AN INVESTIGATION INTO THE FISCHER-TROPSCH SYNTHESIS OVER SUPPORTED RUTHENIUM IN A STIRRED GAS-SOLID REACTOR.

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PREFACE.

The material incorporated in this thesis is my own work (except where specifically indicated to the contrary) and has not been submitted to any other University.

A.R.McK. KIRK.

ACKNOWLEDGEMENTS.

During the course of this work, financial, technical and moral assistance was received from many sources: both individual and corporate. Space considerations prohibit personal mention of all the individuals who contributed, however, special thanks are extended to Dr. R.C. Everson, my research supervisor whose enthusiasm for the project never waned and to Prof. E.T. Woodburn for his Job-like patience.

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ABSTRACT.

A stirred gas-solid reactor has been used to study the Fischer-Tropsch synthesis over a supported ruthenium catalyst.

Detailed catalyst characterisations were conducted on both fresh and used catalyst samples and included such techniques as physisorption and chemisorption, electron microprobe examination, carbon determination and mercury porosimetry.

The product obtained from the synthesis consisted largely of n-alkanes and the product selectivity of individual carbon number fractions is demonstrated to have certain advantages over the corresponding selectivities (adapted from the literature) obtained over iron, cobalt and molybdenum catalyst.

The rate data obtained is fitted to two empirical models: a simple power law model and a previously-described mechanistic model. Energies of activation for methanation and carbon monoxide removal (at approximately 34,3 and 19 kcal/mol respectively) are compared with regressed values obtained by other workers.

Rate data for the synthesis of higher hydrocarbons are fitted to a simple power law model and energies of activation for individual carbon number fractions up to C_8 are presented.

NOMENCLATURE.

Most of the symbols used throughout are defined at the time of use. The following is a listing of the most important symbols used.

A	pre-exponential term in rate expression.
A_m	area of metal atom.
C	constant in the B.E.T. equation.
C_i	concentration of component i.
D	metal dispersion = $\frac{\text{number of surface atoms}}{\text{total number of atoms}}$
D_k	Effective diffusion coefficient.
E_i	activation energy of production (or if -i, removal) of component i.
F	volumetric flow rate.
G	gas uptake in chemisorption.
H	enthalpy of reaction.
K	equilibrium constant.
M	metal atom.
M_T	total number of metal atoms.
M_s	number of surface metal atoms.

M_i	turnover number of component i.
P	pressure.
R	gas constant.
S	specific surface area.
T	temperature.
V	volume.
X, Y	exponents in Vannice methanation regressions.
a, b, c	exponents in empirical power law model.
k	rate constant.
m, n	exponents in Huang & Richardson methanation regression.
P_i	partial pressure of component i.
t	time.
y	number of hydrogen atoms in rate-determining step in Vannice methanation model.
θ_i	fractional surface coverage of component i.
κ	length (or diameter) of metal particle.
λ	thermal conductivity.
ρ	density.
τ	residence time.
ψ	isokinetic temperature.
Φ	fraction of metal atoms exposed.

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CHAPTER 1.

INTRODUCTION.

1.1. GENERAL.

In 1859 Edwin Drake first drilled oil in Pennsylvania. Only six years later, it was stated of oil that "..... it lights our dwellings, lubricates our machinery, and is indispensable in numerous departments of arts, manufactures and domestic life. To be deprived of it now would be setting us back a whole cycle of civilisation." (Bone, 1865). This dependance on oil increased enormously over the ensuing century to the extent that the whole structure of industrialised society is now predicated on the continuing supply of energy.

When considering sources of energy, it must be noted that there are areas of consumption where one type of fuel cannot readily be replaced by another. (Lacey & Roberts, 1976). For example, the general economy of industrialised nations is to a very large extent dependant on liquid fuels, which are of great strategic importance with practically no substitution possibilities. (Petrick, 1975).

The series of dramatic price increases in the price of crude oil announced by the Organisation of Petroleum Exporting Countries (OPEC) in the early nineteen seventies has had the effect of increasing the interest in a more rational utilisation of existing petroleum reserves. This, in turn, has resulted in a renewal of interest (based on both economic and strategic considerations) in the production of liquid fuels from sources other than petroleum.

The opinion expressed to his government by Dmitri Mendeleyev after a tour of the Pennsylvania oil fields in 1872 is probably more relevant to-day than it was at the time of writing: "This material (oil) is far too precious to be burned. When burning oil, we burn money; it should be used as a chemical base material." (Mendeleyev, 1872).

This philosophy has been re-expressed more than a century after Mendeleyev's original report on the utilisation of oil in almost identical terms: "petroleum and natural gas must be reserved for petrochemicals." (Ponder, 1975).

1.2. ENERGY: WORLD CONSUMPTION AND SUPPLY.

In order to appreciate the raison d'être of this study, it is illuminating to consider briefly the historical pattern of energy consumption and supply throughout the world. Since several comprehensive studies of the energy situation (on both local and global scales) have appeared recently (Ion, 1975; Hammond, Metz & Maugh, 1973), no attempt is made here to provide a detailed account; rather a brief resumé of the situation is presented.

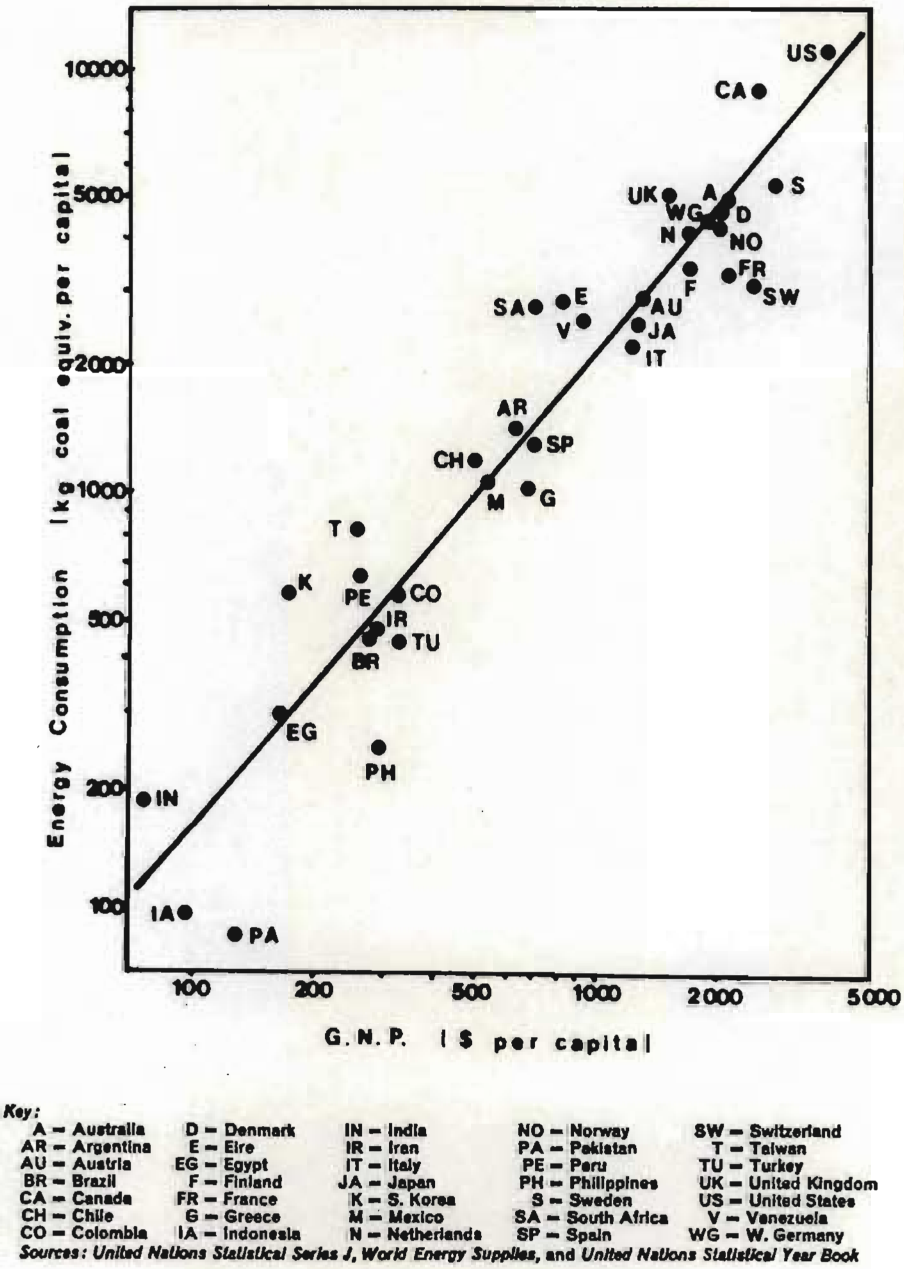
It is, however, important to realise that there is simply no way of accurately assessing total world energy resources. The uncertainty inherent in estimates of world energy resources may be summarised by the following quotation from Schurr (1963): "There is no true measure of the world's endowment of energy resources, nor, in the nature of things is there likely to be one ..... Society's interest is confined to resources that are exploitable now or seem likely to be in the future. As time passes, the standards of exploitability keep changing ..... consequently, resource supply estimates are subject to at least as much uncertainty as energy demand estimates." A further difficulty in the estimation of supply and demand of energy resources is defining just what constitute energy resources. Oil, natural gas and uranium - which must be included in any detailed inventory of present day resources - would not be included in resource estimates compiled more than a century ago. It is therefore reasonable to suppose that future energy resource inventories could well differ greatly from present day inventories and could well include thorium and solar energy for example (Cole et alii, 1973).

With both these important caveats in mind, some perspective on the world energy supply and demand situation may be gained by consideration of various published estimates of world energy supply and demand.

1.2.1. CONSUMPTION.

Throughout history, the pace of industrial and social progress has been closely related to the proportion of energy man has been able to apply to constructive ends.

This is reflected in the fact that consumption of energy may be related directly to standards of living of populations on every continent as can be seen from Figure 1.1. which plots Gross National Product per capita for the year 1968 against per capita energy consumption (in kg of coal equivalent) for the same year (Meadows et alii, 1972).



Sources: United Nations Statistical Series J, World Energy Supplies, and United Nations Statistical Year Book

FIGURE 1.1. - ENERGY CONSUMPTION VERSUS GROSS NATIONAL PRODUCT - 1968.

The world's first coal-burning economy was in England and later in Scotland between the years 1550 and 1700. This substitution of coal in place of wood as a primary energy supply led directly to the Industrial Revolution in the latter part of the 18th century.

Up to the outbreak of World War 1, coal continued to provide the major portion of the world's energy requirements. Since that time, however, drastic changes in the pattern of energy consumption have taken place. From providing some 90 per cent of the world's energy consumption in 1900, the contribution made by coal fell to approximately 40 per cent in 1967. (World Power Conference, 1968). During the same period the contribution made by petroleum and natural gas rose from approximately 4 per cent to almost 60 per cent.

The annual energy consumption of the United States of America (which with approximately 6 per cent of the world's population accounts for almost 35 per cent of the world's energy consumption (Hammond, Metz & Maugh, 1973)) is given in Figure 1.2. (Hottel & Howard, 1973). This Figure also shows the relative contributions made to the total energy consumption by the major individual energy sources. The pattern shown in this Figure does not differ in any major respect from world energy consumption trends.

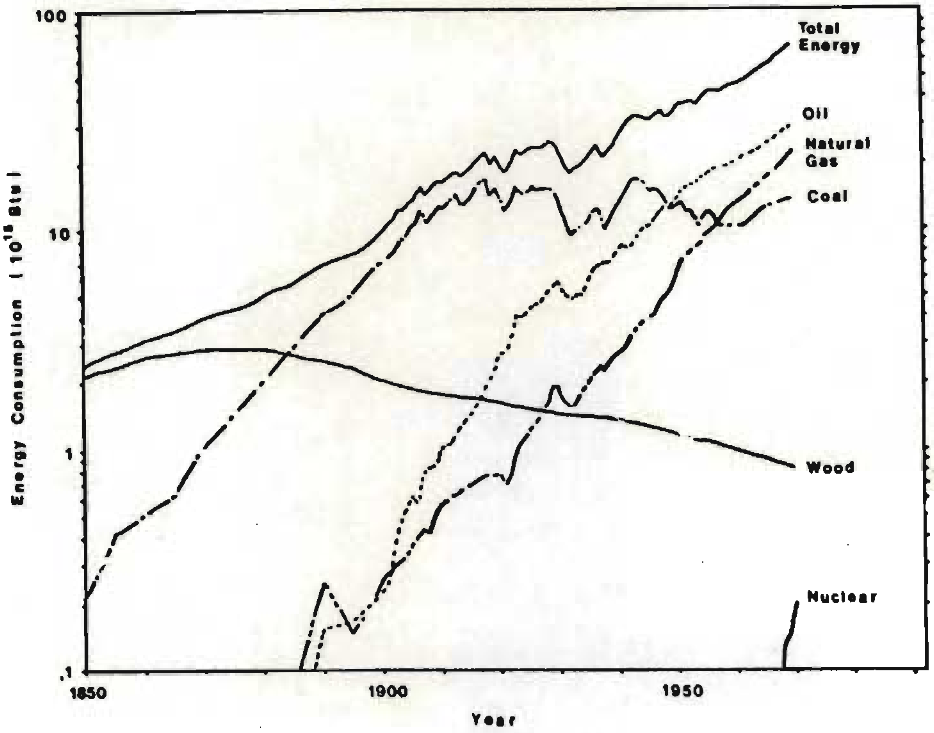


FIGURE 1.2. - ENERGY CONSUMPTION U.S.A. 1850 TO 1970.

The reasons behind the current dominance of oil as an energy source are not difficult to find; firstly, fluids are easier to handle and use than are solids. This is particularly true for mobile consumption sources which account for more than 25 per cent of all energy used in the United States (Hammond, Metz & Maugh, 1973). Secondly, recent concern over air pollution has led to legislation which, in many parts of the world, has resulted in relatively high-sulphur coal being replaced as a fuel by low-sulphur natural gas and residual fuel oils.

Finally, technology is now available for the processing of crude oil into a very wide range of liquid fuels, for removing its sulphur and for converting some of its components into natural gas or hydrogen. The foregoing reasons (together with the fact that enormous amounts of capital have been invested in refineries and other production and processing plants) are sufficient to ensure petroleum's dominance of the energy market as long as it remains available.

This qualification as regards availability leads directly to the question of energy resources and supplies.

1.2.2. SUPPLY.

A basic prerequisite for any study of energy prospects is an estimate of the various energy resources throughout the world and their rates of depletion relative to population changes. With this information, an attempt can then be made to predict the likely changes in energy supply and demand, consideration being given to probable relative costs and advances in science and technology relating to the discovery, exploitation and use of these resources.

One of the most recently-published authoratative figures of the world's likely recoverable energy resources are presented in Table 1.1. (Ion, 1976). Because of the fact that resource estimation is fraught with difficulties, these figures can be regarded as approximations only, although, as will be demonstrated later, even a five-fold increase in resource estimates does not significantly alter the "life expectancy" estimations.

TABLE 1.1.

WORLD ENERGY RESOURCES (IN GIGATONS OF COAL EQUIVALENT.)

	RESERVES			ADDITIONAL RESOURCES	RESOURCE BASE
	PROVED	PROBABLE	POSSIBLE		
COAL	210	-	380	-	30 000
OIL	140	31	321	1 564	2 000
NATURAL GAS	89	91	-		1 360
OIL SANDS	6	36	403	?	?
OIL SHALE	-	162	564	1 416	53 000

It is a truism that the world's total energy resources in the form of fossil fuels is a finite quantity and the utilisation of these energy resources is an irreversible process; once consumed they cannot be replaced. They may, however, be used more effectively and it is to this more effective utilisation that the current interest in coal hydrogenation (be it either direct or indirect hydrogenation) is directed.

The original impetus to coal hydrogenation studies was given by predictions immediately following the First World War of an imminent exhaustion of petroleum reserves. Since that time, the discovery of further petroleum reserves has kept abreast with the world's demands. However, with an ever-increasing demand for energy (at an overall rate of some 4 per cent per annum (Häfele & Sassin, 1976), the depletion date of the probable total petroleum reserves has been estimated at some time before the middle of the next century (Schumann, 1969) and, more pessimistically, by the turn of this century (Richardson, 1971). In any event, the continuing irreversible usage of petroleum must obviously result in eventual reserve depletion. The actual reserve depletion dates do not vary to any great extent, even with the assumption of a five-fold increase in the reserve estimate. This is shown in Table 1.2. (Cole et alii, 1973).

The vast world resources of coal available obviously present a feasible short-term solution; the manufacture of oil from coal, with the utilisation of existing petroleum reserves in a more efficient manner.

Long-term solutions to the problem of energy sufficiency include the rapid development and implementation of nuclear power as the major energy source (with contributions by solar, tidal, geothermal and wind power being assumed to be minor).

With socio-political undertones even more pronounced than those relating to the use of high-sulphur fuels, consideration of implications of intensive implementation of nuclear power-based energy supplies is largely beyond the scope of this introduction. However, several articles on various aspects of the socio-political implications are available in the literature (Hammond, Metz & Maugh, 1973; Farmer, 1977; Ion, 1976; Maxey, 1978.).

TABLE 1.2.

ESTIMATED DEPLETION DATES FOR HYDROCARBON RESERVES (Cole et alii, 1973).

RESOURCE	KNOWN RESERVES*	STATIC[(1)] INDEX (YEARS)	AVERAGE GROWTH RATE* (% PER YEAR)	EXPONENTIAL[(2)] INDEX (YEARS)	EXPONENTIAL INDEX WITH FIVE-FOLD INCREASE IN RESERVE (YEARS)
COAL	5×10^{12} tons	2 300	4,1	111	150
NATURAL GAS	$1{,}14 \times 10^{15}$ cu.ft.	38	4,7	22	49
PETROLEUM	455×10^{9} bbls.	31	3,9	20	50

TERMS:

(1) "Static Index": the number of years known reserves would last at current consumption levels.

(2) "Exponential Index": the number of years known reserves would last with consumption growing exponentially at the average annual rate of growth.

* Based on U.S. Bur. Mines "Mineral Facts & Problems", 1970.

The production of liquid hydrocarbons from coal (by either direct or indirect hydrogenation) has been the subject of study for very many years. However, of all the processes studied, only one is at present in operation on a commercial scale; the route based on the Fischer-Tropsch Synthesis as practiced by the South African Coal, Oil and Gas Corporation (SASOL). The existence of this plant is a result of largely strategic considerations: South Africa has no known reserves of natural gas or oil in economically exploitable quantities, but does possess considerable reserves of coal - albeit of a fairly low quality by world standards. (Falcon, 1977).

1.3. THE FISCHER-TROPSCH REACTION.

1.3.1. GENERAL.

In 1925, Franz Fischer and Hans Tropsch demonstrated the feasibility of producing hydrocarbons from carbon monoxide and hydrogen over an iron catalyst. The reaction of carbon monoxide and hydrogen to produce hydrocarbons above methane is accordingly generally referred to as the "Fischer-Tropsch Reaction" after the two pioneers in this field.

The early work was later extended to include all the Group V111 metals (Fischer, Tropsch & Dilthey, 1925). Of all the metals studied, only four showed significant activity: iron, nickel, cobalt and ruthenium.

The relative costs of these four metals resulted in the general acceptance of iron as the prime Fischer-Tropsch catalyst, much of the work done in the following 50 years being aimed at the development of promoters, supports and preparation techniques to achieve high catalytic activity with the desired product selectivity.

1.3.2. RUTHENIUM AS A FISCHER-TROPSCH CATALYST.

As indicated in the previous section, much of the work conducted into the Fischer-Tropsch synthesis has used iron catalyst. Ruthenium falls directly under iron in the Group V111 metals in the periodic table and for this reason some exploratory work was conducted into the use of ruthenium as a catalyst. Early work by Fischer (Pichler, 1952) indicated that the activity of ruthenium could not be increased by the addition of any promoters nor by support and this, together with the high cost of the metal, led to the abandonment of further investigation of ruthenium as a suitable Fischer-Tropsch catalyst.

Pichler (1952), in a later unsuccessful search for a catalyst to produce synthetic carbohydrates, showed that ruthenium was capable of producing paraffinic waxes with previously unobtainably-high molecular weights (molecular weights of 7-9 000 [Pichler, 1938], 23 000 [Pichler & Buffleb, 1940], 100 000 [Pichler et alii, 1964] and, polymethylene having properties similar to polyethylene with molecular weights above 200 000 [Pichler & Burgert, 1968] being reported).

Ruthenium also has a very high activity for methanation (Schultz, Karn & Anderson, 1967): a characteristic which is reflected in the fact that some 20 to 30 units for gas purification via methanation over ruthenium were in 1974 reported (Mills & Steffgen, 1974) to be in operation in the United States.

The high activity of ruthenium for the synthesis of very high molecular weight hydrocarbons and for methane indicated that its use for a "middle range" molecular weight product (corresponding to some 4 to 15 carbon atoms per molecule) could well be feasible. As has been indicated previously (Karn, Schultz & Anderson, 1965) the cost of ruthenium at $40 per troy ounce (Metal Bulletin 1978) is considerably lower than that of platinum at $350 per troy ounce (Metal Bulletin 1978): a widely-used catalyst in the petroleum industry. Catalyst cost in itself is thus not a prohibiting factor in the choice of catalyst, especially since improved techniques for the preparation of catalysts have, by producing catalysts with dispersions near unity, partly offset the high cost of the metals used. This high dispersion permits the use of catalysts with ruthenium concentrations of less than 1 per cent, yet having an acceptably high activity (Karn, Schultz & Anderson, 1965).

1.3.3. KINETICS OF THE SYNTHESIS.

In spite of the vast body of work reported in the literature on the Fischer-Tropsch synthesis, very little is available in unambiguous form. The overwhelming majority of the reported data on this synthesis is based on the rate of removal of carbon monoxide and hydrogen over undefined catalyst surfaces. Only recently (Vannice, 1975; 1975 (a); Dalla Betta, Piken & Shelef, 1974; 1975) have reports on Fischer-Tropsch synthesis and methanation been presented in terms of "turnover number"; made possible by the detailed characterisation of the catalysts employed.

1.4. SCOPE OF THIS INVESTIGATION.

The purpose of this study was to obtain unambiguous data for the Fischer-Tropsch synthesis over supported ruthenium, with special emphasis being placed on the production of "useful" hydrocarbons; being (arbitrarily) defined as hydrocarbons containing between 5 and 12 carbon atoms per molecule. Towards this end, a stirred gas-solid reactor was used in order to minimise external diffusional effects and also to obtain isothermal conditions over a wide range of conversions.

The choice of catalyst was made with the purpose of minimising internal diffusional effects, and a detailed characterisation of the catalyst was undertaken to enable rates to be expressed in terms of turnover numbers.

A further objective of the study (which presented itself only after work was under way) was to obtain information on the deactivation of the catalyst during synthesis.

CHAPTER 2.

LITERATURE REVIEW.

2.1. INTRODUCTION.

The literature relevant to this study will, for convenience, be reviewed in two distinct sections.

(a) Literature relating to experimental techniques used in this investigation, and

(b) Literature relating to Methanation and the Fischer-Tropsch Synthesis.

Under the first general heading will be reviewed the more pertinent literature concerning reactor types, development of rate equations, catalyst deactivation, and adsorption of gases on metal catalysts. The second heading will review the early theories regarding both methanation and the Fischer-Tropsch synthesis, together with some recent developments in the field of catalysis, with particular reference to the reactions occurring between carbon monoxide and hydrogen.

2.2. LITERATURE RELATING TO EXPERIMENTAL TECHNIQUES.

Under this general heading will be reviewed the literature relating to the more important aspects of the techniques employed in this investigation. Among these, possibly the single most important is the type of reactor employed.

2.2.1. TYPE OF REACTOR.

In any experimental study relating to chemical kinetics, it is important to appreciate the influence that the choice of reactor type may have upon the experimentally determined rates of reaction and product selectivity. This is particularly true when dealing with heterogeneous catalysis, where overall reaction can be regarded as proceeding via five consecutive steps (Walas, 1959):

(a) Diffusion of the reactants from the bulk fluid to the catalyst surface.

(b) Adsorption of the reactants on the catalyst.

(c) Reaction on the catalyst.

(d) Desorption of the products from the catalyst.

(e) Diffusion of the products from the catalyst surface into the bulk fluid.

If it is desired to measure experimentally overall reaction rates, it is important that some type of evaluation of the diffusional effects which are set up by the first and final steps in the above sequence be made. Alternatively, these effects can be minimised (if not altogether removed). The most common technique used in the minimisation of these effects employs a high velocity of fluid relative to the solid catalyst, thus decreasing the thickness of the boundary layer which is the source of diffusional effects. This also results in the minimising of heat transfer effects in which the temperature on the catalyst surface may, in the case of exothermic reactions, be very much higher than the temperature of the bulk phase. (Luss, 1970). Since chemical reaction rates are strongly dependant upon temperature in a non-linear manner, any later attempt to account for temperature gradient effects can result in very large uncertainties.

It can thus be seen that for ease of interpretation of experimental data, a reactor free from mass and heat transfer gradients would be desirable. Carberry (1964) has stated "ideally, the desirable reactor is capable of delivering isothermal chemical rate data at finite, easily measured conversion levels. Furthermore, the device should permit the investigator to quickly deduce differential reaction rates and orders without recourse to differentiation as required with integral reactor data".

In order to appreciate the advantages gained by employing the reactor type selected for this investigation, some of the major advantages of other commonly-used reactor types will be considered.

Only the major features of each reactor will be considered here, since detailed reactor descriptions are plentiful in the literature (Carberry, 1976; Denbigh, 1965; Aris, 1969; Choudhary & Doraiswamy, 1972).

2.2.1.1. THE INTEGRAL FIXED BED REACTOR.

Until fairly recently, this was the most widely-used reactor type. Its major advantage lies in the fact that it most closely resembles an industrial fixed bed reactor and is therefore useful in the immediate evaluation of possible catalysts in terms of probable industrially-realisable values for selectivity, conversion, etc. (Trifiro & Pasquon, 1969). The major disadvantage of the integral reactor for more fundamental laboratory studies lies in the fact that axial and radial concentration and thermal gradients can be considerable (Carberry, 1976). The minimisation of these gradients by the usual method of the employment of high effective Reynold's numbers will, in general, result in the decrease of extent of conversion to approach that obtained in the differential reactor.

2.2.1.2. THE DIFFERENTIAL REACTOR.

The problem of minimising both thermal and concentration gradients can be overcome by use of a differential reactor, which produces only very small conversions across the catalyst bed. The minimum level of conversion which can be tolerated will obviously depend upon the sensitivity of the detection techniques available.

While reactors of this type have been used fairly extensively (Vannice, 1975; 1975 (a); Dalla Betta, Piken & Shelef, 1974 & 1975; Boudart, 1967) it has been pointed out by Boudart that the extrapolation of data obtained by low conversion, differential reactors to regions of higher conversion is fraught with danger. This occurs because of the fact that many chemical reactions are strongly inhibited by reaction products. For example, in a study of ammonia synthesis, inhibition of the synthesis was observed even with conversions as low as 1 per cent (Boudart, 1967).

2.2.1.3. THE MICROCATALYTIC REACTOR.

By arranging a reactor to operate in a stream of carrier gas and exposing the catalyst to a pulse of reactant, the extent of heat release (or absorption in the case of an endothermic reaction) can be minimised while operating at finite conversions. This is the basis of the microcatalytic reactor (Tobin, Kokes & Emmett, 1955). The major disadvantage of this type of reactor is that the activities determined represent initial transient catalyst responses (Emmett, 1959), which may, or may not, be useful in evaluating steady-state behaviour for a particular catalyst/reaction combination (Carberry, 1964).

2.2.1.4. FLUIDISED BED REACTOR.

The physical nature of the fluidised bed reactor is such that near-isothermal operation may be realised without difficulty inter- and intraparticle gradients being very much less pronounced than would be the case with a fixed bed reactor (Carberry, 1976).

Interpretation of kinetic results obtained from fluidised bed reactors is, however, complicated by virtue of the by-passing which is a feature of this reactor type, and further, confident scale-up of such reactors is notoriously problematical.

2.2.1.5. STIRRED GAS-SOLID REACTOR.

The reactor type chosen for this study exhibits many of the characteristics considered desirable in the earlier quotation by Carberry. The catalyst basket rotating rapidly in the bulk fluid in the reactor pot results in perfect (or nearly so) mixing in the bulk phase (Brisk et alii, 1968), thus minimising external heat and mass transfer gradients. The reactants flow continuously through the reactor and the reactor contents attain steady-state operation after a given number of residence times for any given set of operating conditions. (Kempling, 1971). Because of the good mixing characteristics of this reactor type (Brisk et alii, 1968), large conversion levels can be tolerated while thermal and concentration gradients are minimised. A further advantage of this particular type of reactor is that unlike the earlier versions of the S.G.S.R., (Carberry, 1964; Kempling, 1971), operation at elevated pressure is possible without problems of leakage past the stirrer seal.

2.2.2. TYPE OF CATALYST.

With external heat and mass transfer effects minimised by the choice of a suitable reactor type, the remaining non-catalytic aspect of the reactor system which requires consideration is that of internal diffusion. The catalyst type chosen for this investigation was in the form of pellets with the catalytic ruthenium deposited only on the outer shell and was selected in order to minimise intraparticle diffusional effects (Carberry, 1964; Kempling, 1971).

Internal diffusional effects have been considered in detail in the literature (Carberry, 1976). Under steady-state conditions, diffusion of reactants across a boundary must equal the rate of reaction within the surface and the heat released must also be transferred across the same boundary. This is described by the relation: (Prater, 1958):

$$D_k \frac{dc}{dx} \cdot \Delta H = \lambda \cdot \frac{dt}{dx}$$

hence,

$$\Delta T = \frac{(-\Delta H) D_k}{\lambda} \cdot (C_s - C_o)$$

where ΔH = enthalpy of reaction.

D_k = effective diffusion coefficient.

C_s = concentration of reactant at catalyst surface.

C_o = concentration of reactant at some point within the catalyst.

λ = thermal conductivity of catalyst.

This is the maximum temperature gradient which can be set up by virtue of the chemical reaction within a catalyst particle. Using values of 19 000 cal./g.mol. (Kirk, Everson & Woodburn, 1978), 3 x 10^{-3} $cm^2/_s$ (Kempling, 1971) and 5 x 10^{-4} cal/s/cm/C^o (Kempling, 1971) forΔH, D_k and λ, the maximum internal temperature gradient which could be anticipated in this investigation was calculated to be 1,3C^o. An error of this magnitude would result in an error in rate determination of less than 10 per cent.

2.2.3. DEVELOPMENT OF RATE EQUATIONS.

The study of catalytic reactions is generally undertaken with the twin aims of understanding the catalytic process itself and of obtaining data to enable reactor design to be undertaken (Sinfelt, 1968). In order to use the experimental data obtained towards optimal reactor design and operation, it is necessary to establish some relation between rate of reaction and the operating variables of temperature, pressure, conversion and composition (Boudart, 1972). This is generally done by empirically fitting the experimental data to a suitable mathematical model. The most commonly-used models for data fitting of this nature are the power-function models which have the general form

$$\text{rate} = k.p_A{}^a p_B{}^b p_C{}^c \text{ ---}$$

where subscripts A, B, C --- may refer to either reactants or products and the exponents a, b, c --- may or may not be restricted to integral or half-integral values. The rate constant k in the above equation is generally represented over a range of temperatures by an Arrhenius-type dependency:

$$k = Ae^{-E/RT}$$

A further type of rate model frequently used (Kempling, 1971; Phung-Quach & Rouleau, 1978; Huang & Richardson, 1978) is of the form

$$\text{rate} = \frac{k.\,P_A.\,P_B}{(1 + K_A\,P_A + K_B\,P_B)^n}$$

where only two species A and B are considered and is known as the Hougen-Watson (Kempling, 1971) or Langmuir-Hinshelwood (Weller, 1956) type of equation.

The use of the latter type of correlation has been criticised on the grounds that "there appears to be no theoretical justification for applying the extended Langmuir equation to the kinetics of complex heterogeneous reactions" (Weller, 1956). However, this type of mechanistic equation is used because it often leads to some understanding of the reaction mechanism and catalyst behaviour (Kempling, 1971), although this qualitative advantage of the Langmuir-Hinshelwood approach is in part outweighed by the less-wieldy nature of the equation. The great flexibility of an equation of this nature (caused by the abundance of parameters) explains the goodness of fit frequently found with this type of equation. Both Weller (1956) and Boudart (1956) recommend the use of the simplest possible rate equation to give an acceptable fit to the experimental data. This is an equation of the simple power law type.

Weller (1956) has demonstrated that the data of Akers and White (1948) for the methanation reaction over a supported nickel catalyst can be correlated adequately by means of the empirical equation

$$\text{rate} = k\, P_{CO}\, P_{H_2}^{\frac{1}{2}}$$

in place of the less-wieldy equation used by the original investigators, viz.,

$$\text{rate} = \frac{P_{CO}\, P_{H_2}^{\;3}}{(A + B\,P_{CO} + D\,P_{CO_2} + E\,P_{CH_4})^4}$$

Boudart (1956) recommends the following procedure to be adopted where the mechanism of a reaction is unknown:

(1) Empirically fit the data to an equation of the type

$$r = k\, P_A^{\;a} P_B^{\;b} P_C^{\;c} \;---$$

(2) Find a possible mechanism which gives the rate law found empirically in the first step.

(3) Confirm the assumed mechanism by a rigid analysis

of the kinetic constants.

It is accepted that the final step of the above procedure is generally not possible, especially for the case of complex heterogeneous reactions.

2.2.4. CATALYST DEACTIVATION.

Catalyst deactivation by one (or more) of the most common mechanisms (poisoning, coking or sintering) is an inherent feature of almost all catalytic reactions (Butt, 1976), the form taken by the deactivation depending upon the chemical nature of the reaction as well as the catalyst itself. Poisoning occurs by the chemisorption of impurities in the feed on to the active catalytic sites. Typical poisons are the heavy metals, arsenic and sulphur (Gould, 1972). Of these, the most serious in the Fischer-Tropsch synthesis or methanation is sulphur: sulphur is present to varying extents in all coals - the normal source of the carbon monoxide and hydrogen for the synthesis. In general, operation of methanation reactors using industrial catalysts necessitates the use of synthesis gas with sulphur levels of $<0{,}1$ppm (Dalla Betta, Piken & Shelef, 1975). Since the gases used in this investigation were all high purity, the possibility of poisoning by feed impurities was not considered.

Sintering occurs as a consequence of overheating and is generally regarded as being caused by crystallite agglomeration and growth. Overheating can be regarded as an engineering problem inasmuch as it can be avoided by careful reactor design and operation.

Redispersion of the metallic crystallite on supported catalysts is greater in oxygen atmospheres than in hydrogen atmospheres (Somorjai, 1968), further, redispersion in oxygen-containing atmospheres appears, from a study of the available literature, to be restricted to temperatures in excess of 400°C (Wanke & Flynn, 1975). In view of the operational techniques employed in this investigation, no simple thermal sintering is likely to have occurred.

The deactivation of a catalyst used in reactions involving hydrocarbons is quite common: the deactivation occurring by fouling (or "coking") of the catalyst surface by carbonaceous deposits (Butt, 1972). Most of the work into coking has been restricted to cracking catalysts, although even with the large body of work in this field, the chemical mechanism is still ill-defined (Butt, 1976; Lee, Butt & Downing, 1978).

Poisoning and sintering are generally rather slow processes (Butt, 1972) while fouling is more rapid (Rudershausen & Watson, 1959). Dalla Betta, Piken and Shelef (1974) in their study of initial methanation over supported ruthenium likewise reported a very rapid initial deactivation of the catalyst, as indicated by a rapid decrease in the rate of CO removal with time.

2.2.5. ADSORPTION OF GASES.

2.2.5.1. PHYSICAL ADSORPTION.

The fact that a porous solid can take up relatively large amounts of condensable gas has been known for more than two centuries (Gregg & Sing, 1967). The equation for the relation between volume of adsorbed gas and the total surface area of the solid (generally referred to as the B.E.T. equation, after its originators) was, however, not developed until 1938 (Brunauer, Emmett & Teller, 1938).

The derivation of the B.E.T. equation in its most commonly-used form (the two-parameter equation) is presented elsewhere (Flood, 1967) and will not be given here. In its usual form, the B.E.T. equation is

$$\frac{p/po}{V\ (1-p/po)} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C} \cdot p/po$$

This was the relation used in the calculation of the total surface area of all the catalyst samples.

2.2.5.2. CHEMISORPTION.

The preceding section has discussed how the physical adsorption of a gas such as nitrogen may be used to give a measure of the total surface area of a solid. In heterogeneous catalysis, the total area of the catalyst is of secondary importance to the area of the catalytic metal dispersed upon the support. The most commonly-employed method for the determination of metal surface areas utilises the selective chemisorption of a suitable gaseous adsorbate. The technique requires that the adsorbate used form a chemisorbed monolayer, with a known stoichiometry for the metal-adsorbate chemisorption.

The use of chemisorption for the measurement of metal surface areas of catalysis has been reported many times in the literature (Dalla Betta, 1974; 1975; Benson & Boudart, 1965; Buyanova et alii, 1972) and is now a well-established catalyst characterisation technique. Adsorbates which have been used include hydrogen (Dalla Betta, 1974), oxygen (Buyanova et alii, 1972), carbon monoxide (Dalla Betta, 1975) and a hydrogen-oxygen titration method (Benson & Boudart, 1965). Comparison of the relative efficacy of each of these methods is best made by brief consideration of each of the techniques in turn.

HYDROGEN CHEMISORPTION.

The chemisorption of hydrogen on metals was first reported in detail by Langmuir (1912) who determined the monomolecular nature of the adsorbed film. Beeck (1950) demonstrated that the amount of hydrogen adsorbed onto evaporated nickel films corresponded to one atom of hydrogen per metal atom. This atom-for-atom correspondence has been shown to be equally applicable for platinum (Spenadel & Boudart, 1960), cobalt

(Sinfelt, Taylor & Yates, 1965), rhenium (Dalla Betta, Piken & Shelef, 1975) and ruthenium (Dalla Betta, 1974; Taylor, 1975).

The stoichiometry of the chemisorption is established by comparing the chemisorption data for the adsorbate being used on unsupported metal powders or films with the total surface determined by standard B.E.T. measurements. The previously-cited work on ruthenium resulted in H/Ru ratios of 1,17 and 1,1: sufficiently close to unity to justify the assumption of the stoichiometry as given by

$$Ru_s + \tfrac{1}{2}H_2 \longrightarrow Ru_s - H$$

where Ru_s denotes a surface atom of ruthenium

One of the disadvantages of the hydrogen chemisorption technique is that the rate of adsorption is very low at ambient temperatures, frequently requiring several hours for equilibration (Dalla Betta, 1974). This is a direct consequence of the fact that chemisorption is a chemical process and thus only becomes measurable above some minimum temperature . This problem can be overcome either by allowing equilibration over an extended period of time, e.g. overnight (Dalla Betta, 1974), or by conducting chemisorption at an elevated temperature; 100°C frequently being employed (Taylor, 1975).

OXYGEN CHEMISORPTION.

The use of oxygen in chemisorption to determine the metal area of supported catalysts has not received much attention in the literature. Oxygen adsorption on supported and unsupported ruthenium has been evaluated (Buyanova et alii, 1972; Taylor, 1975) using both flow and static methods. While the oxygen chemisorption method has the advantage of equilibrating more rapidly at ambient temperatures than the hydrogen method, the stoichiometry of the chemisorption

$$Ru_s + \tfrac{1}{2}O_2 \longrightarrow Ru_s - O$$

found for the larger particle sizes does not appear to hold for ruthenium particles below 40 Å (Taylor, 1975).

A variable oxygen stoichiometry was also evident in a study of both hydrogen and oxygen chemisorption techniques on supported platinum catalysts conducted by Wilson and Hall (1970) who demonstrated that with increasing catalyst sintering, while the H_2 chemisorption decreased, the O_2 chemisorption remained almost constant (or even exhibited an increase) with decreasing platinum metal area.

Comparison of oxygen and hydrogen chemisorption techniques for the determination of ruthenium areas for supported catalysts (Taylor, Simkevitch & Klimisch, 1970) containing from 0,02 to 1,0 per cent by mass of the metal indicated that for dispersions of greater than 40%, oxygen uptake

CARBON MONOXIDE CHEMISORPTION.

The use of carbon monoxide as an adsorbate for chemisorption is complicated by the fact that adsorbed carbon monoxide can exist in several forms. In an investigation of the mechanism of carbon monoxide chemisorption on supported ruthenium (Guerra, 1969; Guerra & Schulman, 1969) three forms of carbon monoxide bonding were reported: M_2CO (bridged), MCO (linear) and $M(CO)_2$ (multiple). Yates and Garland (1961) reported both linear and bridged forms of bonding of CO on supported nickel and Kavtaradze et alii (1965) (reported in Buyanova et alii, 1972) found both bridged and linear forms on supported ruthenium, with the linear form predominating. The ratio of linear to bridged forms of bonding can vary depending upon surface coverage, with the more strongly-bound bridged form predominating at low surface coverage (Buyanova et alii, 1972).

This leads to difficulty in defining the relative amounts of linear or bridged forms present, thus making it difficult to estimate the number of surface metal atoms present from the amount of CO adsorbed, since bridged and linear forms have different metal-adsorbate stoichiometry.

The effect of ruthenium particle size upon the nature of the chemisorbed CO has been considered by Dalla Betta (1975), who demonstrated that CO/H ratios as high as 4 can occur on small (11 Å) particles of ruthenium; from which can be inferred that multiple adsorption of CO is occurring. The use of both carbon monoxide and hydrogen for the measurement of ruthenium areas of sixteen ruthenium catalysts were compared by King (1978) who found that the CO adsorption gave areas consistently higher (by a factor of 2 or 3) than was obtained with H_2 adsorption, likewise indicating multiple CO adsorption.

This feature of carbon monoxide chemisorption on ruthenium renders its use for area determination generally unsuitable.

HYDROGEN-OXYGEN TITRATION.

The use of a hydrogen-oxygen titration method for the determination of metal areas for supported platinum catalysts with very low platinum contents was first mooted by Benson and Boudart (1965).

Basically the method is one in which hydrogen, instead of being chemisorbed onto the clean metallic catalyst particles, is used to react with the (previously oxidised) metal.

The technique is thus inherently more sensitive than simple hydrogen chemisorption by virtue of the fact that three hydrogen atoms are consumed for each accessible platinum atom:

$$\mathrm{PtO} + \frac{3}{2}\mathrm{H_2} \longrightarrow \mathrm{PtH} + \mathrm{H_2O}$$

The technique has been evaluated for supported ruthenium catalysts

(Taylor, 1975) and it was found that the same limitations applied to this technique as were found for the oxygen chemisorption: that it was suitable for particles greater than 40 Å.

SUMMARY OF CHEMISORPTION TECHNIQUES.

In the light of the above remarks, it may be concluded that the use of a hydrogen chemisorption technique for the determination of metal surface areas is probably the most suitable. The use of hydrogen chemisorption has, in fact, become the most important technique for the measurement of metal surface area of catalysts (Vannice, 1975; 1975[a]; Dalla Betta, 1974; Dalla Betta, Piken & Shelef, 1974; 1975; Taylor, 1975).

PARTICLE SIZE DETERMINATION.

The mean ruthenium particle size can be calculated from the chemisorption data if a number of simplifying assumptions are made (Gregg & Sing, 1967; Taylor, 1975), regarding the shape and size distribution of the particles. If it is assumed that the particles are all of uniform size and further, they are all cubic, then the total area of these cubes may be written as

$$A = \left[\frac{6\kappa^2}{\kappa^3}\right] \quad \text{where } \kappa \text{ is the length of the cube side.}$$

If the density of the material is ρ then the specific surface S is given by

$$S = \frac{6}{\kappa \rho}$$

thus $$\kappa = \frac{6}{\rho S}$$

This then would be a measure of the metal particle size if all six faces of the cube were to be exposed to the adsorbate or, alternatively, if the particles are all assumed to be spherical, with diameter κ. If it is assumed that one of the faces is bonded to the support and is thus unavailable for adsorption, the relation becomes

$$\kappa = \frac{5}{S.\rho}$$

Both of these methods have been used in the literature, and both give very similar results. The assumption of more complicated particle shapes (e.g. hexagonal prisms (Buyanova et alii, 1972)) is probably unjustified in view of error introduced by the primary assumption of particle size uniformity. The above analysis assumes that the chemisorption properties of ruthenium are not affected by particle size effects; an assumption which would appear to be valid, at any rate as far as hydrogen chemisorption is concerned (Taylor, 1975).

The use of the above relation for mean particle diameter based on hydrogen chemisorption has been demonstrated to be valid (Dalla Betta, 1974) by comparison of particle size calculated by this method and particle size determined by electron microscopy; regarded as being the most reliable method (Whyte, 1973) of particle size estimation.

2.2.6. DISPERSION AND TURNOVER NUMBERS.

Having decided upon a suitable adsorbate for the catalyst to be examined, the dispersion or fraction of the metal exposed to the adsorbate may be denoted by

$$\Phi = \left(\frac{G}{M_T} \right) . \left(\frac{M_s}{G} \right)$$

where Φ = fraction exposed

(G/M_T) = adsorbate uptake on the catalyst

(G/M_s) = stoichiometry of the adsorption

The metal surface area may now be determined by

$$S_M = M_T . A_M . \Phi$$

where S_M = metal surface area

M_T = total number of metal atoms in the sample of catalyst

A_M = area occupied by one metal atom

The value A_M for any metal may be estimated by comparison with the generally-accepted (Sinfelt, Taylor & Yates, 1965; Klemperer & Stone, 1958) value for nickel of

$$6,5\ \text{Å}^2\ \text{atom}$$

Thus,

$$A_M = A_{Ni} \left[\frac{r_m}{r_{Ni}}\right]^2$$

where r_m = atomic radius of the metal under consideration

r_{Ni} = atomic radius of nickel

Typical values for A_{Ru} in the literature include 7,6 Å^2 (Sinfelt & Yates, 1972), and 8,17 Å^2 (Dalla Betta, 1974) (based on the assumption of equal participation of the (001), (100) and (101) planes of ruthenium).

With the aid of an estimate of the metal surface area, catalytic rates may now be expressed in terms of surface active sites instead of per unit mass of catalyst. This idea of specific reaction rates or "turnover numbers" is a fairly recent one (Meyer & Burwell, 1973) although a positive linear correlation between rate and the metal surface area of cobalt-based Fischer-Tropsch catalysts had been noted very much earlier (Anderson et alii, 1951).

The major advantage of expressing rates in this manner is that rates obtained by different workers in different laboratories may now be compared directly, a hitherto dangerous task. This has been amply demonstrated by Vannice (1977) who compared turnover numbers for the CO : H_2 reaction obtained from five different laboratories using ten different catalyst preparations. Corrected to identical operating conditions of temperature and pressure, the turnover numbers for catalysts using the same supports agreed to within a factor of two: an agreement which must be regarded as being acceptable.

The rates of formation of methane over various metal catalysts when expressed in terms of turnover numbers (Vannice, 1975) compared with the reactivity expressed in terms of methane formation per gram of metal (Fischer, Tropsch & Dilthey, 1925) showed several major differences, the chief among them being the replacement of iridium by iron as the second most active methanation catalyst, and the demotion of iridium from its previously-held number two position to that of the least active.

The use of supported metal catalysts has decided advantages over the use of their unsupported equivalents. This is especially true in the case of precious metal catalysts, where high dispersion permits use of low metal concentrations, thus alleviating to some extent the high cost of these metals. A further advantage is the stabilising influence achieved by dispersing the metal. However, the use of supported catalysts raises the problems of syngerism and the possible effects of metal particle size upon both reaction rate and product distribution.

One of the interesting aspects of heterogeneous catalysts revealed by measurement of metal areas is that some reactions appear to be structure sensitive (or 'demanding') inasmuch as the turnover number is dependent to some extent upon the metal fraction exposed or upon the metal particle size; while other reactions are structure insensitive (or 'facile') exhibiting no such dependence (Boudart, 1972).

The methanation and Fischer-Tropsch reactions occurring over a number of ruthenium catalysts have recently been demonstrated to be structure sensitive (King, 1978): with metal dispersions varying from 60% to 23% on alumina-supports, the turnover numbers for methanation at 250°C varied from approximately 0,010 s^{-1} to 0,043 s^{-1} respectively. In other words, the more poorly-dispersed catalysts showed a higher specific activity; unsupported ruthenium, with a turnover number of 0,143 s^{-1}, showing the highest activity. The steady-state methanation data of Dalla Betta, Piken & Shelef (1975) show a slightly lower extent of structure sensitivity for three alumina-supported ruthenium catalysts with dispersions ranging from 8,8 to 61% which produced steady-state turnover numbers (at 400^{o}C) of 0,099 s^{-1} to 0,035 s^{-1} respectively; a somewhat surprising result, since they report no evidence of structure sensitivity for initial rates of methanation. (Dalla Betta, Piken & Shelef, 1974).

The direct evaluation of the effect of degree of dispersion upon activity must be undertaken with caution; while it is probably reasonable to compare directly catalysts employing the same support, the use of a different support (e.g. SiO_2 instead of Al_2O_3) can affect the catalyst activity via metal-support interactions (Vannice, 1977).

An interesting result regarding support effects has been reported by King (1978), who found that when a catalyst consisting of 1,8% Ru on γ -alumina was mixed with an ultrastable molecular sieve support, the degree of isomerisation of the C_4 and C_5 carbon number fractions (with iC_4/C_4 = 4,0 and iC_5/C_5 = 11,9) was comparable to that obtained when the ruthenium was impregnated directly onto the molecular sieve (where iC_4/C_4 = 3,5 and iC_5/C_5 = 13,8). This may be contrasted with the degree of isomerisation obtained by the use of ruthenium on γ-alumina catalysts only, where the isobutane and isopentane were below detection limits. This result suggests that the isomerisation reaction is not occurring with the normal synthesis, but rather is a result of subsequent molecular rearrangements.

In order to determine the magnitude and nature of metal-support interactions, Vannice (1975 [b]) investigated specific reaction rates in the CO-H_2 reaction over a number of catalysts employing different supports. In the case of platinum, supported catalysts exhibited specific methanation rates considerably greater (by approximately two orders of magnitude) than those determined over unsupported platinum. (This may be contrasted with the results of King (1978) for ruthenium catalysts referred to above where unsupported ruthenium exhibited an activity higher than any of the supported catalysts). In the case of platinum, the specific methanation rates for different supports varied only slightly; indicating the primarily physical nature of the support's role (viz, in dispersing the metal to varying degrees).

The nature of the metal-support interaction with palladium catalysts appeared to differ from that with platinum insofar as the type of support employed with palladium exercised a considerable influence over the specific methanation rates, while the metal particle size did not appear to have any major effect upon the activity. Again, as was the case for platinum, unsupported palladium exhibited a very much lower activity than did most of the supported catalysts. The one exception to this in the case of supported palladium was the low activity exhibited by silica-supported palladium compared to either alumina- or zeolite-supported palladium. This difference in support influence was not observed for platinum, where the influence of the metal particle size was dominant.

This anomoly may be explained by use of the assumption that any factor which weakens the CO-metal bond will result in an increase in catalytic activity. For platinum catalysis, the formation of the weakly-held linear form of adsorbed CO is favoured by small metal particle size (Freel, 1972; Eischens & Plishin, 1958). This, then, explains the higher activity observed with smaller Pt particles. The nature of the adsorbed CO on palladium, on the other hand, has been shown (van Hardeveld & Hartog, 1972) to be dependent upon the nature of the support: alumina-supported catalysts favouring the linear form, while silica-supported catalysts favouring the (more strongly-bonded) bridged form.

This would likewise explain the fact that ruthenium has the highest methanation activity of all the Group V11 metals (Vannice, 1975): of all the Group V11 metals examined by McKee (1967) ruthenium was unique in that chemisorbed CO could be removed be evacuation at 150°C - indicative of weakly bonded CO.

This assumption of a correlation between CO-metal bond strength and methanation activity is supported by the existence of a correlation between the rate of methanation and heat of CO adsorption, as shown in Figure 2.1. (Vannice, 1975 [a]).

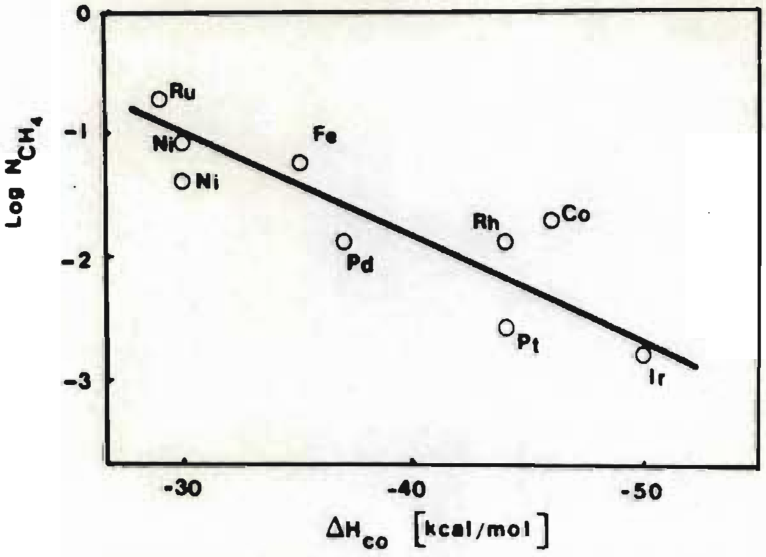


Figure 2.1. - Methanation Activity versus CO Adsorption.

Nickel catalysts (Vannice, 1975 [b]) exhibited a much smaller degree of particle size-support sensitivity, although the average molecular weight of the synthesis product was found to be increased by the use of a support.

The use of graphite-supported metal catalysts for the hydrogenation of carbon monoxide at 1 atm total pressure and 300 - 400°C has been studied by Kikuchi and co-workers (1976). They reported the following order for the activity

$$Co > Rh > Ni > Fe > Ru > Pd > Pt$$

which differs from the order reported by Vannice (1975) for alumina-supported metals viz:

$$Ru > Fe > Ni > Co > Rh > Pd > Pt$$

The relatively high activity of rhodium in the work on graphite-supported catalysts was attributed to a metal-support interaction involving electron transfer between the rhodium and the graphite.

It can thus be seen from the above, that while the nature and magnitude of both metal particle size effects and metal-support interactions can vary from metal to metal and from support to support, it is important in heterogeneous catalysis that the catalyst be characterised as thoroughly as possible. Although the nature of these interactions is not, as yet, fully understood, it is to be hoped that detailed characterisation of catalysts employed in heterogenous catalysis will produce a greater understanding of the nature of such effects, leading perhaps to the "ultimate achievement in catalysis [which] would be the ability to determine without experimentation the optimum catalyst for a given chemical reaction". (Butt, 1976).

2.3. LITERATURE RELATING TO THE FISCHER-TROPSCH REACTION AND METHANATION.

As mentioned in Section 1.3., the "Fischer-Tropsch reaction" is the term generally applied to the synthesis of hydrocarbons higher than methane from carbon monoxide and hydrogen over a suitable catalyst. The synthesis of methane only (carbon dioxide and/or water always being formed) from carbon monoxide and hydrogen is more properly known as methanation. However, since no study of the Fischer-Tropsch reaction could be considered complete without reference to the methanation reaction, this section will include work conducted into methanation under the generic term of the Fischer-Tropsch reaction.

It must be emphasised at the outset that because of the enormous volume of literature available in this field, any review must, of necessity, be restricted in scope. An indication of the amount of work conducted into the Fischer-Tropsch reaction may be obtained by considering that a review conducted by the U.S. Bureau of Mines in 1954 (Anderson, Wiley & Newell, 1954) listed almost 3 000 references to the Fischer-Tropsch reaction and more than 4 000 patents. Work has continued since that date and has, indeed, accelerated enormously over the past few years.

Lately several review articles on methanation and the Fischer-Tropsch synthesis have appeared (Mills & Steffgen, 1974; Vannice, 1977; Vlasenko & Yuzefovich, 1969), and accordingly no attempt will be made here to cover all of the published literature. Rather, a brief resumé of the more relevant literature will be given, with emphasis on the later published work.

2.3.1. HISTORICAL.

The first report of the production of hydrocarbons from carbon monoxide and hydrogen was in 1902 (Sabatier & Senderens, 1902). However, the first detailed examination of the hydrocarbon synthesis was not made until 1923 when Franz Fischer and Hans Tropsch reported the production of hydrocarbons over an iron catalyst (Fischer & Tropsch, 1923). This pioneering work was later extended by the same workers to cover all of the Group V11 metals (Fischer, Tropsch & Dilthey, 1925).

Work on the commercial-scale production of synthetic hydrocarbon fuels received an impetus in Germany in the period immediately preceding the Second World War. This work was aimed at producing liquid hydrocarbon fuels (with coal as a source of carbon monoxide and hydrogen) with the aim of ensuring German self-sufficiency in fuel supplies based on their large reserves of coal. The years 1935 to 1945 saw the construction and operation of nine Fischer-Tropsch plants in Germany (Bussemeier, Frohning & Cornils, 1976).

Following the end of the war in 1945, the attractiveness of this means of liquid fuel production fell away, although the U.S. Bureau of Mines conducted extensive tests into the technical and economic feasibility of various coal hydrogenation processes.

The construction of the oil from coal plant at Sasolburg in the Republic of South Africa was undertaken on largely strategic grounds: South Africa has no known economically-exploitable reserves of oil or natural gas, but does have considerable quantities of coal (Falcon, 1977) which can be mined at a low cost (Bussemeier, Frohning & Cornils, 1976).

2.3.2. FISCHER-TROPSCH AND METHANATION MECHANISMS.

Although, as mentioned earlier, the Fischer-Tropsch synthesis and methanation have been the subject of intensive research for many years, there is still disagreement on the reaction mechanism (or mechanisms, if the two are regarded as proceeding via different mechanisms).

One of the earliest proposals for the synthesis was (not surprisingly) made by Fischer and Tropsch in 1926 (Fischer & Tropsch, 1926). This was the "carbide theory", which was later further developed by Craxford and Rideal (Craxford, 1939; Craxford & Rideal, 1939; 1946).

The carbide theory in its earliest form, postulated that the hydrocarbon synthesis proceeded via the metal carbide of the catalyst, which was hydrogenated with the resultant methylene radicals polymerising and desorbing as olefins or alkanes.

$$M + CO \longrightarrow MC + H_2O$$

$$MC + H_2 \longrightarrow M + (-CH_2-)$$

$$n\ (-CH_2-) \longrightarrow C_nH_{2n}$$

$$C_nH_2 + H_2 \longrightarrow C_nH_{2n+2}$$

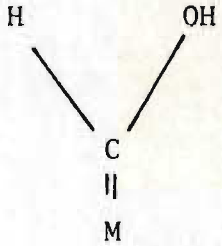
The carbide theory has been criticised on the grounds that it does not adequately explain the synthesis on ruthenium (which does not form a carbide under synthesis conditions) and that for synthesis over nickel catalysts the temperature necessary for the production of methane is lower than the temperature which is required for the hydrogenation of nickel carbide (Fischer & Tropsch, 1926). A further pointer away from the carbide theory was that the rate of synthesis is greater than the rate of carbide formation, (Weller, 1947; Eidus, 1958) although it has been pointed out (Anderson, 1956) that the rate of carbide formation decreases with the extent of carbonisation and an element of arbitrariness is introduced into the calculation of synthesis rates by operation at a fixed level of carbonisation. Possibly one of the major disadvantages of the carbide theory lies in its inability to predict the formation of oxygenated compounds, while synthesis over iron catalysts, for example, can produce appreciable quantities of such compounds (Storch, Golumbic & Anderson, 1951).

In an attempt to overcome this latter objection to the carbide theory, the presence of oxygen-containing surface intermediates was proposed. These included intermediates such as methanol (Elvins & Nash, 1926) and formaldehyde (Storch, Golumbic & Anderson, 1951). However, during methanation over nickel, no evidence was obtained of either methanol or formaldehyde in the product (Tropsch,Schellenberg & Phillipovich, 1925). Further, when methanol was used as a starting material for synthesis over cobalt catalyst the yield of hydrocarbons was lower than that obtained when carbon monoxide and hydrogen were used as starting materials (Tropsch, Schellenberg & Phillipovich, 1925). It would therefore seem that the formation of hydrocarbons from methanol proceeds via the degradation of the methanol into carbon monoxide and hydrogen.

Still utilising the basic idea of oxygenated intermediates, Eidus (1958) and Hamai (1941) both proposed the existance of an intermediate of the form HCOH.

The conclusion that the synthesis proceeds via an unstable intermediate containing carbon, oxygen and hydrogen was also reached by Bashkirov (Kryukov et alii, 1961) and Gibson & Clarke (1961).

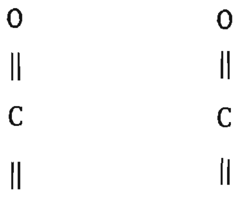
That the reaction proceeds via an unstable intermediate containing carbon, hydrogen and oxygen (in the form HCOH) has been concluded by several investigators employing various experimental techniques to determined the nature of the intermediate. These techniques have included CO-H_2 co-adsorption (McKee, 1957), infrared spectroscopy (Eberly et alii, 1966) and flash desorption (Madey & Yates, 1977). The generally accepted form of the intermediate is the enol form:



a form which featured in the scheme proposed by Storch, Golumbic and Anderson (1951), and one which is still in evidence to-day. The overall scheme proposed can, unlike the original carbide theory, account for the formation of oxygenation products as well as branched isomers of the products. A simplified overall schematic of this reaction scheme is presented in Figure 2.2.

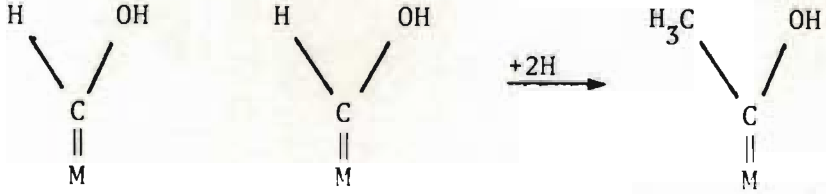
FIGURE 2.2. - SIMPLIFIED STORCH, GOLUMBIC & ANDERSON (1951) MODEL.

1. CHEMISORPTION:

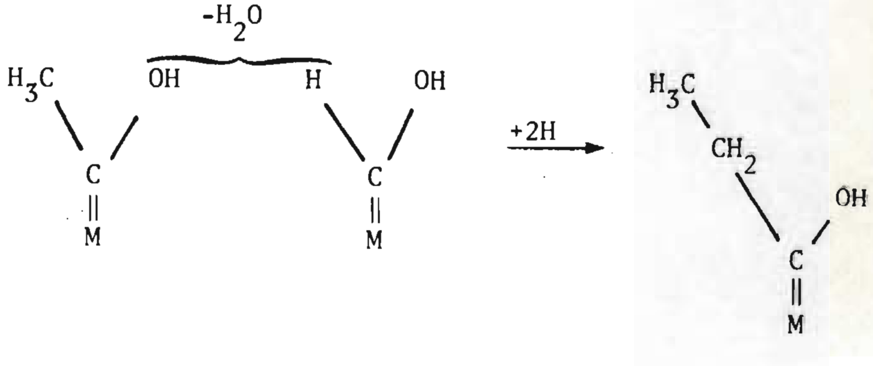


2. FORMATION OF OXYGENATED COMPLEX:

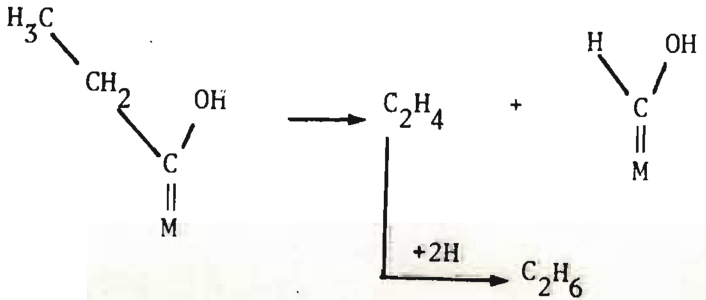
3. CHAIN INITIATION:



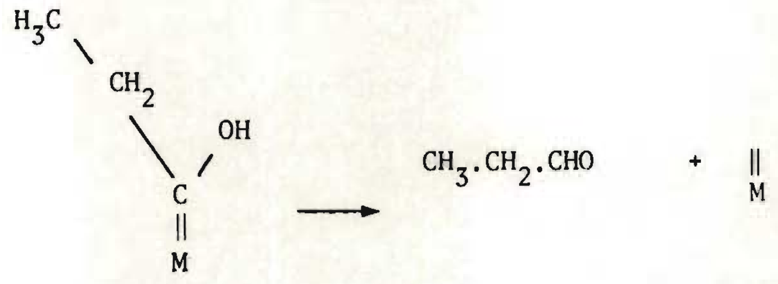
4. CHAIN GROWTH:



5. FORMATION OF HYDROCARBONS:



6. FORMATION OF OXYGENATES:



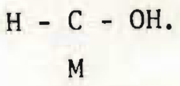
Early investigations into the use of ruthenium as a methanation or Fischer-Tropsch catalyst may be regarded qualitatively only, since no characterisations of the catalysts were undertaken. However, two early reports which give empirically-fitted values of either activation energy or reaction rate exponents are worth considering here. Karn, Schultz and Anderson (1965) studied the CO - H_2 reaction over a supported ruthenium catalyst in an integral reactor operating at a total pressure of between 1 and 21 atm and synthesis gas H_2/CO from 1 to 4. They obtained a satisfactory fit to their experimental data with an equation of the type

$$r = Kp_{H2}^{1,33} \; P_{CO}^{-0,13}$$

No value was given for the activation energy of the reaction (presumably because of the limited range of temperatures covered (222 - 239°C]. Randhava, Rehmat and Camara (1969) studied the methanation of low-concentration carbon monoxide feed gases over supported ruthenium (CO = 505 to 3450 ppm in hydrogen) and reported that for the low concentrations of CO, CO_2 and CH_4 found in their work that the methanation rate was given by

$$r_{CH_4} = K.p_{CO}$$

Evidence was obtained of pore diffusional limitations at the upper end of the temperature range (175 - 275°C) considered, and their reported activation energy of 37,2 Kcal/mole was obtained using the lower temperatures only.

McKee (1967) studied the interaction of hydrogen and carbon monoxide on a series of unsupported noble metal catalysts in a batch reactor. On the basis of his measurements, he concluded that hydrogen and carbon monoxide interact in the adsorbed layer, with $V_{CO}/V_{H_2} \simeq 1$ (where V = adsorbed volume) when a mixture of H_2 and CO were contacted with ruthenium at temperatures between 45°C and 154°C. Ruthenium was found to be unique among the noble metals considered (Pt, Rh, Ir, Ru) in that 50% of adsorbed CO could be removed from the surface by evacuation at 150°C, and total removal could be achieved by treatment with H_2 followed by evacuation. This would indicate that the chemisorbed CO is less-strongly bonded on ruthenium than the other metals considered. If the assumption regarding relative bond strength of M - CO (where M = metal) is recalled (where weakly-held CO is assumed to result in high catalytic activity), this could explain the higher activity of ruthenium as a methanation catalyst when compared to the other noble metal catalysts. The equimolecular interaction of H_2 and CO evident in adsorption on ruthenium would also serve as evidence of the formation of a structure of the form  $H-\underset{M}{C}-OH$. McKee's results for the rate of methanation over ruthenium were fitted to the rate equation

$$r = K P_{H_2}^{2} P_{CO}^{o}$$

over the entire range of initial gas mixture compositions used. An activation energy of 9 Kcal/mol was reported.

Dalla Betta, Piken and Shelef (1974; 1975) studied both the initial and the steady-state activity of CO methanation over ruthenium and nickel catalysts. A differential-type reactor was used with $H_2 : CO = 3 : 1$ and a total synthesis gas pressure of 0,75 atm with total reactor pressure maintained at 1,0 atm by the use of He diluent gas. A power rate law was used to fit the data by relating measured reaction rates to rates obtained under "standard conditions":

$$r = r_o \left[\frac{P}{P_o}\right]^{n}_{H_2} \left[\frac{P}{P_o}\right]^{m}_{CO}$$

where subscript "o" denotes standard conditions. Reaction orders for initial rates of methanation and total hydrocarbon synthesis were found to be dependant upon temperature, as shown in Table 2.1. Activation energies of 17 Kcal/mol and 24 Kcal/mol were reported for total hydrocarbon formation and methanation respectively.

TABLE 2.1.

REACTION ORDERS FOR INITIAL RATES (DALLA BETTA, PIKEN & SHELEF, 1974).

TEMPERATURE °C	EXPONENT	TOTAL H.C.	CH_4
240	n	1,28	1,79
	m	-0,47	-1,14
300	n	1,70	2,04
	m	-1,93	-1,43

Even with the low conversions used, deactivation of the catalyst was initially rapid, with steady-state values (measured after 24 hours operation) being lower than the initial rates by a factor of approximately 25.

Vannice (1975) has reported upon a study made into CO - H_2 reaction over supported Group V111 metals. A flow microreactor system was used to give CO conversions typically less than 5% and total reaction pressure was 1 atm.. H_2 : CO ratios were varied from 0,6 to 15 and reaction temperatures over ruthenium ranged from 207 - 230°C. The product distributions obtained over these metals showed that the use of ruthenium resulted in the highest overall product molecular weight. The rate data obtained were fitted empirically to a power law of the form

$$N_{CH_4} = Ae^{\frac{-Em}{RT}} P_{H_2}^{X} P_{CO}^{Y}$$

The kinetic parameters for ruthenium obtained by this fitting were

$$Em = 24,2 \pm 1,2 \text{ Kcal/mol}$$

$$X = 1,6 \pm 0,1$$

$$Y = -0,6 \pm 0,1$$

$$A = 5,7 \times 10^{8} \text{ molecules/site sec.}$$

while the activation energy for CO removal (E_{CO}) was found to be 18,3 ± 1,0 Kcal/mol. These values for activation energies compare well with the results of the Dalla Betta, Piken & Shelef investigation referred to earlier, although the exponent for the CO partial pressure is considerably lower; the significance of which will be discussed in Chapter 7. In a subsequent publication, Vannice (1975 [a]) presents a kinetic analysis assuming that the rate-determining step is the breaking of the C-O bond. This assumption is shown to be consistent with the data obtained and provides very good agreement between the calculated and regressed values of Y appearing in his empirical rate equation. In a further article, (Ollis & Vannice, 1975) a modification was made to the original kinetic scheme which corrected the rate expression to allow for the fact that in the original derivation the regressed value obtained for n - where n is the exponent in the approximation

$$\frac{K.P_{CO} P_{H_2}}{1 + P_{CO} P_{H_2}} \simeq (K P_{CO} P_{H_2})^n$$

for ruthenium exceeded 1,0 by a degree "well outside any experimental uncertainty".

Details of the Vannice mechanism and the subsequent modification are given in Appendix 2.

The use of a differential reactor to study the hydrogenation of CO over a nickel catalyst has been reported by Huang and Richardson (1978). The proposed mechanism (shown in Appendix 2) results in a Hougen-Watson type of rate equation of the form:

$$\text{rate} = \frac{K.\ K_{CO} P_{CO} P_{H_2}^{\ n}}{(1 + K_{CO} P_{CO})^m}$$

where the values n and m depend upon which step is assumed to be rate-determining. The derivation of values of n and m corresponding to various rate-determining steps is given in Appendix 2.

The kinetics of carbon monoxide hydrogenation over a series of Ru - Cu / SiO_2 catalysts over the temperature range 530 - 670 K has been reported (Bond & Turnham, 1976). By increasing the copper-ruthenium atomic ratio from 0 to 1, the rate of CO hydrogenation was found to decrease by a factor of approximately 50. With the addition of copper, no influence was observed upon the apparent activation energy (which was reported as being approximately 21 Kcal/mol) while the order in H_2 became less positive and the order in CO more positive with increasing copper additions.

The data were fitted to a modified version of the Ollis-Vannice (1975) model, the modification being based upon the dissociative adsorption of H_2 molecules giving a rate-determining step of

$$CHOH_{(ads)} + aH_{(ads)} \longrightarrow CH_{a\,(ads)} + H_2O$$

which leads to a rate expression similar to that derived by Vannice.

The rate-determining step in the hydrogenation of carbon monoxide over supported ruthenium was assumed by Phung-Quach and Rouleau (1978) to be the reaction between the adsorbed CO molecule and adsorbed hydrogen.

Dautzenberg and co-workers (1977) have used a pulsed reactor operated at 10 atm total pressure with H_2/CO = 1/1 and a temperature of 483 K to evaluate the Fischer-Tropsch synthesis over two different ruthenium on γ-alumina catalyst, the metal areas of which were determined by oxygen chemisorption. The rate of propagation of the reaction, with a rate constant of approximately $1,5 \times 10^{-2}\ s^{-1}$, is several orders of magnitude lower than is usually found in heterogeneous catalysis. The rate of initiation was not rate-controlling and all the atoms were found to be active but with an intrinsically low activity. The mechanism considered was one with a close similarity to that proposed by Storch, Golumbic and Anderson (1951).

While the existance of the HCOH intermediate has proved to be a popular assumption, some recent investigators have derived mechanisms for synthesis based on the dissociative adsorption of carbon monoxide. Rabo, Risch and Poutsma (1978) reported that at 300°C the adsorption of CO on silica-gel supported ruthenium was dissociative in nature, resulting in disproportionation of the CO to CO_2 and surface carbon. This surface carbon was found to be more reactive towards H_2 than was chemisorbed non-dissociated CO. On this basis, the ventured the following speculation as to the mechanism of hydrocarbon synthesis: (which is basically the mechanism proposed some 50 years earlier by Fischer and Tropsch):

$$\begin{array}{llcll}
1 & 2M + CO & \longrightarrow & M\text{-}C & + \ M\text{-}O \\
11a & M\text{-}O + H_2 & \longrightarrow & M & + \ H_2O \\
11b & M\text{-}O + CO & \longrightarrow & M & + \ CO_2 \\
111 & M\text{-}C + 2H_2 & \longrightarrow & M & + \ CH_4
\end{array}$$

The rate-controlling step is assumed to be Step 1 in the above sequence, with Step 11a or 11b following: the choice being determined by the relative reactivity of the M-O towards H_2 and CO. At room temperature the adsorption of CO on ruthenium was found to be non-dissociative; a conclusion also reached by Madey and Yates (1977). Since the dissociation energy of gaseous carbon monoxide is 256kcal/mol (Vannice, 1975 [a]; Madey & Yates, 1977), this reported difference in adsorption mechanism over this temperature range is not surprising.

Joyner (1977) has noted that one of the major problems associated with the postulate that synthesis proceeds via the dissociative adsorption of CO is that molybdenum and tungsten dissociate CO more readily than nickel or iron but yet are poor Fischer-Tropsch catalysts.

For temperatures between 80 and 120°C Ku, Gjostein and Bonzel (1977) found no evidence for dissociative adsorption of CO on a clean ruthenium (1010) surface, while for temperatures between 250 and 350°C Sexton and Somorjai (1977) reported evidence for the presence of both molecular and dissociated CO on the surface of polycrystalline rhodium foil during hydrocarbon synthesis. It seems likely that the presence of the molecular or dissociated forms of CO on metallic surfaces would be dependant upon the conditions under which the adsorption states are examined.

As has been mentioned, the most recent publications of work concerning both methanation and the Fischer-Tropsch synthesis have been made on the basis of "specific rates" or "turnover numbers" (terms which are used synonomously throughout this report). In addition, a few studies of the interaction occurring between CO and H_2 on various Group V111 metals have also been reported. While these reports have aided in the understanding of the mechanism of the reaction and have produced empirical correlations based on more fundamental measurements for the rate of methanation, there is still a great deal of work to be done before a reaction as complex as the Fischer-Tropsch reaction can be fully understood.

CHAPTER 3.

EXPERIMENTAL.

3.1. MATERIALS USED.

The catalyst used in this study was a commercial preparation of nominally 0,5 per cent mass ruthenium on γ-alumina in the form of 3,2 mm by 3,2 mm cylindrical pellets from Engelhard Industries. A detailed characterisation of the catalyst is given in Chapter 4.

The gases used were all supplied by African Oxygen. Reducing hydrogen was used for catalyst pretreatment was Matheson U.H.P. grade with a minimum purity of 99,999 per cent and before use was passed through an Engelhard De-Oxo unit and a 5A molecular sieve drier. The synthesis gas ($H_2/CO = 3/1$) was pre-mixed by African Oxygen from Matheson C.P. grade carbon monoxide, with a purity of 99,5 per cent, and Matheson U.H.P. hydrogen. The argon blanket gas was Afrox U.H.P. grade with a minimum purity of 99,999%. Both the synthesis gas and the argon were used as received with no further purification.

All feed and product lines to and from the reactor were stainless steel, as was the reactor itself. The reactor pot gasket seals were annealed copper.

3.2. EXPERIMENTAL SYSTEM.

The apparatus for the synthesis was a continuous flow system designed around the reactor and is most easily described by considering each of the three major components of the system in turn:

(i) the feed system

(ii) the reactor

(iii) the product analysis system

The overall system is shown schematically in Figure 3.1. and a photograph of the overall system is presented in Figure 3.2.

