CATALYTIC HYDROGENATION OF MODEL COAL EXTRACT MID-DISTILLATES

by

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A Thesis submitted for the Degree of Doctor of Philosophy to the University of London and for the Diploma of Imperial College

February 1986

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ABSTRACT

The mid-distillates of coal extract obtained by liquefaction processes generally contains 2 and 3 rings partially hydrogenated aromatics with some nitrogen, oxygen and sulphur heterocyclic compounds being present. This distillate can be converted into diesel fuel by catalytic hydrogenation. To understand the complex nature of the reactivities of the mid-distillates this thesis has investigated the hydrogenation of model feedstocks comprising of tetralin and varying concentration of quinoline and dibenzofuran. In addition two other nitrogen compounds, 1,2,3,4-tetrahydroquinoline and o-propylaniline were investigated. 1,6-dimethylnapthalene was used as a secondary model aromatic compound. The model feed was hydrogenated over a commercial nickel-molybdenum sulphide catalyst in a laboratory trickle-bed reactor which was operated between 500 and 1000 psi and a temperature range of 300 to 330°C which represented conditions close to that of industrial processing.

Tetralin, a partially hydrogenated aromatic compound undergoes slow hydrogenation reaction compared to 1,6-dimethylnapthalene. In the hydrogenation of nitrogen compounds the C-N hydrogenolysis steps were the rate determining steps. In the case of dibenzofuran hydrogenation it appeared that the initial ring hydrogenation was slow with C-O hydrogenolysis being rapid.

Quinoline, 1,2,3,4-tetrahydroquinoline and o-propylaniline poisoned the catalyst during the reaction severely decreasing the rate of tetralin hydrogenation. The effect of quinoline on the hydrogenation rate of 1,6-dimethylnapthalene was minimal. An increase in the activation energy of tetralin hydrogenation was observed due to the influence of nitrogen compounds. Quinoline and 1,2,3,4-tetrahydroquinoline decreased the selectivity towards trans-decalin during tetralin hydrogenation. At lower feed rates, higher temperatures and pressures the poisoning was less severe.

Dibenzofuran had a slight poisoning effect on the hydrogenation rate, but its presence reduced the extent of poisoning arising from the presence of nitrogen compounds. It had a similar effect on the hydrogenation of 1,6-dimethylnapthalene. Dibenzofuran decreased the activation energies of both tetralin and 1,6-dimethylnapthalene hydrogenation in the presence of nitrogen compounds. This effect is attributed to the product water from HDO.

Preliminary experiments on unsupported cobalt-molybdenum catalysts demonstrated that Co-Mo-S phase was responsible for high hydrodesulphurisation activity but its hydrogenation activity was moderate.

DEDICATED TO MY FATHER,

MR. MOINUL ISLAM

- IN LOVING MEMORY

ACKNOWLEDGEMENTS

My sincere thanks are due to Dr D Chadwick for his enthusiasm, guidance and supervision of this thesis.

I gratefully acknowledge the role of Science and Engineering Research Council of U.K. for supporting me with a Co-operative Award in Science and Engineering. I also wish to thank Dr G O Davies and Dr D G Gavin of the Co-operative body, National Coal Board - Coal Research Establishment, Cheltenham, U.K.

Finally, I would like to thank Mrs M Connolly for typing this manuscript.

CONTENTS

		Page
ABSTRACT		2
ACKNOWLEDGEMENTS		4
CONTENTS		5
CHAPTER ONE: INTRODUCTION		
1.1	GENERAL ASPECTS	9
1.2	PROPERTIES OF COAL AND PRODUCTION OF LIQUID FUELS FROM COAL	13
1.2.1	Coalification Process	13
1.2.2	Chemical structures and elemental composition of coal.	14
1.2.3	Liquid fuels - comparison between petroleum-based and coal.	19
1.3	COAL LIQUEFACTION	22
1.3.1	General	22
1.3.2	Pyrolysis processes	23
1.3.3	Solvent extraction processes	25
1.3.4	Distillates from coal extracts	29
1.4	AIMS	35
CHAPTER TWO: HYDROPROCESSING ASPECTS OF COAL EXTRACT MID-DISTILLATES		
2.1	GENERAL	40
2.1.1	Hydrogenation (HG) and hydrocracking (HC)	40
2.1.2	Hydrodesulphurisation (HDS)	43
2.1.3	Hydrodenitrogenation (HDN)	44
2.1.4	Hydrodeoxygenation (HDO)	47
2.2	INTERACTION IN CATALYTIC HYDROPROCESSING	49
2.3	COAL CONVERSION CATALYSTS	53
CHAPTER THREE: EXPERIMENTAL		
3.1	INTRODUCTION	58
3.2	TRICKLE-BED REACTOR SYSTEM	59
3.2.1	General review	59
3.2.2	Present system	67

		Page
3.2.2.1	Description of available system	67
3.2.2.2	Description of modified system	72
3.2.2.3	Performance of reactor	80
3.3	EXPERIMENTAL PROCEDURE	89
3.3.1	Preparation of Feed and Catalyst loading	89
3.3.2	Reaction procedure	91
3.3.3	Preparation of unsupported catalyst and activity test	92
3.4	ANALYTICAL METHODS	96
3.4.1	Gas chromatography	96
3.4.2	Elemental analysis	98
3.4.3	Scanning electron microscopy	102

CHAPTER FOUR: PRELIMINARY EXPERIMENTS

4.1	INTRODUCTION	104
4.2	PURE TETRALIN HYDROGENATION	107
4.3	TETRALIN/QUINOLINE HYDROGENATION	110
4.4	TETRALIN/DIBENZOFURAN HYDROGENATION	114
4.5	SUMMARY	117

CHAPTER FIVE: HYDROGENATION OF PURE TETRALIN AND 1,6-DIMETHYLNAPTHALENE

5.1	INTRODUCTION	119
5.2	PURE TETRALIN HYDROGENATION	121
5.3	PURE 1,6-DIMETHYLNAPTHALENE HYDROGENATION	127
5.4	SUMMARY	132

CHAPTER SIX: HYDROGENATION OF TETRALIN/NITROGEN AND 1,6-DIMETHYLNAPTHALENE/NITROGEN COMPOUND MODEL FEEDSTOCKS

6.1	INTRODUCTION	134
6.2	TETRALIN/QUINOLINE HYDROGENATION	135
6.2.1	Quinoline hydrodenitrogenation (HDN)	135
6.2.2	Influence of quinoline on tetralin hydrogenation.	142
6.2.3	Curve fittings of tetralin hydrogenation under the influence of quinoline poisoning	149

		Page
6.3	TETRALIN/1,2,3,4-TETRAHYDROQUINOLINE AND TETRALIN/O-PROPYLANILINE HYDROGENATION	154
6.3.1	1,2,3,4-tetrahydroquinoline and o-propylaniline hydrodenitrogenation (HDN)	154
6.3.2	Influence of THQ and OPA on tetralin hydrogenation.	158
6.4	1,6-DIMETHYLNAPTHALENE/QUINOLINE HYDROGENATION	161
6.5	SUMMARY	164
CHAPTER SEVEN:	HYDROGENATION OF TETRALIN/NITROGEN/OXYGEN AND 1,6-DIMETHYLNAPTHALENE/NITROGEN/OXYGEN COMPOUND MODEL FEEDSTOCKS	
7.1	INTRODUCTION	167
7.2	TETRALIN/Q/DBF, TETRALIN/THQ/DBF AND TETRALIN/OPA/DBF HYDROGENATION	170
7.2.1	Kinetic results	170
7.3	INTERACTION OF DIFFERENT HYDROPROCESSING REACTION UNDER COMPETITIVE CONDITIONS	174
7.3.1	Effect of DBF of hydrogenation rate constant of tetralin	174
7.3.2	Effect of DBF on HDN reaction rate.	176
7.3.3	Effect of DBF on apparent activation energy of tetralin hydrogenation.	178
7.3.4	Mechanism of HDO	180
7.4	1,6-DIMETHYLNAPTHALENE/QUINOLINE/DIBENZOFURAN HYDROGENATION	187
7.5	SUMMARY	188
CHAPTER EIGHT:	PREPARATION AND ACTIVITY OF UNSUPPORTED CATALYST	
8.1	INTRODUCTION	189
8.2	TRIAL CATALYST PREPARATION AND ELECTRON MICROSCOPY RESULTS	190
8.3	HYDROGENATION OF DIBENZOTHIOPHENE	191
8.4	SUMMARY	197

	Page
CHAPTER NINE: CONCLUSIONS	198
REFERENCES	202
APPENDICES	211
APPENDIX A	212
APPENDIX B	297
APPENDIX C	299

CHAPTER ONE : INTRODUCTION

1.1 GENERAL ASPECTS

With ever increasing demands on petroleum and natural gas and the decreasing reserves of such, the need for better utilisation of fossil fuels as a source of energy is markedly becoming important.

A significant study by Ford Foundation (1979) forecasted that energy supply and demand would show a projected shortfall in liquid hydrocarbons which would become severe by the end of this century. Also, studies (Ezra, 1978) carried out indicated that only an increase of 10-15% in nuclear energy and perhaps about 5% by non-conventional methods in the same period would be achieved. Consequently, there has been a surge of development work on processes for the conversion of coal, oil shale, tar sands and heavy petroleum residue into liquid fuels. For commercially useful liquid products the upgrading of this heavy fossil fuel is normally effected by catalysis. This is carried out by hydrotreating in the presence of catalysts such as cobalt-molybdenum or nickel-molybdenum at 50-200 atms and 300-450°C.

Besides the political constraints as witnessed by the OPEC oil embargoes in 1973, oil production itself is likely to peak during the 1990's (Day,1972), creating a considerable deficiency in energy and chemical feedstocks. Coal will then become a major source for liquid and gaseous fuels in the future along with recoverable oil shales and tar sands. According to the study of the World Energy Conference (1978) the total recoverable coal reserves of the World amounts to 639 x 10^9 tonne coal equivalent. Not only is that coal more widely geographically distributed than oil, it will be enough for another 230 years based on today's coal production. It also corresponds to about 5 times the calorific value of today's proven oil reserves. Fig.1.1 shows the World consumption of primary energy sources.

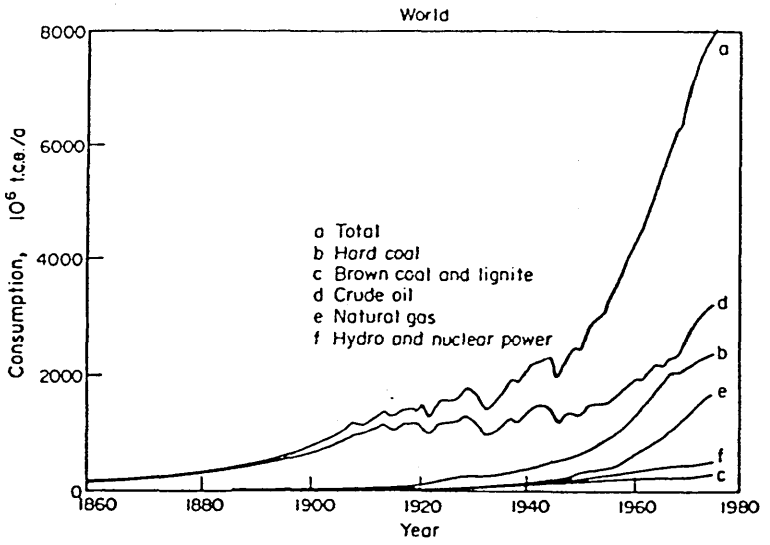


Fig. 1.1 (U.N.Symp., 1979)

A coal-based industry is not something new. Before the Second World War the principal sources of organic chemicals were from tar by-product from coal carbonisation and for the production of synthetic ammonia, the hydrogen required was almost exclusively made from the gasification of coke. During World War Two it was demonstrated that it was feasible to catalytically convert coal into liquid and gaseous fuels. Although based on different technologies, several countries, namely,Germany, Great Britain, U.S.S.R., Czechoslovakia and Spain,operated such coal conversion plants (Donath, 1963; Wu and Storch,1968). At present, the role of coal is highlighted by the formation of an International Workshop (1982),represented by countries which include West Germany, Japan, U.S.A., and Australia, which reviews and discusses the progress being made in increasing our understanding of the properties of coal and its conversion processes.

There are several ways of converting coal into liquid fuels:

(a) Pyrolysis of coal yields gas, liquids and char.

(b) It can be converted into CO and H_2 and thereby carrying out the Fischer-Tropsch type reaction to produce fuels.

(c) Coal can be hydropyrolised to yield gases, naptha range liquids and heavy residua.

(d) It can be liquified by employing a H_2 donor solvent to produce liquid and gaseous products.

Potentially all the conventional fuel products are available from coal liquids. Also, most of the catalytic reactions in coal conversion are similar to those of refining of petroleum and it is not surprising to find that research and development in the coal conversion industries are utilising a significant fraction of presently known catalytic materials and processes. However, the complex nature of coal adds a new dimension to the technical challenge for the development of efficient processes. Therefore, factors such as control of activity and selectivity, catalyst ageing, poisoning, mechanical degradation, development of regeneration procedures and of reactor design for optimum heat and mass transfer are a good deal more complex than those encountered in petroleum refining (Cusumano et al., 1978).

1.2. PROPERTIES OF COAL AND PRODUCTION OF LIQUID FUELS FROM COAL

1.2.1. Coalification process.

Coals are complex organic sedimentary rocks that were derived from plant remains which have accumulated under different conditions that have restricted or inhibited decay. The properties of coal reflect the nature of their original plant material. The process of coalification is believed to progress through several stages and in the sequence: peat, brown coal, sub-bituminous coal, bituminous coal and finally to anthracite. The rate at which this process had occurred was related to a combination of effects of pressures and temperatures over long periods. The principal organic components of plant materials are cellulose and lignin and evidence exists that coals are primarily derived from lignin, whereas the cellulose has biochemically degraded to carbon dioxide and water during accumulation and peat stages.

Coals are inhomogeneous organic solid mass containing microscopically identifiable components known as macerals. They are classified into three groups: vitrinite, exinite and inertinite. The bright components of coal are rich in vitrinite and are

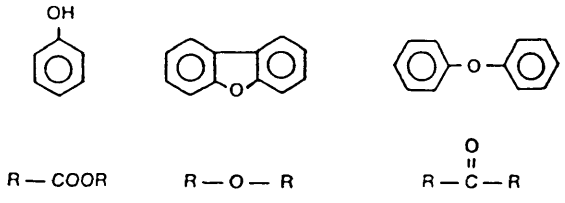
considered to have been derived primarily from wood and the exinite from pollen and plant waxes. Within a coal the properties of each maceral variety differ and as the rank of coal increases their properties also change. However, the properties of vitrinite in different coal ranks vary in a regular manner and is also present in all coals. This useful correlation is used for identifying coal rank e.g., 0.3% vitrinite in brown coals to 2.5% in anthracite.

1.2.2 Chemical structures and elemental composition of coal.

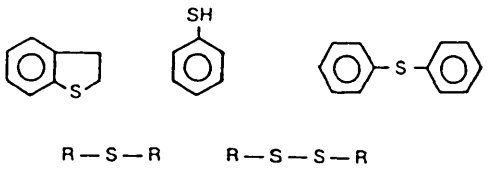
The major elements in coal macerals are carbon and hydrogen but in addition to these they contain oxygen, nitrogen and sulphur. Figure 1.2 shows the different functional groups found in coal.

A typical elemental composition of the macerals is such that vitrinite contains less hydrogen but more oxygen than exinite. The oxygen contents are similar for the vitrinite and the inertinite but the latter is richer in carbon but lower in hydrogen. In the lower rank vitrinite the carbon content is approximately 60wt% (e.g., brown coals) which increases to about 90wt% for high rank vitrinite (e.g., in anthracite), whereas the oxygen content decreases from approximately 30wt% to less

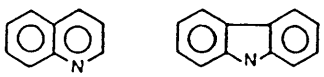
Oxygen:



Sulphur:



Nitrogen:



Metals:

Salts, porphyrins.

Figure 1.2. Functional groups present in coal.

than 4wt% as the vitrinite rank increases. However, the hydrogen essentially remains constant over a wide range of rank.

Due to the many possibilities it is a general practice to propose an average molecular model of coal based on vitrinite. Figures 1.3 and 1.4 examplify such a model.

It is widely accepted (Wender et al.,1981 and Van Krevelen, 1981) that the basic skeletal structure is aromatic and the aromaticity increases with rank. Typically,vitrinites that contain carbon in the range of 78-90wt% have 60-85% of the carbon organised in an aromatic nuclei and such nuclei, on average, contain up to 3 condensed aromatic rings. As the carbon (>92%) increases the proportion of aromatic carbon and the condensed aromatic nuclei size increases rapidly. In low rank coals the condensed aromatic nuclei are highly substituted. The non-aromatic portion of vitrinite mainly constitutes non-aromatic carbon which is present as hydroaromatics and alicyclic ring structures. These are the major substituents | linking the aromatic nuclei.

Both aliphatic and aromatic hydrogens are present in vitrinite. However, aliphatic hydrogen predominates

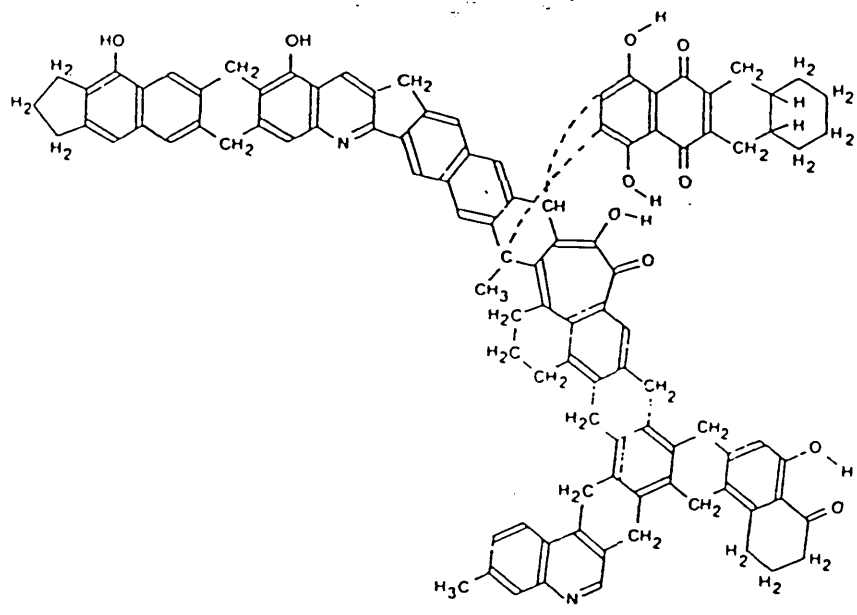


Fig.1.3. Model Structure for an 82%-carbon vitrinite (Given,1960)

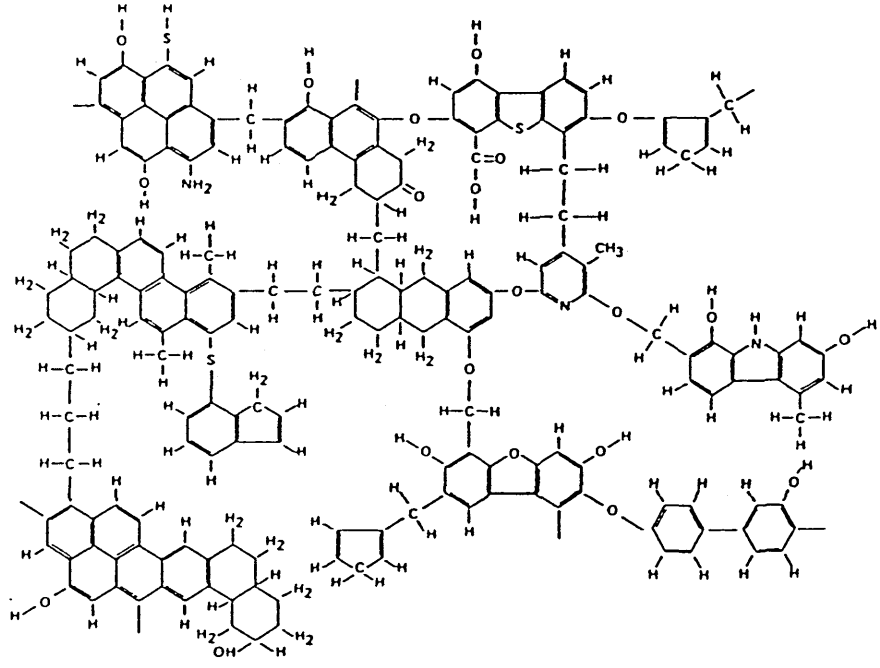


Fig.1.4. Schematic representation of structural groups and connecting bridges in bituminous coal (Wiser,1973)

until the carbon content reaches approximately 90wt%. For higher rank vitrinites the total hydrogen decreases but the ratio of aromatic to aliphatic hydrogen increases. The methyl groups attached to hydroaromatics account for the remainder of the aliphatic hydrogen. The aromatic nuclei also contain methyl group as substituents and account for about 20% of the hydrogen present for vitrinite rank containing carbon in the range 82-90wt%.

The easily identifiable oxygen groups in bituminous coals are phenolic hydroxyl groups which account for 60-80% of organic oxygen. In bituminous coal (carbon content $>$78wt%) there are no carboxyl groups, however in lower rank coals substantial amounts of oxygen occur as carboxyl groups. There is no evidence of aliphatic hydroxyl groups. The unaccounted oxygen is believed to be present mainly as ether groups.

The sulphur and nitrogen content in the organic portion of the coal essentially remains constant for all ranks of coal, particularly more true for nitrogen. Quantitatively speaking, there are approximately 0.5 sulphur atoms per 100 carbon atoms and between 1-2 nitrogen atoms per 100 carbon atoms. Both these elements are believed to be present as heterocyclic structures.

The major inorganic constituents in bituminous coals are kaolinite and other silicate materials. In some coals, carbonate minerals such as calcite and ankerite are also present. Pyrite and marcasite are the main sulphur-bearing minerals that occur in some coals. These minerals usually occur in discrete bands and some are finely disseminated through the coal macerals and particularly associated with the inertinite. In the lower rank coals, cations (e.g., sodium, calcium, magnesium, iron and aluminium) associated with carboxylic acid groups are present (Durie, 1961).

The lower rank coals (e.g., lignites) also contain mineral species such as kaolinite, quartz and pyrite. In the lignites the presence of carbonates is rare (Burns et al.,1962). All the minerals discussed above are the inorganic ash-forming constituents, which also complicate the analysis of organic coal substance and associated structural studies.

1.2.3. Liquid fuels - comparison between petroleum-based and coal

The previous section has briefly described the properties and structures of coal. These provide an insight into the possible change that will take place by breaking the original structure of coal. An analysis of a crude oil (British Petroleum,1972) and coals (Cusumano

et al.,1978) portrays an important picture of the similarities and dissimilarities between them.

Table 1.1 shows that coal conversion involves increasing the hydrogen content, that is, improving the H/C atomic ratios, removing inorganic ash and removing hetero-atoms present in coal. This conversion can be effected by the initial breaking of the complex coal structure by Pyrolysis (FMC Corporation, 1973, White and Neuworth,1976) or by solvent extraction (Davies et al., 1977, Davies,1978) and from the products all the conventional petroleum fuels are potentially available. Table 1.2 gives a comparison between coal liquid and a petroleum crude.

There are important differences in the chemical and physical composition of fuels derived from coal liquids (Cusumano et al.,1978; Solash et al., 1978; Durie,1982) and thus different processes may be needed to produce them.

Motor gasoline is a blend of paraffin, napthenes and aromatics with substantial proportions of benzene, toluene and xylene (BTX) which are the typical high octane components. Jet fuel is characterised by its highly paraffinic kerosene fraction with an aromatic content which must be less than about 20 vol.%, polycyclic aromatics are kept below 3 vol.% and olefins

Table 1.1 Analysis of oil and coal/wt%

	C	H	O	S	N	Ash	Atomic H/C ratio
Bituminous	73	5	9	3	1.5	8.5	0.82
Subbituminous	71	5	16	0.5	1.5	6.0	0.85
Lignite	64	4.6	18	0.5	1.5	11.4	0.86
Crude oil	85.4	12.6	-	2.0	-	10^{-2}	1.7

Table 1.2 Properties of a coal liquid and arabian light

	Syncrude from coal	Arabian light
Density, 15°C (g ml^{-1})	0.950	0.856
Carbon (wt %)	86.60	85.5
Hydrogen (wt %)	9.05	12.6
Sulphur (wt %)	0.10	1.7
Nitrogen (wt %)	0.75	0.2
Oxygen (wt %)	3.50	–
H/C ratio	1.26	1.77
Light oil, IBP–200°C (wt %)	25	23
Middle distillate 200–325°C (wt %)	75	24
VGO 325–500°C (wt %)	–	28
Residue >500°C (wt %)	–	25

below 5 vol.% to avoid formation of polymeric gums. Diesel fuels have long paraffinic molecules (e.g., n-hexadecane which has a cetane number of 100). Cetane number is a measure of ignition quality for diesel fuel and normally for good diesel blends lies in the range of 35 to 50. Gas turbine fuels require a minimum of 11.3wt% of hydrogen and as in the case of heating and residual oils must have a restricted sulphur and nitrogen content of less than 1% to avoid burner corrosion and also to minimise SO_χ and NO_χ emissions which are not accepted for environmental reasons (Hossain et al., 1980).

