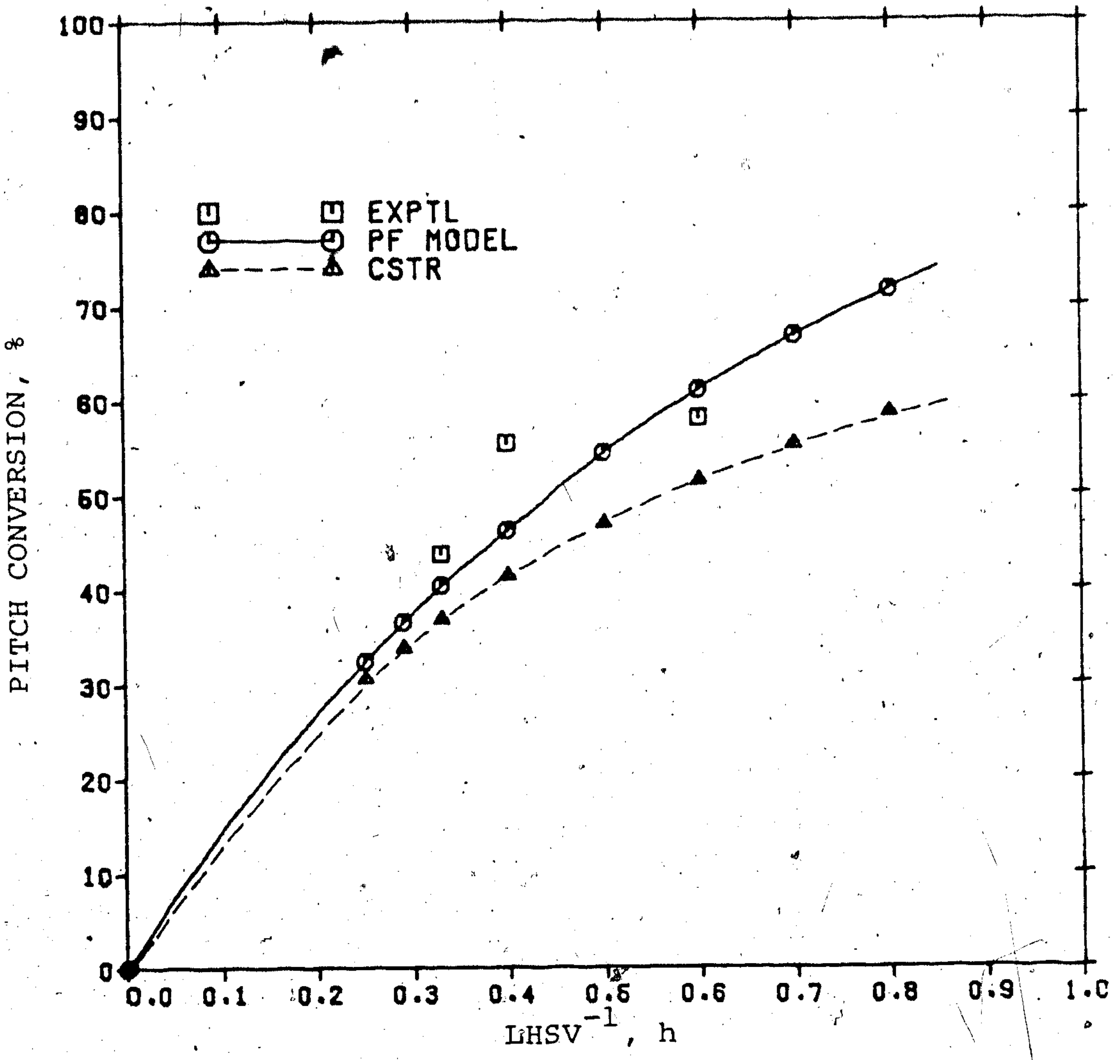

Figure IX.44 Effect of LHSV on Pitch Conversion in the Tubular Reactor at 440 C discrepancies between the predicted and the measured pitch conversions for the tubular reactor. These differences can again be attributed to the possible errors in reactor temperature measurements and errors in the pseudo-first order kinetic equation used in the plug flow model calculations.

Influence of Temperature and LHSV on Sulphur Conversion

Sulphur conversion in the tubular reactor ranges from 8.1 to 25.3 percent for the three temperature levels (400°, 420° and 440°C) studied. The LHSV was maintained at a nominal value of 1.0 h^{-1}. Figure IX.45 shows a plot of sulphur conversion versus temperature in the tubular reactor. Sulphur conversion is observed to increase with temperature. The effect of LHSV on sulphur conversion is shown in Figure IX.46 at 440°C. Sulphur conversion varies from 18.0 to 25.3 percent for the range of LHSV studied and is observed to increase with increasing average liquid residence time. The plug flow model predicted conversions, based on the pseudo-first order kinetic equation for hydrodesulphurization, are presented on the plots as solid curves.

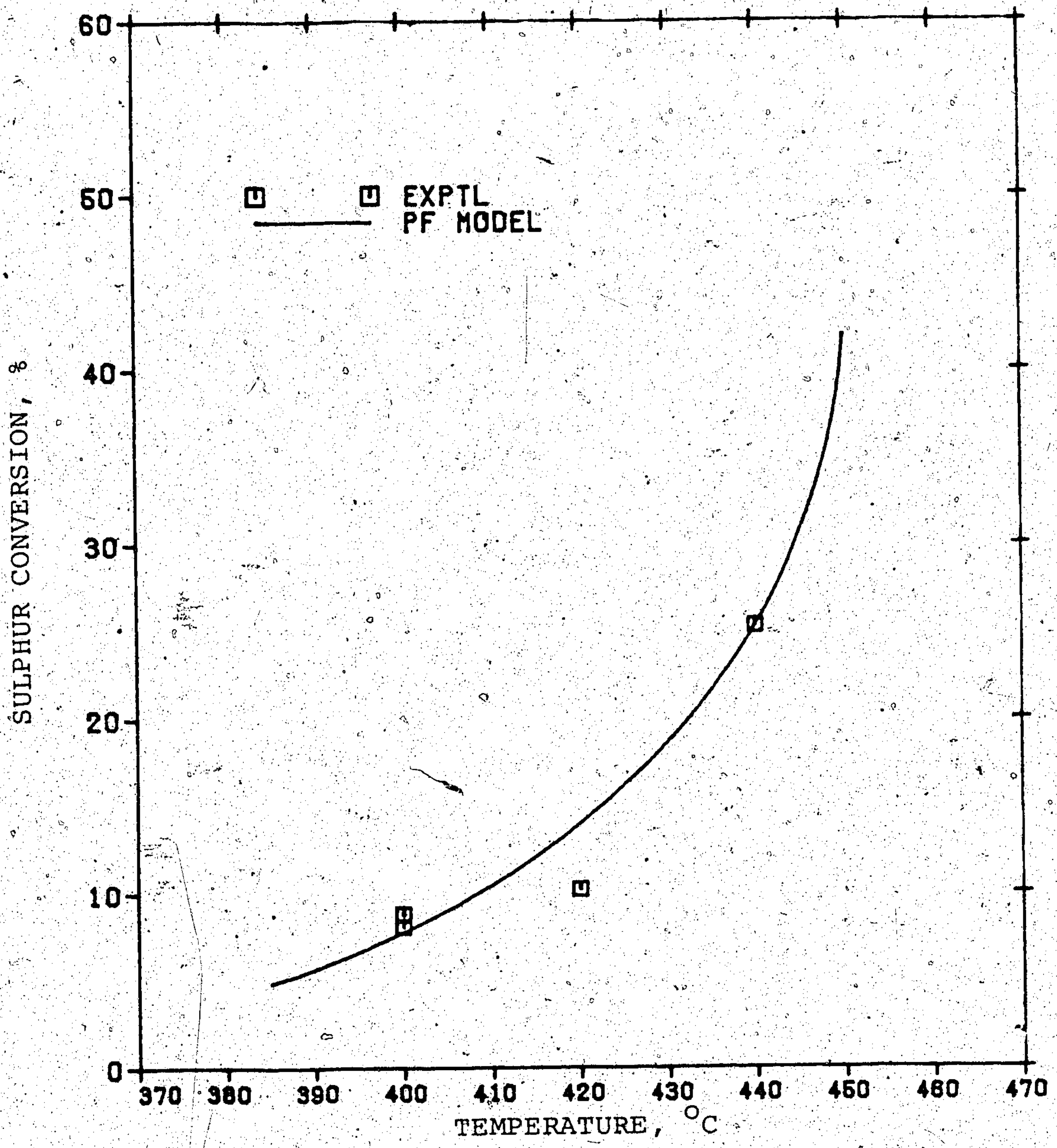

Figure IX.45 Effect of Temperature on Sulphur Conversion in the Tubular Reactor, Nom.LHSV = 1.0

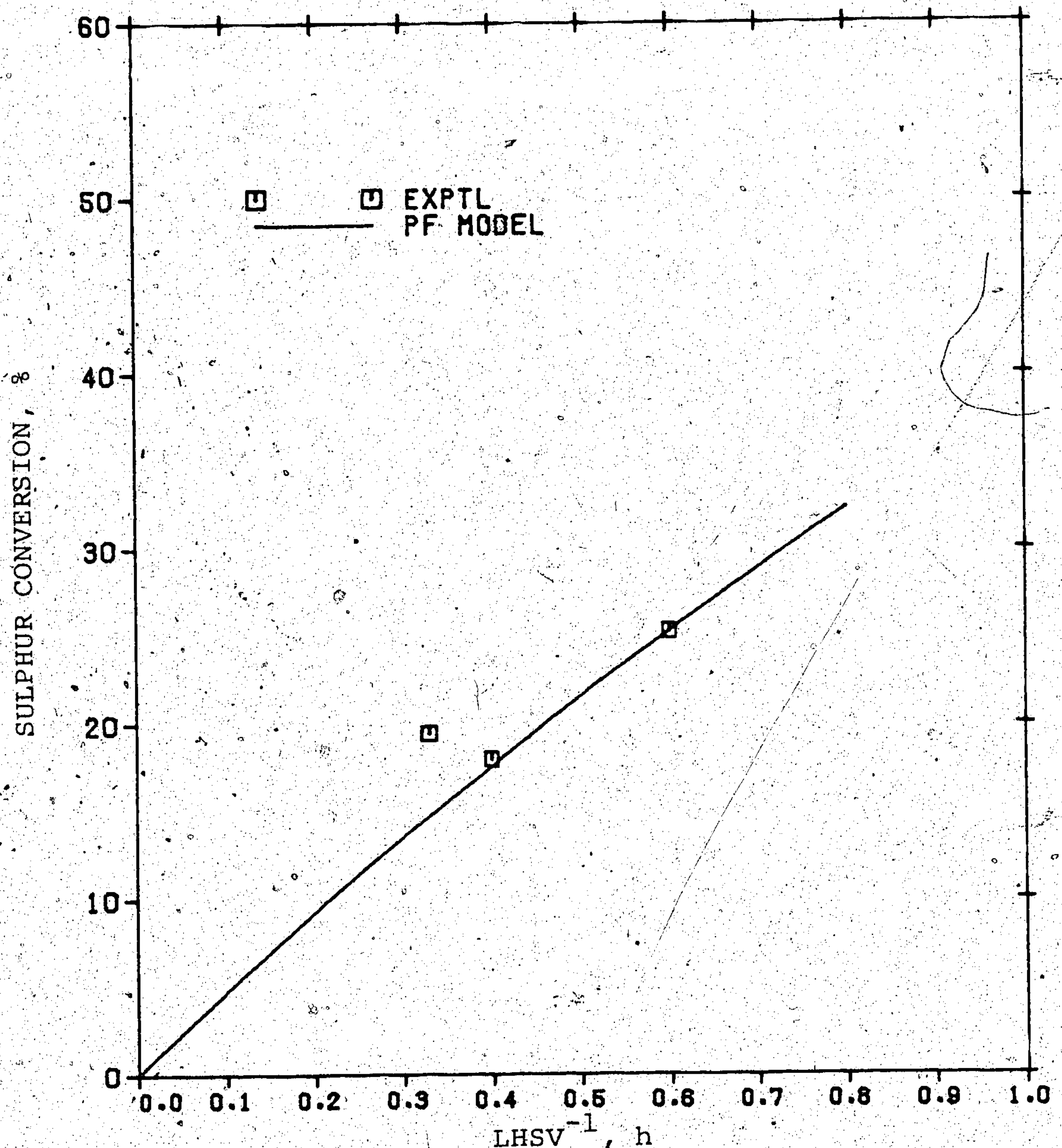

Figure IX.46 Effect of LHSV on Sulphur Conversion in the Tubular Reactor at 440 C

D. Catalytic Processing of CANMET Gas Oil

Product Distributions

The catalytic hydroprocessing of CANMET gas oil was studied at one level of nominal LHSV and at three levels of temperatures. The product distribution results (given in Table VII.9) show that the amounts of lighter fractions increase with increasing temperature. Figure IX.47 presents a plot of liquid product distribution versus temperature while Figure IX.48 presents a similar plot for the gas product distribution.

Effect of Temperature on Pitch Conversion

The effect of temperature on pitch conversion in the catalytic hydroprocessing of CANMET gas oil is presented in Figure IX.49. Pitch conversion approaches 95 percent at a temperature of about 440 °C. Additional runs and replicate runs should help define the shape of the curve in Figure IX.49 more clearly.

Effect of Temperature on Sulphur Conversion

In the catalytic hydroprocessing runs, hydrodesulphurization was almost complete at temperatures of 400°C and above. Over 90.0 percent of the sulphur compounds in the gas oil were converted at 400°C. At 420° and 440°C, sulphur conversion approaches 100 percent. Figure IX.50 shows the sulphur conversion results.

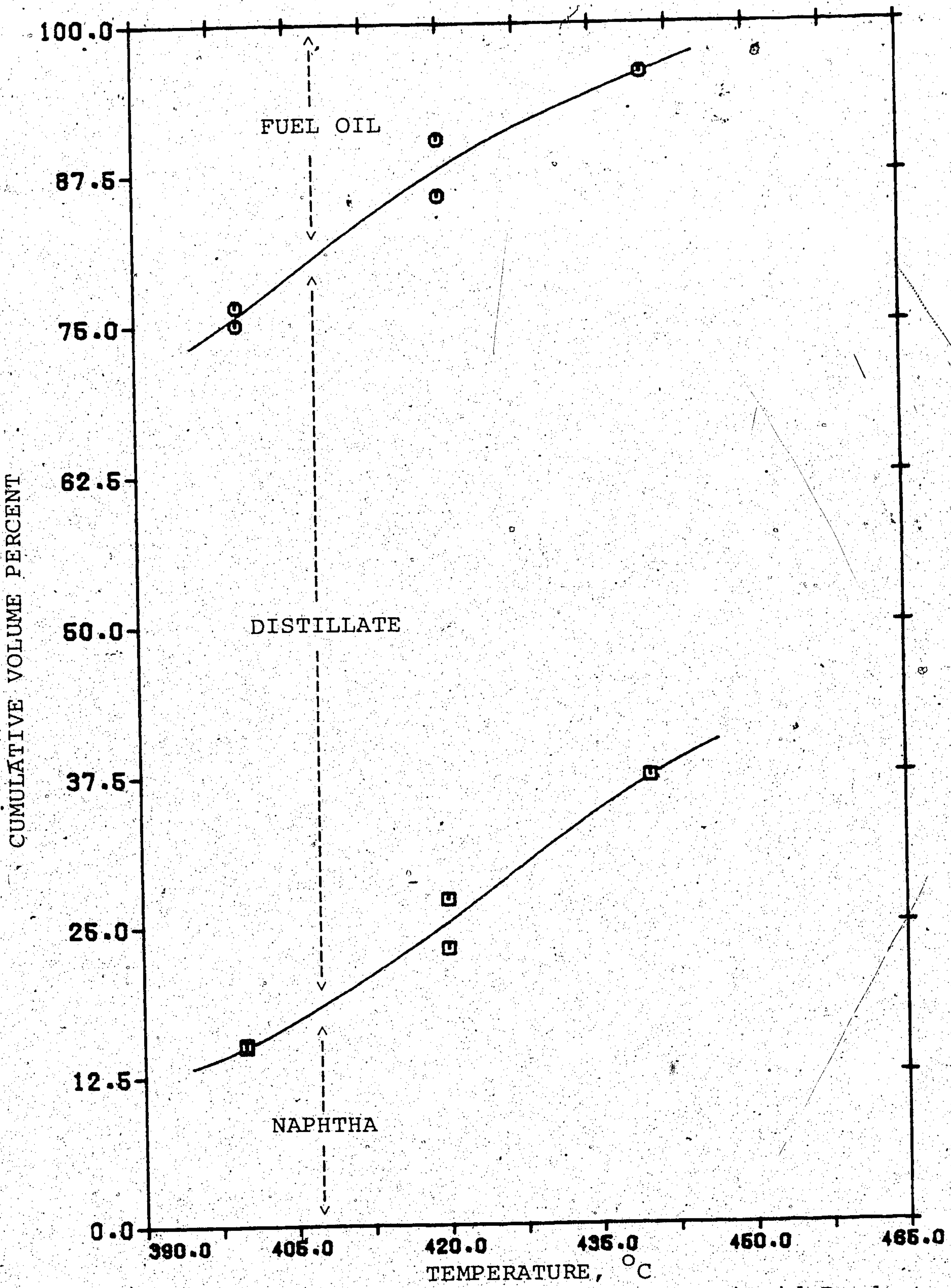

Figure IX.47 Effect of Temperature on Liquid Product Distribution, Nom.LHSV = 0.28, Catalytic Hydroprocessing of EMRGO

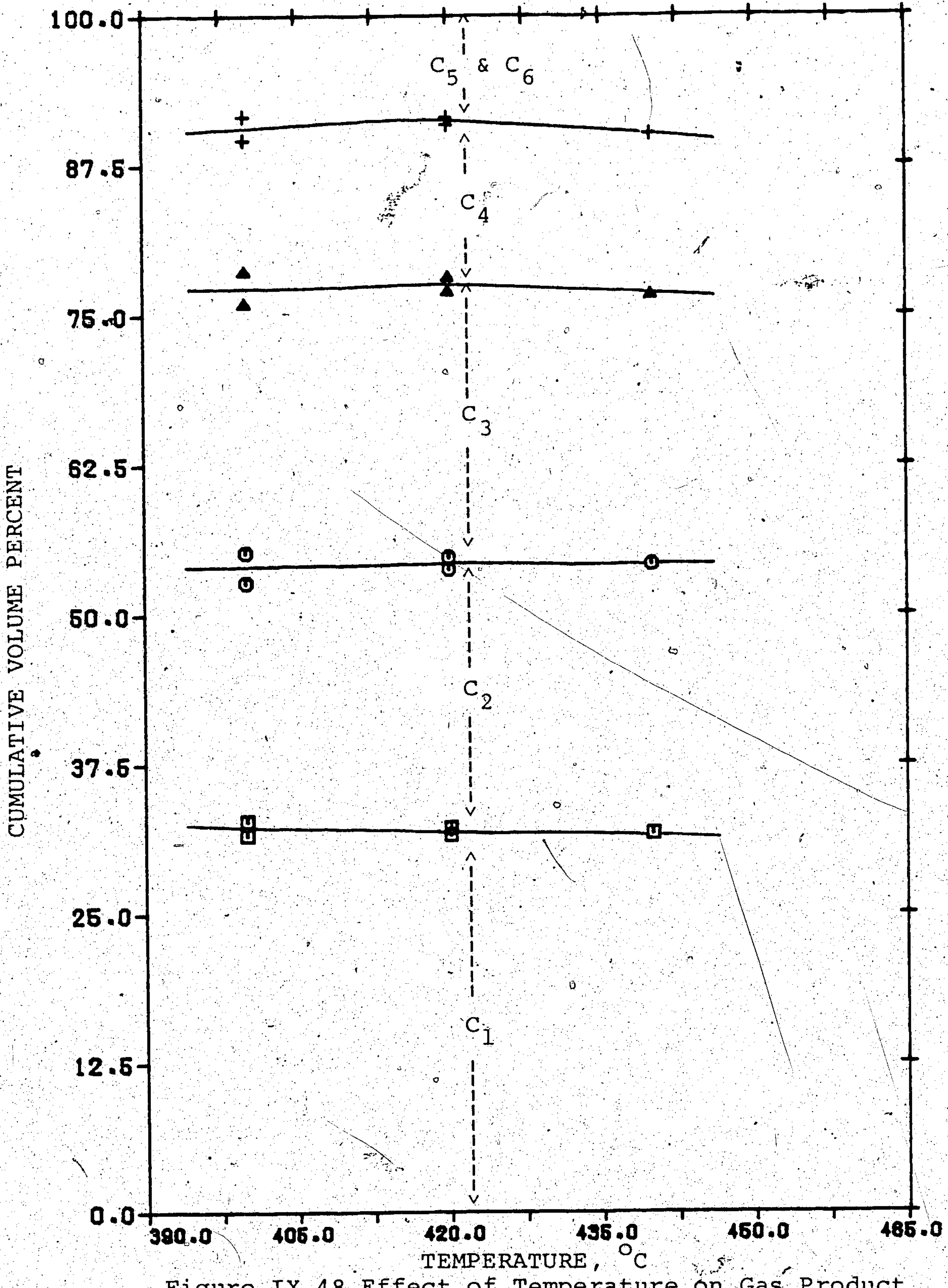

Figure IX.48 Effect of Temperature on Gas Product Distribution, Nom.LHSV = 0.28, Catalytic Hydroprocessing of EMRGO

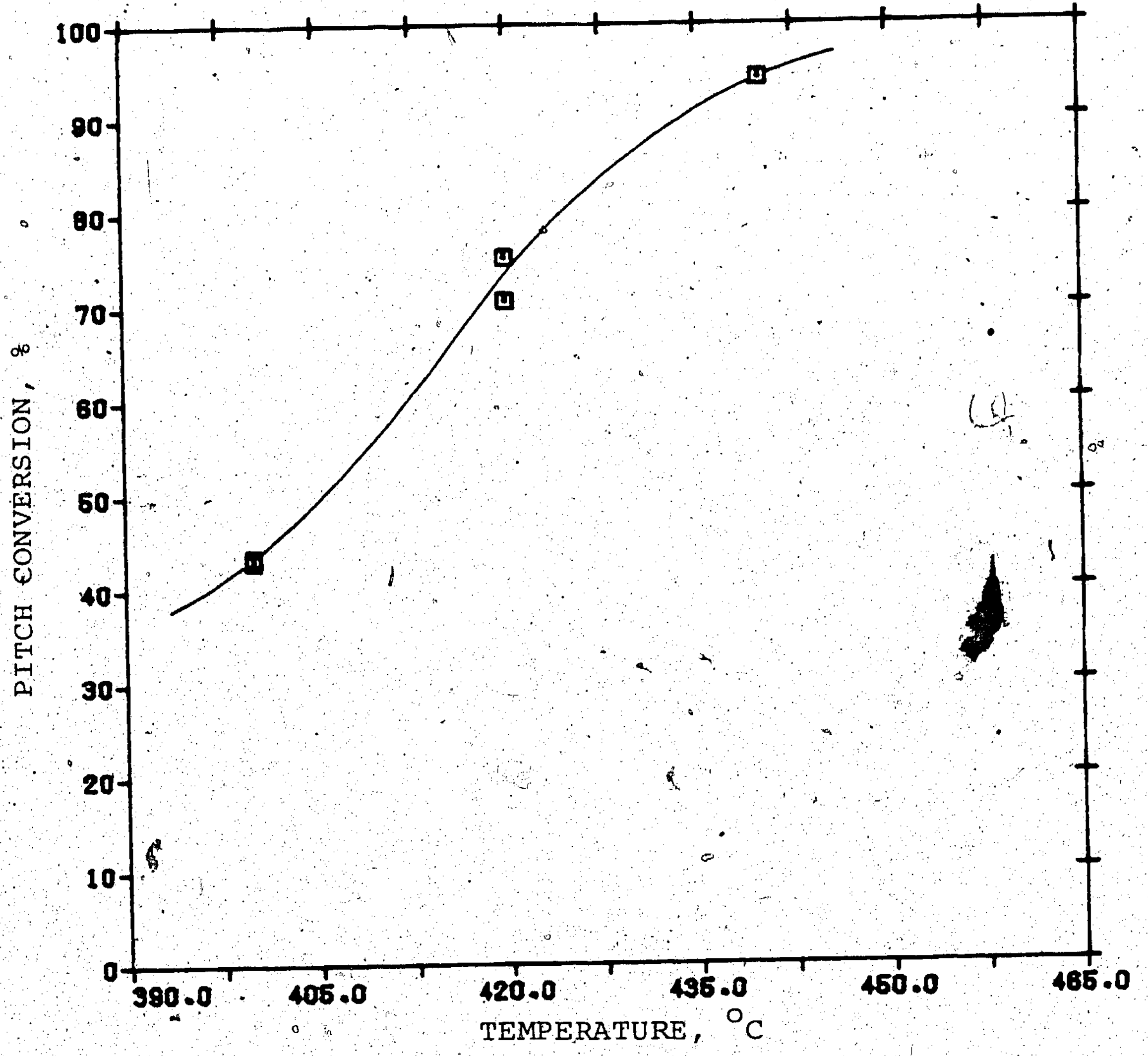

Figure IX.49 Effect of Temperature on Pitch Conversion, Nom.LHSV = 0.28, Catalytic Hydroprocessing of EMRGO

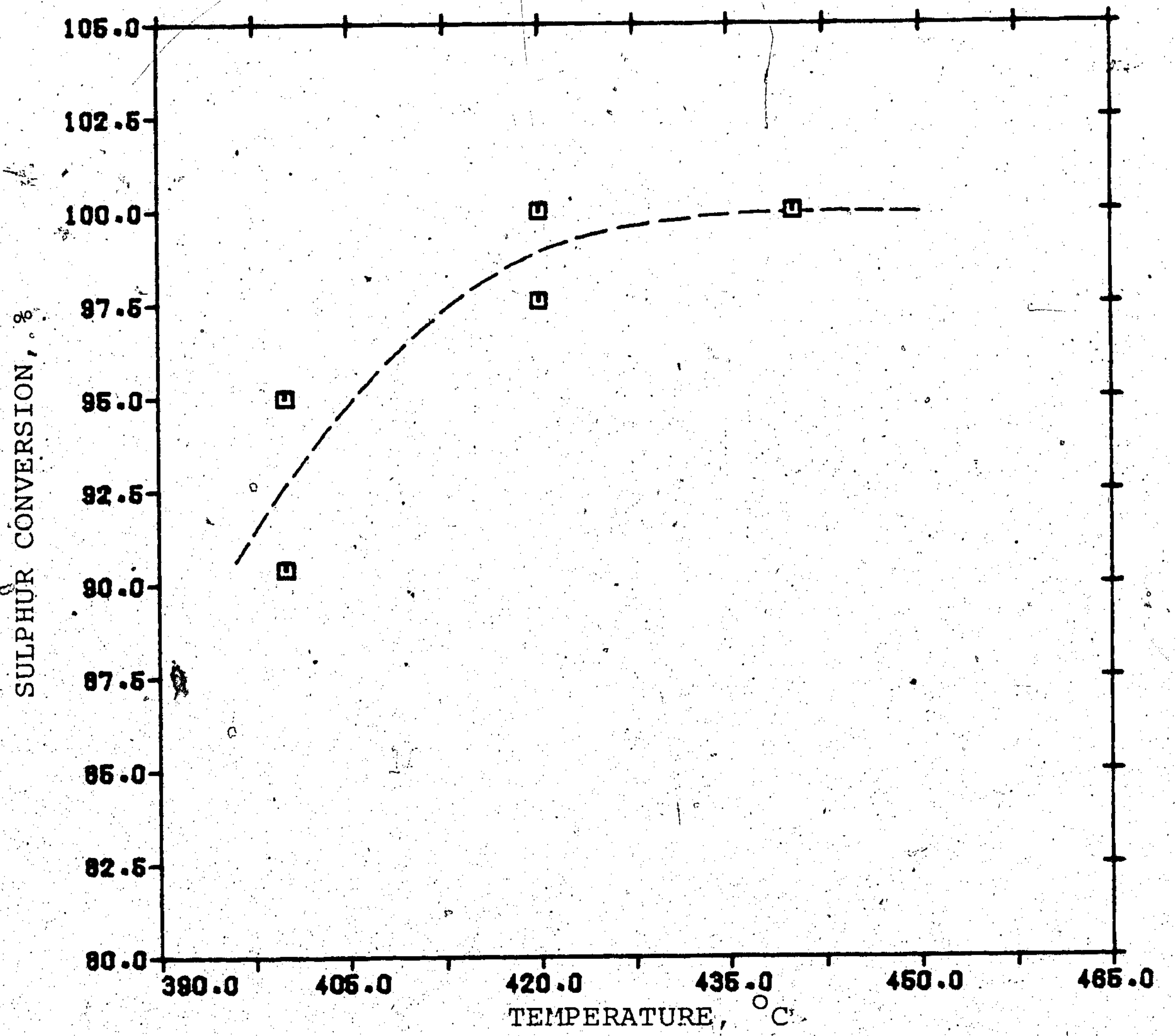

Figure IX.50 Effect of Temperature on Sulphur Conversion, Nom.LHSV = 0.28, Catalytic Hydroprocessing of EMRGO

Kinetic Analysis Results

Modelling the Kinetics of Pitch Conversion

Two models of the form used in the kinetic analysis of thermal hydroprocessing results were used in attempting to model the kinetics of pitch conversion via catalytic hydroprocessing. The catalyst loading used was taken into account in the rate of pitch conversion term. Model 1 relates the rate of pitch conversion to the concentration of pitch in the reactor liquid, while Model 2 relates the rate of pitch conversion to the concentrations of pitch and hydrogen in the reactor liquid.