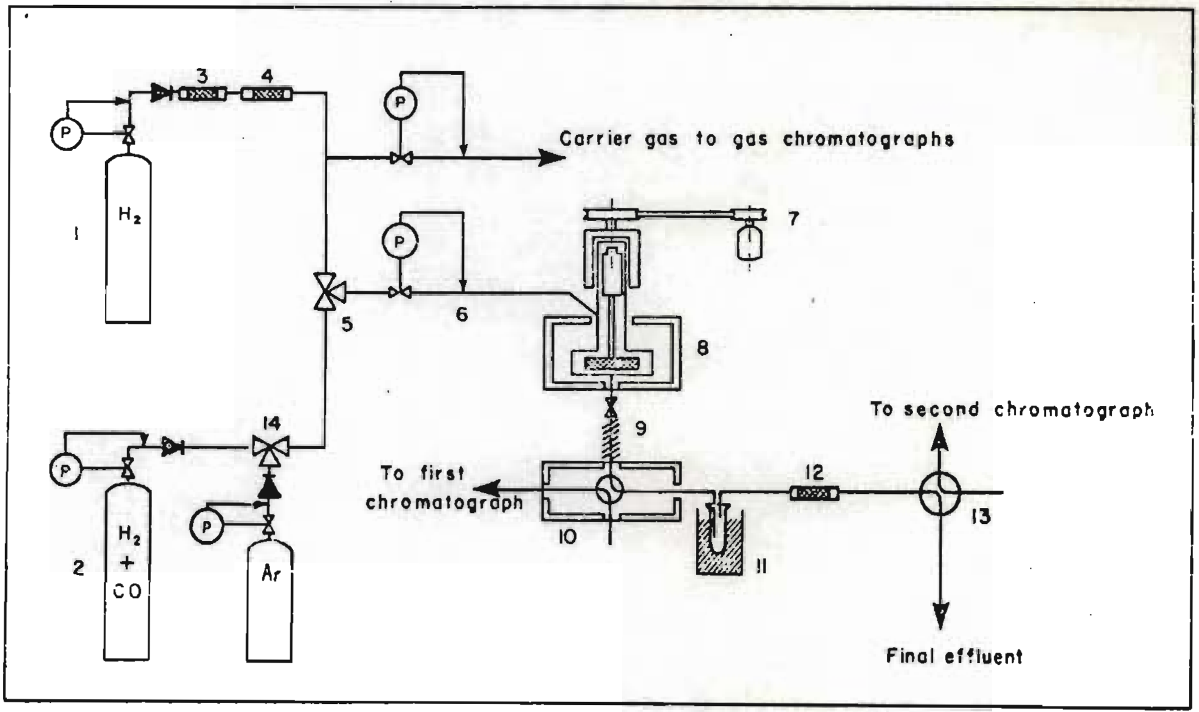


FIGURE 3.1. - SCHEMATIC OF OVERALL SYSTEM

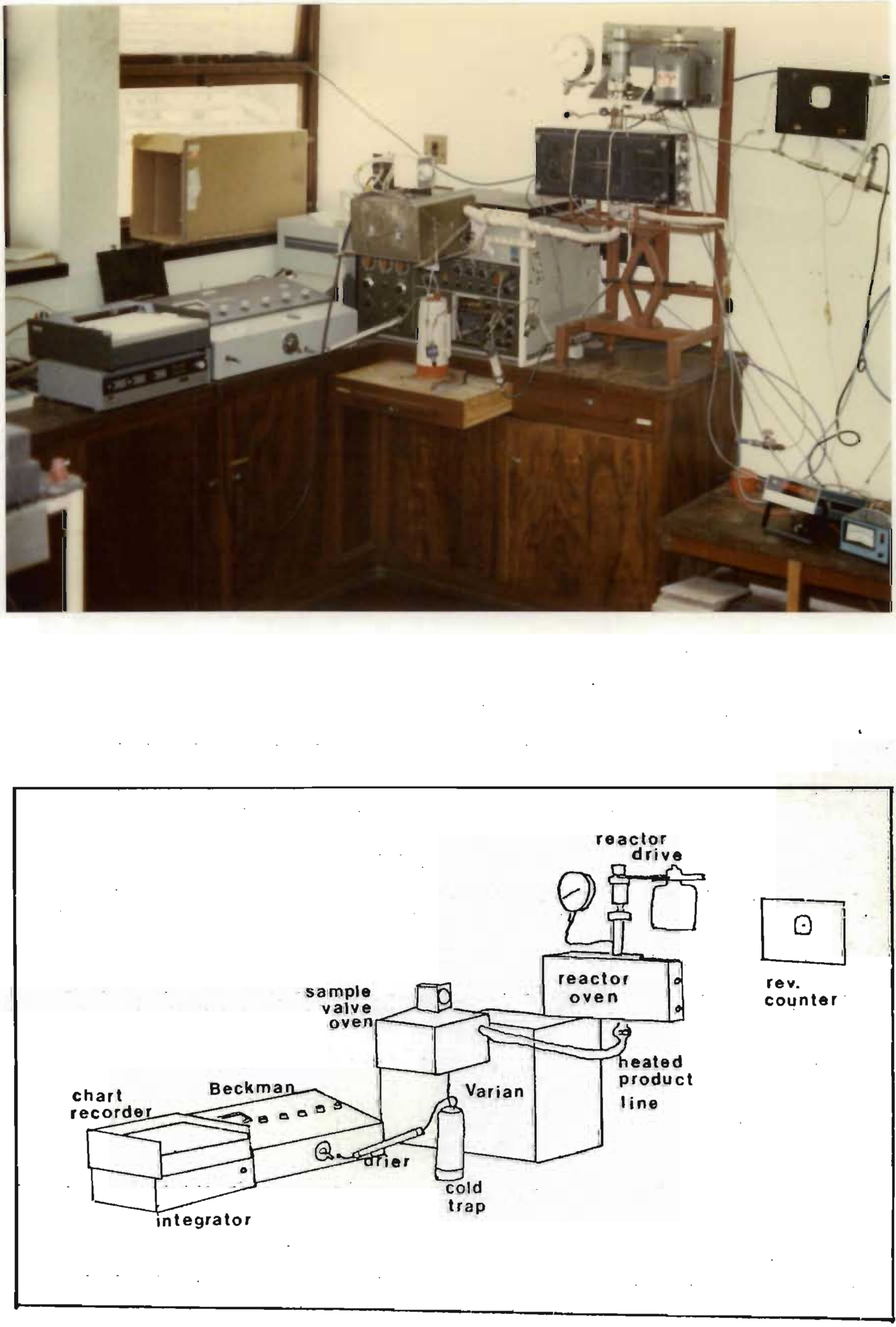


FIGURE 3.2. - PHOTOGRAPH (AND KEY) OF OVERALL EXPERIMENTAL SYSTEM.

3.2.1. THE FEED SYSTEM.

The purpose of the feed system was to enable hydrogen, synthesis gas or argon to be admitted to the reactor at a suitable pre-determined pressure.

Gas was admitted to the reactor from the required cylinder by operation of the two three-way valves numbered 5 and 14 in Figure 3.1. Valve 5 determined whether hydrogen or synthesis gas would be used, while Valve 14 was used to select either the hydrogen/synthesis gas (for catalyst pretreatment or synthesis respectively) or the argon blanket gas. After leaving the second three-way valve, the gas passed into the reactor via an Afrox M-600 pressure regulator pre-set to produce the reactor operating pressure required.

This system enabled the reactor to be operated at a fixed pressure over a range of flow rates into (and hence out of) the reactor, thus facilitating operation of the reactor over a range of synthesis gas conversions.

The flow rate of gas into the reactor was controlled indirectly by means of a stainless steel needle valve on the outlet line of the reactor. Adjustment of this valve controlled the rate of removal of products from the reactor which, in turn, determined the feed rate of gas to the reactor.

The use of synthesis gas without further purification was justified on the grounds that King (1978) found no evidence of carbonyl formation from pre-mixed synthesis gas with a higher CO content (33%) than was used here.

3.2.2. THE REACTOR.

The reactor employed was an I.C.I.-developed stirred gas-solid reactor (S.G.S.R.) Mark V1, which has been described in detail by Brisk et alii (1968). The overall reactor and oven assembly is shown in Figure 3.3. and details of the reactor internals are shown in Figure 3.4.

The drive unit was magnetically-coupled, allowing rotation of the catalyst basket at speeds of up to 6 000 r.p.m. This unit consisted of an electric motor driving a housing which contained six fixed magnets. The stirrer shaft inside the reactor vessel had six similar magnets built into it, and the strong magnetic field between the inner and outer magnets caused the stirrer shaft to rotate at the same speed as the outer housing. This form of drive meant that the reactor vessel could be totally enclosed, enabling operation to be made at elevated pressures with no leakage of gas past the drive shaft.

The reactor vessel contained the stirrer shaft which supported the catalyst basket. The loaded basket is shown in place in Figure 3.5.

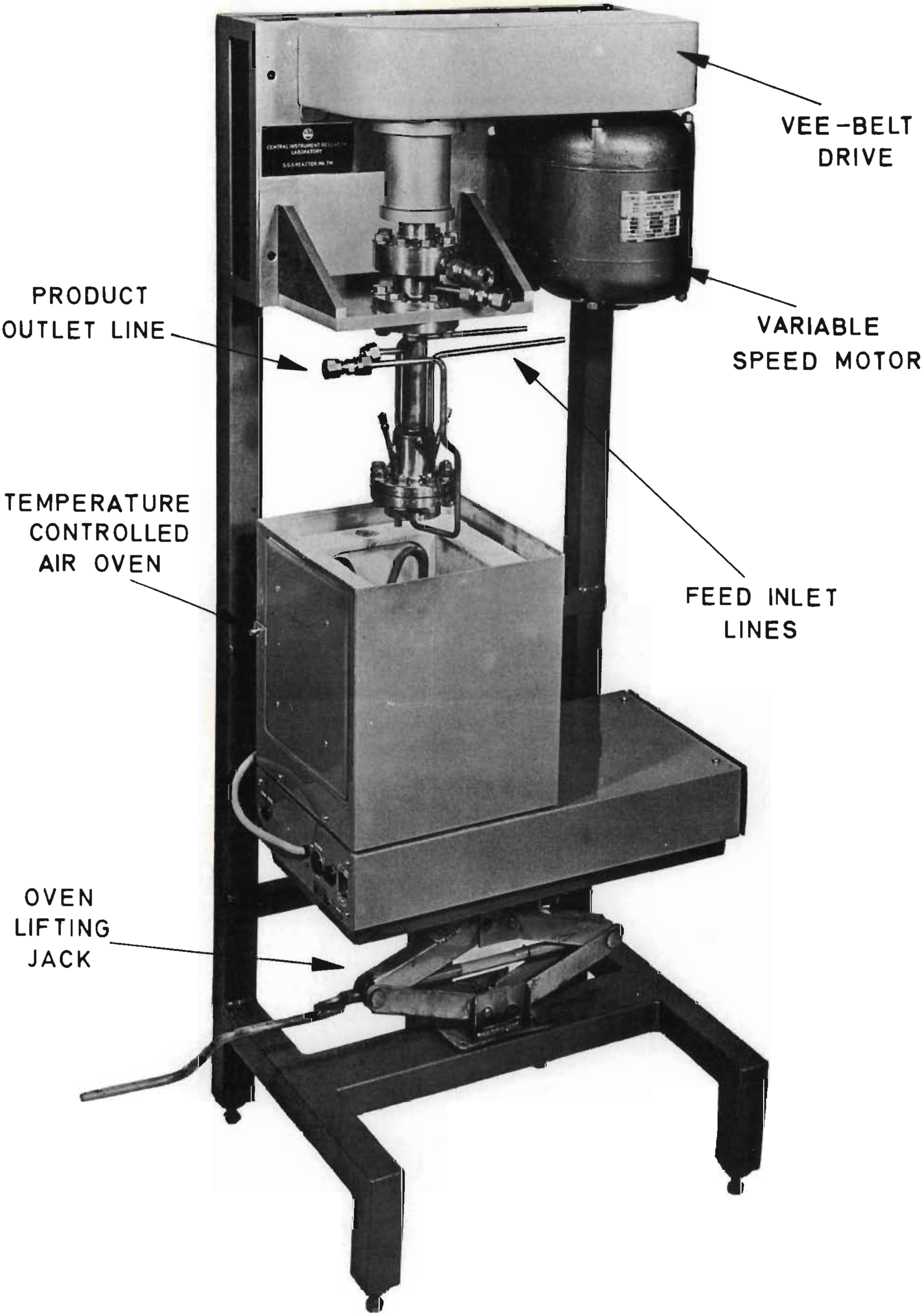
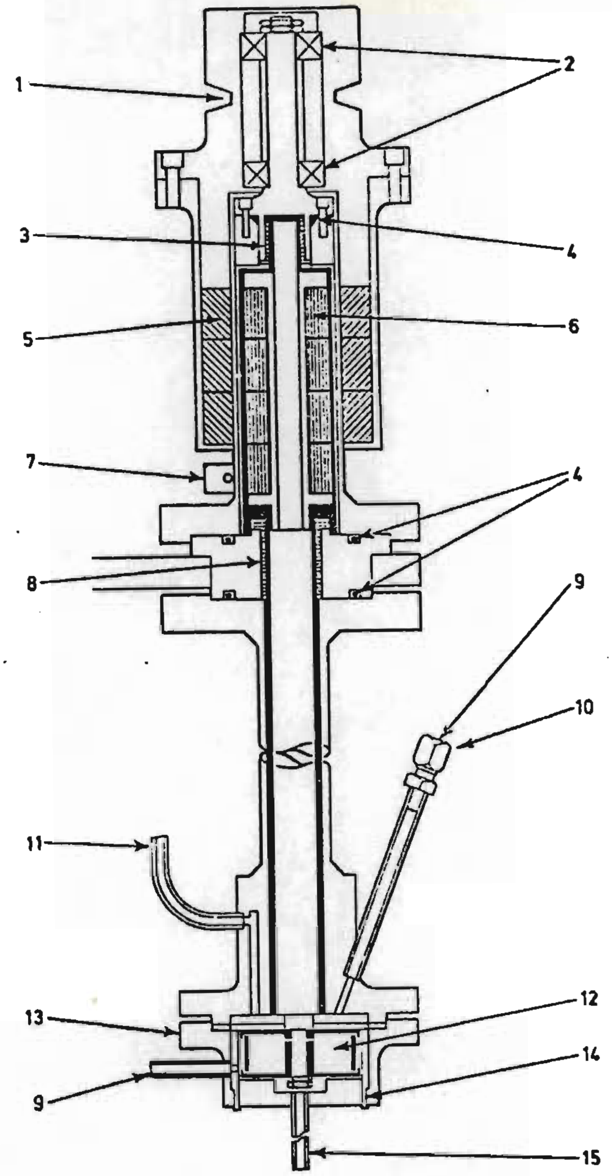


FIGURE 3.3. - REACTOR AND OVEN ASSEMBLY.



1: belt drive groove
2: outer magnet bearings
3: upper bearing
4: O ring seals
5: outer magnet
6: inner magnet
7: reed relay
8: lower bearing
9: thermocouple entries
10: pressure tapping
11: inlet port
12: catalyst basket
13: reactor pot
14: baffles
15: outlet port

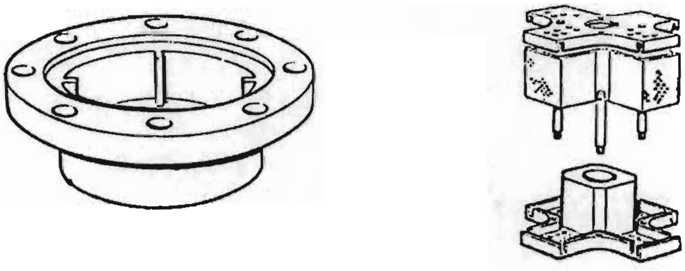


FIGURE 3.4. - DETAILS OF REACTOR INTERNALS.

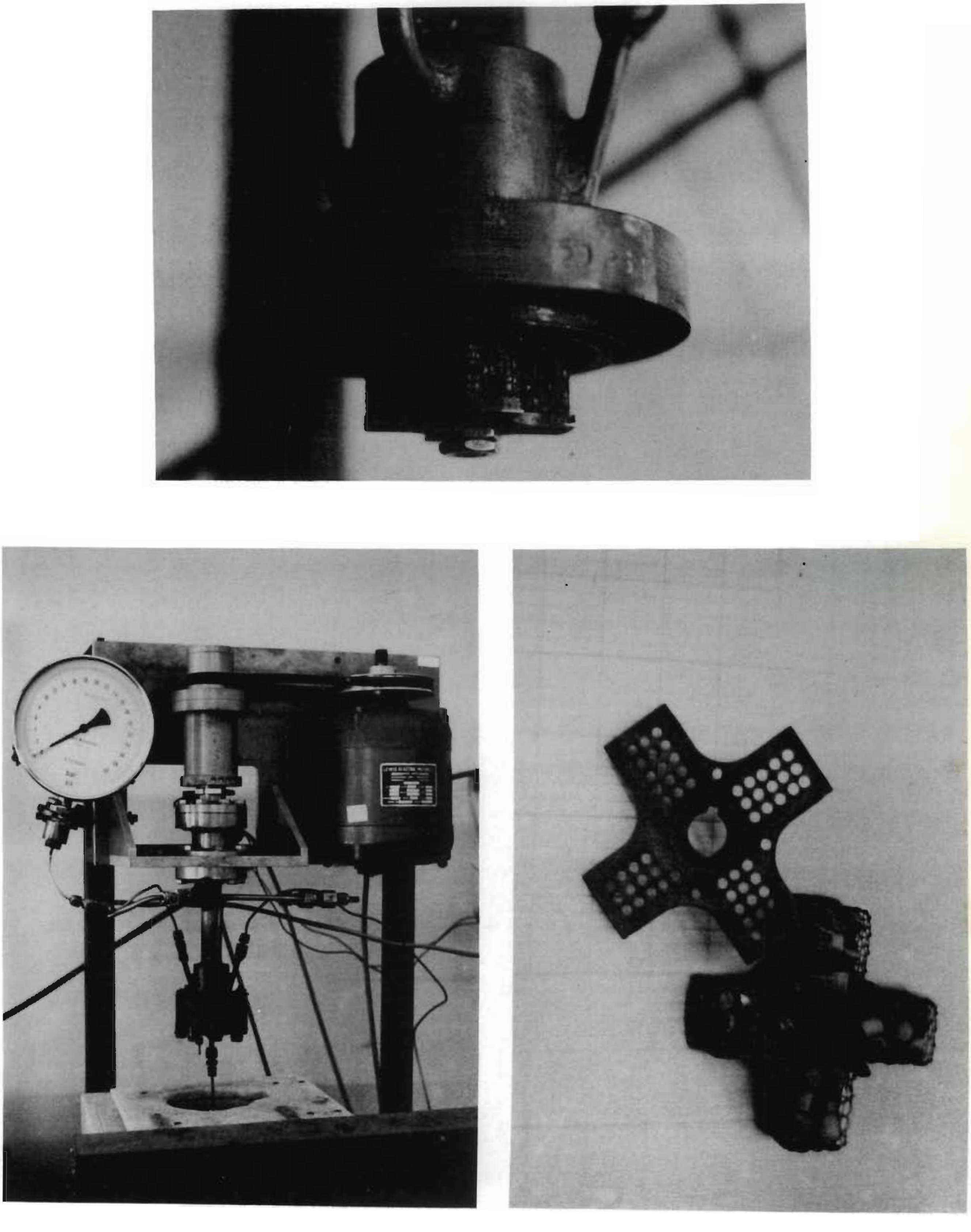


FIGURE 3.5. - DETAILS OF REACTOR.

The shaft was supported by two water-cooled carbon-filled Teflon bearings (the upper being a locating bearing and the lower a thrust bearing) which required no lubrication and which showed superior bearing characteristics to the Rulon bearings which were initially used. Gas entered the reaction vessel through a feed line approximately 18 cm above the catalyst basket, while the reactor outlet was at the bottom of the reactor pot containing the catalyst basket. This configuration resulted in a new downward flow of gas away from the bearing surfaces, thus preventing accumulation of catalyst fines or reaction products in the bearing areas. Accumulation of reaction products and/or catalyst fines can result in excessive wear on the shaft and bearing surfaces, producing rough running of the reactor.

The catalyst basket used was of the cruciform type (shown in Figures 3.4. and 3.5.), which had a total charge volume of 10,4 cm^3. The top and bottom of the basket were constructed of perforated stainless steel plate, while the walls of the basket were of stainless steel mesh. The catalyst basket acted as a catalyst support and as a stirrer rotating in the baffled reactor pot.

Heating of the reactor was achieved by a Perkin-Elmer F100 gas chromatograph over with a 1 Kw heater. The temperature control specification on the oven was $\pm$ 0,5 C^o, but modifications made to the insulating walls resulted in temperature control to $\pm$ 1 C^o (the temperature being measured inside the reactor gas space).

Temperature was originally measured by the use of a millivolt meter in conjunction with a Pyrotenax chromel-alumel thermocouple inside the reactor gas space directly above the catalyst basket, but was later carried out by the use of a Fluke model 2100A digital thermometer with the same thermocouple.

Sealing of the reactor pot was ultimately achieved by the use of annealed copper gaskets; asbestos and asbestos-filled stainless steel gaskets both proving unsatisfactory.

3.2.2.1. REACTOR CHARACTERISATION.

No thorough quantitative characterisation of the mixing characteristics was carried out since this had been done during the development stage (Brisk et alii, 1968). It was necessary, however, to determine the minimum stirrer speed required to ensure adequate mixing of the reactor contents for the range of flow rates to be examined. This was done by examining the extent of mixing under the "worst" conditions prevailing during an experiment, i.e. at the highest flow rate to be used. This was carried out by filling the catalyst basket with glass beads of approximately the same size as the catalyst pellets, activating the stirrer mechanism and employing an inert gas pulse technique to determine the minimum stirrer speed neccessary to produce "good" mixing. The presence of the glass beads was by way of an attempt to keep the hydrodynamics of the system as close as possible to these prevailing during an experiment: glass beads being used in preference to catalyst pellets (or γ-alumina pellets) to minimise adsorption of the pulsed gas. The technique involved injecting a pulse of nitrogen into a stream of hydrogen which was flowing through the reactor into a thermal conductivity detector. Examination of the form of the response of the detector to the nitrogen measured at the outlet of the reactor thus enabled an evaluation to be made of the degree of mixing in the reactor.

No rigorous quantitative analysis was made on the thermal conductivity output signals because of the departure from ideality caused by the substantial dead volume between the reactor outlet and the detector. However, with an outlet flow rate of 370 ml/min (which was the highest flow employed in this investigation) mixing was not improved by any increase in the stirrer speed above 3 000 r.p.m. In light of this, all experiments were conducted at stirrer speeds in excess of 4 000 r.p.m. During the course of some of the preliminary experiments, the stirrer speed was deliberately decreased below 4 000 r.p.m., but kept above 3 000 r.p.m. In these tests no change was observed in the measured rate of reaction, indicating that the reactor contents were well-mixed.

Since the absence of concentration gradients precludes the existence of temperature gradients, it was assumed that the bulk fluid in the reactor was isothermal.

3.2.3. PRODUCT ANALYSIS SYSTEM.

Analysis of the product stream from the reactor was by gas chromatography. For reasons which are outlined in Section 3.3., two chromatographic analyses were necessary for each experiment. The chromatographs used were firstly, a Varian 2800 chromatograph employing dual column thermal conductivity detectors (T.C.D.) operated with temperature programming, and secondly a Beckman G.C. 2A chromatograph with single column T.C.D. operated isothermally. Gas sampling was, in both cases, by by sample valve: the sample for the Varian analysis being taken by a Carle sample valve enclosed in a heated (180^{o}C) modified Beckman G.C. 4A oven, while the sample for analysis on the Beckman chromatograph was taken by a Beckman sample valve operated at ambient temperature.

The product stream from the reactor flowed through an electrically-heated, copper jacketed stainless steel line to the heated Carle sample valve. (The copper jacket fitted tightly over the stainless steel line was to improve heat transfer to the line and prevent cool spots from developing.) From the heated sample valve the product stream was passed through a cold trap maintained at 0^{o}C to remove water and the majority of the higher hydrocarbons and then through a silica gel drier and 5A molecular sieve column before passing through the second sample valve. From the second sample valve, the final effluent gas passed through a bubble flow meter before being vented to atmosphere. Operational details for both of the gas chromatographs are given in the following section.

3.3. ANALYTICAL TECHNIQUES.

In order to appreciate the reason for the analytical system employed, it is necessary to consider the nature of the product stream from the reactor and also the nature of the data which is required from a reactor of the type employed here.

3.3.1. CHROMATOGRAPHIC ANALYSES.

At the outset, it was understood that the product stream would be a complex mixture containing unconverted hydrogen and carbon monoxide together with varying concentrations of the reaction products of water, carbon dioxide and hydrocarbons containing from one carbon atom up to approximately ten or twelve carbon atoms per molecule. It was also considered desirable that a complete analysis of the product stream be conducted in one operation. In other words, one gas sample should be sufficient to give a complete product analysis.

Because of the nature of the product stream, this necessitated the use of thermal conductivity detection techniques since the more sensitive flame ionisation detection technique would not, under normal conditions, detect carbon monoxide, carbon dioxide or water (Schaefer & Douglas, 1971; Williams, Wood & Umstead, 1972). However, the whole principle of operation of the thermal conductivity cell is predicated on the difference in thermal conductivity between the carrier gas and the substance being detected. In order to obtain a measure of the hydrogen concentration, the use of some gas other than hydrogen as a carrier was therefore indicated. This, however, has the attendant disadvantage of generally producing a negative response for hydrogen (relative to all other components) as well as decreasing the sensitivity of the analysis. It was also evident that to separate hydrogen from the other components to an acceptable extent, the initial temperature of the separation would require to be sub-ambient (a facility which was not available) or the column length would have to be such that the elution time for the higher hydrocarbons would be prohibitively long.

A compromise situation was eventually adopted in which hydrogen was used as carrier gas (thus sacrificing the direct analysis of hydrogen) but two distinct analyses were conducted on the reactor product stream. The first of these analyses was conducted on the total product: giving an analysis of all products with the exception of hydrogen. The second analysis was conducted on the product stream after the removal of water and hydrocarbons above ethane. This second analysis thus gave concentrations of carbon monoxide, methane, carbon dioxide and ethane only; the balance of the gas being (undetected) hydrogen. The hydrogen content of the gas subjected to the second analysis could thus be obtained by difference:

$$[H_2]_E = 100. - \{[CO]_E + [CH_4]_E + [C_2H_6]_E\}$$

Meanings of the subscripts employed may be taken from Figure 3.6.

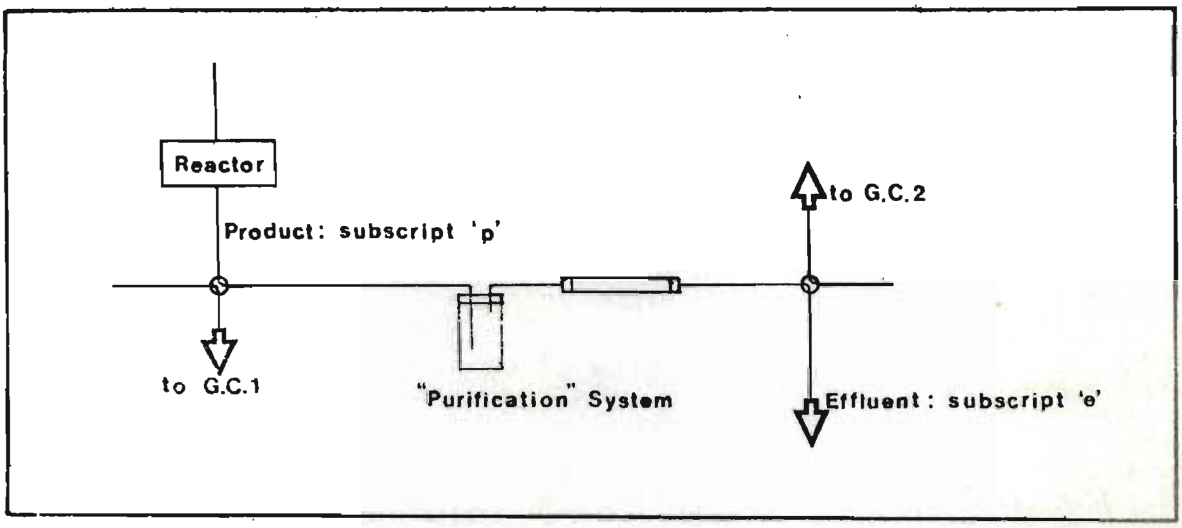


FIGURE 3.6. - SCHEMATIC OF PRODUCT AND EFFLUENT SCHEMES.

The concentration of hydrogen in the product stream could thus be calculated assuming that the purification steps (cold-trap - silica gel - molecular sieve) did not remove carbon monoxide or methane.

Then, $$\frac{[H_2]_E}{[CO]_E} = \frac{[H_2]_P}{[CO]_P}$$

$$\therefore \quad [H_2]_P = [H_2]_E \cdot \frac{[CO]_P}{[CO]_E}$$

$$= [H_2]_E \cdot \frac{[CH_4]_P}{[CH_4]_E}$$

The validity of the assumption that no carbon monoxide or methane removal occurred during purification was demonstrated by passing synthetic mixtures of carbon monoxide, hydrogen and methane through the purification system and measuring the T.C.D. responses of the resultant mixtures. There was no evidence to suggest any removal of carbon monoxide, methane or hydrogen.

A knowledge of the product flow rate from the reactor is necessary to convert the chromatographic data from concentration data to rate data by the relation

$$r_i = F_P [C_i]_P$$

r_i = rate of production of component i

F_P = total product flow rate

$[C_i]_P$ = concentration of product i in the product

While the flow rate of the final effluent stream could be measured directly by any displacement technique, e.g. bubble flow meter as employed in this investigation, the reactor product stream contained varying concentrations of water and other condensable products and thus required indirect measurement. An estimate of the total product flow rate could, however, be obtained by a simple balance over the purification system

$$F_E\ [CH_4]_E \quad = \quad F_P\ [CH_4]_P$$

Thus $$F_P \quad = \quad F_E \cdot \frac{[CH_4]_E}{[CH_4]_P}$$

(or similar relations involving carbon monoxide or hydrogen).

3.3.2. GAS CHROMATOGRAPHIC OPERATION.

Both gas chromatographs were calibrated by means of pre-mixed standard gas mixtures obtained from Afrox Limited. In the case of the Beckman analysis only carbon monoxide, methane, carbon dioxide and ethane were examined. The Varian analysis, however, required calibration for the entire range of reactants and reaction products. Calibration for carbon monoxide, methane, carbon dioxide, ethane, propane and butane was achieved using the standard gas mixtures. For water and hydrocarbons above butane, different techniques were necessary.

The water calibration was carried out by utilising the stoichiometry of the methanation reaction:

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$

In this case, where methane is the only hydrocarbon formed, the molar concentration of water is equal to that of methane. By running the reactor under conditions favourable to methanation and unfavourable for Fischer-Tropsch synthesis (high temperature, low pressure) varying concentrations of methane could be obtained by varying conversion via space velocity. Since calibration for methane was a relatively simple operation, this enabled the calibration for water to be performed. The calibration for pentane and higher hydrocarbons was by an extrapolation method, details of which are given briefly in Appendix 1.

Analysis of all peaks produced by the chromatographs was by area measurement. This was achieved for all component peaks (with the exception of water and C_3 hydrocarbons) by means of a Kipp and Zonen model BC1 digital integrator. Because of the moderately polar nature of the chromatographic columns used, the water and C_3 hydrocarbons appeared as fused peaks (Davé, 1978) and their areas were measured by planimeter after employment of a visual peak-smoothing technique. The method employed is demonstrated in Figure 3.7.

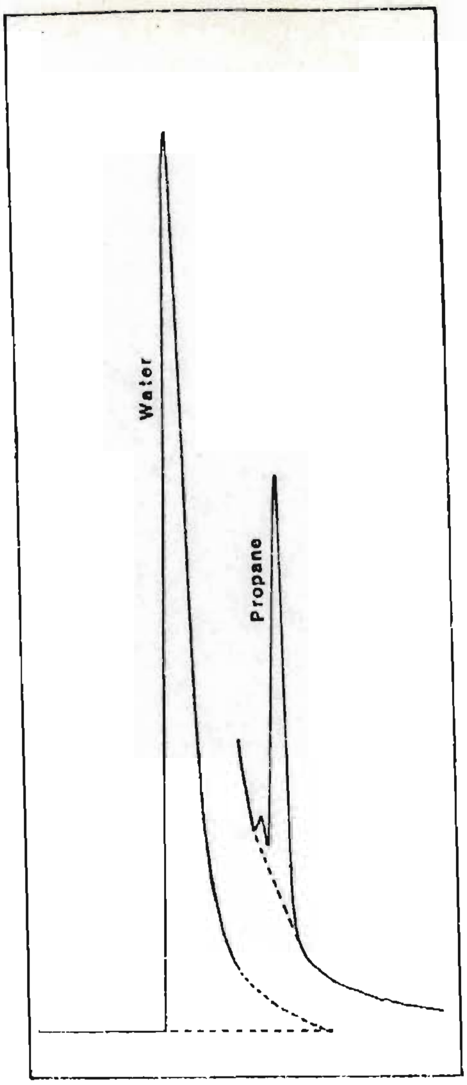


FIGURE 3.7. - PEAK SEGREGATION AND SMOOTHING.

3.4. EXPERIMENTAL PROCEDURE.

An algorithm of the experimental procedure adopted is given in Figure 3.8.

It was originally intended to employ an experimental program similar to that described by Sinfelt (1968) for the rate experiments. This method involves running an experiment at "standard" conditions periodically to ensure that no catalyst deactivation takes place, with regeneration of the catalyst conducted between experiments. This procedure was in fact

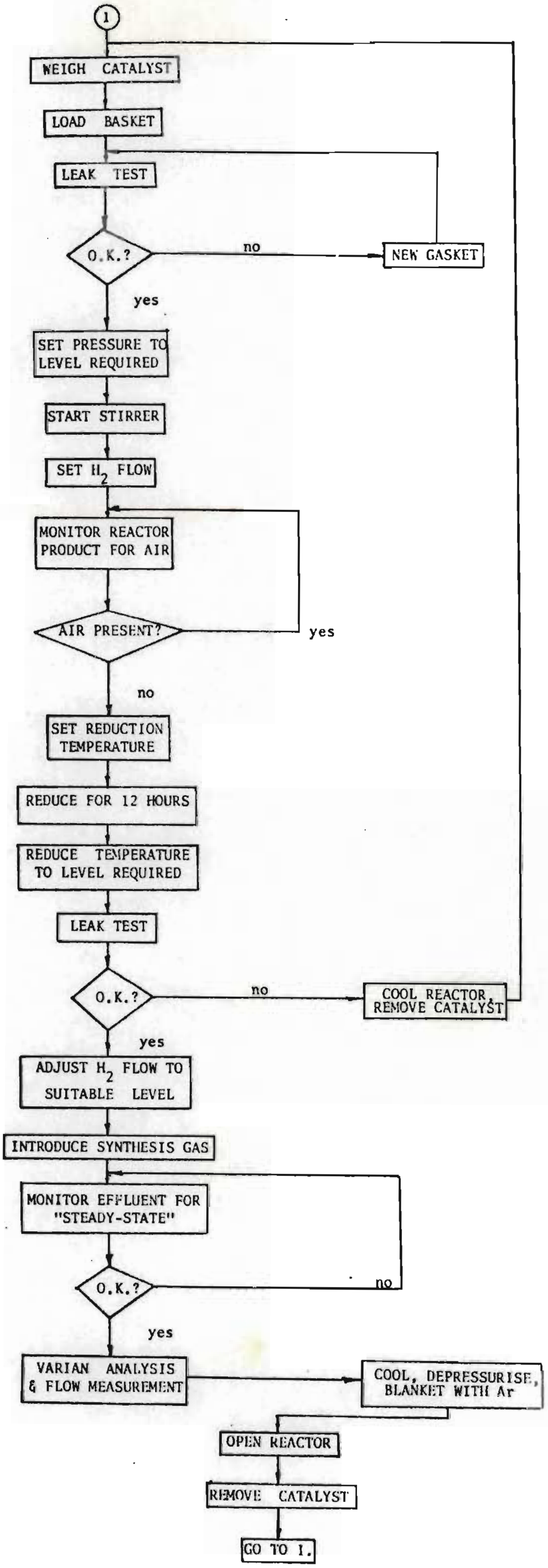


FIGURE 3.8. - ALGORITHM OF EXPERIMENTAL PROCEDURE

adopted for several of the preliminary experiments but was later rejected as being unsuitable for this particular application. The reason for the rejection of this potentially very useful technique was that the catalyst, under certain operating conditions, appeared to deactivate "irreversibly", i.e. inter-experimental treatment with hydrogen at 450°C did not restore the catalyst to its original activity. Because of this apparently irreversible deactivation, each experiment was conducted with a fresh catalyst charge to the reactor. An experiment thus consisted of the following sequence of events:

> catalyst was weighed and loaded into the catalyst basket, with care being taken to obtain uniform load distribution to ensure balanced running of the reactor. The reactor was then pressurised to the level required with hydrogen and leak-tested. The reactor outlet valve was then opened slightly to give a hydrogen outlet flow of some 10 ml per minute and, after a suitable period of time with the stirrer running at a minimum speed of 3 000 r.p.m., the outlet gas was analysed. When this analysis indicated that only hydrogen was present in the reactor, the reactor oven was set to 450°C and the catalyst reduced in situ for twelve hours. The reactor temperature was then decreased to the level required for the scheduled experiment and the reactor leak-tested again by closing off both inlet and outlet valves. Assuming no leaks were evident, the reactor inlet and outlet valves were opened and the hydrogen flow was adjusted to what was considered to be a suitable value depending on the

operating conditions required. Synthesis gas was then admitted to the system.

Flow rates and composition of the effluent stream were then monitored periodically until such time as no appreciable change in either flow rate or composition was observed. A sample of the product stream was then taken for analysis on the Varian chromatograph. At this time, the reactor outlet valve was closed, the system depressurised, blanketed with argon and cooled rapidly. Once cool, the reactor was opened and the catalyst charge removed for subsequent examination. This technique was adopted in order to "freeze" the physical condition of the catalyst. The catalyst removed from the reactor for examination was then regarded as having all the characteristics of the catalyst at the time the reactor product was sampled for analysis.

OPERATING CONDITIONS.

VARIAN 2800.

Dual column operation. Two 4 m x 3,2 mm diameter stainless steel columns packed with 80-100 mesh Chromosorb 102.

200 mA bridge current.

Column oven 50^{o}C to 250^{o}C at 20 C^{o}/min.

Carrier gas : hydrogen at 20 ml/min.

Detector temperature 300°C.
Injector temperature 250°C.
Sample valve temperature 180°C.

BECKMAN G.C. 2A.

Single column operation. 2 m x 3,2 mm diameter stainless steel column packed with 80-100 mesh Chromosorb 102.

200 mA bridge current.

Ambient operation (20°C)

Carrier gas : hydrogen at 20 ml/min.

3.5 OTHER EXPERIMENTAL METHODS.

Although the flow system described in the preceding sections was the principal part of the experimental apparatus, the peripheral equipment used in this investigation was also of considerable importance.

The flow system was used to conduct the rate studies, while the peripheral equipment was used in the characterisation of the catalyst and reaction product examination. Only a general description of the equipment used and methods employed will be presented here, a more detailed description together with the results being given in the following chapters.

3.5.1. ADSORPTION STUDIES.

Conventional glass vacuum systems were used to determine adsorption isotherms by standard volumetric techniques, (Bartholomew, 1978), the system for nitrogen adsorption being based on one described by Lippens (1970).

Two sets of adsorption studies were carried out; nitrogen adsorption which yielded information on the total catalyst surface area, and hydrogen adsorption which yielded information on metal surface area, metal dispersion and particle size.

3.5.1.1. NITROGEN ADSORPTION.

Nitrogen adsorption isotherms were determined at the temperature of liquid nitrogen (77 K) over a range of relative pressures (p/po). Prior to introduction of the gaseous nitrogen for adsorption, the sample was outgassed by heating to 150°C at a total pressure of 10^{-6} torr for approximately 2 hours. This pretreatment was intended to give a reasonably "clean" surface for adsorption.

The standard B.E.T. equation was used as outlined in Chapter 2 to determine the total surface area of the catalyst sample

$$\frac{p/po}{V(1-p/po)} = \frac{1}{V_m C} + \frac{(C-1)\ P/Po}{V_m C}$$

where p/p_o = relative pressure

V = volume adsorbed

V_m = volume corresponding to a monolayer

C = a constant

3.5.1.2. HYDROGEN ADSORPTION.

The measurement of the surface area of a supported metal by the chemisorption of a suitable gas is a well-established technique (Taylor, 1975; Whyte, 1973), the underlying assumption of this technique being that a gas such as hydrogen will adsorb selectively on the metal but not on the support. The hydrogen adsorption in this investigation was carried out at 100°C because of the very slow equilibration of hydrogen on ruthenium (Dalla Betta, 1974). Prior to the introduction of hydrogen, the sample was treated in flowing hydrogen at 200°C for 2 hours before being evacuated at 200°C. This temperature was chosen as being low enough to produce a clean surface without restructuring or regenerating the used, deactivated samples.

3.5.2. CARBON BURN-OFF.

Each of the catalyst samples generated was analysed for total carbon content. This was done by employing a Leco model W.R.12 carbon determinator which operated by burning the sample in a stream of oxygen and quantitatively determining the carbon dioxide so produced.

3.5.3. ELECTRON MICROPROBE EXAMINATION.

Although the ruthenium was distributed only on the outer surface of the γ-alumina support (a fact substantiated by optical microscopic examination), a quantitative determination of the ruthenium distribution was undertaken using an electron microprobe, a tool which has been employed previously for similar catalyst studies (Kempling, 1971; Kempling & Anderson, 1970).

3.5.4. MASS SPECTROMETRY.

A mass spectrometer was used to give a (largely qualitative) indication of the nature of the hydrocarbon and aqueous phases produced during synthesis. This was considered to be useful in providing corroborative evidence of the validity of the assumption of n-alkane production during synthesis and, further, it was hoped this tool would cast some light onto the nature of some of the minor products.

3.5.5. X-RAY DIFFRACTION.

It was hoped that an estimate of the ruthenium crystallite size could be obtained by X-ray diffraction studies. However, the crystallite size was found to be too small to produce satisfactory diffraction patterns. This was also a problem encountered by Dautzenberg and Wolters (1978) in a study of supported platinum catalysts.

3.5.6. I.R. SPECTROPHOTOMETRY.

The use of infra-red spectrophotometry to determine the nature of the carbonaceous material present on cracking catalysts has been reported in the literature (Eberly et alii, 1966). An attempt was made to examine the carbonaceous deposits present on the supported ruthenium catalyst used in this investigation, but the concentrations were too low to yield any meaningful results.

3.5.7. MERCURY POROSIMETRY.

An estimate of the total pore volume and pore size distribution of both fresh and used catalysts was obtained by the use of a mercury porosimeter.

CHAPTER 4.

CHARACTERISATION OF THE CATALYST.

4.1. INTRODUCTION.

In any catalytic investigation, the characterisation of the catalyst is of supreme importance, a remark which is particularly true in heterogeneous catalysis. Because of the possible influence of physical factors such as crystallite size (Carter, Cusumano & Sinfelt, 1966), metallic dispersion (King, 1978), catalyst distribution (Carberry, 1976) and metal-support interactions (Vannice, 1977) on the reaction rate and product selectivity, no catalytic investigation can be considered unambiquous without a rigorous description of the catalyst employed. The lack of such characterisation of the catalysts used in many of the earlier investigations into the Fischer-Tropsch reaction precludes direct comparisons between the work of different investigators employing different catalyst preparation techniques (Vannice, 1975).

The following sections describe the methods employed and the results obtained from a number of characterisation techniques used to describe thoroughly the physical and chemical characteristics of the catalyst used in this study.

As mentioned in the preceding chapter, the catalyst was a commercial preparation from Engelhard Industries, consisting of a nominal 0,5 per cent by mass ruthenium on γ-alumina in the form of 3,2 mm by 3,2 mm cylindrical pellets with the ruthenium present only in the outer shell of the alumina support.

4.2. RADIAL DISTRIBUTION OF RUTHENIUM.

Because of the possible influence of internal diffusion on the product distribution and rate determination, the radial distribution of the ruthenium was examined.

4.2.1. OPTICAL EXAMINATION.

The catalyst was estimated by visual examination to have its ruthenium (evident as a black band) impregnated on the outer shell of the support to a depth of some 200 microns. Microscopic examination of several catalyst pellets confirmed this estimate but indicated that there was some heterogeneity of distribution among the pellets. This may be seen in the photographs of the cross section of several randomly-selected pellets presented in Figure 4.1. where two distinct distribution types are evident: the one type having a shallower penetration of ruthenium than the other. Enlargements of typical pellets from each of these two distribution types are presented in Figure 4.2. (a) and (b).

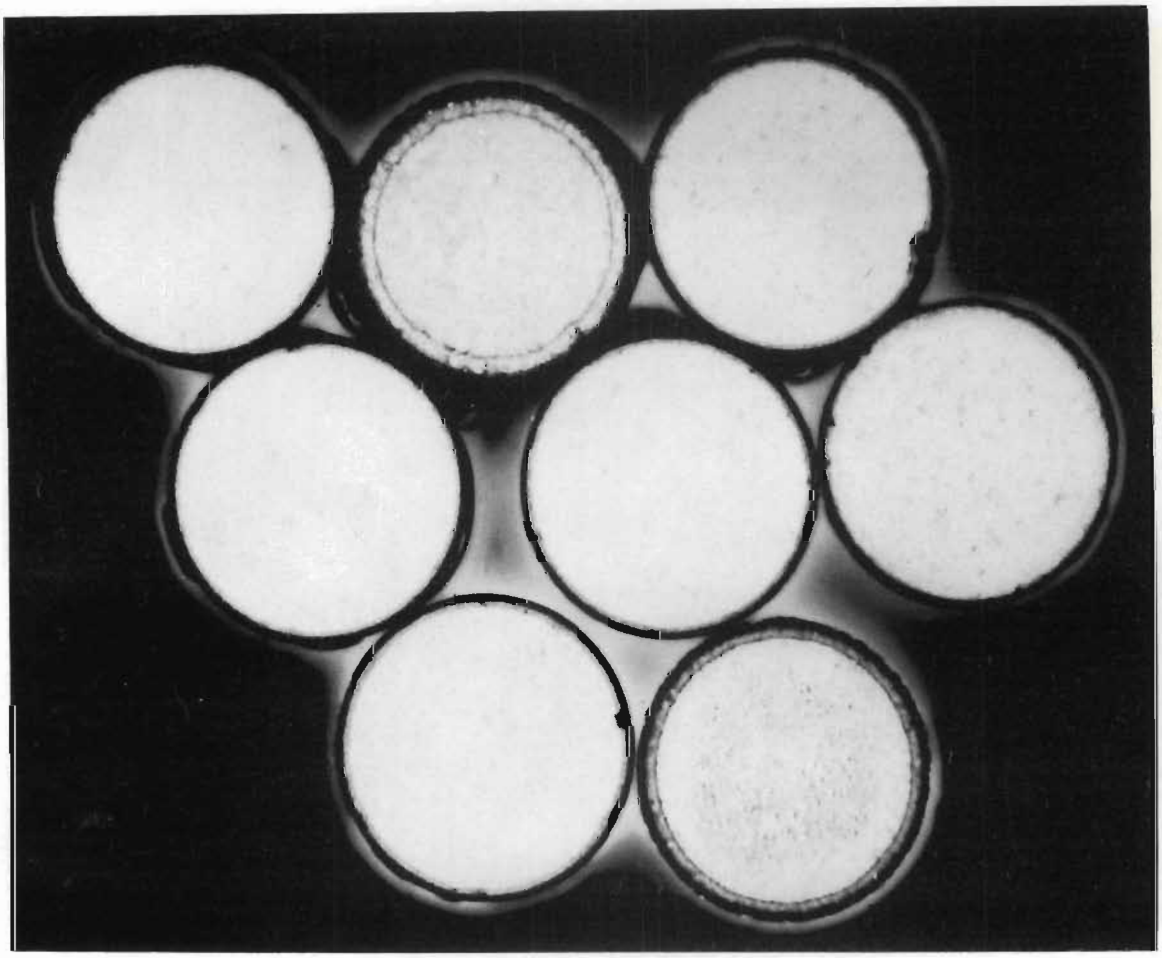
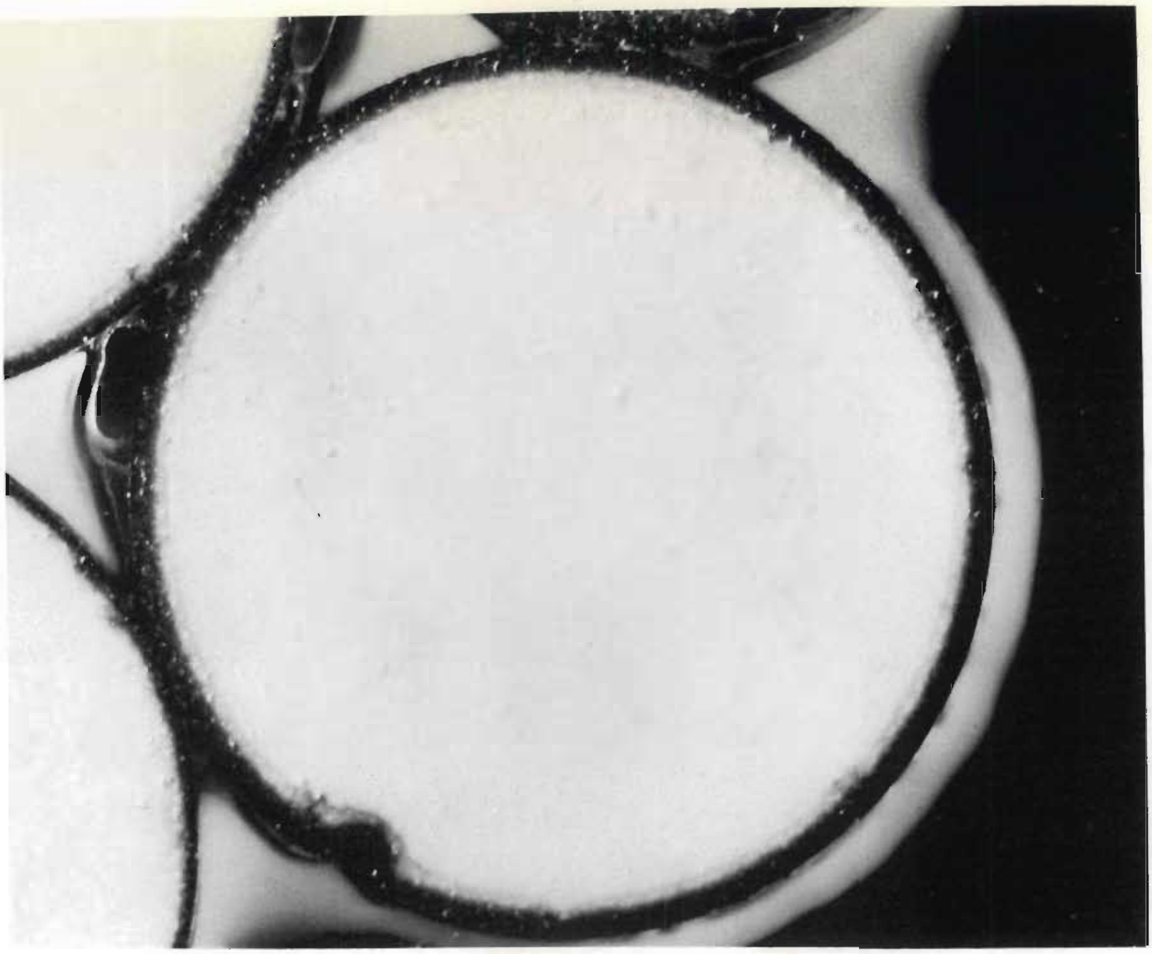


FIGURE 4.1. - PHOTOGRAPH OF CROSS SECTION OF PELLETS.

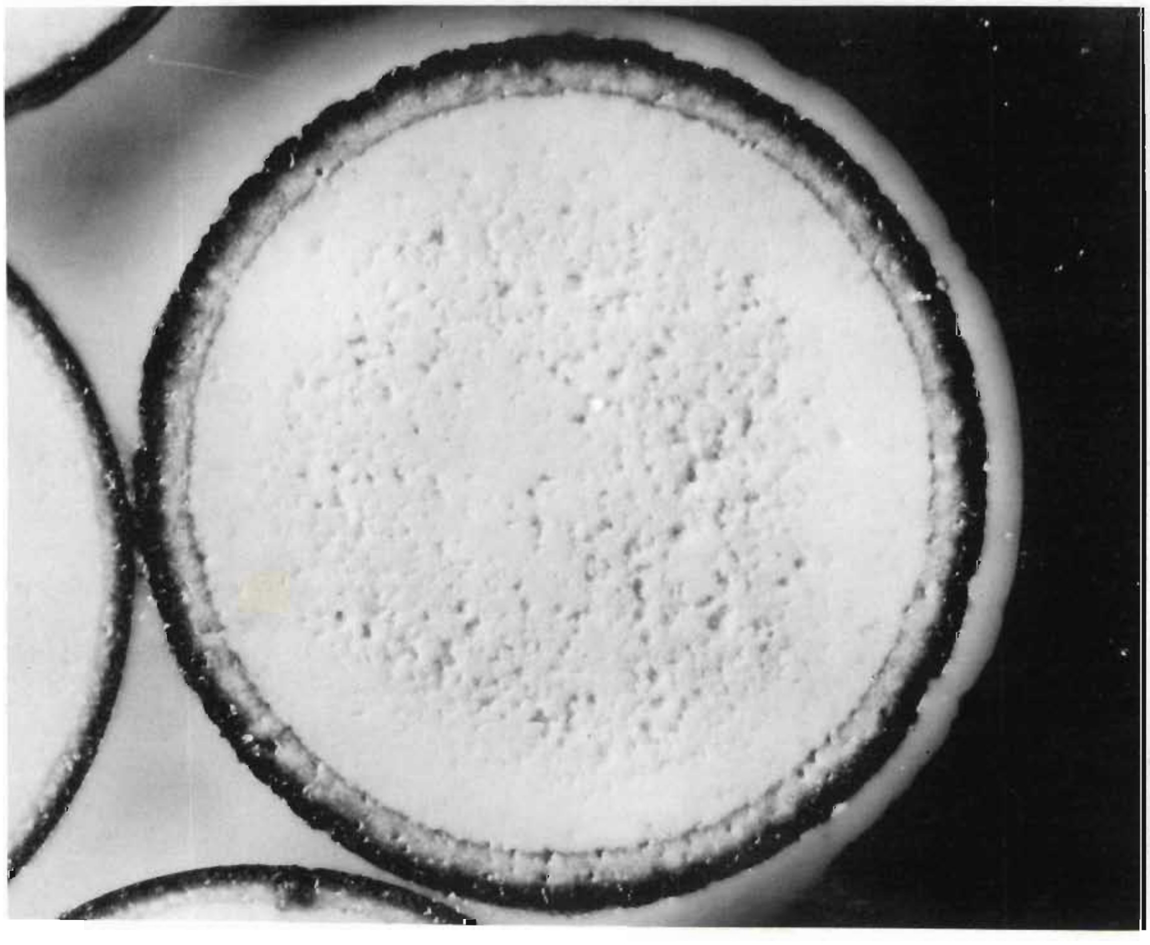
FIGURE 4.2. (Overleaf) - PHOTOGRAPH OF CROSS-SECTION OF RUTHENIUM PELLET.

(a) Shallow Penetration.

(b) Deep Penetration.



(a)



(b)

4.2.2. ELECTRON MICROPROBE EXAMINATION.

Although optical examination of the cross-section of the catalyst pellets indicated that the ruthenium was present only on the outer shell of the support, a more detailed quantitative examination of the radial distribution of the ruthenium was undertaken. An electron microprobe was used to establish a quantitative concentration profile across several catalyst pellets.

Samples of the fresh catalyst were mounted in "Araldite" resin and polished by standard mineralogical techniques (Hutchins, 1974). These polished sections were then step-scanned across the diameter of the pellet at either 2 or 5 micron intervals. Because of the original softness and porosity of the alumina support, the final polished sections were considerably rougher than polished metal sections. Since one of the requirements which should be complied with for good quantitative analysis by electron microprobe is the provision of a perfectly polished section (Hutchins, 1974), this relative surface roughness results in some data scatter due to absorption and scatter of the generated X-rays. However, good agreement was obtained between several samples when two or more radial scans were conducted across each pellet.

Figure 4.3.(a) shows the concentration profile obtained from several such scans across a pellet of fresh catalyst. For the conditions employed here, the ruthenium concentration corresponding to a 95 per cent confidence level of the presence of ruthenium

corresponds to a ruthenium concentration of some 0,82 per cent, which occurred at a distance of approximately 90 microns from the outer edge of the pellet. The solid line in this figure is the curve

$$C_{Ru} = 5,28\ e^{-0,02D}$$

where C_{Ru} = mass concentration of ruthenium

D = distance in microns from outer edge

which was the best regressed fit to the data.

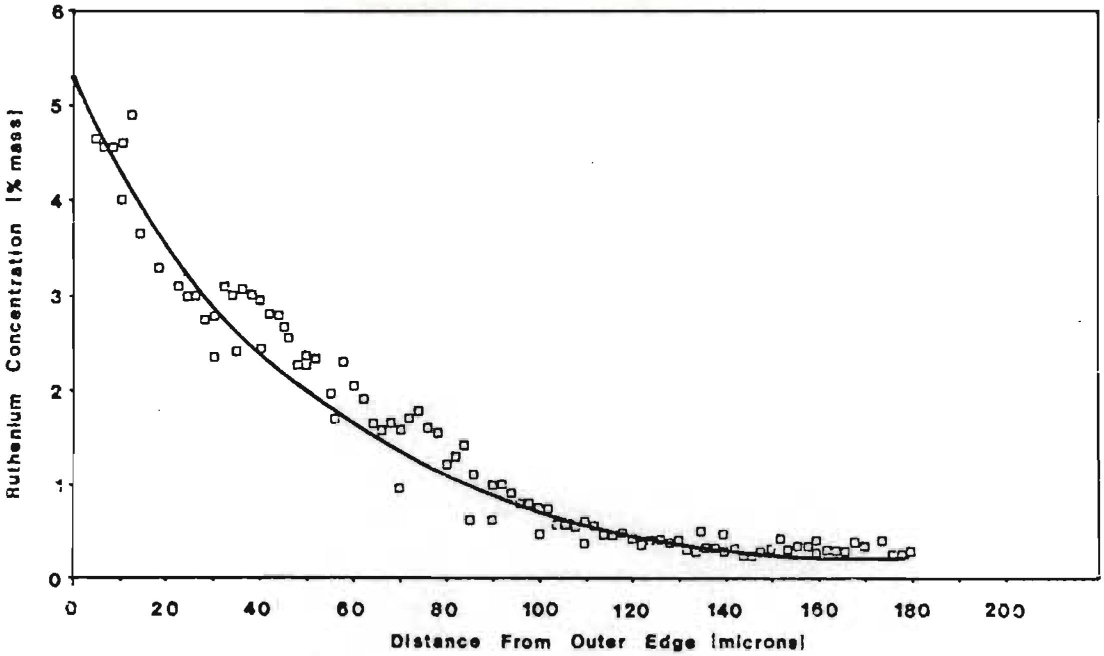


FIGURE 4.3.(a) - RUTHENIUM CONCENTRATION PROFILE ACROSS A FRESH PELLET (SHALLOW PENETRATION).

Figure 4.3.(b) shows the radial distribution of ruthenium on a plot similar to that of Figure 4.3.(a) for a different catalyst pellet. It will be seen that there is a marked difference in

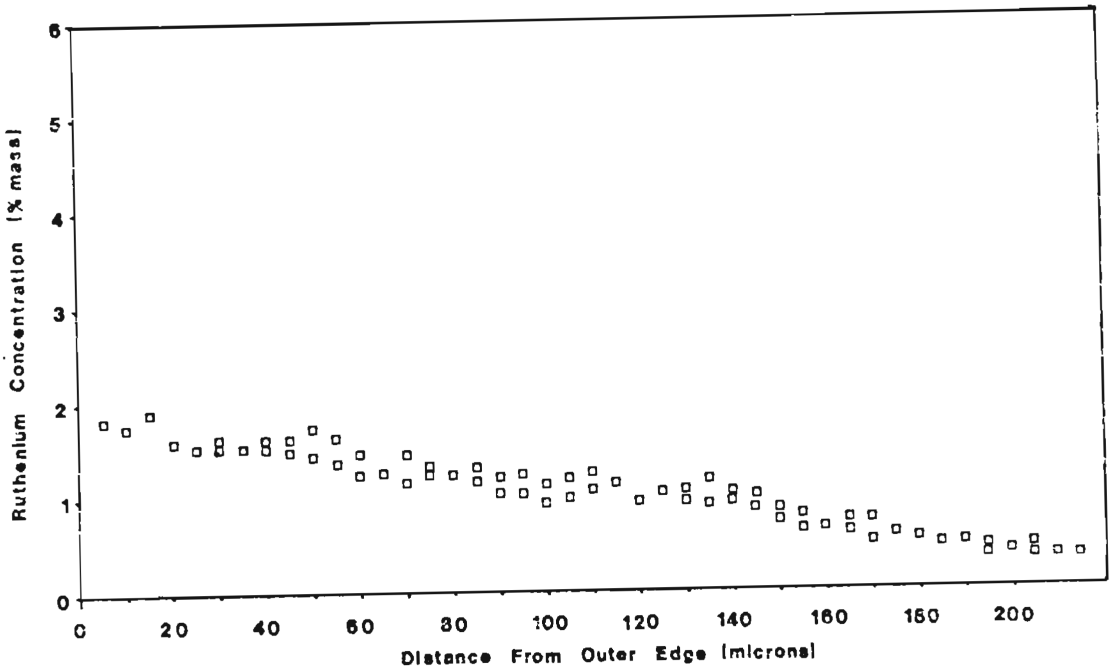


FIGURE 4.3.(b) - RUTHENIUM CONCENTRATION PROFILE ACROSS A FRESH PELLET (DEEP PENETRATION).

the radial concentration profile of ruthenium in this pellet compared to that shown in Figure 4.3.(a) with the ruthenium concentration corresponding to 95 per cent confidence occurring in this case only at some 150 microns. In view of this difference, a random batch of several hundred pellets were visually segregated into the two distribution types. The former distribution type (as shown in Figure 4.2.(a) and 4.3.(a)) represented some 88 per cent of the total, with the latter distribution type making up the difference.

Since loading of the catalyst basket was by random selection and further, all the catalyst characterisation techniques employed were macroscopic in nature (inasmuch as more than one pellet was required for each examination), this microscopic heterogeneity of ruthenium distribution was regarded as having no significance on the macroscopic scale. In other words, the characterisation techniques employed, with the exception of the microscopic work, gave catalyst characterisations averaged over a number of pellets, as did the experimental determination of rates.

In order to establish whether any major changes in ruthenium distribution occurred during pretreatment or synthesis, several pellets from experiments conducted at both high and low temperatures were also examined by the microprobe. The results of these examinations are presented in Figure 4.3.(c) and give no indication of any major redistribution of the metal having occurred.

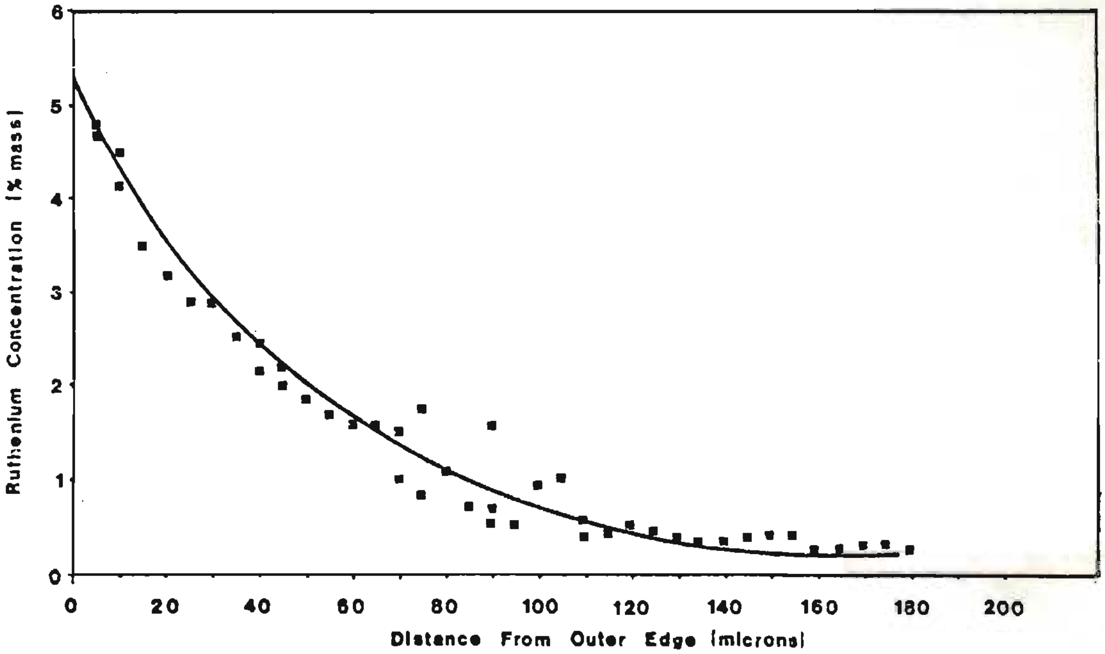


FIGURE 4.3.(c) - RUTHENIUM CONCENTRATION PROFILE ACROSS A USED PELLET (SHALLOW PENETRATION.)

Integration of the regressed fit of the concentration profile obtained for the ruthenium over the whole pellet resulted in an average ruthenium concentration of 0,50 per cent by mass.

4.3. QUANTITATIVE CHEMICAL ANALYSIS.

As mentioned earlier, the nominal ruthenium concentration over the whole catalyst pellet was 0,5 per cent by mass. However, it was considered desirable to conduct a quantitative analysis on a random sample of the pellets to confirm this.

The analysis was carried out by the Analytical Division of the National Institute for Metallurgy and involved a technique in which the catalyst pellets were fused with sodium peroxide, dissolved in hydrochloric acid and quantitatively analysed by atomic absorption spectrophotometry.

Results obtained for ruthenium content of both fresh and used samples are presented in Table 4.1. and, in agreement with the electron microprobe studies, show no loss in metallic content with use in the synthesis.

TABLE 4.1.

RUTHENIUM CONCENTRATION : FRESH & USED CATALYST.

CATALYST FROM RUN No.	CONDITIONS OF RUN		Ru CONCENTRATION (% MASS)
	T (K)	P (kPa)	
Fresh	-	-	0,50
Fresh	-	-	0,48
Fresh	-	-	0,46
2	573	800	0,49
4	551	800	0,47
8	528	800	0,50
19	571	1 200	0,46
49	601	1 600	0,48

4.4. ADSORPTION STUDIES.

As mentioned in Chapter 3, both nitrogen and hydrogen adsorption studies were carried out on the catalyst. Fresh catalyst, a sample of pretreated but unused catalyst and most of the catalyst samples produced during the synthesis experiments were subjected to nitrogen adsorption studies. Hydrogen adsorption was conducted on the fresh catalyst and on samples from twenty of the experiments.

4.4.1. NITROGEN ADSORPTION.

Nitrogen adsorption work was conducted using a conventional glass vacuum system. Nitrogen adsorption isotherms were conducted at the temperature of liquid nitrogen (77 K) and were used to determine total surface area.

4.4.1.1. TOTAL SURFACE AREA.

The standard B.E.T. equation:

$$\frac{p/po}{V(1-p/po)} = \frac{1}{V_m.C} + \frac{(C-1)}{V_m.C} \cdot p/po$$

was used in the manner described in Chapter 2 to determine the total surface area of all the catalyst samples examined. As mentioned earlier, prior to the nitrogen adsorption, the catalysts were "cleaned" by heating at 150°C under vacuum for two hours and then cooled under vacuum to the adsorption temperature.

The results of the nitrogen adsorption work are presented in Table 4.2.

Discussion of these results, along with the results obtained from the other characterisation tests, has been confined to the final portion of this chapter, in order to enable cross-comparisons to be made.

4.4.2. HYDROGEN ADSORPTION.

Because of the very slow equlibration of hydrogen adsorption at ambient temperatures (requiring approximately 3 hours) (Dalla Betta, 1974), hydrogen adsorption tests were conducted at 100°C.

In order to obtain a "clean" surface prior to introduction of the adsorbate, the catalysts were pretreated in flowing hydrogen at 200°C for 2 hours followed by evacuation at 200°C for one hour. This temperature was chosen as being the lowest temperature which could be used to clean the surface of the catalyst without regenerating or restructuring the samples of

TABLE 4.2.

NITROGEN ADSORPTION : TOTAL SURFACE AREA.

CATALYST FROM RUN NO.	TOTAL AREA m^2/g. cat.
Fresh	243,3 : 248,3
Reduced, Unused	246,3
2	199,3
4	184,5
5	191,5
6	168,9 : 160,4
8	164,7 : 163,2
12	180,4
13	109,2 : 139,8
16	192,1
17	177,0
18	169.7
19	168,9 : 184,6
22	203,5
24	177,9
26	170,0
34	134,9 : 171,2
36	134,7 : 168,4
38	168,9
39	133,8
40	166,5
41	180,1
44	195,0
49	190,6
103	200,2
104	157,9
105	163,3
107	120,6
109	175,0
110	155,6

deactivated catalyst. In order to ensure that reduction of the catalyst was possible at 200°C, hydrogen uptakes on catalysts pretreated at temperatures of 200, 250 and 300°C were compared. These results are presented in Table 4.3. and indicate that the surface is certainly cleaned and reduced at 200°C and, if anything, surface area is lost by pretreating at higher temperatures.

TABLE 4.3.

HYDROGEN UPTAKE FOR DIFFERENT CHEMISORPTION PRETREATMENT TEMPERATURES.

REDUCTION(1) AND EVACUATION TEMPERATURE	H_2 UPTAKE μmols/g.cat.
200	8,9
250	7,9
300	7,0

(1) Reduction for 2 hours and evacuation for 1 hour.

The results of the hydrogen adsorption work are presented in Table 4.4.

Values for the dispersion of ruthenium presented in Table 4.4. are based upon the assumption of an H/Ru ratio of unity (as was discussed earlier).

4.5 CARBON CONTENT.

During many chemical reactions involving hydrocarbons, the catalyst loses activity due to fouling. This fouling of the catalyst is caused by the deposition of carbonaceous material on the catalyst either by physical adsorption or by chemisorption on the active sites.

In order to determine to what extent the formation of carbonaceous deposits contributed to the deactivation of the supported ruthenium used in this investigation, total carbon contents were determined for both fresh and used catalyst samples.

The results of these determinations are presented in Table 4.5., along with data taken from the following chapter: the selectivity of the C_5-C_{12} fraction of hydrocarbons formed during synthesis.

TABLE 4.4.

HYDROGEN CHEMISORPTION DATA.

(1) FRESH CATALYST.

H_2 UPTAKE µmols/cat.	SURFACE AREA (S)		DISPERSION (D) %	PARTICLE SIZE (κ) Å
	m^2/g. cat.	m^2/g. Ru		
10,7	1,15	230	43,5	20,2
11,2	1,20	240	45,7	19,3
12,1	1,30	260	49,3	17,9

(2) USED CATALYST.

RUN No.	OPERATING CONDITIONS			H_2 UPTAKE µmols/g. cat.	SURFACE AREA		D %
	PRESSURE kPa	TEMPERATURE K	CO CONVERSION %		m^2/g.cat.	m^2/g. Ru	
2	800	573	72	6,7	0,72	144	27,3
4	800	551	39	8,5	0,91	182	34,6
5	800	551	78	7,6	0,82	164	30,9
6	800	551	65	7,1	0,76	152	28,9
8	800	528	55	7,3	0,78	156	29,7
12	800	529	57	6,9	0,74	148	28,1
16	1 200	573	54	5,7	0,61	122	23,2
17	1 200	571	96	7,8	0,84	168	31,7
18	1 200	571	61	7,8	0,84	168	31,7
19	1 200	571	60	7,5	0,80	160	30,5
23	1 200	577	64	6,8	0,73	146	27,7
24	1 200	548	41	6,9	0,74	148	28,1
26	1 200	545	57	7,7	0,83	166	31,3
28	1 200	573	77	8,5	0,91	182	34,6
34	1 200	498	22	6,1	0,65	130	24,8
36	1 200	523	39	6,0	0,64	128	24,2
37	1 200	545	25	6,0	0,64	128	24,3
38	1 200	551	70	5,1	0,55	110	20,7
39	1 200	573	59	7,0	0,75	150	28,5
42	1 600	577	46	6,2	0,67	134	25,3

TABLE 4.5.

CARBON CONTENT OF USED CATALYSTS.

RUN No.	CARBON CONTENT (% MASS)	C_5 - C_{12} SELECTIVITY (% MASS)
1	0,37	2,68
2	0,14	1,91
3	0,26	3,75
4	0,67	26,77
5	0,20	11,05
6	0,35	21,4
7	2,27 & 2,31	44,82
8	2,26	56,82
9	1,22	50,69
10	3,81	58,63
11	2,48	62,76
12	2,09	56,49
13	5,20	58,58
14	2,45	49,53
15	5,84 & 6,36	59,57
16	0,31	8,94
17	0,07	0
18	0,40	8,13
19	0,50	10,18
20	0,63	7,15
21	1,48	46,72
22	0,05	0
23	0,21	4,44
24	0,91	38,43
26	0,92	37,31
27	1,11	37,98
28	0,25	4,66
29	3,19 & 3,43	52,3
30	3,45	57,3
31	3,61	51,0
32	2,60	56,3
33	4,80	62,4
34	2,76	51,6
35	3,52	52,0
36	3,30	52,0
37	0,58	37,2
38	0,21	27,3
39	0,18	7,2
40	0,42	44,0
41	0,36	6,0
42	0,32	10,1
43	1,56	48,0
44	0,20	0,0
46	4,88	56,8
47	0,58	4,11
48	0,21	1,5
49	0,18	1,0
101	0,42	13,0
103	0,30	4,8
104	0,54	30,9
105	2,21	49,7
107	4,48	54,0

4.6. CATALYST DEACTIVATION.

Although, strictly speaking, not truly a part of the catalyst characterisation techniques employed, the catalyst deactivation (which was evident during synthesis) is conveniently treated here.

As was discussed earlier, the catalyst charge was used for only one experiment, with recharging of the reactor being carried out between experiments. This was because of the apparent irreversibility of the catalyst deactivation occurring during synthesis. While not amenable to direct analysis, the deactivation of the catalyst was briefly examined, albeit somewhat qualitatively. Before presenting the results and discussion of this study, it is helpful to recall the experimental technique adopted.

Upon the completion of catalyst pretreatment and once the reactor had reached the reaction temperature required, synthesis gas was introduced to the reactor, taking the place of hydrogen. This meant that initially the hydrogen pressure of the reactor wasvery much higher than was the case after a period of operation. This would have the effect of increasing the rate of synthesis of methane, both in absolute terms and relative to the synthesis of other hydrocarbon products (Vannice, 1975; Kirk, Everson & Woodburn, 1978). Because of the type of reactor employed, (CSTR), the presence of methane in the reactor product stream could be detected almost immediately upon the introduction of the synthesis gas (since the method of synthesis gas introduction approximated to a pulsed input). Monitoring of the rate of production of methane with respect to time gave a measure of the rate of catalyst deactivation (albeit complicated by the hydrodynamic characteristics of the reactor and the transient nature of the reactor contents during the initial period).

Plots of formation of methane (expressed in rate relative to mass of catalyst charged to the reactor) against process time exhibited considerable data scatter. However, when the same rates were plotted against a function of dimensionless time, the scatter became much less pronounced. The dimensionless time function was calculated from the true dimensionless time t/τ (where t = time and τ = reactor residence time) as follows:

$$\frac{t}{\tau} = \frac{t.F}{V}$$ where V = reactor volume making allowance for operating pressure.

$$= \frac{t.F}{V_o.P}$$ where V_o = reactor volume at S.T.P.

the dimensionless time factor was thus taken as

$$\frac{tF}{P}$$ which is simply the true dimensionless time multiplied by V_o (which is a constant).

In general, the deactivation of catalysts may be caused by one (or more) of the following processes:

(a) POISONING:

caused by the strong chemisorption of the active sites of some impurity (generally present in the reactant stream). Typical poisons include sulphur, arsenic, lead.

(2) FOULING:

caused by reactant or product degradation on the catalyst surface: coke formation is the most commonly-encountered example of this.

(3) AGING:

caused generally by sintering of the catalyst, producing a decrease in the available number of active sites.

In view of the fact that high-purity gases were used as reactants, the loss of activity by catalyst poisoning can be eliminated as a source of deactivation. While carbon monoxide has been cited as a poison for hydrogenation reactions (Butt, 1972), it is hardly realistic in this study to regard CO as a true poison.

The loss of activity by sintering (or in some cases by loss of catalytic metal (e.g. by carbonyl formation)), can likewise be eliminated since chemical analysis and electron microprobe work produced no evidence of any redistribution or loss of ruthenium during the pretreatment, a result in agreement with King (1978).

Since the pretreatment temperature was the highest temperature to which the catalyst was subjected, this would be the most likely time for aging to occur.

Fouling would thus be the only mechanism by which loss of activity could occur.

The plots of the rates of methane formation against the dimensionless time factor $(\frac{tF}{P})$ shown in Figure 4.4. for operating temperatures of 575, 550 and 525 K.

While the nature of the experimental system and procedure adopted did not lend itself well to a quantitative study of the kinetics of deactivation, the overall form of the data presented in Figure 4.4. is in qualitative agreement with published work on deactivation for other catalyst systems (Lee, Butt & Downing, 1978; Ozawa & Bischoff, 1968; Kovach, 1978).

The initially-rapid decline in the rate of methanation can be attributed to both chemical and physical (hydrodynamic) mechanisms: the initial transient period being the direct consequence of major changes in the reactor feed gas composition. However, pulse tests conducted earlier indicated that the transient caused by the step change in the feed gas composition should have been over after some five residence times. This, in most cases, would correspond to a value for $(\frac{tF}{P})$ of approximately 500. The slow decline evident in the latter part of the rate vs time curves is almost certainly a consequence of increasing carbonaceous deposition on the catalyst.