1.3. COAL LIQUEFACTION

1.3.1. General

There are two main approaches to liquefaction: synthesis or degradation. In the synthesis process the coal structure is completely disrupted by gasification to form CO and H_2 (synthesis gas), which can then be converted to a wide range of chemicals and liquid fuels. From synthesis gas methanol can also be produced by the methanol synthesis reaction. The major products of synthesis are almost entirely aliphatic. In the degradation approach, the complex coal structure is

partially broken down into simple molecules which are comparable to crude oils. The products of the degradation are predominantly aromatic. Within the degradation process there are several variants. All involve decomposition by heating but some degree of hydrogenation is used to decrease the molecular complexity. In some cases, solvents are used in the degradative process which plays an important role in breaking down coal structures (Fisher et al., 1978: Davies,1978).

1.3.2 Pyrolysis processes

There are two types of pyrolysis processes: one which can be termed as 'pure' pyrolysis where the coal is treated at high temperatures in the absence of hydrogen, whereas the other process is carried out in a hydrogen atmosphere synonymous to hydrocarbonisation.

A typical example of a pure pyrolysis process is the Char Oil Energy Development (COED) process (Jones, 1975). In this process, pulverised and dried coal is pyrolysed in a series of fluidised beds, with the temperature increasing from bed to bed. This thermal staging prevents agglomerisation of the coal since each reactor temperature is kept below the agglomerisation point. Typical operating bed temperatures used are 500°F,

850°F, 1000°F and 1650°F. The operation of the COED process has been described in detail (Anderson, 1956; Storch et al., 1951; Weitkamp et al., 1953; Karn et al., 1964). The liquid yield is approximately 23 wt % in the COED process. Another well known example is the Occidental Flash Pyrolysis process (White and Neuworth, 1976). In this process the pyrolysis is carried out rapidly in a single fluidised bed reactor kept at a minimum temperature of 1000K. The liquid yield in this process is approximately 38wt%. Both these processes give higher liquid yields compared to the conventional carbonisation process (yield: 9wt%). An example of the hydropyrolysis or hydrocarbonisation process is the COALCON process (Cusumano et al., 1978) which involves the pyrolysis of coal at a hydrogen pressure of 37 bars and a temperature of 550°C. This reaction produces liquid, gaseous and solid products. The gaseous product is separated from the liquid to produce synthetic natural gas (SNG) and liquified petroleum gas (LPG). The liquid products are cut into light and heavy fractions whose characteristics are similar to those of a light to heavy petroleum naptha and a light to medium gas oil respectively. The solid char is used for fuel and hydrogen generation. The overall yield of the COALCON

process which produces the four primary fuel products are 7.3%LPG, 44.7%SNG, 14.3% light oil product and 33.7% heavy oil products.

1.3.3. Solvent extraction processes

In this process, the complex coal structure is broken down into simpler molecules by the action of a suitable solvent. The extraction is usually carried out in the presence of hydrogen and the variant of this is the incorporation of a suitable catalyst. Therefore, the solvent extraction process can be broadly categorised into catalytic or a non-catalytic one (National Research Council,U.S.A., 1980)

In the non-catalytic solvent extraction process, a suitable solvent such as anthracene in the presence of hydrogen (Davies, 1978) can be added to the coal or an appropriate fraction from the liquid product obtained from heating of coal can be returned to the reaction zone.

An example of this is the solvent refined coal (SRC-I and SRC-II) processes (Sullivan et al 1979; Synthetic Fuels, 1979). In this process the temperature in the dissolving vessel is maintained at about 850°F and the pressure at 1000-1500 psi, with the required hydrogen provided from an outside supply. In the SRC-I process

the solvent is taken from the vacuum distillate fraction boiling below 1000°F. The SRC-I product is solid at room temperature and therefore requires further upgrading by hydrogenation. In the SRC-II process, the dissolving conditions are more severe; temperatures and pressures are higher and contact times are longer. The product is liquid at room temperature. Although the H/C ratio has increased compared to the original coal , it still requires further hydrogenation for high quality fuel production.

In the catalytic solvent extraction process, the external catalytic material can be applied in two ways: (i) by addition of the catalyst to the coal in the liquefaction reactor in the presence of hydrogen, as in the H-coal process (Stein et al., 1977, Hydrocarbon Research,1978) or (ii) by adding the catalyst to the reactor in which the solvent is being hydrogenated prior to its transfer to the coal liquefaction reactor, as in the Exxon Donor Solvent process (Fant, 1978; Epperly, 1979). In the H-coal process, this reaction is carried out in a highly ebullient slurry reactor where the catalyst (cobalt-molybdenum) is added directly to the mixture of coal and solvent, operating at 640K and 200 bars. In the Exxon Donor solvent process, the solvent

(400-850°F boiling range material) is hydrogenated in the presence of a catalyst which is then mixed with the coal to form a slurry. This slurry is fed into a liquefaction reactor maintained at a temperature of 800-850°F and a pressure of 1500-2000 psi.

Figure 1.5 shows the scheme of National Coal Board (U.K.)Plant (Davies et al.,1977; Davies,1978; U. N.Symp., 1979) and is important because it is relevant to this thesis.

This coal liquefaction process incorporates a non-catalytic solvent extraction process followed by catalytic hydrogenation. Here, the coal is dissolved in an anthracene oil and digested in a reactor at about 500°C. The liquid products are separated from the untreated coal and the ashes are removed in a filtration stage. The solvent is evaporated and the resulting coal liquid is processed through a catalytic hydro-cracker. Several products are obtained by distillation and are categorised as light, middle and heavy distillates .

In the Synthoil process (Yavorsky et al 1975) the coal is slurried in a recycled aromatic oil. This slurry together with hydrogen is flowed at highly turbulent

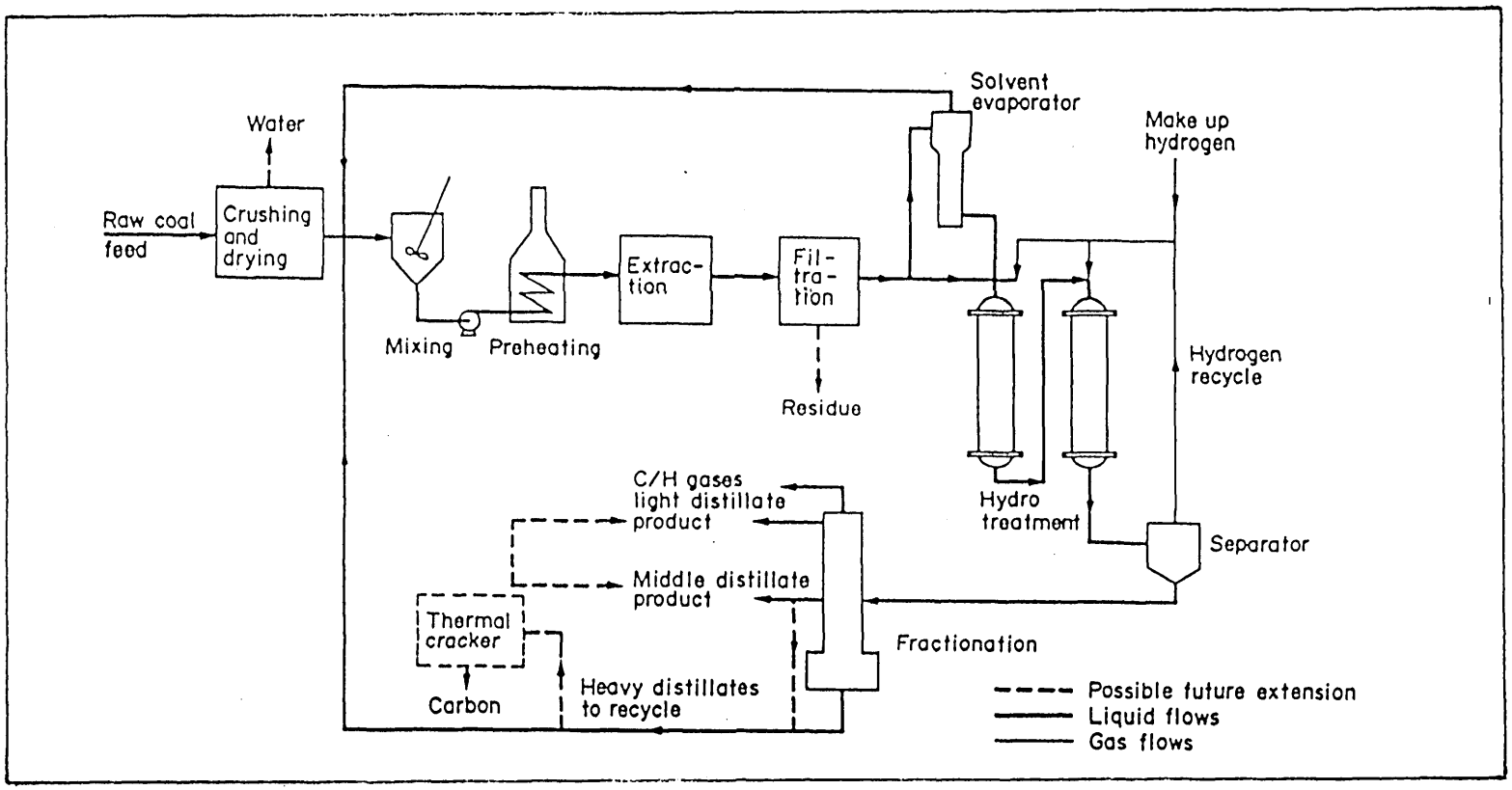


Figure 1.5. Pilot scale plant (NCB-U.K.) for coal liquefaction using liquid solvents.

conditions through a fixed bed of cobalt-molybdenum catalyst. Process conditions are usually either 140 bars or 280 bars at 450°C, depending whether the desired product is a light or a heavy oil. The level of coal conversion is usually very high (90-98%).

1.3.4. Distillates from coal extracts

After reviewing; coal, its properties and its liquefaction processes, an appropriate juncture has been reached, where the distillates from coal extracts need to be discussed as it is of major importance to this Thesis.

From the various liquefaction processes a wide range of gaseous and liquid products are obtained. The liquid products can be divided into different fractions. The heavier fractions which boil above 450K are termed "syncrude" (synthetic crude) and in this range the middle-distillates and the heavy distillates fall. Although the syncrudes produced from a given coal for the different processes (e.g. COED, H-coal, Exxon Donor Solvent and N.C.B. processes) may vary, its compositions are qualitatively similar with respect to the molecular constituents. Therefore, the upgrading processes to different fuels will be similar but may vary in degree. Tables 1.3 and 1.4 illustrate the properties and yields of H-coal and COED process liquids respectively.

TABLE 1.3 Properties and yields of H-Coal process

	Coal feed (dry basis)	Product[a]
Properties		
Analysis, wt %		
Carbon	70.88	88.29
Hydrogen	4.91	9.43
Oxygen	8.57	1.76
Nitrogen	1.47	0.38
Sulfur	3.47	0.14
Ash	10.61	<0.01
Aromatic carbon	--	55
Hydrogen/carbon ratio	0.83	1.28
Kinematic viscosity at 100°F, cSt	--	4.20
Gravity, °API	--	14.1
Yields, wt % dry coal		
Waste gases		6.01
C_1-C_3 gases		10.63
C_4-C_6 gases		4.12
IBP-400°F Naphtha		14.21
400-650°F Distillates		22.26
650-975°F Distillates		6.48
975°F+ Residual oil		19.00
Unconverted coal		5.78
Ash		11.51
Total		100.00

[a]Properties of 350-975°F product; yields include total product yields.

Table 1.4 Typical properties of COED pyrolysis liquids.

	Coal source	
	Utah A seam	Illinois No. 6 seam
Properties of Derived Oil		
Carbon (wt%)	83.8	79.6
Hydrogen (wt%)	9.5	7.1
Nitrogen (wt%)	0.9	1.1
Sulfur (wt%)	0.4	2.8
Oxygen (wt%)	5.0	8.5
Ash (wt%)	0.3	0.9
H/C atom ratio	1.36	1.07
API gravity (60°F)	−3.5	−4
Moisture (wt%)	0.5	0.8
Pour point (°F)	100	100
Viscosity (SUS 210°F)	390	1333
Solids (wt%)	3.8	4.0
Gross heating value (Btu lb^{-1})	16,100	15,050

Taking a further look at the N.C.B. process (U.N.Symp. 1979), Figure 1.6 shows the material balance of the process and from its results that 63% coal can be converted into distillates. Table 1.5 characterises the different distillates. It can be seen that distillates up to 200°C can be successfully utilised as a gasoline component after mild refining. However, the other distillates, that is the middle and the heavy needs further hydrotreatment for them to be utilised as conventional fuels or to be used as a blend in such. Of particular interest to this thesis is the middle distillate which may be hyroprocessed into diesel fuel or its blend.

The COED middle distillate can be processed to both diesel and jet fuel stocks (Cusumano et al., 1978). However, different fractions need to be utilised to fulfil the individual fuel specification (F.M.C. Corporation 1973). In the case of the diesel fuel the 390-650°F fraction is utilised but due to its high aromaticity it still gives an unacceptable low gravity and cetane number. But, hydrotreating the middle distillate to a paraffinic-cycloparaffinic component would just meet the specification. Table 1.6 gives a comparison of a COED diesel fuel fraction with ASTM specification.

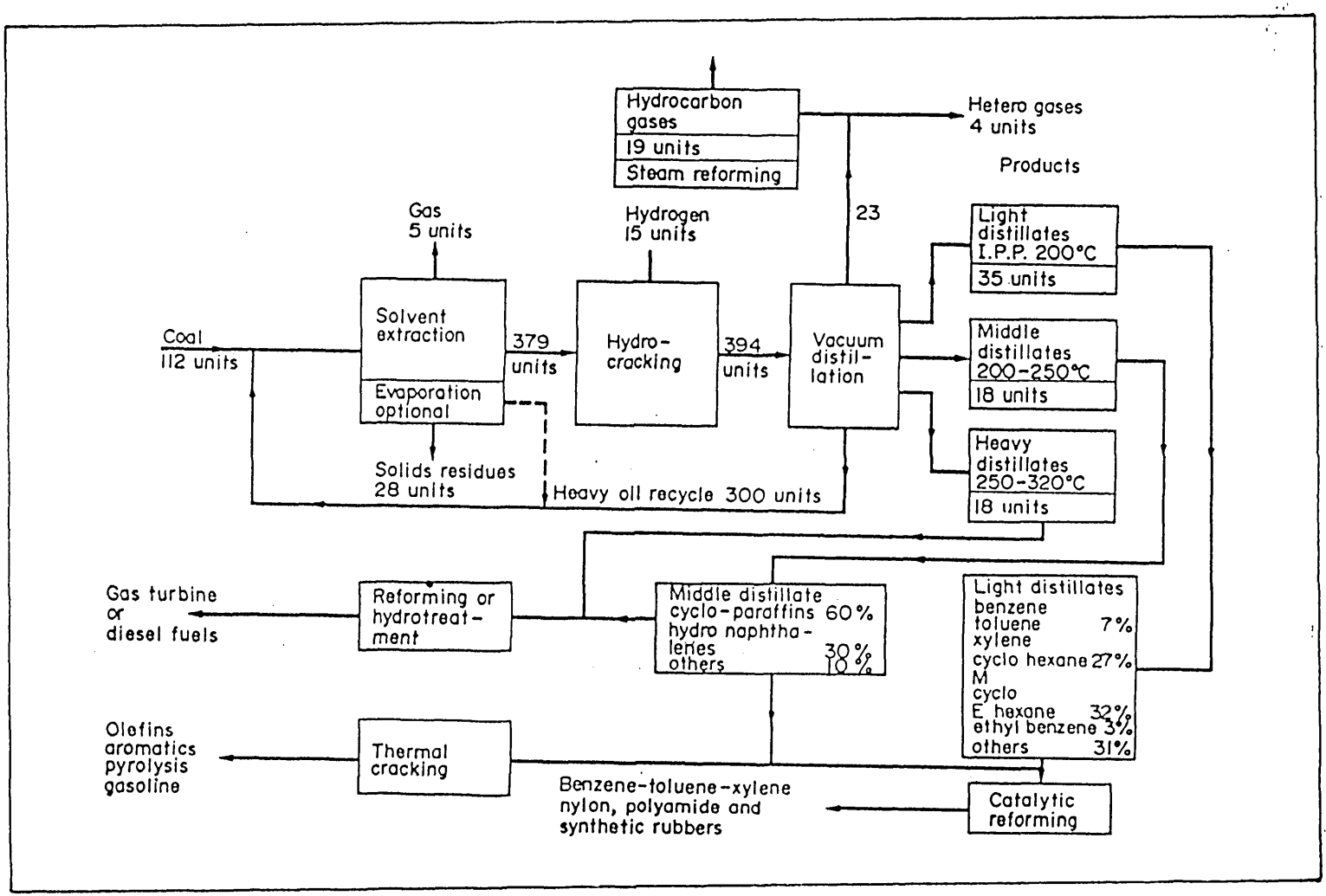


Figure 1.6. Material balance and product utilisation.

Table 1.5. Characterisation of distillates from NCB pilot plant hydrocracking of coal extract.

Light distillate (IBP - 200°C)	
H/C atomic ratio	1.7
Oxygen	<0.1 %
Nitrogen	<0.1 %
Sulphur	0.1 %
Paraffins	20 %
Naphthenes	40 %
Aromatics	40 %
Middle oil 200-300°C	
H/C atomic ratio	1.5
Oxygen	0.4 %
Nitrogen	0.1 %
Sulphur	0.1 %
Paraffins	0.5 %
Naphthenes	45 %
Aromatics	55 %
Heavy oil >300°C	
H/C atomic ratio	1.2
Oxygen	0.2 %
Nitrogen	0.2 %
Sulphur	<0.1 %

Table 1.6

COMPARISON OF A COED DIESEL FUEL FRACTION WITH ASTM SPECIFICATIONS[a]

Properties	Specifications	As distilled			390-525°F Fraction 2-stage HDS[b]
		390-650°F	525-650°F	390-525°F	
Pour point (°F)	0 max.	−70	−20	<−80	<−80
Flash point (°F)	130 min.	215	300	186	156
Sulfur (wt%)	Legal	<.001	<.001	.007	<.001
ASTM distillation (°F)					
10% distilled	460 max.	459	562	436	412
50% distilled	—		588	455	437
90% distilled	620 max.	586	626	494	483
100% distilled	660 max.	613		530	
Gravity (°API, 60°F)	33-37	22.5	19	25.7	33.2
Cetane number[d]	30 min.	18	24	23.0	>30[c]
Aniline point (°C)[e]	—			14.3	58.2
Aromatics (liquid vol%)	—			58.3	5.2

[a] From Project COED
[b] After hydroprocessing of 390-525°F fraction of syncrude.
[c] Estimated.
[d] A measure of the ignition quality of diesel fuel.
[e] A measure of the aromaticity of oil.

Table 1.7

COMPOSITION OF 400-650°F FRACTION FOR H-COAL LIQUIDS FROM ILLINOIS NO. 6 SEAM COAL

Component	Wt%	Component	Wt%
Saturated hydrocarbons		Aromatic hydrocarbons	
n-Paraffins	4.8	Alkylbenzenes	12.6
i-Paraffins	1.7	Indans and tetralin	30.8
Monocycloparaffins	14.0	Indenes	5.7
Dicycloparaffins	7.9	Naphthalene	0.2
Tricycloparaffins	2.6	Naphthalenes	3.5
		Acenaphthenes (C_nH_{2n-14})	4.0
	31.0	Acenaphthylenes (C_nH_{2n-16})	2.2
		Tricyclics (C_nH_{2n-18})	0.4
			59.6
Unsaturated naphthenes		Nonhydrocarbons (phenols)	
Monocycloolefins	4.3	Mol. wt. 108	0.04
		Mol. wt. 122	0.52
	4.3	Mol. wt. 136	0.98
		Mol. wt. 150	0.38
		Mol. wt. 164	0.07
		Mol. wt. 178	0.01
		Other nonhydrocarbons	3.10
			5.10
		Total =	100.00 wt%

The middle and the heavy distillate from the H-coal process are highly aromatic and therefore will not meet the jet and the diesel fuel requirement. However, the 400-650°F fraction (see Table 1.7) may be utilised as a diesel fuel after severe hydrotreating and hydrocracking.

The middle distillate from the Synthoil process contains 27% monoaromatics, 21% diaromatics and 8% polynuclear aromatics. This is substantially more than is allowed for jet fuel (25 vol.%.) However, high pressure hydroprocessing to saturate these aromatics followed by some selective cracking could meet the necessary specifications. To produce diesel fuel or its blend, similar treatment would be required.

Besides the aromatic constituent of the middle distillates from the different processes, all of them contain hetero-atoms (N,O,S) to a varying degree. Therefore, the hydrotreating process must be able to remove such compounds or bring them down to an acceptable level. This is reviewed in the next chapter.

1.4. AIMS

The general aim of this thesis was to investigate the catalytic hydrogenation reactions of mid-distillates from coal extracts. Two approaches were possible.

(i) studying different catalysts

(ii) investigating the reaction of mid-distillates or its model feeds on an established commercial catalyst.

In the first case one could choose different commercial catalysts or prepare some novel one and investigate their performance against the hydrogenation of mid-distillates. But as the mid-distillates contain complex compounds such a study would not have obtained information regarding individual reactions and could have only given a general guideline to the activities of different catalysts. However, if model feeds of mid-distillates were investigated on several catalysts an enormous number of experiments would be required to derive meaningful conclusions.

In the second case, an investigation of the reactions of the model feeds on an established catalyst would be of value, particularly if competitive conditions were explored. Thus, this approach was chosen as the basis of the thesis.

It was indicated earlier in this chapter that hydrogenation of distillates from coal extracts are carried out on cobalt-molybdenum or nickel molybdenum sulphide catalysts. Presently, much attention is given to nickel-molybdenum catalysts. Therefore, the choice

for this thesis was a well established nickel-molybdenum sulphide commercial catalyst (AKZO-153).

As discussed in previous sections the mid-distillates contain 2 and 3 ring partially-hydrogenated aromatics (e.g. tetralin, hydrophenanthrenes) and small quantities of sulphur, nitrogen and oxygen containing heterocyclic compounds. Therefore, in investigating the hydrogenation of the mid-distillates or its model feeds, one encounters the effect of the minor compounds on the hydrogenation of the major aromatic compounds. Preliminary experiments were thus carried out on pure tetralin, tetralin/quinoline and tetralin/dibenzofuran feeds on an aged AKZO-153 catalyst at conditions close to those of industrial operation using a high pressure laboratory scale trickle-bed reactor system to establish the conditions for the main work on which this thesis is based. Following from these results, and to move towards the main aims of this thesis, further experiments were carried out under varying experimental conditions (temperature and pressure) on a fresh batch of AKZO-153 catalyst. The experiments were broadly categorised into three groups:

(i) hydrogenation of tetralin and 1,6-dimethylnapthalene

(ii) hydrogenation of tetralin and 1,6-dimethylnapthalene with nitrogen containing heterocyclic compounds

(iii) hydrogenation of tetralin and 1,6-dimethylnapthalene with nitrogen and oxygen containing heterocyclic compounds.

Under section (i), the catalytic hydrogenation behaviour of major aromatic compounds were investigated, where apparent rate constants and activation energy measurements were made. Types and product distributions were obtained. The effect of pressure was studied.

In section (ii) the influence of quinoline, tetrahydroquinoline and o-propylaniline on the hydrogenation reaction of tetralin was studied. In the case of 1,6-dimethylnapthalene the influence of quinoline only was investigated. The effect of temperature and pressure were investigated.

In section (iii) the influence of dibenzofuran on the hydrogenation reaction of tetralin under competitive reaction conditions due to the effect of quinoline, tetrahydroquinoline and o-propylaniline were investigated. For 1,6-dimethylnapthalene the influence of dibenzofuran under competitive reaction of quinoline was studied. The effect of temperature and pressure were also investigated.

The above experimental studies enabled the main aims of the present research, which were to investigate catalytic hydrogenation reactions (hydrogenation, hydrodenitrogenation and hydrodeoxygenation) under competitive reaction conditions close to industrial processing, to be achieved. The contribution encompassed poisoning effects on hydrogenation rate, selectivity and activation energy. Reaction pathways and mechanism were also evaluated for some of the reactions. Reactivities of different hydroprocessing reactions were also established.

Hydrogenation of sulphur compounds were not carried out on the AKZO-153 catalyst, since a substantial amount of research has been done and their reactive behaviour is reasonably well established.

A secondary aim of this research was to investigate the hydrogenation and hydrodesulphurisation activity of unsupported cobalt-molybdenum catalysts in a trickle-bed reactor at conditions similar to industrial processing as a prelude to further work under competitive conditions. To this effect hydrogenation of dibenzothiophene was carried out on two samples of unsupported cobalt-molybdenum whose structures were previously investigated by other researchers.

CHAPTER TWO : HYDROPROCESSING ASPECTS OF COAL EXTRACT LIQUIDS

2.1. GENERAL

In the upgrading process of coal extract liquids the principal catalytic reactions are hydrogenation (HG), hydrocracking (HC), hydrodesulphurisation (HDS), hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO). Among the slowest of these reactions are the aromatic hydrogenation (Sapre et al., 1981). These reactions proceed at different rates and may take place on the same or different sites of a catalyst. Although each of these reactions incorporate breaking and making of bonds by hydrogen their reaction mechanisms vary. Therefore, each of these reactions needs to be looked into individually.