The Arrhenius plots of the rate constants for both models are given in Figures IX.51 and IX.52. The activation energy estimated based on Model 1 is 154.2 kJ/mol while that estimated for Model 2 is 128.8 kJ/mol. Statistical tests were used to determine how well the experimental kinetic results fit the models. Based on a smaller sum of squares of residuals and coefficients of correlation and determination closer to unity suggests that Model 1 models the kinetics of catalytic pitch conversion better (as shown in Table IX.7).

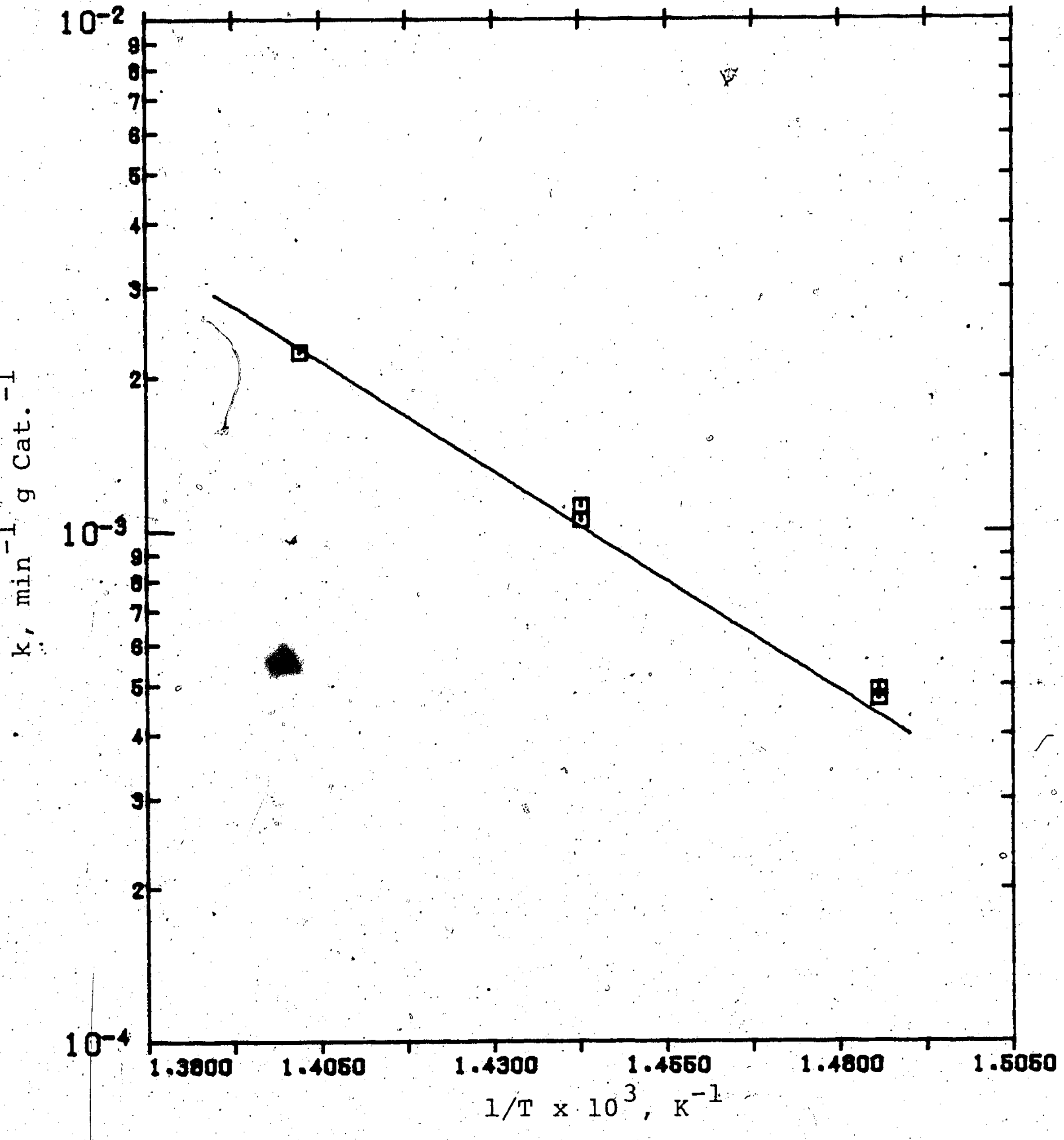

Figure IX.51 Arrhenius Plot of Pitch Conversion Rate Constants Based on Model 1, Catalytic Hydroprocessing of EMRGO

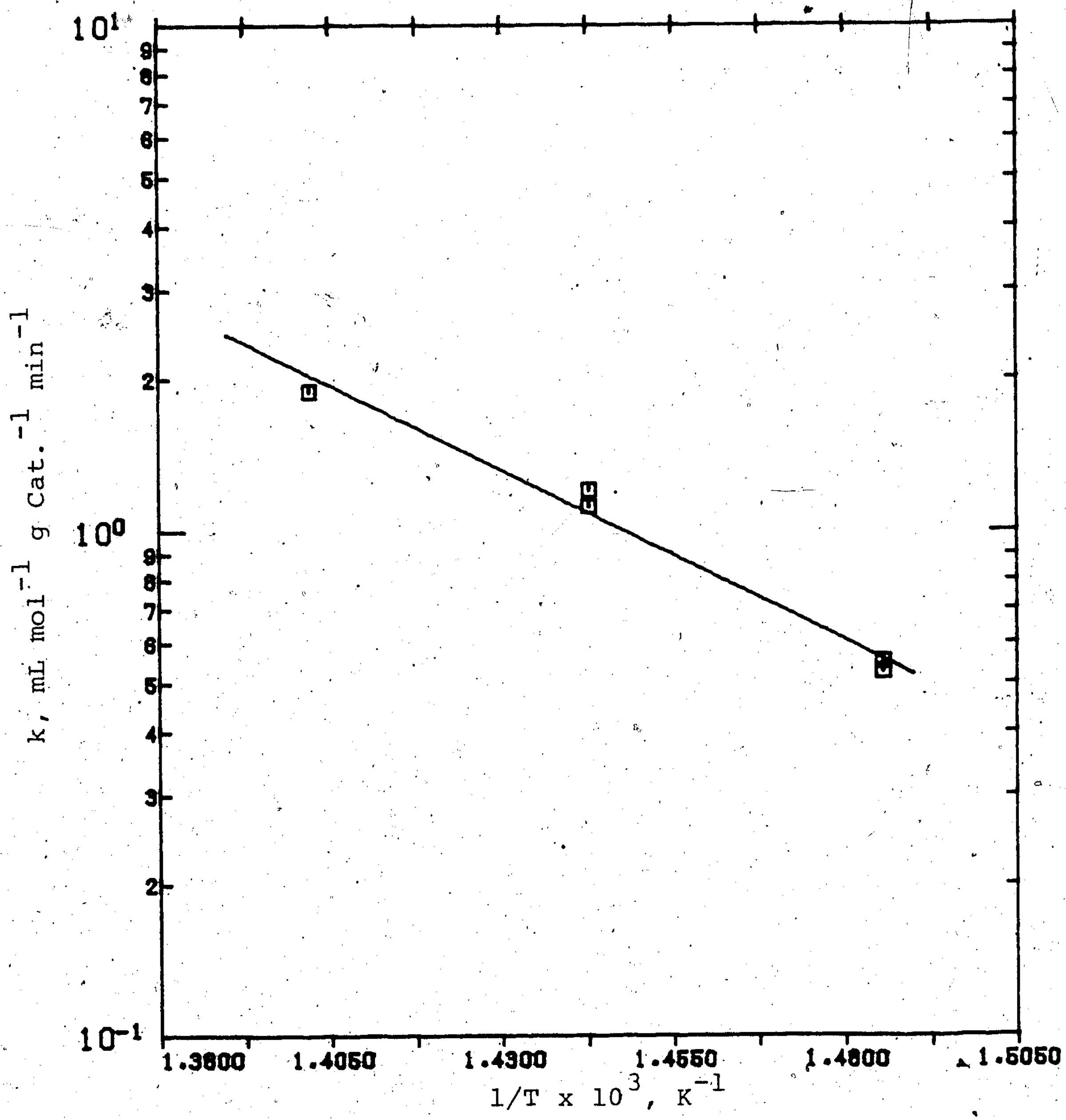

Figure IX.52 Arrhenius Plot of Pitch Conversion Rate Constants Based on Model 2, Catalytic Hydroprocessing of EMRGO

Table IX.7 Statistical Test Results for Kinetic Models Used to Correlate Pitch Conversion Rate Data in the Catalytic Hydroprocessing of EMRGO

Test Coefficient	Model 1 $-r_p = k\ C_{RL}$	Model 2 $-r_p = k\ C_{RL}, C_H$
Residual Sum of Squares	0.0033	0.0201
Coefficient of Determination	0.9980	0.9832
Correlation Coefficient	0.9990	0.9916

X. CONCLUSIONS

The study has demonstrated the usefulness of a mini-CSTR laboratory scale process unit supported by reliable analytical techniques in providing useful insights into the thermal hydroprocessing of heavy gas oils. Much useful information was obtained on the process performance in terms of the level of hydroconversion and hydrodesulphurization, product distributions, the effects of process variables and reaction kinetics. In addition, useful information was obtained on process conditions where coke formation is favoured for six different heavy gas oils. The concentration of reactive constituents in the CSTR liquid phase was measured by sampling the reactor contents at reaction conditions. These concentrations were used to correlate the rate data for the CSTR runs. This approach is superior to other approaches reported in the literature where rate data is simply correlated with compositions of the liquid and gaseous products sampled after pressure reduction and cooling.

Additional information on the performance and product distributions was also obtained on thermal hydroprocessing of Lloydminster vacuum gas oil in a tubular reactor. Difficulties associated with accurate representation of liquid holdup in the reactor were encountered. Preliminary studies on catalytic hydroprocessing in the stirred reactor (CSTR) also provided useful information on performance, product distributions and reaction kinetics for a CANMET gas oil derived from Athabasca bitumen (EMRGO).

Based on the results of the study, a number of relevant observations emerged. A brief summary is given.

1. Lloydminster vacuum gas oil can be thermally hydrocracked in a stirred reactor (CSTR) at 13.9 MPa and temperatures up to about 440°C. Pitch conversions of up to 65 - 70 percent can be attained at these conditions. At temperatures above 440°C, severe coke formation occurs.
2. Coking envelopes for the thermal hydroprocessing of various heavy gas oil feedstocks can be established using the CSTR approach. The boundary between the coking and hydrocracking regimes can be determined based on process variables and the corresponding level of pitch conversion.
3. In the thermal hydrocracking of Lloydminster vacuum gas oil, coke formation was more severe in the tubular reactor than in the CSTR at apparent similar reaction conditions. Higher pitch conversions was observed for tubular reactor runs compared to CSTR runs at the same temperature and nominal LHSV due to the higher average liquid residence time in the tubular reactor.
4. The CSTR approach to kinetic modelling, based on sampling and analysis of actual reactor contents at operating conditions, is the correct approach. The use

of the composition of liquid product sampled after pressure reduction and cooling will lead to erroneous kinetic analysis.

5. Based on experimental rate data from CSTR runs with Lloydminster vacuum gas oil, a kinetic analysis showed that a pseudo-first order kinetic equation relating the rate of pitch conversion to the pitch concentration in the reactor liquid phase fits the data quite well.

6. A CSTR model based on the rate equations derived from Lloydminster vacuum gas oil run data was developed. The model predicted pitch conversion levels in the CSTR quite well. In the analysis, it was found that the ratio of the liquid feedrate to the liquid product rate evaluated at reaction conditions and used in the model, is increasingly greater than unity at the higher temperatures. Taking this ratio to be unity at 440°C will yield large errors in the predicted pitch conversion.

7. Blending Lloydminster vacuum gas oil with other lighter feedstocks allow for thermal processing at higher temperatures with minimal coke formation. There is some indication that coke formation tendency is related to pitch content in the feedstock.

8. The hydrogen concentration results obtained from the thermal hydrocracking of various heavy gas oils were observed to decrease with increasing temperatures. This suggests that the reactor liquid phase is not saturated

with hydrogen and that the hydrogen content in the reactor liquid is dependent on the transfer rate of hydrogen from the gas phase to the liquid phase. The reaction rate could be influenced by the hydrogen transfer rate. This diffusion controlled regime was not evident from hydrogen concentration data for Lloydminster vacuum gas oil where the hydrogen concentration increases with increasing temperature at constant reactor hydrogen partial pressure.

9. The catalytic hydroprocessing of a CANMET heavy gas oil (EMRGO) showed much greater reaction rates than thermal processing and thus a much higher level of hydroconversion and hydrodesulphurization was attained. However coke deposition on the catalyst surface caused rapid catalyst deactivation.

This study has generated much useful information on the thermal hydroprocessing of relatively light feedstocks compared to heavy residuum like bitumen. However, the results of this study should prove useful as reference information in similar studies involving heavier feedstocks.

RECOMMENDATIONS

The hydroprocessing process unit can be used to obtained useful and reliable process data on the thermal hydroprocessing of heavy gas oils. The specialized sampling and analytical procedures enables useful information on process performance and coking characteristics to be obtained. However some difficulties were encountered during the course of the study. Some recommendations that may allow for the interpretation and possible solution of these problems are presented below.

1. For the range of operating conditions used in this study, the measured concentrations of the pitch and of hydrogen in the reactor liquid phase have values that lie in a very narrow range. This causes difficulties in fitting the data to a general rate equation relating the rate of pitch conversion to pitch and hydrogen concentrations in the reacting liquid phase. Additional runs which provide results where the concentration data lie over a wider range would help solve this problem. A wider range of pitch concentration data can be obtained from experiments with blends consisting of a pitch fraction and a diluent light fraction. The range of hydrogen concentration data can be increased by operating at different hydrogen partial pressures.
2. Taking into consideration the large number of compounds

in a gas oil, quite likely each with different reactivity, improving the kinetic analysis to account for this would certainly improve the model predictions. A more sophisticated approach in kinetic analysis where a distribution of narrow boiling range fractions representing a multicomponent system is used to model the gas oil would probably improve the model predictions a great deal. The diversity of compounds in these narrow boiling fractions is less than a wide boiling fraction allowing for the accurate application of simple kinetic equations to the individual fractions.

3. In order to be able to model accurately the conversion of pitch and sulphur compounds in the tubular reactor, the level of mixing in the reactor must be established. The accurate representation of liquid holdup in the reactor must also be determined. The plug flow model used in this study assumes plug flow behaviour of the liquid phase in the reactor. The changing liquid holdup in the reactor due to conversion to vapour phase as the liquid moves up the reactor is roughly accounted for by the introduction of a correction term estimated from CSTR data. Further study of the plug flow model is required to improve its reliability.

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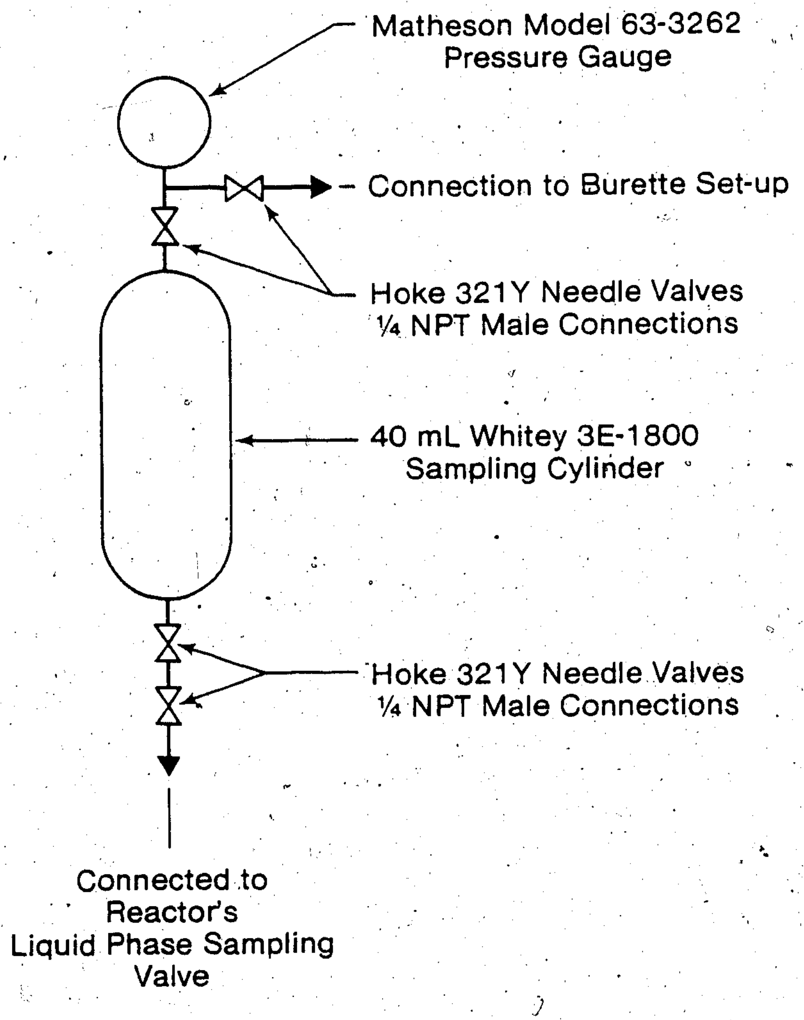
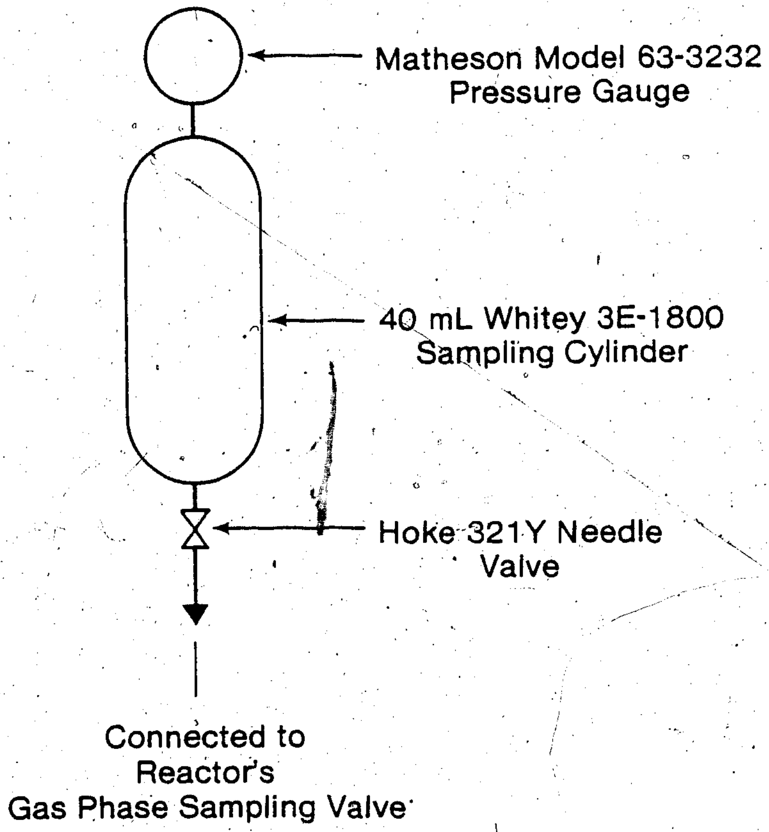
APPENDIX A - Supplementary Equipment Diagrams