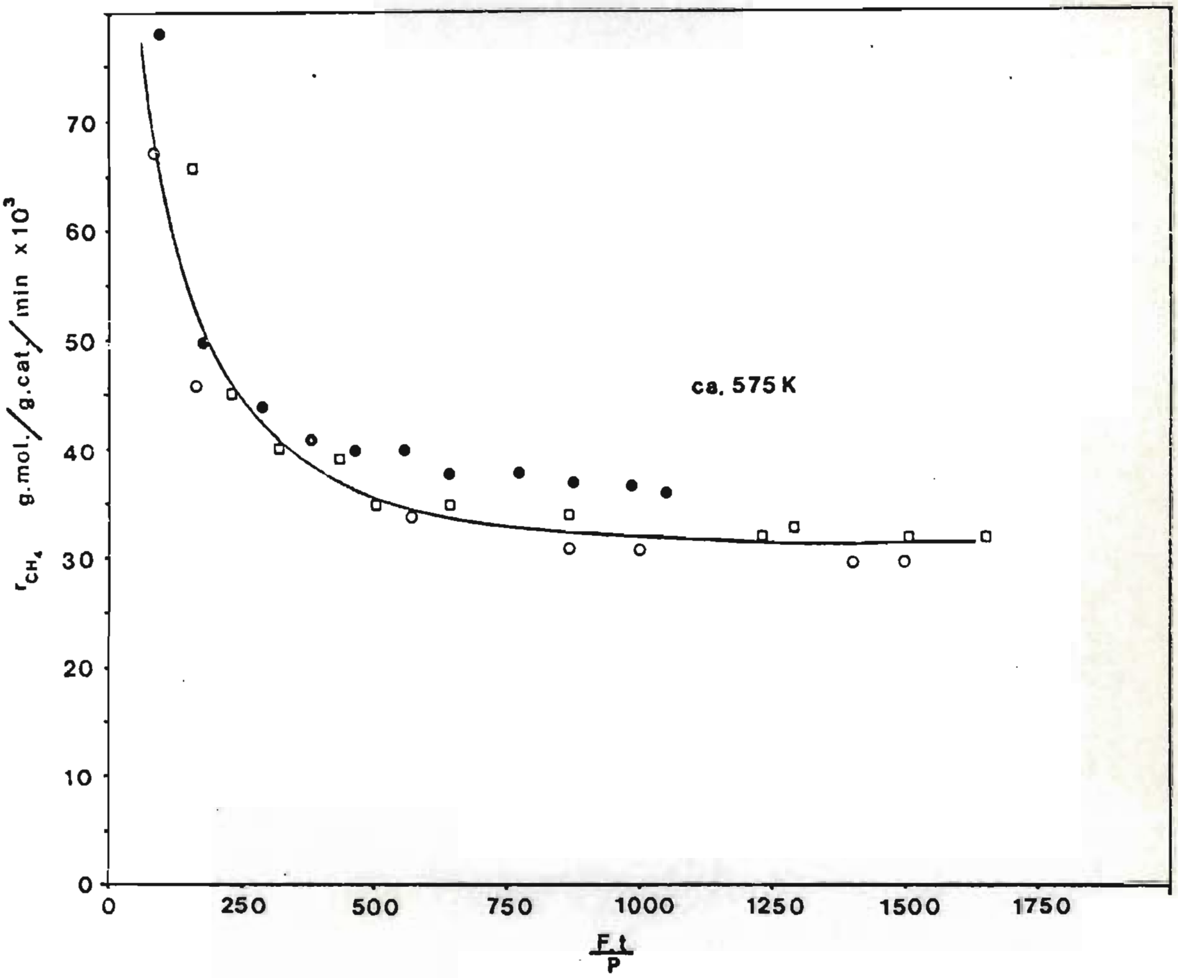
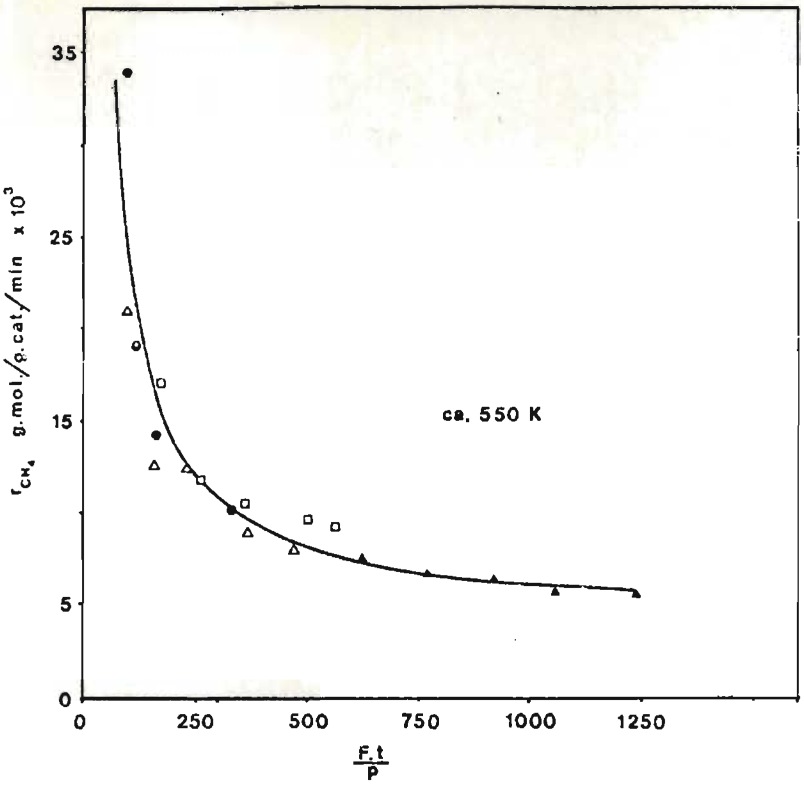
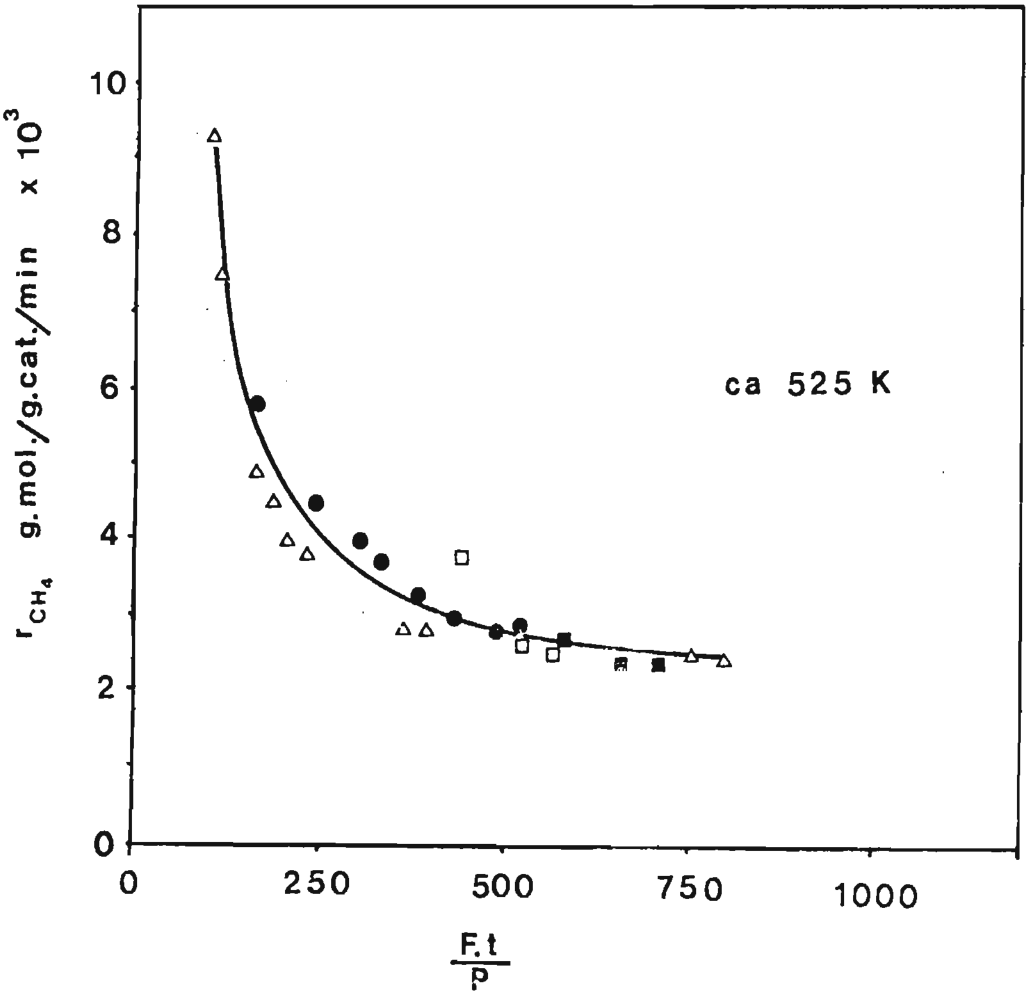


FIGURE 4.4. - RATE OF SYNTHESIS OF METHANE AS A FUNCTION OF DIMENSIONLESS TIME

(a) ca. 575 K
Run Numbers ○ 18; □ 19; • 23



(b) ca. 550 K
Run Numbers □ 24; △ 26; ▲ 37; • 38



(c) ca. 525 K
Run Numbers • 8; △ 9; ■ 46; □ 105

4.7. MERCURY POROSIMETRY.

Mercury porosimetry was employed to compare pore volume and pore size distributions for both fresh and used catalyst samples. Samples of the used catalysts were selected to cover a range of total carbon contents in order to determine if there existed a simple correlation between the carbon content and the pore characteristics.

Table 4.6. presents the total pore volumes obtained for each of the samples examined along with data from Table 4.5. on the carbon content of each of the samples.

The data of Table 4.6. shows no correlation between the carbon content of the used catalyst and total pore volume. Further, with the exception of the catalyst from run number 23, all of the pore volumes are within 10 per cent of that of the reduced, unused catalyst. The extent of deposition of carbonaceous material would therefore not appear to significantly affect the total pore volume.

TABLE 4.6.

TOTAL PORE VOLUME OF CATALYST.

SAMPLE FROM RUN No.	TOTAL CARBON (% MASS)	TOTAL PORE VOLUME (ml/g.)
Fresh	-	0,174
Reduced, Unused	-	0,198
15	6,10	0,179
16	0,31	0,195
17	0,07	0,220
23	0,21	0,243
29	3,31	0,201

4.8. DISCUSSION OF THE CHARACTERISATION RESULTS.

The fact that there was no apparent reduction in catalyst total surface area during the pretreatment period, (indicated by the substantial equality of surface areas for both fresh and reduced, unused catalysts), whereas all the used catalysts exhibited varying extents of area loss, indicates that this loss must have occurred during synthesis. Since the carbon content of the catalyst is likewise a consequence of synthesis, some positive correlation between B.E.T. area and carbon content might reasonably be anticipated. That there is such a correlation is evident from Figure 4.5. which plots the B.E.T. areas from Table 4.2. against the total carbon content of the catalyst from Table 4.5. In spite of the data scatter, it can be seen from this Figure that much of the total area loss occurs at

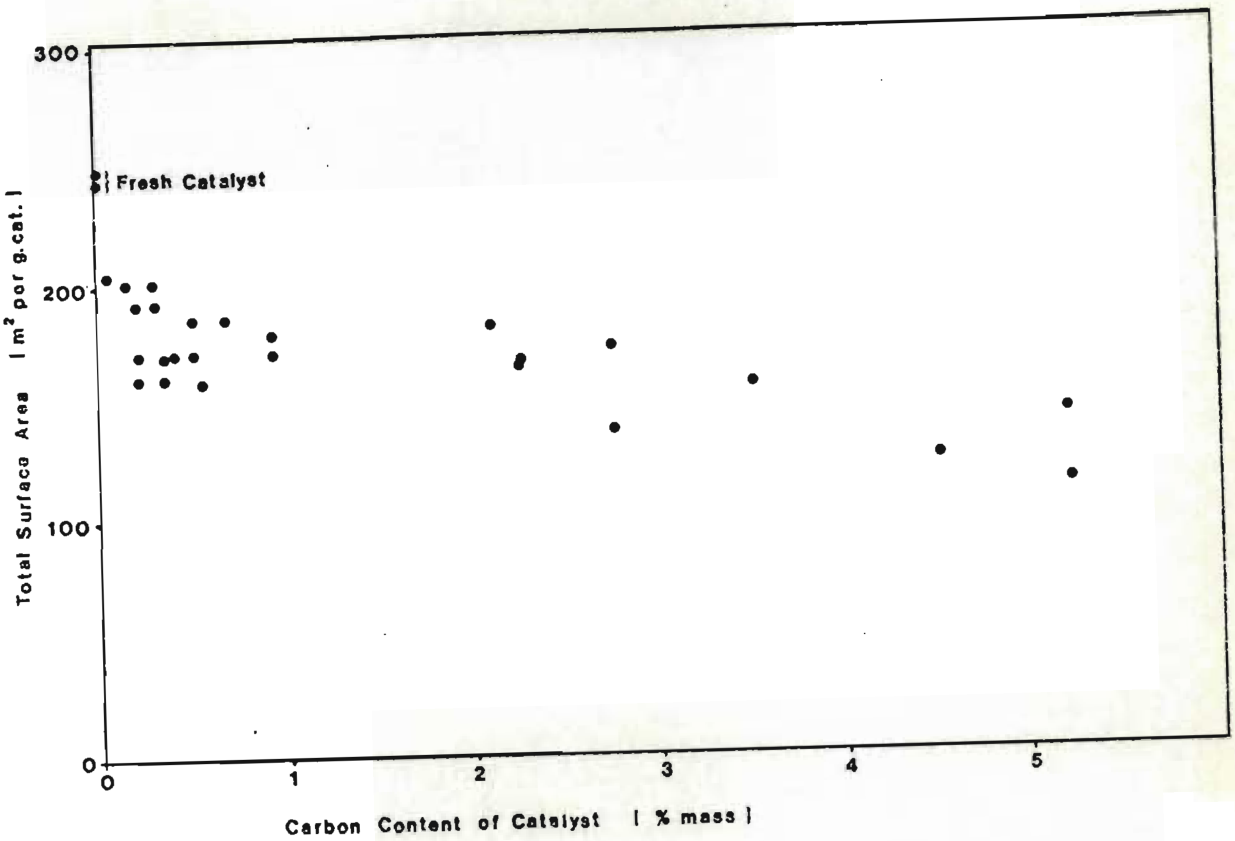


FIGURE 4.5. - CATALYST TOTAL AREA VERSUS CARBON CONTENT.

the onset of synthesis: the major portion of the loss occurring during the initial increment in carbon content.

The decrease in ruthenium metal area (as measured by hydrogen adsorption) shows a similar trend to that exhibited by the total surface area, and is shown in Figure 4.6. If this loss in metal area is regarded as a measure of the extent of catalyst deactivation, it can be inferred that the deactivation proceeds very rapidly in the initial period of synthesis, followed by a slower deactivation period. This is in qualitative agreement with published reports on the rate of coking (Ozawa & Bischoff, 1968) or rate of decrease of conversion occurring during cracking

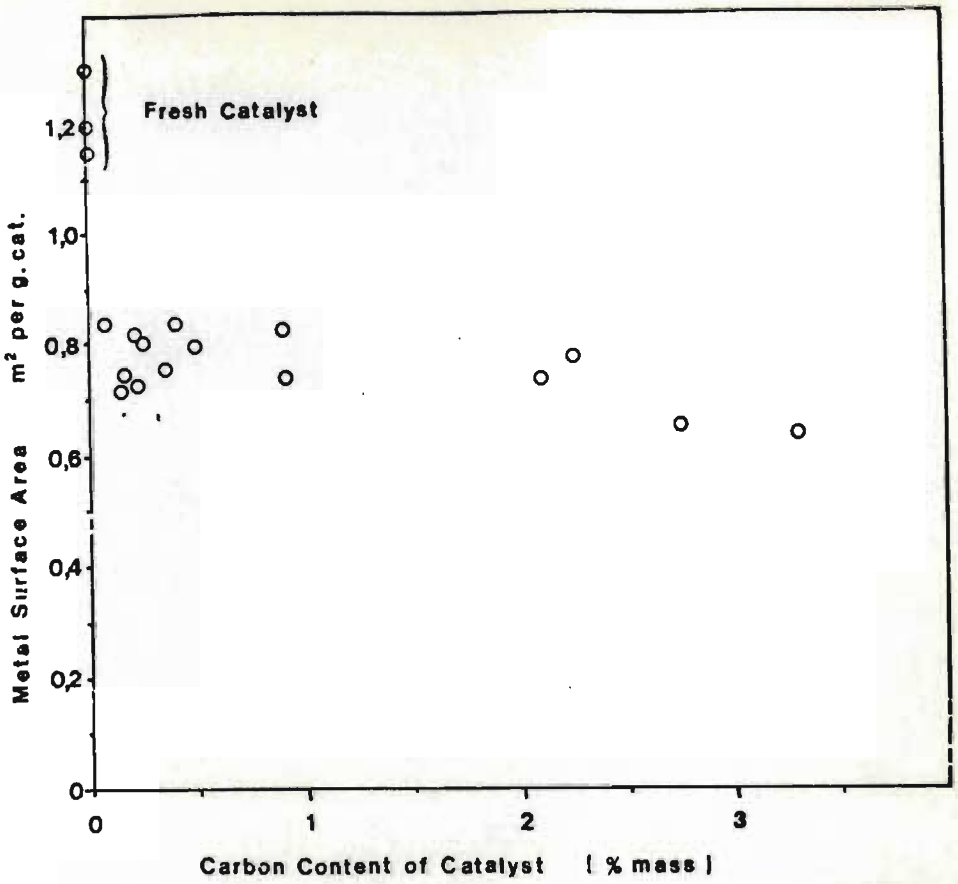


FIGURE 4.6. - CATALYST METAL AREA VERSUS CARBON CONTENT.

reactions (Butt, 1972) and further with the decrease in activity exhibited by the catalytic hydrogenation of carbon monoxide over ruthenium in a microcatalytic reactor (Dalla Betta, Piken & Shelef, 1975).

The sensitivity of the B.E.T. area to relatively minor changes in the carbon content of the catalyst may be compared to the work reported by various workers into the physical properties of new and used cracking catalysts. Ozawa and Bischoff (1968) reported no effect on B.E.T. areas of carbon contents up to almost one per cent: a finding which was confirmed by Haldeman and Botty (1959). Ramser and Hill (1958), on the other hand, found a 27 per cent decrease in surface with a 2,2 mass per cent carbon content and Appleby, Gibson and Good (1962) found decreases in total surface area of 22 and 33 per cent with carbon contents of 2,8 and 10,4 per cent, respectively. Since the catalysts used in each of the above-cited references were all slightly different and, further, the cracking feedstocks were all different, the effect of coke on the physical characteristics of the catalyst may be regarded as being dependent upon both the catalyst structure and the nature of the coke formed.

In a study into the surface areas of new and used Fischer-Tropsch cobalt catalysts, Anderson et alii (1949) reported a decrease in total catalyst area from 80,8 m^2/g for the fresh catalyst to 4,36 m^2/g for the catalyst after 12 weeks of operation under synthesis conditions. While no figures were given for the total carbon content of the used catalyst, the surface area of the catalyst was restored to its original value by treatment in hydrogen at 400°C, with a loss in mass of some 25 per cent. Making the (perhaps rather gross) assumption that only aliphatic, saturated hydrocarbons were present on the catalyst prior to regeneration, this would then correspond to a carbon content of approximately 20 per cent.

Figure 4.7. shows the relation existing between the total area and the metal surface area for the supported ruthenium used in this investigation. The good positive correlation obtained would appear to indicate that the loss in both of these areas is a result of physical blocking of the pores, rather than by chemisorption of products onto the active sites. Such a physical blocking of the pores would have the effect of closing off part of the catalyst interior to the reactants, thus dramatically

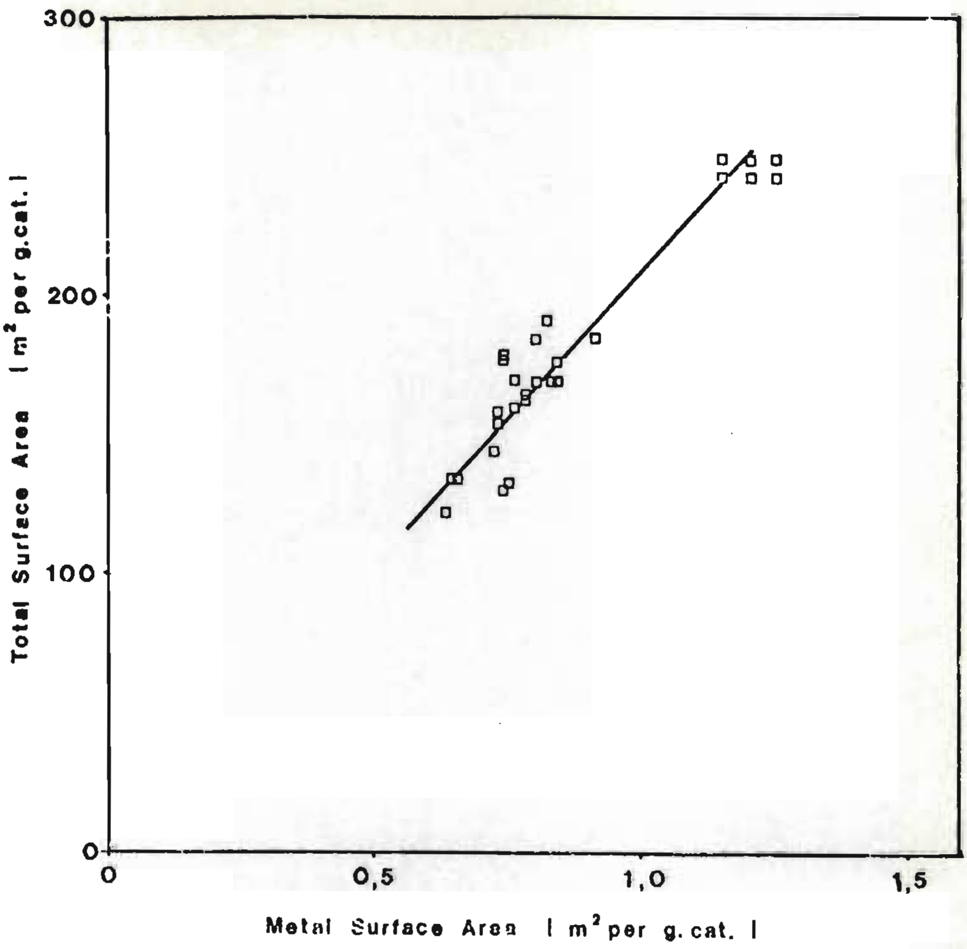


FIGURE 4.7. - RELATION BETWEEN TOTAL AREA AND METAL AREA.

decreasing the total area. If chemisorption were to be the main reason for area loss, it might reasonably be expected that the metal surface area would show a much more pronounced decrease than the total area. The proportionately approximate equal loss in both of these areas would therefore seem to support the contention that area loss is caused by physical means.

For reasons which are outlined in the following chapter on Product Distribution, it is anticipated that the carbon content of the used samples is present not as elemental carbon, but rather as high molecular weight hydrocabons. Additional evidence to support this contention may be inferred from Figure 4.8. which plots the total carbon content of all the catalyst samples against the selectivity of the hydrocarbon fraction containing 5 or more carbon atoms per molecule. Generally, the higher the C_5 to C_{12} selectivity of the synthesis product, the higher is the carbon content of the used catalyst.

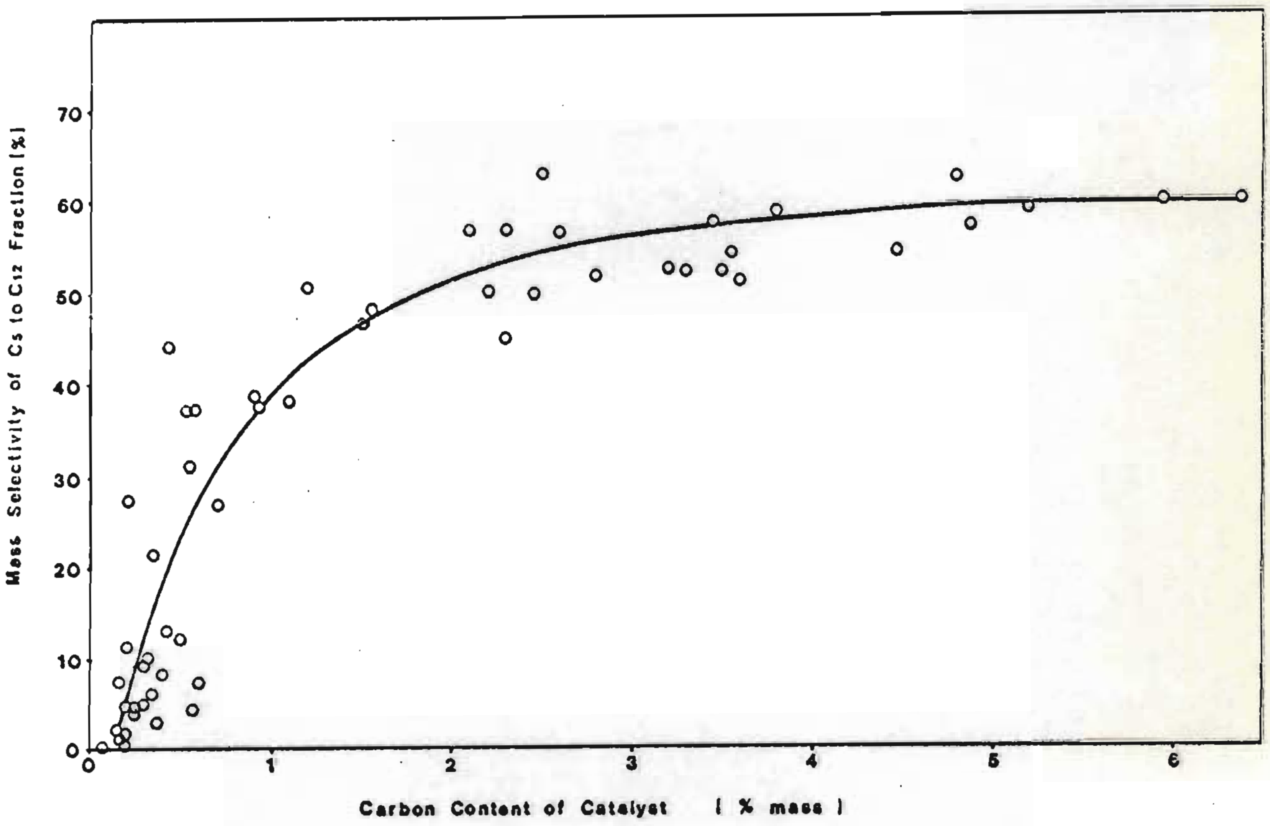


FIGURE 4.8. - RELATION BETWEEN CARBON CONTENT OF CATALYST AND SELECTIVITY OF C_5 TO C_{12} HYDROCARBON FRACTION.

Since the mass distribution of individual carbon number fractions relative to carbon number exhibits a near-exponential decay (again, as discussed in the following chapter), it is to be expected that, although the analysis was terminated at C_{12}, there would in fact be progressively smaller quantities of higher hydrocarbons present (even though undetected hydrocarbons could explain, in part, the fact that at the higher C_5 to C_{12} selectivities plotted in Figure 4.8., the carbon content apparently increases dramatically with only small increases in the C_5 to C_{12} selectivity.

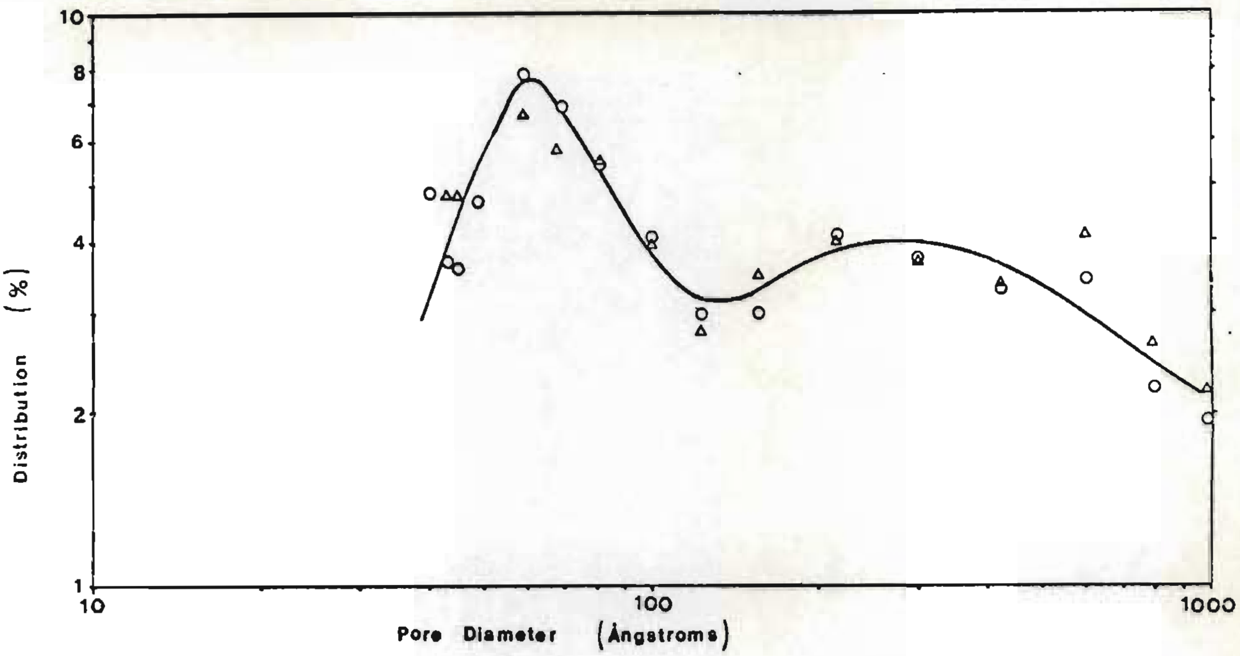
Some of the scatter evident in this Figure can probably be explained by the fact that not all of the experiments were run for the same selectivity-time periods. Although the majority of the experiments were run for approximately the same time, product flow rates and selectivities varied considerably. Thus, the opportunity given to each batch of catalyst to accumulate higher hydrocarbons was not identical from run to run.

The change in metal area (as determined by hydrogen uptake) observed in this study may be compared with that reported by Vannice (1975). Using a 5% Ru-on-Al_2O_3 catalyst in a differential reactor to study the reaction between H_2 and CO, he reported a decrease in dispersion from 7,3% for his fresh catalyst to 6% for used catalyst. This corresponds to a percentage decrease of some 18%.

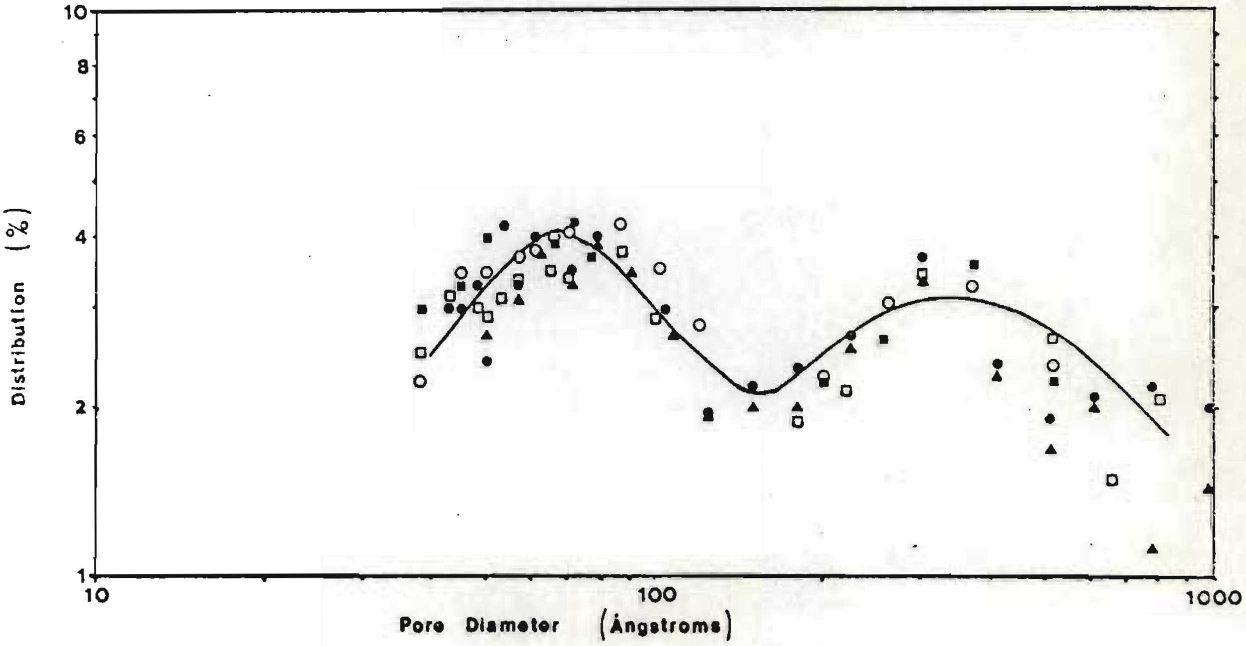
Operation under the conditions employed in this investigation would result in considerably higher values of C_5-C_{12} selectivity than would be the case in Vannice's work. It is therefore not surprising that the loss in metal area observed in this study is considerably higher (at an average loss of some 38%) than reported by Vannice.

Figure 4.9. (a) shows the pore size distribution obtained for fresh and reduced, unused catalysts, while Figure 4.9. (b) shows the pore size distribution for all of the used catalyst samples. The first point of note in both of these Figures is the bimodal distribution of pore diameters. This is a common phenomenon with particulate catalysts and is a consequence of the method of manufacture. (Gregg & Sing, 1967).

Irrespective of the carbon content of the catalyst, the used catalysts all exhibited very similar pore size distributions, with the difference in pore size distribution between fresh and used catalysts being most evident in the region of the smaller-sized pores. While both fresh and used samples show a maximum in the distribution at a pore diameter of approximately 70 Å, the contribution made to the total pore volume by the lower range of pore diameters is greater for the fresh catalyst than is the case for the used catalysts. This is presumably a consequence of blockage of the smaller diameter pores by carbonaceous deposits, although it may be hazardous to place too much reliance on interpretations of this nature based on pore size distributions, since with deposition the pore size



(a)



(b)

FIGURE 4.9. - PORE SIZE DISTRIBUTION OF CATALYST
(a) FRESH
(b) USED

distribution need not necessarily change.

Unfortunately, because of the physical limitations of the mercury porosimeter, the smallest pores capable of being examined were some 38 Å in diameter. This limit on pore size is a consequence of the fact that examination of progressively smaller pores requires substantial increases in mercury pressure, thus, to force the mercury into pores of 200 Å diameter, a pressure of some 700 atmospheres is required, while for pores of 40 Å diameter approximately 3 500 atmospheres is required (Gregg & Sing, 1967).

CHAPTER 5.

PRODUCT DISTRIBUTION.

5.1. INTRODUCTION.

This chapter will consider the nature of the product distributions obtained during the course of the experimentation. The results discussed are taken from Appendix 3 in which are presented data from all of the rate experiments. Also presented in this Appendix are data obtained from experiments employing previously deactivated catalyst which were used in product selectivity spectra only.

Table 5.1. presents the most important of the reactions which can occur during the synthesis over metal catalysts in general (Vannice, 1976). In addition to these, analogous reactions can result in the production of aromatics, aldehydes, ketones and cyclic compounds (Storch, Golumbic & Anderson, 1951). When it is borne in mind that isomerisation can also occur, it can be seen that a very large variety and number of products can result from the Fischer-Tropsch synthesis. Some indication of the complexity which can arise in products of the Fischer-Tropsch synthesis may be gathered from the chromatographic analysis of a C_6 to C_{12} fraction of the products obtained over an iron catalyst where 151 identified compounds (and several unidentified compounds) were reported (Pichler, Schulz & Kühne, 1968).

TABLE 5.1.

PRINCIPAL REACTIONS OCCURRING DURING SYNTHESIS.

Methanation	(a)	$3H_2 + CO \longrightarrow CH_4 + H_2O$
Alkanes		$(2n + 1) H_2 + nCO \longrightarrow C_nH_{2n+2} + nH_2O$
Olefins		$2nH_2 + nCO \longrightarrow C_nH_{2n} + nH_2O$
Methanol	(a)	$2H_2 + CO \longrightarrow CH_3OH$
Alcohols		$2nH_2 + nCO \longrightarrow C_nH_{2n+1}OH + (n-1)H_2O$
Water Gas Shift		$CO + H_2O \longrightarrow CH_2 + H_2$
Boudouard Reaction		$2CO \longrightarrow C + CO_2$
Coke Deposition		$H_2 + CO \longrightarrow C + H_2O$
Carbide Formation	(b)	$xM + C \longrightarrow M_xC$

(a) Methanation and methanol formation can be regarded as special cases of the general alkane and alcohol synthesis respectively.

(b) Carbide formation occurs only when elemental carbon is present on the catalyst surface.

Examination of the product obtained in the present investigation however, does permit considerable simplification of Table 5.1. when applied specifically to synthesis over ruthenium.

5.2. SYNTHESIS OVER RUTHENIUM.

It became apparent from an early stage in the experimentation that the major carbonaceous products of the synthesis were n-alkanes. This was found to be the case over the entire range of operating variables considered. This was a not unexpected result in light of earlier investigations in which are reported the highly paraffinic nature of the high molecular weight waxes produced over ruthenium and the absence of oxygenated products (Pichler, Schulz & Kühne, 1968).

This predominance of alkane production may be regarded as a characteristic of ruthenium as a Fischer-Tropsch catalyst and may be contrasted with the nature of the products of the synthesis over both iron and cobalt catalysts.

One series of reports on an investigation of the synthesis over iron catalysts reports the presence of several classes of compound in both aqueous and non-aqueous phases (Cain, Weitkamp & Bowman, 1953; Cady, Launer & Weitkamp, 1953; Steitz & Barnes, 1953; Weitkamp & Frye, 1953) and further reports "1-olefins are the dominant hydrocarbon class in the synthesis product"(Weitkamp & Frye, 1953).

Typical analyses of both aqueous and non-aqueous product streams as reported in the above-cited investigation are presented in Table 5.2.

TABLE 5.2.

ANALYSES OF TYPICAL OIL & AQUEOUS PRODUCTS : IRON CATALYST.

AQUEOUS		O I L	
COMPOUND CLASS	% wt. of STREAM	COMPOUND CLASS	% wt. of STREAM
Acid	3,1	Acid	8,1
Alcohol	4,3	Alcohol	8.0
Aldehyde	0,6	Aldehyde + Ketone	9,4
Ketone	2,2	Ester	1,5
		Hydrocarbon	73,0

With cobalt catalysts the production of appreciable quantities of olefins in the gaseous products of synthesis has also been reported (Anderson et alii, 1949), although alkanes are the chief product of synthesis. Typical analyses by compound class for the synthesis products over both iron and cobalt catalysts are reproduced in Table 5.3. (Vannice, 1977).

TABLE 5.3.

TYPICAL ANALYSES OVER IRON AND COBALT CATALYSTS.

CATALYST	PARAFFINS % MOL	OLEFINS % MOL	ALCOHOL % MOL
Fe (220^{o}C, 10 atm)	46,4	33,1	20,5
Co (200^{o}C, 7 atm)	79,0	20,0	1,0

While the proportion of olefins in the product for synthesis over iron catalysts reported in this Table does not agree with the earlier quotation where olefins were dominant, it will be demonstrated later in this chapter that the distribution of hydrocarbon classes can vary depending upon the operating conditions; in particular upon the extent of conversion.

In contrast to the product distributions obtained over both iron and cobalt catalysts, a typical chromatogram from an experiment in the present investigation is shown in Figure 5.1. and shows clearly the largely paraffinic nature of the product obtained from the synthesis over ruthenium catalyst. Also

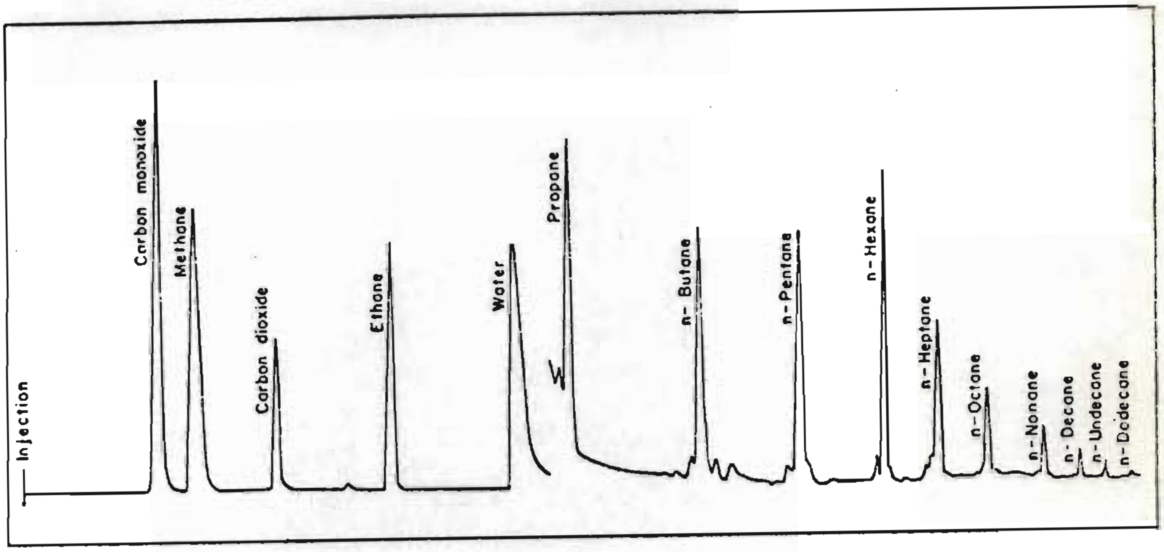


FIGURE 5.1. - CHROMATOGRAM FROM TYPICAL EXPERIMENT : PRESENT INVESTIGATION.

evident from this Figure is that in each carbon number fraction from C_4 to C_{12} the n-alkane has several associated satellite peaks, while the C_3 carbon number fraction has only one such satellite peak. With the exception of the C_3 satellite peak, the compounds responsible for these minor peaks were not positively identified at the time of analysis. However, a sample of the condensable products from the reactor effluent cold trap was accumulated over a number of experiments and examined later by mass spectrometry. The results of this examination, which are presented in Table 5.4., can be used to infer the nature of the compounds producing the satellite peaks evident in Figure 5.1. when read in conjunction with the C_3 satellite identification.

TABLE 5.4.

MASS SPECTROMETRIC ANALYSIS OF CONDENSABLE PRODUCTS.

NON-AQUEOUS LAYER

	% MASS
iso - C_8 alkane	0,34
n - C_8 "	1,52
iso - C_9 "	0,60
n - C_9 "	3,72
iso - C_{10} "	1,27
n - C_{10} "	7,04
iso - C_{11} "	1,81
n - C_{11} "	10,50
iso - C_{12} "	1,94
n - C_{12} "	12,13
iso - C_{13} "	1,78
n - C_{13} "	11,67
iso - C_{14} "	1,65
n - C_{14} "	10,14
iso - C_{15} "	0,71
n - C_{15} "	8,21
iso - C_{16} "	0,35
n - C_{16} "	7,72
iso - C_{17} "	0,29
n - C_{17} "	7,49
iso - C_{18} "	0,20
n - C_{18} "	4,26
iso - C_{19} "	0,13
n - C_{19} "	2,23
n - C_{20} "	1,28
n - C_{21} "	0,72
n - C_{22} "	0,40

AQUEOUS LAYER

	% MASS
Methanol	0,06
Ethanol	0,24
Propanol	0,04
i.Butanol	0,003
n.Butanol	0,03
n.Pentanol	0,009
Water	99,618

Considering the data of Table 5.4., the first point of note is the presence of a considerable proportion of hydrocarbons containing more than twelve carbon atoms per molecule. This is at first sight an anomolous finding since, as was mentioned earlier, the reaction conditions were adjusted for each experiment to terminate the product spectrum at C_{12}. This apparent anomoly is a direct consequence of the relative sensitivities of the gas chromatograph and mass spectrometric analyses and is further accentuated by the technique employed in collecting the sample for mass spectrometric examination. The lower limit of detection of the gas chromatograph under the operating conditions used was in the region of 0,003% (vol.) (based on the total reactor effluent stream) and no hydrocarbons above C_{12} were detected during any experiment. This may be contrasted with the relatively higher sensitivity of mass spectrometric analyses (McCrea, 1974). The method of sample collection in which products condensable under conditions prevailing in the cold trap were the only products examined by mass spectrometry would obviously weight the sample towards the higher molecular weight end of the spectrum. Evaporative losses between the time of sample collection and analysis would further accentuate this bias, although the sample was stored under refrigeration for much of this time.

The most note-worthy feature of the data of Table 5.4. is the totally paraffinic nature of the non-aqueous phase. Further, over the range of carbon numbers examined, some 90% by mass of the non-aqueous phase consisted of n-alkanes, with the contribution made by the iso-alkane in any one carbon number fraction decreasing with decreasing carbon number as can be seen from Table 5.5. Thus, while the contribution made by iso-C_8 to the total C_8 fraction is approximately 18,3%, the contribution made by iso-C_{19} is only some 5,5% of the total C_{19} fraction.

TABLE 5.5.

DISTRIBUTION (MASS %) OF ISOMERS WITHIN CARBON NUMBER FRACTIONS.

CARBON NUMBER	n-ALKANE	i-ALKANE
C8	81,7	18,3
C9	86,1	13,9
C10	84,7	15,3
C11	85,3	14,7
C12	86,2	13,8
C13	86,8	13,2
C14	86,0	14,0
C15	92,0	8,0
C16	95,6	4,4
C17	96,3	3,7
C18	95,5	4,5
C19	94,5	5,5
C20-22	100	0

Other than water, only trace quantities of primary alcohols were detected in the aqueous phase. This absence of any appreciable extent of synthesis of oxygenated products (other than carbon dioxide and water) greatly simplifies the treatment of the product distribution data, as will be apparent in a later section.

While the method of collection of the sample for mass spectrometric examination certainly militates against placing much reliance on a rigorous quantitative consideration of the data in Table 5.4., it is of interest to note that the contribution made by the C_2 alcohol (ethanol) represents a maximum in the distribution of the C_1 to C_5 alcohols detected. This is in contrast to the chromatographic analysis of the C_1 to C_{12} alkanes, where the C_2 alkane (ethane) generally represents a contribution lower than that of either C_1 or C_3 alkanes. A similar compensatory yield of C_2 oxygenated products has been noted by previous workers using iron catalysts (Weitkamp & Frye, 1953) and is illustrated in Figure 5.2.

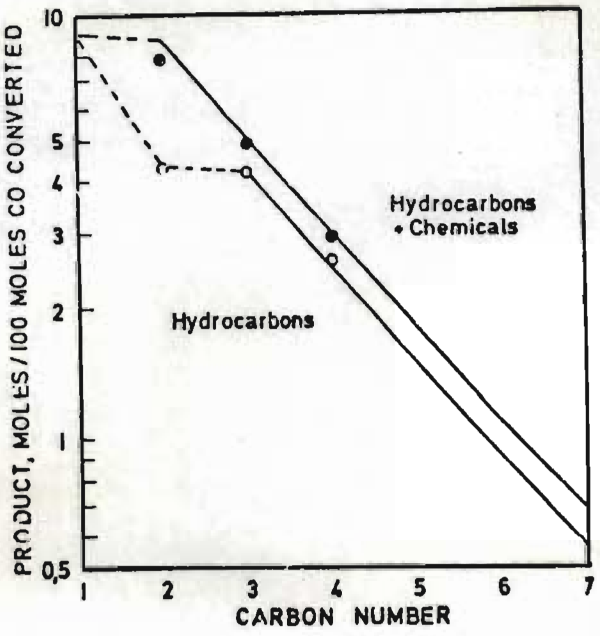


FIGURE 5.2. - PRODUCT DISTRIBUTION OBTAINED OVER IRON CATALYST (WEITKAMP & FRYE, 1953).

In order to identify the minor chromatographic peak associated with the propane in Figure 5.1., several synthetic mixtures of alcohols and olefins were injected into the chromatograph with propane as an internal reference. Comparisons of the retention times obtained with relative retention times in the literature (Davé, 1978) indicated that the most likely compound to produce the minor C_3 peak was propylene. Because of the general similarity in chromatographic response by each of the carbon number fractions from C_3 to C_{12}, it was assumed that the minor peaks associated with each of the alkane homologues above propane were produced by the corresponding alcohols and alkenes. However, in view of the fact that these satellite peaks were always minor relative to the associated n-alkane peak, no attempt was made to segregate the responses: each carbon number fraction was regarded as being the n-alkane only.

The assumption that the satellite peaks were produced by the corresponding alkenes appears at first sight to conflict with the data from the mass spectrometric analyses, where no unsaturates were reported. However, consideration of the relative amounts of alcohol-alkene/alkane produced as a function of conversion may help to explain this apparent anomoly.

While. in general, the satellite peaks remained minor when compared to the n-alkane peak, at low conversions there was evident a bias towards the minor peaks. This is illustrated in the chromatogram in Figure 5.3., where the carbon monoxide conversion (of some 15 per cent) was considerably lower than the conversion (of 63 per cent) corresponding to the earlier chromatogram shown in Figure 5.1. The most obvious difference in the product distribution evident from the two chromatograms is in the relative amounts of propylene/propane produced: the chromatogram corresponding to the experiment with the lower conversion having a greater contribution being made to the total C_3 fraction by propylene. This is also true of the higher carbon number fractions, however the propylene/propane ratio was found in all cases to be the most significant.

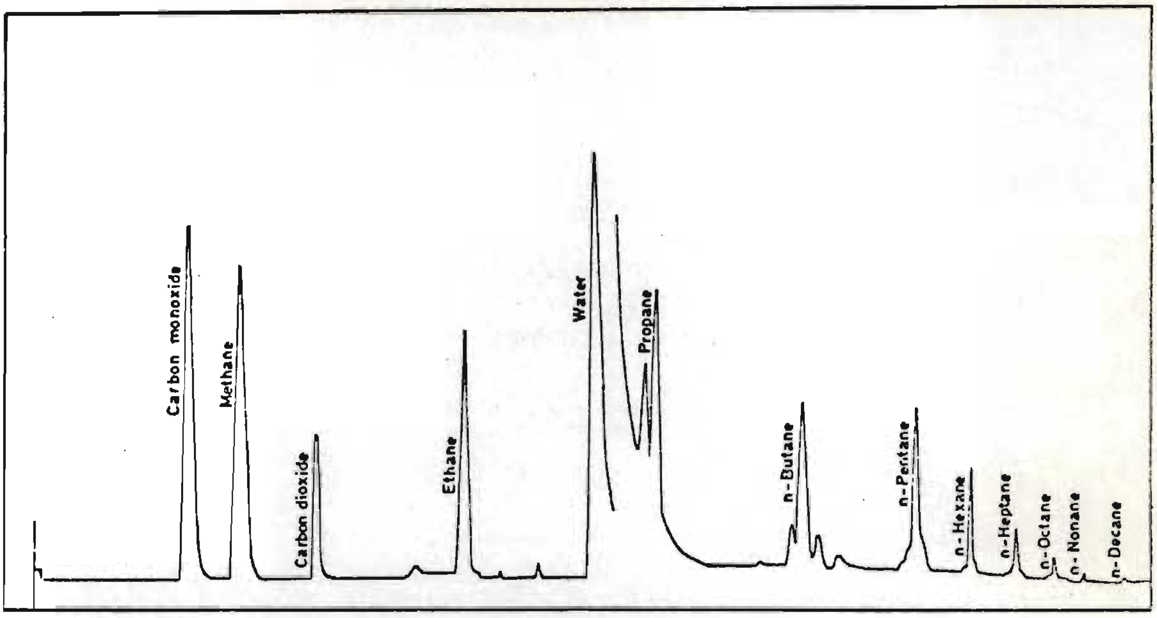


FIGURE 5.3. - CHROMATOGRAM FROM LOW CONVERSION EXPERIMENT: PRESENT INVESTIGATION.

The lower conversion experiments thus produced *relatively* larger amounts of alkenes when compared to the higher conversion experiments. Expressed in *absolute* terms, however, the major component within any single carbon number fraction remained the n-alkane. The higher conversion experiments would thus contribute correspondingly greater amounts of n-alkanes to the sample collected for mass spectrometric examination.

This enhancement of the olefin/saturate ratio with decreasing conversion was also reported by King (1978) who likewise noted the fact that the propylene/propane ratio was the most convenient measure of the overall unsaturate/saturate ratio. Vannice (1975), on the other hand used the ethylene/ethane ratio as an overall indicator of the degree of product unsaturation.

In the study by King (1978) the propylene/propane ratio produced over alumina supported ruthenium was found to range from 1,95 at a carbon monoxide conversion of approximately 3 per cent to 0,33 at 26 per cent carbon monoxide conversion, a trend in qualitative agreement with the present investigation. King further reported that at similar levels of conversion, the propylene/propane ratio was found to be slightly higher for operation at 225^{o}C than was the case for operation at 250^{o}C.

An inferrence which may be made from the increase in the propylene/propane ratio of the product stream with increase in space velocity is that propylene is a precursor of propane in the synthesis (Dry, Shingles & Boshoff, 1972).

In view of the general similarity of the chromatographic responses of each of the carbon number fractions evident from Figure 5.1., Figure 5.3., and the data of Table 5.4., it was considered to be a reasonable assumption that the synthesis product consists of water and carbon dioxide as the sole oxygenated products, with alkanes (predominantly n-alkanes) being the only carbonaceous, non-oxygenated products.

5.3. PRODUCTION OF WATER AND CARBON DIOXIDE.

An assumption frequently made (Anderson, Karn & Schultz, 1964) regarding the products of the Fischer-Tropsch synthesis is that carbon dioxide is a secondary product, being formed via the water-gas shift reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

This assumption has been shown to be valid for synthesis over iron (Dry, Shingles & Boshoff, 1972), cobalt (Anderson et alii, 1949 [a]) and nickel catalysts (Akers & White, 1948). Employing the same argument as used in the cited publication on iron catalysts, it will now be shown that carbon dioxide is likewise a secondary product in the synthesis over ruthenium.

Since the only oxygenated products formed in this investigation were carbon dioxide and water, the rate of production of carbon dioxide and water is a useful measure of the overall rate of synthesis. Table 5.6. presents data for the overall rate of synthesis (expressed as rate of production of carbon dioxide and water) over a range of product flow rates for a fixed reaction temperature and pressure. It can be seen from these data that a change in product flow rate by a factor greater than three resulted in a relatively small change in the overall rate of synthesis. However, the contribution made by the carbon dioxide to the total oxygenated product shows a pronounced decrease with increasing flow rate. Since an increase in flow rate must result in a decrease in mean reaction time, this must produce an enhancement in the ratio of primary to secondary products:

TABLE 5.6.

RELATIVE RATES OF CO_2 AND H_2O FORMATION.

TEMPERATURE 575 K

PRESSURE 1 200 kPa

PRODUCT FLOW RATE ml/min.(STP)	WHSV $hr.^{-1}$	CO CONVERSION (% mol)	$r(CO_2 + H_2O)$ (g mol/min/g Ru)	CO_2/H_2O
71,6	0,425	96	$4,60 \times 10^{-2}$	$9,204 \times 10^{-2}$
84,8	0,443	77	$4,09 \times 10^{-2}$	$1,960 \times 10^{-2}$
118,6	0,602	64	$4,67 \times 10^{-2}$	$1,668 \times 10^{-2}$
134,7	0,662	60	$4,82 \times 10^{-2}$	$1,056 \times 10^{-2}$
223,0	0,901	41	$4,50 \times 10^{-2}$	$0,990 \times 10^{-2}$

Carbon dioxide would therefore appear to be a secondary reaction product, presumably being formed via the water-gas shift reaction.

It is important to realise that the above argument holds only in cases where the extent of the other reactions resulting in the production or removal of carbon dioxide is small enough to be disregarded. Two such reactions which should be considered are the removal of carbon dioxide by methanation (the Sabatier reaction):

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$

and the production of carbon dioxide by the Boudouard reaction:

$$2CO \rightleftharpoons CO_2 + C$$

It has been reported (Dalla Betta, Piken & Shelef, 1975) in a study of the steady state methanation of carbon monoxide over supported ruthenium that carbon deposition via the Boudouard reaction did not occur at a significant rate. This conclusion was based on the relative insensitivity of the overall reaction rate to changes in the H_2 : CO ratio. Table 5.7. presents data obtained in the present investigation showing a similar lack of significant effect produced by a threefold change in the H_2 : CO ratio for operation at a given reactor temperature and pressure.

This absence of elemental carbon deposition via the Boudouard reaction thus confirms the results reported for the methanation study (Dalla Betta, Piken & Shelef, 1975) and further is in agreement with the thermodynamic instability of elemental carbon (Mills & Steffgen, 1974) under the conditions prevailing in this investigation.

TABLE 5.7.

EFFECT OF H_2 : CO RATIO ON OVERALL SYNTHESIS RATE.

TEMPERATURE 575 K

PRESSURE 1 200 kPa

RATE OF SYNTHESIS $r_{(CO_2 + H_2O)}$ g.mol/min/g.Ru.	H_2/CO
$4{,}60 \times 10^{-2}$	10,11
$4{,}50 \times 10^{-2}$	4,77
$4{,}67 \times 10^{-2}$	3,42
$4{,}82 \times 10^{-2}$	2,99

The removal of carbon dioxide by methanation will likewise not affect the treatment since this reaction does not occur in the presence of carbon monoxide (Fischer & Pichler, 1933; Pichler, 1943).

5.4. HYDROCARBON PRODUCTS.

Of greater interest than the production of carbon dioxide and water is the production of hydrocarbons. The remainder of this chapter will therefore be devoted to hydrocarbon production with particular reference to hydrocarbon distributions and individual hydrocarbon selectivities.

As mentioned earlier, to facilitate processing of the raw chromatographic data, it was assumed that only alkanes were produced as non-oxygenated products, with carbon dioxide and water being the sole oxygenated products. This was the basis of all calculations of mass percentages for each of the carbon number fractions examined.

The data obtained in this investigation will be treated by two different (but related) approaches. Firstly, in terms of hydrocarbon distributions where the sensitivity of the composition of the hydrocarbon product to the main operating variables will be considered. Secondly, in terms of the selectivity of each of the individual carbon number fractions relative to the selectivity of methane.

5.4.1. HYDROCARBON DISTRIBUTIONS.

The distribution of carbon number fractions obtained during the Fischer-Tropsch synthesis is a complex function of the operating variables of temperature, pressure and extent of reactant conversion (Everson, Woodburn & Kirk, 1978). This section considers the nature of the hydrocarbon products in relation to each of the main operating variables.

Hydrocarbon product distributions obtained during experiments conducted with various reaction conditions are presented in Figures 5.4.(a) to (d) as a function of temperature, pressure and space velocity (mass flow rate per hour per mass of total catalyst). The use of space velocity rather than contact time as a parameter follows the convention recommended by Boudart (1956) for flow reactors, the relation between space velocity and conversion being shown in Figure 5.5.

The relations shown in Figure 5.4 (a) to (d) are expressed in terms of carbon number fractions with concentrations expressed in terms of mole percentage of total hydrocarbon product.

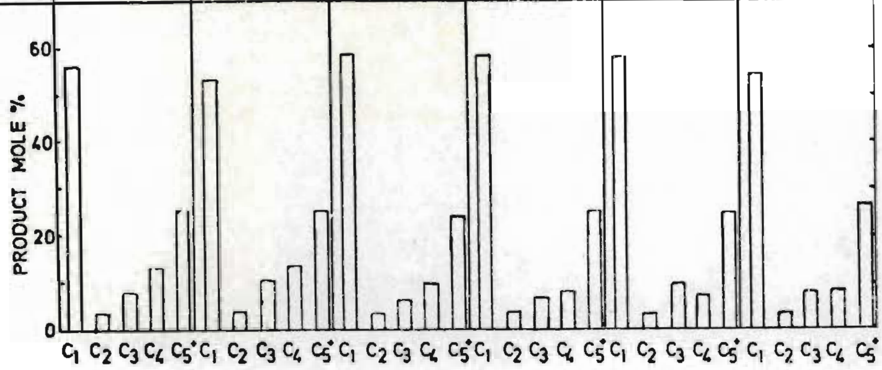
Details of the distribution of the C_5 to C_{12} carbon number fractions for each of the experiments depicted in Figure 5.4.(a) to (d) are presented in Table 5.8 along with molar conversions of carbon monoxide and the concentrations of carbon dioxide and water in the reactor product.

Of all the operating variables considered, the effect of temperature was dominant over the range of operating conditions considered here. That this should be so is a not unexpected result in light of the data presented in Chapter 7 where the activation energies for CO removal and methanation are shown to

FIGURE 5.4. (overleaf) - HYDROCARBON PRODUCT DISTRIBUTIONS.

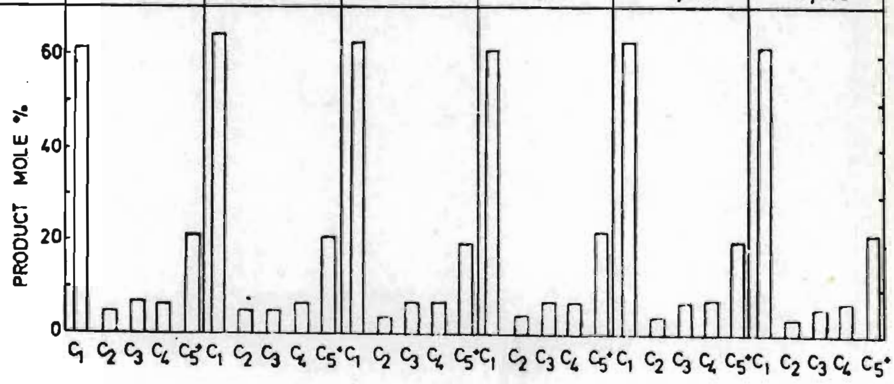
(a)	503-510 K	(c)	548-553 K
(b)	521-529 K	(d)	569-577 K

RUN NO.	111	32	107	13	10	15
PRESS. kPa	1000	1200	1400	800	800	1200
TEMP. K	496	496	496	509	503	510
W.H.S.V.	0,095	0,248	0,107	0,093	0,193	0,102



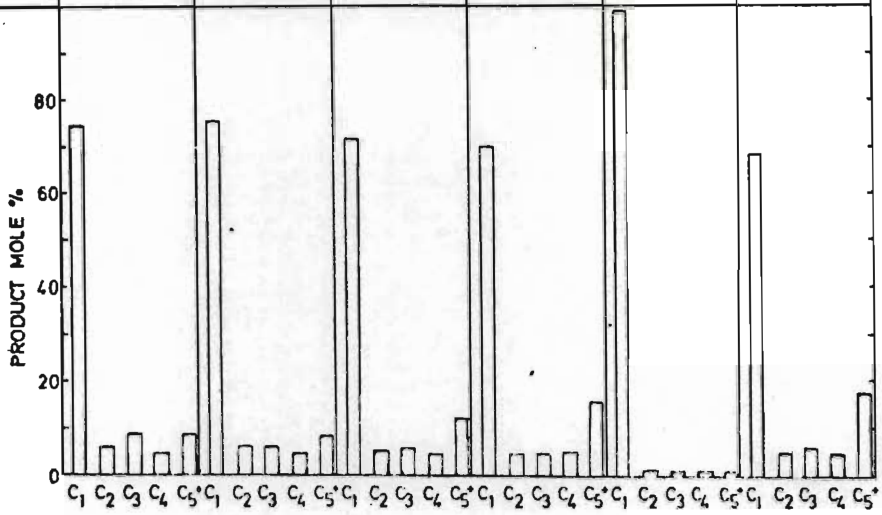
(a)

RUN. NO.	12	110	36	30	29	46
PRESS. kPa	800	1000	1200	1200	1200	1600
TEMP. K	529	519	523	521	521	523
W.H.S.V.	0,178	0,127	0,087	0,153	0,360	0,258



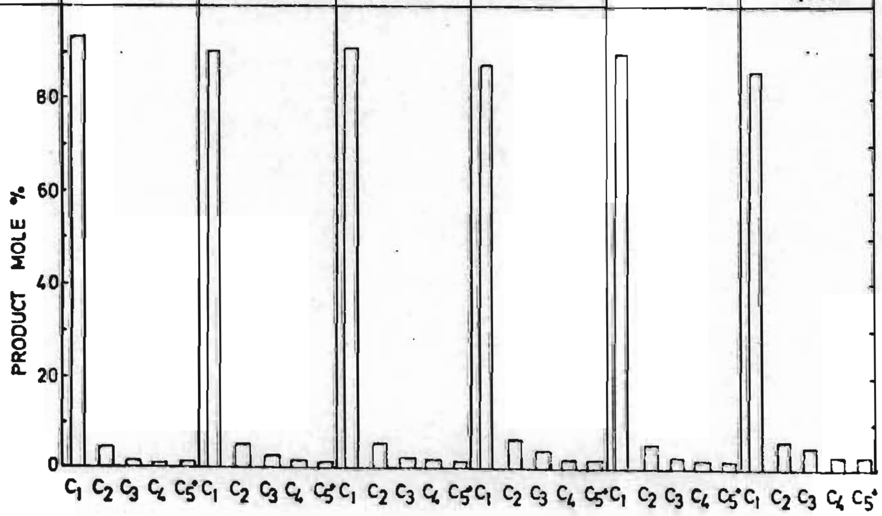
(b)

RUN NO.	4	38	24	21	44	43
PRESS. kPa	800	1200	1200	1200	1600	1600
TEMP. K	551	551	548	548	553	551
WHSV	0,454	0,237	0,414	0,678	0,327	0,677



(c)

RUN NO	2	3	28	20	41	42
PRESS. kPa	800	800	1200	1200	1600	1600
TEMP. K	573	573	573	569	573	577
W.H.S.V.	0,529	0,938	0,446	0,826	0,728	1,348



(d)

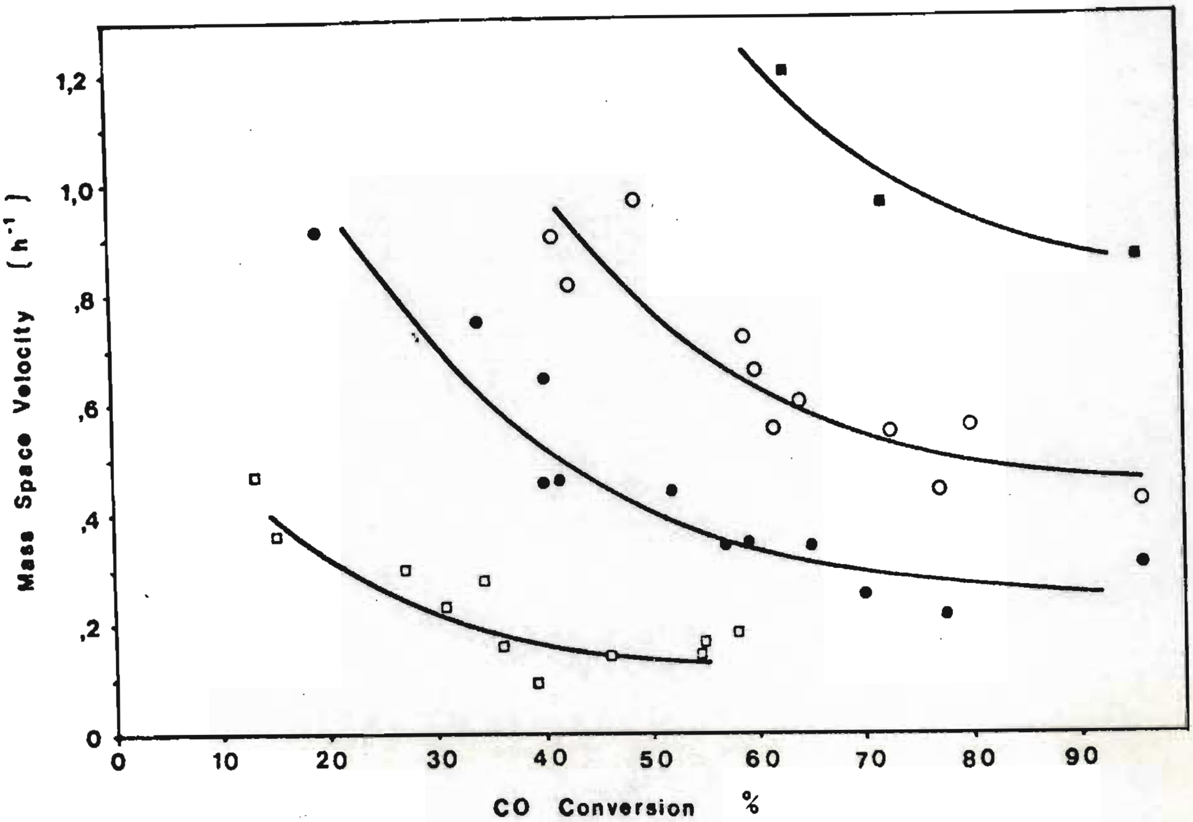


FIGURE 5.5. - RELATION BETWEEN SPACE VELOCITY AND CO CONVERSION.
(■ ~600 K; ○ ~ 575 K; ● ~550 K; □ ~525 K.)

differ considerably (being of the order of 19 and 34 kcal/mol respectively). To a lesser extent, the methane content was dependent upon space velocity and pressure - a dependence which was more evident for the higher operating temperatures: a feature whose significance will be remarked upon later.

For the range of variables considered, the methane content of the hydrocarbon product varied from almost 100 mol % at high temperature to 54,3 mol % at low temperature. This corresponded to mass distributions of almost 100 and some 19,9% respectively. The C_5 to C_{12} fraction was found to be as high as 26,9 mol% (or 59,6% mass), which may be compared to the approximately 17 mol% reported by Vannice (1975) for ruthenium catalyst with operation at 1 bar total pressure and 483 K and the 33,4 mass % (C_5 to C_{11}) obtained over an iron catalyst at 593 - 613 K and 22 bar in an industrial Synthol reactor reported by Frohning and Cornils (1974). Operation with a fixed bed reactor at 26 bar and 493 - 513 (with an H_2/CO ratio of 1,7 - which might be expected to favour higher hydrocarbon synthesis) was reported in the latter reference to produce a C_5 - C_{11} mass selectivity of 24,8%.

Using a reactor similar to the one used in this investigation, Tajbl, Feldkirchner and Lee (1967) studied the methanation reaction over supported ruthenium over a rather limited range of low space velocities and reported that the formation of higher hydrocarbons was lower than expected; a phenomenon which was attributed to the occurrence of hydrogenolysis. The results presented in Figure 5.4. (c) and (d) show the effect of space velocity at total pressures of 12 and 16 bar for reaction temperatures in the region of 550 and 575 K. With increasing space velocities, CO conversions decrease, methane content decreases and the C_5 to C_{12} fraction increases. The methane and C_5 to C_{12} fractions produced with operation at temperature in the region of 525 and 500 K appear to be largely independent of space velocity at CO conversions below 60% as shown in Figure 5.4. (a) and (b) and Table 5.8. This lack of effect of space velocity on methane content of the hydrocarbon product is, in all probability, caused (at least in part) by the experimental technique whereby carbon number fractions above C_{12} were not produced (at any rate, as far as the chromatographic analysis was concerned). This technique could thus be expected to produce a constraint on the measured values of each of the lower carbon number fractions.

The effect of total reactor pressure on the product distributions obtained for operation at a given level of conversion at a particular reaction temperature is indicated in Table 5.9. These data indicate clearly that higher operating pressures favour the production of the C_5 - C_{12} carbon number fraction at the expense of the methane fraction. This is in agreement with other workers using various other catalysts for Fischer-Tropsch synthesis (Vannice, 1975; 1975 [a]; Storch, Golumbic & Anderson, 1951).

The maximum hydrocarbon yield other than C_1 (which was always the major individual carbon number fraction produced), appears to occur over the range C_4 - C_5 (when expressed in molar terms) or C_4 - C_7 (when expressed in mass terms) for operation at 480 to 530 K, whereas for operation with reaction temperatures of 550 K and higher, the maxima occur at C_2 - C_3 (molar or mass). Vannice (1975) reported a maximum at C_3 (molar) for operation with ruthenium at 483 K and 1 bar total pressure, while the data for Frohning and Cornils (1974) on

TABLE 5.8.

DISTRIBUTION OF C_5 TO C_{12} (MOL PER CENT OF TOTAL HC), CO CONVERSION (MOL PER CENT) AND CONCENTRATIONS OF CO_2 AND H_2O (MOL PER CENT OF EXIT STREAM.)

RUN No.	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_5^+	CO CONVERSION	CO_2	H_2O
111	8,07	6,34	4,04	3,57	1,73	1,15	-	-	25,07	13	0,087	2,84
32	5,79	6,05	4,53	3,78	3,53	1,01	-	-	24,69	6	0,018	0,98
107	7,10	5,83	5,07	3,30	2,03	-	-	-	23,33	16	0,138	3,07
13	6,21	5,86	4,35	3,10	2,48	1,86	0,83	-	24,69	19	0,070	4,06
10	5,27	4,81	4,18	4,65	1,86	1,50	-	-	23,27	9	0,030	1,85
15	7,42	6,28	4,28	3,94	3,42	1,54	-	-	26,87	23	0,190	5,04
12	5,08	4,39	3,69	2,61	1,94	1,94	1,14	0,95	21,74	57	0,200	17,10
110	5,44	4,49	3,84	2,60	2,01	1,31	0,85	-	20,53	46	0,290	11,45
36	5,29	4,29	3,19	2,49	1,66	1,25	0,97	0,35	19,48	39	0,198	10,80
30	5,24	4,44	3,46	3,11	2,66	2,31	0,98	0,35	22,54	37	0,156	9,22
29	5,55	4,36	3,56	2,38	1,98	1,19	0,99	-	20,00	15	0,055	3,82
46	5,27	4,28	4,28	2,97	2,14	1,66	0,95	0,48	22,03	27	0,140	6,66
4	3,09	2,02	1,15	0,84	0,52	0,31	-	-	7,94	39	0,090	10,08
38	3,12	2,14	1,16	0,78	0,49	0,17	0,11	-	7,97	70	0,820	24,58
24	4,04	2,99	2,17	1,30	0,68	0,34	0,29	-	11,81	41	0,132	12,57
21	4,24	3,60	2,40	1,84	1,15	0,71	0,57	-	14,50	34	0,080	9,37
44									0,00	96	0,981	40,96
43	4,03	3,35	2,77	2,42	1,68	1,58	0,59	0,20	16,63	46	0,135	6,80
2	0,28	0,10	0,04	-	-	-	-	-	0,43	72	0,400	22,68
3	0,59	0,22	0,08	-	-	-	-	-	0,89	47	0,140	12,85
28	0,67	0,28	0,12	-	-	-	-	-	1,05	77	0,537	27,38
20	1,20	0,47	0,14	-	-	-	-	-	1,81	41	0,110	11,12
41	0,72	0,31	0,17	0,16	-	-	-	-	1,36	74	0,491	27,43
42	1,34	0,76	0,34	0,11	-	-	-	-	2,55	45	0,153	14,07

TABLE 5.9.

EFFECT OF TOTAL PRESSURE ON PRODUCT DISTRIBUTION.

TEMPERATURE (K)	PRESSURE (kPa)	CO CONVERSION (% Mol)	C_5-C_{12}	C_1
551	800	39	26,8	44,1
548	1 200	41	38,4	39,1
551	1 600	46	48,9	31,4
573	800	72	1,9	84,9
573	1 200	77	4,7	78,4
573	1 600	75	6,0	74,8
573	800	47	3,8	78,2
569	1 200	41	7,2	70,8
577	1 600	46	10,1	66,2

the Synthol and fixed-bed reactors appear to indicate maxima at C_3 (16,2 mass % and 6,1 mass % respectively). Cobalt on a mass basis has been reported as having a maximum at C_5 (Storch, Golumbic & Anderson, 1951).

The presentation of data for concentration of individual carbon number fractions as a function of chain length is frequently made in terms of a log-linear plot (similar to that shown in Figure 5.2.) This is demonstrated for the data obtained in the present investigation in Figures 5.6. to 5.8.

The presentation of concentration data in this form results from the mechanistic studies of Herington (1946) who assumed a stepwise growth mechanism, with a constant probability of growth for carbon number fractions above C_5.

While the data presented in Figures 5.6. to 5.8. exhibit some scatter, the effect of temperature, space velocity and total pressure can clearly be seen. The relative regularities found for the higher homologues (C_5 - C_{12}) are not repeated for the lower homologues, especially C_1. Herington (1946) attributed this to the fact that in a homologous series, the first members frequently exhibit abnormality when compared to higher members of the same series.

FIGURE 5.9. (overleaf) - MASS SELECTIVITY OF INDIVIDUAL CARBON NUMBER FRACTIONS RELATIVE TO METHANE.

(a) C_2

(b) C_3

(c) C_4

(d) C_5

(e) C_6

(f) C_7

(g) C_8

(h) C_9

(i) C_{10}

(j) C_{11}

(k) C_{12}

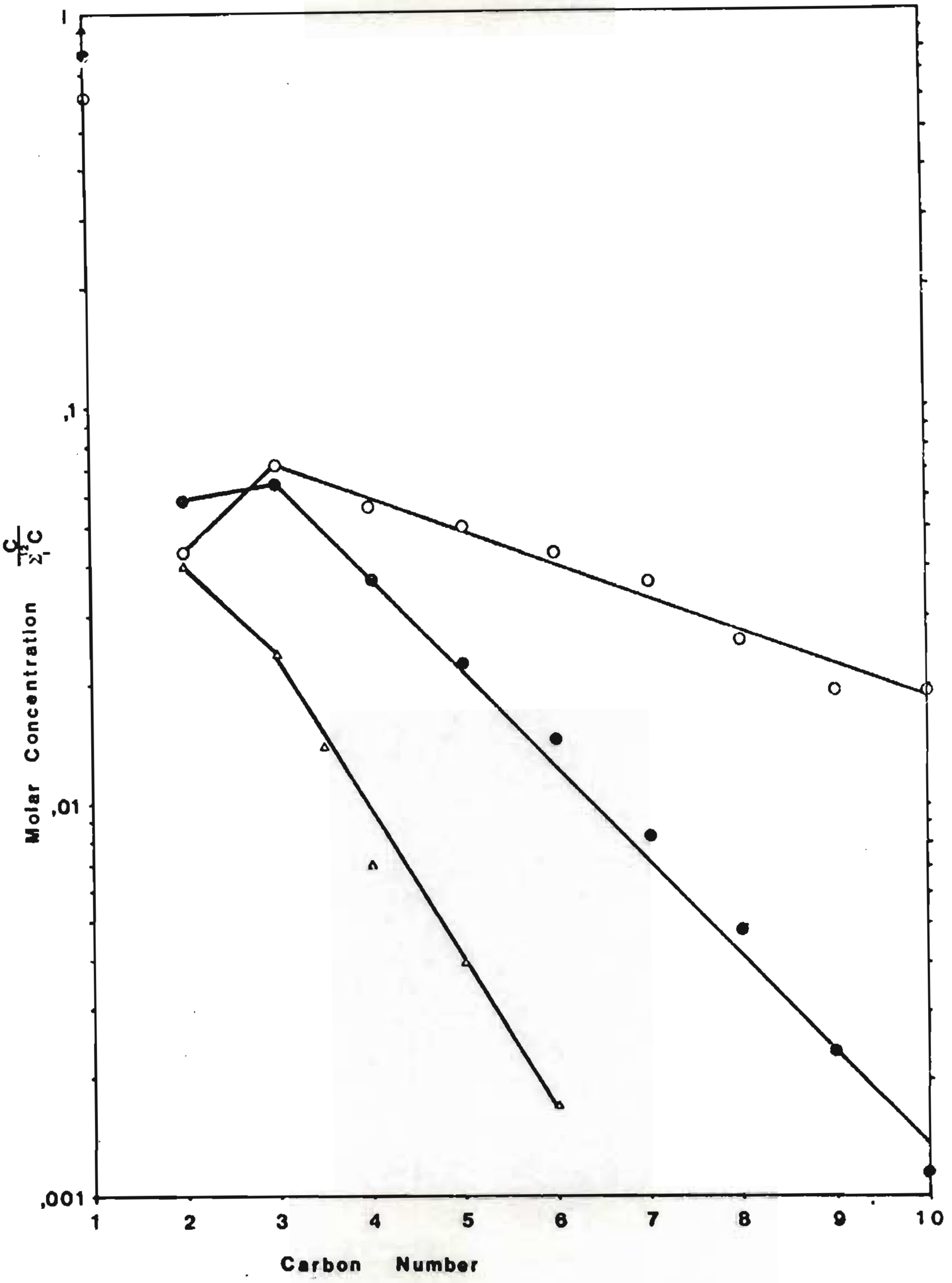


FIGURE 5.6. - EFFECT OF REACTION TEMPERATURE ON PRODUCT DISTRIBUTION.