2.1.1. Hydrogenation (HG) and hydrocracking (HC)

These are the major principal reactions taking place in the upgrading of coal liquids. The simple hydrogenation process increases the H/C atomic ratios and decreases the aromatic content of the liquid. Whereas, the hydrocracking (C-C bond scission) process leads to lighter hydrocarbon fractions as well as branched

compounds. As these reactions are simultaneously occurring with other hydroprocessing reactions it is important to understand their relative rates, types of intermediates formed and selectivity towards different catalytic sites. These will facilitate process and catalyst development.

As discussed earlier, the liquids from coal-liquefaction process (eg. NCB process) contains multi-ring aromatics which require hydrocracking to produce lighter hydrocarbon fractions which are easier to convert into fuels and chemical feedstocks. Only a limited amount of work on the kinetics of catalytic hydrocracking of multi-ring aromatics has been carried out because of the complex nature of the molecules and subsequent product distribution. The hydrocracking of polynuclear aromatics proceeds via several steps which involve hydrogenation, isomerisation, cracking and rehydrogenation (Qader and Hill 1972, Wu and Haynes 1975). These lead to bicyclic and monocyclic aromatics of which some are partially hydrogenated. The illustration below (Fig. 2.1) exemplifies both hydrogenation and hydrocracking of a polynuclear aromatic (phenanthrene). In Fig 2.1 the cracking of the phenanthrene central ring is a minor route (Badilla and Chadwick, 1979).

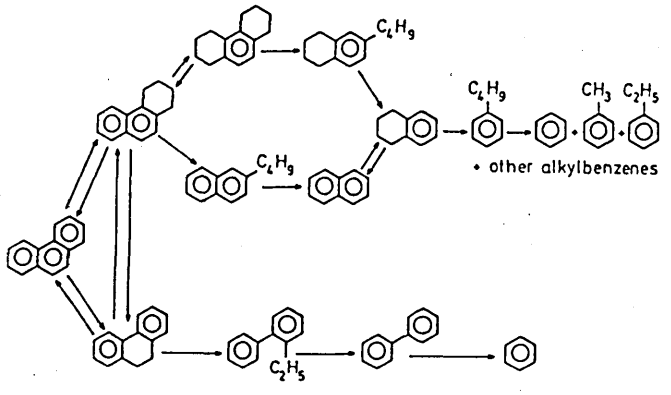


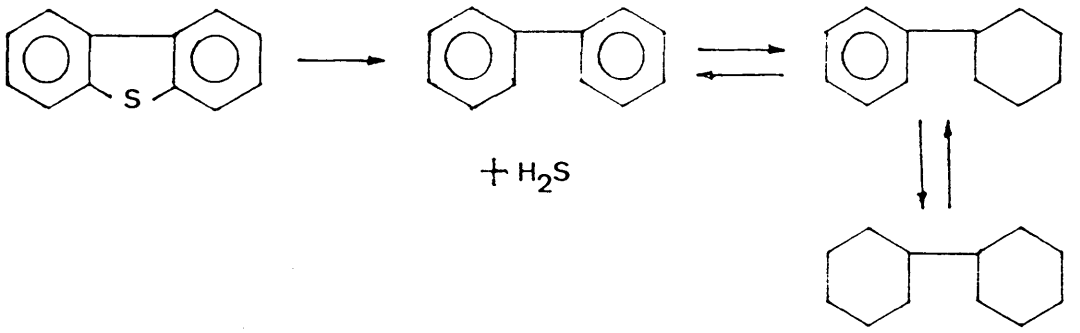
Figure.2.1

However, the coal extract distillates do not necessarily require hydrocracking but pure hydrogenation of the aromatic ring to produce jet or diesel fuels. Sapre et al., (1981) has studied the hydrogenation of aromatic compounds by sulphided Co-Mo/γ-Al_2O_3 catalysts. The different compounds reacted at different rates but do not vary widely. The majority studies were carried out on 2 and 3 ring aromatics or partially hydrogenated aromatics (Sapre et al.,1981; Patzer et al., 1979; Chu et al.,1982). Desikan and Amberg (1964) reported that hydrogen sulphide inhibits hydrogenation activity of Co-Mo/γ-Al_2O_3 catalysts. A recent study (Gültekin et al., 1984) also indicated that hydrogen sulphide inhibited the rate of propylbenzene hydrogenation on a commercial Ni-Mo/Al_2O_3 catalyst.

2.1.2. Hydrodesulphurisation (HDS)

This is the process for the removal of sulphur atom from its compound. Coal liquids contain substantial amounts of sulphur compounds which are similar to those present in petroleum crude and include for example, Benzothiophene,dibenzothiophene and napthobenzothiophene (Akhtar et al.,1974). The chemistry and catalysis of HDS has been well reviewed (Schuman et al.,1970; Schuit et al.,1973; Grange,1980). Contributions to the kinetic study of monocyclic and straight chain sulphur compounds using MoS_2 and WS_2 catalysts has also been made (Wilson et al.,1964; Kemball et al.,1965). Whereas, Givens and Venuto (1970) have carried out work on polycyclic sulphur compounds. Work is still being carried out on HDS but different approaches are being taken. Some workers are looking into the role of the catalyst in HDS and others are studying the kinetics and reaction mechanism. Furimsky (1980) has looked into the role of MoS_2 and WS_2 in HDS, whereas, Singhal et al.,(1981a) and Singhal et al.,(1981b) have looked into the reaction mechanism of HDS and kinetics of dibenzothiophene HDS respectively.

At high partial pressures of hydrogen, the rate of HDS is approximately first order (Hualla et al.,1978) with respect to the sulphur compound but with increasing concentration assumes a negative value in some cases (McKinley,1957) inferring that at high coverage, sulphur compounds act as an inhibitor. One of the products of HDS is hydrogen sulphide which has been found to inhibit butene hydrogenation (Kolboe et al.,1966; Owens et al., 1962). A general reaction path for dibenzothiophene HDS is shown below.



Generally cobalt-molybdenum catalysts have higher HDS activity than Nickel-Molybdenum catalysts.

2.1.3. Hydrodenitrogenation (HDN)

This is the process for the removal of nitrogen from heterocyclic N-compounds present in coal liquids and is of great importance because they can poison acidic

catalysts used in refining. Also the emerging synthetic fuel industry provides a second motivating factor for nitrogen removal due to the need to minimise NO_x emission during the combustion of coal or oil shale liquids.

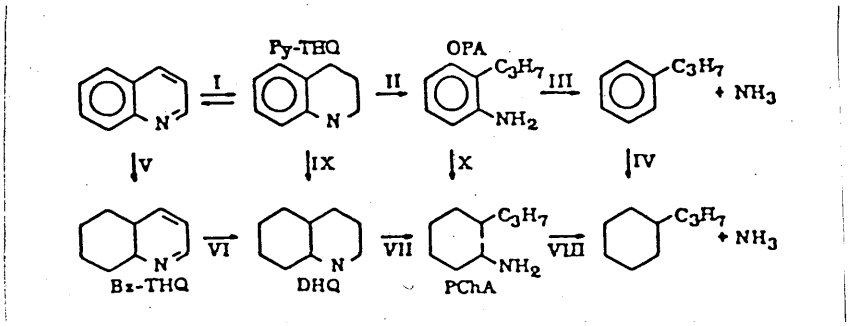
The hydroprocessing catalysts are usually optimised to perform selectively and so far favouring HDS. However, as the chemistry of N-compounds are considerably different than S-compounds; catalysts that are optimised for HDS are not suitable or optimum for HDN. To develop an improved catalyst and processing technique for nitrogen removal the knowledge of the types, quantities and chemical behaviour of the N-compounds present in petroleum and coal liquids are essential.

A brief review of the N-compounds present in petroleum crude and synthetic liquids (e.g.coal liquids) has been done recently (Katzer et al.,1979). Nitrogen concentration in synthetic liquids are typically two to five times greater than in petroleum. The review also indicates that most of the nitrogen compounds in petroleum are also found in synthetic liquids. The N-compounds can generally be divided into weak bases and strong bases (e.g. tetrahydroquinoline is more basic than quinoline) and upon hydrogenation weakly-basic

N-compounds are converted into strongly-basic ones. The increase in basicity creates a problem in hydroprocessing which will be discussed in later sections.

Studies on HDN have been carried out employing different reactors, catalysts and model N-compounds. However, the majority of work has been carried out on quinoline (Doelman and Vlugter,1963; Larson,1967; Madkour et al.,1969; Shih et al.,1977; Satterfield et al.,1978). HDN of pyridine has also been studied (Satterfield and Cocchetto, 1975).

The illustration below gives the reaction network for quinoline HDN (Satterfield et al., 1978).



HDN of quinoline is still given much attention (Satterfield and Cocchetto,1981; Cochetto et al 1981), because this is representative of the major N-compounds present in coal extract distillates. The studies indicate that quinoline HDN with minimum hydrogen consumption is not thermodynamically favourable under conditions of industrial interest and therefore the onus of selectively hydrogenating the heteroring is placed

entirely on the catalyst. These studies were carried out in vapor-phase. To confirm these findings liquid phase studies were carried out very recently (Satterfield et al.,1984) in which they found that the results are very similar to the previous work. The reaction mechanism of HDN of quinoline is complex but it provides an insight into the understanding of the types of intermediates formed, as well as their relative rates of formation and decomposition which will greatly facilitate catalyst development.

Another study of interest (Stern 1979) was HDN of indole, which is a heterocyclic N-compound. This reaction was carried out in an autoclave employing different catalysts. The study looked into the effect of the catalyst as well as the reaction network. The essential steps of HDN of indole are the same as in the case of quinoline. The workers also claim that a novel Rhenium catalyst made by them has an overall HDN activity which is better than Molybdenum catalyst. This offers some hope that scope for an improved catalyst for HDN can be developed.

2.1.4. Hydrodeoxygenation (HDO)

This is the process for the removal of oxygen atoms from coal liquids and is also of importance along with HDS and HDN as this facile reaction in coal

processing is almost unavoidable and a consumer of hydrogen. Considerably less work has been carried out on HDO compared to HDS and HDN. Thus, the application of the catalytic systems are not very clear in this area. In coal extract liquids, the primary heteroatom present are the phenolic oxygen (Palmer and Vahram,1972), also present are fused ring furans and carboxylic acids (Wiesser and Landa 1973). Earlier work (Donath,1956) indicates the inhibiting effect of such compounds on Ni(Co)-W(Mo) systems. Most work has been carried out on the hydrogenolysis of phenols and alcohols but little on heterocyclic oxygen compounds (Rollman,1977). Unlike C-S hydrogenolysis, C-O hydrogenolysis requires prior ring saturation, similar to C-N hydrogenolysis.

Weigold (1982) has studied the behaviour of Co-Mo/Al_2O_3 catalysts in HDO of phenols, whereas Furimsky (1983b) has looked into the deactivation of molybdate catalyst during HDO of tetrahydrofuran, a cyclic oxygen compound. The same worker (Furimsky,1983a) has studied the mechanism of HDO of tetrahydrofuran. One of the products of HDO is water, which has been found to affect catalytic HDN of quinoline (Satterfield and Carter,1981).

An illustration of reaction network of dibenzofuran HDO is shown in figure 2.2.

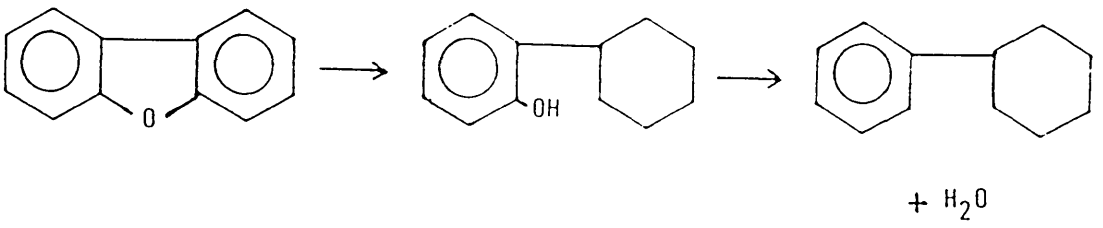


Figure 2.2

2.2. INTERACTIONS IN CATALYTIC HYDROPROCESSING

In the hydrotreating of petroleum or synthetic liquids all the catalytic reactions described above occur simultaneously and therefore one cannot isolate them from each other when studying such processes. Although an earlier worker (Donath,1956) reported the inhibiting effect of nitrogen compounds on Co(Ni)-Mo(W) systems, little attention has been given to its significance. This may be due to the fact that the petroleum refining industries were using crudes with low nitrogen content. However, as such industries are moving towards refining of heavy petroleum residua and synthetic liquids from oil shale and coal, a better understanding of the effect of heteroatom contents and its processing are being sought.

Notably, Satterfield and his co-workers (1975) studied the interaction between catalytic HDS of thiophene

and HDN of pyridine. Studies were carried out in a flow micro-reactor using commercial catalysts consisting of $Ni-Mo/Al_2O_3$, $Co-Mo/Al_2O_3$, $Ni-W/Al_2O_3$, and $Ni-W/SiO_2-Al_2O_3$ In this study they reported that pyridine inhibits the HDS of thiophene consistent with earlier reports (Kiovsky and Berg,1964; Ahuja et al.,1970). However, sulphur compounds have a dual effect on HDN. At low temperature the sulphur compounds compete with the hydrogenation site of the nitrogen compound and at higher temperatures the product of HDS, which is hydrogen sulphide, interacts with the hydrogenolysis function of the catalysts. This hydrogen sulphide interaction improves the cracking function of the catalyst and improves the overall rate of HDN. Desikan and Amberg (1964) reported that pyridine inhibited thiophene HDS in such a manner indicating that there were two sites which have HDS activity on $Co-Mo/Al_2O_3$catalyst.

Rollman (1977) has studied the relative rates of heteroatom removal from model nitrogen, sulphur and oxygen compounds and of hydrogenation of polynuclear aromatics on SiO_2 stabilised Co-Mo catalyst. His report concluded an ordering of reactivity by chemical type and the mechanism of heteroatom removal. Recently, Sivasubramanian and his co-workers (1980) have also

studied the effect of nitrogen concentrations on HDS of a coal-derived liquid. Their results also confirm the existence of two different HDS sites.

More recently, work by Satterfield and Gültekin (1981) reported the effect of H_2S on the catalytic HDN of quinoline. Their study showed that H_2S has an inhibiting effect on the intermediate hydrogenation step of quinoline but a marked accelerating effect on the overall HDN rate. Their study also showed the significance of intermediate secondary amines formed, which are strong bases, retarding the overall HDN rate. These findings indicate the nature of catalytic site as being acidic or having an anionic vacancy. In terms of the energetics of the reaction the presence of H_2S has decreased the activation energy of the C-N hydrogenolysis step (Satterfield and Gültekin,1981), thus indicating that interaction between different reactions are not only on the basis of site blockage or competition but may also involve a change in mechanism of the reaction proceeding via a different path. Another recent study by Satterfield and Carter (1981) reports the effect of water vapour on HDN of quinoline. As water is one of the products of HDO, the study points towards an interaction between HDO and HDN.

Ramachandran and Massoth (1981) have studied the effect of hydrogen sulphide on hydrogenation and cracking of hexene over a Co-Mo catalyst. Although the study does not spell out 'interaction studies', their findings can be related to such between hydrogenation and HDS function of the catalyst. They report that cracking activity linearly increases with partial pressure of H_2S (which is a product of HDS) and postulates a mechanism involving carbonium ions. A very recent study by Gültekin and his co-workers (1984) has looked into the effects of H_2S and NH_3 on catalytic hydrogenation of propylbenzene. H_2S and NH_3 both decrease the hydrogenation rate of propylbenzene on a commercial Ni-Mo/Al_2O_3 catalyst. Further work (Yang et al.,1984) on the effect of H S on the catalytic HDN of quinoline has been carried out but employing a trickle-bed reactor and working in the liquid phase.

Summarising, interaction exists between HDS and HDN, although it is not well understood. There are also strong indications of interactions between HDO and HDN as well as between HDS and hydrogenation functions of different catalysts. Interactions between HDN and hydrogenation have not been well defined and a

preliminary study (Nilsson,1980) showed that N-compounds reduce conversion of aromatic hydrogenation and ammonia reduced the rate of propylbenzene hydrogenation (Gültekin et al.,1984). But as the studies have been carried out mostly on an isolation basis and also under different reaction conditions using different catalysts and reactors, it provides an incoherent picture of the overall interactions that are taking place in the hydroprocessing of heavy fossil fuels (e.g. coal extract liquids). It is noteworthy that previous work has generally failed to correlate the structure of sites of catalysts with their specific hydroprocessing activity. This may be due to the fact that little information of the structure of the catalyst were known or were difficult to study under the reaction conditions employed. But recent (see Sec.2.3) advances in Mossbauer emission spectroscopy may lead to better understanding of such correlations.

2.3. COAL CONVERSION CATALYSTS

Although there have been significant advances in heterogenous catalysis it is biased towards petroleum crude oil refining. Bimetallic systems have been given enormous consideration and much work has been done to establish a relationship between the catalytic activity,

the electronic and geometric structures of these catalysts (Thomas and Thomas,1967; Dowden,1972). However, the findings have led to the establishment of general guidelines for catalyst design (Dowden et al., 1968, Trimm,1978) In the hydrotreatment of coal liquids examples of metal catalysts are tabulated (Cusumano et al.,1978,pp14) which promotes such reactions. But metallic catalysts in general are not expected to survive as metals in an environment of sulphur level exceeding 1% and temperatures over 300°C, which is particularly significant in coal conversion. Metals can form bulk sulphides (Boudart et al.,1975) in such conditions and therefore the true catalyst would be a mixed sulphide although the original form of the catalyst may be a metal or an oxide (Wiesser and Landa,1973). The most widely employed sulphide catalysts in coal conversion processes are mixtures of sulphides from the group IVA (Mo or W) and the group VIII (Ni or Co). Most of the work has been devoted to the Co-Mo system, while somewhat less information is available for the Ni-Mo catalyst. Although the Ni-Mo system is generally less active for HDS compared to Co-Mo they appear to have better hydrorefining properties (Wiesser and Landa,1973).

A recent detailed study (Topsoe et al.,1979; Topsoe et al.,1981) of Co-Mo/Al_2O_3 catalysts by Mossbauer emission spectroscopy have identified a "Co-Mo-S" phase whose presence is correlated with HDS activity. A further study (Breysse et al.,1981; Bennett et al.,1982) of Co-Mo catalysts on alumina and carbon supports are in broad agreement with Topsoe's findings. It has been shown that Co-Mo/Carbon catalyst in sulphided state contain two Co species; Co_9S_8 and a "Co-Mo-S" phase. In the case of the alumina supported catalyst it has also been shown that the "Co-Mo-S" phase is the principal species responsible for high HDS activity. However, it must be noted here that the actual structure of "Co-Mo-S" have not been evaluated. As an extenson of this idea of "Co-Mo-S" phase it will be interesting whether such species ("Ni-Mo-S") are present in Ni-Mo catalysts and whether this unique phase is also responsible for high activity other than HDS, that is, towards HDN and hydrogenation.

The relationship of the structure and activity of Ni-Mo sulphides to composition of the precursor oxides have been studied (Sander and Pratt,1981). Sulphiding transforms the MoO_3 into MoO_2 crystals with a thin skin

of MoS_2 together with some flakes of MoS_2 while the $NiMo_4$ transforms to highly dispersed MoS_2. The above studies were also carried out on both supported and unsupported catalyst and concluded that the support plays very little part in the intrinsic activity of the catalyst. X-ray diffraction study (Laine and Pratt,1981) of Ni-Mo catalysts conclude the presence of highly dispersed, defected MoS_2 species which are responsible for the catalytic activity. However, these studies need to be reconsidered in view of the recent findings described above for the related Co-Mo system.

The preparation and activity of Ni-Mo coal hydrogenation catalysts has been studied (Badilla-Ohlbaum 1979; Badilla-Ohlbaum et al.,1979; Badilla-Ohlbaum et al.,1981). In this study the relationship between the physical properties (pore size distribution, particle size) and the activity of $NiMo/\gamma-Al_2O_3$ has been evaluated. The study also reports the relationship of high activity with high sulphidation of the catalyst.

Existing commercial catalysts are being applied in the majority of coal liquefaction experimental plants. These are the conventional catalyst used in the petroleum refining industry. Tests at N.C.B. (U.K.) have shown that Comox 471 (Co-Mo system catalyst) was the best for

hydrogenation of coal extract (U.N.Symp.,1979). This may be true for the hydro-cracker unit but on the other hand for further hydro-refining (e.g.,the mid-distillates) the Ni-Mo system could be better utilised. The Ni-Mo system is now considered superior particularly for HDN and hydrogenation.

CHAPTER THREE : EXPERIMENTAL

3.1. INTRODUCTION

The major experiments performed during the present research consisted of preparation of model feedstocks and their hydroprocessing reactions employing a laboratory trickle-bed reactor. This high pressure reaction system was operated under conditions close to industrial processing. Analytical experiments included gas chromatographic analysis on reactant and product samples and elemental analysis on catalyst samples. Primary experiments for preliminary studies consisted of preparation of unsupported catalyst and activity test on such type using the trickle-bed reactor. Scanning electron microscopic analyses were carried out to assess pre-determined ratios of nickel and cobalt in the unsupported catalyst.

The model feedstocks were chosen to simulate the mid-distillate of coal extract liquids. This posed a problem as the availability of pure components were restricted and also the cost of such components had to be taken into account. Other difficult factors were choosing components such that both reactant components and products could be separated for quantitative analysis by chromatography.

The trickle-bed reactor system was a difficult apparatus to operate. Firstly, right conditions had to be chosen to avoid mass transfer limitations. Secondly, pressure fluctuation, reactor blockage and temperature control can become a major experimental problem. The trickle-bed reactor system was already built (Badilla-Ohlbaum,1979) but modifications had to be carried out for both safety purposes and to overcome experimental problems mentioned earlier.

Analysis of reactants and products by gas liquid chromatography proved to be another difficult factor and were overcome by trial and error as well as from knowledge of previous work carried out in this field.

The apparatus and procedures are described in later sections.

3.2. TRICKLE-BED REACTOR SYSTEM

3.2.1. General review

In hydrotreating of petroleum fractions where multiphase catalytic reactions with gases and liquid reactants are involved, fixed-bed catalytic reactors are employed. One such type are the trickle-bed reactors.

These reactors have been developed over the past ten to fifteen years by the petroleum industries for hydrotreating (hydrodesulphurisation, hydrocracking,

etc.,) of various petroleum fractions of high boiling point. In these reactors the gas flows either up or down through the void spaces of the catalyst whilst the liquid is allowed to flow down the bed of the catalyst. However, most widely used operation is cocurrent downflow of gas (Figure 3.1.) because it causes better distribution of liquid reactants over the catalyst bed and higher liquid flow rates are attainable without flooding of reactor. It is claimed (Hoog et al.,1953) that in the case of hydrodesulphurisation operation, direct and capital costs are 15-20 percent less for trickle-bed operation than for equivalent exclusively vapour phase operation. Also trickle-bed operation is desirable as reaction with high boiling point hydrocarbon feed in vapour phase would be impossible without excessive cracking. Furthermore, compared to

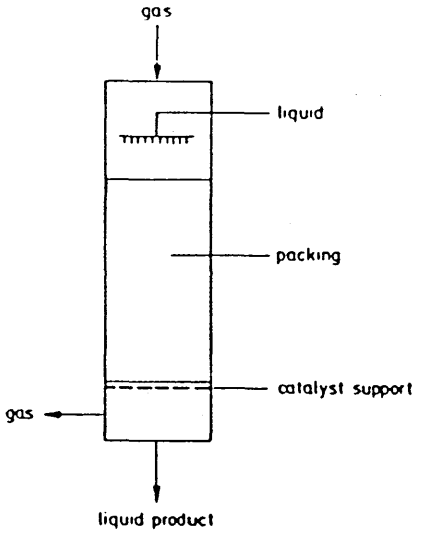


Figure 3.1 Trickle-bed reactor (cocurrent downflow operation.

a slurry-reactor, , a trickle-bed reactor approaches plug-flow pattern and the separation of catalyst from product stream does not arise.

To understand the operating behaviour of trickle-bed reactors, fluid dynamics provide such a basis. Two different flow regimes (Charpentier et al., 1969) can be distinguished where little or no interaction between phases exists:

(a) A liquid phase which is continuous with the gas being transported in independent bubbles and (b) A gas phase which is continuous with liquid trickling through the catalyst packing. Figure 3.2 shows how the different flow regions depend on liquid and gas loadings. This has been compiled from data of several workers (Hofmann 1978). Trickle-bed reactors ideally should be designed so that maximum degree of wetting of catalyst packing by the liquid film is obtained, as incompletely wet catalysts are only partially active. This incomplete wetting can arise due to poor liquid distribution attributable to inadequate design of the liquid distributor at the top of the reactor or too small a liquid load. It could also arise in case of highly exothermic reaction where the heat evolved may cause portions of catalyst bed not to be wetted properly. These affect the contacting efficiency between liquid and catalyst and liquid holdup in the bed.