All Fittings used are ¼ inch Swagelok Tube Fittings

Figure A.1 Schematic Diagram of Liquid Phase Sampling Receiver Set-Up



All Fittings used are ¼ inch Swagelok Tube Fittings

Figure A.2 Schematic Diagram of Gas Phase Sampling Receiver Set-Up

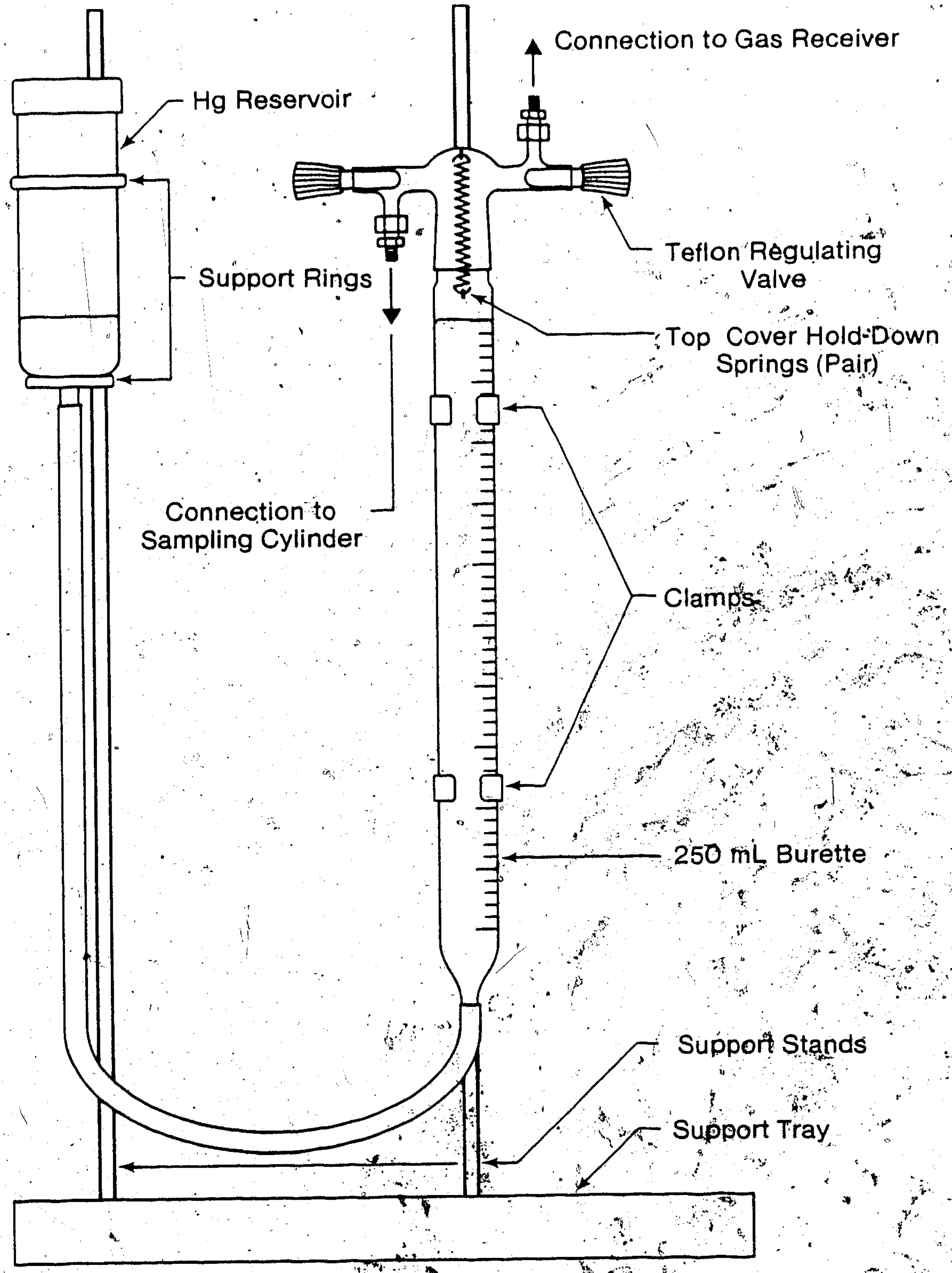
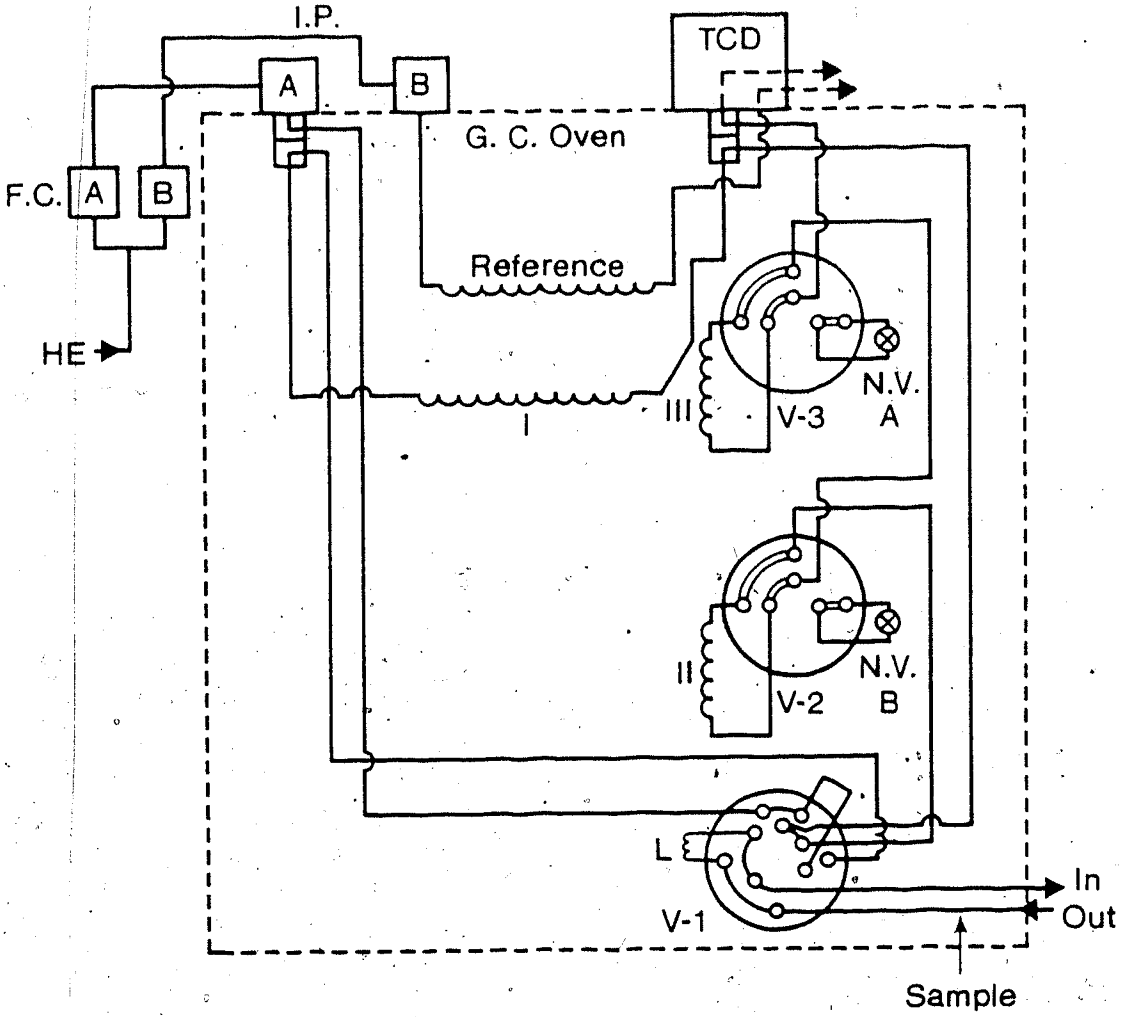


Figure A.3 Schematic Diagram of Burette System Set-Up for volume measurement of dissolved gas from reactor liquid phase samples



Column I	Adipate + Silicone
Column II	Porapak Q
ColumnIII	Molecular Sieve 5A

FC	Flow Controller
NV	Nupro Valve
L	Loop, 0.25 ml
IP	Injection Port

Figure A.4 Plumbing Set-Up for Gas Chromatograph used for Refinery Gas Analysis (RGA)

APPENDIX B - Analytical Methods

B. ANALYTICAL METHODS

This section provides a brief description on the treatment of data obtained from the various analytical methods used.

B.1 Simulated Distillation Analysis (SDA)

There is a linear relationship between the boiling point of aliphatic hydrocarbon compounds and their corresponding retention time. This relationship is established qualitatively by running a SDA on a calibration standard containing a series of n-paraffin compounds. This can be expressed as:

$$(BP)_i = C_1 + C_2(RT)_i \qquad \text{(B.1.1)}$$

where,

$(BP)_i$ = boiling point of component i

$(RT)_i$ = retention time of component i

C_1, C_2 = linear parameters

In the analysis of liquid samples, the response factors of the components in the petroleum mixture were assumed to be unity. This makes the cumulative amount of sample eluted proportional to the cumulative area under the chromatogram.

$$V_t = C_3A_t \qquad \text{(B.1.2)}$$

$$V_T = C_3A_T \qquad \text{(B.1.3)}$$

$$V = V_t/V_T \times 100\ \%$$

$$= A_t/A_T \times 100\ \% \qquad \text{(B.1.4)}$$

where,

V_t, A_t = the cumulative volume of sample eluted and the cumulative area under the chromatogram at retention time t

V_T, A_T = total volume of sample eluted and the total area under the chromatogram

V = volume percent of sample eluted at retention time t

C_3 = proportionality constant

Using equations (B.1.1) and (B.1.4) to obtain the boiling point and volume percentage eluted at any given retention time, a SDA distillation curve can be generated. This is the basis on which the computational procedures followed in program &SIMU5 is based.

B.2 Sulphur Analysis

This method is based on data obtained by X-Ray fluorescence using a Panalyzer 4000. The response for a particular sample is measured as counts per unit time and is found to have a linear relationship with the weight percent sulphur content in the sample.

$$\text{Counts} = K_1 + K_2 W_S \qquad \text{(B.2.1)}$$

where,

Counts = measured response, counts per measurement time

W_S = weight percent sulphur in sample

K_1, K_2 = linear parameters

Calibration standards can be made up of paraffin oil and a known sulphur containing hydrocarbon compound like thiophene. From calibration runs, the linear parameters, K_1 and K_2, can be determined.

B.3 Density Analysis

This method is based on the use of a densimeter. The instrument is set up such that the following relationship between the density of the sample and the frequency reading is observed:

$$\rho_2 - \rho_1 = K_d \left[T_2^{\,2} - T_1^{\,2} \right] \qquad \text{(B.3.1)}$$

where,

ρ_2 = density of sample, g/mL

ρ_1 = density of known reference liquid, g/mL

T_2 = frequency reading for sample

T_1 = frequency reading for known reference liquid

K_d = instrument constant

The instrument constant can be determined from obtaining the frequency readings for two known reference fluids. Air and water for example will make good reference fluids since their densities are well documented and readily available.

B.4 Refinery Gas Analysis (RGA)

The RGA coupled with the absorption-iodimetric titration method provides a complete gas analysis for the product gas. The RGA determines the gas composition in terms of hydrogen and the hydrocarbon gases (C_1 - C_6) as mole fractions and molar flowrates. The absorption-iodimetric titration method determines the hydrogen-sulphide content in the product gases in terms of molar flowrates. Combining these results will yield the overall gas product composition. The computer program &PGA was written for this purpose.

B.5 Hydrogen Sulphide Determination

This method based on the iodimetric-titration technique uses the following equation to determine the molar flowrate of hydrogen sulphide in the gaseous products.

$$M_{H_2S} = \frac{(V_I - V_{Thio})\ (N)\ (V_{Soln})}{V_s\ t_s} \qquad (B.3.2)$$

where,

M_{H_2S} = molar flowrate of H_2S in product gas, mol min^{-1}

V_I = volume of 0.1 N iodine solution used, 10 mL

V_{Thio} = volume of 0.1 N sodium thiosulphate soln. used in titrating the excess iodine, mL

N = normality of sodium thiosulphate soln. used = 0.1 N

V_{Soln} = volume of scrubbing solution used, 50 mL

V_s = volume of scrubbing solution used in titration, mL

t_s = scrubbing time, min

APPENDIX C - Sample Calculations

C. SAMPLE CALCULATIONS

The results for a typical run, LL-18, are used to demonstrate the calculation procedures used. Run No. LL-18 was a thermal hydrocracking run with Lloydminster gas oil as feedstock. The operating conditions and run data obtained during the run are given in Table C.

C.1 Basic Data Reduction

C.1.1 Simulated Distillation Analysis (SDA) Results

The raw SDA results (retention time versus area response) for the liquid feed, liquid product, and reactor liquid samples were converted into basic distillation results (volume percent versus boiling point) by computer program &SIMU5. The calculation procedures used in the computer program are discussed in Appendix B.

Table C.1.1 shows the computer output for the liquid product samples for run LL-18.

C.1.2 Sulphur Content Analysis Results

Sulphur content results for the liquid samples collected during run LL-18 were converted from counts per minute data to weight percent data by using a calibration curve based on thiophene in paraffin oil calibration mixtures. The results are given in Table C.1.2.

The calibration curve can be assumed to be a straight line for the range of sulphur content considered and can be represented by the following equation:

$$w_S = \frac{2.69 - 1.47}{526 - 364}(\text{Count} - 364) + 1.47$$

or

Table C. Operating Data for Run LL-18

Feedstock : Lloydminster Vacuum Gas Oil

Operating Conditions

Reactor Temperature, °C : 440
Reactor Pressure, MPa : 13.9
Hydrogen Feedrate, L/min at 23°C : 2.2
Oil Feedrate, mL/min at 23°C : 3.75
Agitation Speed, rpm : 850

Measured Run Data

Gas Product Flowrate, L/min at 23°C : 2.1
Liquid Product Flowrate, mL/min at 23°C : 3.6
Reactor Liquid Holdup, mL at 23°C : 195
Reactor Liquid Phase Sampling, Sample Weight, g : 12.28
Volume of Dissolved Gases in Reactor Liquid Phase Sample at 23°C, mL : 469

Table C.1.1 Sample Program &SIMU5 Output - SDA Data
Sample LL-18-1 (GC ID. 547)

RT	A	L	AL	VOL	ACC.VOL.	B.P.
.51	8280	21	8259	9.554	9.554	109.52
1.51	2900	168	2732	3.160	12.715	120.90
2.51	3100	288	2812	3.253	15.968	132.28
3.51	2290	386	1904	2.203	18.170	143.66
4.51	2898	466	2432	2.813	20.984	155.03
5.51	2406	534	1872	2.166	23.149	166.41
6.51	2809	585	2224	2.573	25.722	177.79
7.51	2639	626	2013	2.329	28.051	189.17
8.51	2877	657	2220	2.568	30.619	200.54
9.51	2822	680	2142	2.478	33.097	211.92
10.51	3423	694	2729	3.157	36.254	223.30
11.51	3290	699	2591	2.997	39.251	234.68
12.51	3839	702	3137	3.629	42.880	246.06
13.51	3654	706	2948	3.410	46.290	257.42
14.51	4360	705	3655	4.228	50.518	268.81
15.51	3939	701	3238	3.746	54.264	280.19
16.51	4244	698	3546	4.102	58.366	291.57
17.51	4309	689	3620	4.188	62.554	302.94
18.51	4166	681	3485	4.032	66.585	314.32
19.51	4099	675	3424	3.961	70.546	325.70
20.51	4036	668	3368	3.896	74.442	337.08
21.51	3883	661	3222	3.727	78.170	348.45
22.51	3665	657	3008	3.480	81.649	359.83
23.51	3323	647	2676	3.096	84.745	371.21
24.51	2962	640	2322	2.686	87.431	382.59
25.51	2616	628	1988	2.300	89.731	393.96
26.51	2271	621	1650	1.909	91.640	405.34
27.51	1980	613	1367	1.581	93.221	416.72
28.51	1734	606	1128	1.305	94.526	428.10
29.51	1537	599	938	1.085	95.611	439.48
30.51	1331	589	742	.858	96.469	450.85
31.51	1161	580	581	.672	97.141	462.23
32.51	1035	570	465	.538	97.679	473.61
33.51	933	561	372	.430	98.110	484.99
34.51	853	552	301	.348	98.458	496.36
35.51	796	538	258	.298	98.756	507.74
36.51	752	528	224	.259	99.016	519.12
37.51	711	515	196	.227	99.242	530.50
38.51	669	507	162	.187	99.430	541.87
39.51	637	494	143	.165	99.595	553.25
40.51	611	482	129	.149	99.744	564.63
41.51	593	476	117	.135	99.880	576.01
42.51	576	472	104	.120	100.000	587.38
43.51	568	476	0	.000	100.000	598.76
44.51	567	485	0	.000	100.000	610.14

Table C.1.1 Sample Program &SIMU5 Output - SDA Data
(cont'd) Sample LL-18-1 (GC ID. 547)

```
C NO.     BPF       BPC        RT        VOL. %       ACC.VOL
 8       258.0     126.0      2.41       14.05         14.05
 9       303.0     151.0      4.61        5.83         19.88
10       345.0     174.0      6.66        4.96         24.84
11       385.0     196.0      8.61        4.78         29.62
12       421.0     216.0     10.37        4.64         34.26
13       456.0     235.0     12.08        5.27         39.53
14       488.0     253.0     13.64        5.53         45.06
15       519.0     271.0     15.15        6.03         51.09
16       548.0     287.0     16.57        5.51         56.60
17       576.0     302.0     17.94        5.69         62.29
18       602.0     317.0     19.21        5.11         67.40
19       627.0     331.0     20.43        4.81         72.21
20       650.0     344.0     21.55        4.28         76.49
21       674.0     356.0     22.72        4.19         80.68
22       696.0     369.0     23.80        3.43         84.11
23       716.0     380.0     24.77        2.71         86.82
24       736.0     391.0     25.75        2.33         89.15
25       755.0     402.0     26.68        1.87         91.02
26       774.0     412.0     27.60        1.57         92.60
27       792.0     422.0     28.48        1.26         93.85
28       809.0     432.0     29.31        1.01         94.87
29       825.0     441.0     30.09        0.83         95.69
30       841.0     450.0     30.88        0.67         96.36
31       858.0     459.0     31.71        0.58         96.94
32       874.0     468.0     32.49        0.46         97.40
33       889.0     476.0     33.22        0.37         97.77
34       901.0     483.0     33.81        0.25         98.03
35       916.0     491.0     34.54        0.27         98.30
36       928.0     498.0     35.12        0.20         98.50
37       941.0     505.0     35.76        0.19         98.68
38       954.0     512.0     36.39        0.17         98.86
39       964.0     518.0     36.88        0.13         98.99
40       975.0     525.0     37.42        0.13         99.11
41       988.0     531.0     38.05        0.14         99.25
42       999.0     537.0     38.59        0.10         99.35
43      1009.0     543.0     39.08        0.09         99.44
44      1018.0     548.0     39.52        0.07         99.52

45 PLUS FRACTION                          0.48        100.00
```

Table C.1.1 Sample Program &SIMU5 Output - SDA Data
(cont'd) Sample LL-18-1 (GC ID. 547)

```
PRODUCT LIQ. FLOWRATE, ML/MIN          =        3.59
VOL. % PITCH (650-975F FRACTION)       =       22.62
AVERAGE SAMPLE MWT.                    =      233.78
AVERAGE PITCH MWT.                     =      355.72
WT. % PITCH IN SAMPLE                  =       23.75


FRACTION NO.     G/MIN          MOL/MIN          MOL.FRAC.
 1 (C8)         .3447905       .0034407         .2442318
 2 (C9-C11)     .4081116       .0028682         .2035928
 3 (C12-C14)    .4191393       .0022734         .1613712
 4 (C15-C17)    .4780630       .0021111         .1498548
 5 (C18-C20)    .4007953       .0014926         .1059468
 6 (C21-C23)    .2944026       .0009478         .0672797
 7 (C24-C26)    .1660792       .0004709         .0334257
 8 (C27-C29)    .0897131       .0002272         .0161309
 9 (C30-C32)    .0498218       .0001140         .0080953
10 (C33-C35)    .0261414       .0000546         .0038743
11 (C36-C38)    .0164822       .0000316         .0022455
12 (C39+   )     .0336857       .0000557         .0039510
```

Table C.1.2 Sulphur Analysis Results for Run No. LL-18

Data No.	Liquid Feed (LL-18-FD)	Liquid Product (LL-18-PR)	Reactor Liquid (LL-18-RL)
1	494	420	501
2	491	416	480
3	484	420	519
4	504	415	490
5	514	435	491
6	510	427	499
7	477	427	523
8	515	409	512
9	492	418	524
10	497	410	520
11	500	420	519
12	493	432	484
AVERAGE COUNT	498	420	505

Table C.1.2 (cont'd) Sulphur Analysis Results for Calibration Samples

Data No.	THIOPHENE IN PARAFFIN OIL 1.47 WT. % S	THIOPHENE IN PARAFFIN OIL 2.69 WT. % S
1	357	537
2	365	529
3	355	512
4	368	527
5	373	555
6	356	538
7	369	513
8	361	520
9	368	516
10	364	539
11	364	519
12	370	517
AVERAGE COUNT	364	526

$W_S = 0.007531 \text{ (Count} - 364) + 1.47$ (C.1.2)

where,

Count = average count for a sample

W_S = wt. % sulphur in sample

LL-18-FD

Count = 498

$W_S = 0.007531\ (498 - 364) + 1.47 = 2.48$

LL-18-PR

Count = 420

$W_S = 0.007531\ (420 - 364) + 1.47 = 1.89$

LL-18-RL

Count = 505

$W_S = 0.007531\ (505 - 364) + 1.47 = 2.53$.

C.1.3 Density Determination Results

The frequency readings from the digital densimeter were taken for the liquid samples. The instrument was calibrated using air and water.

Experimental conditions were 713.4 mm Hg and 23°C. The frequency readings obtained are listed as follows:

T_{air} = 1584687

T_{H_2O} = 2164083

$T_{LL-18-FD}$ = 2123884

$T_{LL-18-PR}$ = 2108811

$T_{LL-18-RL}$ = 2141343

Physical properties of air and water were obtained from the literature (Chemical Engineers' Handbook, Perry &

Chilton, 5th Edition).

ρ_{air} = 0.0012928 g/mL @ 0°C, 760 mm Hg

ρ_{H_2O} = 0.9975415 g/mL @ 23°C, 760 mm Hg

Density Calculations

Correcting ρ_{air} to analytical conditions:

$$\rho_{air} = 0.0012928 \frac{(713.4)}{(760.0)} \frac{(273)}{(296)}$$

$$= 0.001119 \text{ g/mL}$$

Correlating equation specified for densimeter used:

$$\rho_2 - \rho_1 = K_d \left[T_2^{\ 2} - T_1^{\ 2} \right] \qquad \text{(C.1.3)}$$

where,

ρ_2 = density of sample, g/mL

ρ_1 = density of calibrating liquid, g/mL

T_2 = frequency reading for sample

T_1 = frequency reading for calibrating liquid

K_d = instrument constant

Physical and experimental data for air and water were used to determine the instrument constant K_d.

$$K_d = (\rho_{H_2O} - \rho_{air})/(T_{H_2O}^{\ 2} - T_{air}^{\ 2})$$

$$= (0.9975415 - 0.001119)/(2164083^2 - 1584687^2)$$

$$= 4.5875 \times 10^{-13} \text{ g/mL}$$

Using the value of K_d obtained and equation (C.1.3), the densities of the liquid samples can be determined.

LL-18-FD

$$\rho_{LL-18-FD} = K_d\, (T_{LL-18-FD}^{\ 2} - T_{H_2O}^{\ 2}) + \rho_{H_2O}$$

$$= 4.5875 \times 10^{-13} (2123884^2 - 2164083^2)$$
$$+ 0.9975415$$
$$= 0.9185 \text{ g/mL}$$

LL-18-PR

$$\rho_{LL-18-PR} = 4.5875 \times 10^{-13} (2108811^2 - 2164083^2)$$
$$+ 0.9975415$$
$$= 0.8892 \text{ g/mL}$$

LL-18-RL

$$\rho_{LL-18-RL} = 4.5875 \times 10^{-13} (2141343^2 - 2164083^2)$$
$$+ 0.9975415$$
$$= 0.9526 \text{ g/mL}$$

The density correlation described earlier in the results section was used to correct the measured density at 23°C and 713.4 mm Hg to the API condition of 15°C and 760 mm Hg. Pressure effects on density were neglected.

$$\rho_{LL-18-FD,15^oC} = \sqrt{\rho_{LL-18-FD,23^oC}{}^2 - 0.0011\ (15 - 23)}$$
$$= \sqrt{0.9185^2 - 0.0011\ (15 - 23)}$$
$$= 0.9233 \text{ g/mL}$$

Similarly,

$$\rho_{LL-18-PR,15^oC} = \sqrt{0.8892^2 - 0.0011\ (15 - 23)}$$
$$= 0.8941 \text{ g/mL}$$

$$\rho_{LL-18-RL,15^oC} = \sqrt{0.9526^2 - 0.0011\ (15 - 23)}$$
$$= 0.9572 \text{ g/mL}$$

C.1.4 Bromine Number Determination Results

The method used for bromine number determination is based on the ASTM-1159 standard method which estimates the bromine number by the following equation:

$$\text{Bromine Number} = \frac{(A - B)\ (N)\ (7.99)}{W} \qquad (C.1.4)$$

where,

A = titration volume of bromide-bromate standard solution required for sample aliquot, mL

B = titration volume of bromide-bromate standard solution required for blank, mL

W = weight of sample in the aliquot, g

N = normality of the bromide-bromate solution

The bromine number calculations are demonstrated below based on equation (C.1.4). The value obtained is rounded up to the nearest whole number.

LL-18-FD

Experimental Results: $A = 0.83$ mL, $B = 0.40$ mL

$W = 0.3232$ g, $N = 0.50$

$$\text{Bromine Number} = \frac{(0.83 - 0.40)\ (0.5)\ (7.99)}{0.3232} = 5.3$$

Therefore, Bromine Number for LL-18-FD is 6.

LL-18-PR

Experimental Results: $A = 1.3$ mL, $B = 0.40$ mL

$W = 0.1994$ g, $N = 0.50$

$$\text{Bromine Number} = \frac{(1.3 - 0.40)\ (0.5)\ (7.99)}{0.1994} = 18.0$$

Therefore, Bromine Number for LL-18-PR is 18.

LL-18-RL

Experimental Results: A = 1.70 mL, B = 0.40 mL

W = 0.3719 g, N = 0.50

$$\text{Bromine Number} = \frac{(1.70 - 0.40)\ (0.50)\ (7.99)}{0.3719} = 14.0$$

Therefore, Bromine Number for LL-18-RL is 14.

C.1.5 Refinery Gas Analysis (RGA) Results

The computer program &PGA was used to combine the RGA results (which gives the composition of the sample gas, H_2, C_1 to C_6) and the hydrogen sulphide content of the gas sample as determined by the absorption-iodimetric method. The product gas composition as listed on the program output is given in Table C.1.5.

C.2 Predicting Reactor Contents Composition at Reactor Conditions

The equilibrium flash program, PENG:PR.FIX, developed by D. Robinson & Associates Ltd. was used to estimate the composition of the liquid and vapour phases in the reactor. The composition data for the gaseous and liquid products were used in the equilibrium flash calculations in order to predict the composition of the vapour and liquid phases at reaction conditions.

Table C.2.1 shows the composition of the combined gaseous and liquid products for run LL-18 in flow units, mol min^{-1}. This was used as input data in program PENG:PR.FIX. The program performs flash calculations to predict the composition at conditions of 440°C and 13.9 MPa. The results are given in Table C.2.2.