CO Conversion 57 to 65%
Table Pressure 800 kPa
Reaction Temperature ○ 529 K
● 551 K
△ 573 K

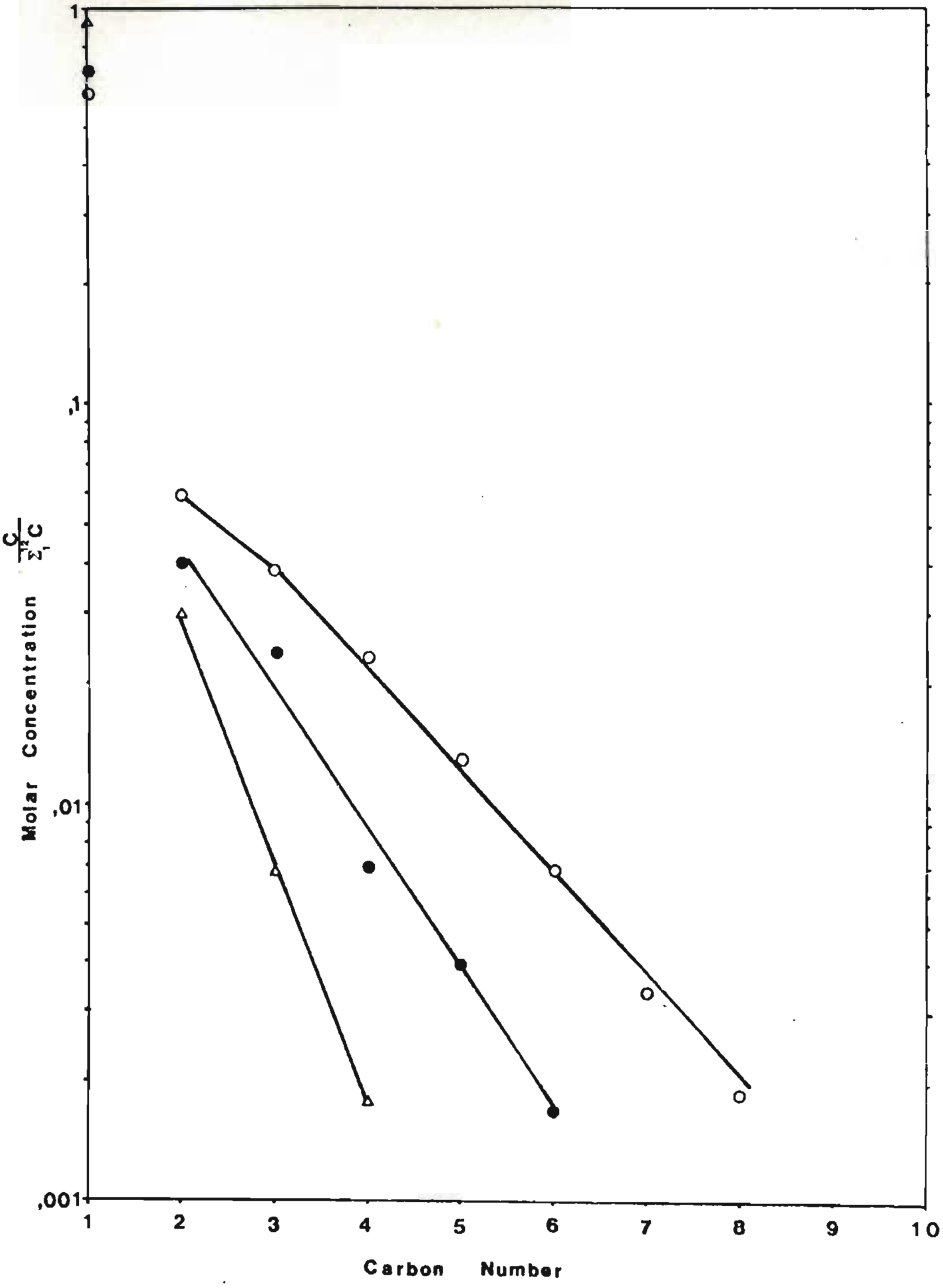


FIGURE 5.7. - EFFECT OF CO CONVERSION ON PRODUCT DISTRIBUTION.

Total Pressure 800 kPa
Reaction Temperature 573 K
CO Conversion ○ 47%
● 64%
△ 81%

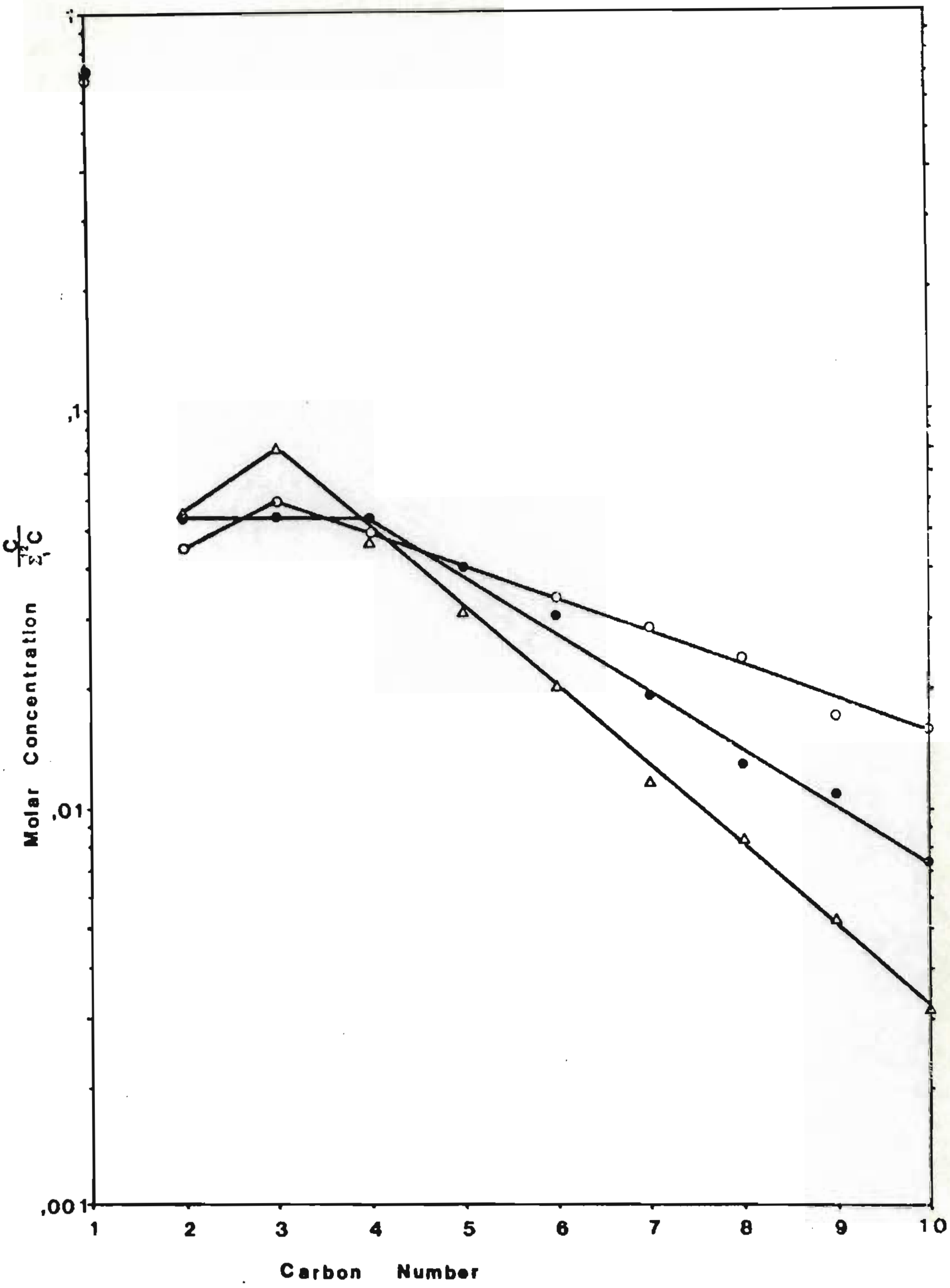


FIGURE 5.8. - EFFECT OF TOTAL PRESSURE ON PRODUCT DISTRIBUTION.

CO Conversion		39 to 46%
Reaction Temperature		550 K
Total Pressure	△	800 kPa
	●	1 200 kPa
	○	1 600 kPa

5.4.2. INDIVIDUAL HYDROCARBON SELECTIVITIES.

If only the hydrocarbon products are considered, a clear relation is established between the selectivity of each individual hydrocarbon and that of methane. This is shown in Figure 5.9 (a) to (k) where the mass selectivity of each of the individual hydrocarbons is plotted against that of methane. It should be noted that the relations shown here result from combining the data from all the experiments conducted over the entire range of operating conditions considered.

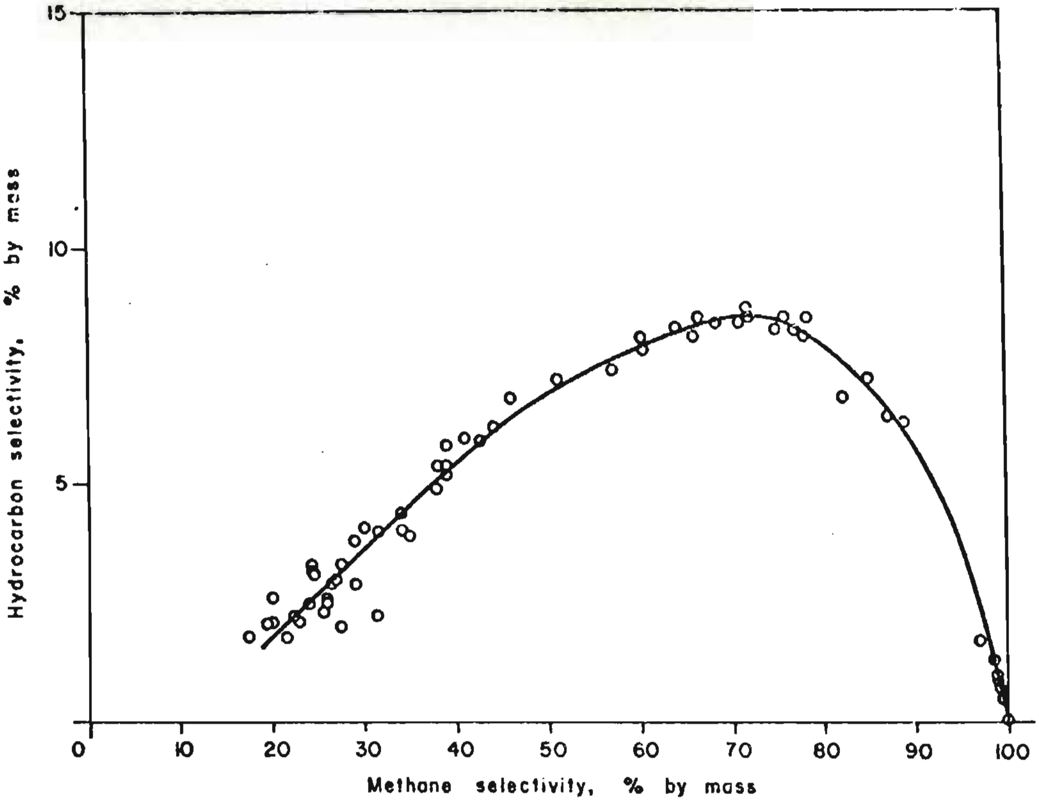
The most notable consequence of the relations shown here is that if the selectivity of methane is fixed, the selectivities of all other hydrocarbons are also fixed. The general form of this relation is similar to that reported for product selectivities over iron catalysts as shown in Figure 5.10.(a) (Dry, 1976)

Direct comparison of work by different workers in the field of heterogeneous catalysis is generally rendered difficult by virtue of the undefined nature of most catalyst surfaces. However, it would appear that data for hydrocarbon product selectivity can be compared directly since these selecticities are the results of *relative* rates of hydrocarbon production and should therefore be unaffected by the overall activity of the catalyst.

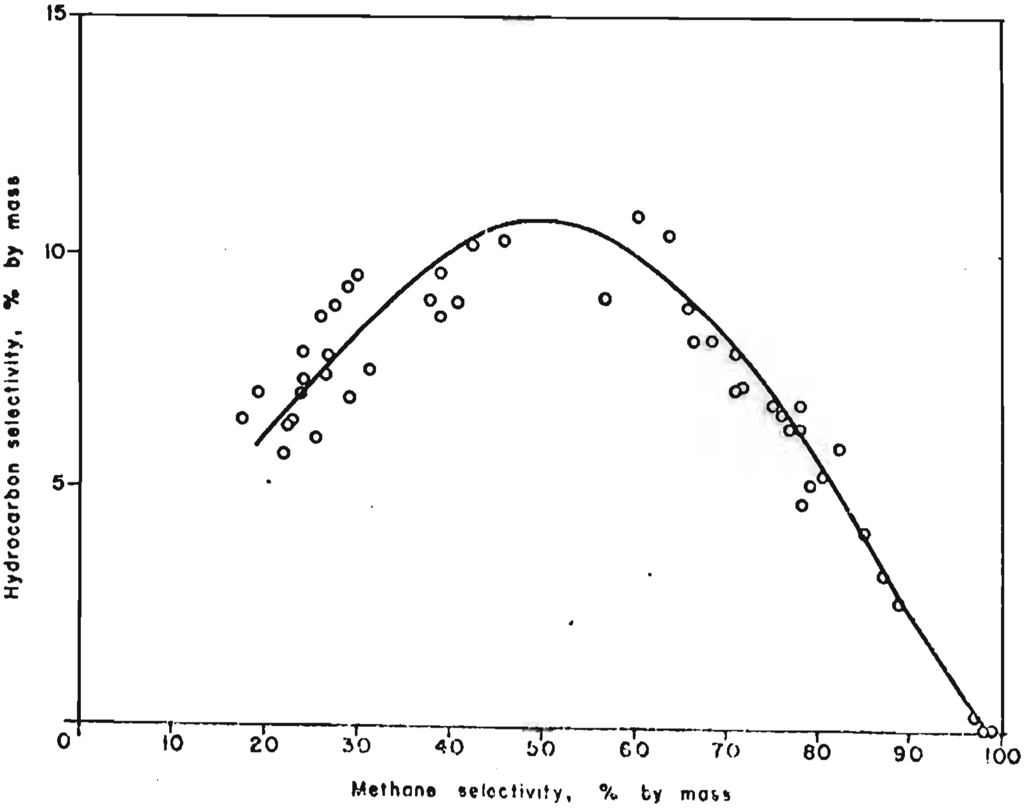
This was confirmed in the present investigation by comparison of product distribution obtained over catalysts previously

FIGURE 5.9. (overleaf) - MASS SELECTIVITY OF INDIVIDUAL CARBON NUMBER FRACTIONS RELATIVE TO METHANE.

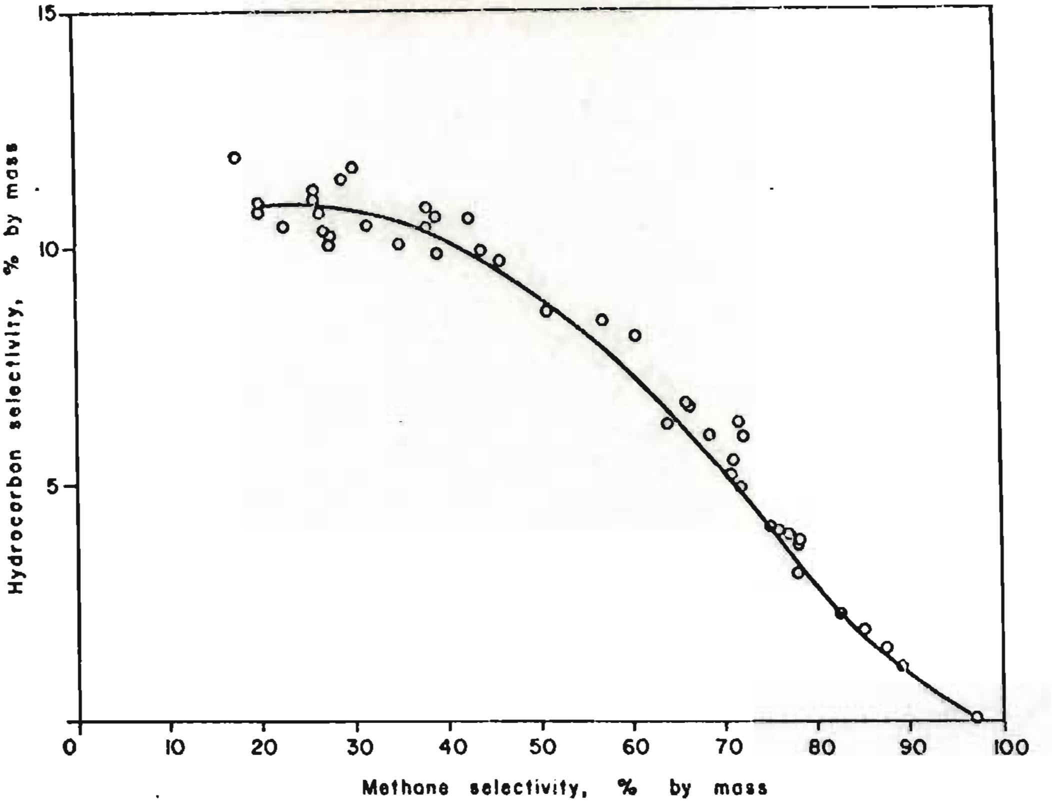
(a) C_2
(b) C_3
(c) C_4
(d) C_5
(e) C_6
(f) C_7
(g) C_8
(h) C_9
(i) C_{10}
(j) C_{11}
(k) C_{12}


Hydrocarbon selectivity, % by mass
Methane selectivity, % by mass
0
5
10
15
0
10
20
30
40
50
60
70
80
90
100

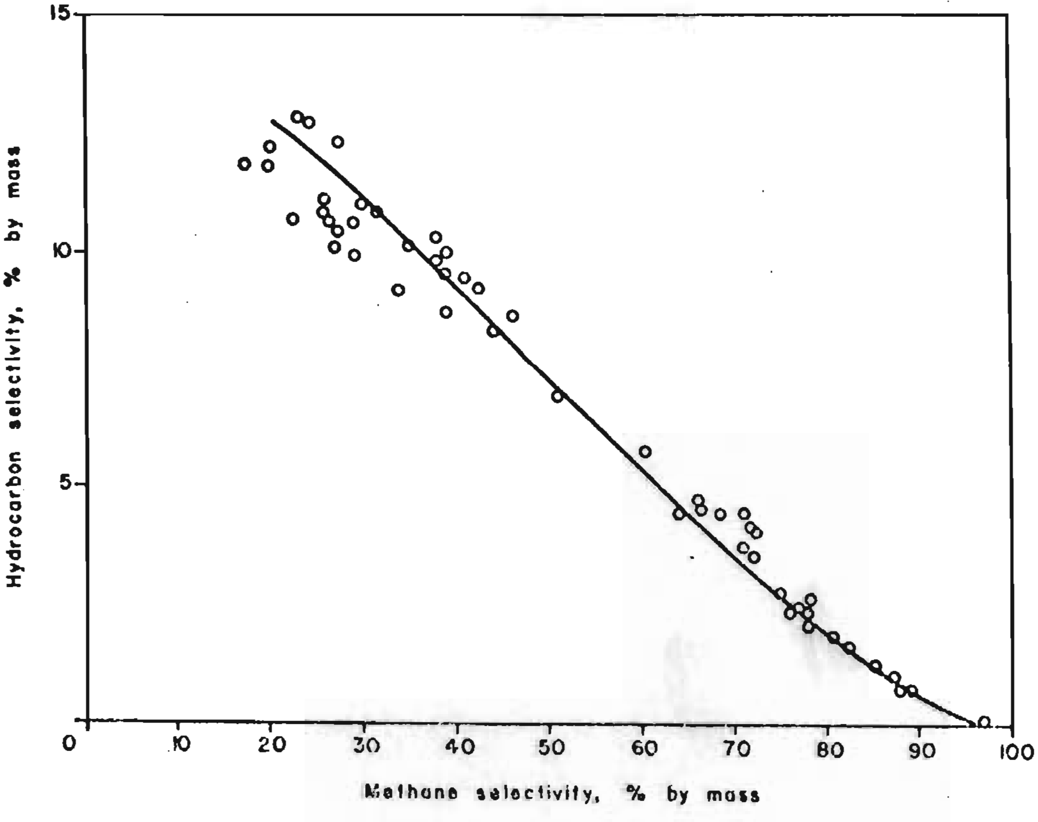
(a)


Hydrocarbon selectivity, % by mass
Methane selectivity, % by mass
0
5
10
15
0
10
20
30
40
50
60
70
80
90
100

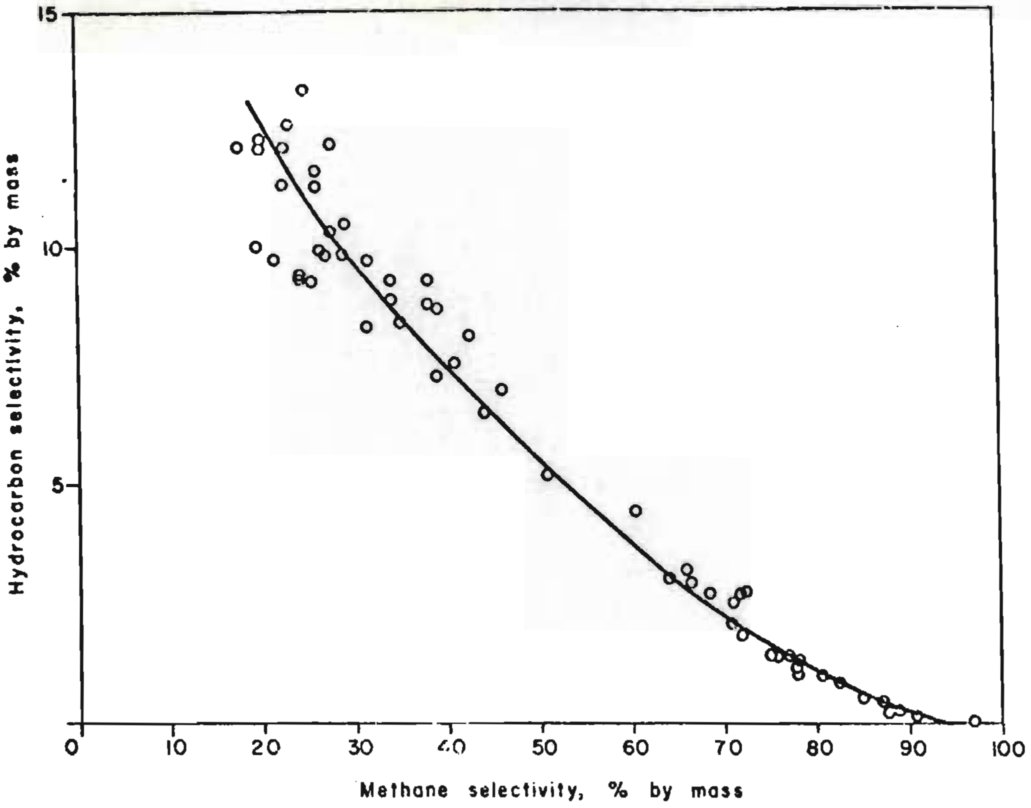
(b)


15
10
5
0
10
20
30
40
50
60
70
80
90
100
Hydrocarbon selectivity, % by mass
Methane selectivity, % by mass

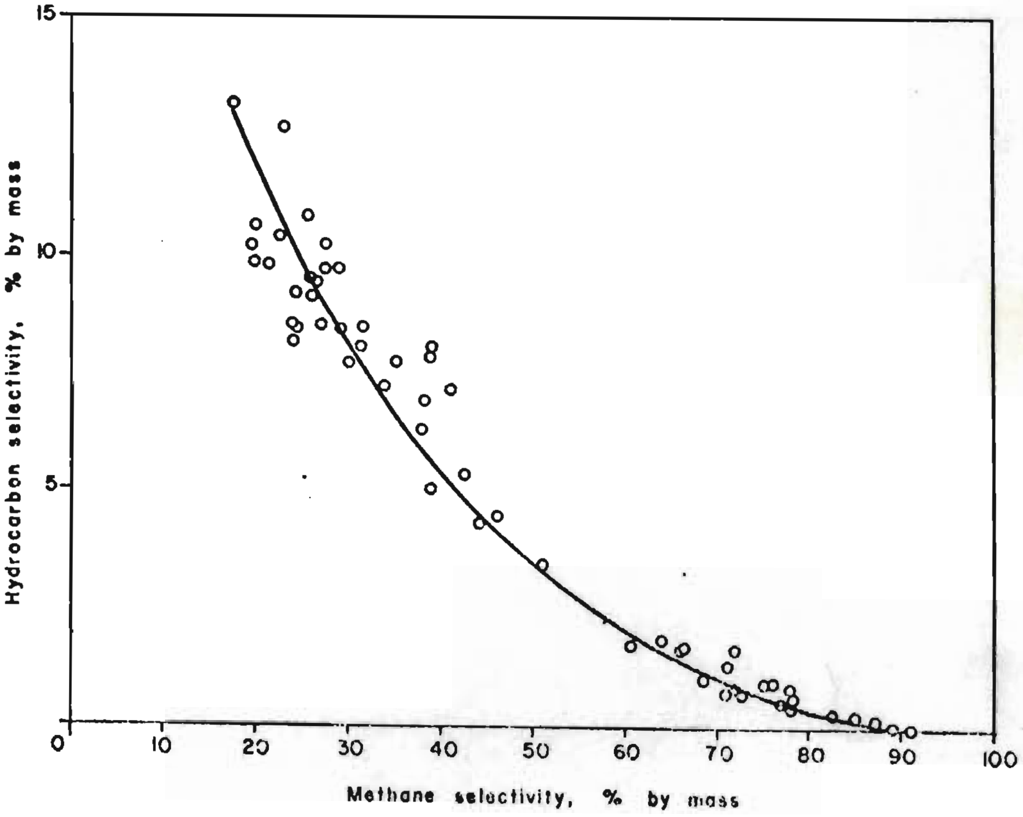
(c)


15
10
5
0
10
20
30
40
50
60
70
80
90
100
Hydrocarbon selectivity, % by mass
Methane selectivity, % by mass

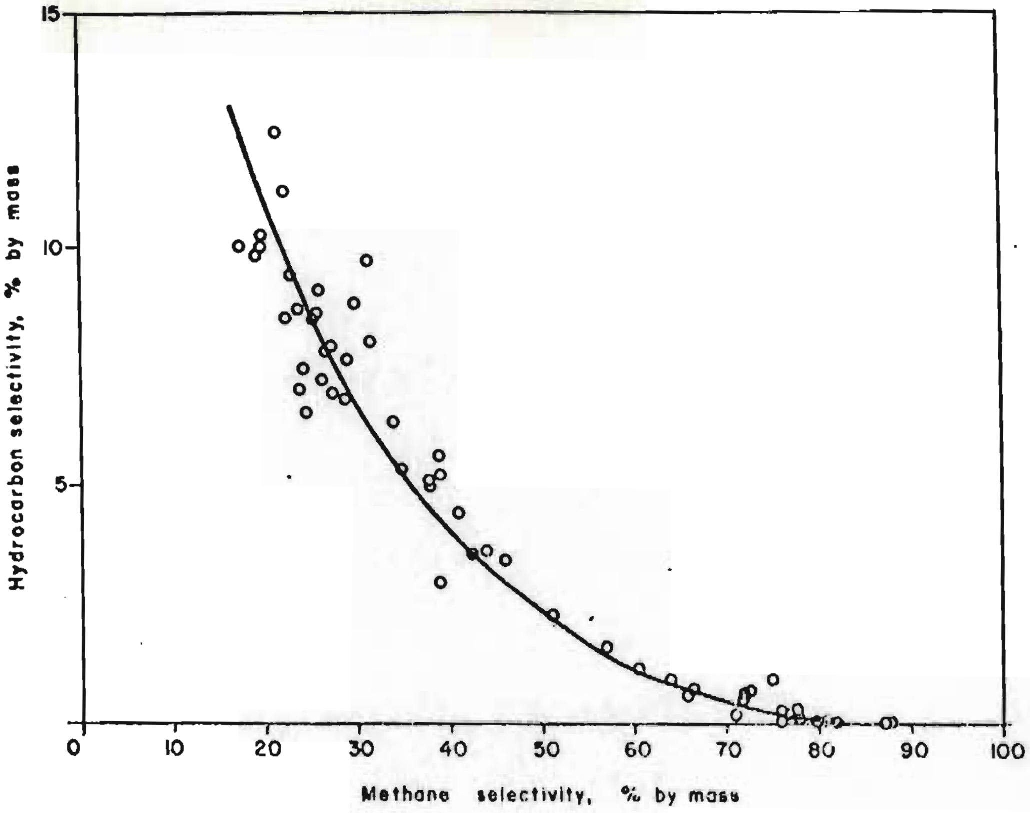
(d)


15
10
5
0
Hydrocarbon selectivity, % by mass
0
10
20
30
40
50
60
70
80
90
100
Methane selectivity, % by mass

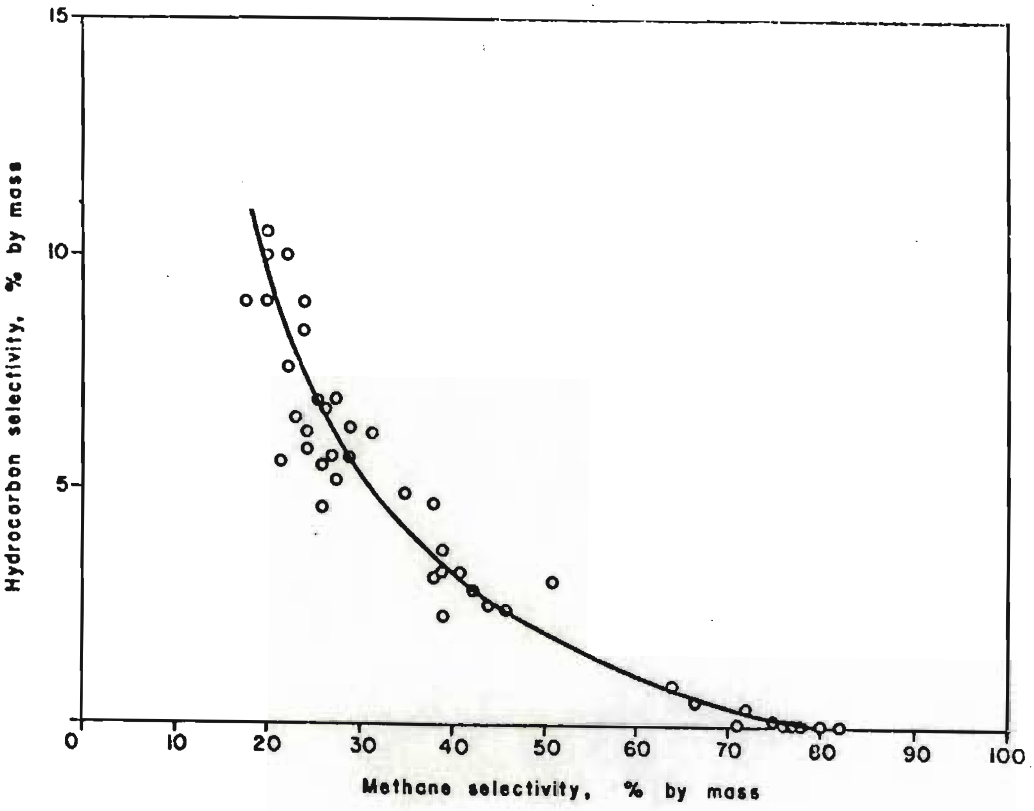
(e)


15
10
5
0
Hydrocarbon selectivity, % by mass
0
10
20
30
40
50
60
70
80
90
100
Methane selectivity, % by mass

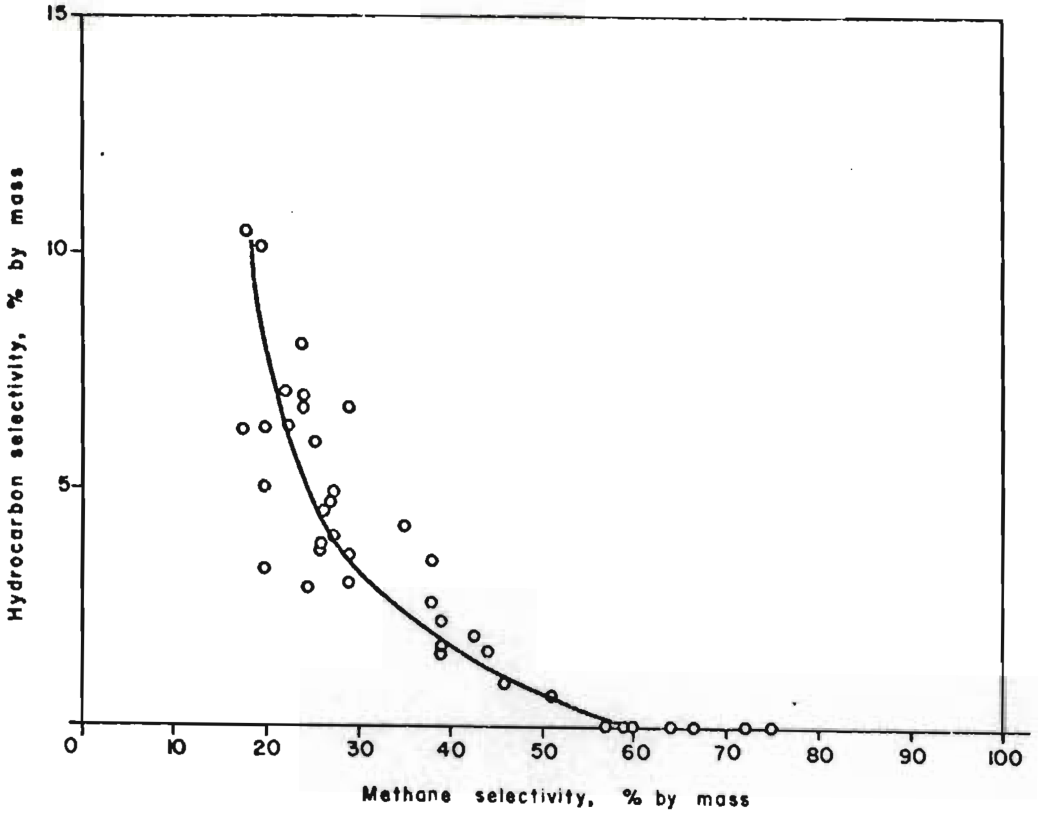
(f)


15
10
5
0
10
20
30
40
50
60
70
80
90
100
Hydrocarbon selectivity, % by mass
Methane selectivity, % by mass

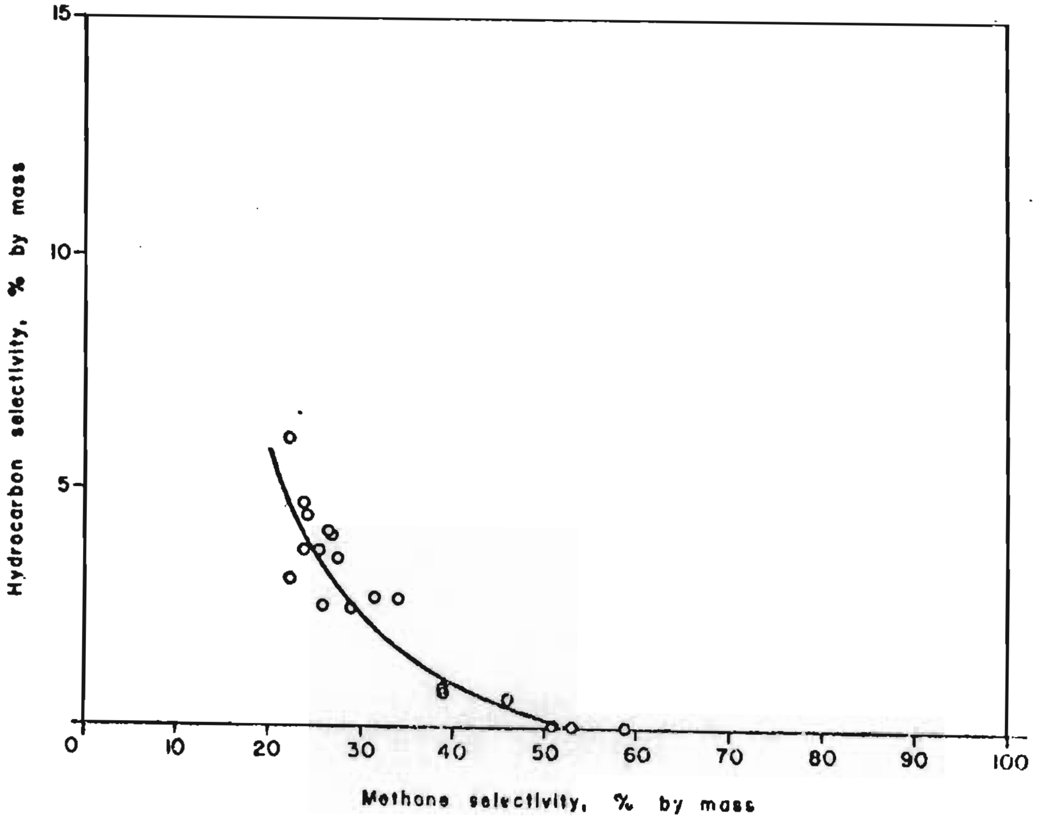
(g)


15
10
5
0
10
20
30
40
50
60
70
80
90
100
Hydrocarbon selectivity, % by mass
Methane selectivity, % by mass

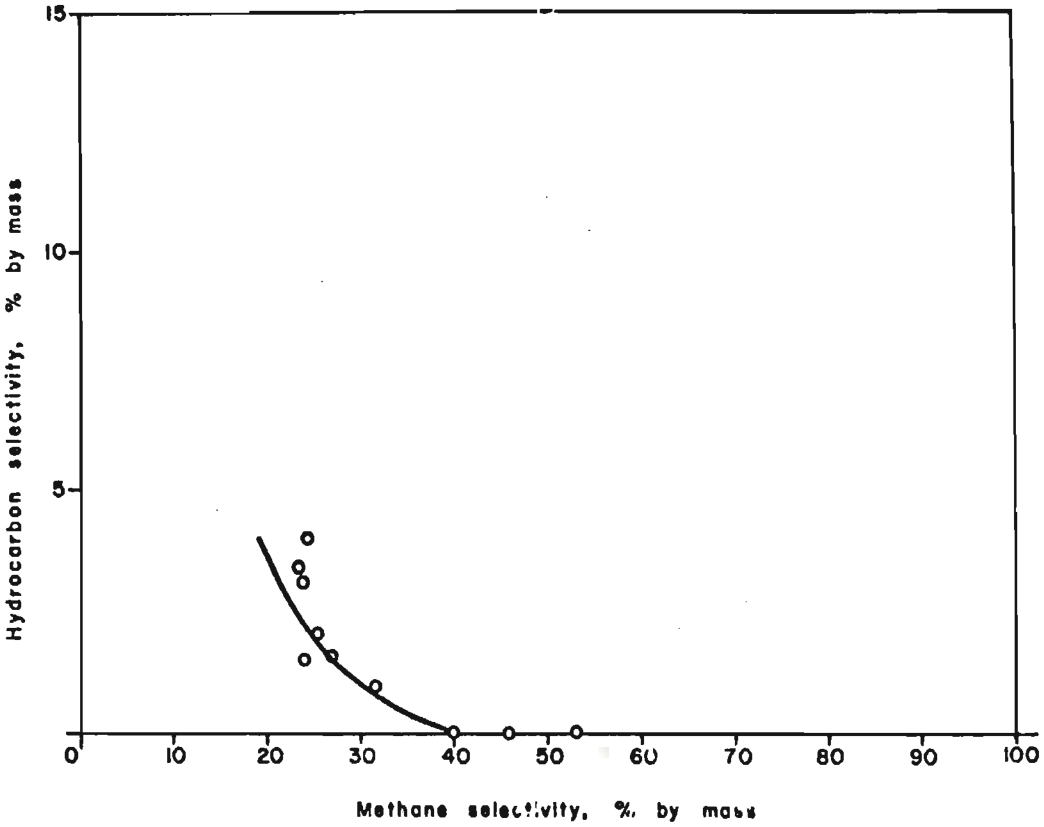
(h)


15
10
5
0
10
20
30
40
50
60
70
80
90
100
Hydrocarbon selectivity, % by mass
Methane selectivity, % by mass

(i)


15
10
5
0
10
20
30
40
50
60
70
80
90
100
Hydrocarbon selectivity, % by mass
Methane selectivity, % by mass

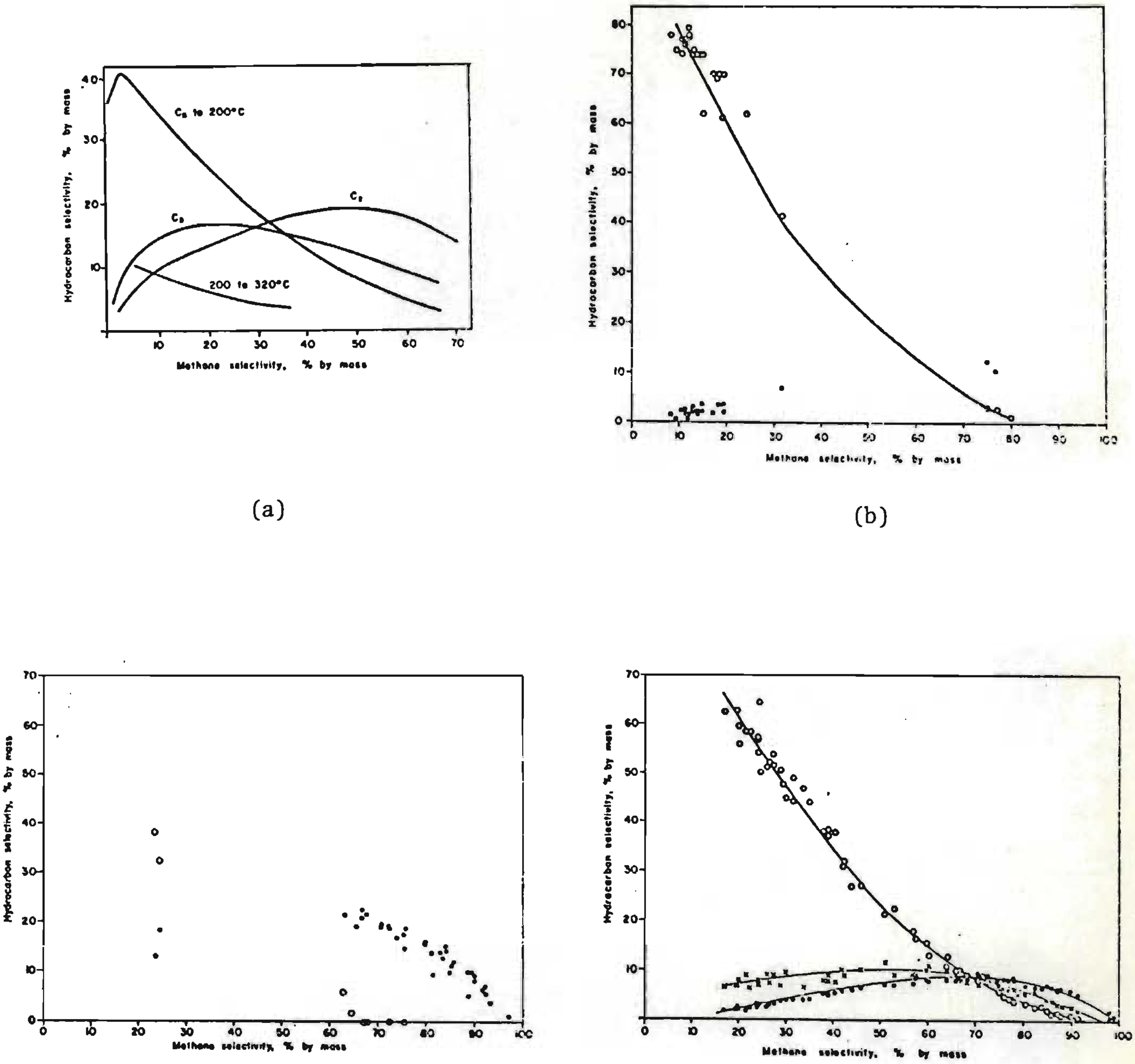
(j)


15
10
5
0
10
20
30
40
50
60
70
80
90
100
Hydrocarbon selectivity, % by mass
Methane selectivity, % by mass

(k)

deactivated to varying degrees (by prior use in the synthesis reaction). It was noted that at a given temperature and pressure, a given conversion produced the same pattern for product selectivity irrespective of the extent of prior deactivation, (although the rate of reaction per unit mass of catalyst varied according to the extent of deactivation).

Since the previously-cited work on iron catalysts (Dry, 1976) was conducted with different types of reactor, different feed compositions of synthesis gas and different techniques for catalyst preparation, it would appear that the product selectivity relation is a function of the catalytic metal only. By extension, although the present investigation was confined to only one catalyst preparation, it is likely that other ruthenium-based catalysts would result in the same selectivity relations as reported here. This contention is partly supported by additional evidence adapted from the literature (Schultz, Karn & Anderson, 1967; Anderson et alii, 1947; 1949; Reisz et alii, 1948) on mass selectivity relations for C_2 and C_5+ carbon number fractions relative to that of methane over various cobalt-based catalysts as shown in Figure 5.10 (b) and a similar relation for molybdenum-based catalysts, as shown in Figure 5.10 (C) (Schultz, Karn & Anderson, 1967). Here again, several types of reactor and catalyst preparation techniques appear to yield fixed selectivity relations unique to the catalytic metal, although some scatter is evident in both Figures and the data is insufficiently complete to allow the construction of the relations over the whole range of methane selectivity.



(a)

(b)

(c)

(d)

FIGURE 5.10. - MASS SELECTIVITY RELATIONS FOR DIFFERENT CATALYSTS.

(a) Iron.
(b) Cobalt.
(c) Molybdenum.
(d) Ruthenium (present investigation).

● C_2 ; × C_3 ; ○ C_5+

In the previously-cited works for cobalt analysis, no upper limit was placed on the C_5+ fraction (unlike the previously-cited [Dry, 1976] work on iron) and hence the values for C_5+ selectivity are higher than would be obtained if they were to have been expressed in terms of C_5 to C_{12}.

Comparison of the relations in Figure 5.10. (in which the selectivities for C_2, C_3 and C_5 - C_{12} are combined) demonstrates that, over ruthenium, the selectivities of the C_2 and C_3 carbon number fractions (with maxima at 8,3 and 10,5 per cent respectively) are considerably lower than those over iron (with maxima of some 20 and 18 per cent respectively). Accordingly, for a given methane selectivity, the selectivity of the C_5 to C_{12} fraction is higher over ruthenium than that obtained over iron-although it should be pointed out that the work on iron catalysts reported selectivity for a fraction designated "C_5 to 200°C", which would approximate to a C_5 to C_{11} fraction (if only n-alkanes are considered).

However, even if the product selectivity shown in Figure 5.10(d) is adjusted to correspond to the fraction C_5 to C_{11}, this results in very little difference in the product selectivity relation obtained (as may be inferred from Figure 5.9. (k) showing the selectivity of the C_{12} fraction).

Consideration of the relations in Figure 5.9. shows that each of the individual hydrocarbons from C_2 to C_{12} begins to make a contribution to the total hydrocarbon product at progressively lower values of methane selectivity. This, while the C_6 carbon number fraction begins to make a measurable contribution at a methane selectivity of approximately 95 per cent, the figures for the methane selectivities corresponding to the appearance of C_8, C_{10} and C_{12} fractions are in the order of 80, 60 and 40 per cent respectively.

Within the range of methane selectivities considered, the $C_{12}+$ fraction is lower over ruthenium than over iron. Thus, while the fraction designated "200 to 320°C" in Figure 5.10 (a) (or approximately C_{12} to C_{19}, if only n-alkanes be considered) contributes some 4 per cent to the total product at a methane selectivity of some 35 per cent, the selectivity of C_{12} carbon number fraction at the same methane selectivity was in the region of 0,5 per cent over ruthenium, with no noticeable production of hydrocarbons containing more than twelve carbon atoms per molecule. However, it is probable that a decrease of the methane selectivity below the lower limit considered here would result in an increase of the selectivity of the $C_{12}+$ fraction over ruthenium to some value greater than that yielded for iron.

In a recent study (King, 1978) of the Fischer-Tropsch synthesis over various ruthenium catalysts in a microreactor at 250°C and 400 kPa it was reported that the mass selectivity of the C_2+ fraction relative to the mass selectivity of methane showed no correlation with degree of carbon monoxide conversion. However, if it is assumed that the H_2/CO usage ratio is the same (at 2/1) as the feed ratio, then with conversions varying from 2,8 to 26 per cent, this results in a variation in the partial pressure of carbon monoxide of only 98,7 to 129,6 kPa when run at only the one total operating pressure of 400 kPa.

By expressing the variation of synthesis gas conversion in terms of partial pressure, comparison with the results obtained in the present investigation becomes possible. Figure 5.11 (a) to (c) present the results obtained in the present investigation for operation with temperatures in the region of 575, 550 and 525 K. It can be seen from these figures that the selectivity of the C_2+ fraction relative to the selectivity of methane does show a dependence on partial pressure of unconverted synthesis gas only below some critical value (which is a function of reaction temperature). Also included in Figure 5.11. (c) is the data of King (1978) showing the lack of correlation referred to over the examined range.

A possible explanation for this dependence upon conversion below a given value of $P_{H_2 + CO}$ may be that since rutheium is one of the most active metals for hydrogenolysis (Dalla Betta, Piken & Shelef, 1974), this relative increase in methane formation could be the result of increasing extents of hydrogenolysis of the higher hydrocarbons becoming apparent at values of the partial pressure of carbon monoxide below the level necessary for complete inhibition of the hydrogenolysis.

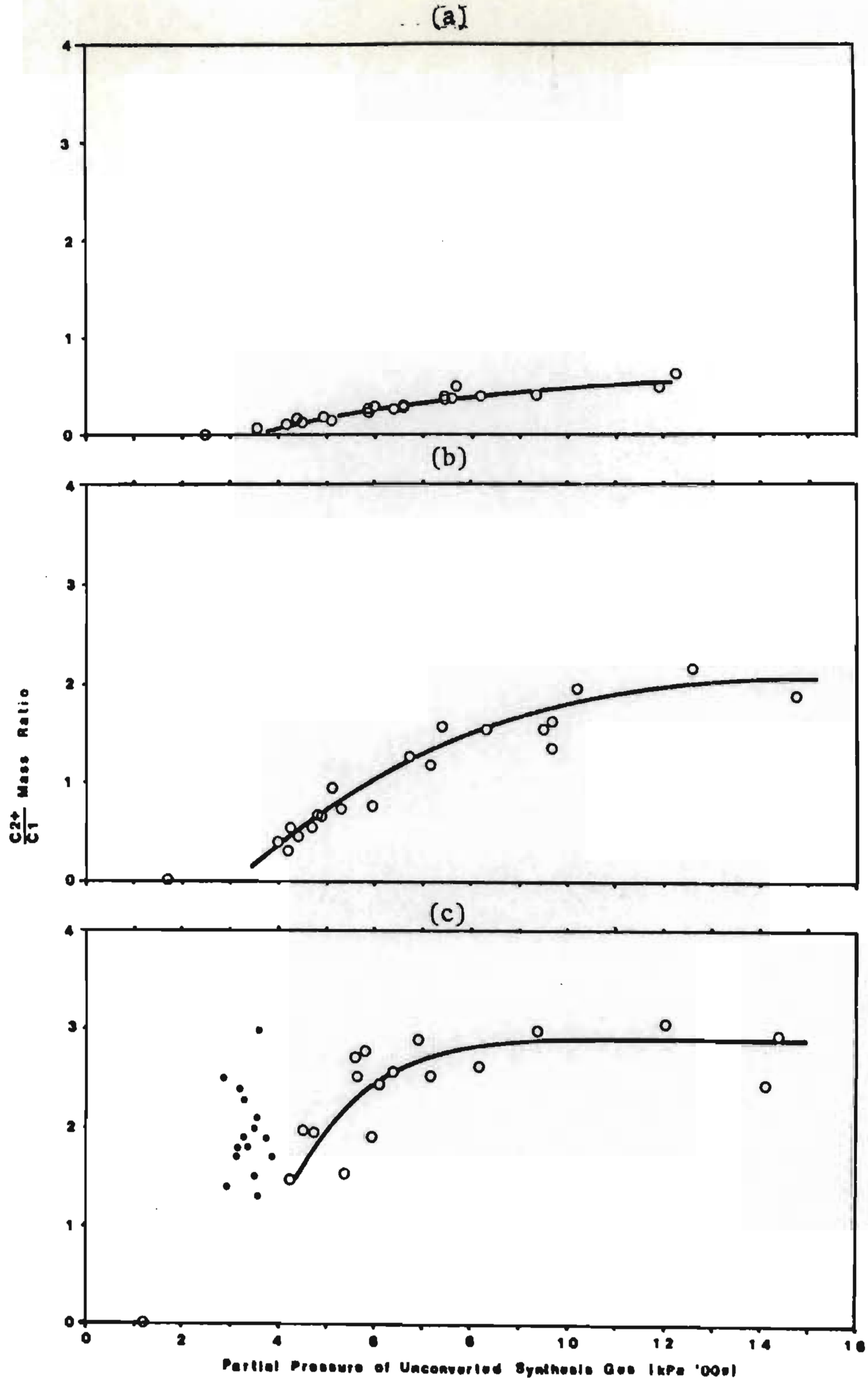
FIGURE 5.11. (overleaf) - MASS RATIO OF FISCHER-TROPSCH PRODUCTS RELATIVE TO METHANE.

(a) ca. 575 K

(b) ca. 550 K

(c) ca. 525 K

○ Present Investigation; ● King (1978).


(a)
(b)
(c)
0
1
2
3
4
C2+/C1 Mass Ratio
0
2
4
6
8
10
12
14
16
Partial Pressure of Unconverted Synthesis Gas (kPa '00s)

The mass selectivity of methane for reaction temperatures in the region of 600, 575, 550 and 525 K is plotted against the partial pressure of synthesis gas $P_{H_2 + CO}$ in Figure 5.12. By virtue of the relations depicted in Figure 5.9. (a) to (k), the mass selectivity of each of the carbon number fractions C_2 to C_{12} can be deduced from the mass selectivity of methane. Accordingly, none of the equivalent relations for the individual carbon number fractions is depicted here. From Figure 5.12. can be seen that for a given value of $P_{H_2 + CO}$, the higher the operating temperature, the higher is the selectivity of methane (and, by extension, the lower the selectivity of higher hydrocarbons). The methane selectivity for temperatures of 525 and 550 K appear to reach limiting values (in the region of 0,25 and 0,37 respectively) for the higher values of $P_{H_2 + CO}$. This apparent lower limit to the selectivity of methane may, in fact, be artificially imposed by the experimental technique adopted. Since the product spectrum was terminated at carbon number fraction C_{12} by adjustment of the space velocity, this would obviously have the effect of imposing an external constraint on the attainable values of selectivity for each of the other carbon number fractions. By removing this constraint, it is highly likely that the methane selectivity plots would not exhibit this limitation.

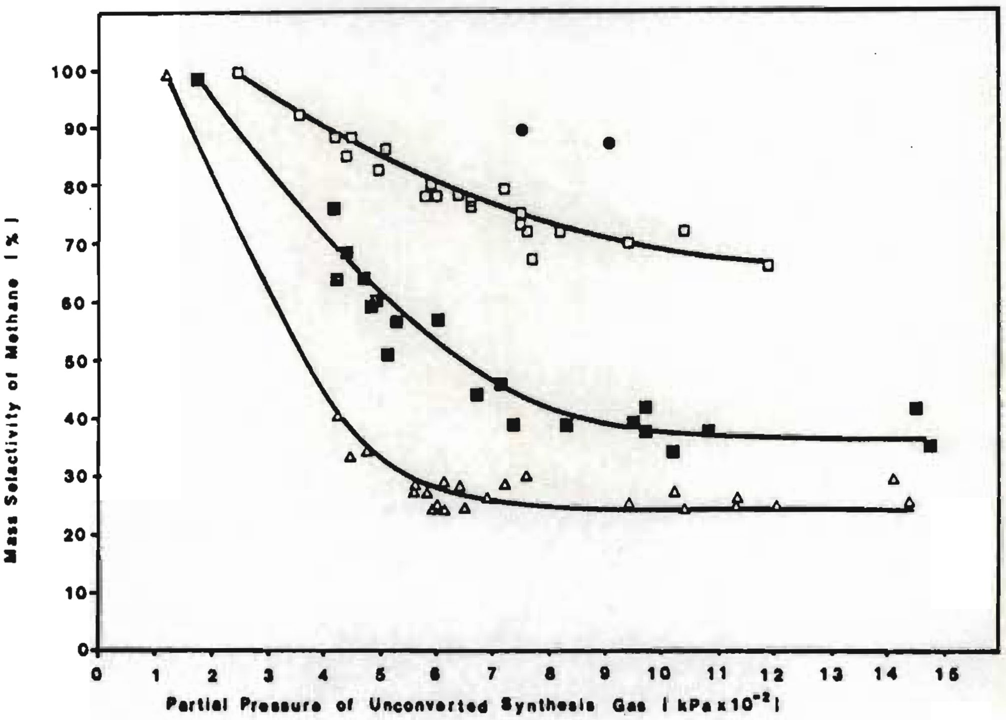


FIGURE 5.12. - MASS SELECTIVITY OF METHANE FOR VARIOUS REACTION TEMPERATURES.

● ca. 600 K; □ ca. 575 K; ■ ca. 550 K; △ ca. 525 K

CHAPTER 6.

RELATIVE RATES OF HYDROCARBON SYNTHESIS.

6.1. INTRODUCTION.

In order to facilitate direct comparisons of the rates of methanation and higher hydrocarbon synthesis, the rates of production of individual hydrocarbon number fractions were expressed relative to the rate of removal of carbon monoxide.

The philosophy behind the adoption of this method for expressing rates was based on the fact that this technique would neutralise any errors which may have been made in the experimental determination of metal surface areas (used in the expression of rates in absolute terms in the following chapter). Since the same estimate of metal area would appear in the rate expression for hydrocarbon synthesis and in the rate expression for CO removal, division of one by the other would obviously neutralise any constant error. A second approach involved the expression of the synthesis rates relative to the methanation rate; the reasoning behind this method being exactly anologous to that employed for the above, with the additional observation that, insofar as methane was always formed as a co-product, the absolute rate of production of individual carbon number fractions is of secondary importance to the rate of formation relative to the rate of formation of methane (an undesirable product).

The underlying assumption in both of these approaches is that there is no difference in the nature of the active metal catalytic sites on the catalyst. The possibility that surface sites may favour either methanation or synthesis of higher hydrocarbons has been raised by King (1978) as a possible explanation for the pronounced difference between the product distribution obtained by synthesis over supported and unsupported ruthenium. However, evidence against such a "twin-site" nature of the catalyst (at any rate, when applied specifically to the catalyst employed here) may be inferred from the results presented in the previous two chapters. If one assumes that the catalyst possesses two fundamentally different types of active site: one favouring methanation and the other favouring synthesis of higher hydrocarbons, it might reasonably be expected that deactivation (mirrored by the total carbon content of the catalyst) would be more severe on the sites favouring synthesis, since the adsorption of high-molecular weight hydrocarbons would occur preferentially on these sites. This, in turn, would have the effect of altering the product selectivity pattern to favour methanation. However, as was mentioned in the previous chapter, no alteration in the product selectivity pattern was observed when catalysts previously deactivated to varying extents (by prior use in the synthesis reaction) were used for synthesis. This would then indicate that the loss of active sites occurred in a random fashion: in contrast to what would be expected should those sites favouring higher hydrocarbon synthesis be preferentially blocked-off.

6.2. SYNTHESIS RATES RELATIVE TO RATE OF CARBON MONOXIDE REMOVAL.

In view of the fact that only one composition of synthesis gas was used for this investigation, the partial pressure of the unconverted synthesis gas $P_{H_2 + CO}$ is a useful indicator of the extent of conversion at a given level of total reactor pressure.

Figures 6.1.(a) to (d) show the relations existing between the molar rates of methanation relative to the rate of removal of carbon monoxide as a function of the partial pressure of unconverted synthesis gas at reaction temperatures in the region of 600, 575, 550 and 525 K respectively. The paucity of results obtained for operation at 600 K perhaps militates against presentation - these results are given only for the sake of completeness.

Because of the stoichiometry of the methanation reaction

$$3H_2 + CO \longrightarrow CH_4 + H_2O$$

the rate of methane formation relative to the rate of removal of carbon monoxide (when expressed in molar terms) will obviously tend towards a limiting value of unity. The extent of the divergence of the relative rate from unity is conversely a measure of the extent of the synthesis reactions relative to that of the methanation reaction.

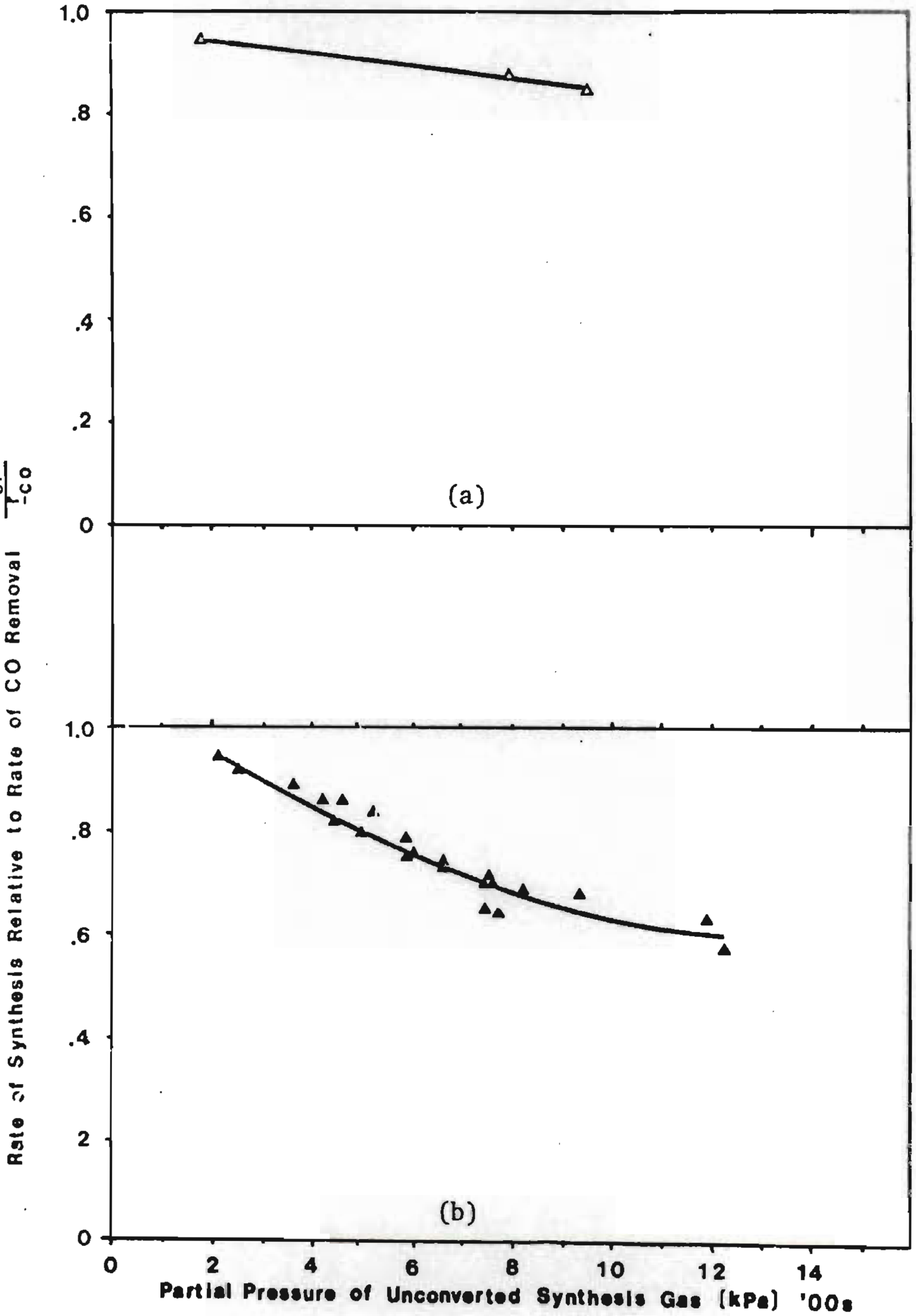
FIGURE 6.1. (overleaf) - RATE OF METHANE SYNTHESIS RELATIVE TO RATE OF CO REMOVAL

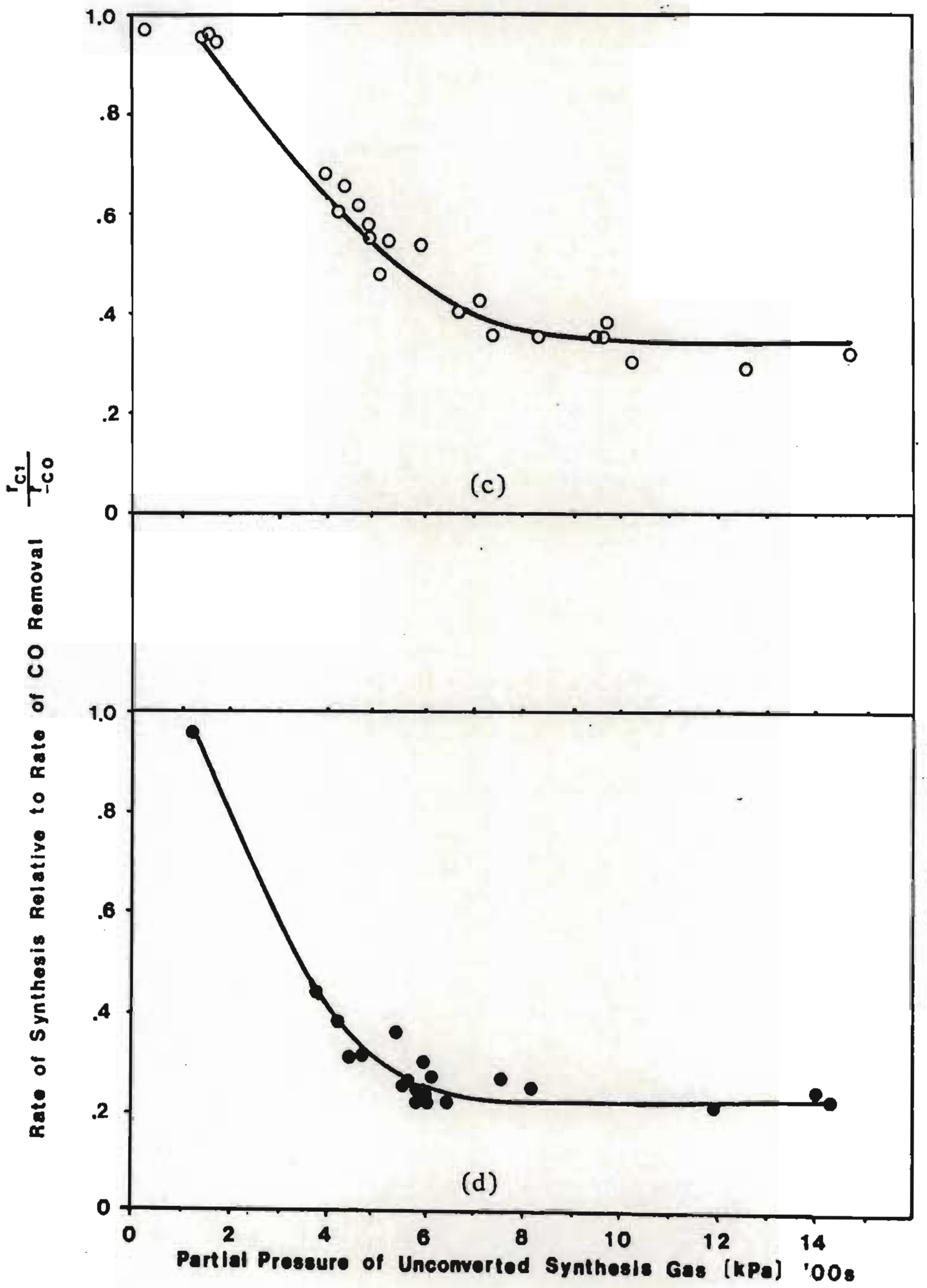
(a) ca. 600 K

(b) ca. 575 K

(c) ca. 550 K

(d) ca. 525 K


1.0
.8
.6
.4
.2
0
(a)
1.0
.8
.6
.4
2
0
(b)
0
2
4
6
8
10
12
14
Partial Pressure of Unconverted Synthesis Gas (kPa) '00s
Rate of Synthesis Relative to Rate of CO Removal
$\frac{r_{C1}}{r_{-CO}}$


1.0
.8
.6
.4
.2
0
(c)
1.0
.8
.6
.4
.2
0
(d)
0
2
4
6
8
10
12
14
Partial Pressure of Unconverted Synthesis Gas (kPa) '00s
Rate of Synthesis Relative to Rate of CO Removal
$\frac{r_{C1}}{r_{-CO}}$

Insofar as methane can be regarded as an undesirable product, it would obviously be advantageous to minimise the rate of formation of methane relative to the rate of removal of carbon monoxide.

It may be seen from Figures 6.1.(a) to (d) that the higher the reaction temperature, the greater is the relative methanation rate for a given partial pressure of unconverted synthesis gas. As the partial pressure of unconverted gas is reduced (as a result of increasing conversion or decreasing reactor total pressure) below a certain critical value, the relative methanation rate begins to increase towards the limiting value of unity. Comparison of these Figures indicates that operation at lower temperatures permits the operation at lower values of the partial pressure of unconverted synthesis gas before this occurrence of increase in relative methanation. This would thus allow operation at higher conversion levels for a given total pressure of reactor (or alternatively, operation at a lower level of total pressure for a given conversion) before this relative loss of higher hydrocarbons would become appreciable. The relative methanation rates obtained for operation at the two higher levels of reaction temperature (600 and 575 K) do not show any obvious levelling-off of rate within the range of $P_{H_2 + CO}$ considered, unlike those for operation at the lower two temperatures. A further point of interest in these Figures is that the ultimate value for the relative methanation rate at 525 K is lower than that for operation at 550 K.

This indicates that relative to CO removal, the extent of synthesis occurring at lower temperatures is greater than that which occurs with operation at higher temperatures for a given value of $P_{H_2 + CO}$.

The relative rates of production for the carbon number fractions C_2 and C_4 at reaction temperatures of 525, 550 and 575 K are given in Figures 6.2. (a) and (b). Before considering them in detail, it is more convenient at this stage to look at the overall reaction scheme.

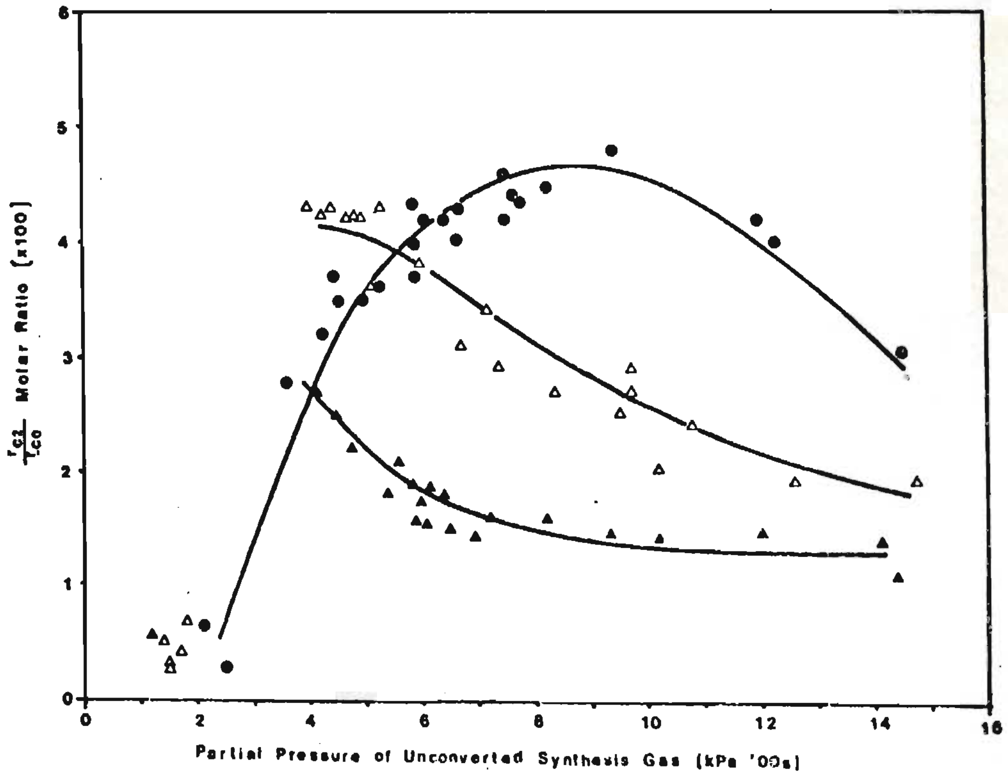


FIGURE 6.2.(a) - RATE OF C_2 SYNTHESIS RELATIVE TO RATE OF CO REMOVAL.

●~575K; △~550K; ▲~525K

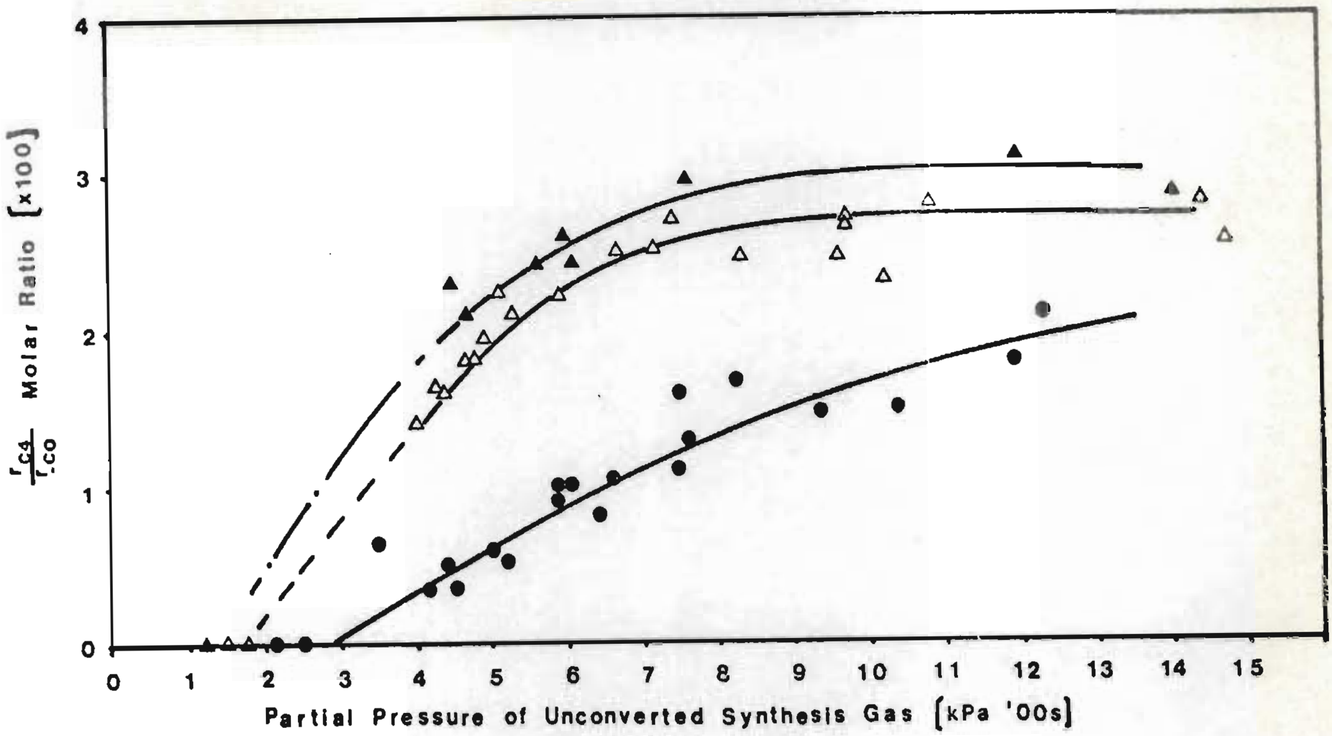


FIGURE 6.2.(b) - RATE OF C_4 SYNTHESIS RELATIVE TO RATE OF CO REMOVAL.
● 575K; △~550K; ▲~525K

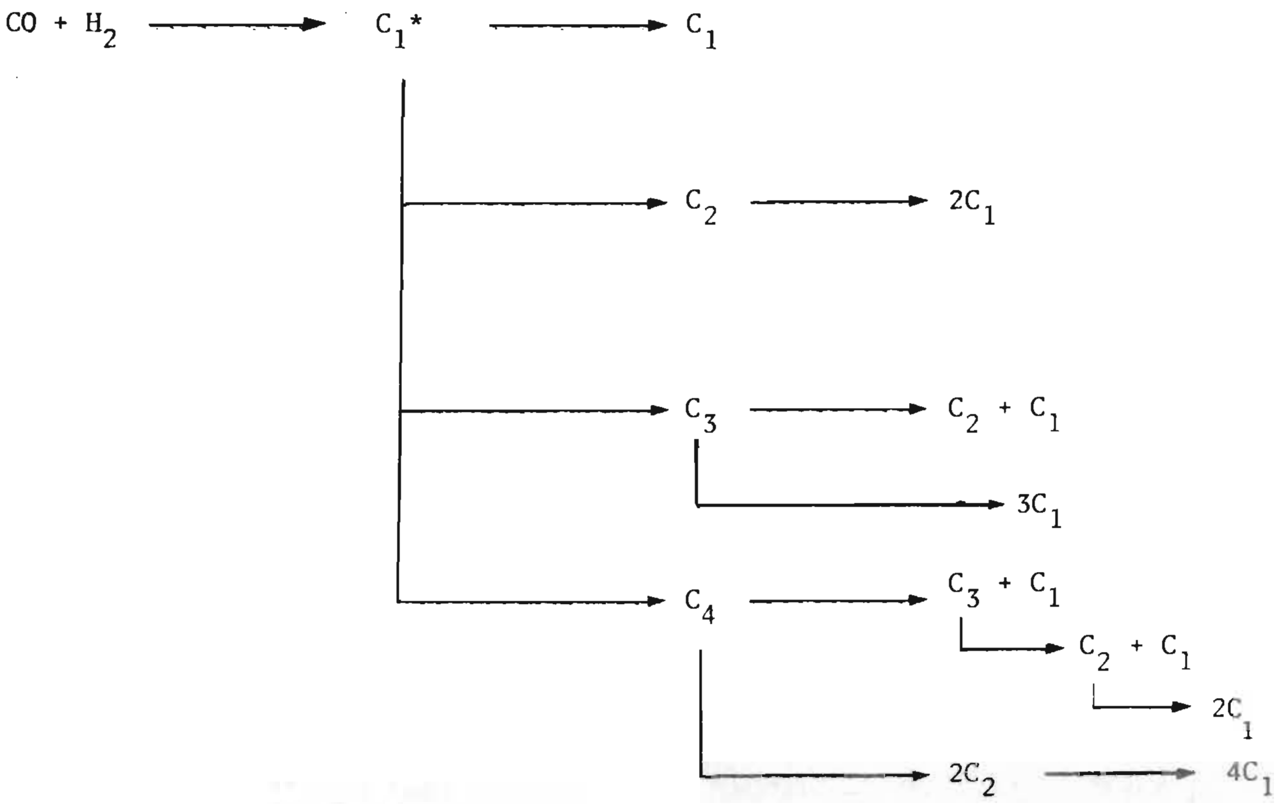
As has been mentioned earlier, ruthenium is one of the most active catalytic materials for hydrogenolysis of alkanes. With operations at low conversions or at high total reactor pressure, the surface coverage of the carbon monoxide is probably sufficiently high to inhibit the hydrogenolysis reaction. As the surface coverage of carbon monoxide is decreased (by virtue of higher conversion) this inhibition becomes less efficient. At some critical value, which is a function of both the reaction temperature and the particular hydrocarbon being considered, hydrogenolysis commences.

The hydrogenolysis of some of the lighter alkanes over ruthenium has been the subject of a number of studies (Sinfelt, 1969; Kempling & Anderson, 1970; Kempling, 1971) which have indicated that the reactivity of the alkane increases with increasing chain length, with ethane exhibiting by far the lowest activity (Kempling, 1971). In general, the hydrogenolysis of alkanes results in the production of a mixture of smaller paraffinic molecules (Kempling, 1971); the actual product distribution obtained depending on the reaction conditions, higher extents of conversion favouring smaller molecules (methane, ethane, etc.). When one considers a schematic of the synthesis - hydrogenolysis reactions which can occur up to a carbon number fraction of C_4, the inter-relationship between the various carbon number fractions becomes clearer. Such a schematic is presented in Table 6.1.