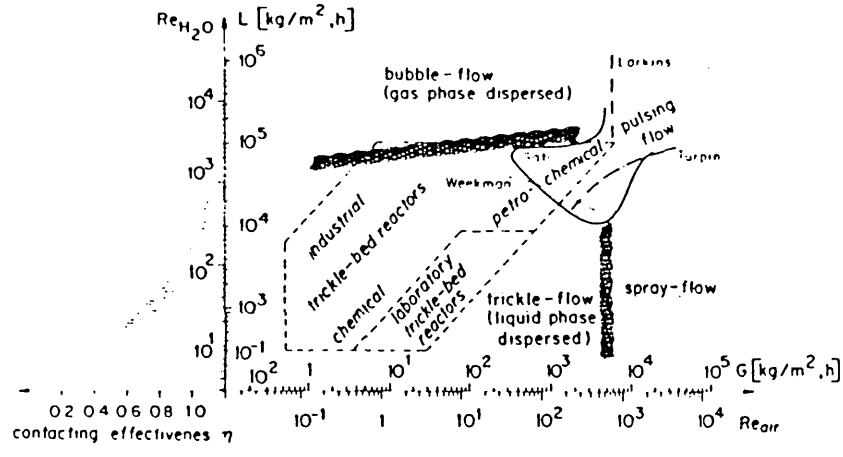


Figure 3.2 Flow regions in trickle-bed reactors (Hofmann, 1978).

To this effect a quantitative approach has been made (Satterfield, 1975) where a so-called contacting-effectiveness is defined. The effectiveness factor (general symbol used - η) is defined as the ratio of the actual reaction rate to that which would occur if all the surface throughout the inside of the catalyst particle were exposed to reactant of the same concentration and temperature as that existing at the outside surface of the catalyst (η value lies between fraction to a maximum of 1.0). However, by virtue of its definition different contacting-effectiveness or effectiveness factor values may not only be attributed to incomplete wetting but also to liquid holdup, mass transfer effects, uneven flow distribution or channeling and axial dispersion.

Little information is available regarding mass transfer limitations in trickle-bed reactors (Satterfield, 1970). However, studies in this field by many authors (Hofmann, 1978) have been based upon plug-flow reactor models neglecting factors such as axial dispersion, dead zones, etc. In the case of heterogenous gas-liquid reactions taking place in a trickle-bed reactor there could be one or more transport processes which could be rate determining. But, in the case of hydrogenation (relevant to this thesis) the gaseous

reactant (e.g. hydrogen) is present in excess amount, thus transport through gas film at gas/liquid interface will not generally be the limiting step. Nevertheless, gaseous reactants after their dissolution in the liquid must be capable of transportation from gas/liquid to liquid/solid interface across the trickling film.

The assumptions that are made in analysing trickle-bed reactor performance under ideal conditions with simple first-order kinetics are as follows:

(a) Flow of liquid is plug flow, that is, no dispersion of liquid in the axial or radial direction.

(b) Absence of mass and heat transfer limitations between gas and liquid, between liquid and solid catalyst or inside catalyst particles. Gas saturation of liquid at all times.

(c) Isothermal first-order irreversible reaction with respect to the reactant in liquid. Presence of gaseous reactant in excess amount.

(d) Complete wetting of catalyst pellets with liquid.

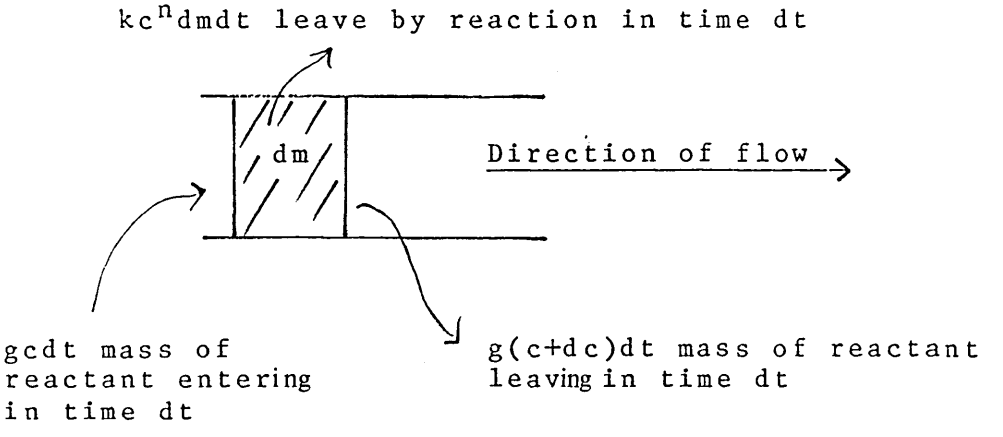
(e) Reaction occurs exclusively at liquid-catalyst interface.

(f) Absence of vaporisation and condensation.

During reaction the liquid feed is usually a vapour-liquid mixture which is reacted at liquid hourly

space velocities (LHSV), defined as volume of liquid feed/(volume of catalyst x hour) or at weight hourly space velocities (WHSV), defined as weight of liquid feed/(weight of catalyst x hour).

The design equation for obtaining pseudo-first order rate constant can be derived by considering a differential mass element of catalyst across the reactor:



where, g = mass of reactant flowing per hour
c = concentration of reactant
dm = mass element of catalyst
n = order of reaction
k = rate constant

Rate of disappearance of reactant is given by:

$$-\frac{dc}{dt} = kc^n$$

Rate of disappearance of reactant in an elemental mass of catalyst dm:

$$kc^n dm$$

At steady state:

$$gcdt = g(c+dc)dt + kc^{n}dmdt$$

$$\text{thus, } -\frac{dc}{c^{n}} = \frac{k}{g}\,dm$$

Integrating over the whole mass of catalyst m_o:

at the entrance $m=0$ and $c=c_i$ (initial concentration)

at the exit $m=m_o$ and $c=c_f$ (final concentration)

$$\int_{c_i}^{c_f} \frac{dc}{c^{n}} = \frac{k}{g} \int_{0}^{m_o} dm$$

$$\text{for } n=1, \quad -\ln \frac{c_f}{c_i} = \frac{m_o}{g}\, k$$

If x is defined as fractional conversion of reactant then, $\frac{c_f}{c_i} = (1-x)$ and $\frac{m_o}{g}$ is the reciprocal of weight hour space velocity (WHSV) which is called the contact time τ. Therefore the final equation becomes $-\ln(1-x) = k\tau$. Hence a plot of $-\ln(1-x)$ vs τ should give a straight line with a slope giving the rate constant value.

The apparent pseudo-first order rate constant obtained by the above assumptions may be compared with studies in stirred autoclave since in the trickle-bed, changes in concentration with distance is considered, whereas in an autoclave concentration with time is measured. In theory as there is one to one correlation

between time in the autoclave and distance travelled in the trickle-bed, the value of rate constants should be the same. But in practical situations rate constants measured in an autoclave are greater than those from a trickle-bed reactor because of loss of contacting effectiveness that often occurs in the latter case. Also differences can occur due to homogenous reactions which are greater in autoclave than in trickle-bed reactor as the ratio of liquid to catalyst volume is much higher in the former. Also modes of poisoning on the catalysts are different in each case as one is stationary and the other is stirred, in which case, the latter catalyst is poisoned uniformly. The overall effect could cause a slower drop in reactivity as a function of time in the trickle-bed than would be expected from studies in the autoclave.

3.2.2. Present system

The trickle-bed reactor system used in this research was designed and built by Badilla-Ohlbaum (1979). Modifications had to be carried out and the descriptions of both are given in the sections that follow.

3.2.2.1. Description of available system

The available experimental trickle-bed reactor system employed for this research is shown in Figure 3.3

and the details of the construction are given in Table 3.1. The trickle-bed reactor shown in Figure 3.4 was made of a 17cm length of 1.27cm ($\frac{1}{2}$ in)o.d. 316s.s.tubing with a 0.16cm (1/16 in) o.d. centrally located thermocouple tubing. To support the catalyst two 316 s.s. sintered discs were placed at each end of the reactor tube. The pre-heater consisted of a 50cm length of 0.32cm (1/8 in)o.d. 316 s.s. tube, coiled around the reactor. All connections were made of Hoke (Gyrolok) stainless steel tube fittings. The reactor was heated by means of an electric furnace, the temperature of which was controlled by a temperature indicator controller (Eurotherm) within a range of $\pm 3°C$. The thermocouple inside the reactor acted as the temperature sensing device for this controller.

The liquid feed was stored in a 3.1tr capacity 316 s.s. storage tank kept under 10 psi of nitrogen to avoid oxidation and evaporation. The feed passes through a removable micro-filter and was pumped by a high pressure metering pump. Hydrogen and the liquid feed were combined prior to entering the pre-heating section of the trickle-bed reactor. The products from the reactor passed through an air cooler (75cm in length, 1/8 in. o.d.), a water-cooled heat exchanger (15cm in length, 1/8 in o.d.) and liquid products were separated

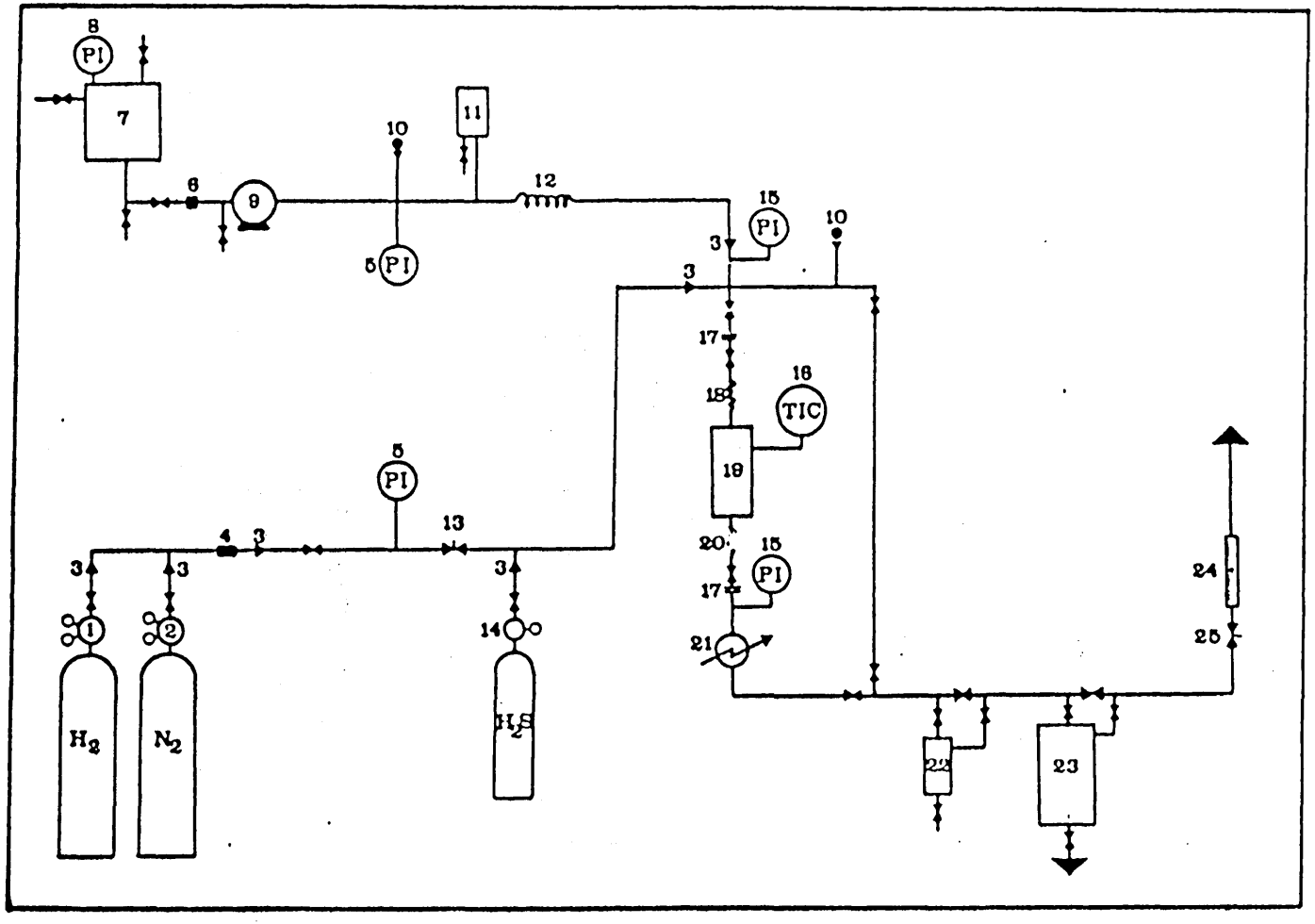


Figure 3.3. High pressure reaction system (Badilla-Ohlbaum,1979)

TABLE 3.1. Key to Figure 3.3.

1. Hydrogen pressure regulator, Pressure Control Ltd., 0-2,000 psig
2. Nitrogen pressure regulator, Pressure Control Ltd., 0-2,000 psig
3. Check valve, Hoke Ball Check Valve, 6133G25.
4. Filter, Hoke Micron In-line Filler, 6312F25.
5. Gauge, U.S. Gauge, 0-4,000 psig, 2½" diamter, 316 ss.
6. Filter, Hoke Micron Removable, 6321G4Y.
7. Liquid feed tank, 3 ℓ capacity, welded 316 ss.
8. Gauge, Gallenkamp, 0-15 psig.
9. Metering pump, Dosapro Milton Roy, Mod 19633, 0-300 cc hr^{-1} 3600 psig.
10. Relief valve, Hale-Hamilton RS12, 2500-3600 psig.
11. Damper (capacitance), Water Dumper Accumulator, 100 cm^3.
12. Damper (resistive), 3 m long, 1/16" O.D. 316 ss tubing.
13. Flow valve, Hoke Milli-Mite Forged Metering Valve, 1315G2Y.
14. Hydrogen sulphide pressure regulator, 0-100 psig, Matheson, Mod 11.
15. Gauge, Budenberg, 0-4,000 psig, 6" diameter.
16. Temperature controller, Eurotherm, Mod 020-088-03-023-12-05.
17. Bulkhead connnector, Hoke, 2BCM2-316.
18. Preheater, 50 cm long, ⅛" O.D., 316 ss tubing.
19. Reactor, 16 cm long, ½" O.D., 316 ss tubing.
20. Air cooler, 30 cm long, ⅛" O.D., 316 ss tubing.
21. Water cooler, 15 cm long, jacket ¼" O.D., tube ⅛" O.D., 316 ss tubing.
22. High pressure sampler, 4 cm^3 capacity.
23. High pressure accumulator, Hoke 6HDY500, 500 cm^3 capacity.
24. Float meter, GEC Elliot Process Instruments, Mod 1100, tube D2.
25. Back pressure valve, Hoke Micro-Mite Forged Metering Valve, 1656G2Y.

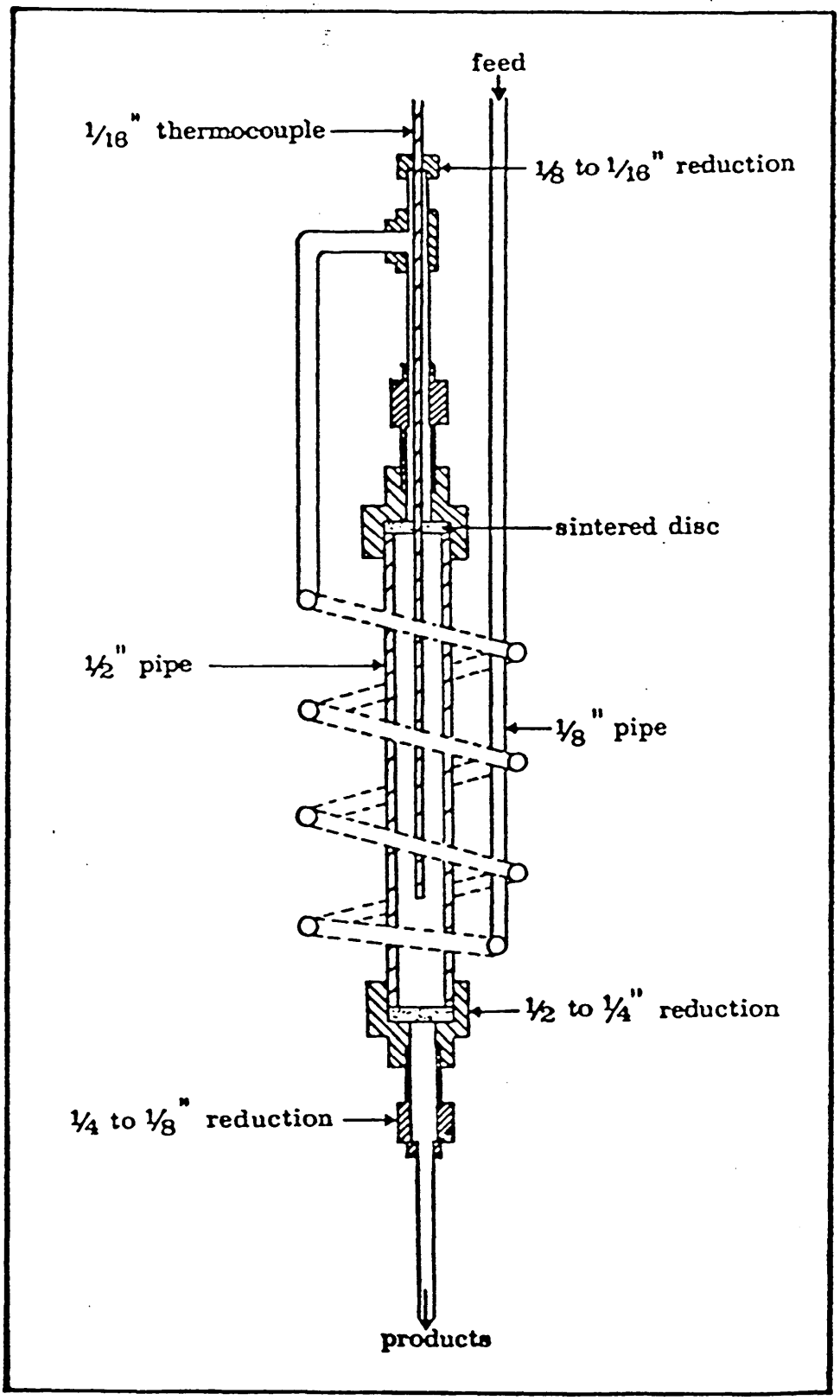


Figure 3.4. The Trickle-bed reactor (Badilla-Ohlbaum, 1979)

from gases in a 500 cm capacity high pressure accumulator. The gases were discharged through a back-pressure valve, which also controlled the gas flow through the reactor. The gas flow was measured by aid of a rotameter placed upstream of the backpressure valve. The liquid product sampling device consisted of a 4cm high pressure sampler placed upstream to the accumulator. This device allowed samples to be taken during an experimental run for analysis.

3.2.2.2. Description of modified system.

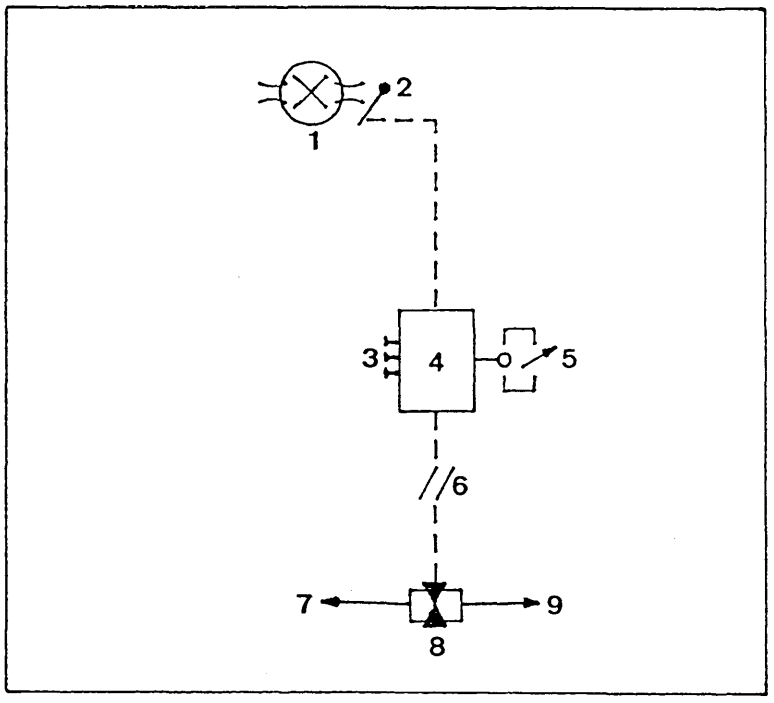
There were two over-riding factors for modifying the existing trickle-bed reactor system. Firstly, with the introduction of a new safety policy, the system had to have a device which automatically shut it off when the extractor for effluent gases (hydrogen, methane, H_2S etc.,) failed. Therefore, even before any trial experiments could be carried out an automatic shut-off system had to be built. While designing and constructing this device, the trickle-bed reactor system was found to have a number of leaks which had to be repaired and included some sections that were completely overhauled. Components such as valves, worn out compression fittings, corroded pipes, had to be renewed. Since the system was a few years old renewable spares were unavailable and therefore complete new sections had to be built.

Secondly, modifications were carried out with a view to improving the system. Some were carried out after trial experimental runs and others were made in later stages when experimental problems such as poor temperature control, pressure fluctuations, poor gas/liquid separation were becoming severe.

The automatic shut-off system essentially consisted of a remotely actuated electro-mechanical on/off gas line valve (Hoke make, imported from U.S.A., to fit existing system), electronic control box and a micro-switch attached to the extractor system. The electronic control box controlled both the gas line valve as well as power to the furnace, high-pressure pump and other electrically powered instruments. The control box had override facilities in case the micro-switch malfunctioned. To incorporate the electro-mechanical valve the gas inlet section of the trickle-bed reactor system had to be modified. Figure 3.5 details the modified section.

After a number of initial trial experimental runs (tetralin-hydrogenation) the essential disadvantage noted was the temperature control. The furnace was being controlled by a centrally located thermocouple placed inside the reactor and the temperature on the indicator of the Eurotherm controller was judged to be the temperature of the reactor-bed. Firstly, to attain a

steady reactor-bed temperature, the furnace output had to be controlled quite accurately but as there was a lag between the reactor and the furnace wall and since the control of the furnace was from the reactor, it was found to be poor. Secondly, reading of the Eurotherm controller could give inaccurate reactor-bed temperature. To overcome this initial disadvantage a second thermocouple (1/8" diameter, stainless steel sheathed) was inserted into the furnace tube where the reactor was housed. This controlled the furnace by aid of the Eurotherm controller. The 1/16" diameter centrally located thermocouple of the reactor was connected to a digital thermometer which gave direct temperature reading of the reactor-bed. This modification showed other immediate advantages. Firstly, it showed the difference between the furnace wall temperature and the reactor-bed temperature which varied between 10-20°C depending upon ambient laboratory temperature and the degree of heat insulation on top and bottom of the furnace tube. Secondly, the time lag between the final furnace temperature and the desired reactor-bed temperature could be observed which varied between approximately 30 mins to 60 mins. and depended upon laboratory conditions as well as on types of reaction carried out, as was later observed.



1. Extractor-fan.
2. Micro-switch.
3. Power supply to furnace, pump and digital thermometers.
4. Electronic control box.
5. Mains supply, 240 Volts.
6. Transformer, 240V to 115V.
7. To experimental rig.
8. Remote actuated on-off valve,Hoke.
9. To gas cylinders.

Figure 3.5. Automatic shut-off section of the trickle-bed reactor system.

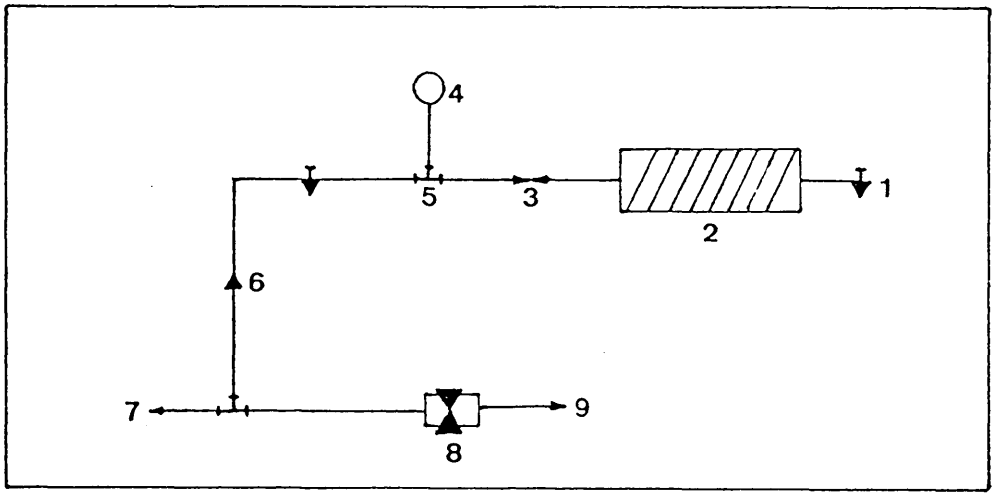
Also, during the trial experimental runs, pressure fluctuations were observed. Investigations revealed that it was due to high cracking-pressure non-return valves being used rather than reactor blockage as was first thought. New non-return valves of low cracking-pressure (8-10 psi) improved the situation drastically.

The high pressure metering pump was accurately calibrated. It was noted that the nitrogen pressure in the feed tank was essential not only for avoiding oxidation and evaporation of liquid feed but to cope with supplying the inlet of the pump via the filter system (see Figure 3.3) during higher feed rate and/or low fluid level (low head pressure) in the feed tank. Inadequate supply of liquid feed gave wrong calibration readings and an erratic feed rate to the system. Further improvement of feed supply to the inlet of the pump was achieved by changing the fine (size 1) removable filter to a coarse (size 4) one. The filter (Hoke) was made of sintered stainless steel material. This also afforded viscous liquid feed to pass through with less resistance. The role of the filter was to avoid damage to the high pressure metering pump (Dosapro Milton-Roy) by fine particles,and size-4 filter was adequate according to the manufacturers of the pump.