Table C.1.5 Analysis of Gas Product

RUN NUMBER : LL-18 ON-LINE SAMPLE

COMPONENT	VOLUME PERCENT	VOLUME FLOW RATE (L/MIN)	MOLECULAR WEIGHT	WEIGHT FLOW RATE (GM/MIN)	WEIGHT PERCENT	MOLAR FLOW RATE (GMOL/MIN)
H2	92.9268	.17536E+01	2.02	.14934E+00	43.4972	.74078E-01
C1	2.1949	.41503E-01	16.04	.28122E-01	8.1909	.17533E-02
C2	1.2175	.22975E-01	30.07	.29184E-01	8.5002	.97054E-03
C3	1.1120	.20984E-01	44.10	.39092E-01	11.3861	.88645E-03
C4	.6664	.12576E-01	58.12	.30876E-01	8.9929	.53124E-03
C5	.2997	.56553E-02	72.15	.17237E-01	5.0204	.23890E-03
C6	.1597	.30137E-02	86.18	.10972E-01	3.1956	.12731E-03
H2S	1.4175	.26750E-01	34.08	.38510E-01	11.2166	.11300E-02
NH3	0.0000	.00000E+00	17.03	.00000E+00	0.0000	.00000E+00
TOTAL		1.8871		.34333		

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C1	31.0944	.41503E-01	16.04	.28122E-01	14.4965	.17533E-02
C2	17.2127	.22975E-01	30.07	.29184E-01	15.0439	.97054E-03
C3	15.7214	.20984E-01	44.10	.39092E-01	20.1515	.88645E-03
C4	9.4217	.12576E-01	58.12	.30876E-01	15.9159	.53124E-03
C5	4.2370	.56553E-02	72.15	.17237E-01	8.8852	.23890E-03
C6	2.2579	.30137E-02	86.18	.10972E-01	5.6556	.12731E-03
H2S	20.0408	.26750E-01	34.08	.38510E-01	19.8514	.11300E-02
NH3	0.0000	.00000E+00	17.03	.00000E+00	0.0000	.00000E+00
TOTAL		.1335		.19399		

Table C.2.1 Composition of the Gaseous and Liquid Products for Run LL-18

COMPONENT	COMPONENT FLOWRATE (mol min^{-1})	MOLE %
H2	0.074078	78.9713
H2S	0.001130	1.2046
C1	0.001753	1.8688
C2	0.009710	1.0351
C3	0.000886	0.9445
C4	0.000531	0.5661
C5	0.000239	0.2548
C6	0.000127	0.1354
C8-	0.003441	3.6683
C9-C11	0.002868	3.0574
C12-C14	0.002273	2.4231
C15-C17	0.002111	2.2504
C18-C20	0.001493	1.5916
C21-C23	0.000948	1.0106
C24-C26	0.000471	0.5021
C27-C29	0.000227	0.2420
C30-C32	0.000114	0.1215
C33-C35	0.000055	0.0586
C36-C38	0.000032	0.0341
C39+	0.000560	0.0597
TOTAL	0.093804	100.0000

Table C.2.2 Results from Program PENG.FIX for sample LL-18

```
PHASE BEHAVIOUR PREDICTION USING THE PENG-ROBINSON EQUATION OF STATE FLASH
CALCULATION AT     13890.0  KPA      713.00  K
COMPONENT              COMPOSITION,  MOLE FRACTION
                     FEED          LIQUID        VAPOR            K-FACTOR

H2                0.7898E+00    0.3284E+00    0.8039E+00        0.2448E+01
H2S               0.1205E-01    0.8763E-02    0.1215E-01        0.1386E+01
METHANE           0.1869E-01    0.1074E-01    0.1894E-01        0.1763E+01
ETHANE            0.1035E-01    0.7322E-02    0.1044E-01        0.1426E+01
PROPANE           0.9451E-02    0.7823E-02    0.9501E-02        0.1215E+01
N-BUTANE          0.5664E-02    0.5486E-02    0.5669E-02        0.1033E+01
N-PENTANE         0.2547E-02    0.2846E-02    0.2538E-02        0.8918E+00
N-HEXANE          0.1357E-02    0.1743E-01    0.1346E-01        0.7718E+00
C8-               0.3668E-01    0.6064E-01    0.3595E-01        0.5928E+00
C9-C11            0.3058E-01    0.7367E-01    0.2926E-01        0.3972E+00
C12-C14           0.2424E-01    0.8215E-01    0.2246E-01        0.2735E+00
C15-C17           0.2251E-01    0.1033E+00    0.2003E-01        0.1939E+00
C18-C20           0.1591E-01    0.9625E-01    0.1345E-01        0.1398E+00
C21-C23           0.1011E-01    0.7931E-01    0.7984E-02        0.1007E+00
C24-C26           0.5021E-02    0.5060E-01    0.3624E-02        0.7163E-01
C27-C29           0.2422E-02    0.3086E-01    0.1551E-02        0.5025E-01
C30-C32           0.1215E-02    0.1905E-01    0.6689E-03        0.3512E-01
C33-C35           0.4821E-03    0.8954E-02    0.2225E-03        0.2485E-01
C36-C38           0.3369E-03    0.7133E-02    0.1287E-03        0.1804E-01
C39+              0.5939E-03    0.1497E-01    0.1534E-03        0.1025E-01
```

C.3 Pitch Conversion Calculations

Pitch conversion calculations were made based on a mass balance equation:

$$X_p = \frac{F_1 C_F - F_2 C_p}{F_1 C_F} \qquad (C.3.1)$$

where,

F_1 = volumetric flowrate of liquid feed at 23°C, mL/min

F_2 = volumetric flowrate of liquid product at 23°C, mL/min

C_F = concentration of pitch in liquid feed at 23°C, mol/mL

C_p = concentration of pitch in liquid product at 23°C, mol/mL

X_p = fraction pitch conversion

The pitch conversion calculations for run LL-18 are demonstrated below. The average molecular weight and weight fraction of the pitch in the liquid samples were estimated by a mass averaging of simulated distillation data based on aliphatic hydrocarbon physical properties. These values were estimated in the simulated distillation data program &SIMU5.

Experimental Results:

Run Results:

F_1 = 3.75 mL/min, F_2 = 3.59 mL/min

Simulated Distillation:

LL-18-FD $MW_F = 373.36$ $W_F = 0.5963$

LL-18-PR $MW_p = 355.72$ $W_p = 0.2375$

Density Analysis:

$\rho_{F,23^oC} = 0.9185$ g/mL

$\rho_{p,23^oC} = 0.8892$ g/mL

Calculations:

$$C_F = \frac{W_F \rho_F}{MW_F} = \frac{0.5963\ (0.9185)}{373.36}\ \text{mol/mL}$$

$$= 1.4670 \times 10^{-3}\ \text{mol/mL}$$

$$C_p = \frac{W_p \rho_p}{MW_p} = \frac{0.2375\ (0.8892)}{355.72}\ \text{mol/mL}$$

$$= 5.9368 \times 10^{-4}\ \text{mol/mL}$$

$$X_p = \frac{3.75\ (1.4670 \times 10^{-3}) - 3.59\ (5.9368 \times 10^{-4})}{3.75\ (1.4670 \times 10^{-3})}$$

$$= 0.6126$$

C.4 Modelling the Kinetics of Pitch Conversion in the Stirred Reactor

Calculations to obtain the rate constants for the two models described earlier are presented in this section for run LL-18.

Model 1. $-r_p = k_1 C_{RL}$

Model 2. $-r_p = k_2 C_{RL} C_H$

Mass balance on the stirred reactor gives the rate of pitch conversion, $-r_p$.

$$-r_p = \frac{F_1C_F - F_2C_p}{V_{RL}}$$

Experimental Results:

V_{RL} = 195 mL at 23°C

P_{rm} = 700.5 mm Hg, T_{rm} = 24°C

Simulated Distillation:

LL-18-RL MW_{RL} = 368.01 W_{RL} = 0.4528

Density Analysis:

$\rho_{RL,23^\circ C}$ = 0.9526 g/mL

Reactor Liquid Phase Sampling:

Wt. Reactor Liquid Sample, W = 12.2830 g

Vol. Dissolved Gases, V_G = 469 mL

Mole Fraction H_2 in Dissolved Gases, X_H = 0.86144*

Calculations:

Correcting reactor liquid volumetric data to reaction conditions,

$$\rho_{RL,440^\circ C} = \sqrt{(0.9526)^2 - 0.0011\ (440 - 23)}$$

$$= 0.6700 \text{ g/mL}$$

$$V_{RL,440^\circ C} = \frac{(V_{RL,23^\circ C})\ (\rho_{RL,23^\circ C})}{(\rho_{RL,440^\circ C})}$$

$$= \frac{195\ (0.9526)}{0.6700} = 277.3 \text{ mL}$$

---

*Measured by RGA of dissolved gases and correcting for H_2S content using predicted value from the equilibrium flash calculations

Calculating the rate of pitch conversion,

$$-r_p = \frac{3.75\ (1.4670 \times 10^{-3}) - 3.59\ (5.9368 \times 10^{-4})}{277.3}$$

$$= 1.2153 \times 10^{-5} \text{ mol mL}^{-1} \text{ min}^{-1}$$

Calculating pitch and hydrogen concentration in reactor liquid phase,

$$C_{RL} = \frac{W_{RL}\rho_{RL}}{MW_{RL}} = \frac{0.4528\ (0.6700)}{368.01}$$

$$= 8.2437 \times 10^{-4} \text{ mol mL}^{-1}$$

$$C_H = (X_H M_G \rho_{RL})/W$$

$$M_G = \text{moles of dissolved gases} = \frac{P_{rm} V_G}{R\ T_{rm}}$$

$$= \frac{(700.5/760.0)\ (469)}{82.05\ (297.15)} = 0.01773 \text{ mol}$$

$$C_H = \frac{0.86144\ (0.01773)\ (0.6700)}{12.2830}$$

$$= 8.3311 \times 10^{-4} \text{ mol mL}^{-1}.$$

Calculating rate constants,

Model 1. $k_1 = -r_p/C_{RL} = \frac{1.2153 \times 10^{-5}}{8.2437 \times 10^{-4}} \text{ min}^{-1}$

$$= 1.4742 \times 10^{-2} \text{ min}^{-1}$$

Model 2. $k_2 = -r_p/(C_{RL}C_H)$

$$= \frac{1.2153 \times 10^{-5}}{(8.2437 \times 10^{-4})(8.3311 \times 10^{-4})}$$

$$= 17.6953 \text{ mL mol}^{-1} \text{ min}^{-1}$$

APPENDIX D - Sample Calculations (Model Predictions)

D. SAMPLE CALCULATIONS (Model Predictions)

D.1 Predicting Pitch Conversion in CSTR

D.1.1 Design Equation Based on First Order Kinetics

For a CSTR, the mass balance equation based on first order kinetic results can be written as:

$$(-r_p) = k\ C_{RL} = \frac{F_1'C_F' - F_2'C_{RL}}{V_{RL}} \qquad (D.1.1.1)$$

Pitch conversion is defined as:

$$X_p = \frac{F_1'C_F' - F_2'C_{RL}}{F_1'C_F'} \qquad (D.1.1.2)$$

where,

$(-r_p)$ = rate of pitch conversion, mol min^{-1} mL^{-1}

k = first order rate constant, min^{-1}

F_1' = volumetric flowrate of liquid feed at reaction conditions, mL min^{-1}

F_2' = volumetric flowrate of liquid product at reaction conditions, mL min^{-1}

C_F' = pitch concentration in the liquid feed at reaction conditions, mol mL^{-1}

C_{RL} = pitch concentration in the reactor liquid at reaction conditions, mol mL^{-1}

V_{RL} = liquid holdup at reaction conditions, mL

X_p = fractional pitch conversion

This analysis assumes that all pitch fractions are in the liquid phase.

Rearranging equations,

$$C_{RL} = \frac{F_1'C_F'}{F_2'}(1 - X_p)$$

By definition,

$$LHSV^{-1} = V_{RL}/F_1'$$

The following simple relation giving X_p in terms of $LHSV^{-1}$ was derived by substitution into equation (D.1.1.1).

$$X_p = \frac{k(F_1'/F_2')(LHSV^{-1})}{1 + k(F_1'/F_2')(LHSV^{-1})} \qquad (D.1.1.3)$$

D.1.2 Design Equation Based on Overall Second Order Kinetics

Similarly, the following mass balance equation can be derived for a CSTR based on overall second order kinetic equation:

$$(-r_p) = kC_{RL}C_H = \frac{F_1'C_F' - F_2'C_{RL}}{V_{RL}} \qquad (D.1.2.1)$$

where,

C_H = concentration of hydrogen in the reactor liquid phase at reaction conditions, mol mL^{-1}

Rearranging equations as in the last section, obtain:

$$X_p = \frac{kC_H(F_1'/F_2')(LHSV^{-1})}{1 + kC_H(F_1'/F_2')(LHSV^{-1})} \qquad (D.1.2.2)$$

D.1.3 Calculations to Predict Pitch Conversion at Different LHSV at a given Temperature

Calculations for predicting the pitch conversion in the CSTR at various LHSV was made at 400°C to demonstrate the calculational procedures involved. The rate constants required for the calculations were obtained from correlations developed earlier for the two kinetic models examined.

The hydrogen concentration term required to evaluate X_p in the overall second order model (Model 2) was obtained based on the experimentally determined C_H versus temperature relationship. Sample calculations are as follows:

Model 1. $(-r_p) = k\ C_{RL}$

At 400°C, $k = 0.2123\ h^{-1}$, av. $F_1'/F_2' = 1.07$

Equation (D.1.1.3),

$$X_p = \frac{k(F_1'/F_2')\ (LHSV^{-1})}{1 + k(F_1'/F_2')\ (LHSV^{-1})}$$

The results are summarized in the following table.

$(LHSV^{-1})$	X_p, %	$(LHSV^{-1})$	X_p, %
0.00	0.00	2.00	31.23
0.50	10.20	2.50	36.22
1.00	18.51	3.00	40.53
1.50	25.41	3.50	44.29

Model 2. $(-r_p) = kC_{RL}C_H$

At 400°C, $k = 304.34$ m[illegible]l^{-1} h^{-1}, av. $F_1'/F_2' = 1.07$

$C_H = 7.0377$ [illegible] 10^{-4} mol mL^{-1} (from correlation relating C_H and temperature developed from experimental results)

Equation (D.1.2.2),

$$X_p = \frac{kC_H(F_1'/F_2')\ (\text{LHSV}^{-1})}{1 + kC_H(F_1'/F_2')\ (\text{LHSV}^{-1})}$$

The results are summarized in the following table.

(LHSV^{-1})	X_p, %	(LHSV^{-1})	X_p, %
0.00	0.00	2.00	31.43
0.50	10.28	2.50	36.42
1.00	18.64	3.00	40.74
1.50	25.59	3.50	44.51

Table IX.4 shows the values of F_1'/F_2' evaluated from CSTR data for LLVGO feedstock.

D.2 Plug Flow Model Calculations

D.2.1 Design Equation Based on the Plug Flow Model

The following assumptions were used in the formulation of the design equation:

(1) Plug-flow behaviour of the fluid, no axial mixing

(2) First order kinetics applies for reaction in the liquid phase

(3) Constant total liquid hold-up in the reactor

The basic plug-flow design equation is given as:

$$\int_0^{V_{RL}} \frac{dV_{RL}}{F' \; C_F'} = \int_0^{X_p} \frac{dX_p}{k \; C_F' \; (1-X_p)} \qquad (D.2.1.1)$$

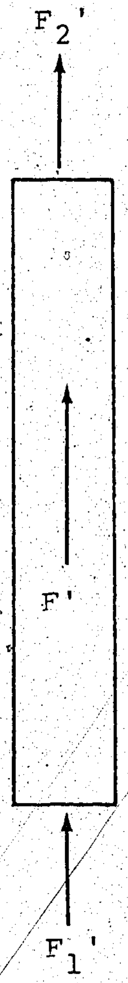
$$F' = (1 - \psi) \; F_1'$$

where,

ψ = $f(X_p)$, [illegible] term used to account for the decrease in volumetric flow of liquid phase as it proceeds up the reactor

Since the functional relationship of ψ to X_p is not known, it is required to estimate an average value of ψ from the following equation. Figure D.1 show a representation of liquid flows in the tubular reactor.

$$\psi_{av} = \frac{F_1' - F_2'}{2F_1'} \qquad (D.2.1.2)$$



$$F' = (1 - \psi)\, F_1'$$

$$F_{av}' = (1 - \psi_{av})\, F_1'$$

Figure D.1 Schematic diagram of Tubular Reactor showing Liquid Flows

$$F_{av}' = (1 - \psi_{av}) F_1' \qquad (D.2.1.3)$$

Substituting equation (D.2.1.3) into (D.2.1.1),

$$\int_0^{V_{RL}} \frac{dV_{RL}}{(1 - \psi_{av}) F_1' C_F'} = \int_0^{X_p} \frac{dX_p}{kC_F' (1 - X_p)}$$

$$\frac{V_{RL}}{F_1' (1 - \psi_{av})} = - \frac{1}{k} \ln (1 - X_p)$$

By definition, $V_{RL}/F_1' = LHSV^{-1}$

Substituting, obtain the following relationship,

$$\frac{LHSV^{-1}}{(1 - \psi_{av})} = - \frac{1}{k} \ln (1 - X_p) \qquad (D.2.1.4)$$

D.2.2 Estimation of term, ψ

Since no reactor liquid phase samples were taken from tubular reactor runs, it is not possible to estimate F_2' from run data. However, that data was obtained for the CSTR runs. Based on CSTR data obtained at similar conversion levels, ψ_{av} was taken as a constant at each temperature level.

$F_1'/F_2' = 1.07$ at 400°C
$F_1'/F_2' = 1.15$ at 420°C
$F_1'/F_2' = 2.00$ at 440°C

Using the above values for F_1'/F_2', it is possible to evaluate an estimate for ψ_{av} at the three temperature levels based on equation (D.2.1.2).

$\psi_{av} = 0.0327$ at 400°C

$\psi_{av} = 0.0652$ at 420°C

$\psi_{av} = 0.2500$ at 440°C

D.2.3 Sample Calculations on Estimating the Effect of LHSV on Pitch Conversion in the Tubular Reactor at 440°C

Run Data:

Run LL-31

LHSV = 2.51 h^{-1}, Temp. = 440°C, k = 1.1804 h^{-1}

Use of equation (D.2.1.4) gives the following:

$$\frac{1.1804}{2.51\ (1 - 0.25)} = -\ln\ (1 - X_p)$$

$X_p = 46.3\ \%$

Similarly, X_p can be evaluated at other $LHSV^{-1}$. A table showing values of X_p evaluated at various $LHSV^{-1}$ is given as Table D.2.1. Values of X_p predicted for a CSTR at 440°C is also presented in Table D.2.1 for comparison purposes.

D.2.4 Sample Calculations on Estimating the Effect of Temperature on Pitch Conversion in the Tubular Reactor at nominal LHSV of 1.0 h^{-1}

Run Data:

Run LL-26

LHSV = 1.46 h^{-1}, Temp. = 400°C, k = 0.2136 h^{-1}

Use of equation (D.2.1.4) gives the following:

$$\frac{0.2136}{1.46\ (1 - 0.0327)} = -\ln\ (1 - X_p)$$

$X_p = 14.0\ \%$

Similarly, X_p can be calculated at other temperatures. A table showing values of X_p evaluated at various temperatures at nominal LHSV of 1.0 h^{-1} is given as Table D.2.2.

D.2.5 Sample Calculations on Estimating the Effect of LHSV on Sulphur Conversion in the Tubular Reactor at 440°C

Run Data:

Run LL-31

LHSV = 2.51 h^{-1}, Temp. = 440°C, k = 0.3652 h^{-1}

Use of equation (D.2.1.4) gives the following:

$$\frac{0.3652}{2.51\ (1 - 0.25)} = -\ln(1 - X_S)$$

$X_S = 17.6\ \%$

Similarly, X_S can be evaluated at other $LHSV^{-1}$. A table showing values of X_S evaluated at various $LHSV^{-1}$ is given as Table D.2.3.

D.2.6 Sample Calculations on Estimating the Effect of Temperature on Sulphur Conversion in the Tubular Reactor at nominal LHSV of 1.0 h^{-1}.

Run Data:

Run LL-26

LHSV = 1.46 h^{-1}, Temp. = 400°C, k = 0.1145 h^{-1}

Use of equation (D.2.1.4) gives the following:

$$\frac{0.1145}{1.46\ (1 - 0.0327)} = -\ \ln(1 - X_S)$$

$X_S = 7.8\ \%$

Similarly, X_S can be evaluated at other temperatures. A table showing values of X_S evaluated at various temperatures at nominal LHSV of 1.0 h^{-1} is given as Table D.2.4.

Table D.2.1 Effect of LHSV on X_p in the Tubular Reactor

Run No.	$LHSV^{-1}$, h	Tubular Reactor		CSTR
		$X_{p,expt}$	$X_{p,pred}$	$X_{p,pred}$
-	0.25	-	32.5	30.7
-	0.29	-	36.6	33.9
LL-32	0.33	43.8	40.5	36.9
LL-31	0.40	55.5	46.3	41.5
-	0.50	-	54.5	47.0
LL-30	0.60	58.1	61.1	51.5
-	0.70	-	66.8	55.3
-	0.80	-	71.6	58.6

Table D.2.2 Effect of Temperature on X_p in the Tubular Reactor at nominal LHSV of 1.0 h^{-1}

Run No.	Temperature ^{o}C	Pitch Conversion, X_p Measured	Pitch Conversion, X_p Predicted
-	385	-	7.3
LL-26	400	18.6	14.0
LL-27	420	35.3	31.2
LL-29	400	15.4	14.3
LL-30	440	58.1	61.1
-	450	-	76.9

Table D.2.3 Effect of LHSV on X_S in the Tubular Reactor

Run No.	$LHSV^{-1}$, h	Sulphur Conversion, X_S	
		Measured	Predicted
-	0.25	-	11.5
-	0.29	-	13.2
LL-32	0.33	19.49	14.8
LL-31	0.40	18.04	17.6
-	0.50	-	21.6
LL-30	0.60	25.33	25.3
-	0.70	-	28.9
-	0.80	-	32.3

Table D.2.4 Effect of Temperature on X_S in the Tubular Reactor at nominal LHSV of 1.0 h^{-1}

Run No.	Temperature °C	Sulphur Conversion, X_S	
		Measured	Predicted
-	385	-	4.9
LL-26	400	8.13	7.8
LL-27	420	10.24	14.0
LL-29	400	8.82	7.9
LL-30	440	25.33	25.3
-	450	-	41.9

APPENDIX E - Computer Program Listings

PROGRAM &SIMU5 LISTINGS

```
FTN4
C      PROGRAM SIMU (),
C      SIMULATED DISTILLATION ANALYSIS
C
C      THIS PROGRAM PROCESS SIMULATED DISTILLATION
C      DATA
C
C      PROGRAM FUNCTIONS:
C      1. CONVERTS AREA RESPONSE VERSUS COLUMN RETENTION
C         TIME DATA TO BOILING POINT VERSUS CUMULATIVE
C         VOLUME PERCENT (OR DISTILLATION) DATA BASED
C         ON A CALIBRATION CURVE
C      2. GENERATE DISTILLATION IN REPORT FORM
C      3. ESTIMATES THE WEIGHT PERCENT OF THE PITCH
C         FRACTION (343-524 C) IN THE SAMPLE
C      4. ESTIMATES THE AVERAGE MOLECULAR WEIGHT OF
C         THE SAMPLE
C      5. ESTIMATES THE AVERAGE MOLECULAR WEIGHT OF
C         THE PITCH FRACTION IN THE SAMPLE
C      6. ESTIMATES THE MOLE FRACTION, MASS & MOLAR
C         FLOWRATES OF 12 INDIVIDUAL NARROW BOILING
C         RANGE FRACTIONS IN THE SAMPLE. THE ABOVE
C         ESTIMATIONS ARE BASED ON PROPERTIES OF PURE
C         ALIPHATIC COMPOUNDS (N-PARAFFINS).
C
C
C      ABSTRACT
C
C      SIMULATED DISTILLATION ANALYSIS OF GAS OIL SAMPLES
C      GENERATES A CHROMATOGRAM WHERE THE ELUTION TIME
C      IS PROPORTIONAL TO THE CONSTANT RISING COLUMN
C      TEMPERATURE. THE AREA RESPONSE IS DIVIDED INTO EQUAL
C      INCREMENTAL TIME SLICES. THE TRUE RESPONSE IS
C      OBTAINED AS THE DIFFERENCE BETWEEN THE SAMPLE RUN
C      AND THE BASELINE RUN AREA RESPONSE.
C
C      THE VOLUMETRIC RESPONSE FACTOR OF EACH SLICE, WHICH
C      REPRESENTS A NARROW BOILING FRACTION IN THE SAMPLE,
C      WAS ASSUMED TO BE EQUAL. THUS VOLUMETRIC PERCENTAGE
C      DATA CAN BE OBTAINED FROM AREA RESPONSE DATA.
C
C      A LINEAR CALIBRATION CURVE BASED ON N-PARAFFINS
C      WAS USED TO CONVERT THE RETENTION TIME DATA INTO
C      CORRESPONDING BOILING POINTS BASED ON THE BOILING
C      POINT OF N-PARAFFINS. A MIXTURE OF N-C9 TO N-C40
C      WAS USED FOR CALIBRATION.
C
C      IN THE ESTIMATION OF AVERAGE MOLECULAR WEIGHTS,
C      PITCH CONTENT, MASS AND MOLAR FLOWRATES, PROPERTIES
C      OF N-PARAFFINS (N-C8 TO N-C44) LIKE DENSITY,
C      BOILING POINT AND MOLECULAR WEIGHT WAS USED. TO
C      FACILITATE A CONTINUITY OF THE DISTILLATION DATA,
```

```
C     LINEAR INTERPOLATION WAS USED TO EVALUATE VALUES
C     THAT DOES NOT FALL ON THE SLICE BOUNDARIES.
C
C
C     INPUT DATA DESCRIPTION
C
C     A0   INTERCEPT - CALIBRATION CURVE (RT VS. BP)
C     A1   SLOPE - CALIBRATION CURVE (RT VS. BP)
C     MA   SAMPLE RUN I.D NO.
C     MC   CALIBRATION RUN I.D. NO.
C     ML   BASELINE RUN I.D. NO.
C     MM   AREA REJECTION (OPTIONAL)
C     MR   PROGRAM RUN I.D. NO.
C
C
C     OUTPUT DATA DESCRIPTION
C
C     A(I)    AREA RESPONSE FOR SLICE I FOR SAMPLE RUN
C     AA      SUM OF TRUE AREA RESPONSE
C     AL(I)   TRUE AREA RESPONSE FOR FRACTION I IN SAMPLE
C     BP(I)   BOILING POINT FOR FRACTION I IN SAMPLE
C     C(J)    CUMULATIVE VOLUME PERCENT - VARIABLE USED
C             TO GENERATE DISTILLATION REPORT
C     L(I)    AREA RESPONSE FOR SLICE I FOR BASELINE RUN
C     R(J)    RETENTION TIME OF FRACTION CORRESPONDING TO
C             C(J)
C     WAC(I) CUMULATIVE VOLUME PERCENT OF SLICES UP TO
C             AND INCULDING SLICE I
C     WT(I)   TRUE VOLUME PERCENT OF SLICE I
C
C
C
C     INITIATION
C
C
      REAL L(45),MWT(40),MWT1(40),MWT2(40),MAFR(40)
      REAL MOFR(40),MFR(40)
      INTEGER OUNIT,SAMPLE(20)
      DIMENSION A(45),WT(45),WAC(45),AL(45),R(14)
      DIMENSION C(14),BP(59),LU(5),P(9),Q(3),RT(81)
      DIMENSION BPC(81),TRT(3),ALPHA(3),WORK(3),IW(6)
      DIMENSION COEF(9),TWAC(3),TEMP(43),WTEC(43),WTEM(43)
      DIMENSION TEMPC(43),RTT(43),DENSI(40)
C
C     DATA FILE
C
      DATA C/0.5,5.,10.,20.,30.,40.,50.,60.,70.,
     *80.,90.,95.,99.5,100./
      DATA TEMP/258.,303.,345.,385.,421.,456.,488.,519.,
     *548.,576.,602.,627.,650.,674.,696.,716.,736.,
     *755.,774.,792.,809.,825.,841.,858.,874.,889.,901.,
     *916.,928.,941.,954.,964.,975.,988.,999.,1009.,1018./
      DATA TEMPC/126.,151.,174.,196.,216.,235.,253.,271.,
     *287.,302.,317.,331.,344.,356.,369.,380.,391.,402.,
```