It will be seen from Table 6.1. that while during synthesis a mixture of hydrocarbon products can result, the onset of hydrogenolysis can complicate interpretation of rate data enormously because of the equally complex mixture of products which can result from the degradation. Thus, the C_4 carbon number fraction can undergo one-step hydrogenolysis to produce either one molecule of each of the C_3 and C_1 carbon number fractions or it can produce two molecules of C_2 carbon number fractions, the relative amounts being dependant upon the relative strengths of the carbon-carbon bonds within the molecule. The C_2 and C_3 carbon number fractions thus formed can either remain as such or undergo further hydrogenolysis; the

TABLE 6.1.

SCHEMATIC OF SYNTHESIS AND HYDROGENOLYSIS REACTIONS.



outcome of such a choice obviously being dependant upon the relative activities of these carbon number fractions and upon the reaction conditions. Ultimately, of course, the final product of hydrogenolysis is methane, but before this is reached a complex mixture of reaction products can result. In view of the fact that ethane is the least active of the alkanes (Kempling, 1971) it could well be expected that progressive hydrogenolysis would result in mixtures favouring ethane, until such a stage was reached that even the ethane would undergo hydrogenolysis to methane.

Bearing the above comments in mind, the relations depicted in Figures 6.2. (a) and (b) can now be considered. Of the relations depicted, perhaps the most interesting is that of the C_2 carbon number fraction. Within the range of temperatures depicted, the relative rate of C_2 formation appears to show a maximum for each reaction temperature. This phenomenon can now be considered in conjunction with the fact that the rates of production for all of the higher hydrocarbons show plateaux with a decrease in relative rates below some critical value of $P_{H_2} + CO$.

If one assumed that hydrogenolysis will occur below some critical value of $P_{H_2} + CO$ (the value being dependant upon both the alkane and the reaction conditions), the relations depicted become qualitatively explicable in terms of synthesis - hydrogenolysis interaction.

Dalla Betta, Piken and Shelef (1974) reported that hydrogenolysis of higher hydrocarbons did not have a significant role in the production of methane in their investigation into methanation of CO using a recirculation reactor and ruthenium catalyst. This was demonstrated by the installation of a liquid nitrogen cold trap in the circulation system which removed some 92% of the higher hydrocarbons formed during reaction. The rate of methane formation was reported to be unchanged whether or not the trap was installed.

However, with differential operation of their reactor, the molar concentration of hydrocarbon products above methane was of the order of 0,2% and it can be expected that the high surface coverage of CO during the reaction conditions used by them would successfully inhibit hydrogenolysis.

Consider Figure 6.3. which depicts the relative rate of formation of the C_5 - C_{12} carbon number fraction relative to changes in $P_{H_2 + CO}$ for operation with reaction temperatures of approximately 525, 550 and 575 K. For operation at a given temperature, the relative rate of formation of the C_5 - C_{12} fraction remains approximately constant for the higher values of $P_{H_2 + CO}$, the actual value of the relative rate being dependant upon the reaction temperature - the higher the temperature, the lower the relative rate. Further, this Figure shows that (for operation at 525 and 550 K respectively), progressively decreasing $P_{H_2 + CO}$ has no effect upon the

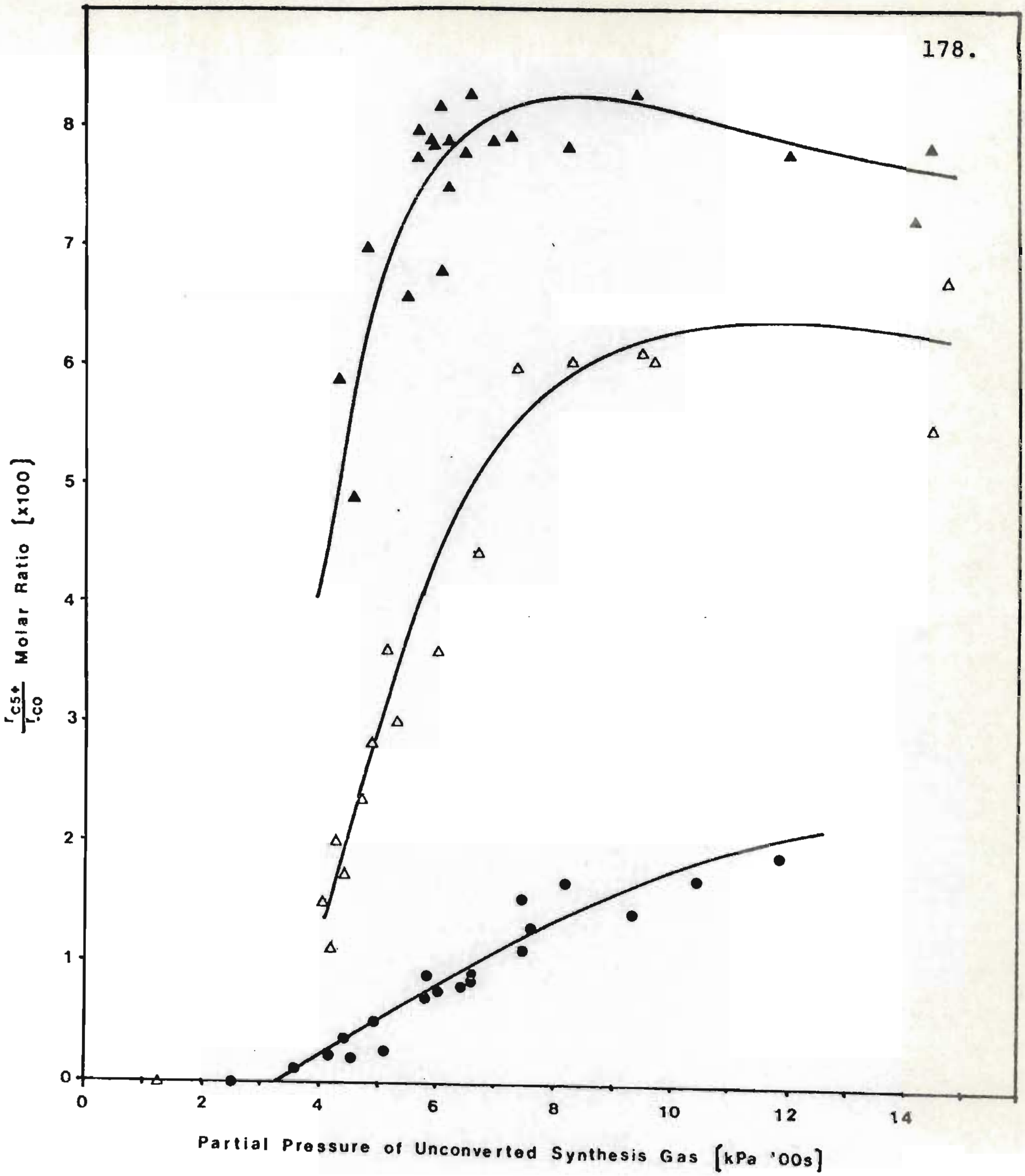


FIGURE 6.3. - RATE OF SYNTHESIS OF C_5 TO C_{12} FRACTION RELATIVE TO RATE OF CO REMOVAL

● ~ 575K; △ ~ 550K; ▲ ~ 525K

relative rate of formation of $C_5 - C_{12}$ until some critical value for $P_{H_2 + CO}$ is reached. Upon reaching this value, further decrease in $P_{H_2 + CO}$ results in a decrease in the relative rate of formation of $C_5 - C_{12}$. For operation at 525 K, the critical value of $P_{H_2 + CO}$ is approximately 600 kPa, while for operation at 550 K, 750 kPa is necessary to prevent a similar decrease. Operation at 575 K would then require a higher value still to prevent a similar decrease, although no estimate can be given since within the range of values of $P_{H_2 + CO}$ considered, the constant value of relative rate was not attained.

This trend is maintained throughout all of the individual carbon number fractions: higher values of $P_{H_2 + CO}$ being required for the higher reaction temperatures in order to prevent a decrease in the relative rate of formation of the carbon number under consideration. Further, the higher the carbon number, the higher the value of $P_{H_2 + CO}$ at which this decline commences. Thus, for operation at 550 K, the critical values of $P_{H_2 + CO}$ for $C_5 - C_{12}$, C_3 and C_2 are approximately 750, 650 and 450 kPa respectively. If this decline below a given value of $P_{H_2 + CO}$ is attributed to the onset of hydrogenolysis, this trend is then in qualitative agreement with the published results on the relative reactivity of alkane to hydrogenolysis (Kempling, 1971; Kempling & Anderson, 1970; 1972; Sinfelt, 1969).

The data for the relative rate of production of the C_2 carbon number fraction is not sufficiently complete to facilitate construction of the whole curve for operation at 525 and 550 K, but the symmetry of the overall system does allow certain inferrences to be made. The maximum occurring for operation at 575 K (at approximately $P_{H_2} + CO = 950$ kPa) can be expected to have its counterpart at some lower value for 550 K and yet lower still for 525 K. This could be interpreted as indicating the hydrogenolysis of the C_2 carbon number fraction is occurring at progressively lower values of $P_{H_2} + CO$ for lower reaction temperatures. The low reactivity of ethane for hydrogenolysis would thus result in ethane contributing relatively more to the product as the higher hydrocarbons succumb to hydrogenolysis.

The product distribution obtained during the reaction in the present investigation can thus be regarded as the net result of synthesis (at high values of $P_{H_2} + CO$) and hydrogenolysis (at low values of $P_{H_2} + CO$).

Insofar as the C_5 - C_{12} carbon number fractions were considered to be the products of value, some consideration should be given to the conditions likely to maximise their rate of production. Figure 6.3. shows relations for the overal production rates of the C_5 to C_{12} carbon number fraction (similar to those presented for individual carbon number fractions in Figure 6.2.) for reaction temperatures of 525, 550 and 575 K. It can be seen from this figure that for maximisation of the relative rates of C_5 - C_{12}, operation at a low reaction temperature is almost mandatory. While there is a significant decrease in the relative rate of C_5 - C_{12} production at 550 K compared with 525, a further increase in temperature to 575 K is disastrous as far as C_5 - C_{12} overall production is concerned.

This would thus indicate that if operation at elevated temperature were to be required, either very low conversions or very much increased reactor total pressures would be required.

A different approach to the expression of rates in relative terms is the expression of the rates relative to the production of the major single carbon number fraction; methane. This approach was utilised in the regression of experimental data (as is outlined later) and is useful in presenting a different perspective on the results obtained.

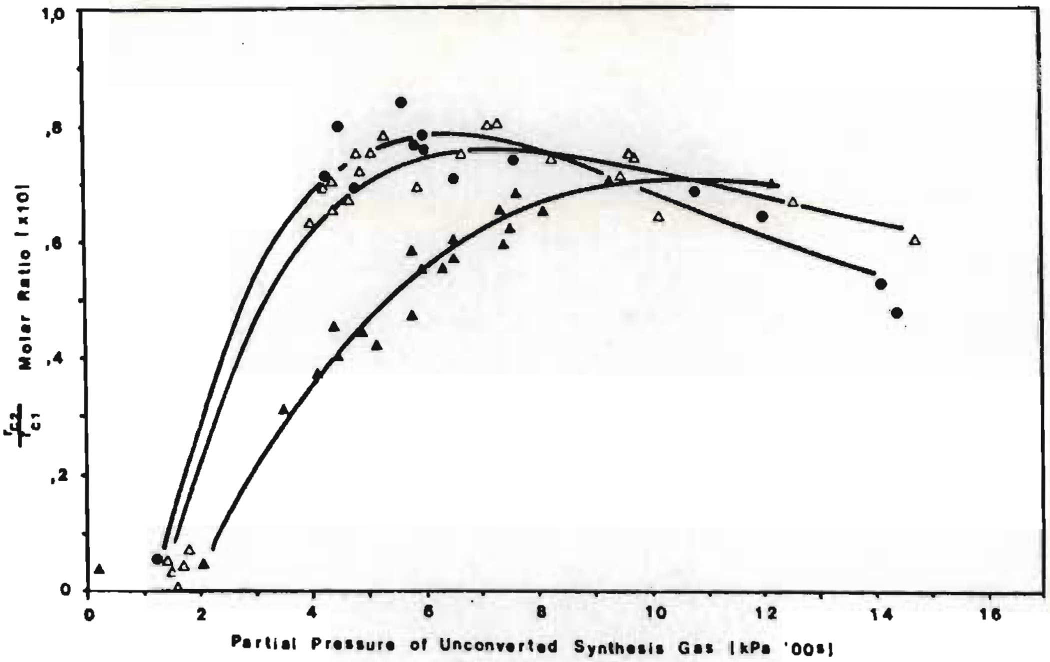
6.3. SYNTHESIS RATES RELATIVE TO RATE OF METHANATION.

Following the method employed in the previous section, the relative rates of individual carbon number fractions were expressed in relation to $P_{H_2 + CO}$ as shown in Figures 6.4. (a) to (f) which present the rates of production of the individual carbon number fractions C_2 to C_7 relative to the rate of methane production for reaction temperatures of 525, 550 and 575 K.

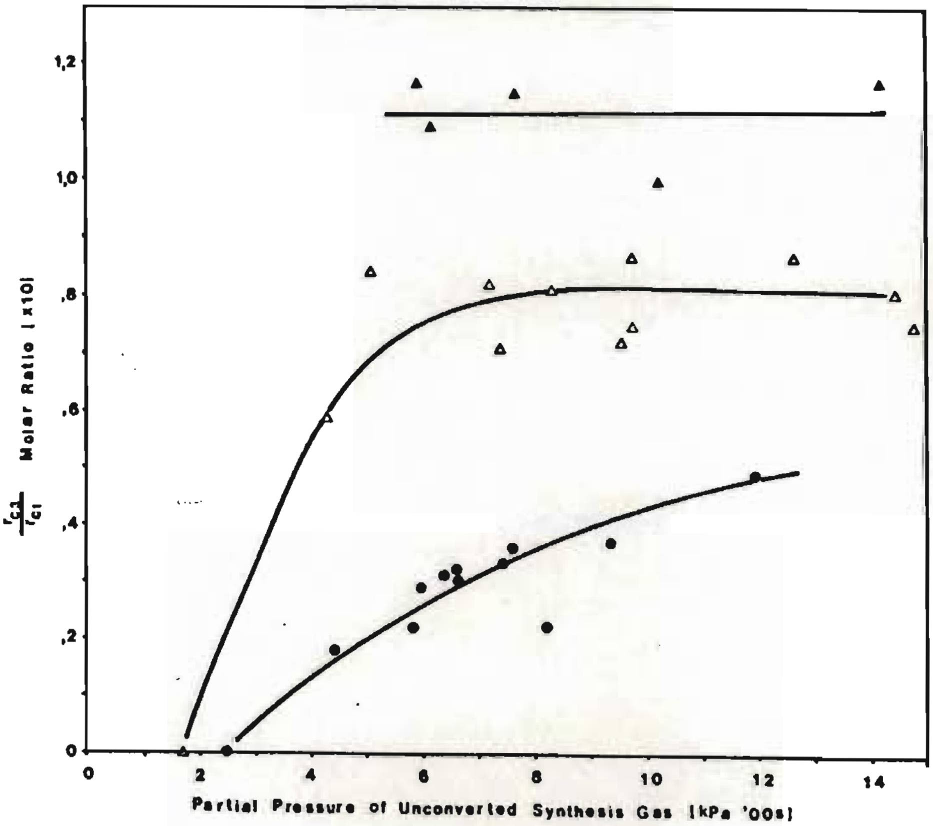
FIGURE 6.4. (overleaf) - RATE OF SYNTHESIS RELATIVE TO RATE OF METHANATION

(a) C_2
(b) C_3
(c) C_4
(d) C_5
(e) C_6
(f) C_7

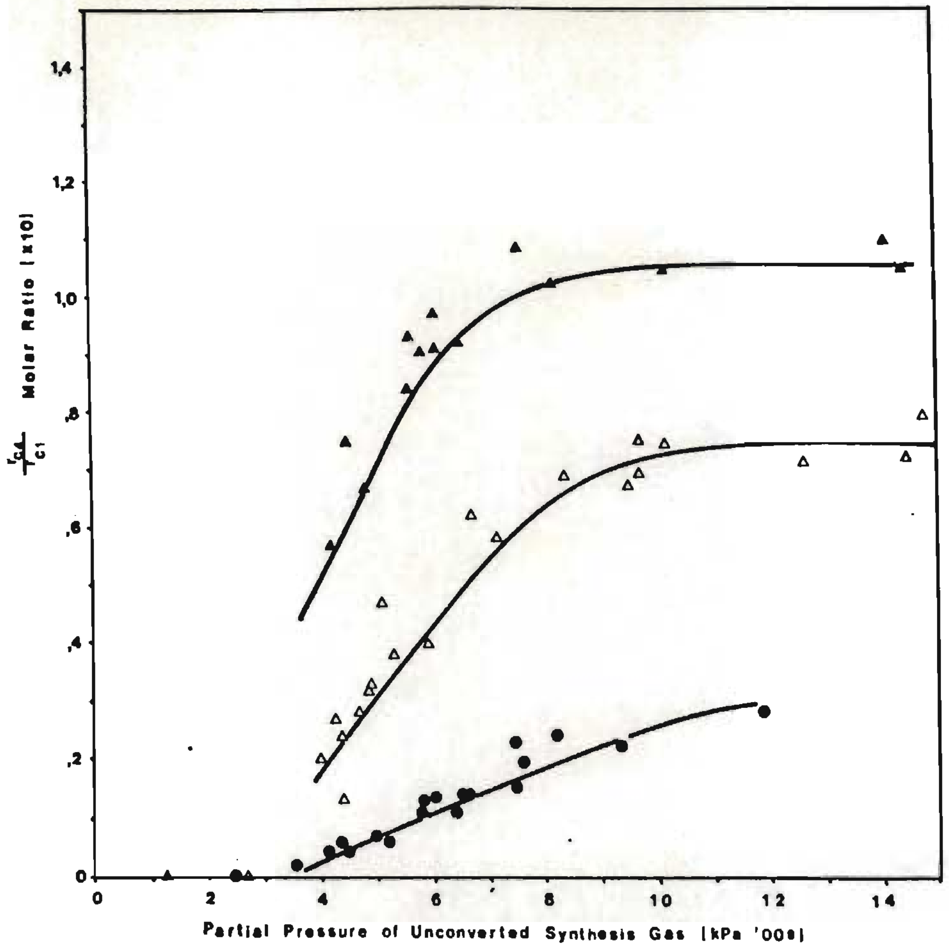
●~575K;△~550K;▲~525K


1,0
,8
,6
,4
,2
0
$\frac{r_{C2}}{r_{C1}}$ Molar Ratio (x10)
0
2
4
6
8
10
12
14
16
Partial Pressure of Unconverted Synthesis Gas (kPa '00s)

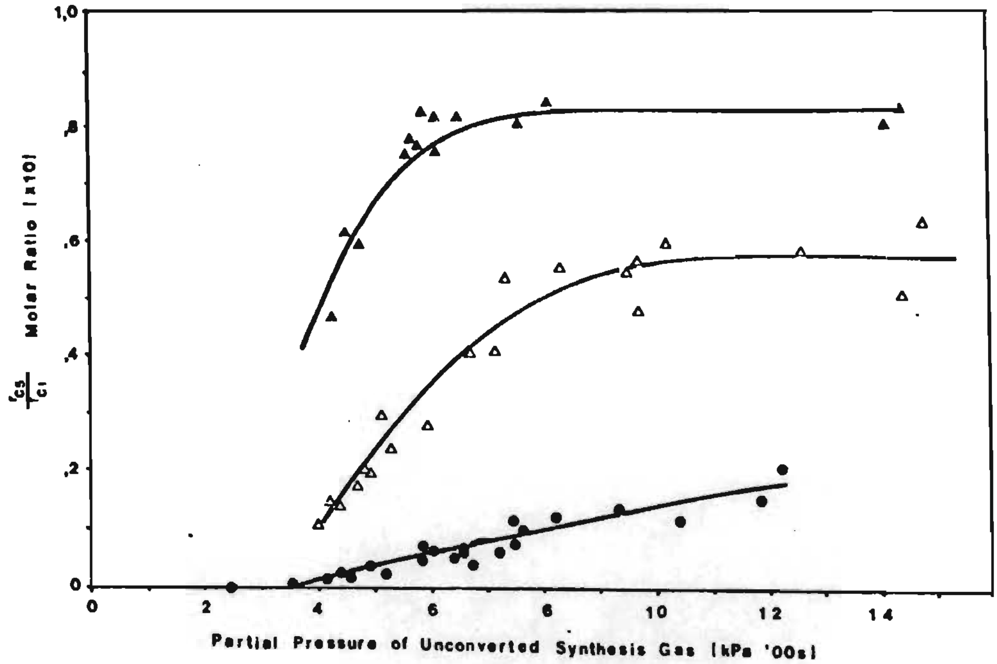
(a)


1,2
1,0
,8
,6
,4
,2
0
$\frac{r_{C3}}{r_{C1}}$ Molar Ratio (x10)
0
2
4
6
8
10
12
14
Partial Pressure of Unconverted Synthesis Gas (kPa '00s)

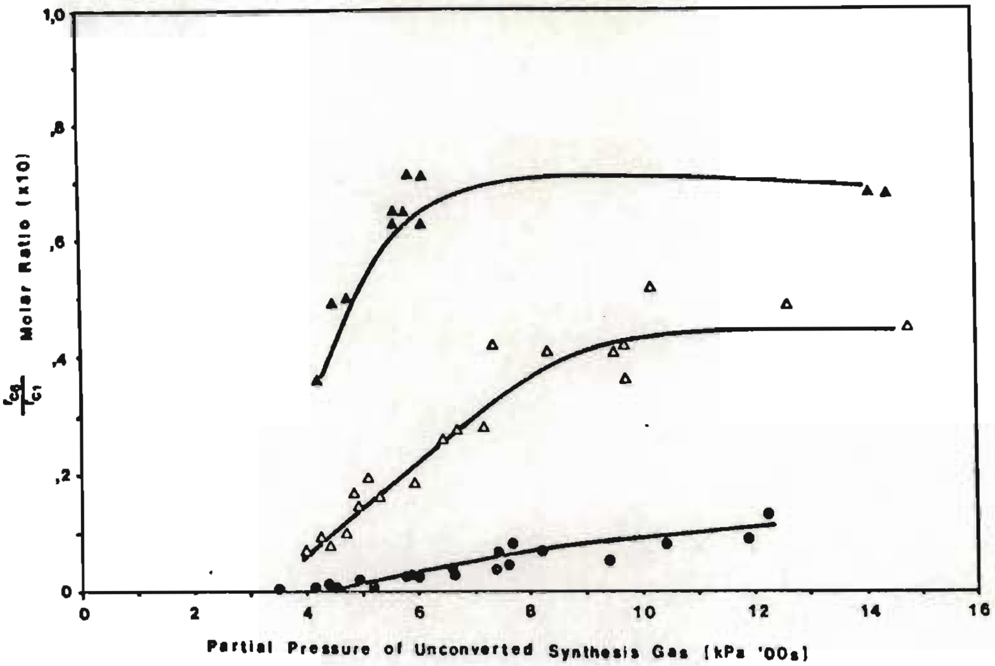
(b)


1,4
1,2
1,0
,8
,6
,4
,2
0
$\frac{r_{C4}}{r_{C1}}$ Molar Ratio (x10)
0
2
4
6
8
10
12
14
Partial Pressure of Unconverted Synthesis Gas (kPa '00s)

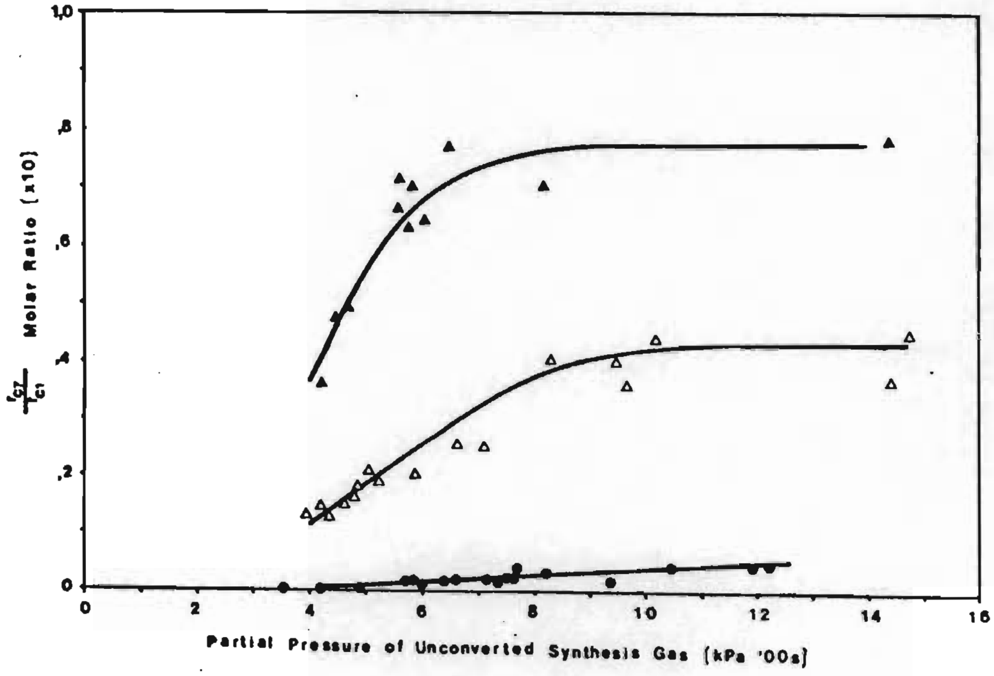
(c)


1,0
,8
,6
,4
,2
0
$\frac{r_{C5}}{r_{C1}}$ Molar Ratio (x10)
0
2
4
6
8
10
12
14
Partial Pressure of Unconverted Synthesis Gas (kPa '00s)

(d)


1,0
,8
,6
,4
,2
0
$\frac{r_{C6}}{r_{C1}}$ Molar Ratio (x10)
0
2
4
6
8
10
12
14
16
Partial Pressure of Unconverted Synthesis Gas (kPa '00s)

(e)


1,0
,8
,6
,4
,2
0
$\frac{r_{C7}}{r_{C1}}$ Molar Ratio (x10)
0
2
4
6
8
10
12
14
16
Partial Pressure of Unconverted Synthesis Gas (kPa '00s)

(f)

Figures 6.4. (g) to (j) depict the relations obtained for the cumulative carbon number fractions C_2+ to C_5+ for operation over the same range of reaction temperatures.

There is an apparent symmetry to the relative rates for each of the individual carbon number fractions which simplifies discussion of the data. Consider the relative rates of the C_2 carbon number fraction depicted in Figure 6.4. (a). The rate of production of the C_2 carbon number fraction shows an increase with reduction in $P_{H_2 + CO}$ until a certain critical value is reached, upon which a decrease in relative rate occurs.

The maximum rate of C_2 production relative to methane formation is seen to be higher the lower is the reaction temperature. However, by operating at a value of $P_{H_2 + CO}$ higher than that below which this increase occurs, the higher the temperature, the higher is the relative rate of C_2 production.

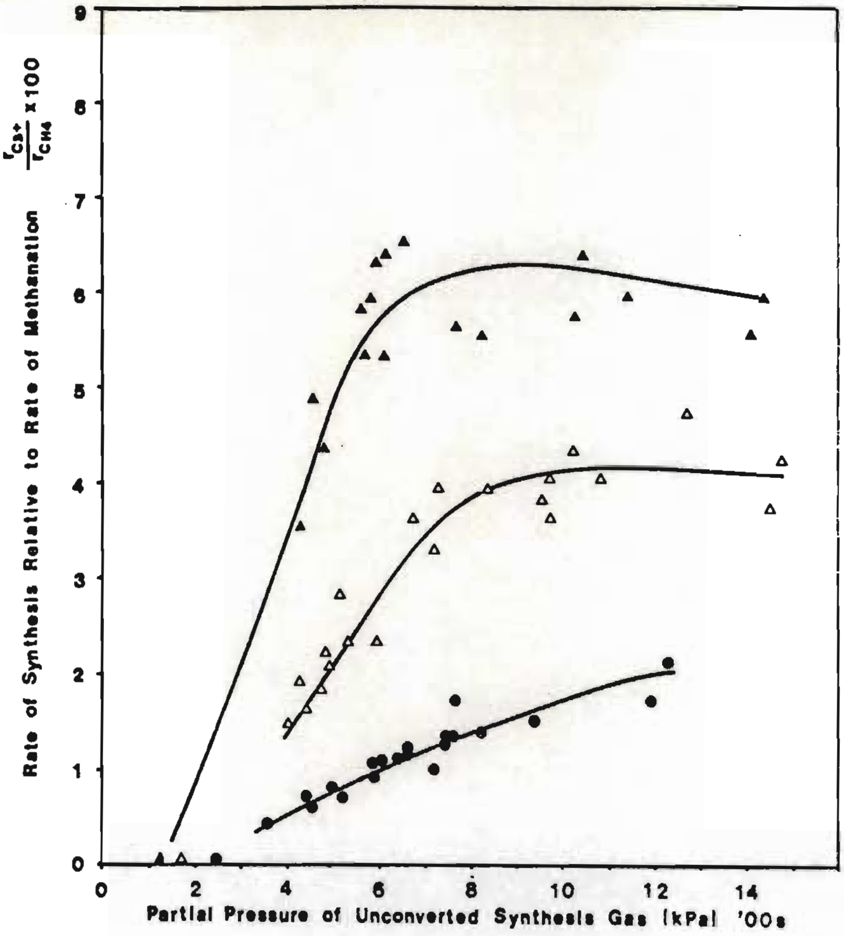
This effect is not obvious for the other carbon number fractions, although extensions of the $P_{H_2 + CO}$ range could well produce such a phenomenon.

As was seen with the previous approach to relative rates, the rates relative to methanation show a decrease with increasing temperature for a given value of $P_{H_2 + CO}$. Again, decreasing the value of $P_{H_2 + CO}$ to below some critical value results in a decrease in the relative rate of production of any individual carbon number fraction.

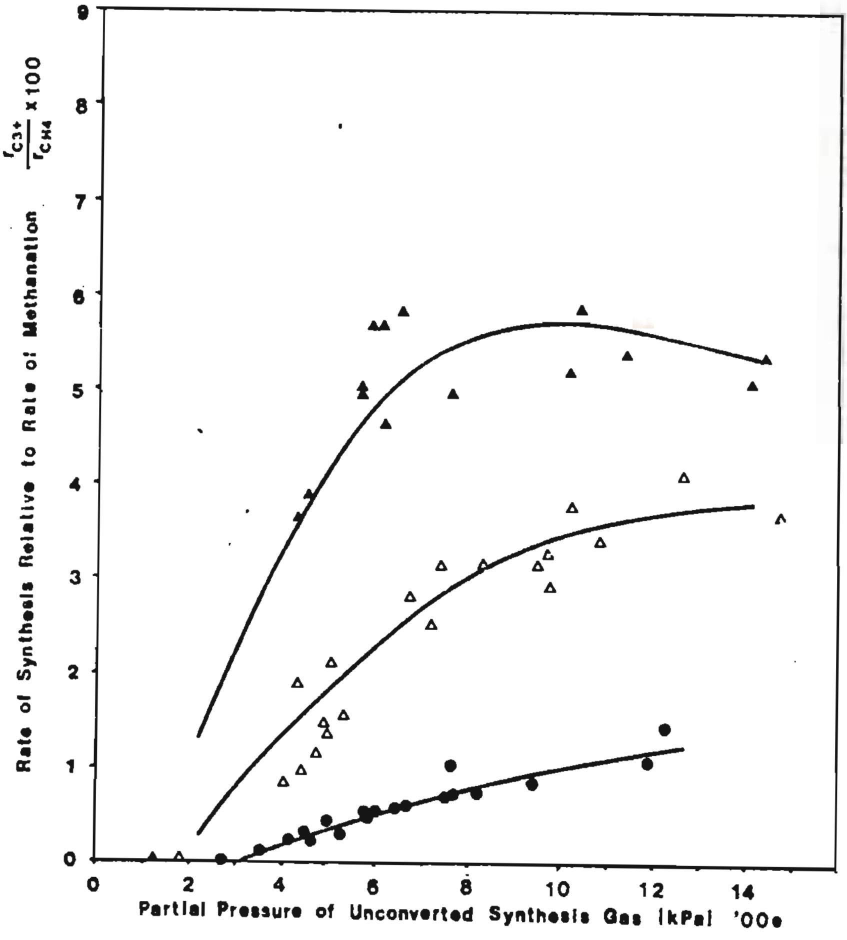
FIGURE 6.4. (overleaf) - RATE OF SYNTHESIS RELATIVE TO RATE OF METHANATION

(g) $C_{2}+$
(h) $C_{3}+$
(i) $C_{4}+$
(j) $C_{5}+$

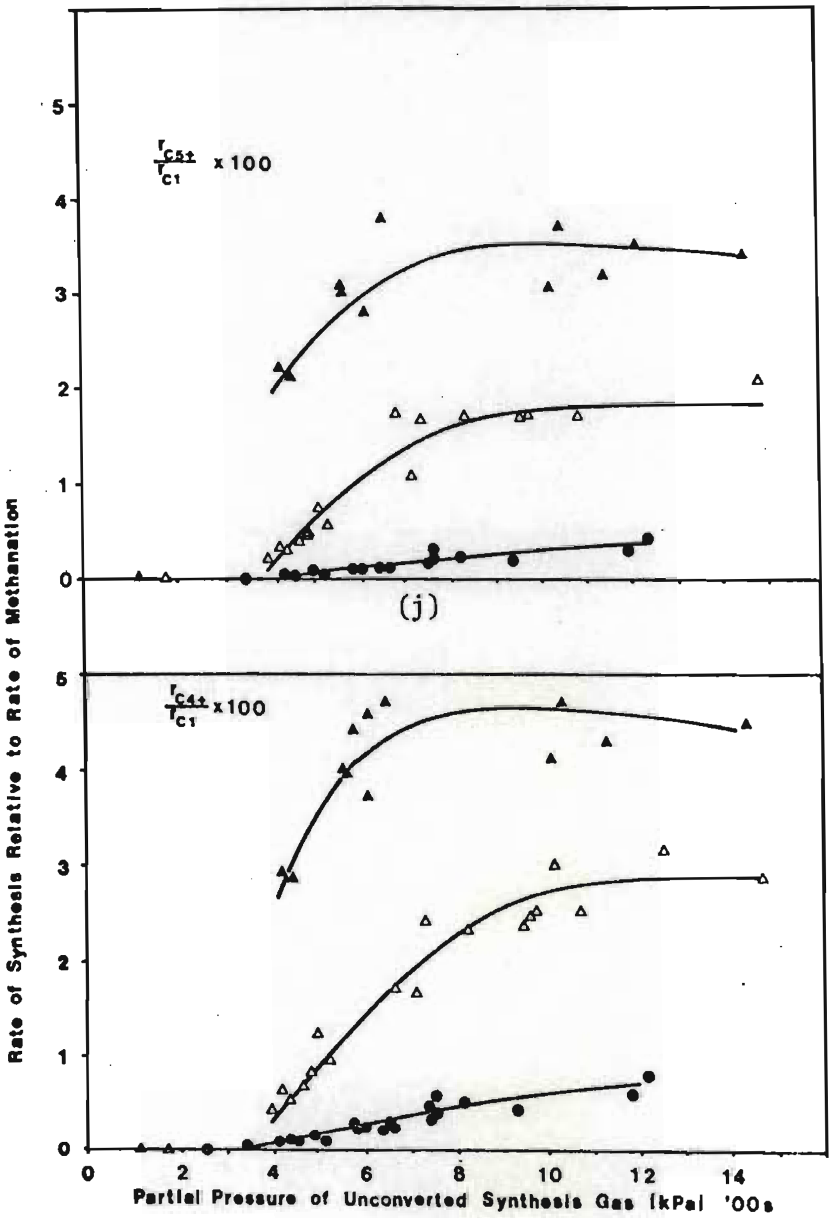
● ~575K; △ ~ 550K; ▲ ~ 525K


Rate of Synthesis Relative to Rate of Methanation $\frac{r_{C3+}}{r_{CH4}}$ x 100
0
1
2
3
4
5
6
7
8
9
0
2
4
6
8
10
12
14
Partial Pressure of Unconverted Synthesis Gas (kPa) '00s

(g)


Rate of Synthesis Relative to Rate of Methanation $\frac{r_{C3+}}{r_{CH4}}$ x 100
0
1
2
3
4
5
6
7
8
9
0
2
4
6
8
10
12
14
Partial Pressure of Unconverted Synthesis Gas (kPa) '00s

(h)


$\frac{r_{C5+}}{r_{C1}}$ x 100
(j)
$\frac{r_{C4+}}{r_{C1}}$ x 100
Rate of Synthesis Relative to Rate of Methanation
0
1
2
3
4
5
0
2
4
6
8
10
12
14
Partial Pressure of Unconverted Synthesis Gas (kPa) '00s

(i)

CHAPTER 7.

ABSOLUTE RATES.

7.1. INTRODUCTION.

The ultimate objective in any study of chemical kinetics is the representation of the measured data by some form of mathematical model which will predict the rate of reaction of the system under consideration over some range of operating conditions such as temperature, pressure, conversion, etc.

As has been emphasised, the rate of reaction in heterogeneous catalytic systems has, until fairly recently, been expressed in terms of rates of production (or removal) per unit mass of catalyst. This practice has now, to a very great extent, been replaced by the expression of rates in the more fundamental form of turnover numbers. In this chapter the rates of synthesis of each of the individual carbon number fractions and the rate of removal of carbon monoxide will be considered in terms of both turnover numbers and rates per unit mass of catalyst. The data will be fitted to a simple power law model and also to a rate equation based upon a previously-proposed mechanistic model.

In view of the fact that methane was always the major individual carbon number fraction in the product, the following sections will deal first with methane formation, then with carbon monoxide removal and finally with the rate of synthesis of each of the higher hydrocarbons.

7.2. METHANATION.

The majority of the literature relating to the development of rate equations for the hydrogenation of carbon monoxide is concerned specifically with methanation (Vannice, 1975; 1975 [a]; Dalla Betta, Piken & Shelef, 1974; 1975), the literature relating to the synthesis reaction being relatively restricted. In recent years, several reports have appeared in the literature relating to methanation and synthesis, although empirical correlations remain, for the most part, confined to methanation.

As was outlined in Chapter 2, the general form of the empirical fits obtained by various investigators for carbon monoxide hydrogenation are similar, with the major differences being found in the absolute values of the regressed exponents for the partial pressure terms of CO and H_2.

The experimental data for the methanation reaction was fitted to a simple power law equation of the form

$$\text{rate}_1 = A_1 e^{-E/RT} P_{CO}^{a_1} P_{H_2}^{b_1}$$

using a multi-linear regression technique on the equation after linearisation by the usual technique of taking logarithms of both sides of the equation.

Thus,

$$\ln \text{rate}_1 = \ln A_1 - E_1/RT + a_1 \ln P_{CO} + b_1 \ln P_{H_2}$$

During the preliminary regressions, terms for the two major reaction products of methane and water were included in the power rate law. However, since inclusion of these terms did not noticeably improve the fit of the data, they were removed in the subsequent regressions. This lack of inhibition by the major reaction products during carbon monoxide hydrogenation is in agreement with the results reported by Vlasenko, Yuzefovich and Rusov (1965)) and by Herwijnen, van Doesburg and de Jong (1973).

This regression technique was adopted for rates of methanation expressed in terms of mass of ruthenium (r_{C1}) and in terms of turnover numbers (N_{C1}). The regressed values obtained are summarised in Table 7.1. along with the only other complete correlation in the literature: that of Vannice (1975 [a]). Also included in this table is the partial correlation of Dalla Betta, Piken and Shelef (1974).

It can be seen from this table, that either convention for the expression of rates results in very similar regressed kinetic parameters. The agreement between the present results and those of Vannice or Dalla Betta et alii however, are not so close. While the values obtained for the reaction order with respect to carbon monoxide and hydrogen are of the same sign as the

TABLE 7.1.

REGRESSED VALUES FOR METHANATION.

PARAMETER	PRESENT INVESTIGATION r_{CH_4} (1)	PRESENT INVESTIGATION N_{CH_4} (1)	VANNICE (2)	DALLA BETTA (3)
ln A	24,91	27,56	20,16	-
E_1 (kcal/mol)	33,3 ± 1,2	34,3 ± 1,8	24,2 ± 1,2	24,0
a_1	-0,46	-0,44	-0,6	-1,14 to -1,43
b_1	0,71	0,71	1,6	1,7 to 2,04
Multiple Correlation Coefficient	0,983	0,986	-	-

(1) 0,5% Ru/Al_2O_3 225 - 300°C

(2) 5% Ru/Al_2O_3 240 - 280°C

(3) 1,5% Ru/Al_2O_3 240 - 300°C

other two investigations, the magnitude (especially of the hydrogen exponent) differs considerably. Further, the activation energy obtained for the methanation reaction (at 34,3 kcal/mol) is appreciably greater than either of the other reported values (24,2 and 24 kcal/mol). Since both of the other investigations were conducted under conditions unfavourable for the formation of higher hydrocarbons, it seems likely that methanation in the presence of higher hydrocarbons proceeds via a difference mechanism. With activation energies for the hydrogenolysis of some of the smaller alkanes (ethane to pentane) over ruthenium being reported in the literature as being between 32 and 48,2 kcal/mol (Kempling, 1971), it is possible that the higher activation energy obtained here is the result of a combination of methanation *per se* and methane formation via hydrogenolysis.

Arrhenius plots for the two forms of the methanation regression using the regressed values for the partial pressure exponents are presented in Figures 7.1 (a) and (b). While there is some scatter of the data, the fit is generally acceptable. Comparisons of the experimental values for methanation and the predicted values (using both regressions) are shown in Figures 7.2. (a) and (b). Again, in spite of the data scatter, agreement between the experimental and predicted values is fairly good.

Vannice (1975 [a]; 1977 [a]) has demonstrated that an activity compensation effect (Boudart, 1968) exists for the methanation reaction over Group V111 supported catalysts. The empirical correlation obtained by Vannice is reproduced in Figure 7.3., upon which is superimposed the values obtained in the present investigation for the ruthenium catalysed methanation reaction. It is gratifying to note that although the value of the activation energy for methanation found in the present study is

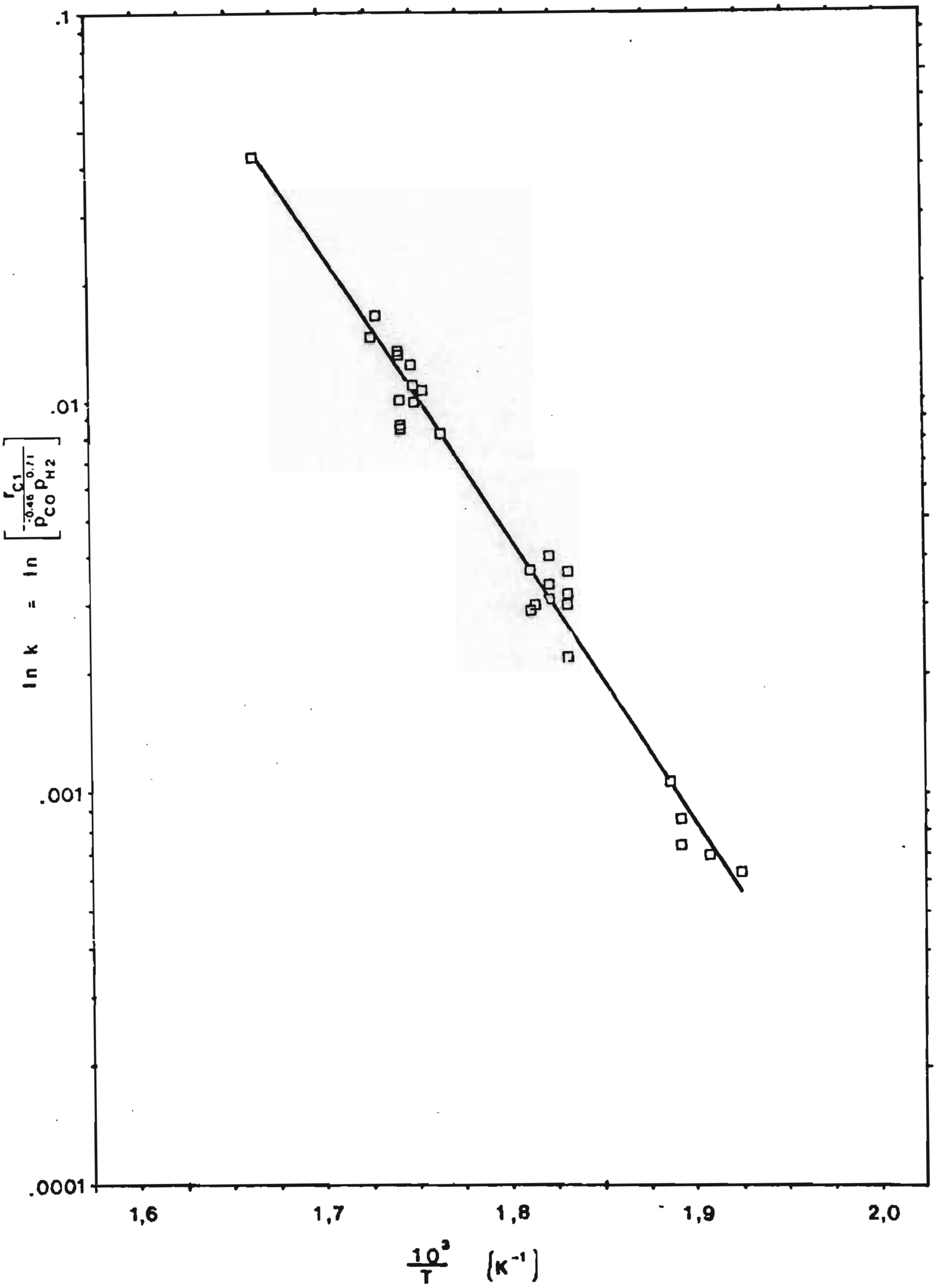


FIGURE 7.1.(a) - ARRHENIUS PLOT FOR RATE OF METHANATION BASED ON RATES/UNIT MASS OF Ru.

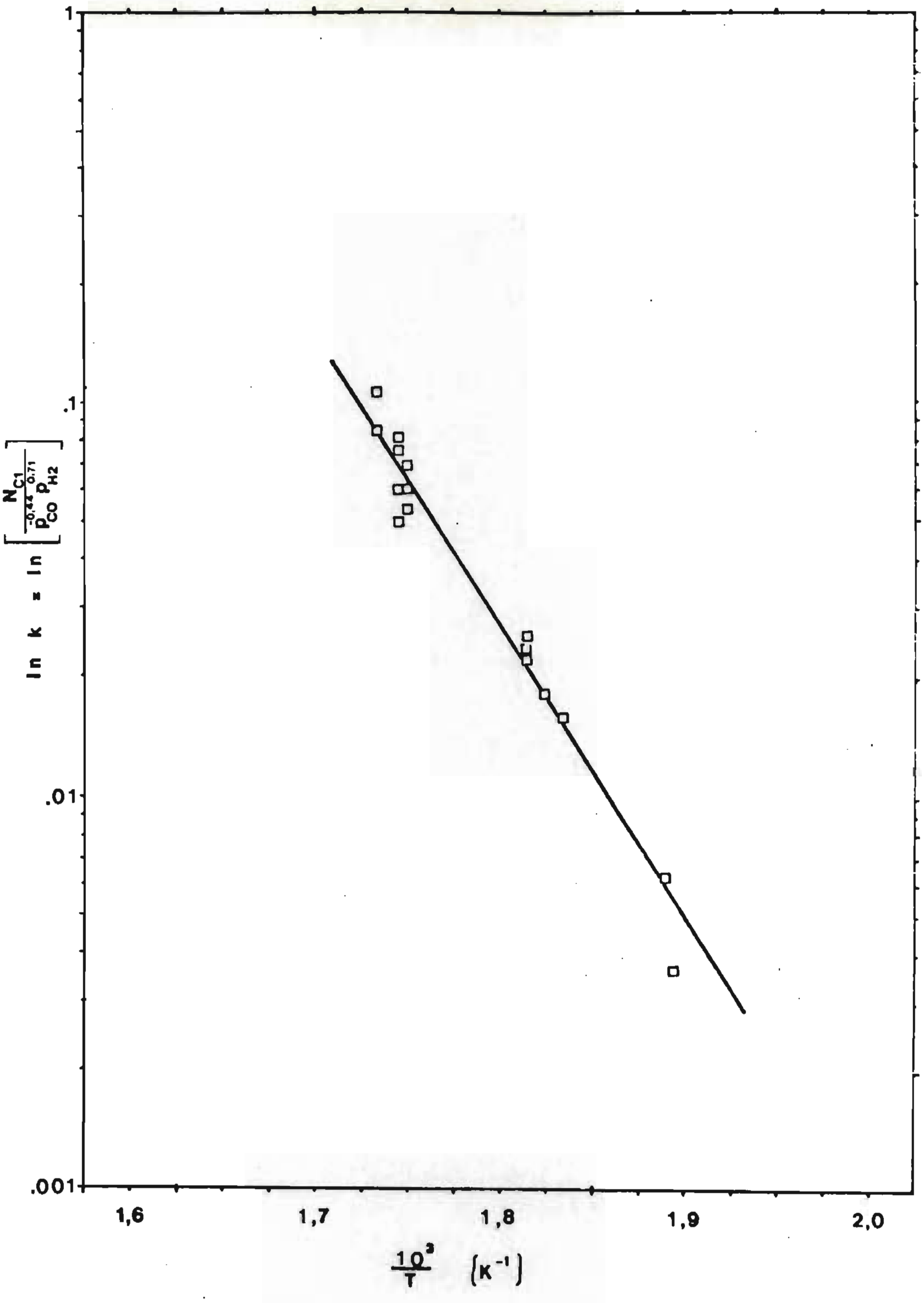


FIGURE 7.1.(b) - ARRHENIUS PLOT FOR RATE OF METHANATION BASED ON TURNOVER NUMBERS.

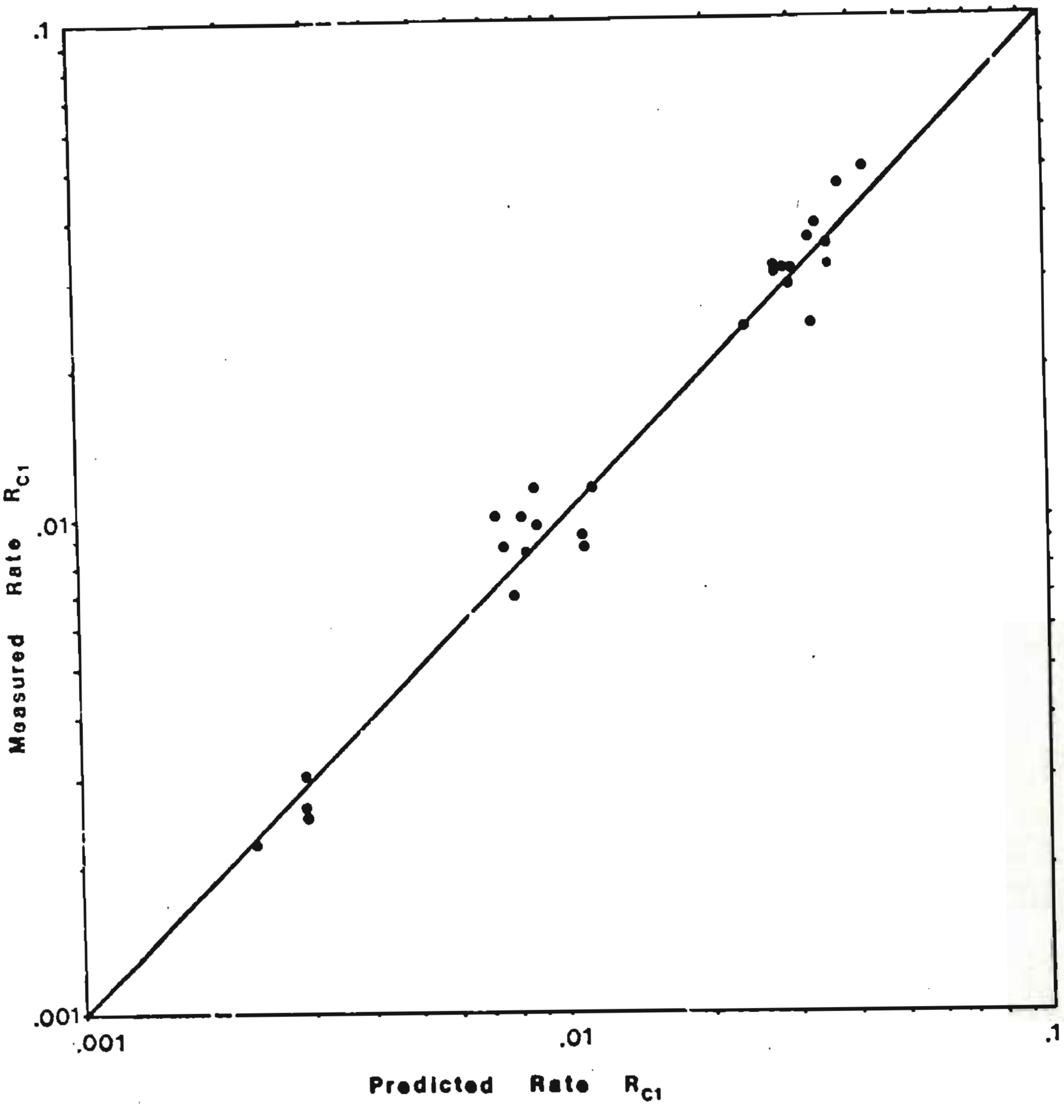


FIGURE 7.2.(a) - COMPARISON OF MEASURED AND PREDICTED METHANATION RATES BASED ON RATES/UNIT MASS OF Ru.

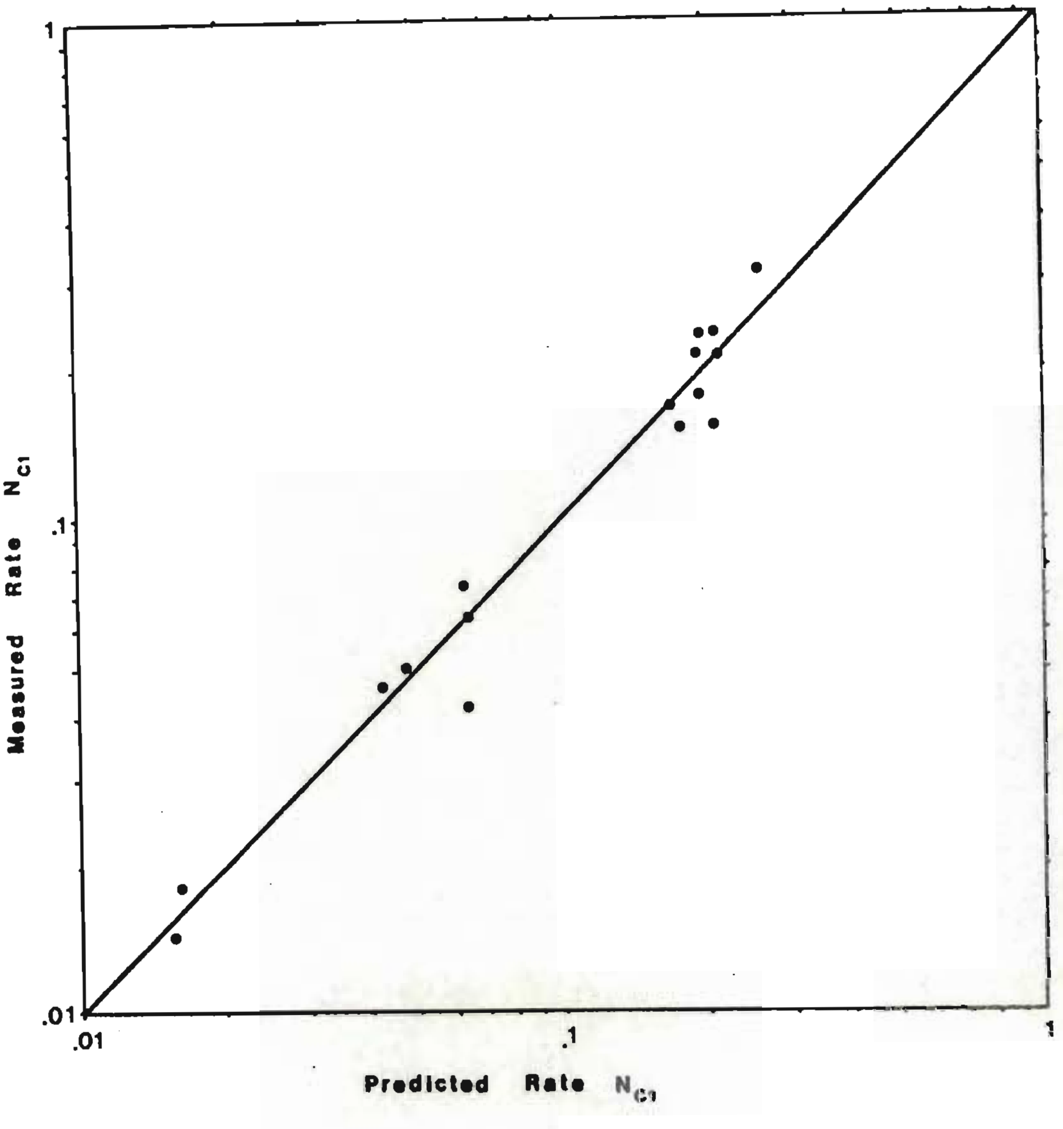


FIGURE 7.2.(b) - COMPARISON OF MEASURED AND PREDICTED METHANATION RATES BASED ON TURNOVER NUMBERS.

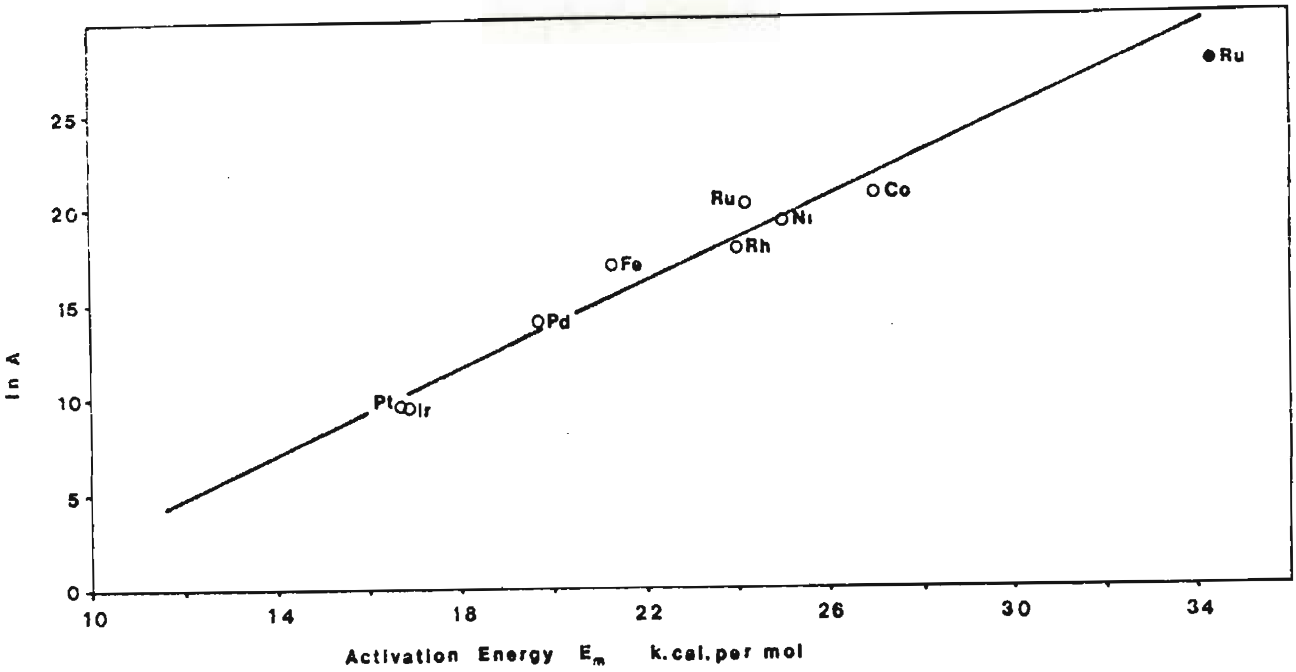


FIGURE 7.3. - ACTIVITY COMPENSATION EFFECT FOR METHANATION (VANNICE, 1975 [a]).

o VANNICE. • PRESENT WORK.

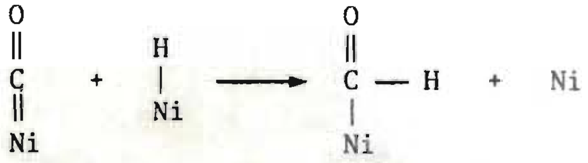
considerably higher than Vannice's, this is compensated for by a correspondingly higher pre-exponential factor. The superimposition of the present result onto Vannice's correlation does not significantly alter the correlation, thus providing additional evidence to support Vannice's conclusion that the correlation is not an experimental artifact. This conclusion was based on the fact that the slope of the correlation is $\frac{1}{R\psi}$ where ψ is the isokinetic temperature. Since the value for ψ obtained by Vannice was 436 K (which was outside the range of reaction temperatures considered) Vannice considered it unlikely that the correlation was the result of errors in kinetic measurement (Boudart, 1968).

The experimental data obtained in the present investigation were also fitted to a Hougen-Watson type model based on the reaction mechanism outlined in Appendix 2. If the assumption is made that neither hydrogen nor products are strongly adsorbed, this mechanism results in a model of the general form

$$\text{rate} = \frac{K.\ K_{CO}.P_{CO}P_{H_2}^{\ n}}{(1 + K_{CO}.P_{CO})^m}$$

The power terms n and m have numerical values which are dependant upon which step in the mechanism are considered to be rate-determining. (The derivation of some typical values is presented in Appendix 2).

This model was originally used by Huang and Richardson (1978) to correlate their data on methanation over supported nickel catalysts. For methanation over nickel at temperatures between 473 and 573 K, the rate-determining step was shown to be



$$\mathrm{O{=}C{=}Ni} + \mathrm{H{-}Ni} \longrightarrow \mathrm{Ni{-}C({=}O){-}H} + \mathrm{Ni}$$

This leads to a rate equation with n = 0,5 and m = 2; values which reportedly have good agreement with the experimental methanation data. By employing the mechanism proposed by

Vannice, values of n = 2 and m = 3 are obtained: values which did not fit the nickel methanation data as well as did the former values.

For the data obtained in this investigation, various values of n and m were used in the regressions employing this model. The non-linear regression program was developed and written by K. Smith of the Chemical Engineering Department, University of Natal.

The values of n and m which gave the best fit (as indicated by the magnitude of the residual mean square) to the experimental data for methanation over ruthenium in the present investigation were n = 0,5 and m = 2,0. The values of Q (the heat of adsorption of CO) and E_{c1} (activation energy for methanation) were 21 kcal/mol and 30,9 kcal/mol respectively.

It is generally accepted that any attempt to identify a mechanism (particularly one relating to a reaction as complex as the Fischer-Tropsch synthesis) simply by obtaining a better fit to a Hougen-Watson model is naïve (Weller, 1956). For this reason, it is important that no conclusion be drawn as to the relative merits of any of the assumed rate-determining steps for the mechanism in Appendix 2, based only on the goodness of fit for a given set of values of n and m.

One of the satisfying features of the results of this regression is the good agreement obtained between the regressed value for activation energy based on the previous power rate law and that obtained here.

A further point of interest which arises from the regressed values obtained from the Huang and Richardson model is the magnitude of Q (the heat of adsorption of carbon monoxide on ruthenium). Vannice (1977 [a]), in his correlation between methanation rates and heat of adsorption of carbon monoxide over Group V111 metals, uses a value for ruthenium of approximately 29 kcal/mol. However, the heat of adsorption of carbon monoxide on Group V111 metals in general has been shown to be a function of the extent of surface coverage, with low surface coverage (corresponding to a predominance of the weakly-bonded bridged form of CO) producing higher values for the heat of adsorption.

Working with polycrystalline nickel films, Wedler, Papp and Schroll (1974) obtained values of 30 kcal/mol for the initial heat of adsorption decreasing to as low as 4 kcal/mol as surface coverage increased. Summarising earlier work on carbon monoxide adsorption on Pd(111) surfaces, Conrad et alii (1975) reported an initial heat of adsorption of 34 kcal/mol, which value showed a continuous decrease with carbon monoxide coverages above $\theta_{CO} = 1/3$.

Ku, Gjostein and Bonzel (1977) reported an initial binding energy of carbon monoxide on a Ru (1010) surface of 31,2 kcal/mol with desorption energies decreasing from 30,1 to 24,4 kcal/mol as surface coverage of carbon monoxide increased.

Goodman et alii (1977) likewise obtained decreasing values of heats of adsorption of carbon monoxide on Ru(110), with a desorption energy of 17,5 kcal/mol being reported.

The value of approximately 21 kcal/mol for the heat of adsorption of CO found in the present investigation can thus be regarded as being in good agreement with the published figures.

7.3. CARBON MONOXIDE REMOVAL RATES.

A similar technique to that employed for the regression of the methanation data was also adopted for the processing of the data obtained for the rate of removal of carbon monoxide.

Following the procedure adopted for methanation, Arrhenius plots for the rate of removal of carbon monoxide are presented in Figures 7.4. (a) and (b), and corresponding comparisons of experimental and predicted values in Figures 7.5 (a) and (b). The data scatter is somewhat more pronounced than was the case for methanation, but agreement could be described as satisfactory.

Unfortunately, comparison with published data is even more difficult for the case of carbon monoxide removal than was the case with methanation since the only reported regressions (those of Vannice, 1975 [a] and Bond & Turnham, 1976) reported on activation energies only.

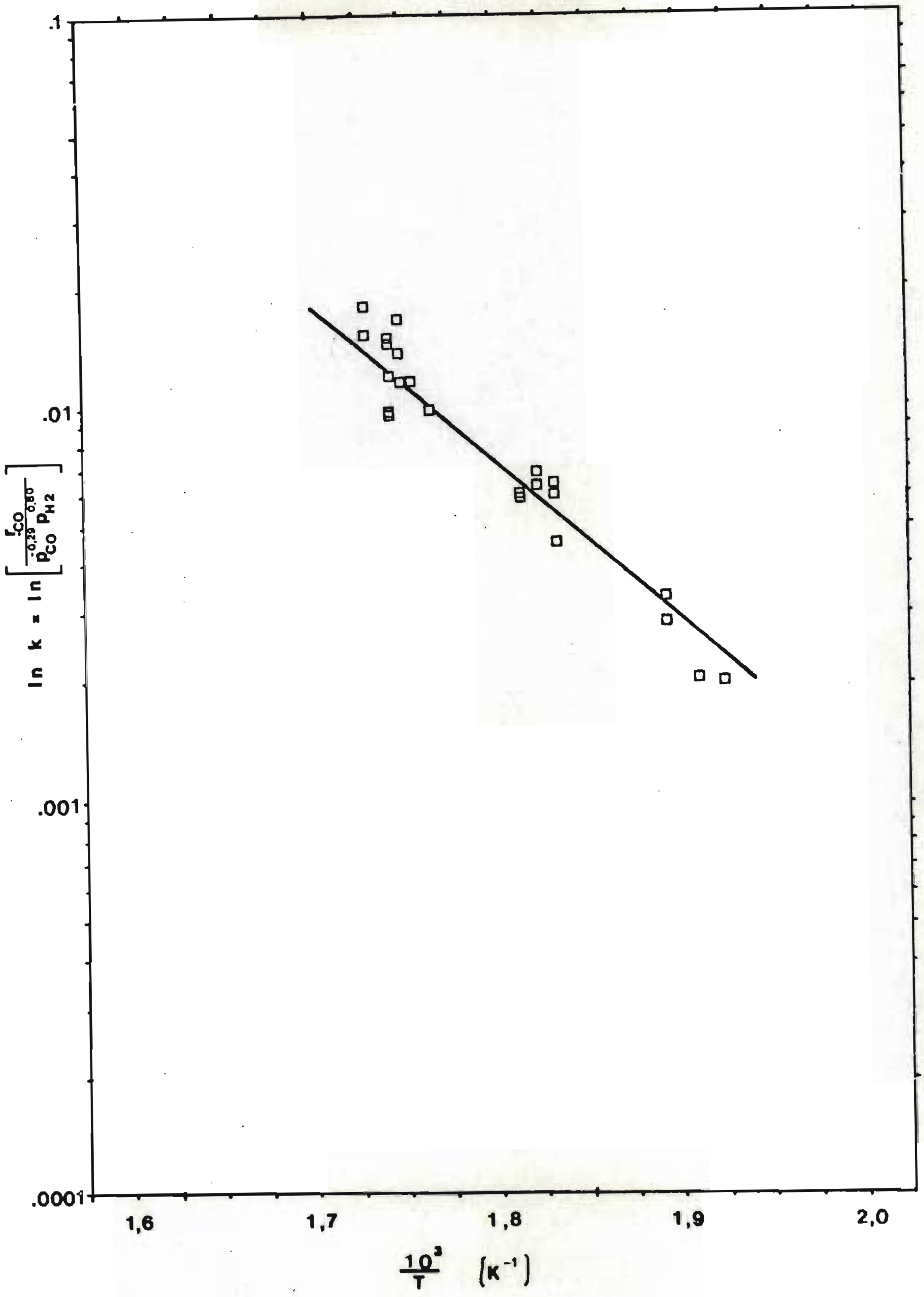


FIGURE 7.4.(a) - ARRHENIUS PLOTS FOR RATE OF CO REMOVAL BASED ON RATES/UNIT MASS OF Ru.

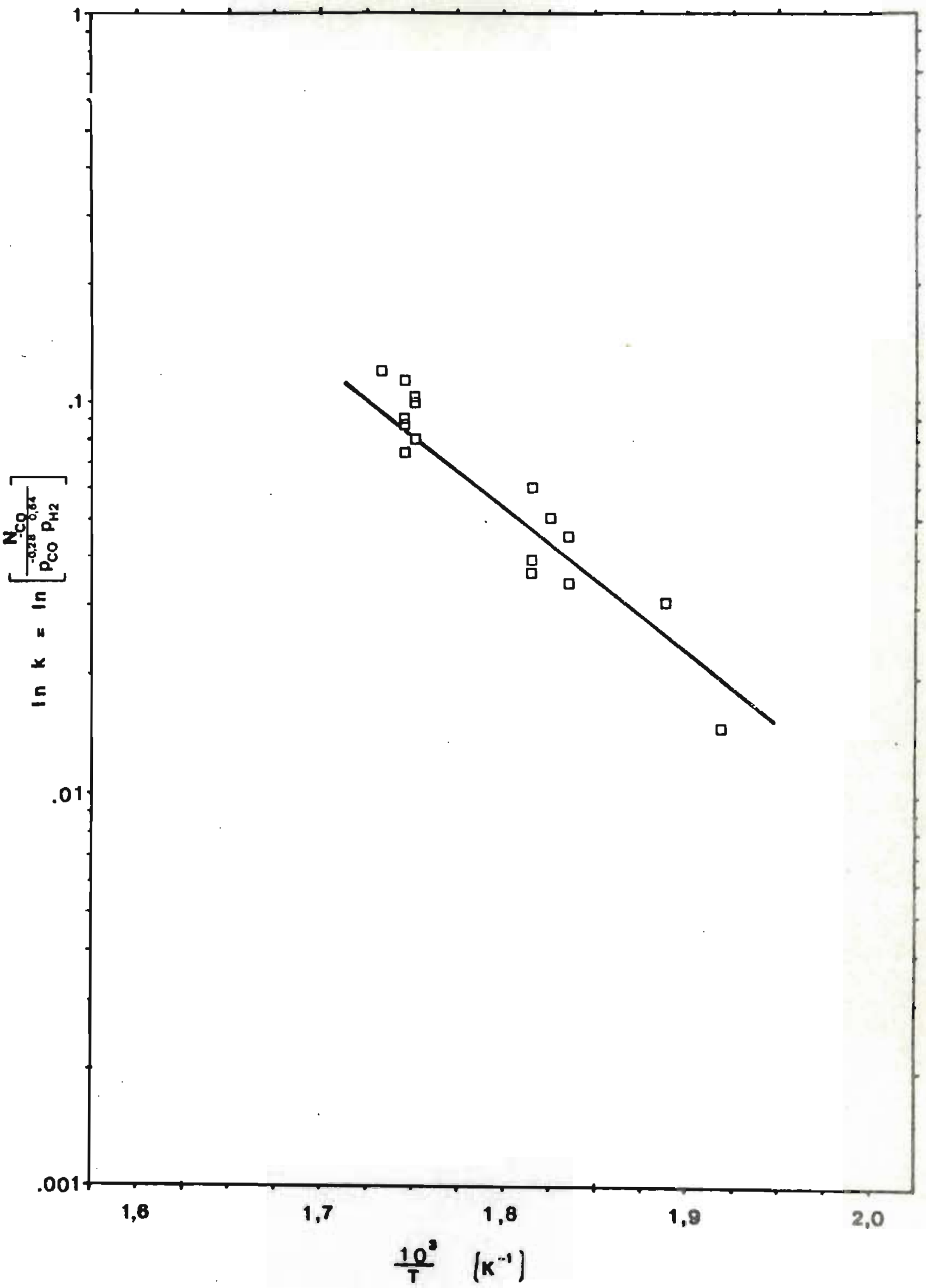


FIGURE 7.4.(b) - ARRHENIUS PLOTS FOR RATE OF CO REMOVAL BASED ON TURNOVER NUMBERS.

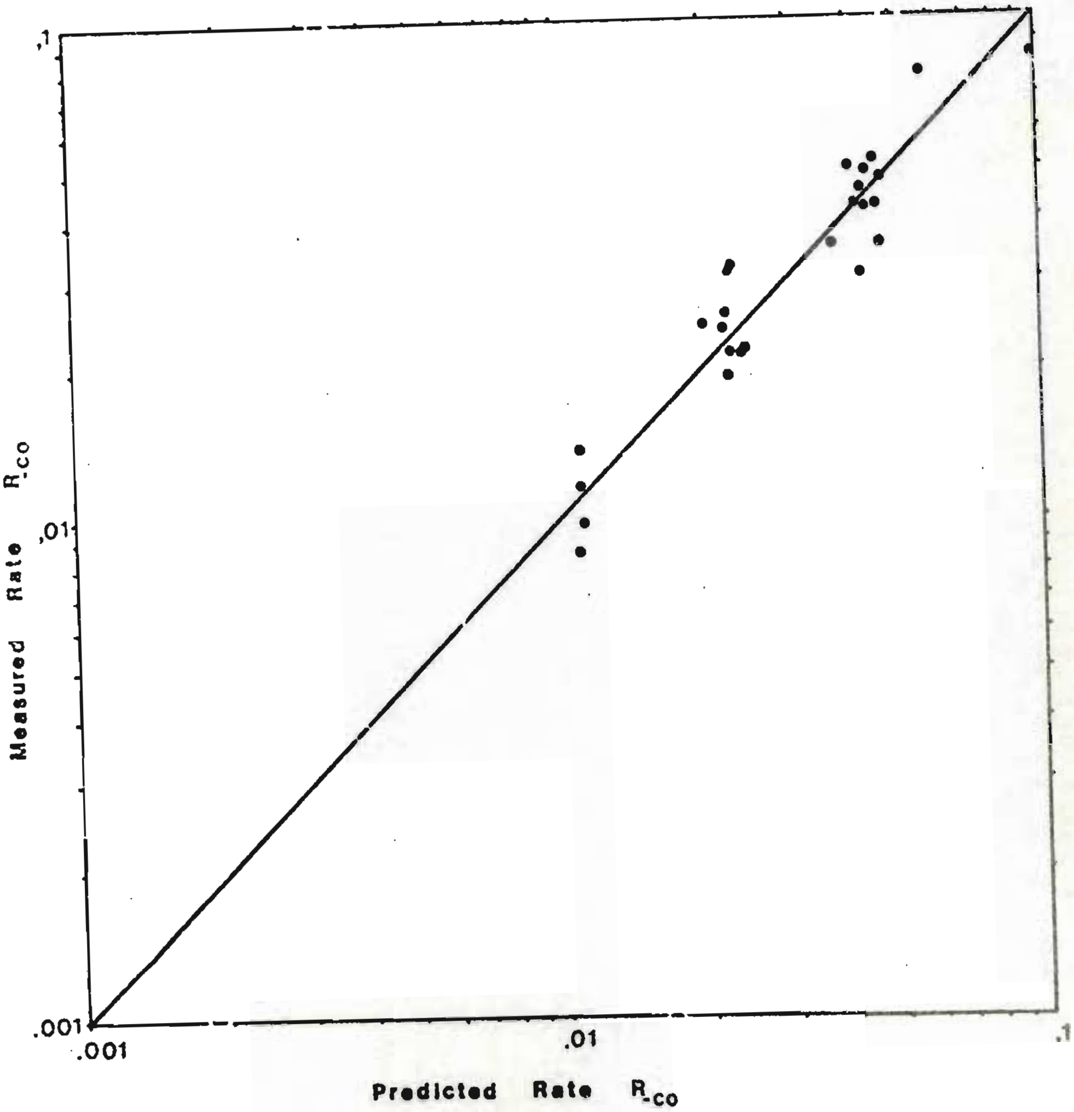


FIGURE 7.5.(a) - COMPARISON OF MEASURED AND PREDICTED CO REMOVAL RATES BASED ON RATES/UNIT MASS OF Ru.