The gas flow through the reactor was measured by means of a rotameter (GEC Eliott, Model-1100, reinforced plastic body). This was calibrated for both hydrogen and nitrogen gases but the removable glass tube (size-D3) previously used was inadequate for the desired nitrogen flow and therefore it was changed to size E3, which accommodated both gases.

The main compression joints ($\frac{1}{4}$" and $\frac{1}{2}$") of the trickle-bed reactor were worn out and after several experimental runs could not hold the pressure. Attempts were made to repair the joints but with closer inspection it was found necessary to rebuild the whole section of the system shown in Figure 3.4. There was a practical problem in pressure testing the trickle-bed reactor while it was inside the furnace as access to the compression joints were restricted. Therefore, certain changes were made to pressure test it outside the furnace. To achieve this a new section (see Figure 3.6) was built at the gas inlet section. To pressure test, the trickle-bed reactor was connected to this section and kept under nitrogen pressure (1500 psi) for 24 hours.

The system was prone to further leaks which were rectified in several stages when investigations revealed such problems. It was discovered that the o-ring material of the liquid non-return valve was made of butyl-nitrile



1. On-off ball valve, Hoke.
2. Trickle-bed reactor.
3. 1/8 in. union, Hoke.
4. Pressure gauge, 0-2000 psig.
5. T-joint, Hoke.
6. Non-return valve, Hoke.
7. To experimental rig.
8. Remote actuated on-off valve, Hoke.
9. To gas cylinders.

Figure 3.6. High Pressure testing section of trickle-bed reactor system.

rubber material which swelled and eventually degraded in an atmosphere of liquid feed containing carbon disulphide (used in this research). This swelling caused leakage through the non-return valve into the liquid line where it eventually reached the metering pump and finally the atmosphere. This leak was not apparent as it was not detectable on the body of the non-return valve itself. The o-ring was then changed to "viton". This was less susceptible to such effects and had approximately ten times the durability than the previous o-ring material.

Approximately, half way through this present research, the metering pump failed to pump against a pressure above 150 psi (required experimental pressures 500 to 1000 psi). The pump had to be completely overhauled and repaired by the original manufacturer, after attempts at the workshop of the department failed to rectify it.

The final stages of the modifications included incorporation of a second high pressure gas/liquid separator to the system and replacement of the reinforced plastic body rotameter by a stainless steel one as the base of the plastic body rotameter cracked after a pressure surge occurred when the back-pressure valve failed. The position of the rotameter was also changed such that any leak through it would not vent effluent

gases into the laboratory. The second gas/liquid separator was essential as poor separation in the first caused entrained liquid to block the narrow orifice of the back-pressure control valve upstream to the system and experiments had to be abandoned. After this modification this problem was completely rectified.

The other addition to the system was the insertion of a thermocouple (1/16") to the furnace element which was connected to a second digital thermometer. This addition had its merits as the temperature of the reactor bed could be controlled within ±1°C and a desired reaction temperature was reproducible for different experimental runs.

The final modified experimental trickle-bed reactor system employed for this research is shown in Figure 3.7 and the details of the construction are given in Table 3.2.

3.2.2.3. Performance of reactor

Studies carried out on some laboratory trickle-bed reactors showed that the rate of reaction appeared to be limited by intrinsic reaction kinetics rather than a mass transfer process (Satterfield, 1970). Le Nobel and Choufoer (1959) found that decrease in catalyst size increased rate of reaction which indicated pore-diffusion limitations. Reduction in liquid

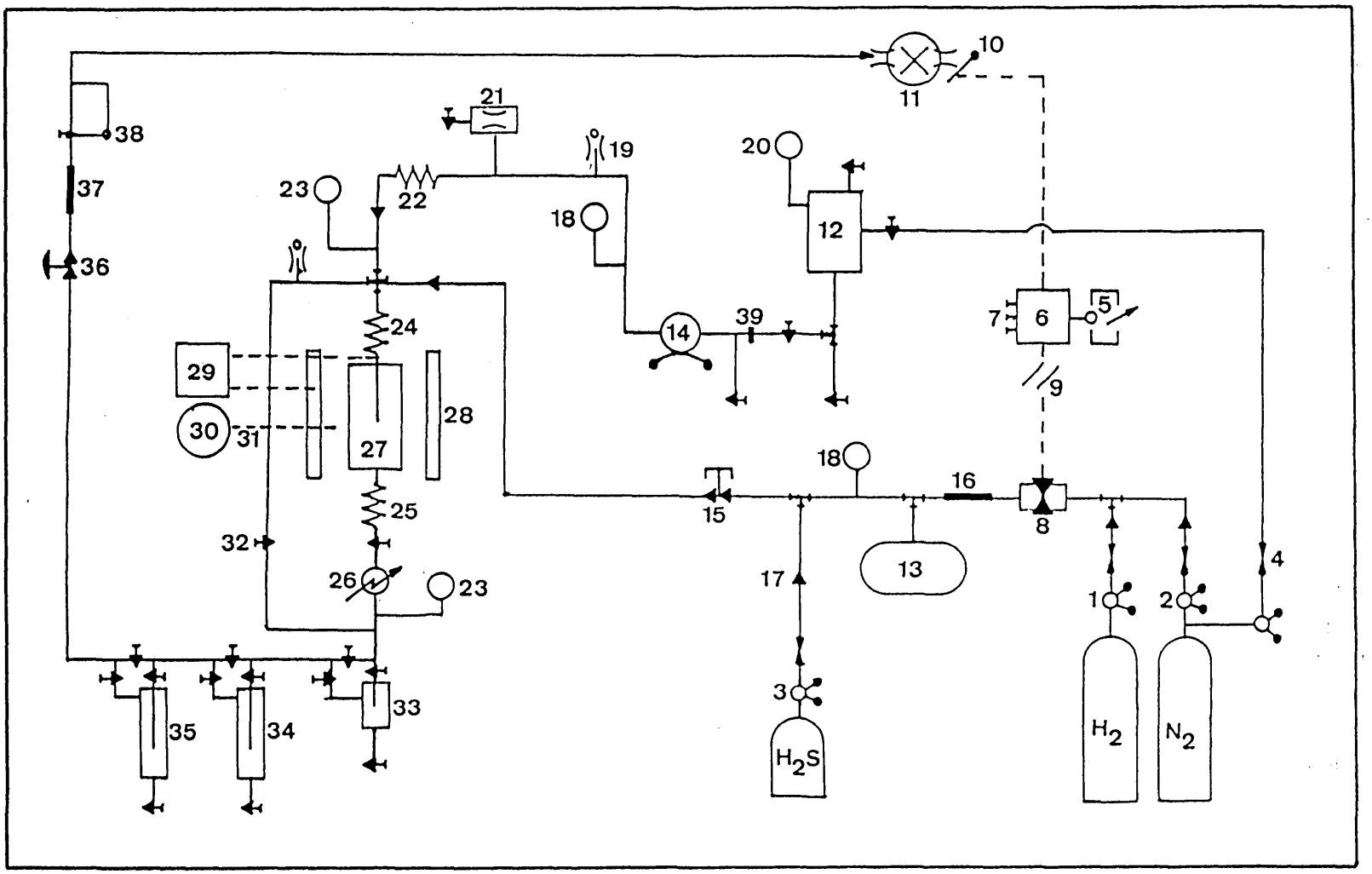


Figure 3.7. Modified high pressure reaction system.

TABLE 3.2. Key to figure 3.7.

1. Hydrogen pressure regulator, Pressure Control Ltd.,0-2000 psig
2. Nitrogen pressure regulator, Pressure Control Ltd.,0-2000 psig
3. Hydrogen sulphide pressure regulator, 0-100 psig, Matheson.
4. Connecting union, Hoke.
5. Mains supply, 240 Volts.
6. Electronic control box.
7. Power supply to electrically controlled apparatus.
8. Remote actuated on-off valve, Hoke.
9. Transformer, 240V to 115V.
10. Micro-switch.
11. Extractor-fan.
12. Liquid feed tank,3ltr capacity,welded 316 ss.
13. High pressure testing section.
14. Metering pump, Dosapro Milton Roy, Mod.19633, 0-300 cc/hr, 3600 psig.
15. Flow valve, Hoke milli-mite Forged Metering valve,1315G2S.
16. Filter, Hoke Micron In-Line filter, 6312F2S.
17. Non-return valve, Ball type, Hoke.
18. Gauge, U.S. gauge, 0-4000 psig, $2\frac{1}{2}$ in. diameter, 316 ss.
19. Relief valve, Hale Hamilton, RS12, 2500-3600 psig.
20. Gauge, Gallenkamp, 0-25 psig.
21. Damper (capacitance), Water dumper accumulator, 100 cm^3.
22. Damper (resistive), 3m long, 1/16 in. O.D., 316 ss tube.
23. Gauge, Budenberg, 0-4000 psig., 6" diameter.
24. Preheater, 50cm long 1/8 in. O.D. 316 ss tube.
25. Air cooler, 30cm long, 1/8 in. O.D., 316 ss tube.
26. Water cooler, 15cm long, jacket $\frac{1}{4}$ in. O.D., tube 1/8 in. O.D., 316 ss tube.
27. Reactor, 17 cm long, $\frac{1}{2}$ in. O.D., 316 ss tube.
28. Electric furnace,45 ohms.
29. Digital thermometers, Eurotherm Mod. 1100.
30. Temperature controller, Eurotherm,Mod.020-088-03-023-12-05.
31. Thermocouple, inconel sheathed.
32. On-off valve, Ball type, Hoke.
33. High pressure sampler, 4 cm^3 capacity.
34. High pressure accumulator, 500 cm^3, Hoke 6HDY500.
35. High pressure gas-liquid separator, 100 cm^3, 316 ss tube.
36. Back pressure valve, Hoke micro-mite forged metering valve, 1656G2S.
37. Float meter, GEC Elliott, Mod.1100 ss body, tube E3.
38. Bubble meter column.
39. Filter, Hoke Micron removable, 6321G4S, size 4.

viscosity also increased reaction rate which points towards ease of diffusivity of organosulphur (in case of hydrodesulphurisation process) molecules through the liquid-filled pores. The above process was further discussed by Van Deemter (1965) who concluded that the effectiveness factor (See Section 3.2.1.) on cobalt-molybdenum catalyst particles of about 1/5" diameter was 0.36 whereas Adlington and Thompson (1965) found the effectiveness factor to be 0.6 for 1/8" diameter catalyst of the same type.

The performances of the trickle-bed reactor used in this present research were studied by previous worker (Badilla-Ohlbaum 1979). Some aspects were also assessed during the present research to confirm previous findings. A process variable study was conducted by the previous worker to select the right conditions for this system. To assess external mass transfer resistance, effects of variations of liquid feed rates in terms of weight hour space velocities (WHSV) were carried out. Whilst for internal mass transfer resistance effects of particle size of the catalyst were carried out. A commercial nickel-molybdenum (AKZO-153) catalyst and a ½" o.d. reactor were used throughout for such studies. Incidentally, the same catalyst (although different

batch) and reactor size has been used throughout the present research.

Table 3.3 gives the conditions for testing the performance of the reactor and the results shown in Figure 3.8 (Badilla-Ohlbaum,1979) assesses the external mass transfer resistance based upon pseudo-first order reaction mechanisms taking place with a plug flow pattern. Straight line dependence (represented by broken lines) indicates no external mass transfer resistance but deviation from it (experimental results - bold line) points towards such resistance. It can be seen that for slower reaction (hydrodeoxygenation) external mass transfer resistance is insignificant.

TABLE 3.3

Experimental conditions for testing performance of reactor.

Weight of catalyst	- 8g
Particle size	- 0.3 - 0.6 mm diameter
Weight Hour Space Velocity(WHSV)	- 1.94 - 4.24 g hr^{-1} g-cat^{-1}
Hydrogen pressure	- 500 and 1000 psi
Hydrogen flow rate	- 480 cm^3 min^{-1}(STP)
Temperature.	- 260 - 375°C

The effect of liquid feed rate on the flow pattern in a ½" o.d. reactor was studied qualitatively by the previous worker. For a homogenous flow the right conditions were met by using catalyst particle size between 0.3 - 0.6mm, feed rate in terms of WHSV between 2-4 and a gas flow rate of 465.9 cm^3 min^{-1}. By using colourant in the feed it was shown that the catalysts were completely surrounded by liquid and wall flow was minimal for catalyst particle size between 0.3 to 0.6mm i.e. by employing a reactor-diameter/particle-diameter ratio of 20-40.

The results shown in Figure 3.9 and Table 3.4 (Badilla-Ohlbaum,1979) indicate that there are no significant difference in conversion for different particle size used and the effectiveness factor which vary from 0.8 to 1.0 shows that pore-diffusion is insignificant under experimental conditions employed.

The experiments carried out previously and presently to assess the performance of this presently used trickle-bed reactor system enabled data to be used from this reactor with reasonable confidence for the use of present research which was undertaken.

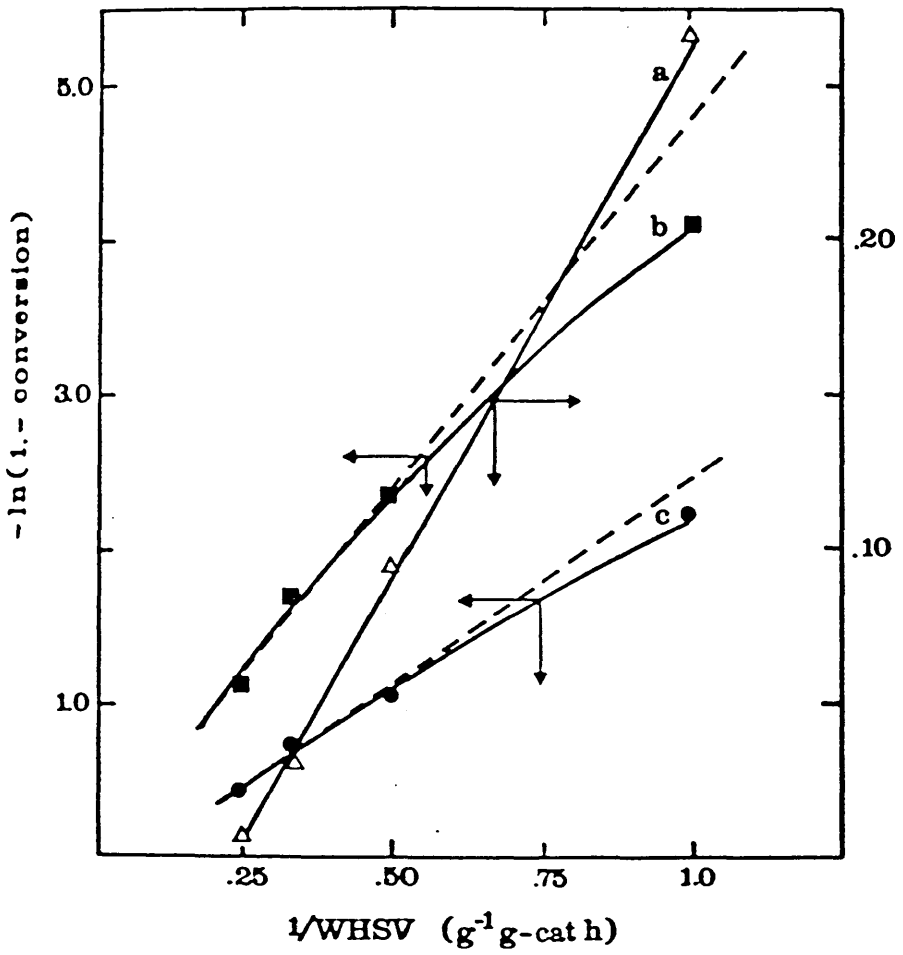


Figure 3.8. Effect of the liquid flow rate. Curves
(a) Dibenzofuran
(b) Phenanthrene hydrogenation
(c) Quinoline HDN.

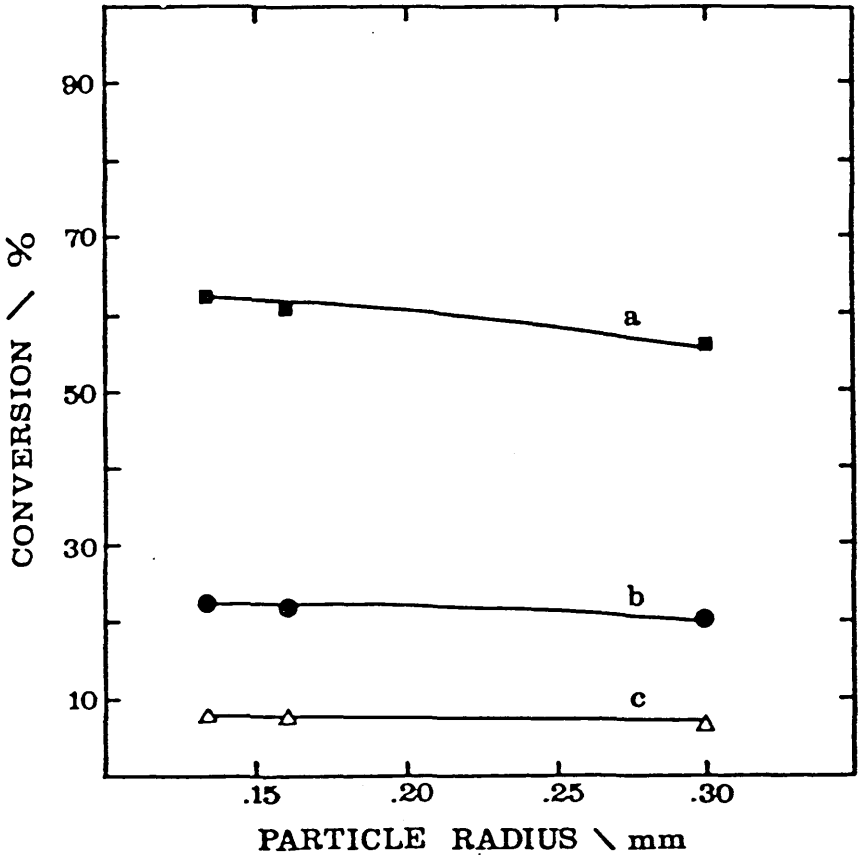


Figure 3.9. Effect of the particle size on the performance of the catalyst.
(a) Phenanthrene hydrogenation
(b) Quinoline HDN
(c) Dibenzofuran HDO

TABLE 3.4 - EFFECTIVENESS FACTORS

	REACTION	CATALYST PARTICLE SIZE/mm 0.135	0.30
CONVERSIONS (%)	Dibenzofuran	7.2	6.4
	Quinoline HDN*	23.1	20.4
	Phenanthrene	62.5	57.4
APPARENT KINETIC CONSTANTS (k_r) g-mol g-cat^{-1} h^{-1}	Dibenzofuran	0.30	0.27
	Quinoline HDN*	1.05	0.91
	Phenanthrene	3.92	3.41
$\frac{\phi_{.30}}{\phi_{.135}} = \frac{.30}{.135}$		-	2.22
$\frac{\eta_{.135}}{\eta_{.30}} = \frac{k_{.135}}{k_{.30}}$	Dibenzofuran	-	1.11
	Quinoline HDN*	-	1.15
	Phenanthrene	-	1.17
EFFECTIVENESS FACTOR	Dibenzofuran	0.97	0.87
	Quinoline HDN*	0.96	0.83
	Phenanthrene	0.95	0.81

* Based on N-removal from organic ring.

3.3. EXPERIMENTAL PROCEDURE

3.3.1. Preparation of feed and catalyst loading

Liquid feedstocks were prepared in batches so as to cover sets of experimental runs. This ensured a consistent percentage of components (particularly important in the case of model feedstocks) for different experimental runs. In each case a small amount of trial feedstock was made prior to making the batch to determine whether individual components would mix or dissolve (in case of solids) and analysed by chromatography to ascertain whether they could be separated. A trial experimental run was also carried out to check whether products could be separated by chromatography. In some cases, the intended feedstock had to be abandoned for reasons mentioned above.

Feed compounds, the majority of which were liquids, were thoroughly mixed in a 3 ltr beaker after weighing them on a top-pan balance (± 0.1 mg). n-decane was added to each feedstock as an internal standard. The choice of n-decane was undertaken after trying other internal standards (n-heptane and n-octane) of which neither could be separated by chromatography from other feed components or its products. The internal standard also did not react under experimental conditions employed. Finally, in a fume cupboard, carbon disulphide (0.1 mol %) was

added to the feedstock by the aid of a pipette. This compound acted as the in-situ sulphiding agent for the catalyst. The feedstock was then stored in winchester bottles. A sample (approximately 4 cm^3) was kept separate for chromatographic analysis.

The commercial nickel-molybdenum catalyst (AKZO-153) was supplied by the National Coal Board, Coal Research Establishment, Cheltenham, U.K. The characteristics (Badilla-Ohlbaum, 1979) of the catalyst were:

MoO_3	-	15 wt %
NiO	-	3 wt %
Surface area[(a)]	-	230 m^2g^{-1}
Pore volume[(a)]	-	0.48 cm^3g^{-1}
Mean pore diameter[(a)]	-	8 nm
Surface acidity[(b)]	-	0.178
Support	-	$\gamma - Al_2O_3$

(a) by nitrogen adsorption
(b) as mgm^{-2} of chemisorbed pyridine.

It was supplied as 1/8" extrudate. These extrudates were crushed in a mortar and sieved by sieve-plates (mesh size 30-50) to obtain particle diameter sizes between 0.3 to 0.6mm. The process was tedious and the sieving had to

be hastened by a mechanical shaker. Careful crushing decreased catalyst wastage. Approximately 40 wt % (optimum) of the required size were obtained while the remainder were smaller in size of which the majority were powder in form. The 30-50 mesh size catalysts were then washed in water to remove some of the adhered powder which would have blocked the sintered disc holding the catalyst in the reactor tube and damaged valve seats downsteam of the reactor. The catalysts were dried by flowing nitrogen in a glass tube heated by a furnace at a temperature of 60°C. Eight grams of the catalysts were then loaded into the reactor tube and sealed. The reactor was pressure tested for 24 hours in the pressure testing section of the experimental rig to check the ½" reactor joints. When successful it was placed in position inside the furnace of the rig and pressure tested for a further 12 hours to check the two connecting joints as well as the whole system. The trickle-bed reactor system was then ready for an experimental run.

3.3.2. Reaction procedure.

A typical reaction procedure is described here. The stored feedstock was transferred from a winchester bottle to the feed tank. A gas mask (type A/B B.S.) was worn during this transfer to avoid inhaling carbon disulphide vapour, which was extremely toxic. The

feed tank was then pressurised by 15 psi of nitrogen. A flow of 500 cm^3/min (STP) of hydrogen sulphide (10% vol. H_2S/H_2 mixture) at approximately 15 psi was established through the reactor. The reactor was allowed to reach the activation temperature (350°C) and was maintained in that condition for one and a half hours. After the catalyst was sulphided the valve situated after the feed tank was opened to allow the feed to reach the inlet section of the metering pump. The pump was then started with the desired setting to introduce feed into the reactor. When a steady flow was obtained the hydrogen sulphide flow was terminated and the pressure (hydrogen) of the reactor was gradually increased to its desired value (500 or 1000 psi) while maintaining a steady flow (480 cm^3/min STP). The temperature of the reactor was then gradually increased or decreased as the case was to its reaction condition value. A steady state was reached after approximately an hour. Samples were withdrawn every 30 minutes for analysis.

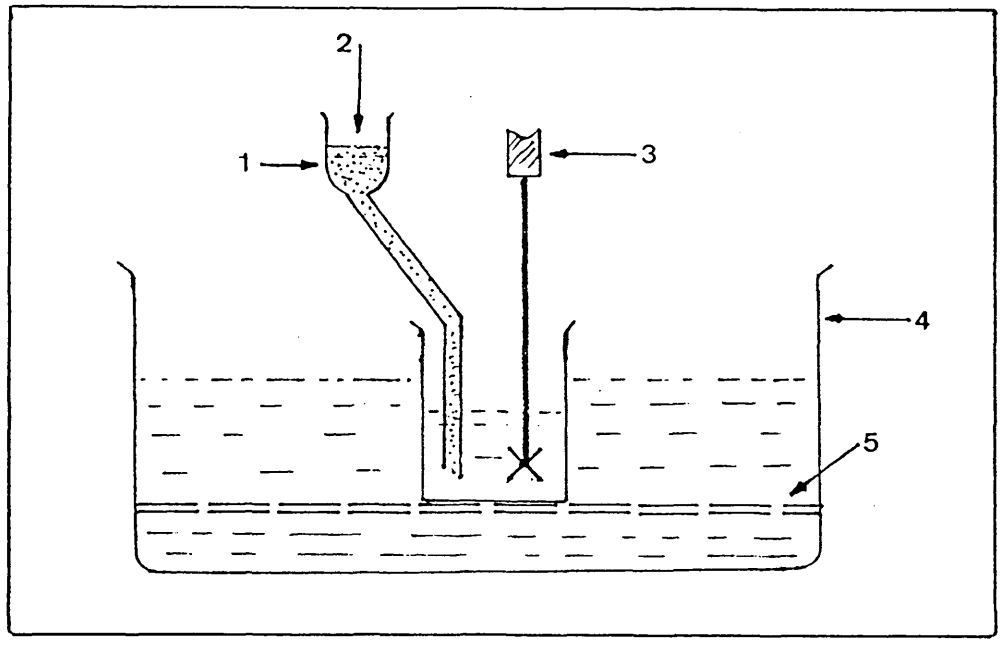
3.3.3. Preparation of unsupported catalyst and activity test.