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     *412.,422.,432.,441.,450.,459.,468.,476.,483.,491.,
     *498.,505.,512.,518.,525.,531.,537.,543.,548./
      DATA DENSI/0.703,0.718,0.73,0.74,0.749,0.756,
     *0.763,0.769,0.773,0.778,0.782,0.786,0.789,0.792,
     *0.794,0.797,0.799,0.801,0.803,0.805,0.807,0.808,
     *0.81,0.811,0.812,0.814,0.815,0.816,0.817,0.818,
     *0.819,0.82,0.821,0.821,0.822,0.822,0.823,0.823,
     *0.829/
      DATA MWT/114.2,128.26,142.29,156.32,170.34,184.37,
     *198.4,212.42,226.45,240.48,254.51,268.53,282.56,
     *296.59,310.61,324.64,338.67,352.69,366.72,380.75,
     *394.78,408.8,422.83,436.86,450.89,464.92,478.95,
     *492.97,507.0,521.03,535.06,549.08,563.11,577.14,
     *591.17,605.2,619.23,703.4/
C
C     SELECT INPUT/OUTPUT MODE
C
      CALL RMPAR(LU)
      WRITE(LU,150)
150   FORMAT(//," INPUT AND OUTPUT ON THIS TERMINAL ?
     *Y - 1    N - 2 ")
      READ(LU,*)IFLAG
      IF(IFLAG.EQ.1)GO TO 203
      LUNIT=LU
      GO TO 202
203   IUNIT=LU
      OUNIT=LU
      GO TO 162
C
C     INPUT VIA TERMINAL
C
162   WRITE(IUNIT,105)
105   FORMAT(//,"ENTER DATE-MONTH-YEAR OF RUN (N1,N2,N3)")
      READ(IUNIT,*)N1,N2,N3
      WRITE(IUNIT,106)
106   FORMAT(//,"ENTER SAMPLE ID. NUMBER (MR).")
      READ(IUNIT,*)MR
      WRITE(IUNIT,101)
101   FORMAT(//,"ENTER SAMPLE NAME. 40 CHAR. MAX.")
      READ(IUNIT,100)(SAMPLE(I),I=1,20)
100   FORMAT(20A2)
      WRITE(IUNIT,107)
107   FORMAT(//,"ENTER HP SAMPLE RUN NO. (MA)")
      READ(IUNIT,*)MA
      WRITE(IUNIT,108)
108   FORMAT(//,"ENTER HP BASELINE RUN NO. (ML)")
      READ(IUNIT,*)ML
      WRITE(IUNIT,109)
109   FORMAT(//,"ENTER AREA OF REJECTION (MM).")
      READ(IUNIT,*)MM
      WRITE(IUNIT,110)
110   FORMAT(//,"ENTER VALUES OF L(1) TO L(5)")
      READ(IUNIT,*)(L(I),I=1,5)
      WRITE(IUNIT,111)
```

```
111    FORMAT(//,"ENTER VALUES OF L(6) TO L(10)")
       READ(IUNIT,*)(L(I),I=6,10)
       WRITE(IUNIT,112)
112    FORMAT(//,"ENTER VALUES OF L(11) TO L(15)")
       READ(IUNIT,*)(L(I),I=11,15)
       WRITE(IUNIT,113)
113    FORMAT(//,"ENTER VALUES OF L(16) TO L(20)")
       READ(IUNIT,*)(L(I),I=16,20)
       WRITE(IUNIT,114)
114    FORMAT(//,"ENTER VALUES OF L(21) TO L(25)")
       READ(IUNIT,*)(L(I),I=21,25)
       WRITE(IUNIT,115)
115    FORMAT(//,"ENTER VALUES OF L(26) TO L(30)")
       READ(IUNIT,*)(L(I),I=26,30)
       WRITE(IUNIT,401)
401    FORMAT(//,"ENTER VALUES OF L(31) TO L(35)")
       READ(IUNIT,*)(L(I),I=31,35)
       WRITE(IUNIT,402)
402    FORMAT(//,"ENTER VALUES OF L(36) TO L(40)")
       READ(IUNIT,*)(L(I),I=36,40)
       WRITE(IUNIT,405)
405    FORMAT(//,"ENTER VALUES OF L(41) TO L(45)")
       READ(IUNIT,*)(L(I),I=41,45)
       WRITE(IUNIT,116)
116    FORMAT(//,"ENTER VALUES OF A(1) TO A(5)")
       READ(IUNIT,*)(A(I),I=1,5)
       WRITE(IUNIT,117)
117    FORMAT(//,"ENTER VALUES OF A(6) TO A(10)")
       READ(IUNIT,*)(A(I),I=6,10)
       WRITE(IUNIT,118)
118    FORMAT(//,"ENTER VALUES OF A(11) TO A(15)")
       READ(IUNIT,*)(A(I),I=11,15)
       WRITE(IUNIT,119)
119    FORMAT(//,"ENTER VALUES OF A(16) TO A(20)")
       READ(IUNIT,*)(A(I),I=16,20)
       WRITE(IUNIT,120)
120    FORMAT(//,"ENTER VALUES OF A(21) TO A(25)")
       READ(IUNIT,*)(A(I),I=21,25)
       WRITE(IUNIT,121)
121    FORMAT(//,"ENTER VALUES OF A(26) TO A(30)")
       READ(IUNIT,*)(A(I),I=26,30)
       WRITE(IUNIT,403)
403    FORMAT(//,"ENTER VALUES OF A(31) TO A(35)")
       READ(IUNIT,*)(A(I),I=31,35)
       WRITE(IUNIT,404)
404    FORMAT(//,"ENTER VALUES OF A(36) TO A(40)")
       READ(IUNIT,*)(A(I),I=36,40)
       WRITE(IUNIT,406)
406    FORMAT(//,"ENTER VALUES OF A(41) TO A(45)")
       READ(IUNIT,*)(A(I),I=41,45)
       WRITE(IUNIT,407)
407    FORMAT(//,"ENTER LIQ. PROD. RATE, ML/MIN")
       READ(IUNIT,*)PFR
       WRITE(IUNIT,122)
```

```
122   FORMAT(//."ENTER CALIBRATION RUN NO. (MC)")
      READ(IUNIT,*)MC
      WRITE(IUNIT,123)
123   FORMAT(//,"ENTER VALUES OF A0 AND A1 FOR "
     *"CALIBRATION RUN")
      READ(IUNIT,*)A0,A1
      WRITE(IUNIT,126)
126   FORMAT(//,"SELECT OUTPUT UNITS, C = 1   F = 2")
      READ(IUNIT,*)ITC
      GO TO 66
C
C     INPUT VIA CARD READER
C
206   WRITE(LU,152)
152   FORMAT(//."CHECK IF ALL THE DATA CARDS ARE IN "
     *"CARD READER - ENTER 1 WHEN READY")
      READ(LU,*)ICARD
      IF(ICARD.EQ.1)GO TO 99
      WRITE(LU,154)
154   FORMAT(//,"WAITING - ENTER 1 WHEN READY")
      GO TO 206
99    READ(IUNIT,*)N1,N2,N3
25    FORMAT(3I2)
      READ(IUNIT,*)MR,MA,ML,MM
2     FORMAT(4I4)
1     READ(IUNIT,100)(SAMPLE(I),I=1,20)
      READ(IUNIT,*)(L(I),I=1,10)
      READ(IUNIT,*)(L(I),I=11,20)
      READ(IUNIT,*)(L(I),I=21,30)
      READ(IUNIT,*)(L(I),I=31,40)
      READ(IUNIT,*)(L(I),I=41,45)
      READ(IUNIT,*)(A(I),I=1,10)
      READ(IUNIT,*)(A(I),I=11,20)
      READ(IUNIT,*)(A(I),I=21,30)
      READ(IUNIT,*)(A(I),I=31,40)
      READ(IUNIT,*)(A(I),I=41,45)
3     FORMAT(10F8.0)
      READ(IUNIT,*)MC,A0,A1
4     FORMAT(I4,2F12.8)
      GO TO 66
C
C     SET INITIAL VALUES
C
66    AA=0.0
      WW=0.0
      DO 21 I=1,45
      RT(I)=I-0.49
      AL(I)=0.0
      WT(I)=0.0
      WAC(I)=0.0
21    CONTINUE
      DO 22 I=1,43
      WTEM(I)=0.0
      WTEC(I)=0.0
```

```
22    CONTINUE
      DO 5 I=1,45
C
C     CORRECT FOR BASELINE RESPONSE
C
      AL(I)=A(I)-L(I)
C
C     SET TRUE SAMPLE RESPONSES THAT ARE LESS THAN
C     PRESET REJECTION AREA TO ZERO
C
      IF(AL(I)-MM)6,7,7
6     AL(I)=0.0
      GO TO 7
C
C     EVALUATE SUM OF AREA RESPONSE FOR SAMPLE
C
7     AA=AA+AL(I)
5     CONTINUE
      DO 12 I=1,45
C
C     EVALUATE VOLUME PERCENT SAMPLE IN INDIVIDUAL
C     SLICES AND CUMULATIVE VOLUME PERCENTAGES UP
C     TO EACH SLICE
C
      WT(I)=AL(I)/AA
      WT(I)=WT(I)*100.0
      WW=WW+WT(I)
      WAC(I)=WW
C
C     EVALUATE BOILING POINT FOR EACH SLICE BASED
C     ON CALIBRATION RUN
C
      BP(I)=(I-A0)/A1
12    CONTINUE
C
C     LINEAR INTERPOLATION TO EVALUATE BOILING POINT
C     AT SPECIFIED VOLUME PERCENT DISTILLED
C
      DO 78 J=1,14
C
C     CHECK IF WAC(I) IS GREATER THAN C(J)
C
      IF(C(J).GT.WAC(1))GO TO 89
C
C     FOR WAC(1) GREATER THAN C(J), EVALUATE CORRES.
C     RETENTION TIME BY LINEAR INTERPOLATION
C
      R(J)=(0.51*C(J))/WAC(1)
      GO TO 84
89    DO 74 I=1,44
      I1=I+1
72    WI=(WAC(I)-C(J))*(WAC(I1)-C(J))
      IF(ABS(WI).LT.1E-6)WI=0.0
      IF(WI-0.0)77,77,74
```

```
77    R(J)=(C(J)-WAC(I))/(WAC(I+1)-WAC(I))+I
84    JJ=J+45
      BP(JJ)=(R(J)-A0)/A1
      GO TO 78
74    CONTINUE
78    CONTINUE
C
C     LINEAR INTERPOLATION - EVALUATE BOILING POINT
C     AT SPECIFIED RETENTION TIMES
C
      DO 61 I=1,37
      IF(TEMP(I)-BP(45))63,63,69
63    RTT(I)=A0+A1*TEMP(I)
      DO 62 J=1,44
      WRI=(RTT(I)-J)*(RTT(I)-J-1)
      IF (WRI-0. )64,64,62
64    WTEC(I)=(RTT(I)-J)*WT(J+1)+WAC(J)
      WTEM(I)=WTEC(I)
      IF (I-1)61,61,57
57    WTEM(I)=WTEC(I)-WTEC(I-1)
      GO TO 61
62    CONTINUE
61    CONTINUE
69    ITEM=I-1
      IF(ITEM-0. )67,67,68
67    WHEY=100.
      GO TO 65
68    WHEY=100.-WTEC(ITEM)
65    J=1.
      PF=WTEC(33)-WTEC(13)
C
C     PRINT PRIMARY OUTPUT
C
75    WRITE(OUNIT,30)MR
30    FORMAT("1"," SAMPLE ID. NUMBER",3X,I4)
      WRITE(OUNIT,33) (SAMPLE(I), I=1,20)
33    FORMAT(" SAMPLE NAME",4X,20A2)
      WRITE(OUNIT,29)N1,N2,N3
29    FORMAT(" DATE",4X,I2,"-",I2,"--",I2)
      WRITE(OUNIT,31)ML,MA
31    FORMAT(" BASELINE HP5730A ID. NUMBER",4X,I4,/,
     1" OIL HP5730A RUN NUMBER",4X,I4)
      WRITE(OUNIT,50)MC
50    FORMAT(" HP5730A CALIBRATION STANDARD",4X,I4)
      WRITE(OUNIT,88)MM
88    FORMAT(" AREA OF REJECTION",4X,I4)
      WRITE(OUNIT,32)
32    FORMAT(/, " RT.",12X,"A",9X,"L",9X,"AL",8X,
     1"VOL",4X,"ACC.VOL.",4X,"B.P.")
      DO 34 I=1,45
      BPC(I)=(BP(I)-32.)*5./9.
      IF(ITC.NE.1)GO TO 39
      WRITE(OUNIT,35)RT(I),A(I),L(I),AL(I),WT(I),
     1WAC(I),BPC(I)
```

```
      GO TO 34
39    WRITE(OUNIT,35)RT(I),A(I),L(I),AL(I),WT(I),
     1WAC(I),BP(I)
35    FORMAT(" ",F5.2,5X,3F10.0.2F10.3,F10.2)
34    CONTINUE
C
C     SECONDARY OUTPUT
C
      WRITE(OUNIT,500)MR
500   FORMAT(1HL,"SAMPLE ID. NUMBER",3X,I4)
      WRITE(OUNIT,501) (SAMPLE(I),I=1,20)
501   FORMAT (" SAMPLE NAME",4X,20A2)
      WRITE(OUNIT,502)N1,N2,N3
502   FORMAT(" DATE",4X,I2," -",I2,"- -",I2)
      WRITE(OUNIT,503)ML,MA
503   FORMAT(" BASELINE HP5730A ID. NUMBER",4X,I4,/,
      4X,I4,/,
     1" OIL HP5730A RUN NUMBER",4X,I4)
      WRITE(OUNIT,504)MC
504   FORMAT(" HP5730A CALIBRATION STANDARD",4X,I4)
      WRITE(OUNIT,505)MM
505   FORMAT(" AREA OF REJECTION",4X,I4)
      WRITE(6,47)AO
47    FORMAT(" AO=",4X,F15.10)
      WRITE(6,48)A1
48    FORMAT(" A1=",4X,F15.10)
      WRITE(OUNIT,38)
38    FORMAT(/," ",7X,"RT",6X,"VOL.PERCENT",
     14X,"B.P.")
      DO 40 I=1,14
      JJ=I+45
      BPC(I)=(BP(JJ)-32.  )*5./9.
      IF(ITC.NE.1)GO TO 42
      WRITEIOUNIT,41)R(I),C(I),BPC(I)
      GO TO 40
42    WRITE(OUNIT,41)R(I),C(I),BP(JJ)
41    FORMAT(1X,F10.2,4X,F10.2,1X,F10.2)
40    CONTINUE
      WRITE(OUNIT,510)MR
510   FORMAT(1H1,"SAMPLE ID. NUMBER",3X,I4)
      WRITE(OUNIT,511) (SAMPLE(I),I=1,20)
511   FORMAT(" SAMPLE NAME",4X,20A2)
      WRITE(OUNIT,512)N1,N2,N3
512   FORMAT("DATE",4X,I2," -",I2," - -"I2)
      WRITE(OUNIT,513)ML,MA
513   FORMAT(" BASELINE HP5730A ID NUMBER",4X,I4,/,
     1" OIL HP5730A RUN NUMBER",4X,I4)
      WRITE(OUNIT,514)MC
514   FORMAT(" HP 5730A CALIBRATION STANDARD",
     14X,I4)
      WRITE(OUNIT,515)MM
515   FORMAT("AREA OF REJECTION",4X,I4)
      WRITE(6,45)
45    FORMAT(//," C NUMBER",3X,"BPF",8X,"BPC",
```

```
      111X,"RT",8X,"VOL PC",5X,"AC VOL")
       DO 55 I=1,ITEM
       CN=I+7
       CX=ITEM+7
       IF(CN.GT.CX)GO TO 55
       WRITE(6,46)CN,TEMP(I),TEMPC(I),RTT(I),
      1WTEM(I),WTEC(I)
 46    FORMAT(2X,I2,4X,F8.2,4X,F8.2,4XF8.2,4X,F8.2,
      14X,F8.2)
 55    CONTINUE
       WRITE(6,52)WHEY
 52    FORMAT(/," WHEY",39X,F8.2,7X,"100.0")
       WRITE(6,53)PF
 53    FORMAT(/,"VOL % OF(650-975F) FRACTION =",2X,
      1F5.2)
 C
 C
 C     ESTIMATE AVERAGE MOLECULAR WEIGHTS
 C
 C
 C     MASS AVERAGING METHOD
 C     MOLECULAR WEIGHT OBTAINED BASED ON
 C     MASS AVERAGING USING MOLECULAR WEIGHTS
 C     OF N-PARAFFINS WITH THE SAME BOILING
 C     POINT RANGE AS THE INDIVIDUAL FRACTIONS
 C     IN THE SAMPLE
 C
 C
 C     SET INITIAL VALUES
 C
       SUM1=0.0
       SUM2=0.0
       SUM3=0.0
       SUM4=0.0
       WTEM(38)=WHEY
 C
 C     COMPUTE
 C
       DO 600 I=1,38
       MWT1(I)=WTEM(I)*DENSI(I)*MWT(I)
       MWT2(I)=WTEM(I)*DENSI(I)
       SUM1=SUM1+MWT1(I)
 600   SUM2=SUM2+MWT2(I)
       AMWT=SUM1/SUM2
       DO 602 I=14,33
       MWT1(I)=WTEM(I)*DENSI(I)*MWT(I)
       MWT2(I)=WTEM(I)*DENSI(I)
       SUM3=SUM3+MWT1(I)
 602   SUM4=SUM4+MWT2(I)
       PMWT=SUM3/SUM4
       PWT=SUM4/SUM2*100.0
 C
 C     PRINT AVERAGE MOL.WT. FOR SAMPLE
 C
```

```
      WRITE(OUNIT,601)AMWT
      WRITE(OUNIT,603)PMWT
      WRITE(OUNIT,604)PWT
601   FORMAT(//,2X,'AVERAGE SAMPLE MOL.WT. = ',
     13X,F8.2)
603   FORMAT(/,2X,'AVERAGE PITCH MOL. WT.  =',
     13X,F8.2)
604   FORMAT(/,2X,'WEIGHT % PITCH = ',3X,F8.2)
C
C
C     ESTIMATE MASS/MOLAR FLOWRATES & MOLE FRACTION
            OF INDIVIDUAL NARROW BOILING RANGE
C                   FRACTION IN SAMPLE
C                     12 FRACTIONS
C
C
      SUM = 0.0
      DO 611 I=1,12
      IF(I.NE.1) GO TO 606
      MAFR(I)=0.6838*WTEM(I)*PFR/100.0
      MOFR(I)=MAFR(I)/100.21
      GO TO 605
606   IF(I.NE.2) GO TO 607
      J=I+1
      GO TO 615
607   IF(I/EQ.12) GO TO 608
      J=J+3
615
615   VOLF=WTEM(J-1)+WTEM(J)+WTEM(J+1)
      MAFR(I)=DENSI(J)*VOLF*PFR/100.0
      MOFR(I)=MAFR(I)/MWT(J)
      GO TO 605
608   VOLF=0.0
      DO 610 J=32,37
      VOLF=VOLF+WTEM(J)
610   CONTINUE
      VOLF=VOLF+WHEY
      MAFR(I)=DENSI(36)*VOLF*PFR/100.0
      MOFR(I)=MAFR(I)/MWT(36)
605   SUM=SUM+MOFR(I)
611   CONTINUE
      DO 612 I=1,12
      MFR(I)=MOFR(I)/SUM
612   CONTINUE
      WRITE(OUNIT,616)PFR
616   FORMAT(/,1X,'PRODUCT LIQUID FLOWRATE =',F8.4,
     12X,' ML/MIN')
      WRITE(OUNIT,609)
609   FORMAT("1",2X,"FRACTION NO.",3X,"GM/MIN.",
     13X,"MOL/MIN.",3X,"MOL.FRAC")
      DO 614 I=1,12
      WRITE(OUNIT,613)I,MAFR(I),MOFR(I),MFR(I)
613   FORMAT (2X,I2,9X,F9.7,4X,F9.7,4X,F9.7)
614   CONTINUE
```

```
      WRITE(OUNIT,617)
617   FORMAT("1")
C
C     INPUT/OUTPUT CONTROL
C
      LUNIT=OUNIT
      IF(OUNIT.EQ.6)LUNIT=LU
      IF(OUNIT.EQ.17.OR.OUNIT.EQ.18)LUNIT=LU
      WRITE(LUNIT,200)
200   FORMAT(//,"  ANOTHER RUN? Y - 1  N - 2")
      READ(LUNIT,*)IFLAG
      IF(IFLAG-1)999,201,999
201   WRITE(LUNIT,102)
102   FORMAT(//,"ALTER I/O SETTING: Y - 1  N - 2")
      READ(LUNIT,*)IO
      IF(IO-1)888,202,888
202   WRITE(LUNIT,103)
103   FORMAT(//,"  ENTER DESIRED INPUT TERMINAL NUMBER.",/,
     1"  CARD READER - 5   TERMINAL - NN.")
      READ(LUNIT,*)NEWI
      WRITE(LUNIT,104)
104   FORMAT(//,"ENTER DESIRED OUTPUT TERMINAL",
     1"NUMBER.",/,"LINEPRINTER - 6 TERMINAL - 1")
      READ(LUNIT,*)NEWO
      IF(NEWI.EQ.6.OR.NEW.EQ.5) GO TO 202
      IUNIT=NEWI
      OUNIT=NEWO
888   LU=LUNIT
      IF(IUNIT.EQ.5) GO TO 206
      IF(IUNIT.EQ.17.OR.IUNIT.EQ.18) GO TO 99
188   WRITE(LUNIT,221)
221   FORMAT(//,"ENTER 1 IF TERMINAL IS READY")
      READ(LUNIT,*)ITERM
      IF(ITERM-1)188,163,188
163   LU=NEWI
      GO TO 162
999   STOP
      END
```

PROGRAM &RATE1 LISTINGS

```
      FTN
      PROGRAM RATE1 () ,         S.Y.K. CHUNG
C
C     THIS PROGRAM CALCULATES THE CONCENTRATIONS
C     OF THE PITCH FRACTION (650 - 975 F CUT)
C     IN VARIOUS LIQUID SAMPLES FOR USE IN THE
C     RATE EQUATION FOR THE CONVERSION OF
C     PITCH.
C
C
C     INITIATION
C
      INTEGER LU(5), SAMPLE (20),N
      REAL FR (2), DENSI(4), WFRAC(3),MWT(3),
     1CONC(4)
      REAL MG,ML,MH2S,MH2,MASS,CONV
C
C     INPUT DATA
C
      CALL RMPAR(LU)
100   WRITE(LU,1)
      READ(LU,107)(SAMPLE(I),I=1,20)
107   FORMAT(20A2)
      WRITE(LU,2)
      READ(LU,*)FR(1),FR(2)
      WRITE(LU,3)
      READ(LU,*)(MWT(I),I=1,3)
      WRITE(LU,4)
      READ(LU,*)(DENSI(I),I=1,3)
      WRITE(LU,5)
      READ(LU,*)(WFRAC(I),I=1,3)
      WRITE(LU,6)
      READ(LU,*)P1,T1,P2,T2,SWT,V
      WRITE(LU,7)
      READ(LU,*)H2F,H2OIL
      WRITE(LU,9)
      READ(LU,*)VG
C
C     COMPUTE
C
      MG=(VG*P1*1.60345E-5)/(273.15+T1)
      MH2=H2F*MG
      DO 200 I=1,3
      CONC(I)=DENSI(I)*WFRAC(I)/MWT(I)
200   CONTINUE
      CONC(4)=MH2*DENSI(3)/SWT
      RATE=(FR(1)*CONC(1)-FR(2)*CONC(2))
C
C     CALCULATE MOLAR CONVERSION OF
C     PITCH
C
      CONV=(RATE/FR(1)/CONC(1))*100.0
C
```