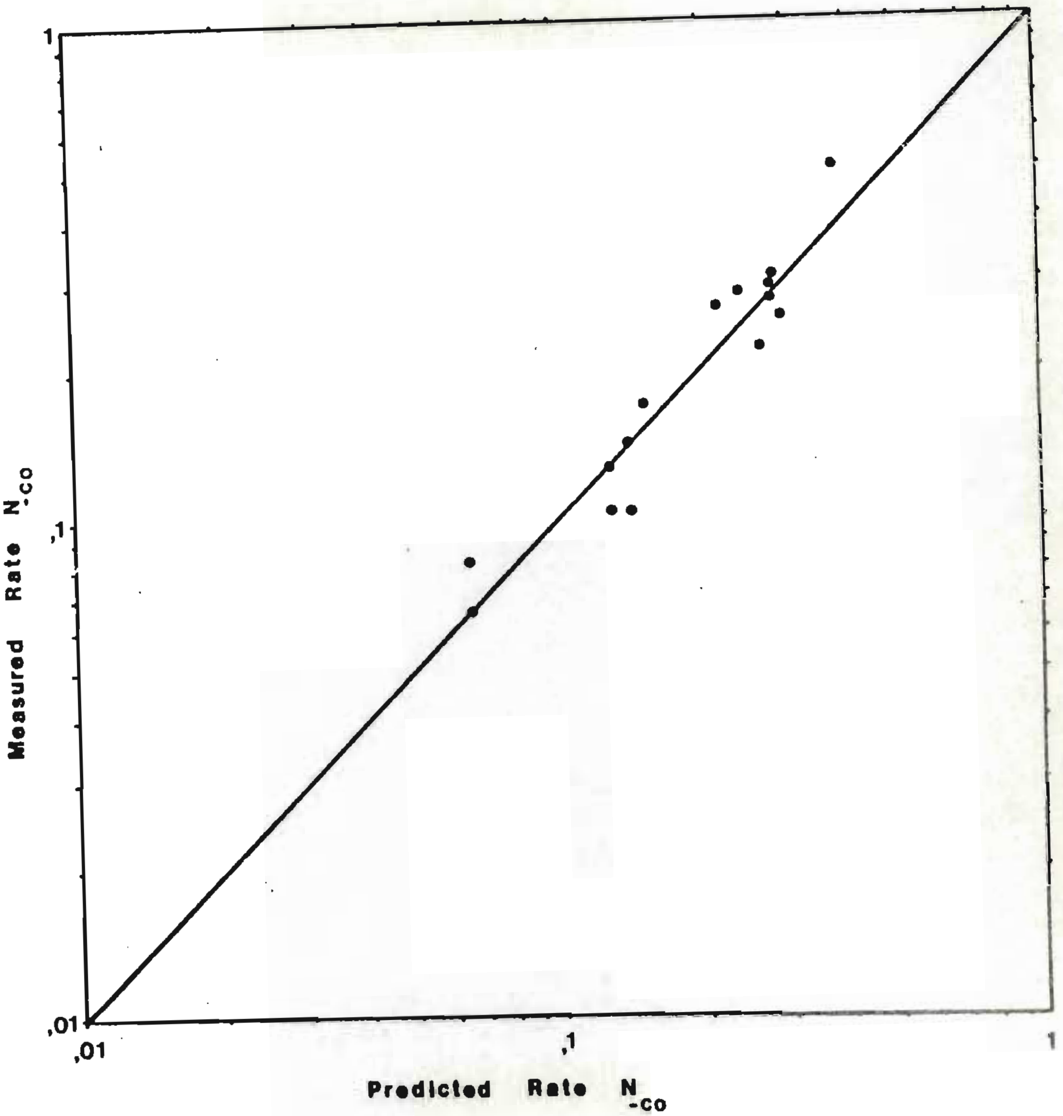


FIGURE 7.5.(b) - COMPARISON OF MEASURED AND PREDICTED CO REMOVAL RATES BASED ON TURNOVER NUMBERS.

Table 7.2. presents the regressed values of the kinetic parameters obtained for the rate of removal of carbon monoxide and the activation energies reported in the previously-cited investigations. As before, agreement is good between the two regressions obtained in the present investigation. An interesting contrast to the methanation reaction regressions is in the good agreement between activation energies in the present work and those of Vannice and Bond & Turnham. Since the reaction conditions varied considerably between the present work and both of the other investigators, this agreement can be interpreted as signifying that the mechanism of removal of carbon monoxide is unaffected by the nature of the reaction products (unlike the methanation mechanism).

In both sets of regressions (as shown in Tables 7.1. and 7.2. the reaction order is negative for carbon monoxide and positive for hydrogen. This is in qualitative agreement with most of the published literature, and is generally taken to indicate coverage by carbon monoxide approaching surface saturation.

7.4. COMPARISON WITH EARLIER WORK.

It is instructive to compare the results obtained in the present investigation with those reported by other investigators. Of the recently-published data on methanation and Fischer-Tropsch synthesis, the publications by King (1978), Vannice (1975, 1975 [a]) and Dalla Betta, Piken and Shelef (1974; 1975) are the most relevant. Table 7.3. presents the experimental conditions

TABLE 7.2.

REGRESSED VALUES FOR CARBON MONOXIDE REMOVAL.

Parameter	THIS INVESTIGATION(1)		VANNICE(2)	BOND & TURNHAM (3)
	R_{-CO}	N_{-CO}		
ln A	12,94	14,19	-	-
E_{-CO} (kcal/mol)	21,9 ± 1,3	19,0 ± 2,0	18,3 ± 1,0	20,5
a	-0,29	-0,28	-	-
b	0,80	0,64	-	-

(1) 0,5/ Ru/Al_2O_3, 8-16 atm, 225 - 300°C

(2) 5% Ru/Al_2O_3, 1 atm, 240 - 280°C

(3) 1% Ru/SiO_2, 20 torr CO, 60 torr H_2

TABLE 7.3.

EXPERIMENTAL OPERATING CONDITIONS OF VARIOUS INVESTIGATORS.

INVESTIGATOR	KING	KING	DALLA BETTA (1)	DALLA BETTA (2)	VANNICE
Catalyst (% mass Ru/Al_2O_3)	0,5	2,5	1,5	1,5	5,0
Dispersion (%)	60	34	35	35	6
C O Conversion (%)	2,8	26	1	1	5
Temperature (K)	523	523	523	523	548
Total Pressure (atm)	4	1	1	1	1
P_{H_2} (3)	2,57	1,95	0,5625	0,5938	0,71
P_{CO} (3)	1,28	0,98	0,1875	0,1562	0,24

(1) Initial rates.

(2) Steady state rates.

(3) Calculated from conversion for King & Vannice.

used by the above-cited investigators. In the case of King and Vannice, the values of the partial pressures of carbon monoxide and hydrogen were not reported in the original articles and so have been estimated from the reported carbon monoxide conversions.

This estimation introduces a certain error into the calculation, since in neither case was H_2/CO usage ratio given. For simplicity, it has been assumed that the usage ratios were in the same ratio as the synthesis gas compositions (2/1 and 3/1 respectively). While this is probably not strictly correct, it is anticipated that the error introduced by this assumption is minimal because of the fairly low conversions used by these authors.

Application of the power rate laws derived from the data of the present investigation viz,

$$N_{CH4} = 9{,}31 \times 10^{11} e^{\frac{-34300}{RT}} P_{CO}^{-0{,}44} P_{H_2}^{0{,}71}$$

and

$$N_{-CO} = 2{,}96 \times 10^{6} e^{\frac{-19000}{RT}} P_{CO}^{-0{,}28} P_{H_2}^{0{,}64}$$

to the values presented in Table 7.3 results in the predicted values for methanation turnover numbers as shown in Table 7.4.(a) In view of the fact that King (1978) has demonstrated the demanding nature of the CO/H_2 reaction, the values of the predicted

TABLE 7.4.

COMPARISON OF PREDICTED AND REPORTED TURNOVER NUMBERS.

(a) $N_{CH4} = 9{,}31 \times 10^{11}\ e^{\frac{-34300}{RT}}\ P_{CO}^{-0{,}44}\ P_{H_2}^{0{,}71}$

INVESTIGATOR	KING	KING	DALLA BETTA	DALLA BETTA	VANNICE
Predicted N(s^{-1})	0,0067	0,0163	0,0052	0,0060	0,0255
Corrected (s^{-1}) Prediction	0,0067	0,0163	0,0052	0,0060	0,1020
Reported N(s^{-1})	0,0104	0,0371	0,0053	0,0110	0,181

(b) $N_{-CO} = 2{,}96 \times 10^{6}\ e^{\frac{-19000}{RT}}\ P_{CO}^{-0{,}28}\ P_{H_2}^{0{,}64}$

INVESTIGATOR	KING	KING	VANNICE
Predicted N(s^{-1})	0,0543	0,0491	0,088
Corrected (S^{-1}) Prediction	0,0543	0,0491	0,282
Reported N(s^{-1})	0,0281	0,0891	0,325

turnover numbers for the conditions used by Vannice have been corrected to a datum dispersion of approximately 40%. This correction was considered to be necessary in view of the fact that the catalyst used by Vannice had a dispersion of only 6%. This correction was not applied in the other cases since it was considered that the additional error which would be introduced by this approximate correction would not be justifiable in correcting from dispersions of some 60 and 35%.

For the case of carbon monoxide removal, only King and Vannice present turnover numbers for CO removal in an unambiguous manner comparisons are therefore restricted to their published results.

With the corrections made to the predicted values of N by use of the correlation between dispersion and turnover number reported by King, it can be seem from Table 7.4. (b) that very good agreement is obtained between the published turnover numbers and those predicted by the rate equations developed in the present study. Considering the approximations and assumptions made, an agreement within a factor of 2 must be considered as being very satisfactory.

As was mentioned in the Literature Review, Vannice (1975 [a]) and later Ollis and Vannice (1975) proposed mechanisms for the methanation reaction over all Group V11 metal catalysts. A detailed description of this mechanism is presented in

Appendix 2 and will not, therefore, be repeated here. In this mechanism, the rate determining step (r.d.s.) is assumed to be the the reaction between the adsorbed CHOH intermediate and y/2 hydrogen molecules. By making the approximation

$$\frac{KP_{CO}P_{H_2}}{1 + KP_{CO}P_{H_2}} \simeq (KP_{CO}P_{H_2})^n$$

the following rate expression was derived:

$$\text{Rate} = K_4 \, K^{n+(n-1)y/2} \, K_{H_2}^{y/2} \, P_{CO}^{n+(n-1)y/2} \, P_{H_2}^{n+ny/2}$$

Comparison with the empirical model

$$\text{Rate} = Ae^{-E/RT} \, P_{H_2}^{X} \, P_{CO}^{Y}$$

results in

$$X = n + ny/2$$

$$\text{and} \quad Y = n + ny/2 - y/2$$

$$= X - y/2$$

$$\text{Thus} \quad y = 2\,(X-Y)$$

$$\text{and} \quad n = \frac{X}{1 + (X-Y)}$$

Bond and Turnham (1976) modified the Ollis-Vannice treatment by employing the assumption of dissociative adsorption of hydrogen to result in a rate equation of the form:

$$\text{Rate} = k_4 K^{n+ny-y} K_{H_2}^{y} P_{CO}^{n+ny-y} P_{H_2}^{n+ny-y/2}$$

and so,

$$X = n+ny - y/2$$

$$\text{and} \quad Y = n+ny - y$$

$$= X - y/2$$

Application of both of these treatments to the data of Vannice, Bond and Turnham, Dalla Betta, Piken and Shelef, and the present investigation produces the results depicted in Table 7.5.

In view of the physical significance of y in both treatments (the number of H atoms involved in the rate-determining step, Bond and Turnham considered their value of 3 as being more reasonable than the 4 obtained by Vannice.

Dalla Betta's partial pressure exponents produce very high values for y on the basis of this analysis. Values of 6 or 7 would mean that the rate-determining step involves the interaction of 6 or 7 hydrogen atoms with the adsorbed HCOH intermediate - an unlikely event.

TABLE 7.5.

CALCULATED AND OBSERVED METHANATION PARAMETERS.

INVESTIGATOR	OBSERVED			CALCULATED	
	X	Y	y	$n^{(a)}$	$n^{(b)}$
VANNICE	1,60	-0,60	4,4	0,5	0,70
BOND-TURNHAM(c)	1,15	-0,45	3,2	0,44	0,65
DALLA BETTA et alii	1,7 2,04	-1,14 -1,43	5,86 6,94	0,44 0,46	0,67 0,69
PRESENT WORK	0,71	-0,46	2,34	0,33	0,56

(a) Based on Ollis-Vannice mechanism.

(b) Based on Bond-Turnham mechanism.

(c) 1% Ru/SiO_2 catalyst.

7.5. SYNTHESIS RATES FOR HIGHER HYDROCARBONS.

Since the regressed values of the kinetic parameters obtained for the rate of methanation based on the simple power rate law showed good agreement whether turnover numbers or rates per gram of ruthenium were used, the regressions for the higher hydrocarbons were based on the relative rates of synthesis. In other words, the rates of synthesis for each of the carbon number fractions were expressed in terms relative to the rate of removal of methane. Thus,

$$\frac{r_{Ci}}{r_{C_1}} = \frac{N_{Ci}}{N_{C_1}}$$

$$N_{Ci} = \frac{r_{Ci}}{r_{C_1}} \cdot N_{C_1}$$

Since a satisfactory correlation had been obtained for N_{C_1}, then the the turnover number for any carbon number fraction C_i (for i = 1 to 12) can be written

$$N_{Ci} = \frac{r_{Ci}}{r_{C_1}} \cdot A_1 \, e^{\frac{-E_1}{RT}} \, P_{CO}^{\,a_1} \, P_{H_2}^{\,b_1}$$

Thus, the correlation obtained previously for turnover number for methanation may be used to determine the turnover number correlation for each of the individual carbon number fractions. This allowed the utilisation of the results from many of the experimental runs for which hydrogen chemisorption characterisation was not conducted. The implicit assumption in this technique is that the same number of active sites participate in both methanation and synthesis reactions (i.e. the "twin-site" theory discussed on Page 167 is, once again, taken to be invalid).

The use of a simple power law model (as was used successfully for methanation) is, however, somewhat restrictive when applied to higher hydrocarbon synthesis. As has been mentioned, under operating conditions of high reaction temperatures or high conversions, the rate of production of the higher hydrocarbons can exhibit a decrease both in relative and absolute terms - probably as a result of hydrogenolysis, since the activation energy for hydrogenolysis is much greater than that for synthesis. This therefore, imposes a restriction on the range of operating conditions over which the simple power rate model can be applied to higher hydrocarbon production, since the inclusion of a simple Arrhenius function in the model results in the prediction of a monotonic increase in reaction rate with temperature - a condition which does not apply to the higher hydrocarbon synthesis. However, for the lower temperature/conversion regions, a simple power rate model suffices.

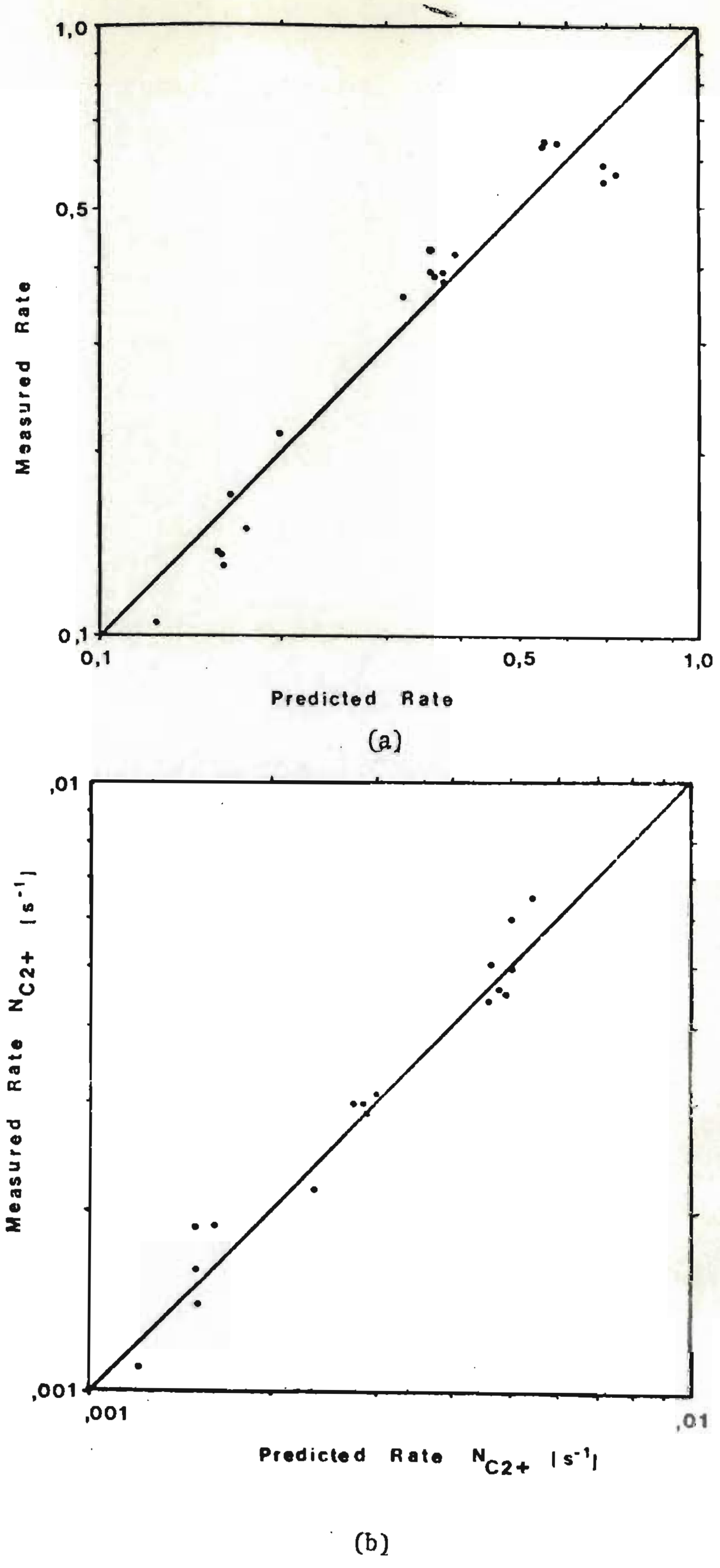
Because of this constraint on the range of operating conditions over which the simple power law model has validity, the data for C_2 and C_3 synthesis rates were not suitable for this treatment. In their place, a regression on the C_2+ fraction (i.e. the total higher hydrocarbon synthesis) was carried out. This approach had the effect of minimising the deviations apparent in the individual C_2 and C_3 fractions.

Figures 7.6. (a) and (b) show the agreement obtained between the predicted and measured values for the rate of synthesis for the C_2+ fraction expressed in terms of rate relative to methanation and absolute rate (after utilisation of the previously-obtained methanation parameters).

Table 7.6. presents the regressed values obtained for the kinetic parameters for rates of synthesis of individual carbon number fractions for which satisfactory correlation coefficients were obtained. Unfortunately, because of the restricted number of experiments in which appreciable quantities of carbon number fractions above C_8 were produced, no satisfactory regressions could be conducted to obtain kinetic parameters for individual carbon number fractions above C_8.

Figure 7.7. shows the agreement obtained between the predicted and experimental values for the rates of synthesis of individual carbon number fractions from C_4 to C_8.

The data of Table 7.6. show that the kinetic parameters obtained in all the regressions conducted exhibited a consistency insofar as all gave a dependance upon carbon monoxide partial pressures opposite in sign to those obtained in the methanation regression.



(a)

(b)

FIGURE 7.6. - COMPARISON OF MEASURED AND PREDICTED RATES OF SYNTHESIS OF C_2+

(a) relative to methanation
(b) expressed as turnover numbers.

TABLE 7.6.

REGRESSED VALUES FOR KINETIC PARAMETERS.

$$r_{Ci} = A_e^{-E/RT} \; P_{CO}^{a} \; P_{H_2}^{b}$$

CARBON NUMBER FRACTION	E	a	b	ln A	CORRELATION COEFFICIENT
C_2^+	15,9	0,39	-0,35	10,59	0,96
C_4	17,0	0,49	-0,63	10,39	0,97
C_5	16,1	0,40	-0,46	7,69	0,92
C_6	16,3	0,22	-0,30	7,50	0,98
C_7	14,7	0,29	-0,49	7,41	0,93
C_8	13,0	0,18	-0,03	1,24	0,98

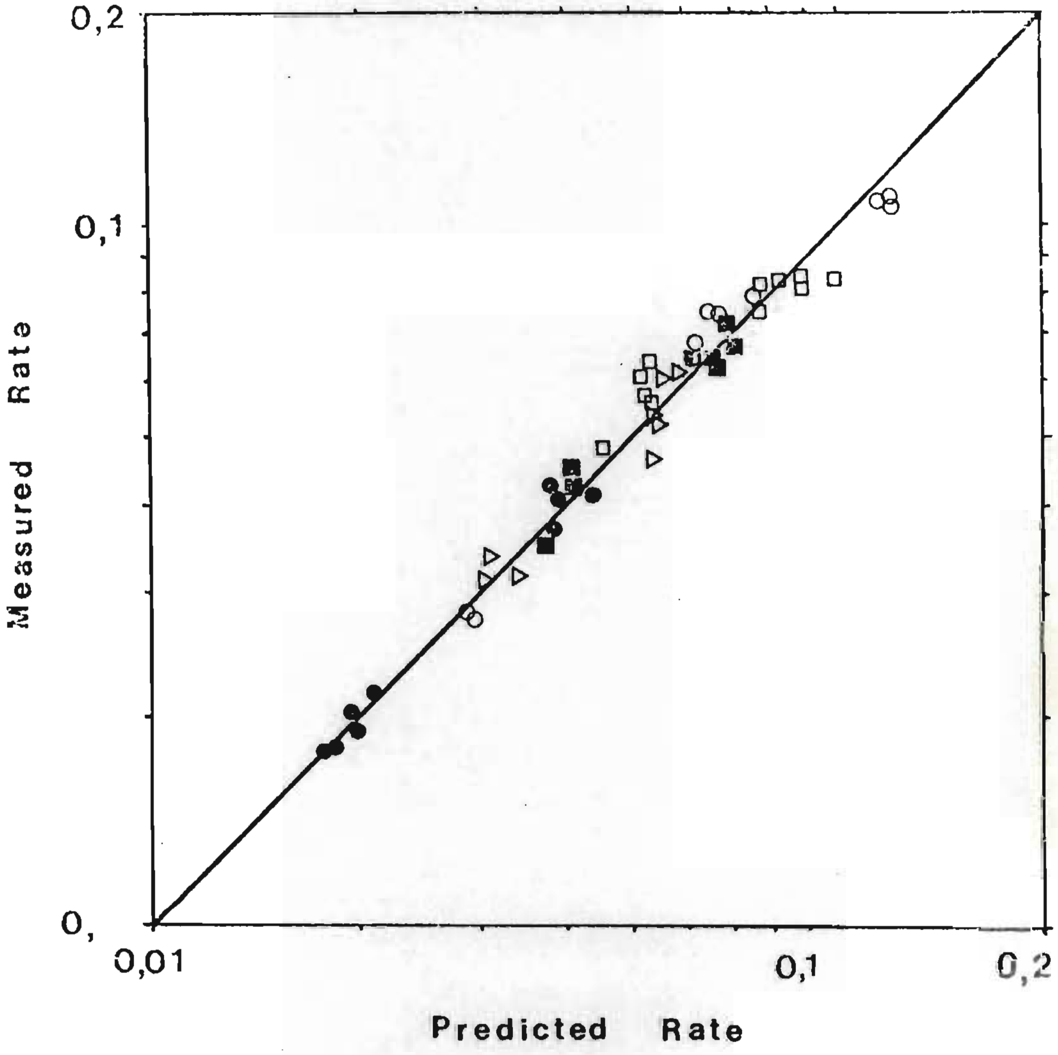


FIGURE 7.7. - COMPARISON OF MEASURED AND PREDICTED RATES OF SYNTHESIS OF C_4 to C_8.

○ C_4; □ C_5; ■ C_6; △ C_7; ● C_8

This would indicate that the rate of production of synthesis of the higher hydrocarbons would be favoured by an increase in the partial pressure of carbon monoxide and a decrease in the partial pressure of hydrogen. The activation energies for higher hydrocarbon synthesis are all very much lower than was found for the methanation reaction.

Consideration of the relative magnitude of the exponents and activation energies obtained for the regressions for methanation and carbon monoxide removal does add some support to these values. If the rate of removal of carbon monoxide be taken as a measure of the rate of production of all hydrocarbons (including methane), then the reduced value of activation energy obtained for carbon monoxide removal (at 19 kcal/mol) compared to the methanation reaction (at approximately 34 kcal/mol) could result only from the activation energy for higher hydrocarbon synthesis being lower than that of carbon monoxide removal. A similar argument may be employed in the case of the partial pressure exponents (where the magnitude of the exponents of the carbon monoxide removal are lower than those obtained for methanation).

CHAPTER 8.

CONCLUSIONS

A stirred gas-solid reactor was used to study the Fischer-Tropsch reaction over a supported ruthenium catalyst. The major conclusions which can be drawn from the experimental data are enumerated below.

1. The stirred gas-solid reactor proved to be a useful tool in the study of the exothermic Fischer-Tropsch synthesis. Operation of an integral reactor at the same level of conversion as employed here would result in thermal gradients of such magnitude as to interfere with the interpretation of the data. Use of the stirred gas-solid reactor has the added advantage of ease of data evaluation.

2. The use of ruthenium as a Fischer-Tropsch catalyst was demonstrated to have certain advantages in product selectivity, particularly in the range C_5 to C_{12}, when compared to data from the literature pertaining to promoted iron, cobalt and molybdenum catalysts.

3. The mass selectivity of each of the individual carbon number fractions examined was demonstrated to have a fixed relation when expressed relative to the mass selectivity of methane.

4. During synthesis the catalyst deactivated as a result of the deposition of carbonaceous material. Indications were that this deposition occurred randomly on the surface of the catalyst, with losses in catalyst total area and metal area both being detected. Reactivation of the catalyst was not considered, although this aspect would obviously require examination before any conclusions could be drawn as to the economic feasibility of the use of ruthenium as a Fischer-Tropsch catalyst.

5. The carbonaceous products of the synthesis over ruthenium were largely paraffinic, with the production of n-alkanes predominating. Traces of primary alcohols were detected in the aqueous product stream, and some degree of isomerisation was evident in the non-aqueous product.

6. Carbon dioxide and water were the only oxygenated products of any significance, with the carbon dioxide being formed via the water-gas shift reaction. Carbon dioxide production was found to be very low compared to other catalysts.

7. Regressions conducted on the methanation data resulted in an activation energy of approximately 34 k cal/mol, which is somewhat higher than most of the reported values. This increase in activation energy is possibly a consequence of methane formation in the presence of higher hydrocarbon. The magnitude

of the partial pressure exponents for both carbon monoxide and hydrogen agree fairly well with the values reported in the literature.

8. Regressions on the data for rate of removal of carbon monoxide produce an activation energy of the order of 19 k cal/mol, which value is in substantial agreement with values available in the literature.

9. Application of the methanation and CO removal rate equations derived in the present investigation to the data of several other workers results in good agreement between predicted values and those reported.

10. The interpretation of the rates synthesis of higher hydrocarbons is complicated by many factors, such as hydrocarbons hydrogenolysis, however a simple power law model can give good agreement between predicted and experimental rates (albeit over a restricted range of operating conditions). This is the first time correlations for the rate of formation of higher hydrocarbons have been presented.

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APPENDIX 1.

GAS CHROMATOGRAPH CALIBRATIONS.

The basic method of calibration for each of the compounds examined in this investigation has been outlined on Page 76 & 77. In this Appendix are presented the calibration curves obtained as well as details of a technique employed to extend the range of calibration concentration beyond those of premixed calibration gases.

In the construction of the calibration curves for both chromatographs, two techniques of sample preparation were used. The first involved direct utilisation of the premixed calibration gases. The second method was used in order to extend the range of compositions (and hence the number of data points): a flow system was set up to prepare gas mixtures using either pure component gas or the premixed calibration gases. This system consisted of two Brooks flow controllers (Model 8744): one controlling the flow rate of the compound for which a calibration curve was being constructed, and the other controlling the flow of hydrogen diluent. By adjusting both of these flow rates to suitable levels (measured by bubble flow meter) before combining them via a 'T' piece, the concentration of the component under investigation could be determined. (For pure gases, the molar concentrations are in the same ratio as their respective flow rates, while for the premixed calibration gases in hydrogen, the initial concentration of the compound being investigated would required to be taken into account). Since the flow controllers did just that, i.e. controlled the flow (irrespective of conditions downstream of the controller), the combined flow could then be passed through the sample valve for chromatographic response measurement.

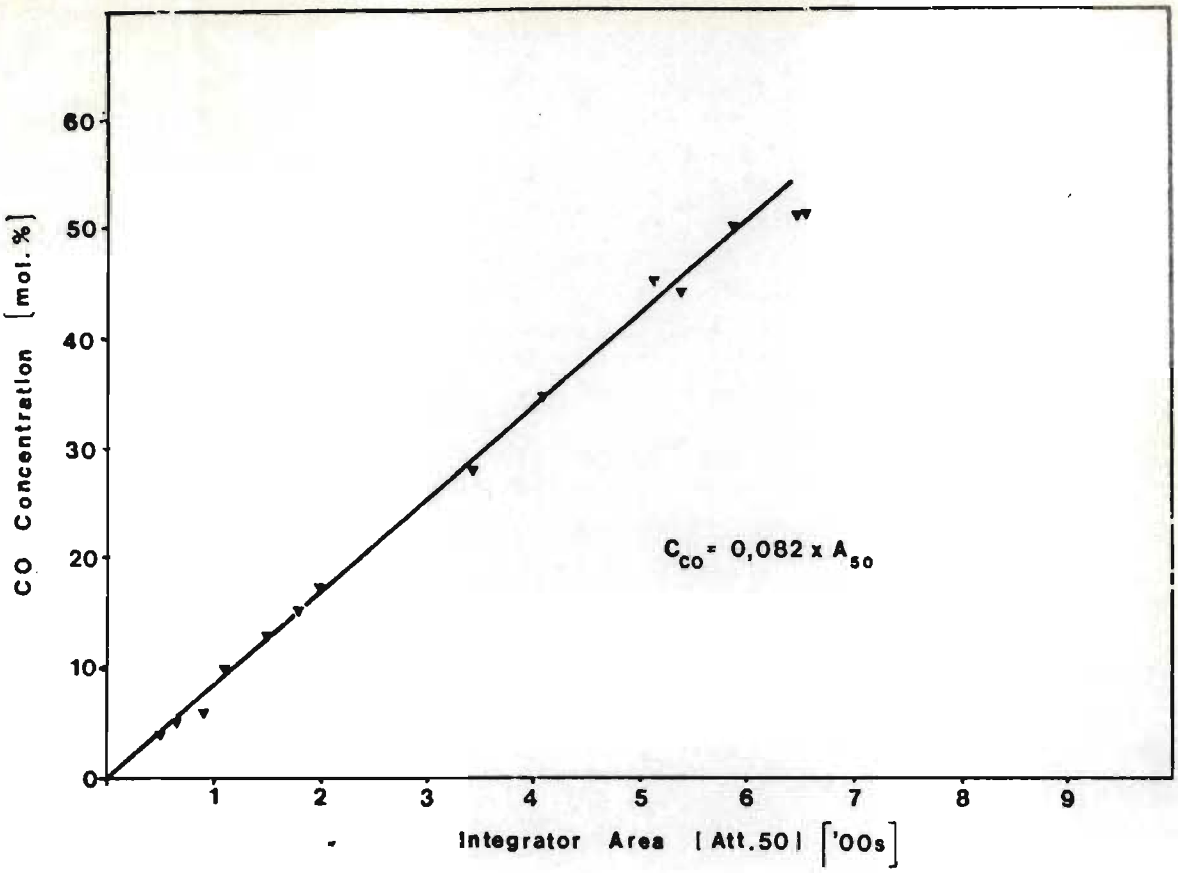
Figures A1 to A4 present the calibration curves for the Beckman gas chromatograph for each of the compounds detected in the final effluent stream.

Figures A5 to A11 present the corresponding calibration curves obtained for the Varian gas chromatograph.

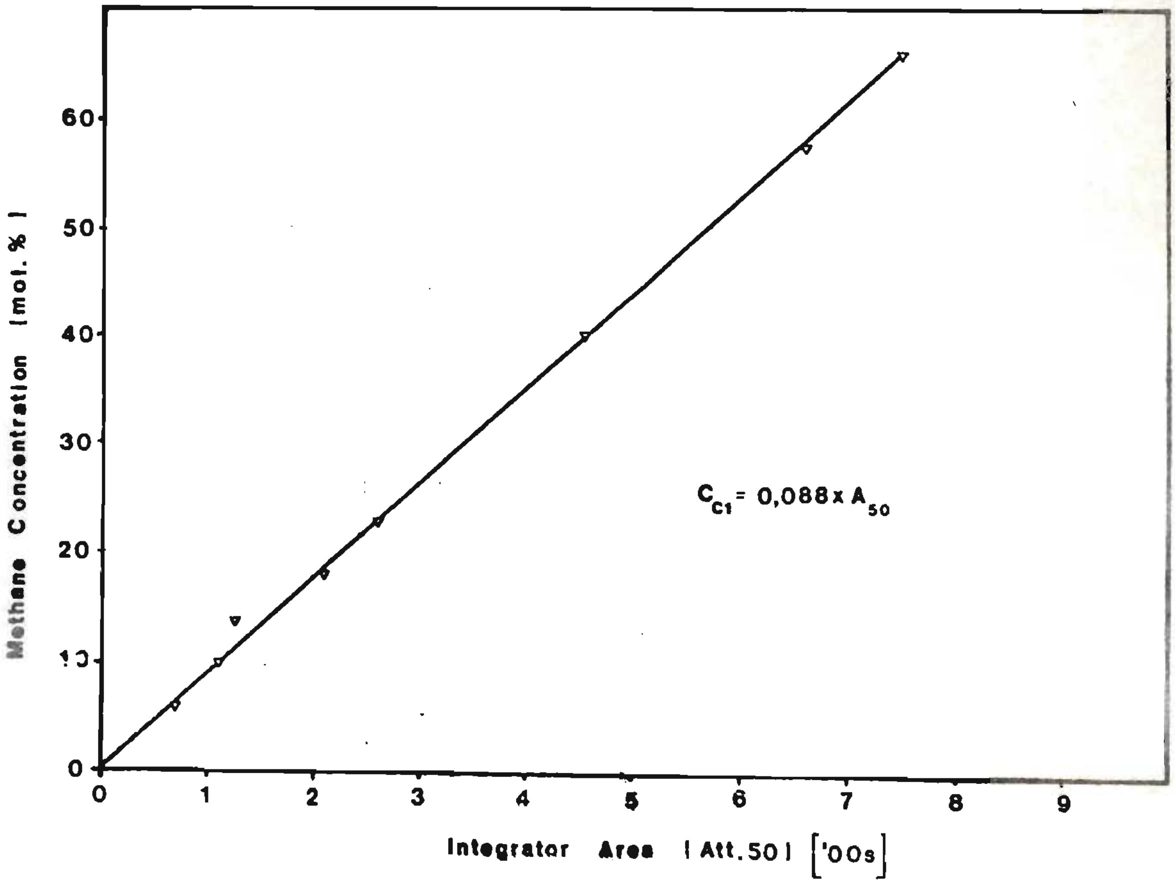
In all cases, the linearity of response was such that a simple linear correlation was used to convert from the measured peak area to the corresponding molar concentration. This correlation is given on each calibration curve.

It should be noted that the areas used for both CO and CH_4 calibration were the areas obtained with a chromatographic signal attentuation of 64 (for the Varian) and 50 (for the Beckman). This attenuation is designation on the symbol A; thus 'A_{64}' denotes the area determined with chromatograph/ recorder combined signal attenuation of 64. The attenuations required for the other compounds were, in general, lower than those for CO or CH_4.

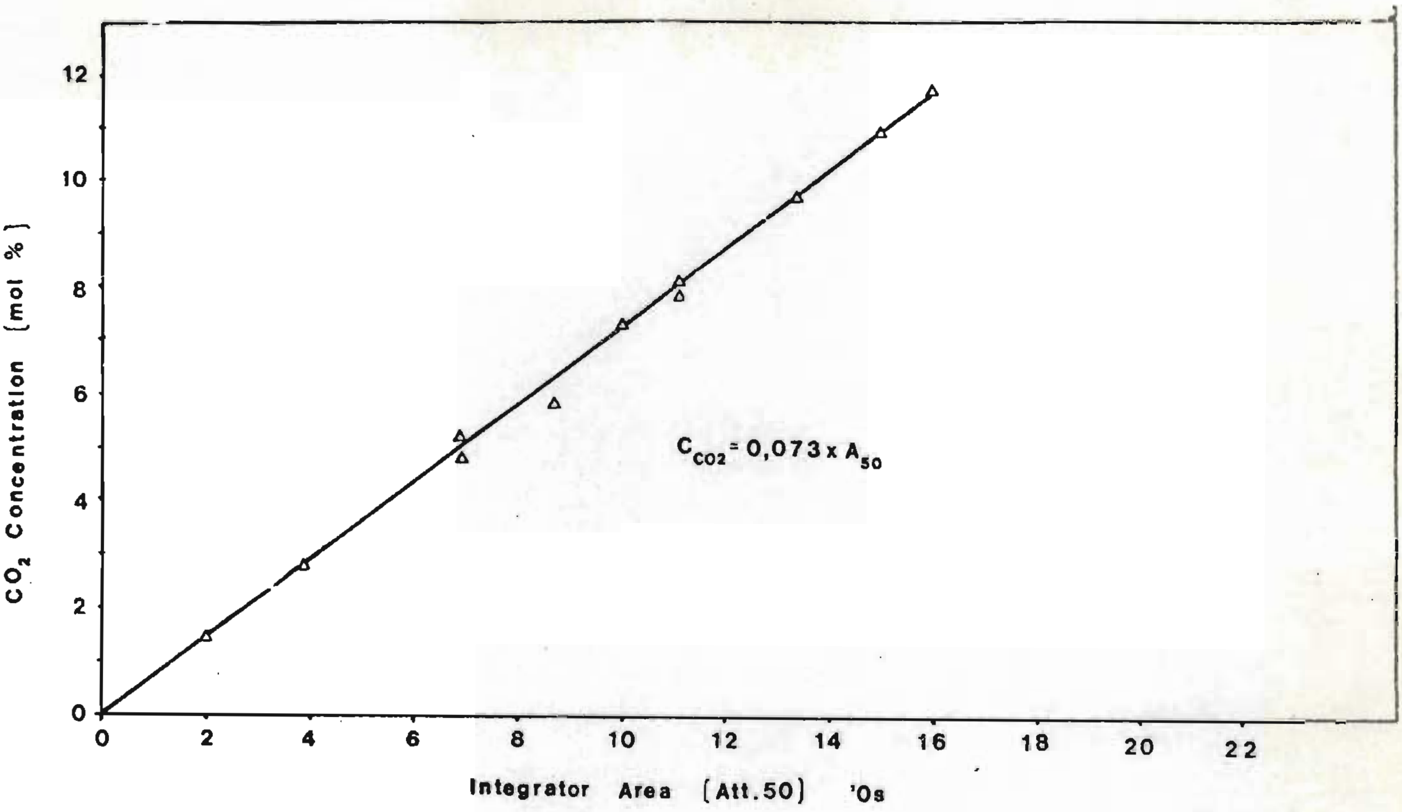
Calibrations for C_5 and higher hydrocarbons were based on the fact that the thermal conductivity of each of the members of the alkane homologous series shows a progressively smaller decrease with increasing carbon number, with the thermal conductivity of the alkanes above C_6 exhibiting only very slight decreases with increasing carbon number. Values of the thermal conductivities of each of the carbon numbers from C_1 to C_{10} are presented in Table A.1. (Touloukian, Liley and Saxena, 1970). Since the thermal conductivity detector response is directly related to the thermal conductivity of the substance being detected, it was considered to be a reasonable assumption that the T.C.D. response to C_6 and higher hydrocarbons would be largely independent of carbon number The C_5 response was taken as being being some 5% lower than the (calibrated) C_4 response, while the responses for C_6 and higher members were taken as being the same as the C_5 response.


CO Concentration [mol. %]
0
10
20
30
40
50
60
1
2
3
4
5
6
7
8
9
Integrator Area (Att.50) ['00s]
$C_{CO} = 0,082 \times A_{50}$

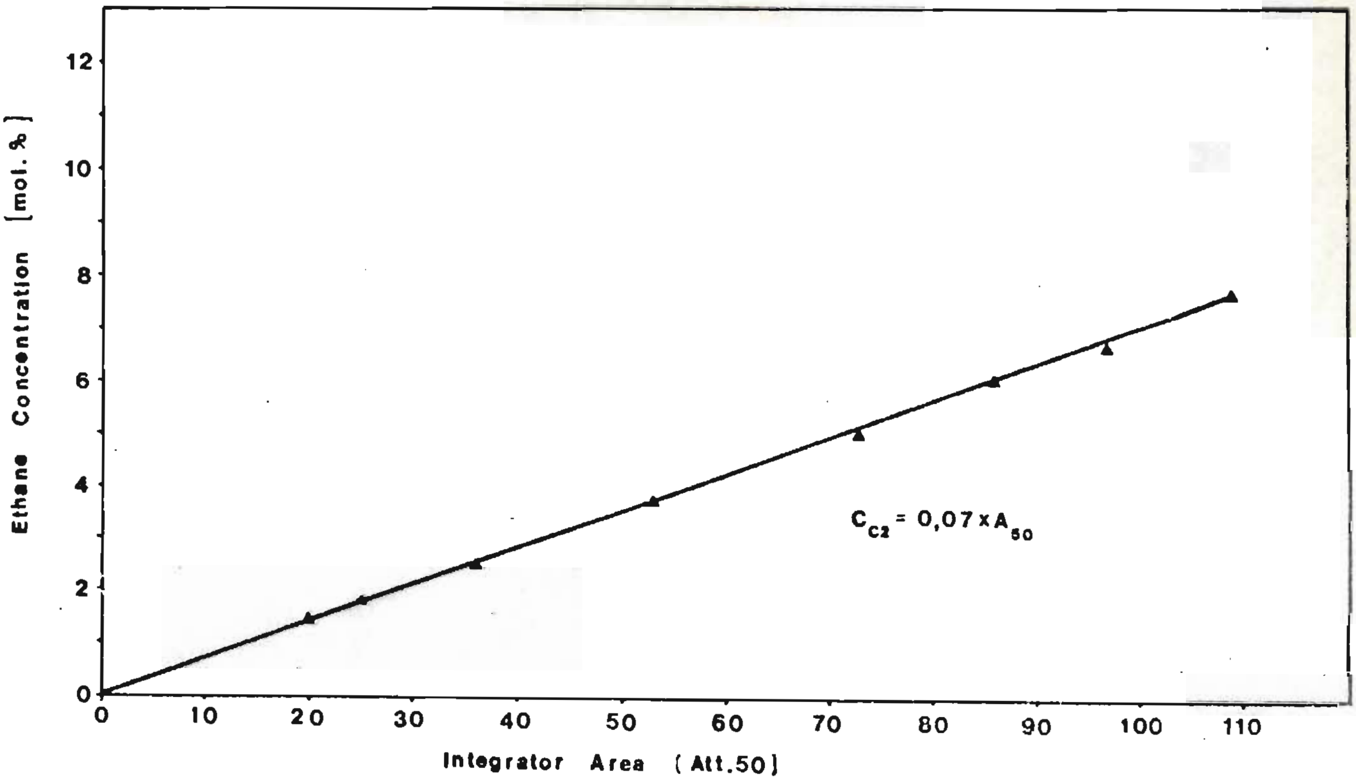
A1


Methane Concentration (mol. %)
0
10
20
30
40
50
60
0
1
2
3
4
5
6
7
8
9
Integrator Area (Att.50) ['00s]
$C_{C1} = 0,088 \times A_{50}$

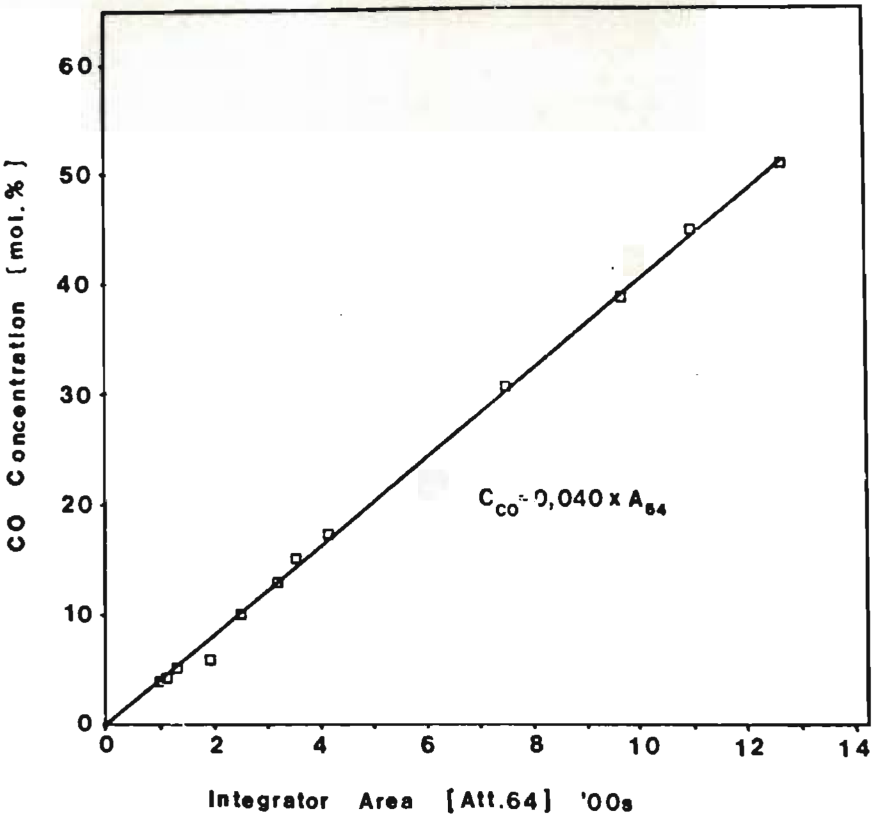
A2


CO$_2$ Concentration (mol %)
0
2
4
6
8
10
12
Integrator Area (Att.50) '0s
0
2
4
6
8
10
12
14
16
18
20
22
$C_{CO2} = 0,073 \times A_{50}$

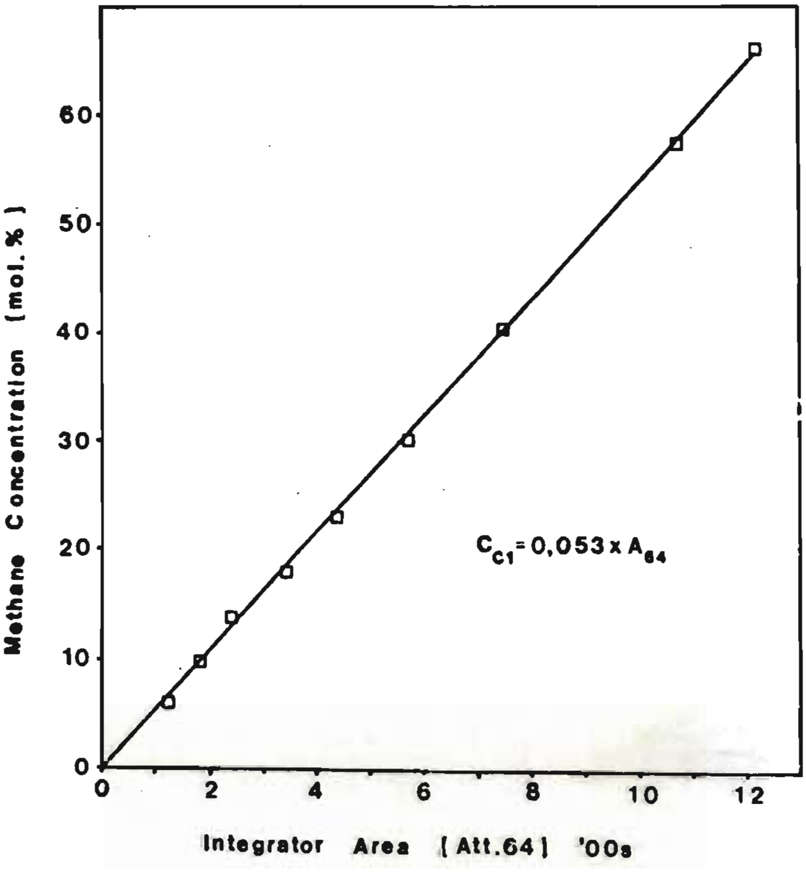
A3


Ethane Concentration (mol. %)
0
2
4
6
8
10
12
Integrator Area (Att.50)
0
10
20
30
40
50
60
70
80
90
100
110
$C_{C2} = 0,07 \times A_{50}$

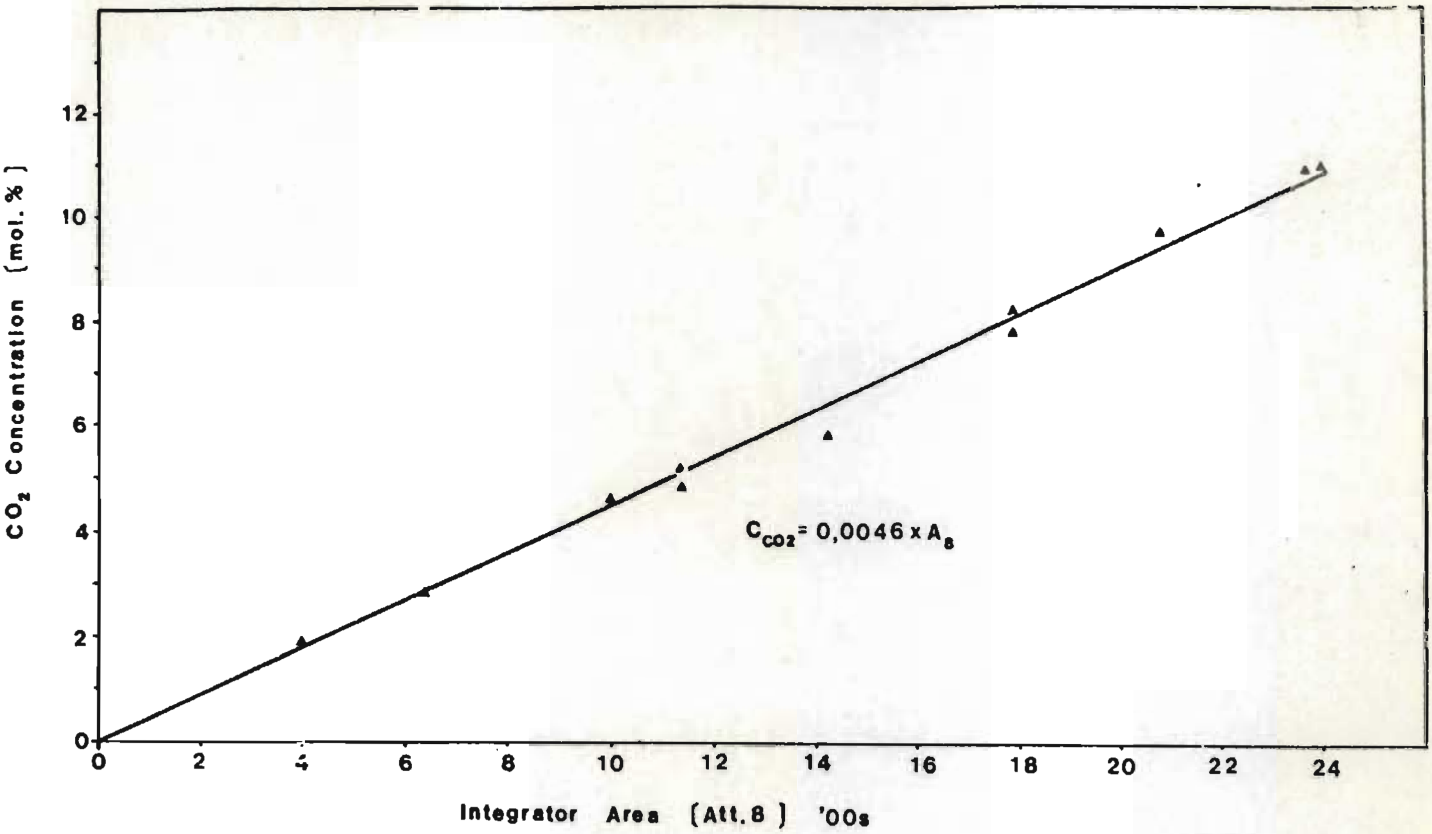
A4


CO Concentration [mol.%]
0
10
20
30
40
50
60
Integrator Area [Att.64] '00s
0
2
4
6
8
10
12
14
C_{CO} = 0,040 x A_{64}

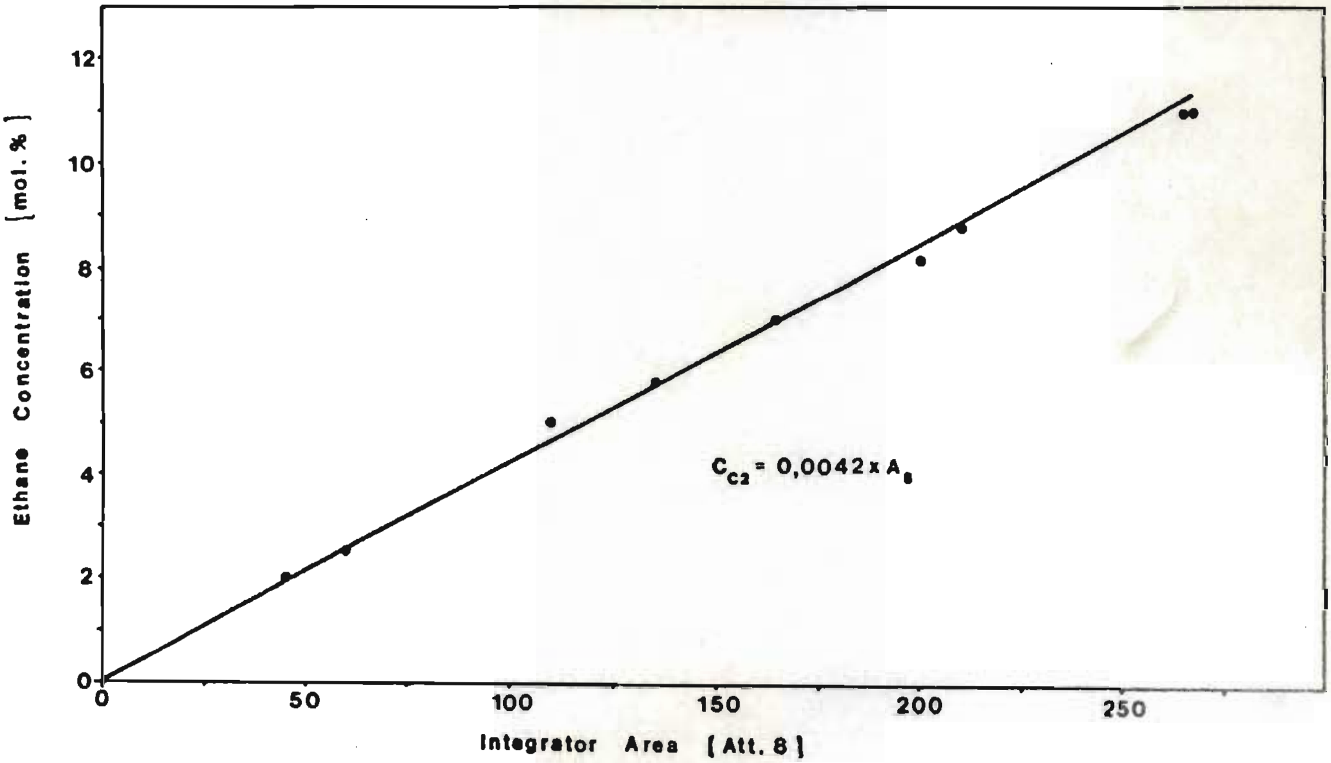
A5


Methane Concentration [mol.%]
0
10
20
30
40
50
60
Integrator Area [Att.64] '00s
0
2
4
6
8
10
12
C_{C1} = 0,053 x A_{64}

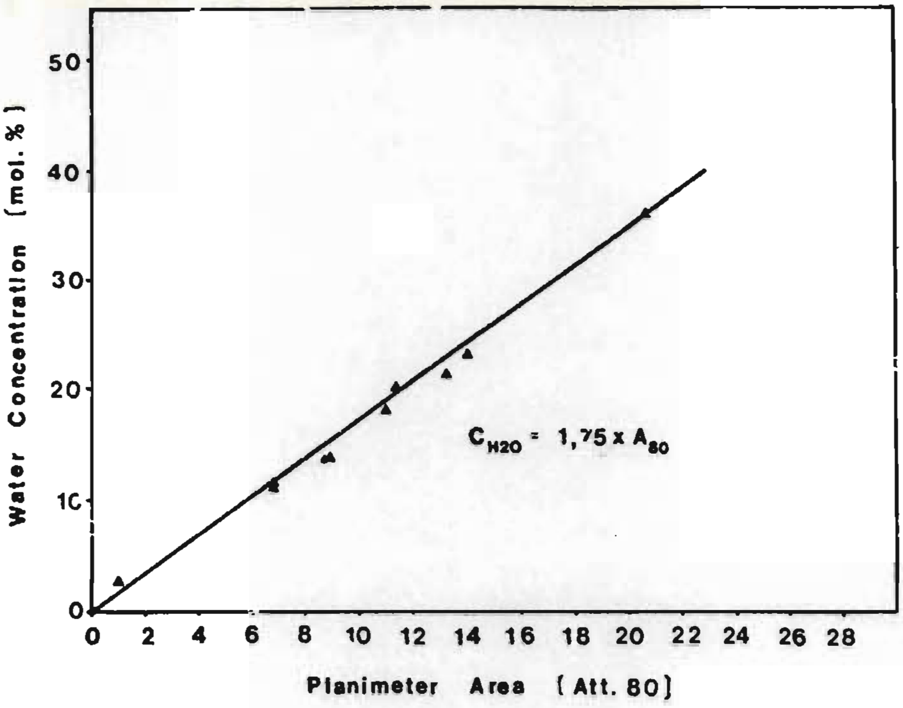
A6


CO$_2$ Concentration [mol. %]
0
2
4
6
8
10
12
Integrator Area [Att. 8] '00s
0
2
4
6
8
10
12
14
16
18
20
22
24
C_{CO2} = 0,0046 x A_8

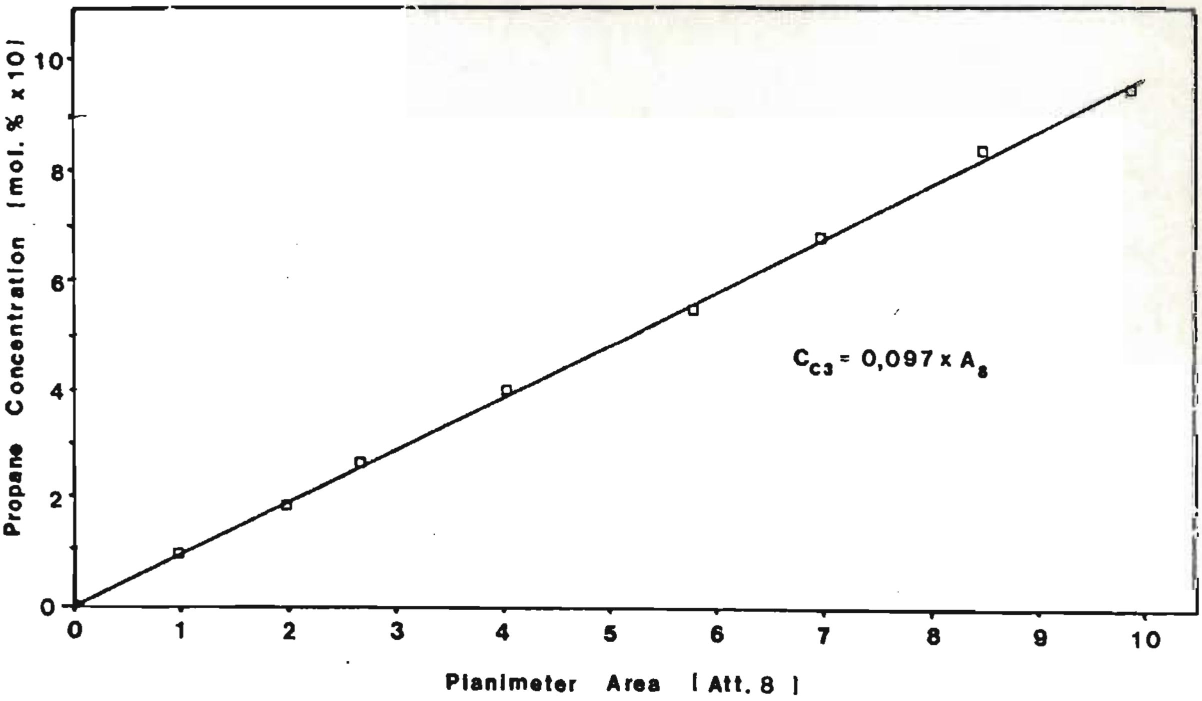
A7


Ethane Concentration [mol. %]
0
2
4
6
8
10
12
Integrator Area [Att. 8]
0
50
100
150
200
250
C_{C2} = 0,0042 x A_8

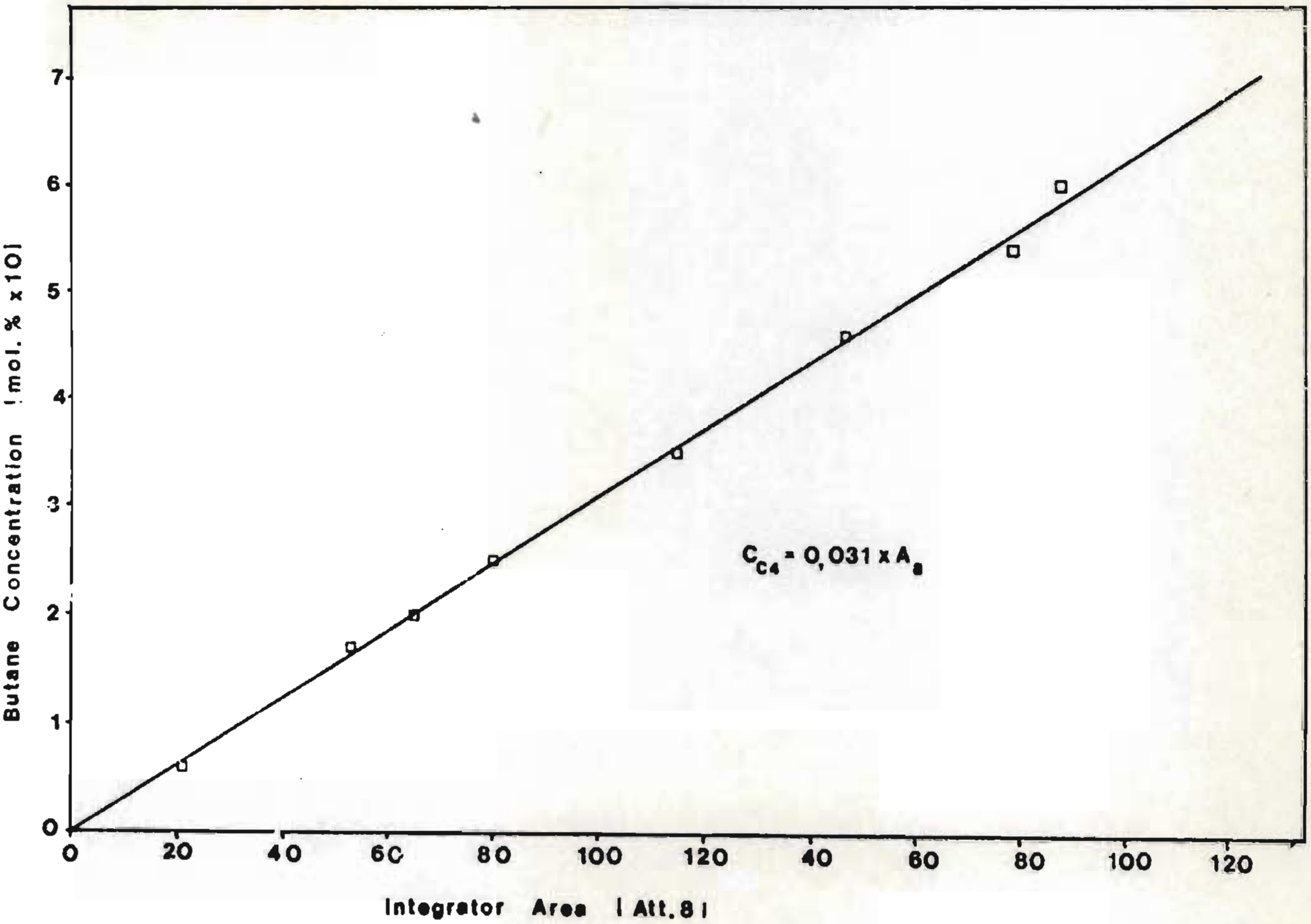
A8


Water Concentration (mol. %)
50
40
30
20
10
0
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28
Planimeter Area (Att. 80)
$C_{H2O} = 1,75 \times A_{80}$

A9


Propane Concentration (mol. % x 10)
10
8
6
4
2
0
0 1 2 3 4 5 6 7 8 9 10
Planimeter Area (Att. 8)
$C_{C3} = 0,097 \times A_8$

A10


Butane Concentration (mol. % x 10)
0
1
2
3
4
5
6
7
Integrator Area (Att. 8)
0
20
40
60
80
100
120
40
60
80
100
120
C_{C4} = 0,031 x A_8

A11

TABLE A.1.

THERMAL CONDUCTIVITY OF n-ALKANES.

(VALUES AT 400 K)

COMPOUND	THERMAL CONDUCTIVITY (mw/cm/K)
CH_4	0,484
C_2H_6	0,360
C_3H_8	0,295
C_4H_{10}	0,264
C_5H_{12}	0,250
C_6H_{14}	0,232
C_7H_{16}	0,214
C_8H_{18}	0,226
C_9H20	0,202
$C_{10}H_{22}$	0,211

APPENDIX 2.

In this appendix, the mechanistic models of Vannice, Huang and Richardson, Bond and Turnham and the Ollis-Vannice modification of Vannice's original reaction scheme are considered.

(a) VANNICE.

The original Vannice (1975 [a]) model was based upon the supposition that the rate-determining step was the hydrogenation of the HCOH surface intermediate, with all preceding steps in quasi-equilibrium, and the final hydrogenation step being very rapid and thus not influencing the kinetics. The basic sequence is thus:

$$CO \overset{K_{CO}}{\longleftrightarrow} CO_{(ads)} \qquad 1.$$

$$H_2 \overset{K_{H_2}}{\longleftrightarrow} H_{2(ads)} \qquad 11.$$

$$CO_{(ads)} + H_{2(ads)} \overset{K_1}{\longleftrightarrow} HCOH_{(ads)} \qquad 111.$$

$$HCOH_{(ads)} + \frac{y}{2} \cdot H_{2(ads)} \xrightarrow{K_2} CH_{y(ads)} + H_2O \qquad 1V.$$

$$CH_y + H_2 \longrightarrow CH_4 \qquad V.$$

with steps 1 and 11 being written as $H_2 + CO \overset{K}{\longleftrightarrow} HCOH$ the surface coverage of the intermediate HCOH may be written as

$$\theta_{HCOH} = \frac{K P_{CO} P_{H_2}}{1 + K P_{CO} P_{H_2}}$$

$$\approx (K P_{CO} P_{H_2})^n$$

with the assumption of high surface coverage of HCOH, the surface fraction available for hydrogen adsorption is

$$1 - \theta_{HCOH} \approx (K P_{CO} P_{H_2})^{-1}$$

and the fraction covered by hydrogen is

$$\theta H_2 \approx \frac{\theta K_{H_2} P_{H_2}}{1 + K_{H_2} P_{H_2}}$$

$$\approx \theta K_{H_2} P_{H_2}$$

Assuming that the adsorbed hydrogen is weakly bonded and thus $K_{H_2} P_{H_2} << 1$

From step 1V,

$$\text{rate of methanation} = K_2 \theta_{HCOH} \theta_{H_2}^{y/2}$$

$$= k_2 K^{n-y/2} K^{y/2} P_{CO}^{n-y/2} P_{H_2}^{n}$$

Vannice's data were fitted to a power rate law of the form

$$\text{rate of methanation} = Ae^{-E/RT} P_{CO}^{\ Y} P_{H_2}^{\ X}$$

$$N_{CH_4} = Ae^{-E/RT} P_{H_2}^{\ X} P_{CO}^{\ Y}$$

and thus,

$$X = n$$

$$\text{and } Y = n - \frac{y}{2}$$

For all of the Group V11 metals considered, Vannice found that the value of X was close to unity, with y varying from 1 to 4.

Since y is the number of hydrogen atoms reacting with the adsorbed CHOH intermediate in step 1V of the mechanism, it m ay be assumed that values of y greater than 4 (thus indicating interation of more than three adsorbed species) is unlikely.

(b) OLLIS-VANNICE MODIFICATION.

Ollis and Vannice (1975) made a modification to the Vannice model by the approximation

$$1 - \theta_{HCOH} \simeq (1 + K\,P_{CO}\,P_{H_2})^{-1}$$

the hydrogen coverage now becomes

$$\theta_{H_2} = \frac{K_{H_2}\,P_{H_2}}{1 + K\,P_{CO}P_{H_2}}$$

$$= \frac{K_{H_2}\,P_{H_2}}{K\,P_{CO}P_{H_2}} \cdot \frac{K\,P_{CO}\,P_{H_2}}{1+K\,P_{CO}P_{H_2}}$$

$$\simeq \frac{K_{H_2}\,P_{H_2}}{K\,P_{CO}P_{H_2}} \cdot (K\,P_{CO}P_{H_2})^n$$

$$= (K\,P_{CO}P_{H_2})^{n-1}\quad K_{H_2}\,P_{H_2}$$

The rate of methanation may now be written

$$\text{rate} = k_{2.}\,\theta_{HCOH}\,(\theta_{H_2})^{y/2}$$

$$= k_{2.}\,(K\,P_{CO}P_{H_2})^n\quad (K\,P_{CO}P_{H_2})^{n-1}\,K_{H_2}P_{H_2}\quad y/2$$

$$= k_2 K^{\,n+(n-1)y/2}\,K_{H_2}^{\,y/2}P_{CO}^{\,n+(n-1)y/2}P_{H_2}^{\,n+n\,y/2}$$

Comparison with the power law equation used in the regression now yields

$$X = n(1 + y/2)$$

$$Y = n(1 + y/2) - y/2 \;] \; X - y/2$$

$$\text{i.e.} \quad y = 2(X - Y)$$

$$\text{and} \quad n = X/(1 + y/2)$$

This modification resulted in the values of n being approximately 0,5 for all the Group V11 metals examined, in agreement with the restriction

$0 \leq n \leq 1$ implied by the approximation

$$\frac{K \, . \, P_{CO} \, P_{H_2}}{1 + K.P_{CO} P_{H_2}} \simeq (K \, P_{CO} \, P_{H_2})^{n}$$

(c) BOND AND TURNHAM.

The Vannice mechanism has been criticised by Bond and Turnham (1976) on the grounds that the participation of one half or three halves of a hydrogen molecule in the rate-determining step is difficult to comprehend. By the use of the assumption of dissociative adsorption of hydrogen, the rate-determining step becomes

$$HCOH_{(ads)} + a\ H_{(ads)} \longrightarrow CH_{a(ads)} + H_2O$$

The rate expression thus becomes

$$r_{CH_4} = k.K^{n+na-a}\ K_{H_2}^{\ a}\ P_{CO}^{\ n+na-a}\ P_{H_2}^{\ n+na-^a/2}$$

as before, comparison with the lower-law regression equation yeilds,

$$X = n+na-{}^a/2$$

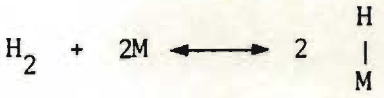
$$\text{and} \quad Y = n+na-a$$

$$= X - {}^a/2$$

Application of the Bond-Turnham modification of the Vannice or Ollis-Vannice model to Vannice's data gave values not far removed from those derived by the Vannice treatment. However, Bond and Turnham's data indicated that their best fit was obtained with y = a = 3, which was regarded by them as being more reasonable than the value of 4 obtained by Vannice: this latter value implying that the rate-determining step results in the formation of methane in one step.

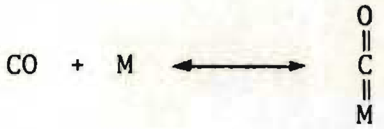
(d) HUANG AND RICHARDSON.

In a study of carbon monoxide hydrogenation over supported nickel catalysts, Huang and Richardson (1978) proposed the following mechanism:



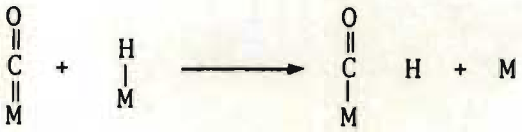
$$H_2 + 2M \longleftrightarrow 2\begin{array}{c}H\\|\\M\end{array}$$

1.



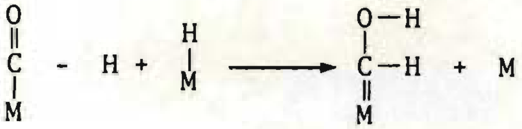
$$CO + M \longleftrightarrow \begin{array}{c}O\\\|\\C\\\|\\M\end{array}$$

11.



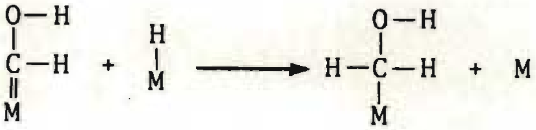
$$\begin{array}{c}O\\\|\\C\\\|\\M\end{array} + \begin{array}{c}H\\|\\M\end{array} \longrightarrow \begin{array}{c}O\\\|\\C\\|\\M\end{array}\quad H + M$$

111.



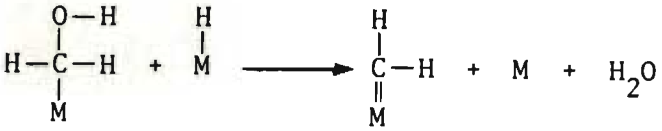
$$\begin{array}{c}O\\\|\\C\\|\\M\end{array} - H + \begin{array}{c}H\\|\\M\end{array} \longrightarrow \begin{array}{l}O-H\\|\\C-H\\\|\\M\end{array} + M$$

1V.



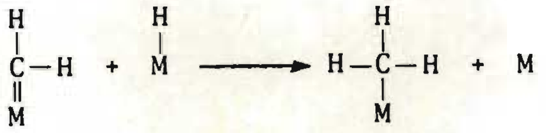
$$\begin{array}{l}O-H\\|\\C-H\\\|\\M\end{array} + \begin{array}{c}H\\|\\M\end{array} \longrightarrow \begin{array}{c}O-H\\|\\H-C-H\\|\\M\end{array} + M$$

V.



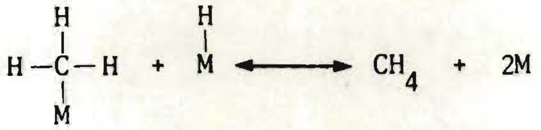
$$\begin{array}{c}O-H\\|\\H-C-H\\|\\M\end{array} + \begin{array}{c}H\\|\\M\end{array} \longrightarrow \begin{array}{l}H\\|\\C-H\\\|\\M\end{array} + M + H_2O$$

V1.



$$\mathrm{H_2C{=}M} + \mathrm{H{-}M} \longrightarrow \mathrm{H_3C{-}M} + \mathrm{M}$$

V11.



$$\mathrm{H_3C{-}M} + \mathrm{H{-}M} \longleftrightarrow \mathrm{CH_4} + 2\mathrm{M}$$

V111.

Relations connecting the surface coverage and the partial pressure of the reactants may be derived on the basis of each of the steps in the proposed mechanism.

STEP 1: $K_{H_2}P_{H_2}\theta^2 = K_{H_2}\theta_H^2$

$$\therefore \theta_H = \sqrt{K_H P_{H_2}}\;\theta$$

STEP 11: $\theta_{CO} = K_{CO}P_{CO}\theta$

STEP 111: $K\theta_{CO}\theta_H = K\theta_{COH}\theta$

$$\therefore \theta_{COH} = K_3 . \frac{\theta_{CO}\,\theta_H}{\theta}$$

STEP 1V: $K\theta_{COH}\theta_H = K\theta_{HCOH}\theta$

$$\therefore \theta_{HCOH} = K_4 \frac{\theta_{COH}\theta_H}{\theta}$$

$$= K_5 . \frac{\theta_{CO}\theta_H^2}{\theta}$$

STEP V: $K\theta_{HCOH}\theta_{H} = K\theta_{CH_2OH}\theta$

$$\therefore \theta_{CH_2OH} = K_6 . \theta_{HCOH} \frac{\theta_H}{\theta}$$

$$= K_7 \frac{\theta_{CO}\theta_{H}{}^3}{\theta^3}$$

if Step 111 is taken as being the rate-determining step, then

$$r_{CH_4} = K\theta_{CO}\theta_{H}$$

$$= K.\ K_{CO}\sqrt{K_H} .\ P_{CO}\sqrt{P_{H_2}}\quad \theta^2$$

now, $\theta + \theta_H + \theta_{CO} = 1$

$$\therefore \theta = \frac{1}{(1 + \sqrt{K_H P_{H_2}} + K_{CO} P_{CO})}$$

if $\sqrt{K_H P_{H_2}}$ be neglected,

then, $\theta = \frac{1}{(1 + K_{CO}P_{CO})}$

thus, rate of methanation $= \frac{K. \sqrt{K_H P_{H_2}} \quad P_{CO}}{(1 + K_{CO} P_{CO})^2}$

$$= \frac{K'.\ P_{CO}\ P_{H_2}{}^{0,5}}{(1 + K_{CO}\ P_{CO})^2}$$

By comparison with the empirical rate equation used in the regression:

$$\text{rate} \quad = \quad \frac{K\, P_{CO}\, P_{H_2}{}^{n}}{(1 + K_{CO}P_{CO})^{m}}$$

$$n \quad = \quad 0{,}5 \qquad\qquad m \quad = \quad 2{,}0$$

which are the values found by Huang and Richardson to give the best fit to their data.

If it is assumed that Steps 111 and 1V are in equilibrium and that the rate-determining step is a combination of Steps V. and V1, one arrives at the same mechanism as was proposed by Vannice (1975). In this case, the same procedure as was adopted above may be followed:

<u>STEP 1:</u> $\theta_H{}^2 \quad = \quad KP_{H_2}\theta^2$

<u>STEP 11:</u> $\theta_{CO} \quad = \quad K_{CO}\, P_{CO}\, \theta$

<u>STEP 111:</u> $\theta_{COH}.\theta \quad = \quad K\theta_{CO}\theta_H$

$$\theta_{COH} \quad = \quad K.\ \frac{\theta_{CO}\ \theta_H}{\theta}$$

<u>STEP 1V:</u> $\theta_{HCOH} \quad = \quad K.\ \frac{\theta_{CO}\ \theta_H}{\theta}$

$$= \quad K.\ \frac{\theta_{CO}\ \theta_H{}^2}{\theta^2}$$

$$r_{CH_4} = K. \theta_{HCOH} \cdot \theta_H^2$$

$$= K. \frac{\theta_{CO}\theta_H^2}{\theta^2} \; . \; \theta_H^2$$

$$= K. \frac{K_{CO}P_{CO}\,\theta \; . \; K\,P_{H_2}\,\theta^2 \; . \; K\,P_{H_2}\,\theta^2}{\theta^2}$$

$$= K. \; K_{CO}\,P_{CO} \, . \, P_{H_2}^2 \, . \, \theta^3$$

As before $\theta = \dfrac{1}{(1 + K_{CO}\,P_{CO})}$

$$\text{rate} = \frac{K_{CO}\,P_{CO}\,P_{H_2}^2}{(1 + K_{CO}\,P_{CO}^3}$$

Thus, by comparison with the Huang and Richardson model, $n = 2$, $m = 3$, which values did not give as satisfactory a fit to Huang and Richardson's methanation data.