As a preliminary study, unsupported catalysts of cobalt-molybdenum and nickel-molybdenum were prepared. In the current state of art there are essentially two

methods of preparation. One of them is the so called co-maceration method (CM) described by Hagenbach et al (1971) and the other known as homogeneous sulphide precipitation (HSP), a method which is described by Candia et al (1981) and named by them. The latter method was adopted for preparation of the unsupported catalysts in this present research and scanning electron microscopy analyses were carried out on these catalysts to determine the Co/Mo and Ni/Mo ratios. The activity tests were however carried out on unsupported cobalt-molybdenum catalyst prepared by both methods and these catalysts were supplied by Institut de Recherches sur la Catalyse, Villerbanne, France.

The preparation procedure for both catalysts are described below. The experimental set up shown in Figure 3.10 were used for both.

(i) Cobalt-molybdenum catalyst : A 100 cm^3 of salt solution comprising cobalt nitrate - $Co(NO_3)_2.6H_2O$ (0.09 moles) and ammonium molybdate-$(NH_4)_6Mo_7O_{24}.4H_2O$ (0.02 moles) were prepared in a conical flask. The cobalt nitrate salt dissolved almost instantaneously but the ammonium molybdate required vigorous stirring for approximately 20 mins., producing an overall red solution. This was then heated in a water bath to a



1. Funnel designed to introduce solution by sub-surface injection.
2. Salt solution.
3. Electrical stirrer.
4. Water-bath.
5. Steel plate.

Figure 3.10. Experimental set up for preparing unsupported catalyst.

temperature of 65°C. On contact, purplish/black precipitate appeared. The solution was then continuously stirred for a further three hours and hot-filtered by means of a Buchner-funnel. A black cake was obtained which was moist. This cake was introduced in a glass boat and dried inside a glass tube at 100°C with a flow of nitrogen (150 cm^3/min). The physical appearance of the catalyst which resembles charcoal was kept in a tightly sealed bottle.

(ii) Nickel-molybdenum catalyst : The preparation was similar to cobalt-molybdenum excepting that the preparation of the salt solution of nickel nitrate - $Ni(NO_3)_2.6H_2O$ and ammonium molybdate required an excess amount of distilled water (150 cm^3) and consequently the final drying time of the catalyst took longer.

The activity test in terms of hydrodesulphurisation (HDS) were carried out on two samples of cobalt-molybdenum catalysts prepared by both CM and HSP methods and having the same Co/Mo atomic ratio of 0.3. The reactions were carried out in the trickle-bed reactor system (procedure and set up described in former sections) at a temperature of 350°C and 375°C and a pressure (H_2) of 500 psi and 1000 psi. The unsupported catalyst (2g) were diluted with 6g. of 0.3 - 0.6mm

diameter γ-Al_2O_3. The HDS feed comprised of dibenzothiophene (DBT) dissolved in n-octane with n-decane as the internal standard. The catalysts were pre-sulphided prior to carrying out the HDS reaction. However, no in-situ sulphiding agent was used in the feed as product of DBT one of which is H_2S acted as such.

3.4. ANALYTICAL METHODS

3.4.1. Gas chromatography

In gas chromatography, the various compounds in a sample mixture are separated in the gas phase and their relative quantities measured. A basic arrangement for chromatographic analysis is shown in Figure 3.11. A carrier gas usually nitrogen, which does not ionise under flame conditions passes through a sample vaporiser in the

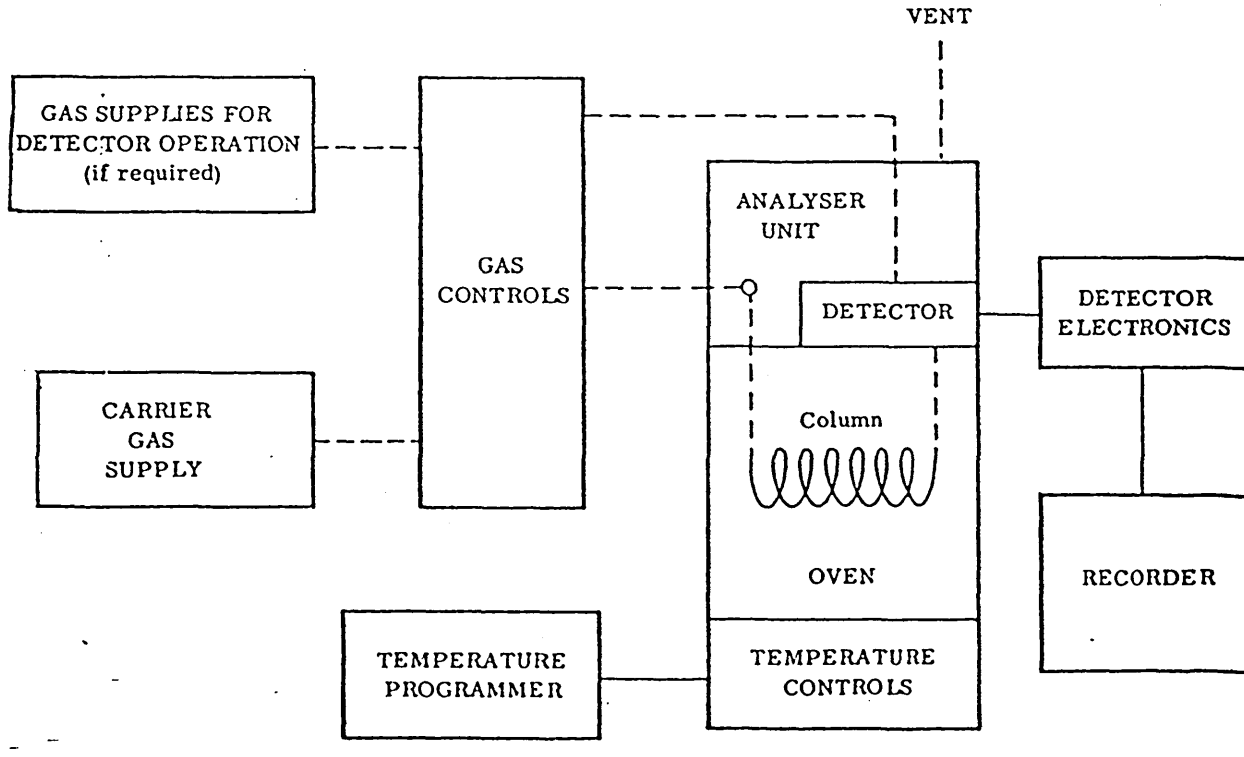


Figure 3.11

analyser section. A typical sample injection consists of 0.5 µl of liquid which is introduced by a hypodermic syringe into a heated block where it vaporises. The carrier gas then carries the sample through a chromatographic column, which is a tube containing relatively non-volatile materials that are capable of reversibly absorbing the sample. The absorption process results in individual compounds being retarded by different degrees depending upon the partition ratio between the stationary and the mobile phase. Therefore, different compounds arrive in sequence at the end of the column, where they pass through a detector. The detector gives an electrical signal to the changing composition of the gas passing through it. This signal is amplified by an electronic unit which converts it into a suitable form for operating a potentiometer recorder. The recorder draws a curve or chromatogram showing the changes in the composition of the gas passing through the detector as a function of time and thus quantifies the components of the sample. There was a choice between two detector systems, a hot-wire detector or a flame ionisation detector (FID) but the flame ionisation detector was the best choice in the present research because it was capable of detecting 10^{-10}g of sample and was the only detector used in this research.

Analysis of feed and product samples were carried out by using a Pye Unicam and/or a Perkin Elmer Sigma-2 gas chromatograph fitted with a FID detector. The sensitivity coefficient of feed and product samples were determined by using n-decane as an internal standard. Table 3.5 shows the retention times and sensitivity coefficients obtained for the main components of the feed and liquid products. Three separate injections were analysed for each sample and an average taken. No analyses of gaseous products were made. Composition data from gas chromatographic analyses are given in Appendix A for main reactions studied.

3.4.2. Elemental Analyses

Elemental analyses to determine carbon, hydrogen and nitrogen (C,H,N) were carried out on different samples of AKZO.153 catalyst obtained from the reactor at different time intervals throughout this present research to assess the level of coke and polymeric nitrogen compound deposition. The analyses were carried out on both the aged catalyst, used during the first part of this research and on the fresh batch employed during the later part. The results of elemental analyses are given in Appendix B.

TABLE 3.5.

Retention time and sensitivity coefficient of the reactant and product components.

Column used - OV 101 (10ft)

Programme - 75°C for 1 min
16°C/min increment
300°C final temperature.

Quantity of Sample - 0.5 µl

Component	Retention time/Min	Sensitivity Coefficient
n-propyl benzene	4.10	0.9259
n-butyl cyclohexane	5.20	0.9706
sec-butyl benzene	4.83	0.9270
n-butyl benzene	5.33	0.9340
tetralin	6.58	0.8642
trans-decalin	5.38	1.0780
cis-decalin	5.88	1.0780
++ n-decane	4.68	1.0000
toluene	1.90	0.8850
ethylbenzene	3.13	0.8642
iso-propyl benzene	3.70	0.8175
m-xylene	3.23	0.9235
o,m,p-xylene	3.13-3.30	0.9235
1,6-dimethyl napthalene	9.13	1.3235
napthalene	6.65	1.2520
quinoline	7.41	0.9625
1,2,3,4-tetrahydro quinoline	8.30	0.7432
o-propyl aniline	6.45	0.9950
benzene	1.20	0.8845
cyclohexane	1.28	0.8839
o-ethyl aniline	6.35	0.9919
dibenzofuran	9.80	1.2350
cyclohexylbenzene	8.40	1.0450
dicyclohexyl	8.40	1.0420
dibenzothiophene	11.90	1.0230
biphenyl	8.70	0.9980
n-octane	2.70	0.9820
1-methylnapthalene	9.05	1.1245
2-methylnapthalene	8.95	1.1260

Table 3.5 (contd)

Column used - Carbowax-400/porasil-F (10ft)

Programme - 140°C for 2 min
32°C/min increment
200°C final temperature

Quantity of sample - 0.5 µl

	Component	Retention time/min	Sensitivity coefficient
	dibenzothiophene	6.20	1.0450
	n-octane	0.80	0.9464
++	n-decane	1.35	1.0000
	biphenyl	3.75	1.0120
	cyclohexylbenzene	3.15	0.9820
	dicyclohexyl	2.75	0.9252

++ internal standard

Note: Sensitivity coefficient based on weights

The instrument used in this present research was CARLO-ERBA Mod.1102. This instrument was specifically designed for the determination of carbon, hydrogen, nitrogen and oxygen content in organic material. C,H,N determination was carried out on samples of materials by means of one analytical channel, while oxygen could be run on a different one (not used for this present work). The instrument was fully automatic except for sample weighing.

The catalyst sample whose percentage C,H,N composition was to be determined, was weighed into a tin container. The container was loaded into an automatic sampler which dropped into the oxidation tube where the catalyst was pyrolised in an oxygen-enriched atmosphere. The decomposed products were carried away by a constant stream of helium through part of the reactor filled with Cr_2O_3 and Co_3O_4 and converted to the desired state of oxidation (CO_2, H_2O and nitrogen oxide). This mixture then passed through a tube packed with reduced copper for reduction of nitrogen oxide to nitrogen, where the excess oxygen was also stopped. The nitrogen along with CO_2 and H_2O was carried to a chromatographic column where they

were separated. As each component emerged from the column it entered a thermal conductivity detector and finally a chromatogram was obtained. Blank analyses were carried out to detect any impurities in the gases or the containers. The C,H and N determination were carried out by comparing the sample peak values with peaks given by a standard.

3.4.3. Scanning electron microscopy

Scanning electron microscopy analyses were carried out on unsupported catalyst to confirm the pre-determined ratios of Ni/Mo and Co/Mo. Analysed results are given in Appendix C.

The different catalyst samples were mounted by compacting it inside the different holes of a previously drilled (3mm x 3mm) 1" aluminium block. This was useful in investigating different samples at the same time. The samples had to be carbon coated prior to the scanning. This was done in a Nanotech Carbon Coater, Model No.CC2 instrument and the procedures were as follows:

(1) The chamber of the carbon coater was vented by depressing the pump button until the vent light extinguished.

(2) The top of the chamber was removed and a piece of carbon fibre put in position.

(3) The 1" sample block was placed inside the chamber and the cover replaced. The pump button was depressed when a vacuum was created.

(4) When vacuum reached was 0.05 torr, the button was depressed again.

(5) The power knob was slowly turned clockwise until carbon fibre was glowing red. It was turned down for the vacuum to recover. The power knob was turned up again until the carbon fibre was glowing white (kept for 15 secs). This gave approximately 200Å of carbon coating on the sample.

(6) The sample block was then removed.

The carbon coated samples were then placed inside a JEOL JSM-35 CF scanning microscope. The microscope was fitted to a computer which logged and analysed the data. The visual display showed the X-ray signal. Photographs of surface could also have been taken but in this instance were not. The analysed results obtained were instantly printed out by a printer attached to the computer.

CHAPTER FOUR : PRELIMINARY EXPERIMENTS

4.1. INTRODUCTION

Preliminary experiments consisted of hydrogenation of pure tetralin, tetralin/quinoline and tetralin/dibenzofuran feed using an aged nickel-molybdenum (AKZO-153s) catalyst. The preliminary experiments served two purposes. Foremost it allowed further experiments for detailed study to be designed and secondly it was used to provide a comparison between an aged catalyst and a fresh one.

Tetralin was chosen as the main component in the model feedstock for studying hydrogenation because substituted napthalenes which are the major components present in mid-distillates are expensive chemicals and furthermore partially hydrogenated compounds of these are not easily available. Moreover, tetralin is the basic skeletal structure and a major reactive part of any partially hydrogenated substituted napthalenes produced as intermediates during mid-distillate hydrogenation. The hydrogenation of tetralin yields two major products which can be separated easily by gas chromatography. The simplicity of the reaction afforded hydrogenation study with other compounds present in the feed with little complication from the reaction network.

Quinoline and dibenzofuran were chosen as secondary

feed components as they are typical nitrogen and oxygen containing compounds present in mid-distillates. Moreover they could be separated from tetralin and its hydrogenated products as well as from their own products produced via hydrodenitrogenation and hydrodeoxygenation reactions respectively. The boiling point of these individual compounds also falls in the mid-distillate range (200-300°C). Thus the choice of compounds for preliminary experiments forms the basis of the model feeds in studying mid-distillate hydrogenation.

The maximum pressure that could be used to study the reactions in the present trickle-bed reactor was 1000 psi. Trial experiments were carried out at different pressures including one at 1000 psi. It was concluded that 500 psi was the minimum pressure that could be studied after considering the ideal product yield which gave reproducible results from quantitative chromatographic analysis. Also a minimum pressure of 500 psi would reflect conditions close to industrial processing of mid-distillates. Thus it was decided to study the reactions at 500 psi for preliminary experiments. Given the condition of pressure, a temperature of 303-304°C was chosen for the hydrogenation of tetralin when it was observed that temperatures exceeding that caused dehydrogenation reactions to take

place, yielding napthalene as the product. This would have complicated preliminary experimental results. Moreover, a balance had to be drawn as temperatures below 300°C yielded only traceable product of hydrodenitrogenation and hydrodeoxygenation. Therefore, when studying the model feeds, reproducibility of quantitative analysis would be poor. Other experimental conditions, that is, catalyst loading, particle size of catalyst, reactant feed rate and hydrogen flow rate were however dictated by the parameters that governed the ideal behaviour of the trickle-bed reactor used (Chapter Three).

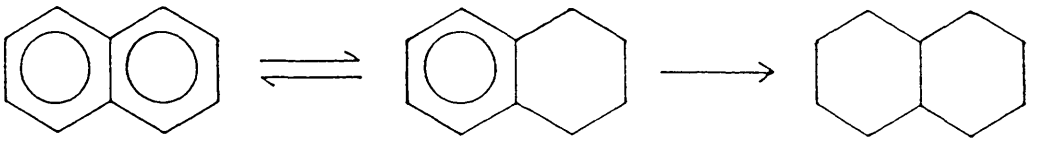
Carbondisulphide (CS_2) was added (0.1 mol %) to each feed to act as an in-situ sulphiding agent for the catalyst.

The experimental conditions were the same for each feed and were as follows:

Weight of catalyst	-	8g
Particle size of catalyst	-	0.3 to 0.6mm
Weight hour space velocity (WHSV)	-	1.94 - 4.24 g hr^{-1} g-cat^{-1}
Hydrogen pressure	-	500 psi
Hydrogen flow rate	-	480 cm^3/min (STP)
Temperature	-	303-304°C

4.2. PURE TETRALIN HYDROGENATION

In discussing the tetralin hydrogenation reaction it will be useful to represent the reaction network which are as follows:



napthalene tetralin trans/cis-decalin

The hydrogenation step of tetralin is essentially irreversible whereas the dehydrogenation step is not. The reaction conditions were such that the dehydrogenation step was avoided.

The kinetic model used for tetralin hydrogenation was based on a pseudo-first order reaction mechanism taking place with a plug flow pattern in a fixed bed reactor under steady state conditions,(Chapter 3, Sec. 3.2.1) which gives the following design equation

$$-\ln(1-x) = k\tau$$

where x is the fractional conversion of tetralin, k is the apparent rate constant and τ is the contact time, which is the reciprocal of WHSV (weight hour space velocity) defined as total liquid feed rate in g/h per g

weight of catalyst. A plot of $-\ell n(1-x)$ vs τ yields a straight line with a slope of k. Results for tetralin hydrogenation shown in Figure 4.1.

The pseudo-first order rate constant obtained was 0.5 hr^{-1} (Temp. 303°C, Press. 500 psi). A comparable value (0.08 hr^{-1}) by Patzer et al (1979) (study carried out in a trickle-bed reactor, Temp-316°C, Press-1000 psi, over ten different catalyst which do not include AKZO-153s) was obtained after adjustment by Sapre and Gates (1981). The difference in rate constant may be attributed to the different commercial catalyst used in the present research with that of Patzer and his co-workers. It appears that the catalyst used in this present research has better hydrogenating activity than those used by Patzer et al (1979). The value of the rate constant of tetralin hydrogenation as a general case has significance in that it is less than the rate constant of napthalene hydrogenation, 1.2 hr^{-1} (Patzer et al, 1979), obtained over the same ten different catalysts mentioned above. This is in agreement with the concept that napthalene is more reactive than tetralin because the π-complex of napthalene experiences greater resonance stabilisation than the benzene ring of tetralin.

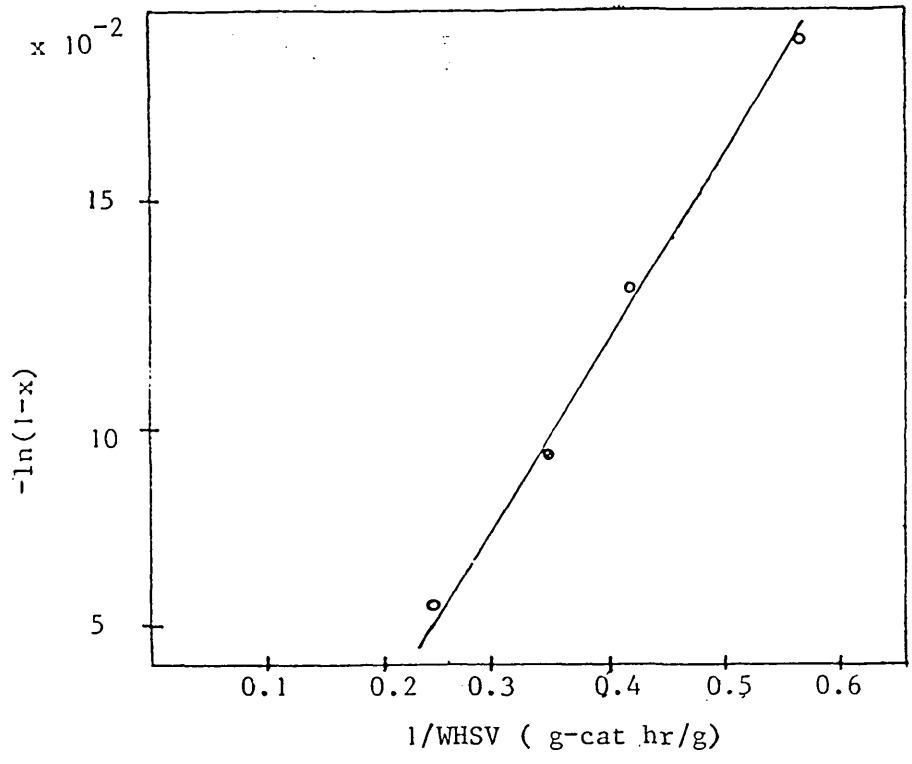


Figure 4.1. Pseudo-first order kinetics of tetralin hydrogenation.

Sapre and Gates (1981) worked with an autoclave where their catalyst and reaction conditions were different but their work is in broad agreement with the present findings that only decalins (trans and cis) were observed as the hydrogenated products and the isomer, trans-decalin was the major one (selectivity towards trans-decalin was 0.78). The selectivity was found to be 0.81 in the present work and was essentially independent of space velocity.

Dziewiecki (1979) and his co-workers studied the activity of nickel-molybdenum catalysts in tetralin and decalin dehydrogenation and have not presented any rate

constant for tetralin hydrogenation. However, their results have a bearing on this present work in that they assessed that dehydrogenation catalyst as being equally effective for hydrogenation of coal extract liquids, given the right conditions. Their work has also the significance of tetralin being a better H_2-donor in solvent extraction reaction (c.f. National Coal Board process Chapter 2, Sec. 1.3.3).

It may be noted in this present work that no catalytically cracked products were observed nor any product of thermal cracking. This is due to the fact that the working temperature was well below 400°C, when thermal cracking of tetralin becomes significant (Hooper et al.,1979).

4.3. TETRALIN/QUINOLINE HYDROGENATION

Table 4.1 and Figure 4.2 summarises the effect of quinoline concentration on tetralin hydrogenation. From the table and figure mentioned above it can be seen that quinoline concentration in the feed has affected the pseudo-first order rate constant of tetralin hydrogenation to the extent that it has reduced the rate by an average of seven times . It clearly shows the inhibiting effect of quinoline on hydrogenation activity.