```
C     ESTIMATE RATE CONSTANT BASED ON 1ST
C     ORDER REACTION
C
      CONST1=RATE/CONC(3)/V
C
C     ESTIMATE RATE CONSTANT BASED ON
C     2ND ORDER REACTION
C
      CONST2=RATE/CONC(3)/CONC(4)/V
      WRITE(LU,10)
      READ(LU,*)IOUT
      WRITE(LU,11)
      READ(LU,*)N
C
C     PRINT OUTPUT
C
300   WRITE(IOUT,50)N
      WRITE(IOUT,49)
      WRITE(IOUT,51)(SAMPLE(I),I=1,20)
      WRITE(IOUT,65)P2,T2
      WRITE(IOUT,70)FR(1)
      WRITE(IOUT,71)FR(2)
      WRITE(IOUT,72)H2OIL
      WRITE(IOUT,108)V
      WRITE(IOUT,73)
      WRITE(IOUT,74)
      WRITE(IOUT,75)(MWT(I),I=1,3)
      WRITE(IOUT,76)(DENSI(I),I=1,3)
      WRITE(IOUT,77)(WFRAC(I),I=1,3)
      WRITE(IOUT,78)SWT
      WRITE(IOUT,52)CONC(1)
      WRITE(IOUT,53)CONC(2)
      WRITE(IOUT,54)CONC(3)
      WRITE(IOUT,55)CONC(4)
      WRITE(IOUT,56)RATE
      WRITE(IOUT,61)CONV
      WRITE(IOUT,57)CONST1
      WRITE(IOUT,58)CONST2
      WRITE(IOUT,120)
C
C     I/O FORMATTING
C
1     FORMAT(/, "ENTER RUN NUMBER - 40 CHAR. MAX")
2     FORMAT(,  "ENTER LIQ. FEED & LIQ.PROD.",
     1"RATE - 2 VALUES")
3     FORMAT(/, "ENTER AV.MOL.WT.,FEED PITCH,",
     1"PROD.PITCH, REACTOR LIQ.PITCH - 3 VALUES")
4     FORMAT(/, "ENTER LIQ. DENSITY FOR FEED,",
     1"PRODUCT, REACTOR LIQ. AT REACT. COND. - 3 VALUES")
5     FORMAT(/, "ENTER PITCH WT. FRACTIONS
     1FEED,PROD.,REACTOR","LIQ., - 3 VALUES")
6     FORMAT(/, "ENTER AMBIENT PRESSURE(MM.HG),",
     1"TEMP.(C),REACTOR, PRESSURE(MPA),TEMP.(C),",
     1"SAMPLE WT.(G), REACT. LIQ. HOLDUP(ML) - 6 VALUES")
```

```
 7     FORMAT(/, "ENTER MOLE FRACTION H2 IN GAS",
      1"DISSOLVED IN REACTOR LIQ., H2/OIL",
      1"FEED RATIO (M3API/M3OIL)")
 9     FORMAT(/, "ENTER MEASURED VOL. OF GAS",
      1"DISSOLVED IN REACTOR LIQ. AT REACTOR",
      1"CONDITIONS")
 10    FORMAT(/, "ENTER DESIRED OUTPUT UNIT")
 11    FORMAT(/, "ENTER PAGE NO. MAX.=99")
 49    FORMAT(5X,18"=")
 50    FORMAT(///,5X,"HYDROCRACKING DATA",30X,
      1"PAGE NO. ",I2)
 51    FORMAT(//,5X,"RUN NUMBER : ",3X,20A2)
 52    FORMAT(///,5X,"PITCH CONC. IN LIQ. ",
      1"FEED =",F10.8," GMOL/ML")
 53    FORMAT(/,5X,"PITCH CONC. IN LIQ. PROD.",
      1"=",F10.8," GMOL/ML")
 54    FORMAT(/,5X,"PITCH CONC. IN REACT.LIQ.=",
      1F10.8," GMOL/ML")
 55    FORMAT(/,5X,"H2 CONC. IN REACTOR LIQ.=",
      1F10.8," GMOL/ML")
 56    FORMAT(//,5X,"RATE OF PITCH CONVERSION =",
      1F10.8," GMOL/MIN")
 61    FORMAT(/////,5X,"PITCH CONVERSION, %      =",
      1F8.4)
 57    FORMAT(/,5X,"RATE CONST. (1ST ORDER EQN.) = ",
      1F10.8," /MIN.")
 58    FORMAT(/,5X,"RATE CONS[illegible]ORDER EQN.)  = ",
      1F10.8," ML/MOL./MIN.",/[illegible]
 65    FORMAT(//,5X"PRESSURE =[illegible].1,
      1" MPA,     TEMP. =",F6.1," C")
 70    FORMAT(/,5X "LIQUID FEED RATE   =",
      1F8.2,3X,"ML/MIN.")
 71    FORMAT(/,5X,"LIQUID PRODUCT RATE  =",
      1F8.2,3X,"ML/MIN.")
 72    FORMAT(/,5X,"H2/OIL FEED RATIO  =",
      1F8.2,3X,"M3API/M3OIL")
 73    FORMAT(//,21X,"FEED SAMPLE",4X,"LIQ. PRODUCT",
      14X,"REACTOR LIQ.")
 74    FORMAT(21X,11"-",4X,11"-",4X,12"-")
 75    FORMAT(/,5X,"PITCH AV.MOL.WT.",F10.2,
      15X,F10.2,5X,F10.2,3X,"G/MOL.")
 76    FORMAT(/,5X,"SAMPLE DENSITY ",F10.4,
      15X,F10.4,5X,F10.4,3X,"G/ML 23.0 C")
 77    FORMAT(/,5X,"WT. FRACT. PITCH",F10.4,
      15X,F10.4,5X,F10.4)
 78    FORMAT(/,5X,"SAMPLE WT.     ",30X,
      1F10.4,3X,"G",///)
 108   FORMAT(/,5X,"LIQ. HOLDUP VOL.    =",
      1F8.2,3X,"ML")
 120   FORMAT("1")
       WRITE(LU,59)
C
C      I/O CONTROL
C
```

```
      READ(LU,*)JFLAG
      IF(JFLAG.EQ.1)GO TO 300
59    FORMAT(12/,"ANOTHER LISTING OF RESULTS ?",
     1"1 - Y  2 - N")
      WRITE(LU,60)
      READ(LU,*)IFLAG
      IF(IFLAG.EQ.1)GO TO 100
60    FORMAT("ANOTHER RUN ? 1-YES  2-NO")
      STOP
      END
```

PROGRAM &PGA LISTINGS

```
      FTN4
      PROGRAM PGA (),      S.Y.K. CHUNG
C
C     THIS PROGRAM PROCESS PRODUCT GAS ANALYSIS DATA
C
C     VARIABLES:
C         C(I)       = COMPONENT
C         FLOW(I)    = MOLAR FOW RATE OF H2S AND
C                      NH3, MOLE/MIN
C         FRAHC(I)   = MOLAR FRACTION OF EACH
C                      COMPONENT IN HYDROCARBON
C         MW(I)      = MOLECULAR WEIGHT OF EACH
C                      COMPONENT
C         PF         = PRODUCT GAS FLOW RATE,L/MIN
C         PTC        = PRODUCT GAS TEMPERATURE,DEG C
C         PP         = PRODUCT GAS PRESSURE, MM HG
C         V(I)       = VOLUME FLOW RATE OF EACH
C                      COMPONENT, L/MIN
C         VPER(I)    = VOLUME % OF EACH COMPONENT
C         W(I)       = WEIGHT % OF EACH COMPONENT
C         WF(I)      = WEIGHT FLOW RATE OF EACH
C                      COMPONENT
C         MF(I)      = MOLAR FLOW RATE OF EACH
C                      COMPONENT
C
C
C     FUNCTION:
C     1. COMBINES REFINERY GAS ANALYSIS DATA WITH
C        H2S FLOWRATE DATA AS OBTAINED FROM THE
C        ABSORPTION-IODIMETRIC METHOD
C     2. CORRECTS FLOW DATA TO STP CONDITIONS
C     3. GENERATES THE GAS PRODUCT COMPOSITION
C        IN A REPORT FORM
C
C
C     INITIATION
C
      REAL MW(9), VH2(9), WH2(9), V(9), VPER(9),
     1W(9), WF(9), FLOW(9)
      REAL FRAHC(9), MF(9)
      INTEGER C (18),LU(5),SAMPLE(20)
      DATA MW/2,016,16,04,30,07,44.10,58.12,72.15,
     186.18,34.08,17.03/
      DATA C/2HH2,2H  ,2HC1,2H  ,2HC2,2H  ,
     12HC3,2H  ,2HC4,2H  ,2HC5,2H  ,2HC6,2H  ,
     12HH2,2HS  ,2HNH,2H3 /
C
C     INPUT DATA
C
      CAL RMPAR(LU)
 999  WRITE(LU,1)
      READ(LU,107)(SAMPLE(I),I=1,20)
 107  FORMAT(20A2)
```

```
      WRITE(LU,2)
      READ(LU,*)PF
      WRITE(LU,3)
      READ(LU,*)PP,PTC
      WRITE(LU,4)
      DO 100 I=1,7
      READ(LU,*)FRAHC(I)
100   CONTINUE
      WRITE(LU,16)
      READ(LU,*)FLOW(1)
      READ(LU,*)FLOW(2)
C
C     RESET INITIAL VALUES
C
      WT=0.0
      VH2(7)=0.0
      WH2(7)=0.0
      PTF=PTC*1.8+32.0
C
C     CONVERSION OF FLOW RATE TO STP
C     (760MM HG & 60 DEG F)
C
      PFSTP=(PF*PP*520.)/760./(460.+PTF)
C
C     CONVERTING MOLAR FLOW RATE OF H2S &
C     NH3 TO VOLUME FLOW RATE
C
      V(8)=FLOW(1)*62.36*288.5/760.
      V(9)=FLOW(2)*62.36*288.5/760
      VHC=PFSTP-V(8)-V(9)
C
C     VOLUME FLOW RATE OF HYDROCARBONS
C     AND HYDROGEN
C
      DO 106 I=1,7
      V(I)=VHC=FRAHC(I)/100.
106   CONTINUE
C
C     CONVERSION FACTOR OF VOLUME FLOW RATE
C     TO MASS & MOLAR FLOW RATES
C
      WFAC=760./62.36/288.5
      DO 101 I=1,9
      WF(I)=WFAC*V(I)*MW(I)
      MF(I)=WFAC*V(I)
      WT=WT+WF(I)
      VPER(I)=V(I)*100//PFSTP
101   CONTINUE
      DO 102 I=1,9
      W(I)=WF(I)*100./WT
102   CONTINUE
C
C
C     ANALYSIS ON A H2-FREE BASIS
```

```
C
      WT2=WT-WF(1)
      VT2=PFSTOP-V(1)
      DO 103 I=2,9
      VH2(I)=V(I)*100./VT2
      WH2(I)=WF(I)*100./WT2
  103 CONTINUE
      WRITE(LU,5)
      READ(LU,*)IOUT
C
C     OUTPUT
C
      WRITE(IOUT,6)
      WRITE(IOUT,7)
      WRITE(IOUT,8)
      WRITE(IOUT,7)
      WRITE(IOUT,15)
      WRITE(IOUT,9)(SAMPLE(I),I=1,20)
      WRITE(IOUT,10)
      DO 104 I=1,9
      J1=I*2
      J=J1-1
      WRITE(IOUT,11))C(J),C(J1),VPER(I),
     1V(I),MW(I),WF(I),W(I),MF(I)
  104 CONTINUE
      WRITE(IOUT,12)PFSTP.WT
      WRITE(IOUT,13)
      DO 105 I=2,9
      J1=I*2
      J=J1-L
      WRITE(IOUT,11)C(J),C(J1),VH2(I),V(I),
     1MW(I),WF(I),WH2(I),MF(I)
  105 CONTINUE
      WRITE(IOUT,12) VT2,WT2
C
C     I/O FORMATTING AND CONTROL
C
      WRITE(LU,14)
      READ(LU,*)IFLAG
      IF(IFLAG.EQ.1)GO TO 999
    1 FORMAT(//," ENTER RUN NUMBER, 40 CHAR.MAX")
    2 FORMAT(//," ENTER GAS FLOW RATE. L/MIN")
    3 FORMAT(//," ENTER MEASURED PRESSURE MMHG,",
     1"AND TEMP. DEG C.")
    4 FORMAT(//," ENTER MOLAR FLOW RATE OF EACH",
     1" COMPONENT IN THE ORDER OF H2,C1,C2,C3,C4,C5,C6")
    5 FORMAT(//," ENTER DESIRED OUTPUT UNIT.")
    6 FORMAT(1H1,//,20X,29"*")
    7 FORMAT(20X,"*",27X,"*")
    8 FORMAT(20X,"*",2X,"ANALYSIS OF GAS",
     1"PRODUCT",2X,"*")
    9 FORMAT(//,3X,"RUN NUMBER :",5X,20A2,//)
   10 FORMAT(3X,"COMPONENT",3X,"VOLUME",5X,
     1"VOLUME",5X,"MOLECULAR",4X,"WEIGHT",5X,
```