APPENDIX 3

(a) Experimental Results Used for Rate Determinations.

```
                  RUN NUMBER=  2
                  --------------

PRESSURE= 800.000 KPA  TEMPERATURE=573.000 K  WHSV=  0.546  % CO CONVERSION= 72.197

------------------------------------------------------------------------------------------------------------
   COMPONENT   PARTIAL PRESSURE   MOLE       MOLE        MASS       MASS        RATE              SELECTIVE
                     KPA         %(TOTAL)   %(HC)      %(TOTAL)    %(HC)   KGMOL/MIN KG RU   RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------------

     C1            159.876       19.985     93.159      27.367     84.920     .37938E-01        .10000E 01
     C2              7.221        0.903      4.208       2.318      7.192     .17136E-02        .45168E-01
     C3              2.809        0.351      1.637       1.322      4.103     .66661E-03        .17571E-01
     C4              0.975        0.122      0.568       0.605      1.877     .23135E-03        .60982E-02
     C5              0.487        0.061      0.284       0.375      1.165     .11568E-03        .30491E-02
     C6              0.174        0.022      0.101       0.160      0.495     .41173E-04        .10853E-02
     C7              0.074        0.009      0.043       0.080      0.247     .17645E-04        .46512E-03
     C8              0.000        0.000      0.000       0.000      0.000     .0                .0
     C9              0.000        0.000      0.000       0.000      0.000     .0                .0
     C10             0.000        0.000      0.000       0.000      0.000     .0                .0
     C11             0.000        0.000      0.000       0.000      0.000     .0                .0
     C12             0.000        0.000      0.000       0.000      0.000     .0                .0
     CO             74.691        9.336      0.000      22.374      0.000     .46023E-01
     CO2             3.305        0.413      0.000       1.556      0.000     .78424E-03        .20672E-01
     H2O           187.340       23.418      0.000      36.076      0.000     .44455E-01        .11718E 01
     H2            363.047       45.381      0.000       7.768      0.000     .11030E 00
------------------------------------------------------------------------------------------------------------
HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 114.081   HYDROGEN IN FROM CARBON BALANCE= 103.482
MOLES OUT/MOLES IN=  0.730   VOLUMETRIC FEED= 169.313 ML/MIN AT NTP   USAGE RATE= .15632E 00   H2/CO USAGE= 2.397

                  RUN NUMBER=  3
                  --------------

PRESSURE= 800.000 KPA  TEMPERATURE=573.000 K  WHSV=  0.967  % CO CONVERSION= 47.692

------------------------------------------------------------------------------------------------------------
   COMPONENT   PARTIAL PRESSURE   MOLE       MOLE        MASS       MASS        RATE              SELECTIVE
                     KPA         %(TOTAL)   %(HC)      %(TOTAL)    %(HC)   KGMOL/MIN KG RU   RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------------

     C1             82.137       10.267     90.299      16.570     78.154     .40832E-01        .10000E 01
     C2              4.536        0.567      4.986       1.716      8.092     .22548E-02        .55221E-01
     C3              2.400        0.300      2.638       1.331      6.279     .11930E-02        .29217E-01
     C4              1.080        0.135      1.188       0.790      3.726     .53705E-03        .13153E-01
     C5              0.536        0.067      0.589       0.487      2.295     .26647E-03        .65261E-02
     C6              0.198        0.025      0.218       0.215      1.012     .98390E-04        .24096E-02
     C7              0.074        0.009      0.082       0.094      0.441     .36896E-04        .90361E-03
     C8              0.000        0.000      0.000       0.000      0.000     .0                .0
     C9              0.000        0.000      0.000       0.000      0.000     .0                .0
     C10             0.000        0.000      0.000       0.000      0.000     .0                .0
     C11             0.000        0.000      0.000       0.000      0.000     .0                .0
     C12             0.000        0.000      0.000       0.000      0.000     .0                .0
     CO            118.752       14.844      0.000      41.925      0.000     .53823E-01
     CO2             1.155        0.144      0.000       0.641      0.000     .57394E-03        .14056E-01
     H2O           105.961       13.245      0.000      24.049      0.000     .52676E-01        .12901E 01
     H2            483.172       60.396      0.000      12.184      0.000     .10759E 00
------------------------------------------------------------------------------------------------------------
HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  98.401   HYDROGEN IN FROM CARBON BALANCE=  87.450
MOLES OUT/MOLES IN=   0.863   VOLUMETRIC FEED= 299.234 ML/MIN AT NTP
```

```
                RUN NUMBER=  4
                --------------

PRESSURE= 800.000 KPA  TEMPERATURE=551.000 K  WHSV=  0.459  % CO CONVERSION= 39.373

------------------------------------------------------------------------------------------------------------------

  COMPONENT  PARTIAL PRESSURE  MOLE      MOLE       MASS      MASS       RATE              SELECTIVE
                  KPA         %(TOTAL)  %(HC)    %(TOTAL)   %(HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------------------

      C1        34.303         4.288    73.971     7.406    44.093    .87189E-02       .10000E 01
      C2         2.581         0.323     5.565     1.045     6.220    .65598E-03       .75236E-01
      C3         3.689         0.461     7.955     2.190    13.041    .93770E-03       .10755E 00
      C4         2.120         0.265     4.571     1.659     9.877    .53877E-03       .61792E-01
      C5         1.432         0.179     3.088     1.391     8.283    .36397E-03       .41745E-01
      C6         0.938         0.117     2.024     1.089     6.484    .23854E-03       .27356E-01
      C7         0.534         0.067     1.151     0.720     4.290    .13572E-03       .15566E-01
      C8         0.388         0.049     0.837     0.597     3.557    .98705E-04       .11321E-01
      C9         0.243         0.030     0.523     0.419     2.496    .61691E-04       .70755E-02
      C10        0.146         0.018     0.314     0.279     1.661    .37014E-04       .42453E-02
      C11        0.000         0.000     0.000     0.000     0.000    .0               .0
      C12        0.000         0.000     0.000     0.000     0.000    .0               .0
      CO       127.828        15.978     0.000    48.295     0.000    .21100E-01
      CO2        0.728         0.091     0.000     0.432     0.000    .18507E-03       .21226E-01
      H2O       81.559        10.195     0.000    19.809     0.000    .20730E-01       .23776E 01
      H2       543.511        67.939     0.000    14.668     0.000    .27001E-01
------------------------------------------------------------------------------------------------------------------
HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  94.216   HYDROGEN IN FROM CARBON BALANCE=  81.218
MOLES OUT/MOLES IN=   0.930   VOLUMETRIC FEED= 142.337 ML/MIN AT NTP   USAGE RATE= .48101E-01   H2/CO USAGE= 1.280

                RUN NUMBER=  5
                --------------

 PRESSURE= 800.000 KPA  TEMPERATURE=551.000 K  WHSV=  0.208  % CO CONVERSION= 77.725

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   COMPONENT  PARTIAL PRESSURE  MOLE      MOLE       MASS      MASS       RATE              SELECTIVE
                   KPA         %(TOTAL)  %(HC)    %(TOTAL)   %(HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------------------

       C1       133.302        16.663    84.174    21.818    63.965    .11517E-01       .10000E 01
       C2         9.240         1.155     5.835     2.836     8.314    .79831E-03       .69318E-01
       C3         7.903         0.988     4.991     3.557    10.429    .68281E-03       .59288E-01
       C4         3.592         0.449     2.268     2.131     6.248    .31030E-03       .26944E-01
       C5         2.057         0.257     1.299     1.515     4.441    .17771E-03       .15430E-01
       C6         1.179         0.147     0.744     1.037     3.040    .10184E-03       .88427E-02
       C7         0.617         0.077     0.390     0.631     1.851    .53312E-04       .46291E-02
       C8         0.261         0.033     0.165     0.304     0.893    .22555E-04       .19585E-02
       C9         0.214         0.027     0.135     0.280     0.820    .18454E-04       .16024E-02
       C10        0.000         0.000     0.000     0.000     0.000    .0               .0
       C11        0.000         0.000     0.000     0.000     0.000    .0               .0
       C12        0.000         0.000     0.000     0.000     0.000    .0               .0
       CO        62.656         7.832     0.000    17.946     0.000    .18889E-01
       CO2        3.085         0.386     0.000     1.389     0.000    .26656E-03       .23145E-01
       H2O      212.460        26.557     0.000    39.121     0.000    .18356E-01       .15938E 01
       H2       363.435        45.429     0.000     7.436     0.000    .43491E-01
------------------------------------------------------------------------------------------------------------------

 HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 118.726   HYDROGEN IN FROM CARBON BALANCE= 108.353
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          RUN NUMBER=  6
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PRESSURE= 800.000 KPA  TEMPERATURE=551.000 K  WHSV=  0.344  % CO CONVERSION= 64.984

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    COMPONENT   PARTIAL PRESSURE   MOLE       MOLE        MASS       MASS        RATE              SELECTIVE
                      KPA        %(TOTAL)   %(HC)       %(TOTAL)    %(HC)   KGMOL/MIN KG RU   RATES (REL TO CH4)

--------------------------------------------------------------------------------------------------------------

       C1           86.520        10.815    78.121      14.563     51.031     .12564E-01      .10000E 01
       C2            6.493         0.812     5.863       2.049      7.181     .94295E-03      .75049E-01
       C3            7.258         0.907     6.554       3.360     11.773     .10540E-02      .83890E-01
       C4            4.029         0.504     3.637       2.458      8.613     .58502E-03      .46562E-01
       C5            2.584         0.323     2.333       1.957      6.858     .37520E-03      .29862E-01
       C6            1.632         0.204     1.473       1.476      5.173     .23697E-03      .18861E-01
       C7            0.935         0.117     0.844       0.983      3.446     .13576E-03      .10806E-01
       C8            0.535         0.067     0.483       0.642      2.250     .77756E-04      .61886E-02
       C9            0.637         0.080     0.576       0.858      3.008     .92567E-04      .73674E-02
       C10           0.127         0.016     0.115       0.190      0.667     .18513E-04      .14735E-02
       C11           0.000         0.000     0.000       0.000      0.000     .0              .0
       C12           0.000         0.000     0.000       0.000      0.000     .0              .0
       CO           96.889        12.111     0.000      28.539      0.000     .26112E-01
       CO2           1.870         0.234     0.000       0.865      0.000     .27153E-03      .21611E-01
       H2O         176.075        22.009     0.000      33.340      0.000     .25569E-01      .20351E 01
       H2          414.414        51.802     0.000       8.719      0.000     .63647E-01
--------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 109.898   HYDROGEN IN FROM CARBON BALANCE= 106.588
MOLES OUT/MOLES IN=   0.708   VOLUMETRIC FEED= 109.664 ML/MIN AT NTP   USAGE RATE= .89760E-01   H2/CO USAGE= 2.437


          RUN NUMBER=  7
          --------------

PRESSURE= 800.000 KPA  TEMPERATURE=528.000 K  WHSV=  0.472  % CO CONVERSION= 12.955

--------------------------------------------------------------------------------------------------------------

    COMPONENT   PARTIAL PRESSURE   MOLE       MOLE        MASS       MASS        RATE              SELECTIVE
                      KPA        %(TOTAL)   %(HC)       %(TOTAL)    %(HC)   KGMOL/MIN KG RU   RATES (REL TO CH4)

--------------------------------------------------------------------------------------------------------------

       C1            7.342         0.918    64.000       1.660     29.922     .19544E-02      .10000E 01
       C2            0.541         0.068     4.720       0.229      4.138     .14414E-03      .73750E-01
       C3            0.844         0.106     7.360       0.525      9.463     .22475E-03      .11500E 00
       C4            0.789         0.099     6.880       0.647     11.660     .21010E-03      .10750E 00
       C5            0.597         0.075     5.200       0.607     10.940     .15879E-03      .81250E-01
       C6            0.670         0.084     5.840       0.814     14.676     .17834E-03      .91250E-01
       C7            0.303         0.038     2.640       0.428      7.714     .80618E-04      .41250E-01
       C8            0.303         0.038     2.640       0.488      8.794     .80618E-04      .41250E-01
       C9            0.083         0.010     0.720       0.149      2.693     .21987E-04      .11250E-01
       C10           0.000         0.000     0.000       0.000      0.000     .0              .0
       C11           0.000         0.000     0.000       0.000      0.000     .0              .0
       C12           0.000         0.000     0.000       0.000      0.000     .0              .0
       CO          179.885        22.486     0.000      71.154      0.000     .71262E-02
       CO2           0.367         0.046     0.000       0.228      0.000     .97719E-04      .50000E-01
       H2O          26.037         3.255     0.000       6.621      0.000     .69307E-02      .35463E 01
       H2          582.239        72.780     0.000      16.450      0.000     .14534E-01
--------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  80.769   HYDROGEN IN FROM CARBON BALANCE=  79.605
MOLES OUT/MOLES IN=   0.948   VOLUMETRIC FEED= 147.360 ML/MIN AT NTP   USAGE RATE= .21660E-01
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                    RUN NUMBER=  8
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PRESSURE= 800.000 KPA  TEMPERATURE=528.000 K  WHSV=  0.178  % CO CONVERSION= 55.449

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   COMPONENT   PARTIAL PRESSURE   MOLE       MOLE       MASS       MASS        RATE              SELECTIVE
                     KPA         %(TOTAL)   %(HC)     %(TOTAL)    %(HC)   KGMOL/MIN KG RU   RATES (REL TO CH4)

-----------------------------------------------------------------------------------------------------------------------

       C1           30.655        3.832    61.149      5.647     24.163     .25397E-02        .10000E 01
       C2            2.168        0.271     4.325      0.749      3.204     .17962E-03        .70725E-01
       C3            3.359        0.420     6.700      1.702      7.280     .27826E-03        .10957E 00
       C4            2.986        0.373     5.955      1.994      8.530     .24734E-03        .97391E-01
       C5            2.506        0.313     4.998      2.077      8.888     .20759E-03        .81739E-01
       C6            2.195        0.274     4.378      2.173      9.298     .18182E-03        .71594E-01
       C7            1.653        0.207     3.297      1.903      8.142     .13692E-03        .53913E-01
       C8            1.253        0.157     2.499      1.644      7.036     .10379E-03        .40870E-01
       C9            1.413        0.177     2.818      2.082      8.909     .11705E-03        .46087E-01
       C10           0.960        0.120     1.914      1.569      6.713     .79502E-04        .31304E-01
       C11           0.613        0.077     1.223      1.101      4.712     .50793E-04        .20000E-01
       C12           0.373        0.047     0.744      0.730      3.125     .30918E-04        .12174E-01
       CO          111.958       13.995     0.000     36.094      0.000     .11544E-01
       CO2           1.511        0.189     0.000      0.765      0.000     .12514E-03        .49275E-01
       H2O         136.322       17.040     0.000     28.253      0.000     .11294E-01        .44470E 01
       H2          500.078       62.510     0.000     11.516      0.000     .22728E-01
-----------------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 103.046   HYDROGEN IN FROM CARBON BALANCE=  96.802

MOLES OUT/MOLES IN=  0.780   VOLUMETRIC FEED=  54.535 ML/MIN AT NTP   USAGE RATE= .34272E-01   H2/CO USAGE= 1.969


                    RUN NUMBER=  9
                    --------------

PRESSURE= 800.000 KPA  TEMPERATURE=528.000 K  WHSV=  0.153  % CO CONVERSION= 54.497

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   COMPONENT   PARTIAL PRESSURE   MOLE       MOLE       MASS       MASS        RATE              SELECTIVE
                     KPA         %(TOTAL)   %(HC)     %(TOTAL)    %(HC)   KGMOL/MIN KG RU   RATES (REL TO CH4)

-----------------------------------------------------------------------------------------------------------------------

       C1           35.654        4.457    65.400      6.688     29.054     .25879E-02        .10000E 01
       C2            2.511        0.314     4.605      0.883      3.836     .18224E-03        .70419E-01
       C3            3.080        0.385     5.650      1.589      6.902     .22356E-03        .86387E-01
       C4            3.257        0.407     5.975      2.215      9.622     .23644E-03        .91361E-01
       C5            2.697        0.337     4.948      2.277      9.891     .19579E-03        .75654E-01
       C6            2.249        0.281     4.126      2.268      9.852     .16327E-03        .63089E-01
       C7            1.652        0.207     3.030      1.937      8.414     .11991E-03        .46335E-01
       C8            1.316        0.165     2.414      1.759      7.641     .95523E-04        .36911E-01
       C9            0.868        0.109     1.592      1.303      5.659     .63004E-04        .24346E-01
       C10           0.924        0.116     1.695      1.538      6.683     .67069E-04        .25916E-01
       C11           0.308        0.039     0.565      0.563      2.447     .22356E-04        .86387E-02
       C12           0.000        0.000     0.000      0.000      0.000     .0                .0
       CO          112.002       14.000     0.000     36.767      0.000     .97365E-02
       CO2           1.680        0.210     0.000      0.867      0.000     .12194E-03        .47120E-01
       H2O         130.781       16.348     0.000     27.599      0.000     .94927E-02        .36681E 01
       H2          501.021       62.628     0.000     11.748      0.000     .18690E-01
-----------------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 102.347   HYDROGEN IN FROM CARBON BALANCE=  94.815

MOLES OUT/MOLES IN=  0.796   VOLUMETRIC FEED=  49.086 ML/MIN AT NTP   USAGE RATE= .28427E-01   H2/CO USAGE= 1.920
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                RUN NUMBER= 12
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PRESSURE= 800.000 KPA  TEMPERATURE=529.000 K  WHSV=  0.195  % CO CONVERSION= 56.999

----------------------------------------------------------------------------------------------------------------
   COMPONENT  PARTIAL PRESSURE   MOLE      MOLE       MASS      MASS        RATE              SELECTIVE
                    KPA        %(TOTAL)  %(HC)     %(TOTAL)   %(HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

----------------------------------------------------------------------------------------------------------------
        C1         34.032         4.254    61.089     5.901    24.299     .30113E-02       .10000E 01
        C2          2.436         0.304     4.373     0.792     3.261     .21554E-03       .71576E-01
        C3          4.010         0.501     7.198     1.912     7.874     .35482E-03       .11783E 00
        C4          3.122         0.390     5.604     1.962     8.080     .27623E-03       .91731E-01
        C5          2.832         0.354     5.083     2.210     9.098     .25056E-03       .83204E-01
        C6          2.445         0.306     4.388     2.279     9.382     .21632E-03       .71835E-01
        C7          2.058         0.257     3.694     2.230     9.183     .18208E-03       .60465E-01
        C8          1.451         0.181     2.605     1.793     7.381     .12839E-03       .42636E-01
        C9          1.082         0.135     1.942     1.500     6.178     .95709E-04       .31783E-01
        C10         1.082         0.135     1.942     1.665     6.854     .95709E-04       .31783E-01
        C11         0.633         0.079     1.137     1.070     4.408     .56025E-04       .18605E-01
        C12         0.528         0.066     0.947     0.972     4.003     .46687E-04       .15504E-01
        CO        116.080        14.510     0.000    35.225     0.000     .13615E-01
        CO2         1.759         0.220     0.000     0.839     0.000     .15562E-03       .51680E-01
        H20       150.350        18.794     0.000    29.330     0.000     .13304E-01       .44178E 01
        H2        476.103        59.513     0.000    10.320     0.000     .26928E-01
----------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 104.284   HYDROGEN IN FROM CARBON BALANCE=  9'.554
MOLES OUT/MOLES IN=   0.762   VOLUMETRIC FEED=  57.669 ML/MIN AT NTP   USAGE RATE= .40543E-01   H2/CO USAGE= 1.978

                RUN NUMBER= 16
                --------------

PRESSURE=1200.000 KPA  TEMPERATURE=573.000 K  WHSV=  0.526  % CO CONVERSION= 53.988

----------------------------------------------------------------------------------------------------------------
   COMPONENT  PARTIAL PRESSURE   MOLE      MOLE       MASS      MASS        RATE              SELECTIVE
                    KPA        %(TOTAL)  %(HC)     %(TOTAL)   %(HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

----------------------------------------------------------------------------------------------------------------
        C1        148.561        12.380    88.058    17.446    71.682     .23983E-01       .10000E 01
        C2          9.638         0.803     5.713     2.122     8.720     .15560E-02       .64878E-01
        C3          3.285         0.274     1.947     1.061     4.359     .53035E-03       .22114E-01
        C4          3.599         0.300     2.133     1.532     6.295     .58105E-03       .24228E-01
        C5          1.908         0.159     1.131     1.008     4.144     .30807E-03       .12846E-01
        C6          1.027         0.086     0.609     0.648     2.663     .16573E-03       .69106E-02
        C7          0.544         0.045     0.322     0.399     1.639     .87742E-04       .36585E-02
        C8          0.145         0.012     0.086     0.121     0.498     .23398E-04       .97561E-03
        C9          0.000         0.000     0.000     0.000     0.000     .0               .0
        C10         0.000         0.000     0.000     0.000     0.000     .0               .0
        C11         0.000         0.000     0.000     0.000     0.000     .0               .0
        C12         0.000         0.000     0.000     0.000     0.000     .0               .0
        CO        183.588        15.299     0.000    37.728     0.000     .34775E-01
        CO2         2.657         0.221     0.000     0.858     0.000     .42896E-03       .17886E-01
        H20       210.099        17.508     0.000    27.756     0.000     .33917E-01       .14142E 01
        H2        634.948        52.912     0.000     9.320     0.000     .83717E-01
----------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 102.209   HYDROGEN IN FROM CARBON BALANCE=  96.128
MOLES OUT/MOLES IN=   0.773   VOLUMETRIC FEED= 158.881 ML/MIN AT NTP   USAGE RATE= .11849E 00   H2/CO USAGE= 2.407
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            RUN NUMBER= 17
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PRESSURE=1200.000 KPA  TEMPERATURE=571.000 K  WHSV=  0.425  % CO CONVERSION= 95.860

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   COMPONENT  PARTIAL PRESSURE  MOLE      MOLE     MASS      MASS      RATE            SELECTIVE
                   KPA          %(TOTAL)  %(HC)    %(TOTAL)  %(HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

-------------------------------------------------------------------------------------------------

     C1          473.366        39.447    99.637   41.320    99.322    .45670E-01      .10000E 01
     C2            1.724         0.144     0.363    0.282     0.678    .16635E-03      .36426E-02
     C3            0.000         0.000     0.000    0.000     0.000    .0              .0
     C4            0.000         0.000     0.000    0.000     0.000    .0              .0
     C5            0.000         0.000     0.000    0.000     0.000    .0              .0
     C6            0.000         0.000     0.000    0.000     0.000    .0              .0
     C7            0.000         0.000     0.000    0.000     0.000    .0              .0
     C8            0.000         0.000     0.000    0.000     0.000    .0              .0
     C9            0.000         0.000     0.000    0.000     0.000    .0              .0
     C10           0.000         0.000     0.000    0.000     0.000    .0              .0
     C11           0.000         0.000     0.000    0.000     0.000    .0              .0
     C12           0.000         0.000     0.000    0.000     0.000    .0              .0
     CO           22.329         1.861     0.000    3.411     0.000    .49880E-01
     CO2          40.191         3.349     0.000    9.648     0.000    .38776E-02      .84906E-01
     H2O         436.623        36.385     0.000   42.876     0.000    .42125E-01      .92238E 00
     H2          225.767        18.814     0.000    2.463     0.000    .12865E 00
-------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 134.525   HYDROGEN IN FROM CARBON BALANCE= 129.937
MOLES OUT/MOLES IN=   0.572   VOLUMETRIC FEED= 125.174 ML/MIN AT NTP   USAGE RATE= .17853E 00   H2/CO USAGE= 2.579

            RUN NUMBER= 18
            --------------

PRESSURE=1200.000 KPA  TEMPERATURE=571.000 K  WHSV=  0.548  % CO CONVERSION= 61.491

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   COMPONENT  PARTIAL PRESSURE  MOLE      MOLE     MASS      MASS      RATE            SELECTIVE
                   KPA          %(TOTAL)  %(HC)    %(TOTAL)  %(HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

-------------------------------------------------------------------------------------------------

     C1          179.060        14.922    88.377   20.143    72.743    .28855E-01      .10000E 01
     C2           11.775         0.981     5.812    2.484     8.969    .18975E-02      .65758E-01
     C3            3.766         0.314     1.859    1.165     4.208    .60695E-03      .21034E-01
     C4            4.042         0.337     1.995    1.648     5.952    .65131E-03      .22572E-01
     C5            2.215         0.185     1.093    1.121     4.049    .35691E-03      .12369E-01
     C6            1.264         0.105     0.624    0.764     2.760    .20366E-03      .70580E-02
     C7            0.263         0.022     0.130    0.185     0.667    .42345E-04      .14675E-02
     C8            0.225         0.019     0.111    0.181     0.652    .36296E-04      .12579E-02
     C9            0.000         0.000     0.000    0.000     0.000    .0              .0
     C10           0.000         0.000     0.000    0.000     0.000    .0              .0
     C11           0.000         0.000     0.000    0.000     0.000    .0              .0
     C12           0.000         0.000     0.000    0.000     0.000    .0              .0
     CO          160.165        13.347     0.000   31.530     0.000    .41214E-01
     CO2           3.378         0.282     0.000    1.045     0.000    .54444E-03      .18868E-01
     H2O         248.994        20.750     0.000   31.511     0.000    .40125E-01      .13906E 01
     H2          584.853        48.738     0.000    8.224     0.000    .99522E-01
-------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 107.402   HYDROGEN IN FROM CARBON BALANCE= 100.203
MOLES OUT/MOLES IN=   0.741   VOLUMETRIC FEED= 159.773 ML/MIN AT NTP   USAGE RATE= .14074E 00   H2/CO USAGE= 2.415
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                    RUN NUMBER= 19
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PRESSURE=1200.000 KPA   TEMPERATURE=571.000 K   WHSV=  0.662   % CO CONVERSION= 60.197

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   COMPONENT   PARTIAL PRESSURE   MOLE       MOLE        MASS        MASS         RATE                SELECTIVE
                     KPA          %(TOTAL)   %(HC)       %(TOTAL)    %(HC)   KGMOL/MIN KG RU    RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------------------

      C1          161.369          13.447     85.482      18.023     66.513     .31109E-01         .10000E 01
      C2           11.008           0.917      5.831       2.305      8.507     .21220E-02         .68213E-01
      C3            7.263           0.605      3.848       2.231      8.233     .14003E-02         .45012E-01
      C4            4.393           0.366      2.327       1.779      6.564     .84689E-03         .27224E-01
      C5            2.434           0.203      1.289       1.223      4.514     .46916E-03         .15081E-01
      C6            1.298           0.108      0.688       0.779      2.876     .25022E-03         .80433E-02
      C7            0.636           0.053      0.337       0.444      1.640     .12270E-03         .39443E-02
      C8            0.225           0.019      0.119       0.179      0.660     .43307E-04         .13921E-02
      C9            0.150           0.012      0.079       0.134      0.494     .28871E-04         .92807E-03
      C10           0.000           0.000      0.000       0.000      0.000     .0                 .0
      C11           0.000           0.000      0.000       0.000      0.000     .0                 .0
      C12           0.000           0.000      0.000       0.000      0.000     .0                 .0
      CO          167.235          13.936      0.000      32.687      0.000     .48759E-01
      CO2           2.621           0.218      0.000       0.805      0.000     .50525E-03         .16241E-01
      H2O         247.683          20.640      0.000      31.122      0.000     .47748E-01         .15349E 01
      H2          593.685          49.474      0.000       8.289      0.000     .11972E 00

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HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 106.704   HYDROGEN IN FROM CARBON BALANCE= 101.225
MOLES OUT/MOLES IN=   0.734   VOLUMETRIC FEED= 183.554 ML/MIN AT NTP   USAGE RATE= .16848E 00   H2/CO USAGE= 2.455

                    RUN NUMBER= 20
                    --------------

PRESSURE=1200.000 KPA   TEMPERATURE=569.000 K   WHSV=  0.901   % CO CONVERSION= 41.168

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   COMPONENT   PARTIAL PRESSURE   MOLE       MOLE        MASS        MASS         RATE                SELECTIVE
                     KPA          %(TOTAL)   %(HC)       %(TOTAL)    %(HC)   KGMOL/MIN KG RU    RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------------------

      C1          101.270           8.439     86.976      13.115     70.781     .30997E-01         .10000E 01
      C2            7.144           0.595      6.136       1.735      9.362     .21866E-02         .70543E-01
      C3            3.729           0.311      3.203       1.328      7.167     .11414E-02         .36822E-01
      C4            2.185           0.182      1.877       1.026      5.536     .66880E-03         .21576E-01
      C5            1.400           0.117      1.202       0.816      4.403     .42851E-03         .13824E-01
      C6            0.550           0.046      0.472       0.383      2.064     .16820E-03         .54264E-02
      C7            0.157           0.013      0.135       0.127      0.686     .48058E-04         .15504E-02
      C8            0.000           0.000      0.000       0.000      0.000     .0                 .0
      C9            0.000           0.000      0.000       0.000      0.000     .0                 .0
      C10           0.000           0.000      0.000       0.000      0.000     .0                 .0
      C11           0.000           0.000      0.000       0.000      0.000     .0                 .0
      C12           0.000           0.000      0.000       0.000      0.000     .0                 .0
      CO          211.961          17.663      0.000      48.037      0.000     .45398E-01
      CO2           1.439           0.120      0.000       0.513      0.000     .44053E-03         .14212E-01
      H2O         145.442          12.120      0.000      21.190      0.000     .44517E-01         .14362E 01
      H2          724.723          60.394      0.000      11.732      0.000     .96988E-01

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HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  94.457   HYDROGEN IN FROM CARBON BALANCE=  86.799
MOLES OUT/MOLES IN=   0.856   VOLUMETRIC FEED= 260.474 ML/MIN AT NTP   USAGE RATE= .14239E 00   H2/CO USAGE= 2.136
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                 RUN NUMBER= 21
                 --------------

PRESSURE=1200.000 KPA  TEMPERATURE=548.000 K  WHSV=  0.747  % CO CONVERSION= 33.869

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  COMPONENT   PARTIAL PRESSURE   MOLE       MOLE       MASS       MASS        RATE              SELECTIVE
                    KPA        %(TOTAL)    %(HC)     %(TOTAL)    %(HC)   KGMOL/MIN KG RU   RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------------------

     C1           39.266         3.272     69.899     4.999     33.764     .96478E-02         .10000E 01
     C2            2.499         0.208      4.448     0.596      4.029     .61395E-03         .63636E-01
     C3            2.697         0.225      4.801     0.944      6.378     .66267E-03         .68687E-01
     C4            2.922         0.243      5.201     1.348      9.107     .71790E-03         .74411E-01
     C5            2.380         0.198      4.236     1.363      9.208     .58471E-03         .60606E-01
     C6            2.023         0.169      3.601     1.384      9.349     .49701E-03         .51515E-01
     C7            1.349         0.112      2.401     1.073      7.247     .33134E-03         .34343E-01
     C8            1.031         0.086      1.836     0.935      6.318     .25338E-03         .26263E-01
     C9            1.296         0.108      2.306     1.320      8.913     .31834E-03         .32997E-01
     C10           0.397         0.033      0.706     0.448      3.027     .97452E-04         .10101E-01
     C11           0.317         0.026      0.565     0.394      2.660     .77962E-04         .80808E-02
     C12           0.000         0.000      0.000     0.000      0.000     .0                 .0
     CO          245.910        20.492      0.000    54.787      0.000     .30944E-01
     CO2           1.058         0.088      0.000     0.370      0.000     .25987E-03         .26936E-01
     H2O         123.827        10.319      0.000    17.735      0.000     .30425E-01         .31535E 01
     H2          773.029        64.419      0.000    12.302      0.000     .74206E-01

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HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  89.826   HYDROGEN IN FROM CARBON BALANCE=  89.587
MOLES OUT/MOLES IN=   0.829   VOLUMETRIC FEED= 220.981 ML/MIN AT NTP   USAGE RATE= .10515E 00   H2/CO USAGE= 2.398

                 RUN NUMBER= 22
                 --------------

PRESSURE=1200.000 KPA  TEMPERATURE=600.000 K  WHSV=  0.860  % CO CONVERSION= 96.165

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  COMPONENT   PARTIAL PRESSURE   MOLE       MOLE       MASS       MASS        RATE              SELECTIVE
                    KPA        %(TOTAL)    %(HC)     %(TOTAL)    %(HC)   KGMOL/MIN KG RU   RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------------------

     C1          529.743        44.145     99.986    42.813     99.974     .94856E-01         .10000E 01
     C2            0.073         0.006      0.014     0.011      0.026     .13016E-04         .13722E-03
     C3            0.000         0.000      0.000     0.000      0.000     .0                 .0
     C4            0.000         0.000      0.000     0.000      0.000     .0                 .0
     C5            0.000         0.000      0.000     0.000      0.000     .0                 .0
     C6            0.000         0.000      0.000     0.000      0.000     .0                 .0
     C7            0.000         0.000      0.000     0.000      0.000     .0                 .0
     C8            0.000         0.000      0.000     0.000      0.000     .0                 .0
     C9            0.000         0.000      0.000     0.000      0.000     .0                 .0
     C10           0.000         0.000      0.000     0.000      0.000     .0                 .0
     C11           0.000         0.000      0.000     0.000      0.000     .0                 .0
     C12           0.000         0.000      0.000     0.000      0.000     .0                 .0
     CO           22.535         1.878      0.000     3.187      0.000     .10118E 00
     CO2          35.183         2.932      0.000     7.819      0.000     .62999E-02         .66415E-01
     H2O         494.706        41.225      0.000    44.979      0.000     .88582E-01         .93386E 00
     H2          117.761         9.813      0.000     1.190      0.000     .28310E 00

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HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 139.348   HYDROGEN IN FROM CARBON BALANCE= 141.567
MOLES OUT/MOLES IN=   0.525   VOLUMETRIC FEED= 248.983 ML/MIN AT NTP   USAGE RATE= .38428E 00   H2/CO USAGE= 2.798
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                RUN NUMBER= 23
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PRESSURE=1200.000 KPA  TEMPERATURE=577.000 K  WHSV=  0.602  % CO CONVERSION= 64.423

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   COMPONENT  PARTIAL PRESSURE   MOLE      MOLE      MASS      MASS        RATE            SELECTIVE
                   KPA         %(TOTAL)   %(HC)    %(TOTAL)   %(HC)   KGMOL/MIN KG RU  RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------------

     C1          222.189        18.516    89.899    22.732    77.094    .35303E-01       .10000E 01
     C2           12.676         1.056     5.129     2.432     8.247    .20141E-02       .57052E-01
     C3            6.628         0.552     2.682     1.865     6.325    .10531E-02       .29832E-01
     C4            3.095         0.258     1.252     1.148     3.893    .49174E-03       .13929E-01
     C5            1.522         0.127     0.616     0.701     2.376    .24177E-03       .68485E-02
     C6            0.735         0.061     0.297     0.404     1.371    .11679E-03       .33082E-02
     C7            0.232         0.019     0.094     0.148     0.503    .36881E-04       .10447E-02
     C8            0.077         0.006     0.031     0.056     0.191    .12294E-04       .34823E-03
     C9            0.000         0.000     0.000     0.000     0.000    .0               .0
     C10           0.000         0.000     0.000     0.000     0.000    .0               .0
     C11           0.000         0.000     0.000     0.000     0.000    .0               .0
     C12           0.000         0.000     0.000     0.000     0.000    .0               .0
     CO          165.062        13.755     0.000    29.553     0.000    .47490E-01
     CO2           4.823         0.402     0.000     1.357     0.000    .76630E-03       .21706E-01
     H2O         289.245        24.104     0.000    33.291     0.000    .45957E-01       .13018E 01
     H2          493.716        41.143     0.000     6.314     0.000    .13467E 00
------------------------------------------------------------------------------------------------------------
HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 110.349   HYDROGEN IN FROM CARBON BALANCE= 111.776
MOLES OUT/MOLES IN=  0.665   VOLUMETRIC FEED= 178.296 ML/MIN AT NTP   USAGE RATE= .18216E 00   H2/CO USAGE= 2.836
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                RUN NUMBER= 24
                --------------

PRESSURE=1200.000 KPA  TEMPERATURE=548.000 K  WHSV=  0.464  % CO CONVERSION= 41.394

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   COMPONENT  PARTIAL PRESSURE   MOLE      MOLE      MASS      MASS        RATE            SELECTIVE
                   KPA         %(TOTAL)   %(HC)    %(TOTAL)   %(HC)   KGMOL/MIN KG RU  RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------------

     C1           60.660         5.055    72.590     7.156    39.087    .85232E-02       .10000E 01
     C2            4.291         0.358     5.134     0.949     5.184    .60286E-03       .70732E-01
     C3            4.371         0.364     5.231     1.418     7.746    .61420E-03       .72062E-01
     C4            4.089         0.341     4.893     1.748     9.551    .57451E-03       .67406E-01
     C5            3.376         0.281     4.040     1.792     9.789    .47435E-03       .55654E-01
     C6            2.502         0.208     2.994     1.586     8.665    .35151E-03       .41242E-01
     C7            1.816         0.151     2.173     1.339     7.313    .25513E-03       .29933E-01
     C8            1.089         0.091     1.304     0.916     5.002    .15308E-03       .17960E-01
     C9            0.565         0.047     0.676     0.533     2.912    .79373E-04       .93126E-02
     C10           0.565         0.047     0.676     0.591     3.231    .79373E-04       .93126E-02
     C11           0.242         0.020     0.290     0.278     1.521    .34017E-04       .39911E-02
     C12           0.000         0.000     0.000     0.000     0.000    .0               .0
     CO          236.724        19.727     0.000    48.868     0.000    .23493E-01
     CO2           1.775         0.148     0.000     0.576     0.000    .24946E-03       .29268E-01
     H2O         163.649        13.637     0.000    21.717     0.000    .22994E-01       .26978E 01
     H2          714.286        59.524     0.000    10.532     0.000    .63716E-01
------------------------------------------------------------------------------------------------------------
HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  93.910   HYDROGEN IN FROM CARBON BALANCE=  97.313
MOLES OUT/MOLES IN=  0.764   VOLUMETRIC FEED= 134.054 ML/MIN AT NTP   USAGE RATE= .87209E-01   H2/CO USAGE= 2.712
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                 RUN NUMBER= 26
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PRESSURE=1200.000 KPA  TEMPERATURE=545.000 K  WHSV=  0.341  % CO CONVERSION= 57.458

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   COMPONENT  PARTIAL PRESSURE  MOLE     MOLE      MASS      MASS       RATE            SELECTIVE
                   KPA        %(TOTAL) %(HC)    %(TOTAL)  %(HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

-------------------------------------------------------------------------------------------------------

      C1          89.052        7.421   72.046    9.814   39.055   .86618E-02        .10000E 01
      C2           6.583        0.549    5.326    1.360    5.413   .64028E-03        .73920E-01
      C3           7.181        0.598    5.810    2.176    8.661   .69849E-03        .80640E-01
      C4           6.013        0.501    4.865    2.402    9.559   .58485E-03        .67520E-01
      C5           5.030        0.419    4.069    2.494    9.926   .48922E-03        .56480E-01
      C6           3.676        0.306    2.974    2.178    8.665   .35756E-03        .41280E-01
      C7           2.907        0.242    2.352    2.002    7.967   .28272E-03        .32640E-01
      C8           1.795        0.150    1.452    1.410    5.610   .17462E-03        .20160E-01
      C9           0.641        0.053    0.519    0.565    2.250   .62365E-04        .72000E-02
      C10          0.556        0.046    0.450    0.544    2.163   .54050E-04        .62400E-02
      C11          0.171        0.014    0.138    0.184    0.731   .16631E-04        .19200E-02
      C12          0.000        0.000    0.000    0.000    0.000   .0                .0
      CO         182.379       15.198    0.000   35.174    0.000   .23959E-01
      CO2          3.391        0.283    0.000    1.028    0.000   .32984E-03        .38080E-01
      H2O        239.544       19.962    0.000   29.699    0.000   .23300E-01        .26899E 01
      H2         651.081       54.257    0.000    8.969    0.000   .57225E-01
-------------------------------------------------------------------------------------------------------
HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 104.764   HYDROGEN IN FROM CARBON BALANCE= 103.284
MOLES OUT/MOLES IN=   0.719   VOLUMETRIC FEED= 101.765 ML/MIN AT NTP   USAGE RATE= .81184E-01   H2/CO USAGE= 2.388

                  RUN NUMBER= 27
                  --------------

PRESSURE=1200.000 KPA  TEMPERATURE=548.000 K  WHSV=  0.653  % CO CONVERSION= 40.025

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   COMPONENT  PARTIAL PRESSURE  MOLE     MOLE      MASS      MASS       RATE            SELECTIVE
                   KPA        %(TOTAL) %(HC)    %(TOTAL)  %(HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

-------------------------------------------------------------------------------------------------------

      C1          55.104        4.592   71.696    6.747   38.303   .11392E-01        .10000E 01
      C2           4.145        0.345    5.394    0.952    5.403   .85700E-03        .75230E-01
      C3           4.132        0.344    5.376    1.391    7.899   .85424E-03        .74988E-01
      C4           4.132        0.344    5.376    1.834   10.412   .85424E-03        .74988E-01
      C5           3.146        0.262    4.093    1.733    9.840   .65033E-03        .57088E-01
      C6           2.359        0.197    3.070    1.553    8.815   .48774E-03        .42816E-01
      C7           1.440        0.120    1.873    1.102    6.254   .29761E-03        .26125E-01
      C8           1.000        0.083    1.301    0.872    4.951   .20667E-03        .18142E-01
      C9           0.840        0.070    1.093    0.823    4.670   .17360E-03        .15239E-01
      C10          0.560        0.047    0.728    0.608    3.454   .11574E-03        .10160E-01
      C11          0.000        0.000    0.000    0.000    0.000   .0                .0
      C12          0.000        0.000    0.000    0.000    0.000   .0                .0
      CO         231.933       19.328    0.000   49.694    0.000   .31998E-01
      CO2          1.346        0.112    0.000    0.453    0.000   .27832E-03        .24432E-01
      H2O        152.089       12.674    0.000   20.948    0.000   .31442E-01        .27600E 01
      H2         737.774       61.481    0.000   11.291    0.000   .78607E-01
-------------------------------------------------------------------------------------------------------
HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  93.346   HYDROGEN IN FROM CARBON BALANCE=  93.168
MOLES OUT/MOLES IN=   0.797   VOLUMETRIC FEED= 193.712 ML/MIN AT NTP   USAGE RATE= .11061E 00   H2/CO USAGE= 2.457
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              RUN NUMBER= 28
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PRESSURE=1200.000 KPA  TEMPERATURE=573.000 K  WHSV=  0.443  % CO CONVERSION= 76.998

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   COMPONENT   PARTIAL PRESSURE   MOLE       MOLE      MASS       MASS       RATE            SELECTIVE
                     KPA        %(TOTAL)   %(HC)    %(TOTAL)    %(HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

--------------------------------------------------------------------------------------------------------

      C1          255.883        21.324    90.512    26.963    78.366    .31483E-01      .10000E 01
      C2           14.770         1.231     5.225     2.918     8.481    .18173E-02      .57722E-01
      C3            5.555         0.463     1.965     1.610     4.679    .68349E-03      .21710E-01
      C4            3.433         0.286     1.214     1.311     3.811    .42241E-03      .13417E-01
      C5            1.884         0.157     0.666     0.893     2.596    .23174E-03      .73608E-02
      C6            0.787         0.066     0.278     0.446     1.295    .96803E-04      .30748E-02
      C7            0.322         0.027     0.114     0.212     0.616    .39601E-04      .12579E-02
      C8            0.072         0.006     0.025     0.054     0.156    .88003E-05      .27952E-03
      C9            0.000         0.000     0.000     0.000     0.000    .0              .0
      C10           0.000         0.000     0.000     0.000     0.000    .0              .0
      C11           0.000         0.000     0.000     0.000     0.000    .0              .0
      C12           0.000         0.000     0.000     0.000     0.000    .0              .0
      CO          101.328         8.444     0.000    18.685     0.000    .41732E-01
      CO2           6.402         0.533     0.000     1.855     0.000    .78763E-03      .25017E-01
      H2O         326.384        27.199     0.000    38.690     0.000    .40157E-01      .12755E 01
      H2          483.181        40.265     0.000     6.364     0.000    .97245E-01
--------------------------------------------------------------------------------------------------------
HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 113.755   HYDROGEN IN FROM CARBON BALANCE= 106.129
MOLES OUT/MOLES IN=   0.700   VOLUMETRIC FEED= 121.171 ML/MIN AT NTP   USAGE RATE= .13898E 00   H2/CO USAGE= 2.330

              RUN NUMBER= 29
              --------------

PRESSURE=1200.000 KPA  TEMPERATURE=521.000 K  WHSV=  0.359  % CO CONVERSION= 15.397

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   COMPONENT   PARTIAL PRESSURE   MOLE       MOLE      MASS       MASS       RATE            SELECTIVE
                     KPA        %(TOTAL)   %(HC)    %(TOTAL)    %(HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

--------------------------------------------------------------------------------------------------------

      C1           11.407         0.951    62.970     1.735    26.442    .16423E-02      .10000E 01
      C2            0.658         0.055     3.630     0.187     2.880    .94684E-04      .57652E-01
      C3            1.160         0.097     6.403     0.485     7.449    .16699E-03      .10168E 00
      C4            1.267         0.106     6.997     0.699    10.731    .18248E-03      .11111E 00
      C5            1.004         0.084     5.545     0.687    10.556    .14461E-03      .88050E-01
      C6            0.789         0.066     4.356     0.645     9.907    .11362E-03      .69182E-01
      C7            0.646         0.054     3.564     0.614     9.425    .92962E-04      .56604E-01
      C8            0.430         0.036     2.376     0.466     7.163    .61975E-04      .37736E-01
      C9            0.359         0.030     1.980     0.436     6.702    .51646E-04      .31447E-01
      C10           0.215         0.018     1.188     0.290     4.461    .30987E-04      .18868E-01
      C11           0.179         0.015     0.990     0.266     4.084    .25823E-04      .15723E-01
      C12           0.000         0.000     0.000     0.000     0.000    .0              .0
      CO          258.281        21.523     0.000    83.726     0.000    .67673E-02
      CO2           0.658         0.055     0.000     0.275     0.000    .94684E-04      .57652E-01
      H2O          45.689         3.807     0.000     7.815     0.000    .65779E-02      .40052E 01
      H2          877.257        73.105     0.000    16.673     0.000    .76851E-03
--------------------------------------------------------------------------------------------------------
HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  82.284   HYDROGEN IN FROM CARBON BALANCE=  73.550
MOLES OUT/MOLES IN=   1.010   VOLUMETRIC FEED= 111.095 ML/MIN AT NTP   USAGE RATE= .75358E-02   H2/CO USAGE= 0.134
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            RUN NUMBER= 30
            --------------

PRESSURE=1200.000 KPA  TEMPERATURE=521.000 K  WHSV=  0.160  % CO CONVERSION= 36.467

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  COMPONENT   PARTIAL PRESSURE  MOLE      MOLE       MASS      MASS       RATE             SELECTIVE
                    KPA        %(TOTAL)  %(HC)     %(TOTAL)   %(HC)  KGMOL/MIN KG RU   RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------

     C1           25.832        2.153    61.136     3.639    23.970    .15446E-02       .10000E 01
     C2            1.412        0.118     3.342     0.373     2.457    .84443E-04       .54669E-01
     C3            2.724        0.227     6.448     1.055     6.952    .16291E-03       .10547E 00
     C4            2.762        0.230     6.537     1.410     9.290    .16515E-03       .10692E 00
     C5            2.212        0.184     5.235     1.402     9.237    .13227E-03       .85631E-01
     C6            1.875        0.156     4.437     1.419     9.350    .11209E-03       .72569E-01
     C7            1.462        0.122     3.461     1.287     8.480    .87432E-04       .56604E-01
     C8            1.312        0.109     3.106     1.317     8.676    .78465E-04       .50798E-01
     C9            1.125        0.094     2.662     1.268     8.350    .67256E-04       .43541E-01
     C10           0.975        0.081     2.307     1.219     8.028    .58288E-04       .37736E-01
     C11           0.412        0.034     0.976     0.566     3.731    .24660E-04       .15965E-01
     C12           0.150        0.012     0.355     0.224     1.479    .89674E-05       .58055E-02
     CO          207.457       17.288     0.000    51.141     0.000    .71201E-02
     CO2           1.950        0.162     0.000     0.755     0.000    .11658E-03       .75472E-01
     H2O         115.176        9.598     0.000    18.252     0.000    .68870E-02       .44586E 01
     H2          833.164       69.430     0.000    14.671     0.000    .66287E-02
------------------------------------------------------------------------------------------------------
HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  92.310   HYDROGEN IN FROM CARBON BALANCE=  78.668
MOLES OUT/MOLES IN=  0.944   VOLUMETRIC FEED=  45.183 ML/MIN AT NTP   USAGE RATE= .13749E-01   H2/CO USAGE= 0.931

            RUN NUMBER= 36
            --------------

PRESSURE=1200.000 KPA  TEMPERATURE=523.000 K  WHSV=  0.087  % CO CONVERSION= 39.417

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  COMPONENT   PARTIAL PRESSURE  MOLE      MOLE       MASS      MASS       RATE             SELECTIVE
                    KPA        %(TOTAL)  %(HC)     %(TOTAL)   %(HC)  KGMOL/MIN KG RU   RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------

     C1           32.996        2.750    63.712     4.493    27.164    .10317E-02       .10000E 01
     C2            1.913        0.159     3.693     0.488     2.953    .59808E-04       .57971E-01
     C3            3.347        0.279     6.464     1.253     7.578    .10466E-03       .10145E 00
     C4            3.443        0.287     6.648     1.699    10.275    .10765E-03       .10435E 00
     C5            2.738        0.228     5.286     1.678    10.142    .85600E-04       .82971E-01
     C6            2.224        0.185     4.294     1.627     9.840    .69526E-04       .67391E-01
     C7            1.650        0.137     3.186     1.404     8.489    .51584E-04       .50000E-01
     C8            1.291        0.108     2.493     1.253     7.574    .40370E-04       .39130E-01
     C9            0.861        0.072     1.662     0.938     5.669    .26913E-04       .26087E-01
     C10           0.646        0.054     1.247     0.780     4.717    .20185E-04       .19565E-01
     C11           0.502        0.042     0.970     0.667     4.030    .15700E-04       .15217E-01
     C12           0.179        0.015     0.346     0.259     1.569    .56070E-05       .54348E-02
     CO          205.629       17.136     0.000    48.998     0.000    .41832E-02
     CO2           2.367        0.197     0.000     0.886     0.000    .74012E-04       .71739E-01
     H2O         129.056       10.755     0.000    19.769     0.000    .40351E-02       .39112E 01
     H2          811.158       67.597     0.000    13.806     0.000    .53191E-02
------------------------------------------------------------------------------------------------------
HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  93.619   HYDROGEN IN FROM CARBON BALANCE=  81.773
MOLES OUT/MOLES IN=  0.909   VOLUMETRIC FEED=  25.206 ML/MIN AT NTP   USAGE RATE= .95022E-02   H2/CO USAGE= 1.272
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              RUN NUMBER= 37
              --------------

PRESSURE=1200.000 KPA  TEMPERATURE=545.000 K  WHSV=  0.506  % CO CONVERSION= 25.016

------------------------------------------------------------------------------------------------------------

   COMPONENT   PARTIAL PRESSURE   MOLE       MOLE        MASS       MASS         RATE               SELECTIVE
                     KPA          %(TOTAL)   %(HC)       %(TOTAL)   %(HC)   KGMOL/MIN KG RU   RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------------

      C1           28.753          2.396     71.279      4.120     38.127     .54833E-02         .10000E 01
      C2            1.977          0.165      4.901      0.531      4.916     .37705E-03         .68763E-01
      C3            2.459          0.205      6.097      0.969      8.968     .46901E-03         .85535E-01
      C4            2.242          0.187      5.559      1.165     10.779     .42763E-03         .77987E-01
      C5            1.724          0.144      4.274      1.112     10.287     .32877E-03         .59958E-01
      C6            1.302          0.109      3.228      1.003      9.280     .24830E-03         .45283E-01
      C7            0.832          0.069      2.062      0.745      6.894     .15864E-03         .28931E-01
      C8            0.543          0.045      1.345      0.554      5.126     .10346E-03         .18868E-01
      C9            0.289          0.024      0.717      0.332      3.069     .55178E-04         .10063E-01
      C10           0.217          0.018      0.538      0.276      2.554     .41383E-04         .75472E-02
      C11           0.000          0.000      0.000      0.000      0.000     .0                 .0
      C12           0.000          0.000      0.000      0.000      0.000     .0                 .0
      CO          243.525         20.294      0.000     61.068      0.000     .15494E-01
      CO2           0.820          0.068      0.000      0.323      0.000     .15634E-03         .28512E-01
      H2O          79.604          6.634      0.000     12.833      0.000     .15181E-01         .27686E 01
      H2          835.713         69.643      0.000     14.969      0.000     .19682E-01
------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  86.340   HYDROGEN IN FROM CARBON BALANCE=  78.243
MOLES OUT/MOLES IN=   0.950   VOLUMETRIC FEED= 159.248 ML/MIN AT NTP   USAGE RATE= .35176E-01   H2/CO USAGE= 1.270

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              RUN NUMBER= 38
              --------------

PRESSURE=1200.000 KPA  TEMPERATURE=551.000 K  WHSV=  0.248  % CO CONVERSION= 69.773

------------------------------------------------------------------------------------------------------------

   COMPONENT   PARTIAL PRESSURE   MOLE       MOLE        MASS       MASS         RATE               SELECTIVE
                     KPA          %(TOTAL)   %(HC)       %(TOTAL)   %(HC)   KGMOL/MIN KG RU   RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------------

      C1          133.734         11.145     75.506     14.046     45.936     .91092E-02         .10000E 01
      C2           10.593          0.883      5.981      2.086      6.822     .72152E-03         .79208E-01
      C3           10.918          0.910      6.164      3.153     10.313     .74365E-03         .81636E-01
      C4            7.757          0.646      4.380      2.953      9.659     .52838E-03         .58005E-01
      C5            5.534          0.461      3.124      2.615      8.554     .37693E-03         .41379E-01
      C6            3.785          0.315      2.137      2.137      6.988     .25781E-03         .28302E-01
      C7            2.061          0.172      1.164      1.353      4.425     .14039E-03         .15412E-01
      C8            1.387          0.116      0.783      1.038      3.393     .94445E-04         .10368E-01
      C9            0.862          0.072      0.487      0.724      2.368     .58709E-04         .64450E-02
      C10           0.300          0.025      0.169      0.279      0.914     .20420E-04         .22417E-02
      C11           0.187          0.016      0.106      0.192      0.628     .12763E-04         .14011E-02
      C12           0.000          0.000      0.000      0.000      0.000     .0                 .0
      CO          134.909         11.242      0.000     24.796      0.000     .21212E-01
      CO2           3.997          0.333      0.000      1.155      0.000     .27227E-03         .29890E-01
      H2O         303.420         25.285      0.000     35.851      0.000     .20667E-01         .22688E 01
      H2          580.557         48.380      0.000      7.622      0.000     .48346E-01
------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 114.043   HYDROGEN IN FROM CARBON BALANCE= 107.528
MOLES OUT/MOLES IN=   0.691   VOLUMETRIC FEED=  73.530 ML/MIN AT NTP   USAGE RATE= .69558E-01   H2/CO
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              RUN NUMBER= 39
              --------------

PRESSURE=1200.000 KPA  TEMPERATURE=573.000 K  WHSV=  0.717  % CO CONVERSION= 59.108

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   COMPONENT   PARTIAL PRESSURE   MOLE       MOLE       MASS       MASS        RATE            SELECTIVE
                     KPA        %(TOTAL)   %(HC)     %(TOTAL)    %(HC)  KGMOL/MIN KG RU   RATES (REL TO CH4)

--------------------------------------------------------------------------------------------------------------

      C1           171.729       14.311    88.012     19.349    72.344     .36192E-01       .10000E 01
      C2            10.726        0.894     5.497      2.266     8.472     .22604E-02       .62457E-01
      C3             6.197        0.516     3.176      1.920     7.179     .13059E-02       .36083E-01
      C4             3.181        0.265     1.630      1.299     4.858     .67040E-03       .18524E-01
      C5             1.868        0.156     0.958      0.947     3.542     .39377E-03       .10880E-01
      C6             0.780        0.065     0.400      0.473     1.767     .16448E-03       .45448E-02
      C7             0.319        0.027     0.164      0.225     0.841     .67289E-04       .18592E-02
      C8             0.213        0.018     0.109      0.171     0.639     .44860E-04       .12395E-02
      C9             0.106        0.009     0.055      0.096     0.359     .22430E-04       .61975E-03
      C10            0.000        0.000     0.000      0.000     0.000     .0               .0
      C11            0.000        0.000     0.000      0.000     0.000     .0               .0
      C12            0.000        0.000     0.000      0.000     0.000     .0               .0
      CO           170.287       14.191     0.000     33.575     0.000     .51875E-01
      CO2            2.732        0.228     0.000      0.846     0.000     .57570E-03       .15907E-01
      H2O          240.684       20.057     0.000     30.507     0.000     .50724E-01       .14015E 01
      H2           591.178       49.265     0.000      8.326     0.000     .12914E 00
--------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 105.866   HYDROGEN IN FROM CARBON BALANCE= 100.328
MOLES OUT/MOLES IN=   0.741   VOLUMETRIC FEED= 213.417 ML/MIN AT NTP   USAGE RATE= .18101E 00   H2/CO USAGE= 2.489

              RUN NUMBER= 40
              --------------

PRESSURE=1600.000 KPA  TEMPERATURE=545.000 K  WHSV=  0.914  % CO CONVERSION= 18.834

--------------------------------------------------------------------------------------------------------------

   COMPONENT   PARTIAL PRESSURE   MOLE       MOLE       MASS       MASS        RATE            SELECTIVE
                     KPA        %(TOTAL)   %(HC)     %(TOTAL)    %(HC)  KGMOL/MIN KG RU   RATES (REL TO CH4)

--------------------------------------------------------------------------------------------------------------

      C1            27.515        1.720    70.343      2.868    34.865     .67746E-02       .10000E 01
      C2             1.647        0.103     4.211      0.322     3.913     .40551E-03       .59857E-01
      C3             2.077        0.130     5.309      0.595     7.236     .51129E-03       .75472E-01
      C4             2.184        0.137     5.584      0.825    10.032     .53774E-03       .79375E-01
      C5             1.772        0.111     4.531      0.831    10.106     .43636E-03       .64411E-01
      C6             1.235        0.077     3.158      0.692     8.413     .30413E-03       .44893E-01
      C7             0.967        0.060     2.471      0.630     7.656     .23801E-03       .35133E-01
      C8             0.591        0.037     1.510      0.439     5.334     .14545E-03       .21470E-01
      C9             0.483        0.030     1.236      0.403     4.900     .11901E-03       .17567E-01
      C10            0.376        0.023     0.961      0.348     4.228     .92561E-04       .13663E-01
      C11            0.269        0.017     0.686      0.273     3.318     .66115E-04       .97593E-02
      C12            0.000        0.000     0.000      0.000     0.000     .0               .0
      CO           368.775       23.048     0.000     67.262     0.000     .21069E-01
      CO2            0.967        0.060     0.000      0.277     0.000     .23801E-03       .35133E-01
      H2O           83.637        5.227     0.000      9.807     0.000     .20593E-01       .30397E 01
      H2          1107.506       69.219     0.000     14.429     0.000     .50727E-01
--------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  82.179   HYDROGEN IN FROM CARBON BALANCE=  82.096
MOLES OUT/MOLES IN=   0.905   VOLUMETRIC FEED= 279.345 ML/MIN AT NTP   USAGE RATE= .71796E-01   H2/CO USAGE= 2.408
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        RUN NUMBER= 41
        --------------

PRESSURE=1600.000 KPA  TENPERATURE=573.000 K  WHSV=  0.761  % CO CONVERSION= 74.356

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   COMPONENT   PARTIAL PRESSURE  MOLE      MOLE      MASS       MASS      RATE             SELECTIVE
                    KPA          %(TOTAL)  %(HC)     %(TOTAL)   %(HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

--------------------------------------------------------------------------------------------------------

      C1           342.567       21.410    89.070    25.193    74.751    .49697E-01      .10000E 01
      C2            20.163        1.260     5.242     2.780     8.249    .29251E-02      .58858E-01
      C3            11.399        0.712     2.964     2.305     6.840    .16537E-02      .33276E-01
      C4             5.204        0.325     1.353     1.387     4.117    .75501E-03      .15192E-01
      C5             2.753        0.172     0.716     0.911     2.704    .39943E-03      .80372E-02
      C6             1.209        0.076     0.314     0.478     1.418    .17536E-03      .35285E-02
      C7             0.655        0.041     0.170     0.301     0.893    .94985E-04      .19113E-02
      C8             0.604        0.038     0.157     0.317     0.940    .87679E-04      .17643E-02
      C9             0.050        0.003     0.013     0.030     0.088    .73066E-05      .14702E-03
      C10            0.000        0.000     0.000     0.000     0.000    .0              .0
      C11            0.000        0.000     0.000     0.000     0.000    .0              .0
      C12            0.000        0.000     0.000     0.000     0.000    .0              .0
      CO           164.526       10.283     0.000    21.175     0.000    .69205E-01
      CO2            8.243        0.515     0.000     1.667     0.000    .11958E-02      .24063E-01
      H2O          460.556       28.785     0.000    38.105     0.000    .66814E-01      .13444E 01
      H2           582.070       36.379     0.000     5.351     0.000    .18464E 00
--------------------------------------------------------------------------------------------------------
HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 118.502   HYDROGEN IN FROM CARBON BALANCE= 115.925
MOLES OUT/MOLES IN=   0.641   VOLUMETRIC FEED= 230.388 ML/MIN AT NTP   USAGE RATE= .25384E 00   H2/CO USAGE= 2.668


        RUN NUMBER= 42
        --------------

PRESSURE=1600.000 KPA  TEMPERATURE=577.000 K  WHSV=  1.386  % CO CONVERSION= 45.521

--------------------------------------------------------------------------------------------------------

   COMPONENT   PARTIAL PRESSURE  MOLE      MOLE      MASS       MASS      RATE             SELECTIVE
                    KPA          %(TOTAL)  %(HC)     %(TOTAL)   %(HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

--------------------------------------------------------------------------------------------------------

      C1           150.019        9.376    85.308    13.603    66.166    .48980E-01      .10000E 01
      C2             9.808        0.613     5.577     1.668     8.111    .32023E-02      .65380E-01
      C3             7.340        0.459     4.174     1.830     8.902    .23964E-02      .48925E-01
      C4             4.213        0.263     2.396     1.385     6.736    .13755E-02      .28082E-01
      C5             2.353        0.147     1.338     0.960     4.671    .76834E-03      .15687E-01
      C6             1.333        0.083     0.758     0.650     3.160    .43521E-03      .88855E-02
      C7             0.592        0.037     0.337     0.336     1.633    .19343E-03      .39491E-02
      C8             0.197        0.012     0.112     0.128     0.621    .64476E-04      .13164E-02
      C9             0.000        0.000     0.000     0.000     0.000    .0              .0
      C10            0.000        0.000     0.000     0.000     0.000    .0              .0
      C11            0.000        0.000     0.000     0.000     0.000    .0              .0
      C12            0.000        0.000     0.000     0.000     0.000    .0              .0
      CO           283.055       17.691     0.000    44.917     0.000    .77221E-01
      CO2            2.518        0.157     0.000     0.626     0.000    .82207E-03      .16784E-01
      H2O          231.480       14.467     0.000    23.614     0.000    .75577E-01      .15430E 01
      H2           907.092       56.693     0.000    10.282     0.000    .19427E 00
--------------------------------------------------------------------------------------------------------
HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  96.777   HYDROGEN IN FROM CARBON BALANCE=  93.881
MOLES OUT/MOLES IN=   0.791   VOLUMETRIC FEED= 427.300 ML/MIN AT NTP   USAGE RATE= .27149E 00   H2/CO USAGE= 2.516
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            RUN NUMBER= 43
            --------------

PRESSURE=1600.000 KPA  TEMPERATURE=551.000 K  WHSV=  0.706  % CO CONVERSION= 45.972

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   COMPONENT   PARTIAL PRESSURE   MOLE       MOLE      MASS       MASS       RATE             SELECTIVE
                      KPA        %(TOTAL)   %(HC)    %(TOTAL)    %(HC)   KGMOL/MIN KG RU  RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------------

      C1          69.019        4.314     68.061     6.259    31.439     .11490E-01       .10000E 01
      C2           4.625        0.289      4.560     0.786     3.950     .76988E-03       .67005E-01
      C3           5.994        0.375      5.910     1.495     7.508     .99778E-03       .86841E-01
      C4           4.908        0.307      4.840     1.614     8.105     .81713E-03       .71118E-01
      C5           4.090        0.256      4.034     1.669     8.385     .68094E-03       .59265E-01
      C6           3.406        0.213      3.359     1.660     8.339     .56699E-03       .49347E-01
      C7           2.805        0.175      2.766     1.590     7.985     .46693E-03       .40639E-01
      C8           2.454        0.153      2.420     1.586     7.965     .40856E-03       .35559E-01
      C9           1.703        0.106      1.679     1.235     6.206     .28349E-03       .24673E-01
      C10          1.603        0.100      1.581     1.290     6.479     .26682E-03       .23222E-01
      C11          0.601        0.038      0.593     0.531     2.669     .10006E-03       .87083E-02
      C12          0.200        0.013      0.198     0.193     0.970     .33352E-04       .29028E-02
      CO         280.485       17.530      0.000    44.513     0.000     .39731E-01
      CO2          2.254        0.141      0.000     0.562     0.000     .37521E-03       .32656E-01
      H2O        234.155       14.635      0.000    23.889     0.000     .38980E-01       .33926E 01
      H2         981.698       61.356      0.000    11.128     0.000     .86430E-01
------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  97.104   HYDROGEN IN FROM CARBON BALANCE=  93.805
MOLES OUT/MOLES IN=   0.792   VOLUMETRIC FEED= 217.693 ML/MIN AT NTP   USAGE RATE= .12616E 00   H2/CO USAGE= 2.175

            RUN NUMBER= 44
            --------------

PRESSURE=1600.000 KPA  TEMPERATURE=553.000 K  WHSV=  0.342  % CO CONVERSION= 96.147

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   COMPONENT   PARTIAL PRESSURE   MOLE       MOLE      MASS       MASS       RATE             SELECTIVE
                      KPA        %(TOTAL)   %(HC)    %(TOTAL)    %(HC)   KGMOL/MIN KG RU  RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------------

      C1         710.711       44.419     99.598    43.917    99.249     .39038E-01       .10000E 01
      C2           2.870        0.179      0.402     0.333     0.751     .15763E-03       .40380E-02
      C3           0.000        0.000      0.000     0.000     0.000     .0               .0
      C4           0.000        0.000      0.000     0.000     0.000     .0               .0
      C5           0.000        0.000      0.000     0.000     0.000     .0               .0
      C6           0.000        0.000      0.000     0.000     0.000     .0               .0
      C7           0.000        0.000      0.000     0.000     0.000     .0               .0
      C8           0.000        0.000      0.000     0.000     0.000     .0               .0
      C9           0.000        0.000      0.000     0.000     0.000     .0               .0
      C10          0.000        0.000      0.000     0.000     0.000     .0               .0
      C11          0.000        0.000      0.000     0.000     0.000     .0               .0
      C12          0.000        0.000      0.000     0.000     0.000     .0               .0
      CO          29.382        1.836      0.000     3.177     0.000     .40273E-01
      CO2         16.758        1.047      0.000     2.848     0.000     .92046E-03       .23579E-01
      H2O        699.693       43.731      0.000    48.640     0.000     .38432E-01       .98450E 00
      H2         140.588        8.787      0.000     1.086     0.000     .11338E 00
------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 141.894   HYDROGEN IN FROM CARBON BALANCE= 137.793
MOLES OUT/MOLES IN=   0.539   VOLUMETRIC FEED= 106.788 ML/MIN AT NTP   USAGE RATE= .15365E 00   H2/CO USAGE= 2.815
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               RUN NUMBER= 45
               --------------

PRESSURE=1600.000 KPA  TEMPERATURE=523.000 K  WHSV=  0.227  % CO CONVERSION= 30.764

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   COMPONENT   PARTIAL PRESSURE  MOLE      MOLE       MASS      MASS         RATE              SELECTIVE
                    KPA         %(TOTAL)  %(HC)     %(TOTAL)   %(HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

-----------------------------------------------------------------------------------------------------------

      C1           36.295         2.268    64.286     3.757    28.920      .22342E-02       .10000E 01
      C2            1.921         0.120     3.403     0.373     2.870      .11827E-03       .52935E-01
      C3            4.242         0.265     7.513     1.208     9.295      .26112E-03       .11688E 00
      C4            3.957         0.247     7.008     1.485    11.429      .24356E-03       .10901E 00
      C5            2.949         0.184     5.222     1.373    10.572      .18150E-03       .81237E-01
      C6            2.454         0.153     4.346     1.365    10.510      .15105E-03       .67610E-01
      C7            1.940         0.121     3.437     1.255     9.663      .11944E-03       .53459E-01
      C8            1.198         0.075     2.123     0.884     6.804      .73771E-04       .33019E-01
      C9            0.989         0.062     1.752     0.819     6.305      .60890E-04       .27254E-01
      C10           0.514         0.032     0.910     0.472     3.632      .31616E-04       .14151E-01
      C11           0.000         0.000     0.000     0.000     0.000      .0               .0
      C12           0.000         0.000     0.000     0.000     0.000      .0               .0
      CO          311.972        19.498     0.000    56.514     0.000      .85328E-02
      CO2           3.253         0.203     0.000     0.926     0.000      .20023E-03       .89623E-01
      H2O         132.113         8.257     0.000    15.385     0.000      .81323E-02       .36399E 01
      H2         1096.203        68.513     0.000    14.184     0.000      .12710E-01
-----------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  88.759   HYDROGEN IN FROM CARBON BALANCE=  81.418
MOLES OUT/MOLES IN=   0.913   VOLUMETRIC FEED=  70.108 ML/MIN AT NTP   USAGE RATE= .21243E-01   H2/CO USAGE= 1.490

               RUN NUMBER= 46
               --------------

PRESSURE=1600.000 KPA  TEMPERATURE=523.000 K  WHSV=  0.294  % CO CONVERSION= 26.953

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   COMPONENT   PARTIAL PRESSURE  MOLE      MOLE       MASS      MASS         RATE              SELECTIVE
                    KPA         %(TOTAL)  %(HC)     %(TOTAL)   %(HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

-----------------------------------------------------------------------------------------------------------

      C1           27.136         1.696    62.995     2.678    25.388      .22207E-02       .10000E 01
      C2            1.297         0.081     3.011     0.258     2.275      .10615E-03       .47799E-01
      C3            2.321         0.145     5.388     0.677     5.972      .18994E-03       .85535E-01
      C4            2.833         0.177     6.577     1.089     9.608      .23184E-03       .10440E 00
      C5            2.270         0.142     5.269     1.083     9.556      .18575E-03       .83648E-01
      C6            1.843         0.115     4.279     1.051     9.269      .15084E-03       .67925E-01
      C7            1.843         0.115     4.279     1.222    10.778      .15084E-03       .67925E-01
      C8            1.280         0.080     2.971     0.967     8.532      .10475E-03       .47170E-01
      C9            0.922         0.058     2.139     0.782     6.898      .75419E-04       .33962E-01
      C10           0.717         0.045     1.664     0.675     5.952      .58659E-04       .26415E-01
      C11           0.410         0.026     0.951     0.424     3.736      .33520E-04       .15094E-01
      C12           0.205         0.013     0.475     0.231     2.036      .16760E-04       .75472E-02
      CO          320.853        20.053     0.000    59.558     0.000      .96885E-02
      CO2           2.389         0.149     0.000     0.697     0.000      .19553E-03       .88050E-01
      H2O         113.613         7.101     0.000    13.557     0.000      .92975E-02       .41868E 01
      H2         1120.068        70.004     0.000    14.851     0.000      .12260E-01
-----------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  87.047   HYDROGEN IN FROM CARBON BALANCE=  79.367
MOLES OUT/MOLES IN=   0.936   VOLUMETRIC FEED=  90.074 ML/MIN AT NTP   USAGE RATE= .21948E-01   H2/CO USAGE= 1.265
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                RUN NUMBER= 47
                --------------

PRESSURE=1600.000 KPA  TEMPERATURE=575.000 K  WHSV=  0.563  % CO CONVERSION= 80.455

--------------------------------------------------------------------------------------------------------------

   COMPONENT   PARTIAL PRESSURE   MOLE      MOLE       MASS      MASS        RATE              SELECTIVE
                     KPA         %(TOTAL)  %(HC)     %(TOTAL)   %(HC)  KGMOL/MIN KG RU   RATES (REL TO CH4)

--------------------------------------------------------------------------------------------------------------

       C1            396.294      24.768    90.235    28.324    77.953    .41460E-01        .10000E 01
       C2             22.014       1.376     5.012     2.950     8.119    .23030E-02        .55549E-01
       C3             12.478       0.780     2.841     2.453     6.750    .13054E-02        .31487E-01
       C4              4.309       0.269     0.981     1.117     3.073    .45085E-03        .10874E-01
       C5              2.251       0.141     0.513     0.724     1.993    .23552E-03        .56807E-02
       C6              1.013       0.063     0.231     0.389     1.071    .10598E-03        .25563E-02
       C7              0.627       0.039     0.143     0.280     0.771    .65609E-04        .15825E-02
       C8              0.193       0.012     0.044     0.098     0.270    .20187E-04        .48691E-03
       C9              0.000       0.000     0.000     0.000     0.000    .0                .0
       C10             0.000       0.000     0.000     0.000     0.000    .0                .0
       C11             0.000       0.000     0.000     0.000     0.000    .0                .0
       C12             0.000       0.000     0.000     0.000     0.000    .0                .0
       CO            128.641       8.040     0.000    16.090     0.000    .55401E-01
       CO2            11.288       0.706     0.000     2.219     0.000    .11810E-02        .28484E-01
       H2O           506.973      31.686     0.000    40.764     0.000    .53039E-01        .12793E 01
       H2            513.919      32.120     0.000     4.591     0.000    .14531E 00
--------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 123.646   HYDROGEN IN FROM CARBON BALANCE= 118.929
MOLES OUT/MOLES IN=   0.625   VOLUMETRIC FEED= 163.547 ML/MIN AT NTP   USAGE RATE= .20071E 00   H2/CO USAGE= 2.623

                RUN NUMBER= 48
                --------------

PRESSURE=1600.000 KPA  TEMPERATURE=603.000 K  WHSV=  1.244  % CO CONVERSION= 63.135

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   COMPONENT   PARTIAL PRESSURE   MOLE      MOLE       MASS      MASS        RATE              SELECTIVE
                     KPA         %(TOTAL)  %(HC)     %(TOTAL)   %(HC)  KGMOL/MIN KG RU   RATES (REL TO CH4)

--------------------------------------------------------------------------------------------------------------

       C1            312.674      19.542    94.216    25.143    87.236    .81143E-01        .10000E 01
       C2             12.324       0.770     3.714     1.858     6.447    .31983E-02        .39415E-01
       C3              4.201       0.263     1.266     0.929     3.223    .10901E-02        .13435E-01
       C4              1.529       0.096     0.461     0.446     1.546    .39678E-03        .48899E-02
       C5              0.772       0.048     0.233     0.279     0.969    .20039E-03        .24696E-02
       C6              0.278       0.017     0.084     0.120     0.417    .72141E-04        .88906E-03
       C7              0.093       0.006     0.028     0.047     0.162    .24047E-04        .29635E-03
       C8              0.000       0.000     0.000     0.000     0.000    .0                .0
       C9              0.000       0.000     0.000     0.000     0.000    .0                .0
       C10             0.000       0.000     0.000     0.000     0.000    .0                .0
       C11             0.000       0.000     0.000     0.000     0.000    .0                .0
       C12             0.000       0.000     0.000     0.000     0.000    .0                .0
       CO            216.212      13.513     0.000    30.425     0.000    .96092E-01
       CO2             8.062       0.504     0.000     1.783     0.000    .20921E-02        .25783E-01
       H2O           354.155      22.135     0.000    32.038     0.000    .91908E-01        .11327E 01
       H2            689.701      43.106     0.000     6.932     0.000    .26104E 00
--------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 108.621   HYDROGEN IN FROM CARBON BALANCE= 105.973
MOLES OUT/MOLES IN=   0.701   VOLUMETRIC FEED= 376.088 ML/MIN AT NTP   USAGE RATE= .35713E 00   H2/CO USAGE= 2.717
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              RUN NUMBER= 49
              --------------

PRESSURE=1600.000 KPA  TEMPERATURE=601.000 K  WHSV=  0.944  % CO CONVERSION= 71.875

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   COMPONENT   PARTIAL PRESSURE  MOLE       MOLE      MASS       MASS        RATE             SELECTIVE
                    KPA         %(TOTAL)  %(HC)     %(TOTAL)   %(HC)   KGMOL/MIN KG RU  RATES (REL TO CH4)

---------------------------------------------------------------------------------------------------------------

      C1          387.572        24.223    94.911    29.116    89.117    .71243E-01      .10000E 01
      C2           14.513         0.907     3.554     2.044     6.257    .26677E-02      .37446E-01
      C3            4.050         0.253     0.992     0.837     2.561    .74446E-03      .10450E-01
      C4            1.334         0.083     0.327     0.363     1.112    .24521E-03      .34418E-02
      C5            0.691         0.043     0.169     0.234     0.715    .12703E-03      .17831E-02
      C6            0.193         0.012     0.047     0.078     0.238    .35451E-04      .49762E-03
      C7            0.000         0.000     0.000     0.000     0.000    .0              .0
      C8            0.000         0.000     0.000     0.000     0.000    .0              .0
      C9            0.000         0.000     0.000     0.000     0.000    .0              .0
      C10           0.000         0.000     0.000     0.000     0.000    .0              .0
      C11           0.000         0.000     0.000     0.000     0.000    .0              .0
      C12           0.000         0.000     0.000     0.000     0.000    .0              .0
      CO          176.790        11.049     0.000    23.242     0.000    .83048E-01
      CO2          13.099         0.819     0.000     2.706     0.000    .24077E-02      .33796E-01
      H20         425.598        26.600     0.000    35.969     0.000    .78233E-01      .10981E 01
      H2          576.159        36.010     0.000     5.410     0.000    .22814E 00
---------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 115.551   HYDROGEN IN FROM CARBON BALANCE= 113.580
MOLES OUT/MOLES IN=   0.654   VOLUMETRIC FEED= 285.006 ML/MIN AT NTP   USAGE RATE= .31119E 00   H2/CO USAGE= 2.747


              RUN NUMBER=101
              --------------

PRESSURE=1600.000 KPA  TEMPERATURE=566.000 K  WHSV=  0.807  % CO CONVERSION= 42.722

---------------------------------------------------------------------------------------------------------------

   COMPONENT   PARTIAL PRESSURE  MOLE       MOLE      MASS       MASS        RATE             SELECTIVE
                    KPA         %(TOTAL)  %(HC)     %(TOTAL)   %(HC)   KGMOL/MIN KG RU  RATES (REL TO CH4)

---------------------------------------------------------------------------------------------------------------

      C1          127.657         7.979    82.469    11.582    60.378    .24171E-01      .10000E 01
      C2            8.832         0.552     5.705     1.502     7.832    .16722E-02      .69182E-01
      C3            8.254         0.516     5.332     2.059    10.735    .15627E-02      .64654E-01
      C4            4.721         0.295     3.050     1.553     8.094    .89386E-03      .36981E-01
      C5            2.682         0.168     1.732     1.095     5.707    .50774E-03      .21006E-01
      C6            1.734         0.108     1.120     0.846     4.409    .32836E-03      .13585E-01
      C7            0.578         0.036     0.373     0.328     1.709    .10945E-03      .45283E-02
      C8            0.337         0.021     0.218     0.218     1.136    .63847E-04      .26415E-02
      C9            0.000         0.000     0.000     0.000     0.000    .0              .0
      C10           0.000         0.000     0.000     0.000     0.000    .0              .0
      C11           0.000         0.000     0.000     0.000     0.000    .0              .0
      C12           0.000         0.000     0.000     0.000     0.000    .0              .0
      CO          298.669        18.667     0.000    47.420     0.000    .42179E-01
      CO2           3.244         0.203     0.000     0.809     0.000    .61415E-03      .25409E-01
      H20         216.278        13.517     0.000    22.075     0.000    .40951E-01      .16942E 01
      H2          927.015        57.938     0.000    10.513     0.000    .10991E 00
---------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  94.851   HYDROGEN IN FROM CARBON BALANCE=  94.218
MOLES OUT/MOLES IN=   0.789   VOLUMETRIC FEED= 240.085 ML/MIN AT NTP   USAGE RATE= .15209E 00
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                  RUN NUMBER=102
                  --------------

PRESSURE=1600.000 KPA  TEMPERATURE=549.000 K  WHSV=  0.599  % CO CONVERSION= 21.934

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    COMPONENT   PARTIAL PRESSURE   MOLE       MOLE       MASS       MASS        RATE              SELECTIVE
                      KPA         %(TOTAL)   %(HC)     %(TOTAL)    %(HC)   KGMOL/MIN KG RU   RATES (REL TO CH4)

-----------------------------------------------------------------------------------------------

      C1            38.959          2.435     73.017     4.042     41.570     .62827E-02       .10000E 01
      C2             3.048          0.190      5.712     0.593      6.098     .49151E-03       .78233E-01
      C3             3.138          0.196      5.880     0.895      9.206     .50597E-03       .80534E-01
      C4             2.815          0.176      5.276     1.059     10.887     .45393E-03       .72250E-01
      C5             2.008          0.126      3.763     0.938      9.642     .32382E-03       .51542E-01
      C6             1.345          0.084      2.520     0.750      7.712     .21684E-03       .34514E-01
      C7             1.076          0.067      2.016     0.698      7.174     .17348E-03       .27612E-01
      C8             0.592          0.037      1.109     0.437      4.498     .95412E-04       .15186E-01
      C9             0.377          0.024      0.706     0.313      3.214     .60716E-04       .96641E-02
      C10            0.000          0.000      0.000     0.000      0.000     .0               .0
      C11            0.000          0.000      0.000     0.000      0.000     .0               .0
      C12            0.000          0.000      0.000     0.000      0.000     .0               .0
      CO           354.986         22.187      0.000    64.456      0.000     .16084E-01
      CO2            0.251          0.016      0.000     0.072      0.000     .40478E-04       .64427E-02
      H2O           99.235          6.202      0.000    11.583      0.000     .16003E-01       .25472E 01
      H2          1092.173         68.261      0.000    14.165      0.000     .35874E-01
-----------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  84.016   HYDROGEN IN FROM CARBON BALANCE=  82.164
MOLES OUT/MOLES IN=   0.904   VOLUMETRIC FEED= 181.199 ML/MIN AT NTP   USAGE RATE= .51958E-01   H2/CO USAGE= 2.230

                  RUN NUMBER=103
                  --------------

PRESSURE=1400.000 KPA  TEMPERATURE=573.000 K  WHSV=  0.685  % CO CONVERSION= 70.519

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    COMPONENT   PARTIAL PRESSURE   MOLE       MOLE       MASS       MASS        RATE              SELECTIVE
                      KPA         %(TOTAL)   %(HC)     %(TOTAL)    %(HC)   KGMOL/MIN KG RU   RATES (REL TO CH4)

-----------------------------------------------------------------------------------------------

      C1           299.347         21.382     89.441    24.580     76.089     .55875E-01       .10000E 01
      C2            17.830          1.274      5.327     2.745      8.497     .33280E-02       .59561E-01
      C3             9.480          0.677      2.832     2.141      6.626     .17694E-02       .31668E-01
      C4             4.305          0.307      1.286     1.281      3.966     .80351E-03       .14380E-01
      C5             2.030          0.145      0.607     0.750      2.322     .37896E-03       .67823E-02
      C6             1.007          0.072      0.301     0.445      1.376     .18806E-03       .33656E-02
      C7             0.550          0.039      0.164     0.282      0.873     .10258E-03       .18358E-02
      C8             0.137          0.010      0.041     0.080      0.249     .25644E-04       .45895E-03
      C9             0.000          0.000      0.000     0.000      0.000     .0               .0
      C10            0.000          0.000      0.000     0.000      0.000     .0               .0
      C11            0.000          0.000      0.000     0.000      0.000     .0               .0
      C12            0.000          0.000      0.000     0.000      0.000     .0               .0
      CO           170.968         12.212      0.000    24.568      0.000     .76336E-01
      CO2            7.159          0.511      0.000     1.617      0.000     .13363E-02       .23916E-01
      H2O          394.646         28.189      0.00C    36.456      0.000     .73664E-01       .13184E 01
      H2           492.541         35.181      0.000     5.055      0.000     .22102E 00
-----------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 115.977   HYDROGEN IN FROM CARBON BALANCE= 119.758
MOLES OUT/MOLES IN=   0.620   VOLUMETRIC FEED= 265.593 ML/MIN AT NTP   USAGE RATE= .29735E 00   H2/CO USAGE= 2.895
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                RUN NUMBER=104
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PRESSURE=1400.000 KPA  TEMPERATURE=545.000 K  WHSV=  0.352  % CO CONVERSION= 58.995

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   COMPONENT  PARTIAL PRESSURE   MOLE      MOLE      MASS      MASS      RATE           SELECTIVE
                   KPA         %(TOTAL)  %(HC)    %(TOTAL)   %(HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

-----------------------------------------------------------------------------------------------------

      C1        110.976        7.927    73.541    10.839   42.407    .99644E-02     .10000E 01
      C2          8.265        0.590     5.477     1.513    5.921    .74206E-03     .74471E-01
      C3          9.692        0.692     6.423     2.603   10.185    .87025E-03     .87336E-01
      C4          7.662        0.547     5.077     2.713   10.613    .68794E-03     .69039E-01
      C5          5.362        0.383     3.553     2.356    9.220    .48141E-03     .48313E-01
      C6          3.950        0.282     2.617     2.074    8.113    .35465E-03     .35592E-01
      C7          2.237        0.160     1.482     1.365    5.342    .20083E-03     .20154E-01
      C8          1.285        0.092     0.851     0.894    3.498    .11537E-03     .11578E-01
      C9          0.904        0.065     0.599     0.706    2.764    .81185E-04     .81475E-02
      C10         0.571        0.041     0.378     0.495    1.937    .51275E-04     .51458E-02
      C11         0.000        0.000     0.000     0.000    0.000    .0             .0
      C12         0.000        0.000     0.000     0.000    0.000    .0             .0
      CO        196.698       14.050     0.000    33.619    0.000    .25410E-01
      CO2         5.473        0.391     0.000     1.470    0.000    .49138E-03     .49314E-01
      H2O       272.046       19.432     0.000    29.892    0.000    .24427E-01     .24514E 01
      H2        774.880       55.349     0.000     9.460    0.000    .54944E-01
-----------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 105.382   HYDROGEN IN FROM CARBON BALANCE=  99.058
MOLES OUT/MOLES IN=   0.750   VOLUMETRIC FEED= 108.867 ML/MIN AT NTP   USAGE RATE= .80354E-01   H2/CO USAGE= 2.162

                RUN NUMBER=105
                --------------

PRESSURE=1400.000 KPA  TEMPERATURE=521.000 K  WHSV=  0.279  % CO CONVERSION= 34.901

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   COMPONENT  PARTIAL PRESSURE   MOLE      MOLE      MASS      MASS      RATE           SELECTIVE
                   KPA         %(TOTAL)  %(HC)    %(TOTAL)   %(HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

-----------------------------------------------------------------------------------------------------

      C1         32.088        2.292    58.377     3.619   24.463    .26333E-02     .10000E 01
      C2          2.135        0.152     3.884     0.451    3.052    .17520E-03     .66534E-01
      C3          4.939        0.353     8.986     1.532   10.355    .40532E-03     .15392E 00
      C4          4.493        0.321     8.174     1.837   12.417    .36871E-03     .14002E 00
      C5          3.712        0.265     6.754     1.884   12.736    .30464E-03     .11569E 00
      C6          3.250        0.232     5.913     1.970   13.319    .26672E-03     .10129E 00
      C7          1.769        0.126     3.217     1.247    8.427    .14513E-03     .55114E-01
      C8          1.195        0.085     2.174     0.960    6.491    .98061E-04     .37239E-01
      C9          0.956        0.068     1.739     0.863    5.830    .78448E-04     .29791E-01
      C10         0.430        0.031     0.783     0.431    2.911    .35302E-04     .13406E-01
      C11         0.000        0.000     0.000     0.000    0.000    .0             .0
      C12         0.000        0.000     0.000     0.000    0.000    .0             .0
      CO        270.855       19.347     0.000    53.461    0.000    .11916E-01
      CO2         3.155        0.225     0.000     0.978    0.000    .25888E-03     .98312E-01
      H2O       138.901        9.921     0.000    17.625    0.000    .11399E-01     .43287E 01
      H2        932.122       66.580     0.000    13.142    0.000    .22218E-01
-----------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  90.575   HYDROGEN IN FROM CARBON BALANCE=  85.919
MOLES OUT/MOLES IN=   0.865   VOLUMETRIC FEED=  85.409 ML/MIN AT NTP   USAGE RATE= .34134E-01   H2/CO USAGE= 1.864
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                RUN NUMBER=109
                --------------

PRESSURE=1000.000 KPA  TEMPERATURE=545.000 K  WHSV=  0.439  % CO CONVERSION= 52.135

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   COMPONENT  PARTIAL PRESSURE  MOLE       MOLE      MASS       MASS       RATE            SELECTIVE
                   KPA          %(TOTAL)   %(HC)     %(TOTAL)   %(HC)   KGMOL/MIN KG RU   RATES (REL TO CH4)

----------------------------------------------------------------------------------------------------------------

     C1            63.853        6.385     71.913     8.857    38.877    .10090E-01        .10000E 01
     C2             5.100        0.510      5.744     1.326     5.822    .80593E-03        .79874E-01
     C3             4.518        0.452      5.088     1.723     7.564    .71391E-03        .70755E-01
     C4             4.789        0.479      5.393     2.408    10.570    .75675E-03        .75000E-01
     C5             3.454        0.345      3.890     2.156     9.462    .54575E-03        .54088E-01
     C6             2.650        0.265      2.985     1.976     8.674    .41883E-03        .41509E-01
     C7             2.048        0.205      2.307     1.776     7.794    .32364E-03        .32075E-01
     C8             1.205        0.120      1.357     1.191     5.226    .19038E-03        .18868E-01
     C9             0.753        0.075      0.848     0.836     3.668    .11899E-03        .11792E-01
     C10            0.301        0.030      0.339     0.371     1.628    .47594E-04        .47170E-02
     C11            0.120        0.012      0.136     0.163     0.715    .19038E-04        .18868E-02
     C12            0.000        0.000      0.000     0.000     0.000    .0                .0
     CO           162.644       16.264      0.000    39.481     0.000    .27993E-01
     CO2            2.128        0.213      0.000     0.812     0.000    .33633E-03        .33333E-01
     H2O          172.895       17.289      0.000    26.980     0.000    .27321E-01        .27077E 01
     H2         . 573.541       57.354      0.000     9.945     0.000    .64602E-01
----------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 101.025   HYDROGEN IN FROM CARBON BALANCE=  98.237
MOLES OUT/MOLES IN=   0.756   VOLUMETRIC FEED= 132.677 ML/MIN AT NTP   USAGE RATE= .92595E-01   H2/CO USAGE= 2.308
```

APPENDIX 3.