Table 4.1. Apparent rate constants of tetralin hydrogenation

$k(hr^{-1})$ -	0.30	0.16	0.09	0.06
quinoline conc^{n} (wt%) -	0.20	0.50	0.78	1.44
Temperature(°C) -	304	304	303	304
Pressure(psi) -	500	500	500	500

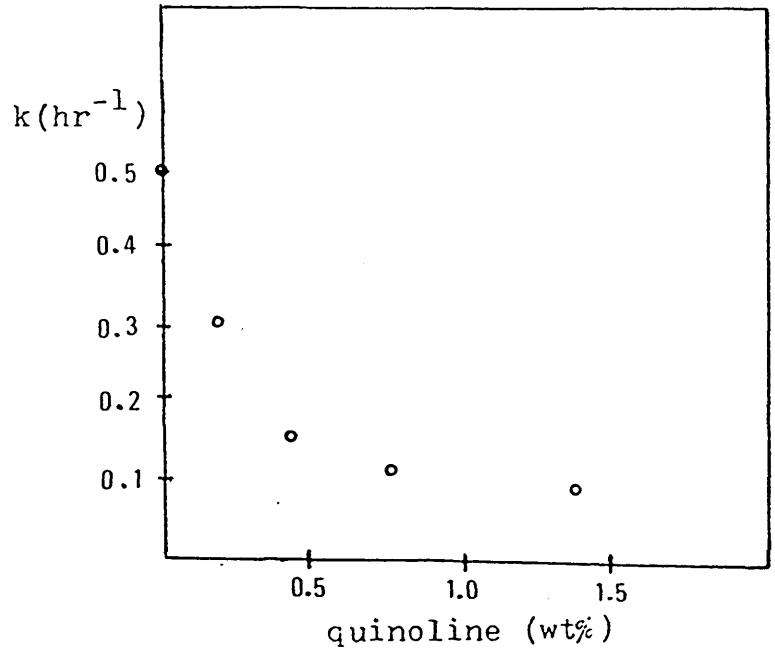


Figure 4.2. Effect of quinoline concentration on the pseudo-first order rate constant of tetralin hydrogenation

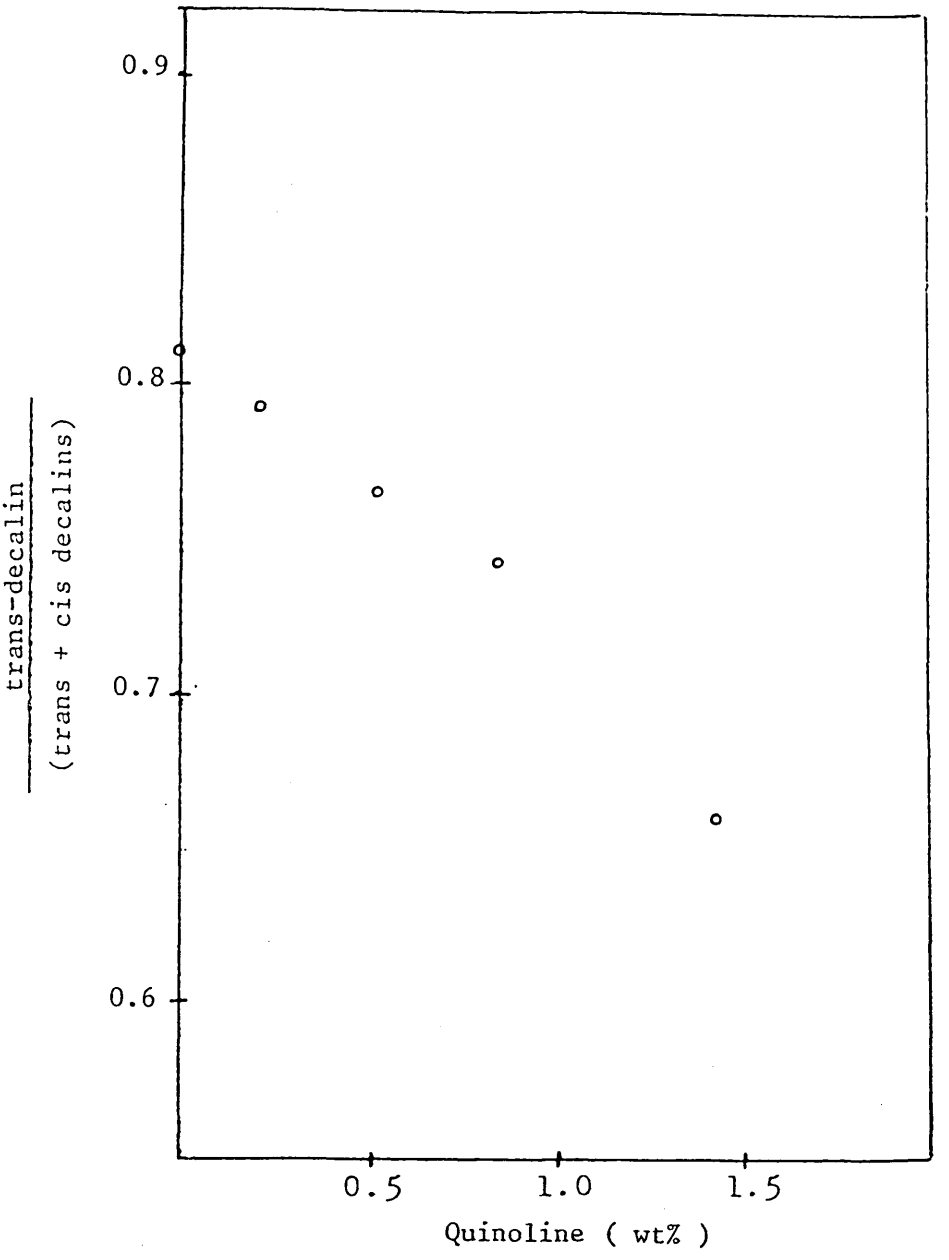
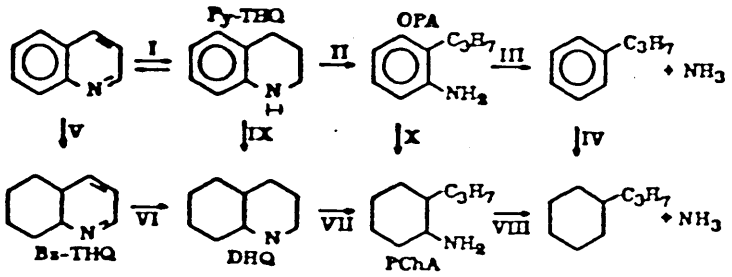


Figure 4.3. Influence of quinoline on the selectivity of trans/cis decalins

Another effect of quinoline on the tetralin reaction step is the decrease of selectivity (figure 4.3) towards trans-decalin with increasing quinoline concentration. This would be a convenient point to present the reaction network of quinoline HDN by previous workers (Satterfield et al., 1978):



It should be noted here that although several routes exist for quinoline HDN, it has been found in this present work that the route has been via 1,2,3,4-tetrahydroquinoline and the subsequent steps have been II and III (see quinoline network). Evidence of the other route has not been found. Only n-propylbenzene was obtained as the HDN product and no propyl cyclohexane was detected, which further confirmed the single route taken.

An attempt can now be made to rationalise the experimental results. The initial hydrogenated product (1,2,3,4-tetrahydroquinoline) of quinoline is a strongly

basic compound which may poison an acidic or an anionic vacant site by strong adsorption. This strong adsorption is responsible for the suppression of the rate constant of tetralin hydrogenation. The selectivity measurement indicates that quinoline or its intermediate products in some way affect the intermediate activated complex of tetralin hydrogenation or an isomerisation site of the catalyst. Preliminary experimental results on the effect of temperature on tetralin/quinoline reaction indicated that formation of napthalene proceeds at a temperature exceeding 310°C. This confirmed the reversibility of the napthalene to tetralin hydrogenation reaction. The reversible reaction may be assigned to two types of reaction: tetralin is undergoing dehydrogenation on an active site and/or acting as an H_2-donor (Dziewiecki et al.,1979) to an acceptor molecule (e.g. tetralin). However, with increasing temperature tetralin to decalin conversion also increases.

The effect of pressure has also been studied on the above reactions. Both hydrogenation and HDN were found to increase with increasing hydrogen pressure.

4.4. TETRALIN/DIBENZOFURAN HYDROGENATION

Table 4.2 and Figure 4.4 summarises the effect of dibenzofuran concentration on tetralin hydrogenation.

Table 4.2 Apparent rate constants of tetralin hydrogenation

$k(hr^{-1})$	-	0.5	0.5	0.46
dibenzofuran (wt%)	-	0.2	0.5	1.5
temperature (°C)	-	304	303	304
pressure (psi)	-	500	500	500

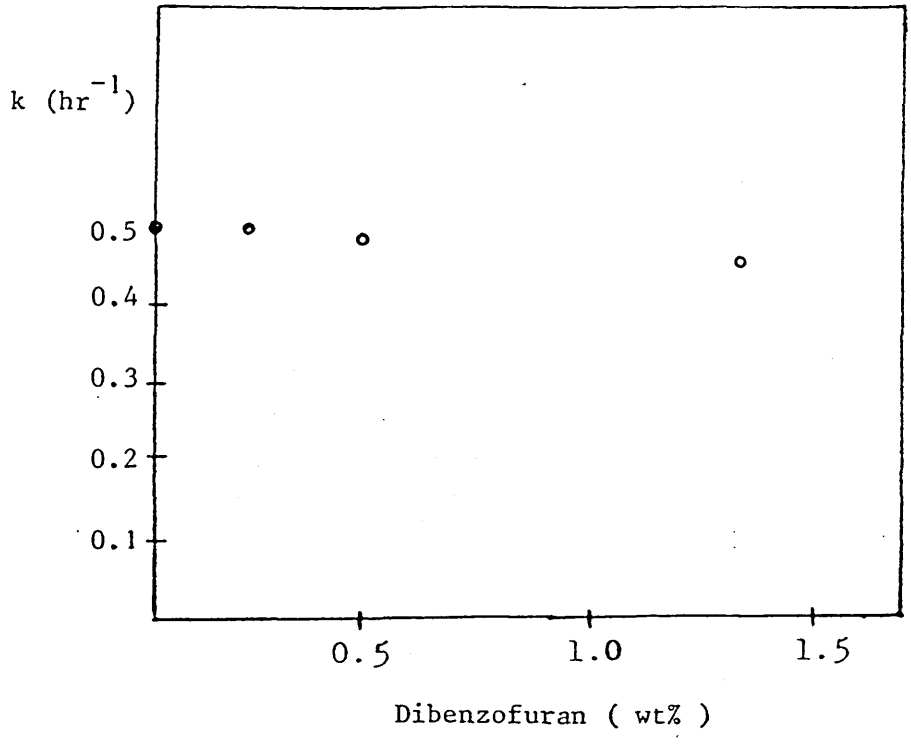
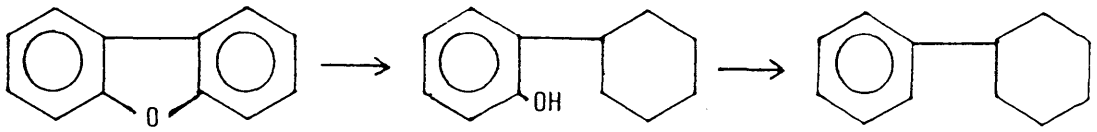


Figure 4.4 Effect of dibenzofuran on the pseudo-first order rate constant of tetralin hydrogenation

It is seen that dibenzofuran has very little effect on the hydrogenation of tetralin. The reaction network of dibenzofuran HDO has been illustrated in Chapter Two but is once again shown here for ease of discussion of experimental results:



$+ H_2O$

Only cyclohexylbenzene was observed as the product of dibenzofuran HDO. Water was however present as one of the products of HDO but was not detected as the detector system of the chromoatograph was a flame-ionisation one. The intermediate phenolic compound shown in the network was not observed and therefore either the initial ring saturation of dibenzofuran and subsequent C-O hydrogenolysis step takes place on the same site or the initial ring saturation is the slower step with C-O hydrogenolysis being rapid. The slight suppression of the rate constant of tetralin hydrogenation by dibenzofuran at a concentration of 1.5 wt% may be due to site blockage or the water acting as a weak base adsorbing on an anionic vacant site of the catalyst.

There was no effect on the selectivity of tetralin hydrogenation to decalins.

4.5. SUMMARY

Preliminary experiments have established conditions for further experiments. It has demonstrated near ideal behaviour of the trickle-bed reactor for the range of temperature, pressure and space velocities used.

Hydrogenation of tetralin, a partially hydrogenated aromatic compound, undergoes slow reaction compared to napthalene: Tetralin, $k=0.5\ hr^{-1}$ (present work), $k=0.08\ hr^{-1}$ (Patzer et al., 1979); Napthalene, $k=1.2\ hr^{-1}$ (Patzer et al., 1979).

There seems to be no apparent threshold for poisoning of tetralin hydrogenation by quinoline.

Selectivity measurements indicate isomerisation sites which are affected by quinoline poisoning.

Dibenzofuran at low concentrations i.e., 0.5 wt% and less, has no effect on the rate of tetralin hydrogenation. However at concentration of about 1.5 wt% it suppresses the rate slightly. Selectivity towards trans-decalin remained essentially constant.

It is likely that initial ring saturation of dibenzofuran and subsequent oxygen atom removal takes place at the same site or the initial ring saturation is a slower step with C-O hydrogenolysis being rapid.

The major product of HDO was cyclohexylbenzene and no deep hydrogenation was observed.

The preliminary results have, therefore, set the scene for more detailed investigation.

CHAPTER FIVE : HYDROGENATION OF PURE TETRALIN AND 1,6-DIMETHYLNAPTHALENE

5.1. INTRODUCTION

Following from the results of preliminary experiments, tetralin was the final choice of the hydrocarbon compound for the model feedstock of coal extract mid-distillate. Thus, further experimental programmes for this thesis were mainly concentrated on the reaction of tetralin. For comparison and better understanding of the behaviour of mid-distillate hydrogenation, a second hydrocarbon compound, namely, 1,6-dimethylnapthalene was also chosen for the model feedstock.

Hydrogenation of pure tetralin and 1,6-dimethylnapthalene feed were carried out by using a fresh charge of nickel-molybdenum catalyst (AKZO-153). This fresh charge was from a different batch than that used in the preliminary experiments. A set of reactions was carried out on both compounds to assess the effect of temperature and pressure. However, due to the high cost and later shortage due to the unavailability of 1,6-dimethylnapthalene, the reactions were carried out at 500 psi only as opposed to two pressures (500 and 1000 psi) used in the tetralin reaction. The range of temperatures used for each compound were the same which enabled direct comparison to be made in terms of their reactivity.

The experimental conditions with respect to catalyst loading, catalyst particle size, reactant feed rate and hydrogen flow rate were already established (Chapter Four). The condition of temperature and pressure were mainly ascertained from results of preliminary experiments. Four reaction temperatures in the range of 300-330°C were studied. They were suitable for both tetralin and 1,6-dimethylnapthalene hydrogenation that gave ideal product yield for quantitative analysis by gas chromatography. This temperature range was also ideally suited to study the model feedstock which included nitrogen and oxygen containing compounds. The temperature range included one of the reaction temperatures studied in the preliminary experiments which enabled comparison to be made between a fresh and an aged catalyst.

The reasons for choosing only two pressures (500 and 1000 psi) for studying the hydrogenation of the pure compounds were that it was adequate to establish the effect of pressure and to keep the number of experiments to a practical limit that could be carried out for this thesis.

Carbon disulphide (CS_2) was added (0.1 mol %) to each feed to act as an in-situ sulphiding agent for the catalyst.

The experimental conditions were the same for both feeds and are summarised below:

Weight of catalyst	- 8 g
Particle size of catalyst	- 0.3 to 0.6mm
Weight hour space velocity(WHSV)	- 1.75-4.09 g $hr^{-1}g\text{-}cat^{-1}$
Hydrogen pressure	- 500 and *1000 psi *(Tetralin only)
Hydrogen flowrate	- 490 cm^3/min (STP)
Reaction temperature	- 300 to 330°C

5.2. PURE TETRALIN HYDROGENATION

Catalytic hydrogenation of pure tetralin yielded two products, trans and cis decalins at 300°C and at a pressure of 500 psi. Napthalene appeared as a third product at temperatures exceeding 310°C and at a pressure of 500 psi. However, at 1000 psi and at all reaction temperatures (300 - 330°C) studied, trans and cis decalins were the only two products of the hydrogenation reaction. There was no evidence of deactivation of the catalyst over a period of approximately 150 hours when measurements were made.

Apparent rate constants for tetralin hydrogenation were obtained (data used from Appendix A, D.1. to D.8.) by assuming pseudo-first order reaction mechanism and were justified by the high correlation (0.98 to 0.99) of $-\ln(1-x)$ vs τ curves obtained for all tetralin reactions. The log plot of the Arrhenius equation, $k = Ae^{-E/RT}$, also gave high correlation curves. Figures 5.1 and 5.2 exemplify such correlations and are typical of plots that were drawn to calculate the rate constants and activation energies respectively.

Table 5.1 summarises the results of tetralin feed hydrogenation reactions;

Table 5.1. Apparent rate constant and activation energy of tetralin hydrogenation

Pressure (psi)	-	500	500	500	500	1000	1000	1000	1000
Temp (°C)	-	300	315	324	330	300	315	324	329
$k_{HG}(hr^{-1})$	-0.20	0.27	0.44	0.51	0.40	0.69	0.85	0.92	
$E_{app}(HG)$	-		93 ± 7 kJ mol^{-1}				84 ± 3 kJ mol^{-1}		

k_{HG} - pseudo-first order rate constant of tetralin to decalin hydrogenation.

$E_{ap}(HG)$ - Apparent activation energy of tetralin to decalin hydrogenation.

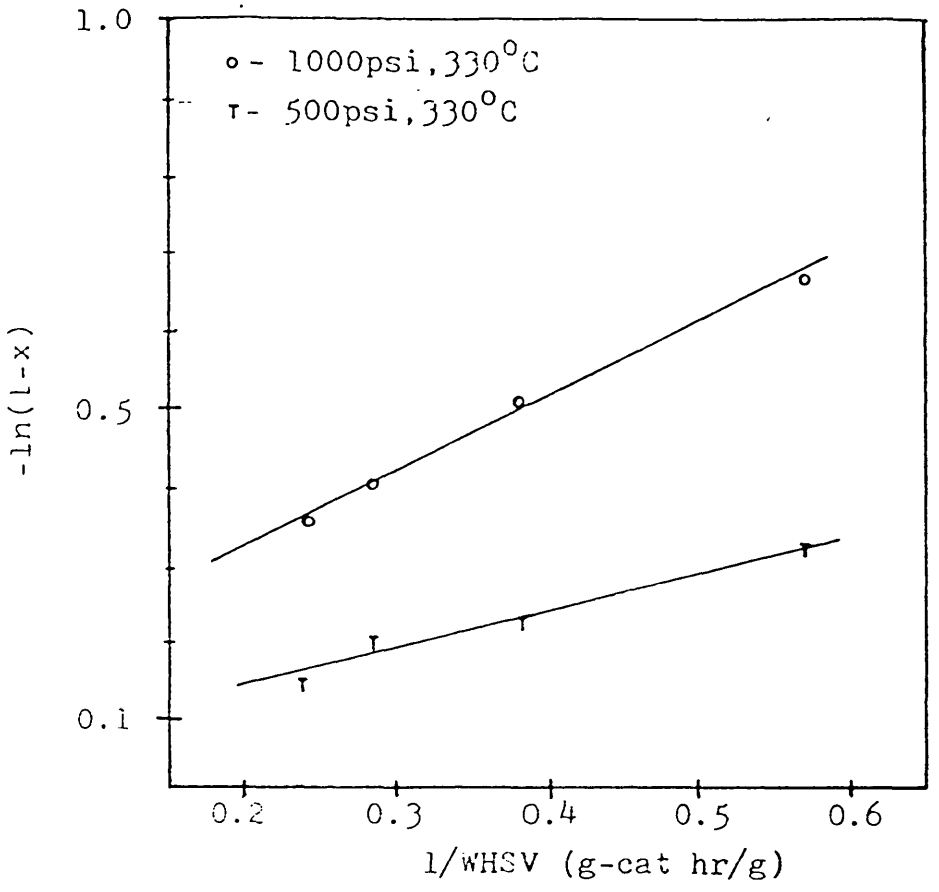


Figure 5.1. Pseudo-first order kinetics of tetralin hydrogenation

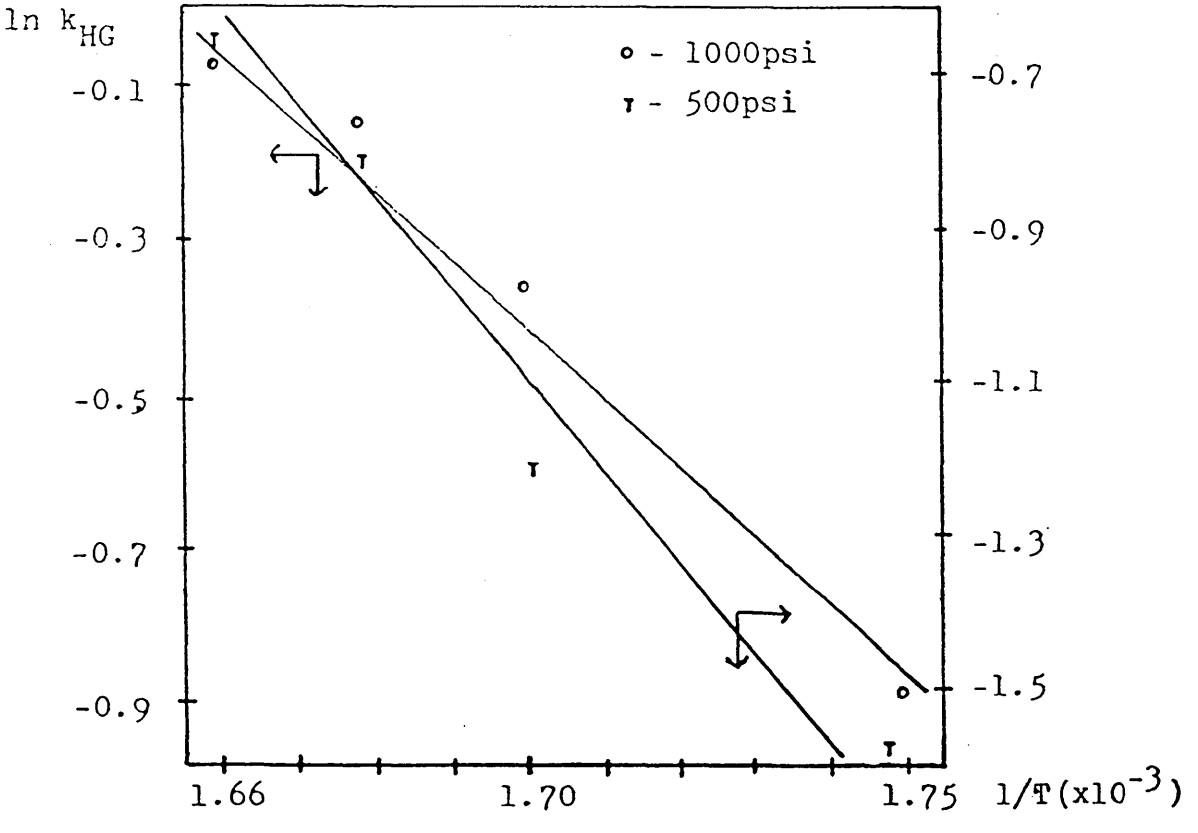


Figure 5.2. Arrhenius plot of the apparent rate constant of tetralin hydrogenation.

One of the rate constant values obtained here can be directly compared with work of Patzer et al (1979) as the experimental conditions with respect to temperature and pressure were very close. $k = 0.69\ hr^{-1}$ at T = 315°C, P = 1000 psi; $k = 0.08\ hr^{-1}$ at T = 316°C, P = 1000 psi (Patzer et al, 1979). It appears from the rate constant values that AKZO 153 has better hydrogenating activity than the commercial catalysts used by Patzer et al (1979). It is not unusual to find such differences as studies carried out by Chu et al (1982), found that the rate constant of napthalene hydrogenation over four different commercial catalysts varied between 0.5 to 4.5 hr^{-1} under the same experimental conditions.

It may be noted here that the hydrogenation rate constant (k) was 0.5 hr^{-1} at T = 300°C, P = 5000 psi on the aged nickel-molybdenum catalyst. Whereas, k was 0.2 hr^{-1} on the fresh nickel-molybdenum catalyst under the same experimental conditions. The difference in activity of the same commercial catalyst, where it appears that the aged catalyst is more active than the fresh one, is believed to be due to the different batches of catalyst used. In which case, investigation of the variability of the catalysts was beyond the scope of this

thesis. However, steady activity during hydrogenation reactions were observed for both the aged and the fresh catalyst. This demonstrates the robust nature found in many commercial sulphided nickel-molybdenum catalyst (Wiesser and Landa, 1973) used in petroleum refining. The results from the aged and fresh catalysts illustrate the difficulty when making direct comparison with other studies where different catalysts have been used. In any case the findings of the present research are in agreement with the concept that partially hydrogenated aromatics undergo slow reactions. $k = 0.20\ hr^{-1}$ at T = 300°C, P = 500 psi for tetralin (present work), whereas $k = 2.6\ hr^{-1}$ at T = 300°C, P = 500 psi for napthalene hydrogenation (Chu et al.,1982).

The selectivity towards trans-decalin was 0.83 (average value) as compared to the value of 0.78 obtained by Sapre and Gates (1981). The high selectivity towards the trans-isomer is as one would expect from a steric viewpoint. Trans-isomer is sterically more stable than the cis-isomer. Hydrogenation selectivity towards trans and cis decalins on both catalysts were similar (aged - 0.81 and fresh - 0.83).

Other features to note regarding tetralin hydrogenation were the appearance of napthalene at 315°C

(16 mol % in product, for τ = 0.57 hr) and that for a given contact time the ratio of napthalene to decalins increased with temperature. This can be rationalised from an equilibrium consideration. The equilibrium conversion of napthalene decreases from 100% at 300°C to 95% at 330°C (Wilson et al, 1958, Frye, 1962). Thereby, the tetralin dehydrogenation steps to napthalene are slightly favoured at higher temperatures. However, with increasing contact time (for a given temperature) the ratio of napthalene to decalins decreases. For the range of reaction temperature (300-330°C) used, the dehydrogenation step was favoured only at 500 psi, 330°C and short contact times but at 1000 psi hydrogenation dominated and napthalene was not detected. These results are in broad agreement with other findings (Sapre, 1980), where he studied bipheryl hydrogenation and found that at higher temperature dehydrogenation reactions became more important while at higher hydrogen pressures it was not. Therefore, Sapre's (1980) and present results suggest that the strategy of maximising high yields of hydrogenated products would be to work at low temperatures and high pressures.

It must be pointed out that it was difficult to qualify the process of tetralin dehydrogenation as being via normal catalytic mechanism or by tetralin acting as

an H_2-donor. The disadvantage of being unable to do so could largely be ignored as the hydrogenation step was considered to be more important to this thesis and was the focus of attention throughout the present research.

5.3. PURE 1,6-DIMETHYLNAPTHALENE HYDROGENATION

The reaction yielded quite a number of products. The two initial hydrogenated products (dimethyl tetralins) were identified but the dimethyldecalins although identified and obtained as separate peaks (some overlapping) could not be assigned to individual isomers as pure components were not available of such compounds. Hence, they were grouped together in the composition data. Only traces of a dealkylated product namely, 1-methylnapthalene were observed at higher temperatures.

The kinetic model used for 1,6-dimethylnapthalene hydrogenation was based on a pseudo-first order reaction mechanism taking place with a plug flow pattern in a fixed bed reactor under steady-state condition, which gives the following design equation (reversible reaction):

$$-\ell n(1 - \frac{x_i}{x_{eq}}) = k\tau$$

This design equation is similar to that in section 3.2.1 except that x_i is the observed fractional conversion of 1,6-dimethylnapthalene and x_{eq} is the

equilibrium conversion. However, the equilibrium conversion is approximately 100% at operating temperatures below 330°C, then the above equation is essentially the same as that in section 4.2.

Apparent rate constants for 1,6-dimethylnapthalene hydrogenation were obtained (data used from Appendix A, D.73 to D.76) by assuming pseudo-first order reaction mechanism. The model was a good fit and figures 5.3 and 5.4 illustrate the high correlation of $-\ell n(1-x)$ vs τ and the log plot of the Arrhenius equation respectively.

Table 5.2 summarises the results of pure 1,6-dimethylnapthalene feed hydrogenation reactions.

Table 5.2. Apparent rate constants and activation energy of 1,6-dimethylnapthalene hydrogenation.