```
      1"WEIGHT",6X,"MOLAR",/,
      115X,"PERCENT",3X,"FLOW RATE",4X,"WEIGHT",
      15X,"FLOW RATE",3X,"PERCENT",3X,"FLOW RATE",
      1/,26X,"(L[illegible]IN)",17X,"(GM/MIN)",16X,
      1"(GMOL/MIN)",//)
 11    FORMAT(3X,2A2,8X,F7.4,3X,E10.5,4X,F5.2,
      14X,E10.5,4X,F7.4,2X,E10.5)
 12    FORMAT(/,3X,"TOTAL",18X,F7.4,16X,F8.5,/)
 13    FORMAT(3X,"ANALYSIS ON A HYDROGEN-FREE BASIS",/)
 15    FORMAT(20X,29"*")
 14    FORMAT(//," ANOTHER RUN ? 1-YES  2-NO")
 16    FORMAT(//," ENTER MOLAR FLOW RATE OF",
      1"H2S & NH3.  MOLE/MIN")
       STOP
       END
```

APPENDIX F - Experimental Results

HYDROCRACKING DATA

Run No. : LL-05
Run Type : Thermal Hydrocracking
Feedstock: LLVGO

Process Data

Pressure = 13.9 MPa Temperature = 420.0 C
Liquid Feedrate = 3.75 mL/min
Liquid Product Rate = 3.75 mL/min
H2/OIL Feed Ratio = 225.70 M3API/M3OIL
Liquid Holdup Vol. = 296.90 mL (at 420 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	379.17	361.81	365.93
S.G. (g/mL)	0.9174	0.8967	0.6308
Pitch Wt.Frac.	0.6100	0.4100	0.5000
Sample Wt. (g)			14.116

Computed Results

Pitch Conc. in Liq.Feed = 0.00147589 mol/mL
Pitch Conc. in Liq.Prod. = 0.00101613 mol/mL
Pitch Conc. in Reactor Liq. = 0.00086191 mol/mL
H2 Conc. in Reactor Liq. = 0.00065867 mol/mL

Rate of Pitch Conversion = 0.00000581 mol/mL/min
Pitch Conversion, % = 31.1513

Rate Const.(1st Order Eqn.) = 0.00673733 /min
Rate Const.(2nd Order Eqn.) = 10.2286870 mL/mol/min

Sulphur Conversion, % = 16.38

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No.: LL-06 Thermal Run
Run Type : Thermal Hydrocracking
Feedstock: LLVGO

Process Data

Pressure = 13.9 MPa Temperature = 440.0 C
Liquid Feedrate = 3.75 mL/min
Liquid Product Rate = 3.75 mL/min
H2/OIL Feed Ratio = 198.60 M3API/M3OIL
Liquid Holdup Vol. = 274.10 mL (at 440 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	379.17	355.78	363.51
S.G. (g/mL)	0.9174	0.8686	0.6514
Pitch Wt.Frac.	0.6100	0.2124	0.3765
Sample Wt. (g)			7.9110

Computed Results

Pitch Conc. in Liq.Feed = 0.00147589 mol/mL
Pitch Conc. in Liq.Prod. = 0.00051855 mol/mL
Pitch Conc. in Reactor Liq. = 0.00067468 mol/mL
H2 Conc. in Reactor Liq. = 0.00068519 mol/mL

Rate of Pitch Conversion = 0.00001310 mol/mL/min
Pitch Conversion, % = 64.8651

Rate Const.(1st Order Eqn.) = 0.01941297 /min
Rate Const.(2nd Order Eqn.) = 28.3321950 mL/mol/min

Sulphur Conversion, % = 27.99

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No.: LL-07 Thermal Run
Run Type : Thermal Hydrocracking
Feedstock: LLVGO

Process Data

Pressure = 13.9 MPa   Temperature = 420.0 C
Liquid Feedrate = 3.75 mL/min
Liquid Product Rate = 3.75 mL/min
H2/OIL Feed Ratio = 210.80 M3API/M3OIL
Liquid Holdup Vol. = 275.10 mL (at 420 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	379.17	371.17	372.14
S.G. (g/mL)	0.9170	0.8965	0.6247
Pitch Wt.Frac.	0.6100	0.4301	0.4746
Sample Wt. (g)			14.116

Computed Results

Pitch Conc. in Liq.Feed = 0.00147525 mol/mL
Pitch Conc. in Liq.Prod. = 0.00103884 mol/mL
Pitch Conc. in Reactor Liq. = 0.00079670 mol/mL
H2 Conc. in Reactor Liq. = 0.00064753 mol/mL

Rate of Pitch Conversion = 0.00000595 mol/mL/min
Pitch Conversion, % = 29.5823

Rate Const.(1st Order Eqn.) = 0.00746699 /min
Rate Const.(2nd Order Eqn.) = 11.5314290 mL/mol/min

Sulphur Conversion, % = 16.36

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : LL-08
Run Type : Thermal Hydrocracking
Feedstock : CLVGO

Process Data

Pressure = 13.9 MPa   Temperature = 440.0 C
Liquid Feedrate = 3.75 mL/min
Liquid Product Rate = 3.75 mL/min
H2/OIL Feed Ratio = 215.50 M3API/M3OIL
Liquid Holdup Vol. = 262.10 mL (at 440 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	375.32	360.44	365.93
S.G. (g/mL)	0.9159	0.8763	0.6203
Pitch Wt.Frac.	0.6500	0.2624	0.3635
Sample Wt. (g)			6.0060

Computed Results

Pitch Conc. in Liq.Feed = 0.00158621 mol/mL
Pitch Conc. in Liq.Prod. = 0.00063795 mol/mL
Pitch Conc. in Reactor Liq. = 0.00061618 mol/mL
H2 Conc. in Reactor Liq. = 0.00071956 mol/mL

Rate of Pitch Conversion = 0.00001357 mol/mL/min
Pitch Conversion, % = 59.7817

Rate Const.(1st Order Eqn.) = 0.02201831 /min
Rate Const.(2nd Order Eqn.) = 30.5995790 mL/mol/min

Sulphur Conversion, % = 21.47

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : LL-10
Run Type : Thermal Hydrocracking
Feedstock: LLVGO

Process Data

Pressure = 13.9 MPa Temperature = 400.0 C
Liquid Feedrate = 3.75 mL/min
Liquid Product Rate = 3.75 mL/min
H2/OIL Feed Ratio = 304.10 M3API/M3OIL
Liquid Holdup Vol. = 274.10 mL (at 400 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	369.24	365.83	368.48
S.G. (g/mL)	0.9191	0.9090	0.6517
Pitch Wt.Frac.	0.6000	0.5173	0.5490
Sample Wt. (g)			14.123

Computed Results

Pitch Conc. in Liq.Feed = 0.00149350 mol/mL
Pitch Conc. in Liq.Prod. = 0.00128537 mol/mL
Pitch Conc. in Reactor Liq. = 0.00097097 mol/mL
H2 Conc. in Reactor Liq. = 0.00076348 mol/mL

Rate of Pitch Conversion = 0.00000285 mol/mL/min
Pitch Conversion, % = 13.9360

Rate Const.(1st Order Eqn.) = 0.00293264 /min
Rate Const.(2nd Order Eqn.) = 3.84112690 mL/mol/min

Sulphur Conversion, % = 11.53

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : LL-11
Run Type : Thermal Hydrocracking
Feedstock: LLVGO

Process Data

Pressure = 13.9 MPa Temperature = 400.0 C
Liquid Feedrate = 4.92 mL/min
Liquid Product Rate = 4.92 mL/min
H2/OIL Feed Ratio = 254.50 M3API/M3OIL
Liquid Holdup Vol. = 267.50 mL (at 400 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	372.10	366.24	366.77
S.G. (g/mL)	0.9171	0.9081	0.6499
Pitch Wt.Frac.	0.6100	0.5288	0.5684
Sample Wt. (g)			30.168

Computed Results

Pitch Conc. in Liq.Feed = 0.00150344 mol/mL
Pitch Conc. in Liq.Prod. = 0.00131117 mol/mL
Pitch Conc. in Reactor Liq. = 0.00100718 mol/mL
H2 Conc. in Reactor Liq. = 0.00069876 mol/mL

Rate of Pitch Conversion = 0.00000354 mol/mL/min
Pitch Conversion, % = 12.7888

Rate Const.(1st Order Eqn.) = 0.00351115 /min
Rate Const.(2nd Order Eqn.) = 5.02483180 mL/mol/min

Sulphur Conversion, % = 4.99

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : LL-12
Run Type : Thermal Hydrocracking
Feedstock : LLVGO

Process Data

Pressure = 13.9 MPa Temperature = 420.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 5.00 mL/min
H2/OIL Feed Ratio = 240.40 M3API/M3OIL
Liquid Holdup Vol. = 279.80 mL (at 420 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	368.39	364.52	366.10
S.G. (g/mL)	0.9172	0.9062	0.6295
Pitch Wt.Frac.	0.6050	0.4318	0.4967
Sample Wt. (g)			12.498

Computed Results

Pitch Conc. in Liq.Feed = 0.00150630 mol/mL
Pitch Conc. in Liq.Prod. = 0.00107346 mol/mL
Pitch Conc. in Reactor Liq. = 0.00085406 mol/mL
H2 Conc. in Reactor Liq. = 0.00068446 mol/mL

Rate of Pitch Conversion = 0.00000773 mol/mL/min
Pitch Conversion, % = 28.7354

Rate Const.(1st Order Eqn.) = 0.00905651 /min
Rate Const.(2nd Order Eqn.) = 13.2316060 mL/mol/min

Sulphur Conversion, % = 16.83

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : LL-13
Run Type : Thermal Hydrocracking
Feedstock: LLVGO

Process Data

Pressure = 13.9 MPa Temperature = 440.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 5.00 mL/min
H2/OIL Feed Ratio = 298.80 M3API/M3OIL
Liquid Holdup Vol. = 252.50 mL (at 440 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	381.59	359.46	367.23
S.G. (g/mL)	0.9172	0.8937	0.6511
Pitch Wt.Frac.	0.6418	0.2756	0.4343
Sample Wt. (g)			12.366

Computed Results

Pitch Conc. in Liq.Feed = 0.00154265 mol/mL
Pitch Conc. in Liq.Prod. = 0.00068520 mol/mL
Pitch Conc. in Reactor Liq. = 0.00077002 mol/mL
H2 Conc. in Reactor Liq. = 0.00065867 mol/mL

Rate of Pitch Conversion = 0.00001698 mol/mL/min
Pitch Conversion, % = 55.5826

Rate Const.(1st Order Eqn.) = 0.02205029 /min
Rate Const.(2nd Order Eqn.) = 31.3017850 mL/mol/min

Sulphur Conversion, % = 22.86

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : LL-14
Run Type : Thermal Hydrocracking
Feedstock: LLVGO

Process Data

Pressure = 13.9 MPa Temperature = 400.0 C
Liquid Feedrate = 7.50 mL/min
Liquid Product Rate = 7.50 mL/min
H2/OIL Feed Ratio = 187.10 M3API/M3OIL
Liquid Holdup Vol. = 281.90 mL (at 400 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	377.22	367.98	368.17
S.G. (g/mL)	0.9176	0.9126	0.6483
Pitch Wt.Frac.	0.6235	0.5424	0.5582
Sample Wt. (g)			14.095

Computed Results

Pitch Conc. in Liq.Feed = 0.00151668 mol/mL
Pitch Conc. in Liq.Prod. = 0.00134517 mol/mL
Pitch Conc. in Reactor Liq. = 0.00098292 mol/mL
H2 Conc. in Reactor Liq. = 0.00063105 mol/mL

Rate of Pitch Conversion = 0.00000456 mol/mL/min
Pitch Conversion, % = 11.3088

Rate Const.(1st Order Eqn.) = 0.00464257 /min
Rate Const.(2nd Order Eqn.) = 7.35688020 mL/mol/min

Sulphur Conversion,% = 3.79

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : LL-15
Run Type : Thermal Hydrocracking
Feedstock: LLVGO

Process Data

Pressure = 13.9 MPa Temperature = 460.0 C
Liquid Feedrate = 3.75 mL/min
Liquid Product Rate = 3.75 mL/min
H2/OIL Feed Ratio = 388.50 M3API/M3OIL
Liquid Holdup Vol. = 200.30 mL (at 460 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	371.76	347.71	367.63
S.G. (g/mL)	0.9176	0.8747	0.7275
Pitch Wt.Frac.	0.6095	0.1518	0.3467
Sample Wt. (g)			10.149

Computed Results

Pitch Conc. in Liq.Feed = 0.00150440 mol/mL
Pitch Conc. in Liq.Prod. = 0.00038187 mol/mL
Pitch Conc. in Reactor Liq. = 0.00068608 mol/mL
H2 Conc. in Reactor Liq. = 0.00050010 mol/mL

Rate of Pitch Conversion = 0.00002102 mol/mL/min
Pitch Conversion, % = 74.6166

Rate Const.(1st Order Eqn.) = 0.03063196 /min
Rate Const.(2nd Order Eqn.) = 61.2516940 mL/mol/min

Sulphur Conversion, % =

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : LL-16
Run Type : Thermal Hydrocracking
Feedstock: LLVGO

Process Data

Pressure = 13.9 MPa Temperature = 420.0 C
Liquid Feedrate = 7.50 mL/min
Liquid Product Rate = 7.39 mL/min
H2/OIL Feed Ratio = 309.90 M3API/M3OIL
Liquid Holdup Vol. = 286.90 mL (at 420 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	387.87	365.63	367.32
S.G. (g/mL)	0.9168	0.9056	0.6304
Pitch Wt.Frac.	0.6422	0.4680	0.5123
Sample Wt. (g)			12.635

Computed Results

Pitch Conc. in Liq.Feed = 0.00151795 mol/mL
Pitch Conc. in Liq.Prod. = 0.00115915 mol/mL
Pitch Conc. in Reactor Liq. = 0.00087922 mol/mL
H2 Conc. in Reactor Liq. = 0.00059213 mol/mL

Rate of Pitch Conversion = 0.00000982 mol/mL/min
Pitch Conversion, % = 24.7572

Rate Const.(1st Order Eqn.) = 0.01117365 /min
Rate Const.(2nd Order Eqn.) = 18.8701630 mL/mol/min

Sulphur Conversion, % = 14.83

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : LL-17
Run Type : Thermal Hydrocracking
Feedstock: LLVGO

Process Data

Pressure = 13.9 MPa Temperature = 440.0 C
Liquid Feedrate = 7.50 mL/min
Liquid Product Rate = 7.38 mL/min
H2/OIL Feed Ratio = 348.20 M3API/M3OIL
Liquid Holdup Vol. = 280.70 mL (at 440 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	371.46	360.67	366.45
S.G. (g/mL)	0.9171	0.9014	0.6287
Pitch Wt.Frac.	0.5893	0.3206	0.4426
Sample Wt. (g)			12.718

Computed Results

Pitch Conc. in Liq.Feed = 0.00145493 mol/mL
Pitch Conc. in Liq.Prod. = 0.00080126 mol/mL
Pitch Conc. in Reactor Liq. = 0.00075935 mol/mL
H2 Conc. in Reactor Liq. = 0.00071474 mol/mL

Rate of Pitch Conversion = 0.00001781 mol/mL/min
Pitch Conversion, % = 45.8092

Rate Const.(1st Order Eqn.) = 0.02345162 /min
Rate Const.(2nd Order Eqn.) = 32.8112640 mL/mol/min

Sulphur Conversion, % = 18.40

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : LL-18
Run Type : Thermal Hydrocracking
Feedstock: LLVGO

Process Data

Pressure = 13.9 MPa Temperature = 440.0 C
Liquid Feedrate = 3.75 mL/min
Liquid Product Rate = 3.59 mL/min
H2/OIL Feed Ratio = 526.20 M3API/M3OIL
Liquid Holdup Vol. = 277.30 mL (at 440 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	373.36	355.72	368.01
S.G. (g/mL)	0.9185	0.8892	0.6700
Pitch Wt.Frac.	0.5963	0.2375	0.4528
Sample Wt. (g)			12.2830

Computed Results

Pitch Conc. in Liq.Feed = 0.00146759 mol/mL
Pitch Conc. in Liq.Prod. = 0.00059388 mol/mL
Pitch Conc. in Reactor Liq. = 0.00082437 mol/mL
H2 Conc. in Reactor Liq. = 0.00083302 mol/mL

Rate of Pitch Conversion = 0.00001216 mol/mL/min
Pitch Conversion, % = 61.2600

Rate Const.(1st Order Eqn.) = 0.01474832 /min
Rate Const.(2nd Order Eqn.) = 17.7046280 mL/mol/min

Sulphur Conversion, % = 29.51

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : LL-19
Run Type : Thermal Hydrocracking
Feedstock: LLVGO

Process Data

Pressure = 13.9 MPa Temperature = 400.0 C
Liquid Feedrate = 3.75 mL/min
Liquid Product Rate = 3.74 mL/min
H2/OIL Feed Ratio = 343.60 M3API/M3OIL
Liquid Holdup Vol. = 274.60 mL (at 400 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	371.01	366.80	378.57
S.G. (g/mL)	0.9189	0.9105	0.6496
Pitch Wt.Frac.	0.6263	0.5154	0.5617
Sample Wt. (g)			13.537

Computed Results

Pitch Conc. in Liq.Feed = 0.00155119 mol/mL
Pitch Conc. in Liq.Prod. = 0.00127937 mol/mL
Pitch Conc. in Reactor Liq. = 0.00096384 mol/mL
H2 Conc. in Reactor Liq. = 0.00078166 mol/mL

Rate of Pitch Conversion = 0.00000376 mol/mL/min
Pitch Conversion, % = 17.7435

Rate Const.(1st Order Eqn.) = 0.00389969 /min
Rate Const.(2nd Order Eqn.) = 4.98898320 mL/mol/min

Sulphur Conversion, % = 9.96

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : LL-20
Run Type : Thermal Hydrocracking
Feedstock: LLVGO

Process Data

Pressure = 13.9 MPa Temperature = 420.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 5.00 mL/min
H2/OIL Feed Ratio = 367.90 M3API/M3OIL
Liquid Holdup Vol. = 283.10 mL (at 420 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	368.86	365.36	366.62
S.G. (g/mL)	0.9178	0.9038	0.6340
Pitch Wt.Frac.	0.5943	0.4469	0.5136
Sample Wt. (g)			13.002

Computed Results

Pitch Conc. in Liq.Feed = 0.00147874 mol/mL
Pitch Conc. in Liq.Prod. = 0.00110551 mol/mL
Pitch Conc. in Reactor Liq. = 0.00088817 mol/mL
H2 Conc. in Reactor Liq. = 0.00075140 mol/mL

Rate of Pitch Conversion = 0.00000659 mol/mL/min
Pitch Conversion, % = 25.2400

Rate Const.(1st Order Eqn.) = 0.00742187 /min
Rate Const.(2nd Order Eqn.) = 9.87739180 mL/mol/min

Sulphur Conversion, % = 13.58

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : LL-21
Run Type : Thermal Hydrocracking
Feedstock: LLVGO

Process Data

Pressure = 13.9 MPa   Temperature = 440.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 4.83 mL/min
H2/OIL Feed Ratio = 587.80 M3API/M3OIL
Liquid Holdup Vol. = 258.60 mL (at 440 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	368.77	353.13	366.69
S.G. (g/mL)	0.9169	0.8944	0.6639
Pitch Wt.Frac.	0.5969	0.2654	0.4700
Sample Wt. (g)			11.674

Computed Results

Pitch Conc. in Liq.Feed = 0.00148412 mol/mL
Pitch Conc. in Liq.Prod. = 0.00067220 mol/mL
Pitch Conc. in Reactor Liq. = 0.00085094 mol/mL
H2 Conc. in Reactor Liq. = 0.00081935 mol/mL

Rate of Pitch Conversion = 0.00001614 mol/mL/min
Pitch Conversion, % = 56.2471

Rate Const.(1st Order Eqn.) = 0.01896740 /min
Rate Const.(2nd Order Eqn.) = 23.1493490 mL/mol/min

Sulphur Conversion, % = 26.32

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : LL-22
Run Type : Thermal Hydrocracking
Feedstock: LLVGO

Process Data

Pressure = 13.9 MPa   Temperature = 400.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 5.00 mL/min
H2/OIL Feed Ratio = 271.10 M3API/M3OIL
Liquid Holdup Vol. = 273.60 mL (at 400 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	368.51	365.08	367.56
S.G. (g/mL)	0.9175	0.9134	0.6544
Pitch Wt.Frac.	0.5939	0.5192	0.5705
Sample Wt. (g)			14.513

Computed Results

Pitch Conc. in Liq.Feed = 0.00147867 mol/mL
Pitch Conc. in Liq.Prod. = 0.00129900 mol/mL
Pitch Conc. in Reactor Liq. = 0.00101571 mol/mL
H2 Conc. in Reactor Liq. = 0.00073732 mol/mL

Rate of Pitch Conversion = 0.00000328 mol/mL/min
Pitch Conversion, % = 12.1509

Rate Const.(1st Order Eqn.) = 0.00323266 /min
Rate Const.(2nd Order Eqn.) = 4.38431840 mL/mol/min

Sulphur Conversion, % = 7.77

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : LL-23
Run Type : Thermal Hydrocracking
Feedstock: 50 - 50 Vol.% LLVGO - EMRGO Blend

Process Data

Pressure = 13.9 MPa Temperature = 450.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 4.82 mL/min
H2/OIL Feed Ratio = 702.30 M3API/M3OIL
Liquid Holdup Vol. = 247.70 mL (at 450 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	360.77	338.68	365.04
S.G. (g/mL)	0.9154	0.8926	0.6998
Pitch Wt.Frac.	0.5190	0.1409	0.4947
Sample Wt. (g)			13.417

Computed Results

Pitch Conc. in Liq.Feed = 0.00131688 mol/mL
Pitch Conc. in Liq.Prod. = 0.00037135 mol/mL
Pitch Conc. in Reactor Liq. = 0.00094836 mol/mL
H2 Conc. in Reactor Liq. = 0.00081992 mol/mL

Rate of Pitch Conversion = 0.00001936 mol/mL/min
Pitch Conversion, % = 72.8164

Rate Const.(1st Order Eqn.) = 0.02041012 /min
Rate Const.(2nd Order Eqn.) = 24.8927880 mL/mol/min

Sulphur Conversion, % = 33.0

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : LL-24
Run Type : Thermal Hydrocracking
Feedstock: 75 - 25 Vol.% LLVGO - EMRGO Blend

Process Data

Pressure = 13.9 MPa Temperature = 450.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 4.97 mL/min
H2/OIL Feed Ratio = 849.90 M3API/M3OIL
Liquid Holdup Vol. = 260.90 mL (at 450 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	356.38	342.49	369.06
S.G. (g/mL)	0.9159	0.8982	0.7122
Pitch Wt.Frac.	0.5629	0.1603	0.5495
Sample Wt. (g)			14.222

Computed Results

Pitch Conc. [illegible] Liq.Feed = 0.00144666 mol/mL
Pitch Conc. in Liq.Prod. = 0.00042020 mol/mL
Pitch Conc. in Reactor Liq. = 0.00106041 mol/mL
H2 Conc. in Reactor Liq. = 0.00071917 mol/mL

Rate of Pitch Conversion = 0.00001972 mol/mL/min
Pitch Conversion, % = 71.1145

Rate Const.(1st Order Eqn.) = 0.01859292 /min
Rate Const.(2nd Order Eqn.) = 25.8532410 mL/mol/min

Sulphur Conversion, % = 34.5

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : LL-25
Run Type : Thermal Hydrocracking
Feedstock: EMRGO

Process Data

Pressure = 13.9 MPa   Temperature = 450.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 4.91 mL/min
H2/OIL Feed Ratio = 507.00 M3API/M3OIL
Liquid Holdup Vol. = 239.40 mL (at 450 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	351.95	345.61	360.63
S.G. (g/mL)	0.9118	0.8966	0.6751
Pitch Wt.Frac.	0.4405	0.1418	0.4425
Sample Wt. (g)			13.393

Computed Results

Pitch Conc. in Liq.Feed = 0.00114121 mol/mL
Pitch Conc. in Liq.Prod. = 0.00036787 mol/mL
Pitch Conc. in Reactor Liq. = 0.00082836 mol/mL
H2 Conc. in Reactor Liq. = 0.00076299 mol/mL

Rate of Pitch Conversion = 0.00001629 mol/mL/min
Pitch Conversion, % = 68.3455

Rate Const.(1st Order Eqn.) = 0.01966531 /min
Rate Const.(2nd Order Eqn.) = 25.7738880 mL/mol/min

Sulphur Conversion, % = 24.6

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : EC1-2
Run Type : Catalytic Hydrocracking
Feedstock: EMRGO

Process Data

Pressure = 13.9 MPa Temperature = 400.0 C
Liquid Feedrate = 1.41 mL/min
Liquid Product Rate = 1.38 mL/min
H2/OIL Feed Ratio = 702.80 M3API/M3OIL
Liquid Holdup Vol. = 277.40 mL (at 400 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	354.14	342.84	345.36
S.G. (g/mL)	0.9096	0.8671	0.6052
Pitch Wt.Frac.	0.4579	0.2684	0.3828
Sample Wt. (g)			11.799

Computed Results

Pitch Conc. in Liq.Feed = 0.00117610 mol/mL
Pitch Conc. in Liq.Prod. = 0.00067883 mol/mL
Pitch Conc. in Reactor Liq. = 0.00067081 mol/mL
H2 Conc. in Reactor Liq. = 0.00085486 mol/mL

Rate of Pitch Conversion = 0.000002601 mol/mL/min
Pitch Conversion, % = 43.5097

Rate Const.(1st Order Eqn.) = 0.00387745 /min
Rate Const.(2nd Order Eqn.) = 4.53577900 mL/mol/min

Sulphur Conversion, % = 95.0

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : EC1-3
Run Type : Catalytic Hydrocracking
Feedstock: EMRGO

Process Data

Pressure = 13.9 MPa   Temperature = 400.0 C
Liquid Feedrate = 1.38 mL/min
Liquid Product Rate = 1.40 mL/min
H2/OIL Feed Ratio = 655.50 M3API/M3OIL
Liquid Holdup Vol. = 250.00 mL (at 400 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	354.14	339.63	351.83
S.G. (g/mL)	0.9096	0.8666	0.6037
Pitch Wt.Frac.	0.4579	0.2592	0.4051
Sample Wt. (g)			9.8650

Computed Results

Pitch Conc. in Liq.Feed = 0.00117610 mol/mL
Pitch Conc. in Liq.Prod. = 0.00066137 mol/mL
Pitch Conc. in Reactor Liq. = 0.00069511 mol/mL
H2 Conc. in Reactor Liq. = 0.00092643 mol/mL

Rate of Pitch Conversion = 0.000002788 mol/mL/min
Pitch Conversion, % = 42.9507

Rate Const.(1st Order Eqn.) = 0.00401148 /min
Rate Const.(2nd Order Eqn.) = 4.33002950 mL/mol/min

Sulphur Conversion, % = 90.4

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : EC1-5
Run Type : Catalytic Hydrocracking
Feedstock: EMRGO

Process Data

Pressure = 13.9 MPa Temperature = 420.0 C
Liquid Feedrate = 1.39 mL/min
Liquid Product Rate = 1.40 mL/min
H2/OIL Feed Ratio = 845.00 M3API/M3OIL
Liquid Holdup Vol. = 244.70 mL (at 420 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	368.14	329.07	340.18
S.G. (g/mL)	0.9089	0.8474	0.5838
Pitch Wt.Frac.	0.5088	0.1195	0.3240
Sample Wt. (g)			9.898

Computed Results

Pitch Conc. in Liq.Feed = 0.00125618 mol/mL
Pitch Conc. in Liq.Prod. = 0.00030773 mol/mL
Pitch Conc. in Reactor Liq. = 0.00055603 mol/mL
H2 Conc. in Reactor Liq. = 0.00100401 mol/mL

Rate of Pitch Conversion = 0.000005375 mol/mL/min
Pitch Conversion, % = 75.3265

Rate Const.(1st Order Eqn.) = 0.00966671 /min
Rate Const.(2nd Order Eqn.) = 9.62813570 mL/mol/min

Sulphur Conversion, % = 100.0

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : EC1-6
Run Type : Catalytic Hydrocracking
Feedstock: EMRGO

Process Data

Pressure = 13.9 MPa Temperature = 440.0 C
Liquid Feedrate = 1.39 mL/min
Liquid Product Rate = 1.35 mL/min
H2/OIL Feed Ratio = 847.50 M3API/M3OIL
Liquid Holdup Vol. = 182.60 mL (at 440 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	351.95	318.01	340.19
S.G. (g/mL)	0.9089	0.8385	0.5819
Pitch Wt.Frac.	0.4548	0.0268	0.2554
Sample Wt. (g)			10.415

Computed Results

Pitch Conc. in Liq.Feed = 0.00117451 mol/mL
Pitch Conc. in Liq.Prod. = 0.00007066 mol/mL
Pitch Conc. in Reactor Liq. = 0.00043687 mol/mL
H2 Conc. in Reactor Liq. = 0.00118317 mol/mL

Rate of Pitch Conversion = 0.000008418 mol/mL/min
Pitch Conversion, % = 94.1567

Rate Const.(1st Order Eqn.) = 0.01926961 /min
Rate Const.(2nd Order Eqn.) = 16.2863660 mL/mol/min

Sulphur Conversion, % = 100.0

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : EC1-7
Run Type : Catalytic Hydrocracking
Feedstock: EMRGO

Process Data

Pressure = 13.9 MPa Temperature = 420.0 C
Liquid Feedrate = 1.39 mL/min
Liquid Product Rate = 1.39 mL/min
H2/OIL Feed Ratio = 727.80 M3API/M3OIL
Liquid Holdup Vol. = 245.40 mL (at 420 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	363.05	332.69	341.58
S.G. (g/mL)	0.9089	0.8536	0.5870
Pitch Wt.Frac.	0.5047	0.1443	0.3247
Sample Wt. (g)			13.638

Computed Results

Pitch Conc. in Liq.Feed = 0.00126352 mol/mL
Pitch Conc. in Liq.Prod. = 0.00037024 mol/mL
Pitch Conc. in Reactor Liq. = 0.00055799 mol/mL
H2 Conc. in Reactor Liq. = 0.00087478 mol/mL

Rate of Pitch Conversion = 0.000005060 mol/mL/min
Pitch Conversion, % = 70.6979

Rate Const.(1st Order Eqn.) = 0.00906781 /min
Rate Const.(2nd Order Eqn.) = 10.3658100 mL/mol/min

Sulphur Conversion, % = 97.6

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : AHGO1-1
Run Type : Thermal Hydrocracking
Feedstock: AHGO1

Process Data

Pressure = 13.9 MPa Temperature = 450.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 5.07 mL/min
H2/OIL Feed Ratio = 460.00 M3API/M3OIL
Liquid Holdup Vol. = 290.90 mL (at 450 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	365.83	362.14	369.07
S.G. (g/mL)	0.9023	0.9030	0.6368
Pitch Wt.Frac.	0.5077	0.2988	0.4781
Sample Wt. (g)			11.600

Computed Results

Pitch Conc. in Liq.Feed = 0.00125221 mol/mL
Pitch Conc. in Liq.Prod. = 0.00074506 mol/mL
Pitch Conc. in Reactor Liq. = 0.00082492 mol/mL
H2 Conc. in Reactor Liq. = 0.00090906 mol/mL

Rate of Pitch Conversion = 0.000008538 mol/mL/min
Pitch Conversion, % = 39.6675

Rate Const.(1st Order Eqn.) = 0.01034969 /min
Rate Const.(2nd Order Eqn.) = 11.3850990 mL/mol/min

Sulphur Conversion, % = 0.0

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : AHGO1-2
Run Type : Thermal Hydrocracking
Feedstock: AHGO1

Process Data

Pressure = 13.9 MPa   Temperature = 460.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 4.99 mL/min
H2/OIL Feed Ratio = 478.00 M3API/M3OIL
Liquid Holdup Vol. = 270.00 mL (at 460 C)