(b) Experimental Results Used for Product Distributions.

```
              RUN NUMBER=  1
              --------------

PRESSURE= 800.000 KPA  TEMPERATURE=573.000 K  WHSV=  0.405  % CO CONVERSION= 64.128

------------------------------------------------------------------------------------------------------------

   COMPONENT  PARTIAL PRESSURE  MOLE       MOLE      MASS      MASS       RATE            SELECTIVE
                    KPA        %(TOTAL)  %(HC)    %(TOTAL)   %(HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------------

     C1          132.136       16.517    92.237    23.575   82.406    .24155E-01      .10000E 01
     C2            5.840        0.730     4.077     1.954    6.829    .10676E-02      .44196E-01
     C3            3.411        0.426     2.381     1.674    5.850    .62360E-03      .25816E-01
     C4            0.991        0.124     0.692     0.641    2.240    .18109E-03      .74970E-02
     C5            0.567        0.071     0.396     0.455    1.592    .10369E-03      .42926E-02
     C6            0.240        0.030     0.167     0.230    0.803    .43812E-04      .18138E-02
     C7            0.072        0.009     0.050     0.080    0.280    .13144E-04      .54414E-03
     C8            0.000        0.000     0.000     0.000    0.000    .0              .0
     C9            0.000        0.000     0.000     0.000    0.000    .0              .0
     C10           0.000        0.000     0.000     0.000    0.000    .0              .0
     C11           0.000        0.000     0.000     0.000    0.000    .0              .0
     C12           0.000        0.000     0.000     0.000    0.000    .0              .0
     CO           92.671       11.584     0.000    28.934    0.000    .30285E-01
     CO2           2.876        0.360     0.000     1.411    0.000    .52575E-03      .21765E-01
     H2O         159.914       19.989     0.000    32.097    0.000    .29233E-01      .12102E 01
     H2          401.282       50.160     0.000     8.949    0.000    .72175E-01
------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 108.405   HYDROGEN IN FROM CARBON BALANCE=  99.512
MOLES OUT/MOLES IN=   0.759   VOLUMETRIC FEED= 125.215 ML/MIN AT NTP   USAGE RATE= .10246E 00   H2/CO USAGE= 2.383

              RUN NUMBER= 10
              --------------

PRESSURE= 800.000 KPA  TEMPERATURE=503.000 K  WHSV=  0.218  % CO CONVERSION=  8.875

------------------------------------------------------------------------------------------------------------

   COMPONENT  PARTIAL PRESSURE  MOLE       MOLE      MASS      MASS       RATE            SELECTIVE
                    KPA        %(TOTAL)  %(HC)    %(TOTAL)   %(HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------------

     C1            3.322        0.415    57.364     0.795   21.452    .43712E-03      .10000E 01
     C2            0.153        0.019     2.636     0.068    1.848    .20084E-04      .45946E-01
     C3            0.521        0.065     8.992     0.343    9.248    .68521E-04      .15676E 00
     C4            0.377        0.047     6.512     0.327    8.827    .49619E-04      .11351E 00
     C5            0.305        0.038     5.271     0.329    8.871    .40168E-04      .91892E-01
     C6            0.278        0.035     4.806     0.358    9.661    .36623E-04      .83784E-01
     C7            0.242        0.030     4.186     0.362    9.784    .31898E-04      .72973E-01
     C8            0.269        0.034     4.651     0.459   12.393    .35442E-04      .81081E-01
     C9            0.108        0.013     1.860     0.206    5.566    .14177E-04      .32432E-01
     C10           0.216        0.027     3.721     0.457   12.350    .28354E-04      .64865E-01
     C11           0.000        0.000     0.000     0.000    0.000    .0              .0
     C12           0.000        0.000     0.000     0.000    0.000    .0              .0
     CO          175.994       21.999     0.000    73.671    0.000    .22553E-02
     CO2           0.269        0.034     0.000     0.177    0.000    .35442E-04      .81081E-01
     H2O          16.603        2.075     0.000     4.468    0.000    .21844E-02      .49973E 01
     H2          601.342       75.168     0.000    17.980    0.000   -.81181E-03
------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  80.076   HYDROGEN IN FROM CARBON BALANCE=  74.397
MOLES OUT/MOLES IN=   1.015   VOLUMETRIC FEED=  67.142 ML/MIN AT NTP   USAGE RATE= .14435E-02   H2/CO USAGE=-0.360
```

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                F-SERIES RUN NUMBER= 11
                --------------

PRESSURE= 800.000 KPA  TEMPERATURE=523.000 K  WHSV=  0.682  % CO CONVERSION= 81.491

------------------------------------------------------------------------------------------------------------

   COMPONENT   PARTIAL PRESSURE   MOLE       MOLE       MASS       MASS        RATE              SELECTIVE
                      KPA         %(TOTAL)   %(HC)      %(TOTAL)   %(HC)  KGMOL/MIN KG RU   RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------------

      C1          75.472         9.434    68.239    11.730   33.616     .21182E-01       .10000E 01
      C2           6.048         0.756     5.468     1.762    5.051     .16974E-02       .80136E-01
      C3           7.448         0.931     6.734     3.183    9.123     .20903E-02       .98686E-01
      C4           5.632         0.704     5.092     3.173    9.094     .15807E-02       .74624E-01
      C5           4.664         0.583     4.217     3.262    9.348     .13090E-02       .61798E-01
      C6           3.720         0.465     3.363     3.108    8.906     .10441E-02       .49290E-01
      C7           2.784         0.348     2.517     2.704    7.750     .78135E-03       .36888E-01
      C8           1.872         0.234     1.693     2.073    5.941     .52539E-03       .24804E-01
      C9           1.440         0.180     1.302     1.790    5.131     .40415E-03       .19080E-01
      C10          1.440         0.180     1.302     1.986    5.692     .40415E-03       .19080E-01
      C11          0.080         0.010     0.072     0.121    0.347     .22453E-04       .10600E-02
      C12          0.000         0.000     0.000     0.000    0.000     .0               .0
      CO          55.040         6.880     0.000    14.970    0.000     .68011E-01
      CO2          1.544         0.193     0.000     0.660    0.000     .43334E-03       .20458E-01
      H2O        239.240        29.905     0.000    41.830    0.000     .67145E-01       .31699E 01
      H2         393.576        49.197     0.000     7.646    0.000     .13082E 00
------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 123.025   HYDROGEN IN FROM CARBON BALANCE= 107.463
MOLES OUT/MOLES IN=   0.691   VOLUMETRIC FEED= 203.679 ML/MIN AT NTP   USAGE RATE= .19883E 00   H2/CO USAGE= 1.924


                F-SERIES RUN NUMBER= 12
                --------------

PRESSURE= 800.000 KPA  TEMPERATURE=523.000 K  WHSV=  0.254  % CO CONVERSION= 66.589

------------------------------------------------------------------------------------------------------------

   COMPONENT   PARTIAL PRESSURE   MOLE       MOLE       MASS       MASS        RATE              SELECTIVE
                      KPA         %(TOTAL)   %(HC)      %(TOTAL)   %(HC)  KGMOL/MIN KG RU   RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------------

      C1          44.096         5.512    65.331     7.953   28.366     .53970E-02       .10000E 01
      C2           1.680         0.210     2.489     0.568    2.026     .20562E-03       .38099E-01
      C3           4.232         0.529     6.270     2.099    7.487     .51796E-03       .95972E-01
      C4           4.120         0.515     6.104     2.694    9.608     .50425E-03       .93433E-01
      C5           3.472         0.434     5.144     2.818   10.051     .42494E-03       .78737E-01
      C6           2.880         0.360     4.267     2.792    9.958     .35249E-03       .65312E-01
      C7           2.688         0.336     3.982     3.030   10.807     .32899E-03       .60958E-01
      C8           1.824         0.228     2.702     2.344    8.360     .22324E-03       .41364E-01
      C9           1.704         0.213     2.525     2.459    8.769     .20855E-03       .38643E-01
      C10          0.800         0.100     1.185     1.281    4.567     .97913E-04       .18142E-01
      C11          0.000         0.000     0.000     0.000    0.000     .0               .0
      C12          0.000         0.000     0.000     0.000    0.000     .0               .0
      CO          84.800        10.600     0.000    26.766    0.000     .20685E-01
      CO2          0.992         0.124     0.000     0.492    0.000     .12141E-03       .22496E-01
      H2O        167.024        20.878     0.000    33.890    0.000     .20442E-01       .37877E 01
      H2         479.688        59.961     0.000    10.815    0.000     .31098E-01
------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 110.278   HYDROGEN IN FROM CARBON BALANCE=  91.721
MOLES OUT/MOLES IN=   0.810   VOLUMETRIC FEED=  75.810 ML/MIN AT NTP   USAGE RATE= .51783E-01   H2/CO USAGE=
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          RUN NUMBER= 13
          --------------

PRESSURE= 800.000 KPA  TEMPERATURE=509.000 K  WHSV=  0.108  % CO CONVERSION= 18.570

-----------------------------------------------------------------------------------------------------------

  COMPONENT   PARTIAL PRESSURE  MOLE      MOLE       MASS       MASS       RATE              SELECTIVE
                   KPA         %(TOTAL)  %(HC)      %(TOTAL)   %(HC)  KGMOL/MIN KG RU   RATES (REL TO CH4)

-----------------------------------------------------------------------------------------------------------

    C1            7.892          0.986    58.621     1.752    22.419     .49714E-03        .10000E 01
    C2            0.427          0.053     3.172     0.178     2.275     .26904E-04        .54118E-01
    C3            0.808          0.101     6.000     0.493     6.310     .50884E-04        .10235E 00
    C4            1.012          0.127     7.517     0.814    10.421     .63751E-04        .12824E 00
    C5            0.836          0.104     6.207     0.835    10.682     .52638E-04        .10588E 00
    C6            0.789          0.099     5.862     0.942    12.050     .49714E-04        .10000E 00
    C7            0.585          0.073     4.345     0.812    10.385     .36847E-04        .74118E-01
    C8            0.418          0.052     3.103     0.661     8.456     .26319E-04        .52941E-01
    C9            0.334          0.042     2.483     0.594     7.596     .21055E-04        .42353E-01
    C10           0.251          0.031     1.862     0.494     6.320     .15792E-04        .31765E-01
    C11           0.111          0.014     0.828     0.241     3.086     .70185E-05        .14118E-01
    C12           0.000          0.000     0.000     0.000     0.000     .0                .0
    CO          170.833         21.354     0.000    66.363     0.000     .24541E-02
    CO2           0.650          0.081     0.000     0.397     0.000     .40941E-04        .82353E-01
    H20          37.658          4.707     0.000     9.404     0.000     .23722E-02        .47718E 01
    H2          577.397         72.175     0.000    16.021     0.000     .18343E-02
-----------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  83.353   HYDROGEN IN FROM CARBON BALANCE=  75.814
MOLES OUT/MOLES IN=   0.980   VOLUMETRIC FEED=  31.849 ML/MIN AT NTP   USAGE RATE= .42884E-02   H2/CO USAGE= 0.747
          F-SERIES RUN NUMRER= 14
          --------------

PRFSSURE= 800.000 KPA  TEMPERATURF=523.000 K  WHSV=  1.020  % CO CONVERSION= 99.584

-----------------------------------------------------------------------------------------------------------

  COMPONENT   PARTIAL PRESSURE  MOLE      MOLE       MASS       MASS       RATE              SELECTIVE
                   KPA         %(TOTAL)  %(HC)      %(TOTAL)   %(HC)  KGMOL/MIN KG RU   RATES (REL TO CH4)

-----------------------------------------------------------------------------------------------------------

    C1          337.080         42.135    99.436    44.607    98.948     .11982E 00        .10000E 01
    C2            1.912          0.239     0.564     0.474     1.052     .67967E-03        .56722E-02
    C3            0.000          0.000     0.000     0.000     0.000     .0                .0
    C4            0.000          0.000     0.000     0.000     0.000     .0                .0
    C5            0.000          0.000     0.000     0.000     0.000     .0                .0
    C6            0.000          0.000     0.000     0.000     0.000     .0                .0
    C7            0.000          0.000     0.000     0.000     0.000     .0                .0
    C8            0.000          0.000     0.000     0.000     0.000     .0                .0
    C9            0.000          0.000     0.000     0.000     0.000     .0                .0
    C10           0.000          0.000     0.000     0.000     0.000     .0                .0
    C11           0.000          0.000     0.000     0.000     0.000     .0                .0
    C12           0.000          0.000     0.000     0.000     0.000     .0                .0
    CO            1.600          0.200     0.000     0.371     0.000     .12422F 00
    CO2           8.536          1.067     0.000     3.166     0.000     .30343E-02        .25323E-01
    H20         332.368         41.546     0.000    49.481     0.000     .11815E 00        .98602E 00
    H2          118.504         14.813     0.000     1.960     0.000     .31864F 00
-----------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 141.346   HYDROGEN IN FROM CARBON BALANCE= 126.859
MOLES OUT/MOLES IN=   0.586   VOLUMETRIC FEED= 304.536 ML/MIN AT NTP   USAGE RATE= .44285E 00   H2/CO USAGE= 2.565
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```
              RUN NUMBER= 15
              --------------

PRESSURE=1200.000 KPA  TEMPERATURE=510.000 K  WHSV=  0.117  % CO CONVERSION= 23.745

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   COMPONENT   PARTIAL PRESSURE   MOLE      MOLE        MASS       MASS        RATE               SELECTIVE
                    KPA         %(TOTAL)   %(HC)     %(TOTAL)    %(HC)  KGMOL/MIN KG RU   RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------------------

       C1           13.088        1.091    54.193      1.928    19.814    .59390E-03        .10000E 01
       C2            0.758        0.063     3.137      0.209     2.151    .34384E-04        .57895E-01
       C3            1.874        0.156     7.758      0.759     7.801    .85021E-04        .14316E 00
       C4            1.943        0.162     8.043      1.037    10.661    .88147E-04        .14842E 00
       C5            1.791        0.149     7.416      1.187    12.201    .81270E-04        .13684E 00
       C6            1.515        0.126     6.275      1.200    12.332    .68767E-04        .11579E 00
       C7            1.033        0.086     4.278      0.951     9.777    .46887E-04        .78947E-01
       C8            0.951        0.079     3.936      0.998    10.254    .43136E-04        .72632E-01
       C9            0.827        0.069     3.423      0.974    10.011    .37509E-04        .63158E-01
       C10           0.372        0.031     1.540      0.486     4.998    .16879E-04        .28421E-01
       C11           0.000        0.000     0.000      0.000     0.000    .0                .0
       C12           0.000        0.000     0.000      0.000     0.000    .0                .0
       CO          239.719       19.977     0.000     61.795     0.000    .33877E-02
       CO2           2.618        0.218     0.000      1.060     0.000    .11878E-03        .20000E 00
       H20          69.422        5.785     0.000     11.504     0.000    .31502E-02        .53042E 01
       H2          864.090       72.008     0.000     15.910     0.000    .20323E-02
------------------------------------------------------------------------------------------------------------------

 HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  85.809   HYDROGEN IN FROM CARBON BALANCE=  75.740
 MOLES OUT/MOLES IN=   0.981   VOLUMETRIC FEED=  34.193 ML/MIN AT NTP   USAGE RATE= .54200E-02   H2/CO USAGE= 0.600

            F-SERIES RUN NUMBER= 16
            --------------

PRESSURE= 800.000 KPA  TEMPERATURF=548.000 K  WHSV=  0.667  % CO CONVERSION= 98.825

------------------------------------------------------------------------------------------------------------------
   COMPONENT   PARTIAL PRESSURE   MOLE      MOLE        MASS       MASS        RATE               SELECTIVE
                    KPA         %(TOTAL)   %(HC)     %(TOTAL)    %(HC)  KGMOL/MIN KG RU   RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------------------

       C1          307.400       38.425    99.295     43.358    98.685    .76770E-01        .10000E 01
       C2            2.184        0.273     0.705      0.578     1.315    .54543E-03        .71047E-02
       C3            0.000        0.000     0.000      0.000     0.000    .0                .0
       C4            0.000        0.000     0.000      0.000     0.000    .0                .0
       C5            0.000        0.000     0.000      0.000     0.000    .0                .0
       C6            0.000        0.000     0.000      0.000     0.000    .0                .0
       C7            0.000        0.000     0.000      0.000     0.000    .0                .0
       C8            0.000        0.000     0.000      0.000     0.000    .0                .0
       C9            0.000        0.000     0.000      0.000     0.000    .0                .0
       C10           0.000        0.000     0.000      0.000     0.000    .0                .0
       C11           0.000        0.000     0.000      0.000     0.000    .0                .0
       C12           0.000        0.000     0.000      0.000     0.000    .0                .0
       CO            3.840        0.480     0.000      0.948     0.000    .80654E-01
       CO2          11.184        1.398     0.000      4.338     0.000    .27931E-02        .36383E-01
       H20         300.584       37.573     0.000     47.696     0.000    .75068E-01        .97783E 00
       H2          174.808       21.851     0.000      3.082     0.000    .19229E 00
------------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 137.093   HYDROGEN IN FROM CARBON BALANCE= 118.097
MOLES OUT/MOLES IN=   0.629   VOLUMETRIC FEED= 199.174 ML/MIN AT NTP   USAGE RATE= .27295E 00   H2/CO USAGF= 2.384
```

```
              F-SERIES RUN NUMBER= 18
              --------------

PRESSURE= 800.000 KPA  TEMPERATURE=571.000 K  WHSV=  1.606  % CO CONVERSION= 74.125

--------------------------------------------------------------------------------------------------------
   COMPONENT  PARTIAL PRESSURE  MOLE      MOLE      MASS      MASS      RATE              SELECTIVE
                   KPA          %(TOTAL)  %(HC)     %(TOTAL)  %(HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

--------------------------------------------------------------------------------------------------------

      C1        173.840        21.730    94.598    29.370    88.188    .12559E 00      .10000E 01
      C2          6.448         0.806     3.509     2.043     6.133    .46582E-02      .37092E-01
      C3          2.328         0.291     1.267     1.082     3.248    .16818E-02      .13392E-01
      C4          0.688         0.086     0.374     0.421     1.265    .49703E-03      .39577E-02
      C5          0.272         0.034     0.148     0.207     0.621    .19650E-03      .15647E-02
      C6          0.144         0.018     0.078     0.131     0.393    .10403E-03      .82835E-03
      C7          0.048         0.006     0.026     0.051     0.152    .34676E-04      .27612E-03
      C8          0.000         0.000     0.000     0.000     0.000    .0              .0
      C9          0.000         0.000     0.000     0.000     0.000    .0              .0
      C10         0.000         0.000     0.000     0.000     0.000    .0              .0
      C11         0.000         0.000     0.000     0.000     0.000    .0              .0
      C12         0.000         0.000     0.000     0.000     0.000    .0              .0
      CO         70.400         8.800     0.000    20.815     0.000    .14570E 00
      CO2         2.648         0.331     0.000     1.230     0.000    .19130E-02      .15232E-01
      H2O       196.384        24.548     0.000    37.327     0.000    .14187E 00      .11297E 01
      H2        346.800        43.350     0.000     7.324     0.000    .31772E 00
--------------------------------------------------------------------------------------------------------
HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 115.748   HYDROGEN IN FROM CARBON BALANCE=  98.325
MOLES OUT/MOLES IN=   0.756   VOLUMETRIC FEED= 479.692 ML/MIN AT NTP   USAGE RATE= .46342E 00   H2/CO USAGE= 2.181

              F-SERIES RUN NUMBER= 20
              --------------

 PRESSURE= 800.000 KPA  TEMPERATURE=573.000 K  WHSV=  1.061  % CO CONVERSION= 97.089

--------------------------------------------------------------------------------------------------------
   COMPONENT  PARTIAL PRESSURE  MOLE      MOLE      MASS      MASS      RATE              SELECTIVE
                   KPA          %(TOTAL)  %(HC)     %(TOTAL)  %(HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

--------------------------------------------------------------------------------------------------------

      C1        292.560        36.570    99.316    42.263    98.724    .11920E 00      .10000E 01
      C2          2.016         0.252     0.684     0.546     1.276    .82138E-03      .68909E-02
      C3          0.000         0.000     0.000     0.000     0.000    .0              .0
      C4          0.000         0.000     0.000     0.000     0.000    .0              .0
      C5          0.000         0.000     0.000     0.000     0.000    .0              .0
      C6          0.000         0.000     0.000     0.000     0.000    .0              .0
      C7          0.000         0.000     0.000     0.000     0.000    .0              .0
      C8          0.000         0.000     0.000     0.000     0.000    .0              .0
      C9          0.000         0.000     0.000     0.000     0.000    .0              .0
      C10         0.000         0.000     0.000     0.000     0.000    .0              .0
      C11         0.000         0.000     0.000     0.000     0.000    .0              .0
      C12         0.000         0.000     0.000     0.000     0.000    .0              .0
      CO          9.280         1.160     0.000     2.346     0.000    .12612E 00
      CO2        12.952         1.619     0.000     5.145     0.000    .52771E-02      .44271E-01
      H2O       283.640        35.455     0.000    46.096     0.000    .11556E 00      .96951E 00
      H2        199.552        24.944     0.000     3.603     0.000    .29424E 00
--------------------------------------------------------------------------------------------------------
HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 134.295   HYDROGEN IN FROM CARBON BALANCE= 115.217
MOLES OUT/MOLES IN=   0.645   VOLUMETRIC FEED= 317.015 ML/MIN AT NTP   USAGE RATE=
```

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                 F-SERIES RUN NUMBER= 24
                 --------------

PRESSURE= 800.000 KPA  TEMPERATURE=568.000 K  WHSV=  0.962  % CO CONVERSION= 49.469

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  COMPONENT   PARTIAL PRESSURE   MOLE      MOLE       MASS      MASS        RATE              SELECTIVE
                     KPA       %(TOTAL)   %(HC)     %(TOTAL)   %(HC)  KGMOL/MIN KG RU   RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------

    C1              91.160      11.395    91.659     17.892   80.662    .45827E-01       .10000E 01
    C2               4.264       0.533     4.287      1.569    7.074    .21436E-02       .46775E-01
    C3               2.176       0.272     2.188      1.174    5.295    .10939E-02       .23870E-01
    C4               1.048       0.131     1.054      0.746    3.362    .52684E-03       .11496E-01
    C5               0.448       0.056     0.450      0.396    1.784    .22522E-03       .49144E-02
    C6               0.216       0.027     0.217      0.228    1.027    .10859E-03       .23695E-02
    C7               0.144       0.018     0.145      0.177    0.796    .72391E-04       .15796E-02
    C8               0.000       0.000     0.000      0.000    0.000    .0               .0
    C9               0.000       0.000     0.000      0.000    0.000    .0               .0
    C10              0.000       0.000     0.000      0.000    0.000    .0               .0
    C11              0.000       0.000     0.000      0.000    0.000    .0               .0
    C12              0.000       0.000     0.000      0.000    0.000    .0               .0
    CO             118.400      14.800     0.000     40.668    0.000    .58270E-01
    CO2              0.960       0.120     0.000      0.518    0.000    .48260E-03       .10531E-01
    H2O            113.992      14.249     0.000     25.170    0.000    .57305E-01       .12505E 01
    H2             467.192      58.399     0.000     11.462    0.000    .10568E 00
------------------------------------------------------------------------------------------------------
HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  99.449   HYDROGEN IN FROM CARBON BALANCE=  88.676
MOLES OUT/MOLES IN=   0.877   VOLUMETRIC FEED= 287.466 ML/MIN AT NTP   USAGE RATE= .16395E 00   H2/CO USAGE= 1.814
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                  F-SERIES RUN NUMBER= 27
                  --------------

  PRESSURE= 800.000 KPA  TEMPERATURE=525.000 K  WHSV=  0.282  % CO CONVERSION= 69.512

  ----------------------------------------------------------------------------------------------------

    COMPONENT   PARTIAL PRESSURE   MOLE      MOLE       MASS      MASS        RATE              SELECTIVE
                       KPA       %(TOTAL)   %(HC)     %(TOTAL)   %(HC)  KGMOL/MIN KG RU   RATES (REL TO CH4)

  ----------------------------------------------------------------------------------------------------

      C1              43.248       5.406    63.280      7.823   26.886    .59172E-02       .10000E 01
      C2               3.632       0.454     5.314      1.232    4.234    .49693E-03       .83981E-01
      C3               4.272       0.534     6.251      2.125    7.303    .58449E-03       .98779E-01
      C4               3.632       0.454     5.314      2.381    8.185    .49693E-03       .83981E-01
      C5               3.296       0.412     4.823      2.683    9.221    .45096E-03       .76212E-01
      C6               2.712       0.339     3.968      2.637    9.062    .37106E-03       .62708E-01
      C7               2.424       0.303     3.547      2.740    9.418    .33165E-03       .56049E-01
      C8               2.160       0.270     3.160      2.784    9.568    .29553E-03       .49945E-01
      C9               1.176       0.147     1.721      1.702    5.849    .16090E-03       .27192E-01
      C10              1.080       0.135     1.580      1.734    5.959    .14777E-03       .24972E-01
      C11              0.712       0.089     1.042      1.256    4.316    .97416E-04       .16463E-01
      C12              0.000       0.000     0.000      0.000    0.000    .0               .0
      CO              76.800       9.600     0.000     24.310    0.000    .23958E-01
      CO2              1.032       0.129     0.000      0.513    0.000    .14120E-03       .23862E-01
      H2O            173.040      21.630     0.000     35.211    0.009    .23675E-01       .40011E 01
      H2             480.784      60.098     0.000     10.870    0.000    .33861E-01
  ----------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 112.030   HYDROGEN IN FROM CARBON BALANCE=  91.033
MOLES OUT/MOLES IN=   0.816   VOLUMETRIC FEED=  84.112 ML/MIN AT NTP   USAGE RATE= .57818E-01   H2/CO USAGE= 1.413
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                F-SERIES RUN NUMBER= 28
                ---------------

PRESSURE= 800.000 KPA  TEMPERATURE=548.000 K  WHSV=  0.388  % CO CONVERSION= 99.326

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   COMPONENT   PARTIAL PRESSURE   MOLE      MOLE       MASS      MASS        RATE              SELECTIVE
                     KPA        %(TOTAL)  %(HC)     %(TOTAL)   %(HC)   KGMOL/MIN KG RU   RATES (REL TO CH4)

-----------------------------------------------------------------------------------------------------------

     C1           322.240        40.280    99.740    44.698    99.514   .46040E-01        .10000E 01
     C2             0.840         0.105     0.260     0.218     0.486   .12001E-03        .26068E-02
     C3             0.000         0.000     0.000     0.000     0.000   .0                .0
     C4             0.000         0.000     0.000     0.000     0.000   .0                .0
     C5             0.000         0.000     0.000     0.000     0.000   .0                .0
     C6             0.000         0.000     0.000     0.000     0.000   .0                .0
     C7             0.000         0.000     0.000     0.000     0.000   .0                .0
     C8             0.000         0.000     0.000     0.000     0.000   .0                .0
     C9             0.000         0.000     0.000     0.000     0.000   .0                .0
     C10            0.000         0.000     0.000     0.000     0.000   .0                .0
     C11            0.000         0.000     0.000     0.000     0.000   .0                .0
     C12            0.000         0.000     0.000     0.000     0.000   .0                .0
     CO             2.240         0.280     0.000     0.544     0.000   .47153E-01
     CO2            6.112         0.764     0.000     2.331     0.000   .87324E-03        .18967E-01
     H2O          317.808        39.726     0.000    49.594     0.000   .45406E-01        .98625E 00
     H2           150.760        18.845     0.000     2.614     0.000   .11571E 00
-----------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 139.446   HYDROGEN IN FROM CARBON BALANCE= 120.077
MOLES OUT/MOLES IN=   0.619   VOLUMETRIC FEED= 115.856 ML/MIN AT NTP   USAGE RATE= .16286E 00   H2/CO USAGE= 2.454

                F-SERIES RUN NUMBER= 29
                ---------------

PRESSURE= 800.000 KPA  TEMPERATURE=548.000 K  WHSV=  0.550  % CO CONVERSION= 63.322 .

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   COMPONENT   PARTIAL PRESSURE   MOLE      MOLE       MASS      MASS        RATE              SELECTIVE
                     KPA        %(TOTAL)  %(HC)     %(TOTAL)   %(HC)   KGMOL/MIN KG RU   RATES (REL TO CH4)

-----------------------------------------------------------------------------------------------------------

     C1            88.192        11.024    81.310    16.006    57.627   .23470E-01        .10000E 01
     C2             6.920         0.865     6.380     2.355     8.478   .18415E-02        .78465E-01
     C3             5.200         0.650     4.794     2.595     9.344   .13838E-02        .58962E-01
     C4             3.376         0.422     3.113     2.221     7.997   .89842E-03        .38280E-01
     C5             2.112         0.264     1.947     1.725     6.210   .56204E-03        .23948E-01
     C6             1.392         0.174     1.283     1.358     4.889   .37044E-03        .15784E-01
     C7             0.816         0.102     0.752     0.926     3.332   .21715E-03        .92525E-02
     C8             0.456         0.057     0.420     0.590     2.123   .12135E-03        .51705E-02
     C9             0.000         0.000     0.000     0.000     0.000   .0                .0
     C10            0.000         0.000     0.000     0.000     0.000   .0                .0
     C11            0.000         0.000     0.000     0.000     0.000   .0                .0
     C12            0.000         0.000     0.000     0.000     0.000   .0                .0
     CO            92.800        11.600     0.000    29.474     0.000   .42636E-01
     CO2            0.808         0.101     0.000     0.403     0.000   .21502E-03        .91618E-02
     H2O          158.600        19.825     0.000    32.382     0.000   .42206E-01        .17983E 01
     H2           439.328        54.916     0.000     9.967     0.000   .77748E-01
-----------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 108.225   HYDROGEN IN FROM CARBON BALANCE=  91.435
MOLES OUT/MOLES IN=   0.813   VOLUMETRIC FEED= 164.322 ML/MIN AT NTP   USAGE RATE= .12038E 00
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                  F-SERIES RUN NUMBER= 32
                  ---------------

PRESSURE=1200.000 KPA  TEMPERATURE=525.000 K  WHSV=  0.289  % CO CONVERSION= 88.742

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    COMPONENT   PARTIAL PRESSURE   MOLE      MOLE      MASS      MASS        RATE              SELECTIVE
                      KPA        %(TOTAL)  %(HC)    %(TOTAL)   %(HC)   KGMOL/MIN KG RU   RATES (REL TO CH4)

--------------------------------------------------------------------------------------------------------------

      C1          132.288        11.024    69.473    13.025    34.272    .99849E-02       .10000E 01
      C2           10.284         0.857     5.401     1.899     4.995    .77622E-03       .77739E-01
      C3           10.476         0.873     5.502     2.837     7.463    .79071E-03       .79191E-01
      C4            9.060         0.755     4.758     3.234     8.508    .68384E-03       .68487E-01
      C5            8.184         0.682     4.298     3.626     9.541    .61772E-03       .61865E-01
      C6            6.372         0.531     3.346     3.372     8.873    .48095E-03       .48168E-01
      C7            5.040         0.420     2.647     3.102     8.161    .38041E-03       .38099E-01
      C8            3.312         0.276     1.739     2.323     6.113    .24999E-03       .25036E-01
      C9            2.448         0.204     1.286     1.928     5.074    .18477E-03       .18505E-01
      C10           2.124         0.177     1.115     1.856     4.884    .16032E-03       .16056E-01
      C11           0.720         0.060     0.378     0.691     1.819    .54345E-04       .54427E-02
      C12           0.108         0.009     0.057     0.113     0.297    .81517E-05       .81640E-03
      CO           52.800         4.400     0.000     9.098     0.000    .31415E-01
      CO2           2.268         0.189     0.000     0.614     0.000    .17119E-03       .17144E-01
      H2O         411.672        34.306     0.000    45.601     0.000    .31072E-01       .31119E 01
      H2          542.844        45.237     0.000     6.681     0.000    .61370E-01
--------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 129.906   HYDROGEN IN FROM CARBON BALANCE= 112.994
MOLES OUT/MOLES IN=   0.656   VOLUMETRIC FEED=  86.393 ML/MIN AT NTP   USAGE RATE= .92785E-01   H2/CO USAGE= 1.954


                  RUN NUMBER= 32
                  ---------------

  PRESSURE=1200.000 KPA  TEMPERATURE=496.000 K  WHSV=  0.252  % CO CONVERSION=  5.087

--------------------------------------------------------------------------------------------------------------

    COMPONENT   PARTIAL PRESSURE   MOLE      MOLE      MASS      MASS        RATE              SELECTIVE
                      KPA        %(TOTAL) . %(HC)   %(TOTAL)   %(HC)   KGMOL/MIN KG RU   RATES (REL TO CH4)

--------------------------------------------------------------------------------------------------------------

      C1            2.610         0.218    53.401     0.423    19.897    .28258E-03       .10000E 01
      C2            0.185         0.015     3.778     0.056     2.640    .19994E-04       .70755E-01
      C3            0.492         0.041    10.076     0.219    10.324    .53318E-04       .18868E 00
      C4            0.394         0.033     8.060     0.231    10.887    .42654E-04       .15094E 00
      C5            0.283         0.024     5.793     0.206     9.714    .30658E-04       .10849E 00
      C6            0.295         0.025     6.045     0.257    12.107    .31991E-04       .11321E 00
      C7            0.222         0.018     4.534     0.224    10.558    .23993E-04       .84906E-01
      C8            0.185         0.015     3.778     0.213    10.031    .19994E-04       .70755E-01
      C9            0.172         0.014     3.526     0.223    10.511    .18661E-04       .66038E-01
      C10           0.049         0.004     1.008     0.071     3.332    .53318E-05       .18868E-01
      C11           0.000         0.000     0.000     0.000     0.000    .0               .0
      C12           0.000         0.000     0.000     0.000     0.000    .0               .0
      CO          270.875        22.573     0.000    76.787     0.000    .15715E-02
      CO2           0.222         0.018     0.000     0.099     0.000    .23993E-04       .84906E-01
      H2O          14.073         1.173     0.000     2.565     0.000    .15236E-02       .53915E 01
      H2          909.942        75.829     0.000    18.425     0.000   -.91871E-02
--------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  78.600   HYDROGEN IN FROM CARBON BALANCE=  68.757
MOLES OUT/MOLES IN=   1.081   VOLUMETRIC FEED=  69.073 ML/MIN AT NTP   USAGE RATE=-.76155E-02   H2/CO USAGE=-5.846
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                F-SERIES RUN NUMBER= 33
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PRESSURE= 800.000 KPA  TEMPERATURE=525.000 K  WHSV=  0.275  % CO CONVERSION= 67.608

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  COMPONENT   PARTIAL PRESSURE  MOLF       MOLF       MASS       MASS        RATE              SELECTIVE
                   KPA          %(TOTAL)   %(HC)      %(TOTAL)   %(HC)   KGMOL/MIN KG RU   RATES (REL TO CH4)

---------------------------------------------------------------------------------------------------------------

    C1            63.456         7.932     74.619     11.321     39.232     .83285E-02        .10000E 01
    C2             3.088         0.386      3.631      1.033      3.580     .40530E-03        .48664E-01
    C3             3.648         0.456      4.290      1.790      6.202     .47880E-03        .57489E-01
    C4             3.328         0.416      3.913      2.152      7.459     .43680E-03        .52446E-01
    C5             3.000         0.375      3.528      2.408      8.346     .39375E-03        .47277E-01
    C6             2.592         0.324      3.048      2.486      8.614     .34020E-03        .40847E-01
    C7             1.944         0.243      2.286      2.168      7.512     .25515E-03        .30635E-01
    C8             2.112         0.264      2.484      2.685      9.303     .27720E-03        .33283E-01
    C9             0.960         0.120      1.129      1.370      4.748     .12600E-03        .15129E-01
    C10            0.912         0.114      1.072      1.444      5.004     .11970E-03        .14372E-01
    C11            0.000         0.000      0.000      0.000      0.000     .0                .0
    C12            0.000         0.000      0.000      0.000      0.000     .0                .0
    CO            83.200        10.400      0.000     25.976      0.000     .22788E-01
    CO2            0.920         0.115      0.000      0.451      0.000     .12075E-03        .14498E-01
    H2O          171.784        21.473      0.000     34.478      0.000     .22546E-01        .27071E 01
    H2           459.056        57.382      0.000     10.237      0.000     .37201E-01
---------------------------------------------------------------------------------------------------------------
HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 111.073   HYDROGEN IN FROM CARBON BALANCE=  92.811
MOLES OUT/MOLES IN=   0.801   VOLUMETRIC FEED=  82.263 ML/MIN AT NTP   USAGE RATE= .59988E-01   H2/CO USAGE= 1.632

                 F-SERIES RUN NUMBER= 34
                 --------------

 PRESSURE= 800.000 KPA  TEMPERATURE=573.000 K  WHSV=  0.844  % CO CONVERSION= 81.243

---------------------------------------------------------------------------------------------------------------

   COMPONENT   PARTIAL PRESSURE  MOLF       MOLE       MASS       MASS        RATE              SELECTIVE
                    KPA          %(TOTAL)   %(HC)      %(TOTAL)   %(HC)   KGMOL/MIN KG RU   RATES (REL TO CH4)

---------------------------------------------------------------------------------------------------------------

     C1           207.760        25.970     96.039     33.362     91.710     .74854E-01        .10000E 01
     C2             6.448         0.806      2.981      1.941      5.337     .23232E-02        .31036E-01
     C3             1.472         0.184      0.680      0.650      1.787     .53035E-03        .70851E-02
     C4             0.384         0.048      0.178      0.224      0.614     .13835E-03        .18483E-02
     C5             0.192         0.024      0.089      0.139      0.381     .69176E-04        .92414E-03
     C6             0.072         0.009      0.033      0.062      0.171     .25941E-04        .34655E-03
     C7             0.000         0.000      0.000      0.000      0.000     .0                .0
     C8             0.000         0.000      0.000      0.000      0.000     .0                .0
     C9             0,000         0,000      0,000      0,000      0,000     .0                .0
     C10            0.000         0.000      0.000      0.000      0.000     .0                .0
     C11            0.000         0.000      0.000      0.000      0.000     .0                .0
     C12            0.000         0.000      0.000      0.000      0.000     .0                .0
     CO            53.760         6.720      0.000     15.107      0.000     .83896E-01
     CO2            4.856         0.607      0.000      2.144      0.000     .17496E-02        .23373E-01
     H2O          223.144        27.893      0.000     40.311      0.000     .80397E-01        .10740E 01
     H2           301.912        37.739      0.000      6.060      0.000     .18977E 00
---------------------------------------------------------------------------------------------------------------
HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 121.173   HYDROGEN IN FROM CARBON BALANCE= 103.578
MOLES OUT/MOLES IN=   0.717   VOLUMETRIC FEED= 252.465 ML/MIN AT NTP   USAGE RATE=
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              F-SERIES RUN NUMBER= 35
              ---------------

PRESSURE= 800.000 KPA  TEMPERATURE=573.000 K  WHSV=  0.952  % CO CONVERSION= 69.487

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  COMPONENT  PARTIAL PRESSURE  MOLE      MOLE      MASS      MASS       RATE               SELECTIVE
                   KPA        %(TOTAL)  %(HC)    %(TOTAL)   %(HC)  KGMOL/MIN KG RU   RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------------
     C1        156.880        19.610    94.379    27.472    87.990    .69681E-01       .10000E 01
     C2          6.320         0.790     3.802     2.075     6.646    .28071E-02       .40286E-01
     C3          2.016         0.252     1.213     0.971     3.110    .89544E-03       .12851E-01
     C4          0.664         0.083     0.399     0.422     1.350    .29493E-03       .42325E-02
     C5          0.272         0.034     0.164     0.214     0.687    .12081E-03       .17338E-02
     C6          0.072         0.009     0.043     0.068     0.217    .31980E-04       .45895E-03
     C7          0.000         0.000     0.000     0.000     0.000    .0               .0
     C8          0.000         0.000     0.000     0.000     0.000    .0               .0
     C9          0.000         0.000     0.000     0.000     0.000    .0               .0
     C10         0.000         0.000     0.000     0.000     0.000    .0               .0
     C11         0.000         0.000     0.000     0.000     0.000    .0               .0
     C12         0.000         0.000     0.000     0.000     0.000    .0               .0
     CO         80.000        10.000     0.000    28.516     0.000    .80920E-01
     CO2         2.168         0.271     0.000     1.044     0.000    .96296E-03       .13819E-01
     H2O       177.848        22.231     0.000    35.037     0.000    .78994E-01       .11337E 01
     H2        373.760        46.720     0.000     8.181     0.000    .17066E 00
------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 112.231   HYDROGEN IN FROM CARBON BALANCE=  94.748
MOLES OUT/MOLES IN=   0.784   VOLUMETRIC FEED= 284.709 ML/MIN AT NTP   USAGE RATE= .25158E 00   H2/CO USAGE= 2.109

              F-SERIES RUN NUMBER= 36
              ---------------

PRESSURE= 800.000 KPA  TEMPERATURE=573.000 K  WHSV=  0.124  % CO CONVERSION= 57.770

------------------------------------------------------------------------------------------------------------
  COMPONENT  PARTIAL PRESSURE  MOLE      MOLE      MASS      MASS       RATE               SELECTIVE
                   KPA        %(TOTAL)  %(HC)    %(TOTAL)   %(HC)  KGMOL/MIN KG RU   RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------------
     C1        123.808        15.476    93.601    22.557    86.076    .73897E-02       .10000E 01
     C2          5.240         0.655     3.962     1.790     6.831    .31276E-03       .42324E-01
     C3          2.136         0.267     1.615     1.070     4.084    .12749E-03       .17253E-01
     C4          0.720         0.090     0.544     0.476     1.815    .42975E-04       .58155E-02
     C5          0.296         0.037     0.224     0.243     0.926    .17667E-04       .23908E-02
     C6          0.072         0.009     0.054     0.071     0.269    .42975E-05       .58155E-03
     C7          0.000         0.000     0.000     0.000     0.000    .0               .0
     C8          0.000         0.000     0.000     0.000     0.000    .0               .0
     C9          0.000         0.000     0.000     0.000     0.000    .0               .0
     C10         0.000         0.000     0.000     0.000     0.000    .0               .0
     C11         0.000         0.000     0.000     0.000     0.000    .0               .0
     C12         0.000         0.000     0.000     0.000     0.000    .0               .0
     CO        107.200        13.400     0.000    38.179     0.000    .87530E-02
     CO2         1.160         0.145     0.000     0.581     0.000    .69237E-04       .93693E-02
     H2O       144.328        18.041     0.000    29.582     0.000    .86145E-02       .11657E 01
     H2        415.040        51.880     0.000     9.452     0.000    .19031E-01
------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 104.641   HYDROGEN IN FROM CARBON BALANCE=  91.736
MOLES OUT/MOLES IN=   0.810   VOLUMETRIC FEED=  37.043 ML/MIN AT NTP   USAGE RATE= .27784E-01   H2/CO USAGE= 2.174
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          F-SERIES RUN NUMBER= 37
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PRESSURE= 800.000 KPA  TEMPERATURE=548.000 K  WHSV= 0.390  % CO CONVERSION= 69.654

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  COMPONENT  PARTIAL PRESSURE  MOLE      MOLE     MASS      MASS      RATE              SELECTIVE
                  KPA          %(TOTAL)  %(HC)    %(TOTAL)  %(HC)  KGMOL/MIN KG RU   RATES (REL TO CH4)

---------------------------------------------------------------------------------------------------

     C1          106.000      13.250    82.963   18.467   60.372    .19187E-01       .10000E 01
     C2            7.664       0.958     5.998    2.504    8.184    .13872E-02       .72302E-01
     C3            5.512       0.689     4.314    2.641    8.633    .99771E-03       .52000E-01
     C4            3.480       0.435     2.724    2.198    7.185    .62991E-03       .32830E-01
     C5            2.160       0.270     1.691    1.693    5.536    .39098E-03       .20377E-01
     C6            1.560       0.195     1.221    1.461    4.776    .28237E-03       .14717E-01
     C7            0.816       0.102     0.639    0.889    2.905    .14770E-03       .76981E-02
     C8            0.432       0.054     0.338    0.536    1.753    .78195E-04       .40755E-02
     C9            0.144       0.018     0.113    0.201    0.656    .26065E-04       .13585E-02
     C10           0.000       0.000     0.000    0.000    0.000    .0               .0
     C11           0.000       0.000     0.000    0.000    0.000    .0               .0
     C12           0.000       0.000     0.000    0.000    0.000    .0               .0
     CO           80.000      10.000     0.000   24.391    0.000    .33237E-01
     CO2           1.216       0.152     0.000    0.583    0.000    .22011E-03       .11472E-01
     H2O         181.192      22.649     0.000   35.513    0.000    .32797E-01       .17094E 01
     H2          409.824      51.228     0.000    8.925    0.000    .63774E-01
---------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 112.649   HYDROGEN IN FROM CARBON BALANCE=  95.269
MOLES OUT/MOLES IN=   0.780   VOLUMETRIC FEED= 116.662 ML/MIN AT NTP   USAGE RATE= .97011E-01   H2/CO USAGE= 1.919

          F-SERIES RUN NUMBER= 38
          --------------

PRESSURE= 800.000 KPA  TEMPERATURE=548.000 K  WHSV=  0.273  % CO CONVERSION= 99.058

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  COMPONENT  PARTIAL PRESSURE  MOLE      MOLE     MASS      MASS      RATE              SELECTIVE
                  KPA          %(TOTAL)  %(HC)    %(TOTAL)  %(HC)  KGMOL/MIN KG RU   RATES (REL TO CH4)

---------------------------------------------------------------------------------------------------

     C1          326.480      40.810    99.498   44.458   99.062    .32111E-01       .10000E 01
     C2            1.648       0.206     0.502    0.421    0.938    .16209E-03       .50478E-02
     C3            0.000       0.000     0.000    0.000    0.000    .0               .0
     C4            0.000       0.000     0.000    0.000    0.000    .0               .0
     C5            0.000       0.000     0.000    0.000    0.000    .0               .0
     C6            0.000       0.000     0.000    0.000    0.000    .0               .0
     C7            0.000       0.000     0.000    0.000    0.000    .0               .0
     C8            0.000       0.000     0.000    0.000    0.000    .0               .0
     C9            0.000       0.000     0.000    0.000    0.000    .0               .0
     C10           0.000       0.000     0.000    0.000    0.000    .0               .0
     C11           0.000       0.000     0.000    0.000    0.000    .0               .0
     C12           0.000       0.000     0.000    0.000    0.000    .0               .0
     CO            3.200       0.400     0.000    0.763    0.000    .33090E-01
     CO2           6.664       0.833     0.000    2.496    0.000    .65543E-03       .20412E-01
     H2O         323.112      40.389     0.000   49.499    0.000    .31779E-01       .98968E 00
     H2          138.896      17.362     0.000    2.364    0.000    .82914E-01
---------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 139.989   HYDROGEN IN FROM CARBON BALANCE= 122.740
MOLES OUT/MOLES IN=   0.605   VOLUMETRIC FEED=  81.669 ML/MIN AT NTP   USAGE RATE= .11600E 00   H2/CO USAGE= 2.506
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                    F-SERIES RUN NUMBER= 40
                    --------------

PRESSURE= 800.000 KPA   TEMPERATURE=545.000 K   WHSV=  0.300   % CO CONVERSION= 75.395

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   COMPONENT   PARTIAL PRESSURE   MOLE        MOLE       MASS        MASS          RATE              SELECTIVE

                     KPA          %(TOTAL)   %(HC)      %(TOTAL)    %(HC)   KGMOL/MIN KG RU    RATES (REL TO CH4)

----------------------------------------------------------------------------------------------------------------

      C1         135.680          16.960     86.288     72.809     68.406     .18246E-01         .10000E 01

      C2           8.872           1.109      5.642      2.796      8.387     .11931E-02         .65389E-01

      C3           5.896           0.737      3.750      2.726      8.175     .79290E-03         .43455E-01

      C4           3.280           0.410      2.086      1.999      5.995     .44110E-03         .24175E-01

      C5           1.936           0.242      1.231      1.465      4.392     .26036E-03         .14269E-01

      C6           0.992           0.124      0.631      0.896      2.688     .13341E-03         .73113E-02

      C7           0.320           0.040      0.204      0.336      1.008     .43034E-04         .23585E-02

      C8           0.264           0.033      0.168      0.316      0.948     .35503E-04         .19458E-02

      C9           0.000           0.000      0.000      0.000      0.000     .0                 .0

      C10          0.000           0.000      0.000      0.000      0.000     .0                 .0

      C11          0.000           0.000      0.000      0.000      0.000     .0                 .0

      C12          0.000           0.000      0.000      0.000      0.000     .0                 .0

      CO          67.200           8.400      0.000     19.769      0.000     .27691E-01

      CO2          1.696           0.212      0.000      0.784      0.000     .22808E-03         .12500E-01

      H2O        202.520          25.315      0.000     38.101      0.000     .27235E-01         .14926E 01

      H2         371.344          46.418      0.000      7.803      0.000     .56245E-01
----------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 116.915    HYDROGEN IN FROM CARBON BALANCE=  98.696

MOLES OUT/MOLES IN=    0.753    VOLUMETRIC FEED=  89.795 ML/MIN AT NTP    USAGE RATE= .83936E-01    H2/CO USAGE= 2.051


                    F-SERIES RUN NUMBER= 39
                    --------------

PRESSURE= 800.000 KPA   TEMPERATURE=545.000 K   WHSV=  0.340   % CO CONVERSION= 71.892

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   COMPONENT   PARTIAL PRESSURE   MOLE        MOLE       MASS        MASS          RATE              SELECTIVE

                     KPA          %(TOTAL)   %(HC)      %(TOTAL)    %(HC)   KGMOL/MIN KG RU    RATES (REL TO CH4)

----------------------------------------------------------------------------------------------------------------

      C1         118.720          14.840     84.824     20.382     64.336     .18459E-01         .10000E 01

      C2           8.000           1.000      5.716      2.575      8.128     .12439E-02         .67385E-01

      C3           5.432           0.679      3.881      2.565      8.095     .84458E-03         .45755E-01

      C4           3.376           0.422      2.412      2.101      6.632     .52491E-03         .28437E-01

      C5           2.080           0.260      1.486      1.607      5.072     .32340E-03         .17520E-01

      C6           1.152           0.144      0.823      1.063      3.355     .17912E-03         .97035E-02

      C7           0.576           0.072      0.412      0.618      1.951     .89558E-04         .48518E-02

      C8           0.576           0.072      0.412      0.705      2.224     .89558E-04         .48518E-02

      C9           0.048           0.006      0.034      0.066      0.208     .74632E-05         .40431E-03

      C10          0.000           0.000      0.000      0.000      0.000     .0                 .0

      C11          0.000           0.000      0.000      0.000      0.000     .0                 .0

      C12          0.000           0.000      0.000      0.000      0.000     .0                 .0

      CO          75.200           9.400      0.000     22.593      0.000     .29905E-01

      CO2          1.432           0.179      0.000      0.676      0.000     .22265E-03         .12062E-01

      H2O        189.472          23.684      0.000     36.595      0.000     .29460E-01         .15960E 01

      H2         393.936          49.242      0.000      8.454      0.000     .59010E-01
----------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 114.284    HYDROGEN IN FROM CARBON BALANCE=  96.683

MOLES OUT/MOLES IN=    0.768    VOLUMETRIC FEED= 101.698 ML/MIN AT NTP    USAGE RATE= .88914E-01    H2/CO USAGE= [illegible]
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                    F-SERIES RUN NUMBER= 41
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PRESSURE= 800.000 KPA   TEMPERATURE=545.000 K   WHSV=  0.261   % CO CONVERSION= 79.602

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    COMPONENT   PARTIAL PRESSURE   MOLE        MOLE        MASS        MASS        RATE                 SELECTIVE

                     KPA           %(TOTAL)    %(HC)       %(TOTAL)    %(HC)   KGMOL/MIN KG RU   RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------------------------------------

        C1           153.488        19.186     87.281      24.976     70.797     .17338E-01        .10000E 01

        C2             9.744         1.218      5.541       2.973      8.427     .11007E-02        .63484E-01

        C3             6.208         0.776      3.530       2.778      7.875     .70126E-03        .40446E-01

        C4             3.120         0.390      1.774       1.840      5.217     .35244E-03        .20327E-01

        C5             1.760         0.220      1.001       1.289      3.653     .19881E-03        .11467E-01

        C6             1.032         0.129      0.587       0.903      2.559     .11658E-03        .67237E-02

        C7             0.456         0.057      0.259       0.464      1.315     .51510E-04        .29709E-02

        C8             0.048         0.006      0.027       0.056      0.158     .54221E-05        .31273E-03

        C9             0.000         0.000      0.000       0.000      0.000     .0                .0

        C10            0.000         0.000      0.000       0.000      0.000     .0                .0

        C11            0.000         0.000      0.000       0.000      0.000     .0                .0

        C12            0.000         0.000      0.000       0.000      0.000     .0                .0

        CO            57.600         7.200      0.000      16.403      0.000     .25392E-01

        CO2            2.136         0.267      0.000       0.956      0.000     .24128E-03        .13916E-01

        H2O          220.512        27.564      0.000      40.368      0.000     .24909E-01        .14367E 01

        H2           343.896        42.987      0.000       6.995      0.000     .53373E-01
------------------------------------------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 120.364   HYDROGEN IN FROM CARBON BALANCE= 102.048

MOLES OUT/MOLES IN=   0.726   VOLUMETRIC FEED=  77.986 ML/MIN AT NTP   USAGE RATE= .78764E-01   H2/CO USAGE= 2.102


                    F-SERIES RUN NUMBER= 42
                    --------------

PRESSURE= 800.000 KPA   TEMPERATURE=545.000 K   WHSV=  0.151   % CO CONVERSION= 99.434

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     COMPONENT   PARTIAL PRESSURE   MOLE        MOLE        MASS        MASS        RATE                 SELECTIVE

                      KPA           %(TOTAL)    %(HC)       %(TOTAL)    %(HC)   KGMOL/MIN KG RU   RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------------------------------------

         C1           322.240        40.280     99.668      44.024     99.380     .17615E-01        .10000E 01

         C2             1.072         0.134      0.332       0.275      0.620     .58599E-04        .33267E-02

         C3             0.000         0.000      0.000       0.000      0.000     .0                .0

         C4             0.000         0.000      0.000       0.000      0.000     .0                .0

         C5             0.000         0.000      0.000       0.000      0.000     .0                .0

         C6             0.000         0.000      0.000       0.000      0.000     .0                .0

         C7             0.000         0.000      0.000       0.000      0.000     .0                .0

         C8             0.000         0.000      0.000       0.000      0.000     .0                .0

         C9             0.000         0.000      0.000       0.000      0.000     .0                .0

         C10            0.000         0.000      0.000       0.000      0.000     .0                .0

         C11            0.000         0.000      0.000       0.000      0.000     .0                .0

         C12            0.000         0.000      0.000       0.000      0.000     .0                .0

         CO             1.920         0.240      0.000       0.459      0.000     .18426E-01

         CO2           12.696         1.587      0.000       4.770      0.000     .69401E-03        .39399E-01

         H2O          311.688        38.961      0.000      47.905      0.000     .17038E-01        .96725E 00

         H2           150.384        18.798      0.000       2.568      0.000     .45353E-01

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HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 138.721   HYDROGEN IN FROM CARBON BALANCE= 122.508

MOLES OUT/MOLES IN=   0.606   VOLUMETRIC FEED=  45.305 ML/MIN AT NTP   USAGE RATE= .63780E-01   H2/CO USAGE= 2.461
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            F-SERIES RUN NUMBER= 46
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PRESSURE= 800.000 KPA  TEMPERATURE=523.000 K  WHSV=  0.108  % CO CONVERSION= 77.361

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  COMPONENT  PARTIAL PRESSURE  MOLE      MOLE      MASS      MASS       RATE              SELECTIVE
                 KPA          %(TOTAL)  %(HC)    %(TOTAL)  %(HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

------------------------------------------------------------------------------------------------------------

    C1          70.384         8.798    69.831    11.232   33.870    .32153E-02       .10000E 01
    C2           4.840         0.605     4.802     1.448    4.367    .22110E-03       .68766E-01
    C3           5.120         0.640     5.080     2.247    6.775    .23390E-03       .72744E-01
    C4           4.736         0.592     4.699     2.740    8.261    .21635E-03       .67288E-01
    C5           4.216         0.527     4.183     3.028    9.130    .19260E-03       .59900E-01
    C6           3.432         0.429     3.405     2.944    8.877    .15678E-03       .48761E-01
    C7           2.760         0.345     2.738     2.753    8.301    .12608E-03       .39213E-01
    C8           1.992         0.249     1.976     2.265    6.830    .91000E-04       .28302E-01
    C9           1.800         0.225     1.786     2.298    6.929    .82229E-04       .25574E-01
    C10          1.032         0.129     1.024     1.462    4.407    .47145E-04       .14662E-01
    C11          0.480         0.060     0.476     0.747    2.252    .21928E-04       .68197E-02
    C12          0.000         0.000     0.000     0.000    0.000    .0               .0
    CO          65.600         8.200     0.000    18.320    0.000    .10240E-01
    CO2          1.064         0.133     0.000     0.467    0.000    .48607E-04       .15117E-01
    H2O        222.032        27.754     0.000    39.862    0.000    .10143E-01       .31546E 01
    H2         410.512        51.314     0.000     8.189    0.000    .19516E-01
------------------------------------------------------------------------------------------------------------
HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 119.554   HYDROGEN IN FROM CARBON BALANCE= 104.714
MOLES OUT/MOLES IN=   0.710   VOLUMETRIC FEED=  32.362 ML/MIN AT NTP   USAGE RATE= .29756E-01   H2/CO USAGE= 1.906
            F-SERIES RUN NUMBER= 48
            --------------

 PRESSURE= 800.000 KPA  TEMPERATURE=523.000 K  WHSV=  0.142  % CO CONVERSION= 83.827

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   COMPONENT  PARTIAL PRESSURE  MOLE      MOLE      MASS      MASS       RATE              SELECTIVE
                  KPA          %(TOTAL)  %(HC)    %(TOTAL)  %(HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

 -----------------------------------------------------------------------------------------------------------

     C1          94.128        11.766    73.972    14.614   40.525    .55188E-02       .10000E 01
     C2           6.720         0.840     5.281     1.956    5.425    .39400E-03       .71392E-01
     C3           6.360         0.795     4.998     2.715    7.530    .37289E-03       .67568E-01
     C4           5.376         0.672     4.225     3.026    8.390    .31520E-03       .57114E-01
     C5           4.464         0.558     3.508     3.119    8.649    .26173E-03       .47425E-01
     C6           3.432         0.429     2.697     2.864    7.942    .20122E-03       .36461E-01
     C7           2.424         0.303     1.905     2.352    6.523    .14212E-03       .25752E-01
     C8           1.656         0.207     1.301     1.832    5.080    .97092E-04       .17593E-01
     C9           1.272         0.159     1.000     1.580    4.381    .74578E-04       .13514E-01
     C10          1.032         0.129     0.811     1.422    3.943    .60507E-04       .10964E-01
     C11          0.384         0.048     0.302     0.581    1.612    .22514E-04       .40796E-02
     C12          0.000         0.000     0.000     0.000    0.000    .0               .0
     CO          48.000         6.000     0.000    13.042    0.000    .84586E-01
     CO2          1.512         0.189     0.000     0.646    0.000    .88649E-04       .16063E-01
     H2O        245.760        30.720     0.000    42.926    0.000    .14409E-01       .26109E 01
     H2         377.480        47.185     0.000     7.326    0.000    .28174E-01
------------------------------------------------------------------------------------------------------------
HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 124.720   HYDROGEN IN FROM CARBON BALANCE= 107.252
MOLES OUT/MOLES IN=   0.693   VOLUMETRIC FEED=  42.541 ML/MIN AT NTP   USAGE RATE= .42760E-01   H2/CO USAGE= 1.932
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              F-SERIES RUN NUMBER= 51
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PRESSURE= 800.000 KPA  TEMPERATURE=501.000 K  WHSV=  0.094  % CO CONVERSION= 90.323

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   COMPONENT   PARTIAL PRESSURE  MOLE      MOLE      MASS      MASS       RATE            SELECTIVE
                     KPA         %(TOTAL)  %(HC)     %(TOTAL)  %(HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

--------------------------------------------------------------------------------------------------

      C1          146.280        18.285    85.165    22.067    55.988    .55287E-02      .10000E 01
      C2            4.600         0.575     2.678     1.301     3.301    .17386E-03      .31447E-01
      C3            4.504         0.563     2.622     1.868     4.741    .17023E-03      .30790E-01
      C4            3.944         0.493     2.296     2.157     5.472    .14907E-03      .26962E-01
      C5            3.424         0.428     1.993     2.324     5.897    .12941E-03      .23407E-01
      C6            2.688         0.336     1.565     2.180     5.530    .10159E-03      .18376E-01
      C7            1.872         0.234     1.090     1.765     4.478    .70753E-04      .12797E-01
      C8            1.200         0.150     0.699     1.290     3.272    .45355E-04      .82034E-02
      C9            0.936         0.117     0.545     1.130     2.866    .35377E-04      .63987E-02
      C10           0.960         0.120     0.559     1.285     3.261    .36284E-04      .65628E-02
      C11           0.912         0.114     0.531     1.341     3.403    .34470E-04      .62346E-02
      C12           0.440         0.055     0.256     0.705     1.789    .16630E-04      .30079E-02
      CO           29.440         3.680     0.000     7.772     0.000    .10386E-01
      CO2           0.736         0.092     0.000     0.305     0.000    .27818E-04      .50314E-02
      H2O         273.320        34.165     0.000    46.385     0.000    .10330E-01      .18685E 01
      H2          324.744        40.593     0.000     6.124     0.000    .20969E-01
--------------------------------------------------------------------------------------------------

HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 130.485   HYDROGEN IN FROM CARBON BALANCE= 109.944
MOLES OUT/MOLES IN=   0.676   VOLUMETRIC FEED=  28.112 ML/MIN AT NTP   USAGE RATE= .31355E-01   H2/CO USAGE= 2.019


              F-SERIES RUN NUMBER= 55
              --------------

PRESSURE=1200.000 KPA  TEMPERATURE=573.000 K  WHSV=  0.598  % CO CONVERSION= 54.416

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   COMPONENT   PARTIAL PRESSURE  MOLE      MOLE      MASS      MASS       RATE            SELECTIVE
                     KPA         %(TOTAL)  %(HC)     %(TOTAL)  %(HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

--------------------------------------------------------------------------------------------------

      C1          147.552        12.296    90.506    18.915    77.934    .30181E-01      .10000E 01
      C2            6.960         0.580     4.283     1.673     6.893    .14236E-02      .47170E-01
      C3            3.900         0.325     2.400     1.375     5.665    .79772E-03      .26431E-01
      C4            1.992         0.166     1.226     0.926     3.814    .40745E-03      .13500E-01
      C5            1.008         0.084     0.620     0.581     2.396    .20618E-03      .68315E-02
      C6            0.684         0.057     0.421     0.471     1.942    .13991E-03      .46357E-02
      C7            0.288         0.024     0.177     0.231     0.951    .58908E-04      .19519E-02
      C8            0.108         0.009     0.066     0.099     0.406    .22091E-04      .73195E-03
      C9            0.000         0.000     0.000     0.000     0.000    .0              .0
      C10           0.000         0.000     0.000     0.000     0.000    .0              .0
      C11           0.000         0.000     0.000     0.000     0.000    .0              .0
      C12           0.000         0.000     0.000     0.000     0.000    .0              .0
      CO          163.200        13.600     0.000    36.612     0.000    .39849E-01
      CO2           1.656         0.138     0.000     0.584     0.000    .33872E-03      .11223E-01
      H2O         191.508        15.959     0.000    27.619     0.000    .39172E-01      .12979E 01
      H2          681.144        56.762     0.000    10.915     0.000    .72390E-01
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HYDROGEN OUT ASSUMING NORMAL PARAFFINS= 102.359   HYDROGEN IN FROM CARBON BALANCE=  86.254
MOLES OUT/MOLES IN=   0.861   VOLUMETRIC FEED= 179.035 ML/MIN AT NTP   USAGE RATE= .11224E 00   H2/CO USAGE=
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                 RUN NUMBER=107
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PRESSURE=1400.000 KPA  TEMPERATURE=496.000 K  WHSV=  0.134  % CO CONVERSION= 15.667

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   COMPONENT   PARTIAL PRESSURE  MOLE      MOLE      MASS      MASS       RATE             SELECTIVE
                     KPA         %(TOTAL)  %(HC)     %(TOTAL)  %(HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

--------------------------------------------------------------------------------------------------------

     C1            11.181         0.799    58.242    1.489   23.331     .52808E-03      .10000E 01
     C2             0.552         0.039     2.874    0.138    2.159     .26059E-04      .49347E-01
     C3             1.120         0.080     5.833    0.410    6.425     .52885E-04      .10015E 00
     C4             1.866         0.133     9.721    0.901   14.116     .88141E-04      .16691E 00
     C5             1.363         0.097     7.101    0.817   12.800     .64381E-04      .12192E 00
     C6             1.120         0.080     5.833    0.802   12.559     .52885E-04      .10015E 00
     C7             0.974         0.070     5.072    0.810   12.698     .45987E-04      .87083E-01
     C8             0.633         0.045     3.297    0.601    9.410     .29891E-04      .56604E-01
     C9             0.389         0.028     2.029    0.415    6.502     .18395E-04      .34833E-01
     C10            0.000         0.000     0.000    0.000    0.000     .0              .0
     C11            0.000         0.000     0.000    0.000    0.000     .0              .0
     C12            0.000         0.000     0.000    0.000    0.000     .0              .0
     CO           292.096        20.864     0.000   68.079    0.000     .25630E-02
     CO2            2.239         0.160     0.000    0.820    0.000     .10577E-03      .20029E 00
     H2O           49.786         3.556     0.000    7.460    0.000     .23514E-02      .44528E 01
     H2          1036.681        74.049     0.000   17.259    0.000    -.16689E-02
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HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  82.692   HYDROGEN IN FROM CARBON BALANCE=  71.525
MOLES OUT/MOLES IN=   1.039   VOLUMETRIC FEED=  39.211 ML/MIN AT NTP   USAGE RATE= .89412E-03   H2/CO USAGE=-0.651


                RUN NUMBER=111
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PRESSURE=1000.000 KPA  TEMPERATURE=496.000 K  WHSV=  0.095  ( CO CONVERSION= 12.764

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  COMPONENT   PARTIAL PRESSURE  MOLE      MOLE      MASS      MASS       RATE             SELECTIVE
                    KPA         ((TOTAL)  ((HC)     ((TOTAL)  ((HC)  KGMOL/MIN KG RU  RATES (REL TO CH4)

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    C1             5.830         0.583    56.004    1.130   21.663     .28769E-03      .10000E 01
    C2             0.340         0.034     3.266    0.124    2.369     .16778E-04      .58319E-01
    C3             0.800         0.080     7.685    0.426    8.175     .39477E-04      .13722E 00
    C4             0.830         0.083     7.973    0.583   11.180     .40957E-04      .14237E 00
    C5             0.840         0.084     8.069    0.732   14.046     .41451E-04      .14408E 00
    C6             0.660         0.066     6.340    0.687   13.182     .32568E-04      .11321E 00
    C7             0.420         0.042     4.035    0.509    9.754     .20725E-04      .72041E-01
    C8             0.390         0.039     3.746    0.538   10.325     .19245E-04      .66895E-01
    C9             0.180         0.018     1.729    0.279    5.351     .88823E-05      .30875E-01
    C10            0.120         0.012     1.153    0.206    3.957     .59215E-05      .20583E-01
    C11            0.000         0.000     0.000    0.000    0.000     .0              .0
    C12            0.000         0.000     0.000    0.000    0.000     .0              .0
    C+             2.610         0.261    25.072    2.953   56.614     .12879E-03      .44768E 00
    CO           206.000        20.600     0.000   69.858    0.000     .14873E-02
    CO2            0.870         0.087     0.000    0.464    0.000     .42931E-04      .14923E 00
    H2O           28.400         2.840     0.000    6.191    0.000     .14014E-02      .48714E 01
    H2           754.320        75.432     0.000   18.272    0.000    -.35345E-02
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HYDROGEN OUT ASSUMING NORMAL PARAFFINS=  82.240   HYDROGEN IN FROM CARBON BALANCE=  68.269
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