Sample Data

	Liq. Feed	Liq. Prod.	React. Liq.
Pitch Av.MWT	369.63	353.67	378.03
S.G. (g/mL)	0.9020	0.8998	0.6943
Pitch Wt.Frac.	0.5272	0.2030	0.5480
Sample Wt. (g)			12.000

Computed Results

Pitch Conc. in Liq.Feed = 0.00128651 mol/mL
Pitch Conc. in Liq.Prod. = 0.00051647 mol/mL
Pitch Conc. in Reactor Liq. = 0.00100647 mol/mL
H2 Conc. in Reactor Liq. = 0.00088776 mol/mL

Rate of Pitch Conversion = 0.000014279 mol/mL/min
Pitch Conversion, % = 59.9355

Rate Const.(1st Order Eqn.) = 0.01418743 /min
Rate Const.(2nd Order Eqn.) = 15.9810940 mL/mol/min

Sulphur Conversion, % = 9.93

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : AHGO1-4
Run Type : Thermal Hydrocracking
Feedstock: AHGO1

Process Data

Pressure = 13.9 MPa Temperature = 450.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 5.01 mL/min
H2/OIL Feed Ratio = 469.00 M3API/M3OIL
Liquid Holdup Vol. = 268.00 mL (at 450 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	361.59	356.25	374.36
S.G. (g/mL)	0.9010	0.9075	0.6526
Pitch Wt.Frac.	0.4695	0.2603	0.5220
Sample Wt. (g)			12.000

Computed Results

Pitch Conc. in Liq.Feed = 0.00116989 mol/mL
Pitch Conc. in Liq.Prod. = 0.00066308 mol/mL
Pitch Conc. in Reactor Liq. = 0.00090997 mol/mL
H2 Conc. in Reactor Liq. = 0.00092183 mol/mL

Rate of Pitch Conversion = 0.000009431 mol/mL/min
Pitch Conversion, % = 43.2077

Rate Const.(1st Order Eqn.) = 0.01036363 /min
Rate Const.(2nd Order Eqn.) = 11.2424560 mL/mol/min

Sulphur Conversion, % = 19.26

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : AHGO1-5
Run Type : Thermal Hydrocracking
Feedstock: AHGO1

Process Data

Pressure = 13.9 MPa Temperature = 440.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 5.01 mL/min
H2/OIL Feed Ratio = 463.00 M3API/M3OIL
Liquid Holdup Vol. = 292.10 mL (at 440 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	376.39	356.14	364.50
S.G. (g/mL)	0.9006	0.8966	0.6282
Pitch Wt.Frac.	0.5337	0.3238	0.5157
Sample Wt. (g)			11.937

Computed Results

Pitch Conc. in Liq.Feed = 0.00127700 mol/mL
Pitch Conc. in Liq.Prod. = 0.00081518 mol/mL
Pitch Conc. in Reactor Liq. = 0.00088879 mol/mL
H2 Conc. in Reactor Liq. = 0.00092733 mol/mL

Rate of Pitch Conversion = 0.000007877 mol/mL/min
Pitch Conversion, % = 36.0366

Rate Const.(1st Order Eqn.) = 0.00886381 /min
Rate Const.(2nd Order Eqn.) = 9.55845070 mL/mol/min

Sulphur Conversion, % = 17.98

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : AHGO2-1
Run Type : Thermal Hydrocracking
Feedstock: AHGO2

Process Data

Pressure = 13.9 MPa Temperature = 450.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 4.87 mL/min
H2/OIL Feed Ratio = 472.00 M3API/M3OIL
Liquid Holdup Vol. = 264.50 mL (at 450 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	385.57	364.02	386.53
S.G. (g/mL)	0.9205	0.9176	0.7051
Pitch Wt.Frac.	0.5507	0.2398	0.5070
Sample Wt. (g)			14.393

Computed Results

Pitch Conc. in Liq.Feed = 0.00131473 mol/mL
Pitch Conc. in Liq.Prod. = 0.00060447 mol/mL
Pitch Conc. in Reactor Liq. = 0.00092483 mol/mL
H2 Conc. in Reactor Liq. = 0.00075617 mol/mL

Rate of Pitch Conversion = 0.000013723 mol/mL/min
Pitch Conversion, % = 55.2188

Rate Const.(1st Order Eqn.) = 0.01483771 /min
Rate Const.(2nd Order Eqn.) = 19.6223220 mL/mol/min

Sulphur Conversion, % = 26.02

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : AHGO2-2
Run Type : Thermal Hydrocracking
Feedstock: AHGO2

Process Data

Pressure = 13.9 MPa Temperature = 460.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 4.91 mL/min
H2/OIL Feed Ratio = 489.00 M3API/M3OIL
Liquid Holdup Vol. = 236.40 mL (at 460 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	386.96	355.70	386.00
S.G. (g/mL)	0.9205	0.9080	0.8337
Pitch Wt.Frac.	0.5463	0.1527	0.5463
Sample Wt. (g)			15.377

Computed Results

Pitch Conc. in Liq.Feed = 0.00129954 mol/mL
Pitch Conc. in Liq.Prod. = 0.00038980 mol/mL
Pitch Conc. in Reactor Liq. = 0.00117992 mol/mL
H2 Conc. in Reactor Liq. = 0.00065921 mol/mL

Rate of Pitch Conversion = 0.000019392 mol/mL/min
Pitch Conversion, % = 70.5447

Rate Const.(1st Order Eqn.) = 0.01643459 /min
Rate Const.(2nd Order Eqn.) = 24.9305920 mL/mol/min

Sulphur Conversion, % = 21.58

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : AHGO2-3
Run Type : Thermal Hydrocracking
Feedstock: AHGO2

Process Data

Pressure = 13.9 MPa   Temperature = 440.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 4.99 mL/min
H2/OIL Feed Ratio = 465.00 M3API/M3OIL
Liquid Holdup Vol. = 272.70 mL (at 440 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	386.95	371.74	382.88
S.G. (g/mL)	0.9206	0.9169	0.6692
Pitch Wt.Frac.	0.5459	0.3197	0.5156
Sample Wt. (g)			12.841

Computed Results

Pitch Conc. in Liq.Feed = 0.00129876 mol/mL
Pitch Conc. in Liq.Prod. = 0.00078854 mol/mL
Pitch Conc. in Reactor Liq. = 0.00090117 mol/mL
H2 Conc. in Reactor Liq. = 0.00082107 mol/mL

Rate of Pitch Conversion = 0.000009384 mol/mL/min
Pitch Conversion, % = 39.4064

Rate Const.(1st Order Eqn.) = 0.01041374 /min
Rate Const.(2nd Order Eqn.) = 12.6831020 mL/mol/min

Sulphur Conversion, % = 8.06

S.G.(Liq.Feed & Liq.Prod.) measured at 23
S.G.(React.Liq.) corrected to reactor conc

HYDROCRACKING DATA

Run No. : AHGO2-4
Run Type : Thermal Hydrocracking
Feedstock: AHGO2

Process Data

Pressure = 13.9 MPa Temperature = 450.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 4.92 mL/min
H2/OIL Feed Ratio = 476.00 M3API/M3OIL
Liquid Holdup Vol. = 263.50 mL (at 450 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	386.95	367.79	385.98
S.G. (g/mL)	0.9206	0.9219	0.7106
Pitch Wt.Frac.	0.5459	0.2559	0.5016
Sample Wt. (g)			12.475

Computed Results

Pitch Conc. in Liq.Feed = 0.00129876 mol/mL
Pitch Conc. in Liq.Prod. = 0.00064144 mol/mL
Pitch Conc. in Reactor Liq. = 0.00092351 mol/mL
H2 Conc. in Reactor Liq. = 0.00077610 mol/mL

Rate of Pitch Conversion = 0.000012668 mol/mL/min
Pitch Conversion, % = 51.4018

Rate Const.(1st Order Eqn.) = 0.01371530 /min
Rate Const.(2nd Order Eqn.) = 17.6719860 mL/mol/min

Sulphur Conversion, % = 8.85

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : AVGO-1
Run Type : Thermal Hydrocracking
Feedstock: AVGO

Process Data

Pressure = 13.9 MPa Temperature = 440.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 4.96 mL/min
H2/OIL Feed Ratio = 486.00 M3API/M3OIL
Liquid Holdup Vol. = 259.60 mL (at 440 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	403.74	370.01	388.30
S.G. (g/mL)	0.9388	0.9319	0.7480
Pitch Wt.Frac.	0.6837	0.2588	0.5265
Sample Wt. (g)			14.424

Computed Results

Pitch Conc. in Liq.Feed = 0.00158978 mol/mL
Pitch Conc. in Liq.Prod. = 0.00065181 mol/mL
Pitch Conc. in Reactor Liq. = 0.00101418 mol/mL
H2 Conc. in Reactor Liq. = 0.00063181 mol/mL

Rate of Pitch Conversion = 0.000018166 mol/mL/min
Pitch Conversion, % = 59.3281

Rate Const.(1st Order Eqn.) = 0.01791212 /min
Rate Const.(2nd Order Eqn.) = 28.3505330 mL/mol/min

Sulphur Conversion, % = 20.13

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : AVGO-2
Run Type : Thermal Hydrocracking
Feedstock: AVGO

Process Data

Pressure = 13.9 MPa Temperature = 420.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 5.03 mL/min
H2/OIL Feed Ratio = 487.00 M3API/M3OIL
Liquid Holdup Vol. = 282.70 mL (at 420 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	405.12	385.80	386.35
S.G. (g/mL)	0.9388	0.9364	0.6932
Pitch Wt.Frac.	0.6680	0.4543	0.6147
Sample Wt. (g)			14.997

Computed Results

Pitch Conc. in Liq.Feed = 0.00154798 mol/mL
Pitch Conc. in Liq.Prod. = 0.00110266 mol/mL
Pitch Conc. in Reactor Liq. = 0.00110291 mol/mL
H2 Conc. in Reactor Liq. = 0.00068379 mol/mL

Rate of Pitch Conversion = 0.000007759 mol/mL/min
Pitch Conversion, % = 28.3405

Rate Const.(1st Order Eqn.) = 0.00703470 /min
Rate Const.(2nd Order Eqn.) = 10.2877710 mL/mol/min

Sulphur Conversion, % = 10.81

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : AVGO-3
Run Type : Thermal Hydrocracking
Feedstock: AVGO

Process Data

Pressure = 13.9 MPa Temperature = 440.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 4.97 mL/min
H2/OIL Feed Ratio = 480.00 M3API/M3OIL
Liquid Holdup Vol. = 267.90 mL (at 440 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	404.68	377.31	390.27
S.G. (g/mL)	0.9388	0.9355	0.7241
Pitch Wt.Frac.	0.6788	0.3100	0.5466
Sample Wt. (g)			15.336

Computed Results

Pitch Conc. in Liq.Feed = 0.00157472 mol/mL
Pitch Conc. in Liq.Prod. = 0.00076861 mol/mL
Pitch Conc. in Reactor Liq. = 0.00101415 mol/mL
H2 Conc. in Reactor Liq. = 0.00064766 mol/mL

Rate of Pitch Conversion = 0.000015131 mol/mL/min
Pitch Conversion, % = 51.4834

Rate Const.(1st Order Eqn.) = 0.01491875 /min
Rate Const.(2nd Order Eqn.) = 23.0348820 mL/mol/min

Sulphur Conversion, % = 17.46

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : AVGO-4
Run Type : Thermal Hydrocracking
Feedstock: AVGO

Process Data

Pressure = 13.9 MPa Temperature = 450.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 4.97 mL/min
H2/OIL Feed Ratio = 489.00 M3API/M3OIL
Liquid Holdup Vol. = 234.90 mL (at 450 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	404.68	368.78	389.78
S.G. (g/mL)	0.9388	0.9650	0.7725
Pitch Wt.Frac.	0.6788	0.2209	0.5358
Sample Wt. (g)			16.074

Computed Results

Pitch Conc. in Liq.Feed = 0.00157472 mol/mL
Pitch Conc. in Liq.Prod. = 0.00057804 mol/mL
Pitch Conc. in Reactor Liq. = 0.00106190 mol/mL
H2 Conc. in Reactor Liq. = 0.00060024 mol/mL

Rate of Pitch Conversion = 0.000021287 mol/mL/min
Pitch Conversion, % = 63.5129

Rate Const.(1st Order Eqn.) = 0.02004628 /min
Rate Const.(2nd Order Eqn.) = 33.3972780 mL/mol/min

Sulphur Conversion, % = 6.91

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : CLGO1-1
Run Type : Thermal Hydrocracking
Feedstock: CLGO1

Process Data

Pressure = 13.9 MPa   Temperature = 440.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 4.67 mL/min
H2/OIL Feed Ratio = 494.00 M3API/M3OIL
Liquid Holdup Vol. = 259.00 mL (at 440 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	401.17	367.29	390.36
S.G. (g/mL)	0.9293	0.8899	0.7145
Pitch Wt.Frac.	0.6499	0.2447	0.5105
Sample Wt. (g)			13.621

Computed Results

Pitch Conc. in Liq.Feed = 0.00150548 mol/mL
Pitch Conc. in Liq.Prod. = 0.00059288 mol/mL
Pitch Conc. in Reactor Liq. = 0.00093440 mol/mL
H2 Conc. in Reactor Liq. = 0.00068739 mol/mL

Rate of Pitch Conversion = 0.000018373 mol/mL/min
Pitch Conversion, % = 63.2177

Rate Const.(1st Order Eqn.) = 0.01965999 /min
Rate Const.(2nd Order Eqn.) = 28.6008680 mL/mol/min

Sulphur Conversion, % = 21.82

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : CLGO1-2
Run Type : Thermal Hydrocracking
Feedstock: CLGO1

Process Data

Pressure = 13.9 MPa   Temperature = 450.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 4.71 mL/min
H2/OIL Feed Ratio = 511.00 M3API/M3OIL
Liquid Holdup Vol. = 224.90 mL (at 450 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	401.17	359.17	388.16
S.G. (g/mL)	0.9293	0.8565	0.7702
Pitch Wt.Frac.	0.6499	0.1854	0.5335
Sample Wt. (g)			15.164

Computed Results

Pitch Conc. in Liq.Feed = 0.00150548 mol/mL
Pitch Conc. in Liq.Prod. = 0.00044212 mol/mL
Pitch Conc. in Reactor Liq. = 0.00105859 mol/mL
H2 Conc. in Reactor Liq. = 0.00066486 mol/mL

Rate of Pitch Conversion = 0.000024211 mol/mL/min
Pitch Conversion, % = 72.3361

Rate Const.(1st Order Eqn.) = 0.02287186 /min
Rate Const.(2nd Order Eqn.) = 34.4008180 mL/mol/min

Sulphur Conversion, % = 32.97

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : CLGO1-3
Run Type : Thermal Hydrocracking
Feedstock: CLGO1

Process Data

Pressure = 13.9 MPa   Temperature = 440.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 4.78 mL/min
H2/OIL Feed Ratio = 525.00 M3API/M3OIL
Liquid Holdup Vol. = 262.30 mL (at 440 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	401.17	370.73	386.80
S.G. (g/mL)	0.9293	0.8940	0.7115
Pitch Wt.Frac:	0.6499	0.2485	0.5326
Sample Wt. (g)			15.447

Computed Results

Pitch Conc. in Liq.Feed = 0.00150548 mol/mL
Pitch Conc. in Liq.Prod. = 0.00059925 mol/mL
Pitch Conc. in Reactor Liq. = 0.00097969 mol/mL
H2 Conc. in Reactor Liq. = 0.00060183 mol/mL

Rate of Pitch Conversion = 0.000017777 mol/mL/min
Pitch Conversion, % = 61.9469

Rate Const.(1st Order Eqn.) = 0.01814440 /min
Rate Const.(2nd Order Eqn.) = 30.1487430 mL/mol/min

Sulphur Conversion, % = 18.98

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : CLGO1-4
Run Type : Thermal Hydrocracking
Feedstock: CLGO1

Process Data

Pressure = 13.9 MPa Temperature = 420.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 4.16 mL/min
H2/OIL Feed Ratio = 495.00 M3API/M3OIL
Liquid Holdup Vol. = 286.20 mL (at 420 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	401.17	387.36	389.32
S.G. (g/mL)	0.9293	0.9082	0.6648
Pitch Wt.Frac.	0.6499	0.4551	0.5849
Sample Wt. (g)			14.053

Computed Results

Pitch Conc. in Liq.Feed = 0.00150548 mol/mL
Pitch Conc. in Liq.Prod. = 0.00106702 mol/mL
Pitch Conc. in Reactor Liq. = 0.00099877 mol/mL
H2 Conc. in Reactor Liq. = 0.00069763 mol/mL

Rate of Pitch Conversion = 0.000010792 mol/mL/min
Pitch Conversion, % = 41.0311

Rate Const.(1st Order Eqn.) = 0.01080417 /min
Rate Const.(2nd Order Eqn.) = 15.4869690 mL/mol/min

Sulphur Conversion, % = 25.05

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : CVGO-1
Run Type : Thermal Hydrocracking
Feedstock: CVGO

Process Data

Pressure = 13.9 MPa Temperature = 440.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 5.00 mL/min
H2/OIL Feed Ratio = 485.00 M3API/M3OIL
Liquid Holdup Vol. = 264.20 mL (at 440 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	365.45	355.77	368.94
S.G. (g/mL)	0.9267	0.9267	0.6700
Pitch Wt.Frac.	0.6206	0.3513	0.6094
Sample Wt. (g)			13.700

Computed Results

Pitch Conc. in Liq.Feed = 0.00157370 mol/mL
Pitch Conc. in Liq.Prod. = 0.00091506 mol/mL
Pitch Conc. in Reactor Liq. = 0.00110668 mol/mL
H2 Conc. in Reactor Liq. = 0.00071790 mol/mL

Rate of Pitch Conversion = 0.000012465 mol/mL/min
Pitch Conversion, % = 41.8533

Rate Const.(1st Order Eqn.) = 0.01126337 /min
Rate Const.(2nd Order Eqn.) = 15.6893330 mL/mol/min

Sulphur Conversion, % = 4.70

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : CVGO-2
Run Type : Thermal Hydrocracking
Feedstock: CVGO

Process Data

Pressure = 13.9 MPa   Temperature = 450.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 4.73 mL/min
H2/OIL Feed Ratio = 480.00 M3API/M3OIL
Liquid Holdup Vol. = 275.20 mL (at 450 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	365.45	357.51	365.44
S.G. (g/mL)	0.9267	0.9367	0.7100
Pitch Wt.Frac.	0.6206	0.3297	0.5580
Sample Wt. (g)			14.600

Computed Results

Pitch Conc. in Liq.Feed = 0.00157370 mol/mL
Pitch Conc. in Liq.Prod. = 0.00086384 mol/mL
Pitch Conc. in Reactor Liq. = 0.00108412 mol/mL
H2 Conc. in Reactor Liq. = 0.00055719 mol/mL

Rate of Pitch Conversion = 0.000013745 mol/mL/min
Pitch Conversion, % = 48.0723

Rate Const.(1st Order Eqn.) = 0.01267881 /min
Rate Const.(2nd Order Eqn.) = 22.7550200 mL/mol/min

Sulphur Conversion, % = 7.42

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : CVGO-3
Run Type : Thermal Hydrocracking
Feedstock: CVGO

Process Data

Pressure = 13.9 MPa Temperature = 440.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 5.08 mL/min
H2/OIL Feed Ratio = 490.00 M3API/M3OIL
Liquid Holdup Vol. = 265.20 mL (at 440 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	360.15	356.46	363.34
S.G. (g/mL)	0.9260	0.9243	0.6663
Pitch Wt.Frac.	0.6179	0.4073	0.6164
Sample Wt. (g)			14.300

Computed Results

Pitch Conc. in Liq.Feed = 0.00158871 mol/mL
Pitch Conc. in Liq.Prod. = 0.00105613 mol/mL
Pitch Conc. in Reactor Liq. = 0.00113037 mol/mL
H2 Conc. in Reactor Liq. = 0.00071528 mol/mL

Rate of Pitch Conversion = 0.000009723 mol/mL/min
Pitch Conversion, % = 32.4595

Rate Const.(1st Order Eqn.) = 0.00860066 /min
Rate Const.(2nd Order Eqn.) = 12.0241090 mL/mol/min

Sulphur Conversion, % = 1.66

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

HYDROCRACKING DATA

Run No. : CVGO-5
Run Type : Thermal Hydrocracking
Feedstock: CVGO

Process Data

Pressure = 13.9 MPa Temperature = 430.0 C
Liquid Feedrate = 5.00 mL/min
Liquid Product Rate = 5.00 mL/min
H2/OIL Feed Ratio = 486.00 M3API/M3OIL
Liquid Holdup Vol. = 263.20 mL (at 430 C)

Sample Data

	Liq. Feed	Liq. Prod	React. Liq.
Pitch Av.MWT	361.83	356.37	371.37
S.G. (g/mL)	0.9261	0.9265	0.6685
Pitch Wt.Frac.	0.6015	0.4321	0.6590
Sample Wt. (g)			14.000

Computed Results

Pitch Conc. in Liq.Feed = 0.00153953 mol/mL
Pitch Conc. in Liq.Prod. = 0.00112338 mol/mL
Pitch Conc. in Reactor Liq. = 0.00118626 mol/mL
H2 Conc. in Reactor Liq. = 0.00075729 mol/mL

Rate of Pitch Conversion = 0.000007907 mol/mL/min
Pitch Conversion, % = 27.0308

Rate Const.(1st Order Eqn.) = 0.00666553 /min
Rate Const.(2nd Order Eqn.) = 8.80177310 mL/mol/min

Sulphur Conversion, % = 4.29

S.G.(Liq.Feed & Liq.Prod.) measured at 23.0 C
S.G.(React.Liq.) corrected to reactor conditions

Table F.1 Sulphur Concentration in Reactor Liquid Phase at Reaction Conditions - CSTR Runs With LLVGO

RUN NO.	TEMP.,C	LHSV,/h	C_S, mmol/mL
LL-05	420	1.10	0.4321
LL-06	440	1.18	0.4932
LL-07	420	1.19	0.4338
LL-08	440	1.27	0.4350
LL-10	400	0.99	0.4423
LL-11	400	1.55	0.4351
LL-12	420	1.55	0.4512
LL-13	440	1.71	0.5241
LL-14	400	2.25	0.4707
LL-16	420	2.20	0.4479
LL-17	440	2.36	0.4626
LL-18	440	1.15	0.5286
LL-19	400	1.15	0.4634
LL-20	420	1.53	0.4398
LL-21	440	1.66	0.5195
LL-22	400	1.54	0.4438

Table F.2 Tubular Reactor Runs Results - Thermal Hydroprocessing of Lloydminster Gas Oil

RUN NO.	T, ^{o}C	Actual LHSV, h^{-1}	F_1, mL min^{-1}	ρ_F, g mL^{-1}	C_F, mol mL^{-1}	F_2, mL min^{-1}	ρ_p, g mL^{-1}	C_p, mol mL^{-1}	X_p, %
LL-26	400	1.46	5.00	0.9220	0.001525	4.97	0.9169	0.001242	18.6
LL-27	420	1.47	5.00	0.9220	0.001525	5.00	0.9149	0.000986	35.3
LL-29	400	1.43	5.00	0.9228	0.001526	5.03	0.9204	0.001284	15.4
LL-30	440	1.66	5.00	0.9228	0.001526	4.94	0.9086	0.000647	58.1
LL-31	440	2.51	7.50	0.9228	0.001546	7.45	0.9175	0.000693	55.5
LL-32*	440	3.04	3.75	0.9231	0.001555	3.70	0.9123	0.000886	43.8

*Heavy coke formation encountered, high hydrogen feedrate used (H_2/Oil = 1054.5 m^3API/m^3Oil), Liquid holdup measurements unreliable.

ρ_F, ρ_p are density measurements of the liquid feed and liquid product at 23.0°C

C_F, C_p are concentration of pitch in the liquid feed and liquid product at 23.0°C

X_p is the percent pitch conversion

Table F.3 Mass Balance Results for CSTR Runs with Lloydminster Gas Oil

RUN NO.	F_1, mL min^{-1}	ρ_F, g mL^{-1}	F_2, mL min^{-1}	ρ_p, g mL^{-1}	$\dot{m}_{H2}$, g min^{-1}	$\dot{m}_{PG}$, g min^{-1}	ABS. ERROR (g min^{-1})	% ERROR
LL-05	3.75	0.9174	3.75	0.8967	0.072	0.121	+ 0.029	+ 0.83
LL-06	3.75	0.9174	3.75	0.8686	0.063	0.233	+ 0.013	+ 0.37
LL-07	3.75	0.9170	3.75	0.8965	0.067	0.137	+ 0.007	+ 0.20
LL-08	3.75	0.9159	3.75	0.8763	0.068	0.224	- 0.008	- 0.23
LL-10	3.75	0.9191	3.75	0.9090	0.096	0.117	+ 0.017	+ 0.48
LL-11	4.92	0.9171	4.92	0.9081	0.106	0.128	+ 0.022	+ 0.48
LL-12	5.00	0.9172	5.00	0.9062	0.102	0.167	- 0.010	- 0.21
LL-13	5.00	0.9172	5.00	0.8937	0.126	0.387	- 0.144	- 3.06
LL-14	7.50	0.9176	7.50	0.9126	0.119	0.127	+ 0.030	+ 0.43
LL-15*	3.75	0.9176	3.75	0.8747	0.123	0.579	- 0.295	- 8.28
LL-16	7.50	0.9168	7.39	0.9056	0.197	0.312	+ 0.069	+ 0.98
LL-17	7.50	0.9171	7.38	0.9014	0.221	0.544	- 0.097	- 1.37
LL-18	3.75	0.9189	3.59	0.8895	0.167	0.343	+ 0.077	+ 2.13
LL-19	3.75	0.9189	3.74	0.9105	0.109	0.132	+ 0.018	+ 0.51
LL-20	5.00	0.9178	5.00	0.9038	0.156	0.267	- 0.041	- 0.86
LL-21	5.00	0.9169	4.83	0.8944	0.249	0.552	- 0.038	- 0.74
LL-22	5.00	0.9175	5.00	0.9134	0.115	0.178	- 0.043	- 0.91
LL-23	5.00	0.9154	4.82	0.8926	0.297	0.630	- 0.058	- 1.19
LL-24	5.00	0.9159	4.97	0.8982	0.359	0.713	- 0.239	- 4.84
LL-25	5.00	0.9118	4.91	0.8966	0.214	0.550	- 0.179	- 3.75

* Run not completed due to excessive coking - reliability of data questionable

% ERROR = $(F_1\rho_F - F_2\rho_p + \dot{m}_{H2} - \dot{m}_{PG})/(F_1\rho_F + \dot{m}_{H2})\ ) \times 100$ %

Table F.4 Mass Balance Results for CSTR Runs with EMRGO and Tubular Reactor Runs with Lloydminster Gas Oil

RUN NO.	F_1, mL min^{-1}	ρ_F, g mL^{-1}	F_2, mL min^{-1}	ρ_p, g mL^{-1}	$\dot{m}_{H2}$, g min^{-1}	$\dot{m}_{PG}$, g min^{-1}	ABS. ERROR (g min^{-1})	% ERROR
EC1-2	1.41	0.9096	1.38	0.8671	0.084	0.121	+ 0.049	+ 3.59
EC1-3	1.38	0.9096	1.40	0.8666	0.077	0.111	+ 0.008	+ 0.60
EC1-5	1.39	0.9089	1.40	0.8474	0.099	0.170	+ 0.006	+ 0.44
EC1-6	1.39	0.9089	1.35	0.8385	0.100	0.201	+ 0.030	+ 2.20
EC1-7	1.39	0.9089	1.39	0.8536	0.086	0.148	+ 0.015	+ 1.11
LL-26	5.00	0.9166	4.97	0.9115	0.136	0.185	+ 0.004	+ 0.08
LL-27	5.00	0.9166	5.00	0.9095	0.150	0.287	- 0.102	- 2.16
LL-29	5.00	0.9174	5.03	0.9150	0.120	0.171	- 0.066	- 1.40
LL-30	5.00	0.9174	4.94	0.9032	0.315	0.579	- 0.139	- 2.84
LL-31	7.50	0.9174	7.45	0.9121	0.343	0.690	- 0.262	- 3.63
LL-32	3.75	0.9177	3.70	0.9069	0.335	0.518	- 0.097	- 2.57

$$\% \text{ ERROR} = \left((F_1\rho_F - F_2\rho_p + \dot{m}_{H2} - \dot{m}_{PG}) / (F_1\rho_F + \dot{m}_{H2}) \right) \times 100 \%$$

Table F.5 Sulphur Balance Results for CSTR Runs with Lloydminster Gas Oil

RUN NO.	F_1, mL min^{-1}	ρ_F, g mL^{-1}	w_{SF}	F_2, mL min^{-1}	ρ_p, g mL^{-1}	w_{SP}	$\dot{m}_{PG}$, gS min^{-1}	ABS. ERROR (gS min^{-1})	% ERROR
LL-05	3.75	0.9174	0.0242	3.75	0.8967	0.0207	0.0149	- 0.0013	- 1.56
LL-06	3.75	0.9174	0.0242	3.75	0.8686	0.0184	0.0230	+ 0.0003	+ 0.39
LL-07	3.75	0.9170	0.0242	3.75	0.8965	0.0207	0.0143	- 0.0007	- 0.81
LL-08	3.75	0.9159	0.0234	3.75	0.8763	0.0192	0.0215	- 0.0042	- 5.25
LL-10	3.75	0.9191	0.0237	3.75	0.9090	0.0212	0.0111	- 0.0017	- 2.06
LL-11	4.92	0.9171	0.0222	4.92	0.9081	0.0213	0.0130	- 0.0080	- 7.98
LL-12	5.00	0.9172	0.0259	5.00	0.9062	0.0218	0.0228	- 0.0028	- 2.36
LL-13	5.00	0.9172	0.0259	5.00	0.8937	0.0205	0.0385	- 0.0113	- 9.54
LL-14	7.50	0.9176	0.0245	7.50	0.9126	0.0237	0.0121	- 0.0057	- 3.38
LL-15*	3.75	0.9176	0.0245	3.75	0.8747	0.0182	0.0385	- 0.0139	-16.48
LL-16	7.50	0.9168	0.0248	7.39	0.9056	0.0217	0.0317	- 0.0064	- 3.75
LL-17	7.50	0.9171	0.0243	7.38	0.9014	0.0205	0.0486	- 0.0178	-10.67
LL-18	3.75	0.9189	0.0248	3.59	0.8895	0.0189	0.0362	- 0.0111	-12.98
LL-19	3.75	0.9189	0.0248	3.74	0.9105	0.0224	0.0119	- 0.0027	- 3.18
LL-20	5.00	0.9178	0.0237	5.00	0.9038	0.0208	0.0227	- 0.0079	- 7.30
LL-21	5.00	0.9169	0.0243	4.83	0.8944	0.0190	0.0416	- 0.0123	-11.02
LL-22	5.00	0.9175	0.0231	5.00	0.9134	0.0214	0.0077	+ 0.0005	+ 0.51
LL-23	5.00	0.9154	0.0230	4.82	0.8926	0.0158	0.0480	- 0.0107	-10.17
LL-24	5.00	0.9159	0.0232	4.97	0.8982	0.0155	0.0480	- 0.0109	-10.30
LL-25	5.00	0.9118	0.0241	4.91	0.8966	0.0185	0.0464	- 0.0180	-16.36

* Run not completed due to excessive coking - reliability of data questioned

% ERROR = $((F_1 \rho_F w_{SF} - F_2 \rho_p w_{SP} - \dot{m}_{PG})/(F_1 \rho_F w_{SF})) \times 100$ %

Table F.6 Sulphur Balance Results for CSTR with EMRGO and Tubular Reactor Runs with Lloydminster Gas Oil

RUN NO.	F_1,mL min^{-1}	ρ_F,g mL^{-1}	w_{SF}	F_2,mL min^{-1}	ρ_p,g mL^{-1}	w_{SP}	$\dot{m}_{PG}$,gS min^{-1}	ABS.ERROR (gS min^{-1})	% ERROR
EC1-2	1.41	0.9096	0.0261	1.38	0.8671	0.0014	0.0413	- 0.0095	-28.38
EC1-3	1.38	0.9096	0.0261	1.40	0.8666	0.0026	0.0394	- 0.0098	-29.89
EC1-5	1.39	0.9089	0.0269	1.40	0.8474	0.00	0.0474	- 0.0134	-39.47
EC1-6	1.39	0.9089	0.0269	1.35	0.8385	0.00	0.0454	- 0.0114	-33.59
EC1-7	1.39	0.9089	0.0269	1.39	0.8536	0.0007	0.0451	- 0.0119	-35.15
LL-26	5.00	0.9166	0.0241	4.97	0.9115	0.0224	0.0141	- 0.0051	- 4.64
LL-27	5.00	0.9166	0.0241	5.00	0.9095	0.0218	0.0224	- 0.0111	-10.04
LL-29	5.00	0.9174	0.0241	5.03	0.9150	0.0219	0.0134	- 0.0036	- 3.30
LL-30	5.00	0.9174	0.0241	4.94	0.9032	0.0185	0.0413	- 0.0133	-12.03
LL-31	7.50	0.9174	0.0241	7.45	0.9121	0.0200	0.0445	- 0.0146	- 8.79
LL-32	3.75	0.9177	0.0241	3.70	0.9069	0.0199	0.0272	- 0.0110	-13.31

% ERROR = $(F_1\rho_F w_{SF} - F_2\rho_p w_{SP} - \dot{m}_{PG})/(F_1\rho_F w_{SF})\ )\times 100$

APPENDIX G - Supplementary Information

Table G.1 Chemical analysis and physical properties of NM-502 catalyst.

Chemical Analysis, wt. % dry basis

Mo O_3	14.0 %
Ni O	2.8 %
Alumina Base	Balance

Physical Properties

Form	Extrudate
Size	1/16"
Surface Area, m^2/g	270
Total Pore Volume, cm^3/g	0.55
Density, g/cm^3	0.68 - 0.71
Strength, lbs crush	14 - 16
Attrition Index*	95

* % retained on a 20 mesh sieve after tumbling for 1 hour.