Pressure (psi)	-	500	500	500	500
Temperature (°C)	-	300	315	325	330
k_{HG} (hr^{-1})	-	2.85	4.90	6.74	8.27
$E_{app(HG)}$	-		101 $\pm$2 kJ mol^{-1}		

k_{HG} - pseudo-first order rate constant of 1,6-dimethylnapthalene to hydronapthalene.

$E_{app(HG)}$ - apparent activation energy of 1,6-dimethylnapthalene to hydronapthalenes.

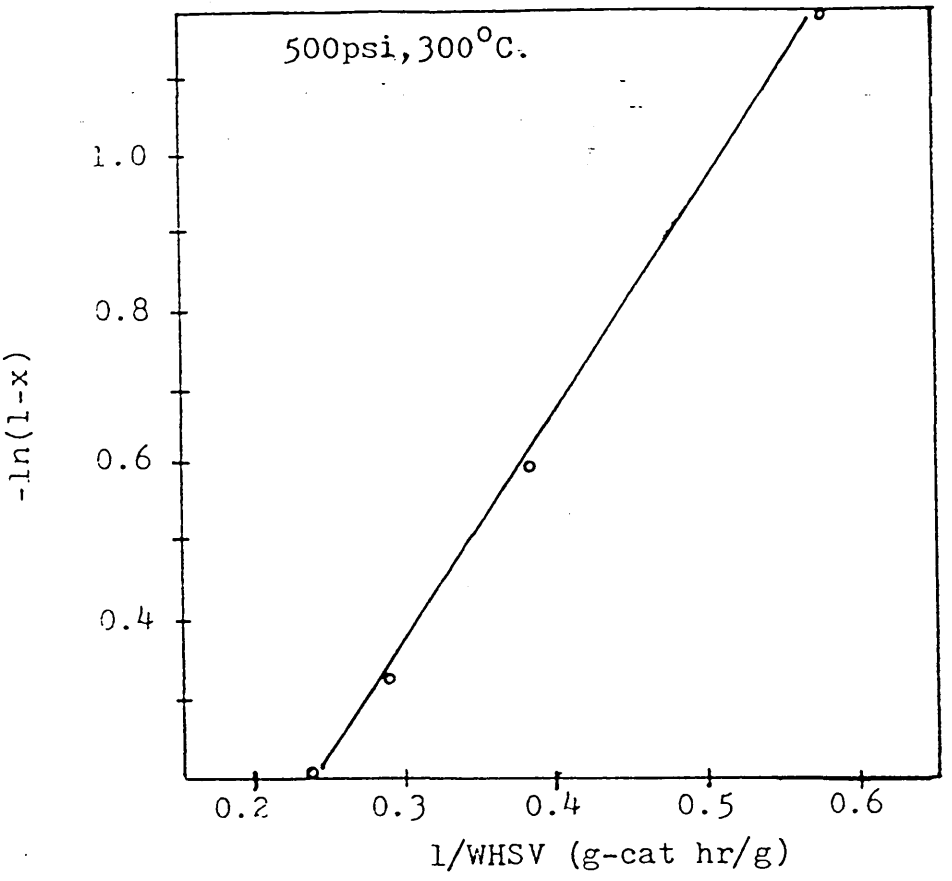


Figure 5.3. Pseudo-first order kinetics of 1,6-dimethylnapthalene hydrogenation

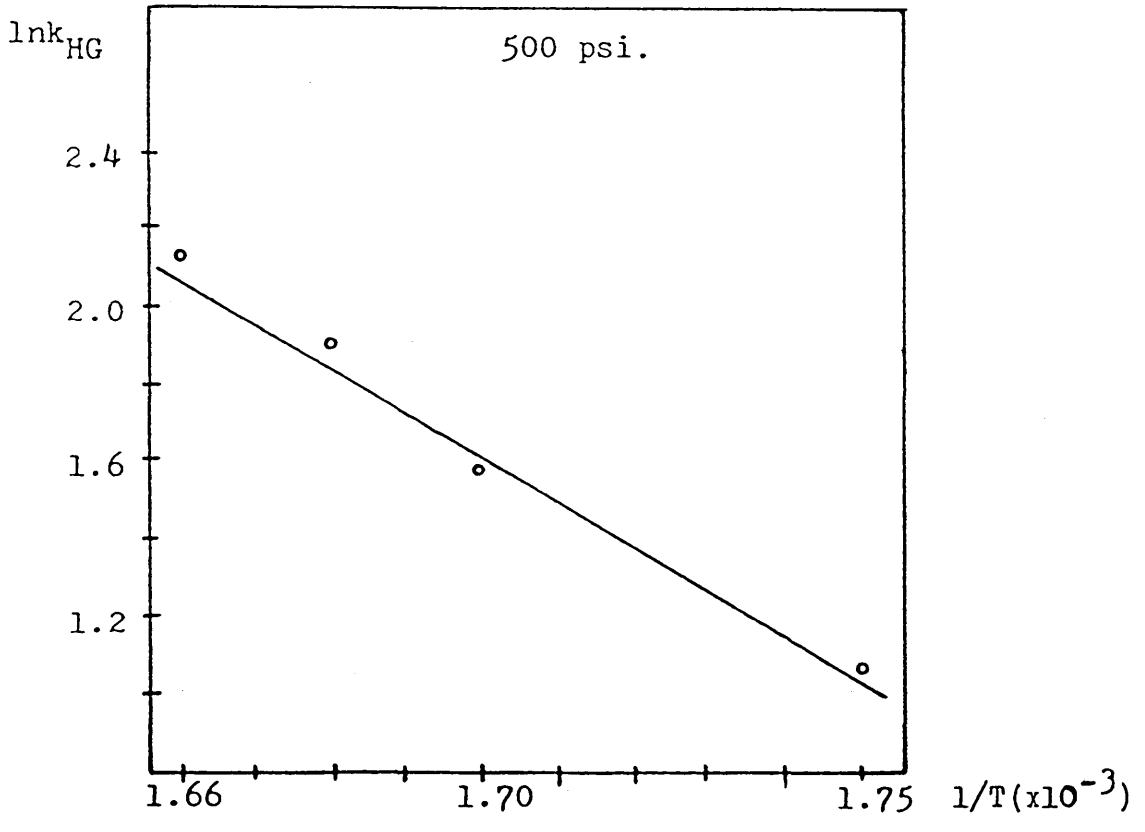
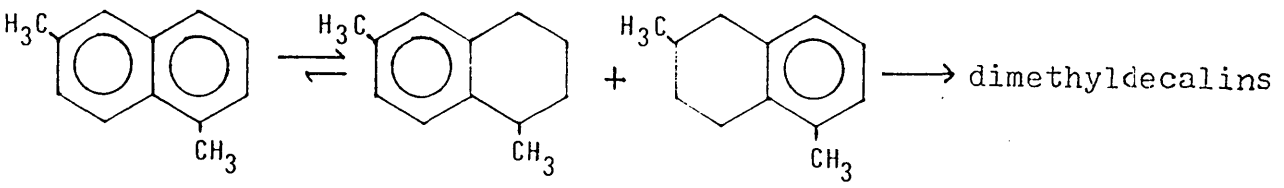


Figure 5.4. Arrhenius plot of the apparent rate constant of 1,6-dimethylnapthalene hydrogenation.

In discussing the reaction of 1,6-dimethylnapthalene it will be useful to illustrate the reaction network which are as follows:



There were some salient features which were observed from the product distribution. Firstly, the dealkylated product obtained was 1-methylnapthalene only, indicating that the meta position of napthalene ring are prone to dealkylation reaction under present experimental conditions. Dealkylation of substituted napthalenes are not unknown as was observed in hydrogenation of 1-methylnapthalene (Patzer et al, 1979). As a matter of interest, in the U.S.A., hydrodealkylation is used for the production of napthalene from petroleum derived methylnapthalenes, achieving a yield of around 99%. Both thermal and catalytic dealkylation are possible (Wiseman, 1972) but these reactions only become significant at high

pressures and temperatures exceeding 500°C. In the present case, the dealkylation could have been either via thermal or catalytic mechanism as there was no scope to identify the process. But one inference that could be drawn whichever the process, is that the meta position is more reactive from a steric viewpoint and hence 1-methylnapthalene was obtained as the dealkylated product

The hydrogenation of the napthalene ring preferentially takes place on the meta substituted (6-position in this case) ring (selectivity - 0.62). This can again be attributed to the steric effect but more importantly the methyl substituent at the meta position causes better resonance stabilisation of the activated π-complex of napthalene by positive (+I) inductive effect (ability to share σ-electrons). For steric hindrance the capability of the ortho methyl substituents (1-position in this case) inductive effect is reduced.

Product composition indicates that the hydrogenation of the partially hydrogenated aromatic intermediates (dimethyltetralins) were slow.

Literature values of rate constants of 1,6-dimethylnapthalene hydrogenation were unavailable so a direct comparison could not be made. However, some indication could be drawn from work carried out on

2,3-dimethylnapthalene (Rollman, 1977). Reaction of 2,3-dimethylnapthalene was shown to be 1.4 times faster than napthalene. Nevertheless, one important comparison that could be made was that 1,6-dimethylnapthalene reacts substantially faster than tetralin. In general, partially hydrogenated aromatics undergo slow hydrogenation reaction, e.g., reaction of 2-phenyl napthalene hydrogenates approximately 8 times faster than 2-phenyltetralin (Sapre and Gates, 1981)).

The apparent activation energy of 1,6-dimethylnapthalene hydrogenation on AKZO-153 was 101 kJ mol . Literature (Chu et al, 1982) value for comparison with respect to napthalene hydrogenation was between 109-130 kJ mol^{-1}, on five different catalysts.

5.4. SUMMARY

1,6-dimethylnapthalene reacts approximately 16 times faster than the partially hydrogenated aromatic, tetralin.

Alkyl substituted napthalenes are not prone to dealkylation reaction in temperature range studied.

Steric factor and position of methyl substituent of 1,6-dimethylnapthalene dictates selectivity of initial ring hydrogenation.

Reactivities of alkyl/aryl substituted napthalenes compared to napthalene are faster or slower depending on

whether steric or the π-complex stabilisation by the substituent is dominant or not. 2,3-dimethylnapthalene is 1.4 times faster than napthalene (Rollman, 1977), but 2-phenylnapthalene is approximately 1.3 times slower than napthalene (Sapre and Gates, 1981). Although phenyl group is a better electron donor than methyl group, the bulkiness of the former causes more steric hindrance.

The initial hydrogenated products of 1,6-dimethylnapthalene undergoes further slow reactions to dimethyl decalins.

Increasing the hydrogen pressure by two-fold increases the rate of tetralin hydrogenation by an average of 2.1 times, thus first order with respect to hydrogen.

CHAPTER SIX : HYDROGENATION OF TETRALIN/NITROGEN AND 1,6-DIMETHYLNAPTHALENE/NITROGEN COMPOUND MODEL FEEDSTOCKS

6.1. INTRODUCTION

Hydrogenation of six model feedstocks were carried out on the same charge of AKZO-153 catalyst used for the tetralin and 1,6-dimethylnapthalene studies. These feedstocks consisted of variation in quinoline concentration and the comparison of quinoline with two other nitrogen-containing compounds. Both pressure and temperature variations were included in these sets of experiments.

The standard experimental conditions for each feedstock were as follows:

Weight of catalyst	- 8 g
Particle size of catalyst	- 0.3 to 0.6mm
Weight hour space velocity(WHSV)	- 1.75 - 4.09 g hr^{-1} g-cat^{-1}
Hydrogen pressure	- 500 and *1000psi
Hydrogen flow rate	- 490 cm^3/min (STP)
Reaction temperature	- 300 - 330°C

*tetralin containing feed only.

6.2. TETRALIN/QUINOLINE HYDROGENATION

6.2.1. Quinoline Hydrodenitrogenation (HDN)

The major products of quinoline HDN were found to be 1,2,3,4-tetrahydroquinoline (THQ), o-propylaniline (OPA) and n-propylbenzene. Under some conditions small quantities of polymeric nitrogen compounds were also detected.

Hydrodenitrogenation (HDN) of quinoline is an irreversible reaction. If it is assumed that the heterocyclic molecule (in this case quinoline) and hydrogen adsorb on different catalytic sites and the rate-determining steps are the surface reactions between adsorbed quinoline molecules and adsorbed hydrogen the model of the rate of reaction can be expressed as a Langmuir-Hinshelwood type:

$$-r_i = \frac{k_i' K_i P_i}{(1 + \Sigma K_i P_i + \Sigma K_j P_j + \Sigma K_s P_s)} \cdot \frac{K_{H_2} P_{H_2}}{(1 + K_{H_2} P_{H_2})}$$

where, k_i' is the reaction rate constant, P_i is the partial pressure of the ith component in reactants, P_j is the partial pressure of the jth component in the products, P_s is the partial pressure of sth component in solvents and P_{H_2} is the partial pressure of hydrogen. K_i, K_j, K_s and K_{H_2} are adsorption constants. Here, concentration of quinoline and its products are low and there is a large excess of hydrogen and assuming that adsorptivity difference between reactants and products are

small, the denominator of the above Langmuir-Hinshelwood type equation could be considered as a constant value. Thus, the above equation can be rewritten for a pseudo-first order rate and expressed as:

$$-r_i = k_i P_i$$

Insertion of this rate expression into the mass balance of a fixed-bed reactor (in this case trickle-bed) and then integrating it gives the following design equation for a pseudo-first order reaction.

$$-\ln (1-x) = k\tau$$

This design equation is the same as that used for the kinetics of tetralin hydrogenation excepting that x here is the fractional conversion of quinoline to its denitrogenated products and k is the pseudo-first order rate constant for quinoline HDN. These pseudo-first order kinetics were also proposed by many other researchers (Houalla et al., 1980; Stern, 1979; Shih et al., 1977; Aboul-Gheit et al., 1973; Frye and Mosby, 1967).

Apparent rate constants of quinoline HDN were obtained from data in Appendix A, D.9 to D.32 by assuming a pseudo-first order reaction mechanism and were justified by

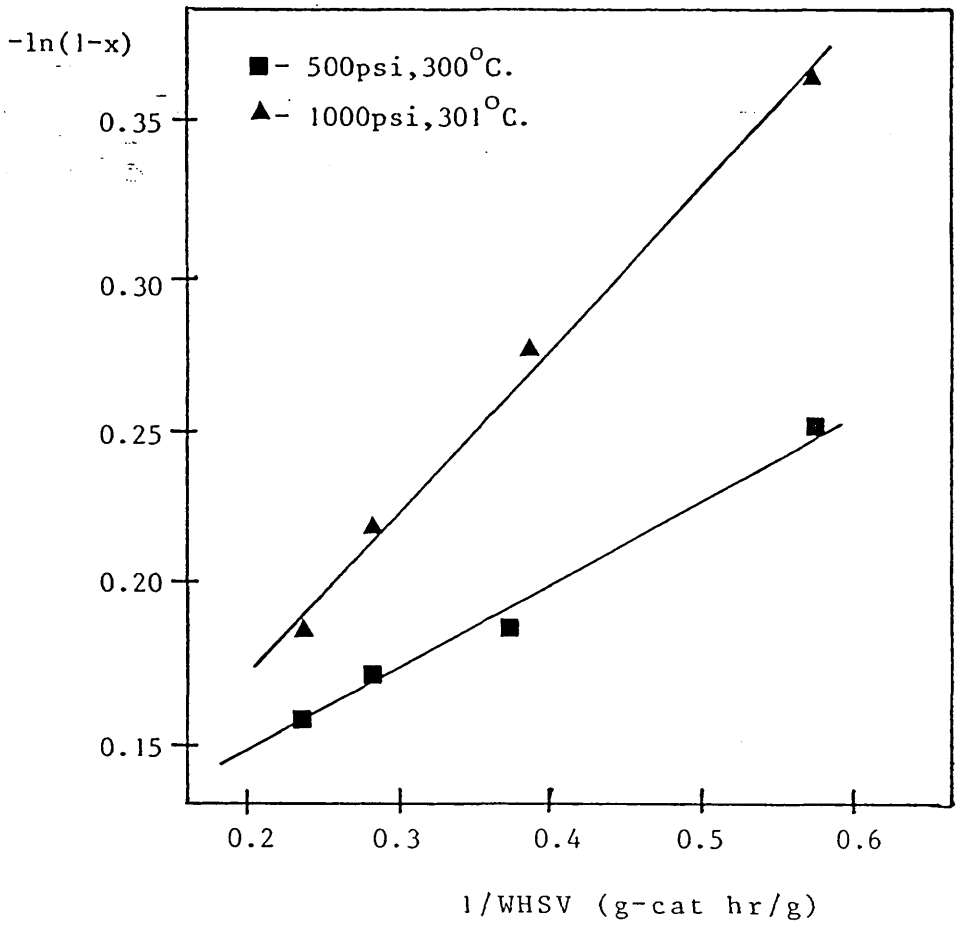


Figure 6.1. Pseudo-first order kinetics of quinoline HDN

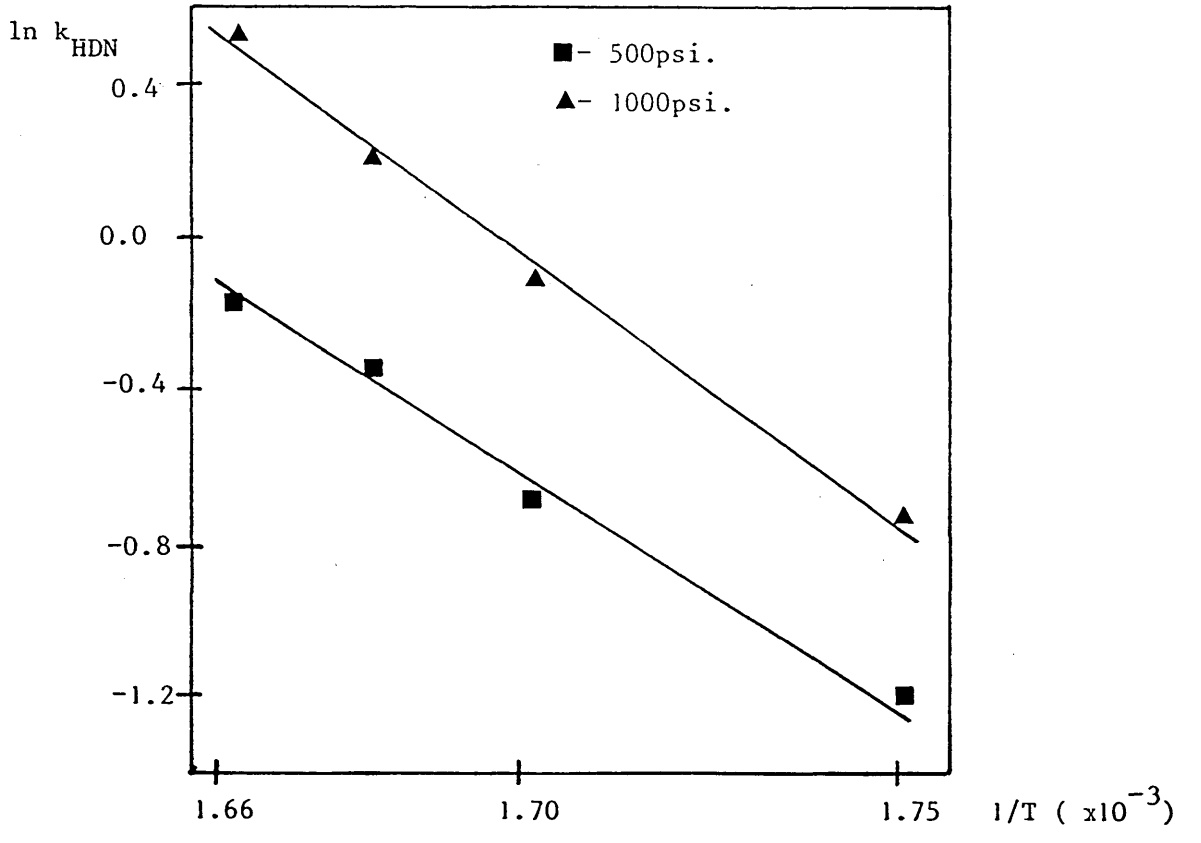


Figure 6.2. Arrhenius plot of the apparent rate constant of quinoline HDN

the high correlation of $-\ell n(1-x)$ vs τ plots (Figure 6.1). Similar plots were obtained for the extremes of quinoline concentrations studied.

Activation energy were determined by an Arrhenius plot, an example of which is given in Figure 6.2.

Table 6.1. illustrates the effect of temperature and pressure on HDN.

*Table 6.1.

1/WHSV(hr)	0.57	0.57	0.57	0.57	0.57	0.57	0.57	0.57
Temp.(°C)	300	315	325	330	301	315	324	330
Press.(psi)	500	500	500	500	1000	1000	1000	1000
% HDN	23.27	35.56	42.12	47.20	30.05	40.25	50.80	58.28

*Data from Appendix A, D.9. to D.16.

It can be seen that both an increase in temperature and pressure favours HDN. This is naturally reflected on the rate constant measurement of quinoline HDN which are summarised in Table 6.2.

Table 6.2. Apparent rate constant and activation energy of quinoline HDN.

Feedstock. No.1. Tetralin/Quinoline (0.21 wt %)/CS_2 (0.1 mol %)

Pressure (psi)	-	500	500	500	500	1000	1000	1000	1000
Temp. (°C)	-	300	315	325	330	301	315	324	330
$k_{HDN}(hr^{-1})$	-0.31	0.51	0.69	0.86	0.50	0.88	1.25	1.61
$E_{app(HDN)}$	-		95 $\pm$2 kJ mol^{-1}			108 $\pm$3 kJ mol^{-1}		

Table 6.2 (Cont)

Feedstock No.2. Tetralin/Quinoline (0.63 wt %)/CS_2 (0.1 mol %)								
Pressure (psi)	-	500	500	500	500	1000	1000	1000	1000
Temp. (°C)	-	300	315	324	331	301	317	324	330
$k_{HDN}(hr^{-1})$		-0.31	0.51	0.69	0.86	0.50	0.88	1.25	1.61
$E_{app(HDN)}$	-	95 ±2 kJ mol^{-1}				108 ±3 kJ mol^{-1}			
Feedstock No.3. Tetralin/Quinoline (1.34 wt %)/CS_2 (0.1 mol %)								
Pressure (psi)	-	500	500	500	500	1000	1000	1000	1000
Temp(°C)	-	300	320	325	330	300	320	324	331
$k_{HDN}hr^{-1})$		-0.31	0.59	0.69	0.86	0.50	0.88	1.25	1.61
$E_{app}(HDN)$	-	95 ±2 kJ mol^{-1}				108 ±3 kJ mol^{-1}			

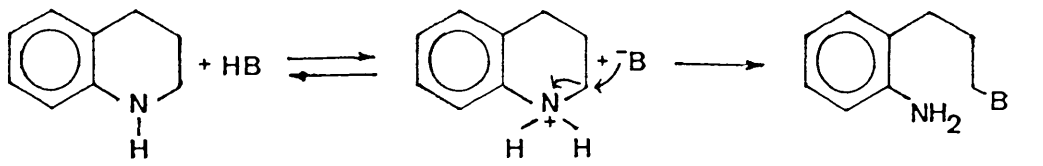
From Table 6.2. it can be seen that k_{HDN} increases with both temperature and pressure. The k_{HDN} values were not affected by quinoline concentration (0.21 to 1.34 wt%) indicating that within this range, quinoline was not self-inhibiting towards HDN. Therefore, the assumptions made on the Langmuir-Hinshelwood model still holds.

At this juncture it will be useful to discuss the findings from the experimental data of quinoline HDN before looking into the effect of quinoline towards tetralin

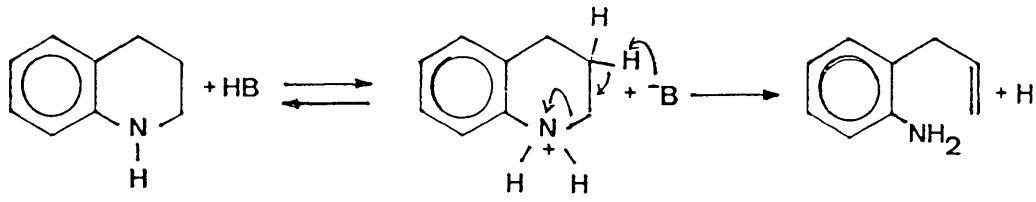
hydrogenation. The quinoline HDN network has already been illustrated (Chapter Four) and in these experiments the route of HDN has been found to be the same as found in the preliminary experiments.

In the HDN of quinoline the initial hydrogenation step reaches rapid equilibrium but favouring 1,2,3,4-tetrahydroquinoline (THQ). With increasing contact time the conversion of quinoline slightly increases towards THQ as equilibrium is reached. However, with increasing reaction temperature equilibrium favours quinoline and between 300°C to 330°C the quinoline conversion decreases from 88% to 84% (contact time - 0.24 hr). This is consistent with earlier findings (Shih et al., 1977; Satterfield et al., 1978). At increasing hydrogen pressure from 500 psi to 1000 psi the quinoline conversion to THQ was unaffected. Thus, the extent of hydrogenation of the quinoline ring is a function of catalyst activity.

The next step of quinoline HDN is the C-N hydrogenolysis step of THQ to o-propylaniline (OPA). This is favoured with increasing temperature. The final step is another C-N hydrogenolysis step of OPA to n-propylbenzene, but here the nitrogen is completely removed as ammonia. This step is favoured at both high temperature and pressure. This would be a convenient point to illustrate C-N hydrogenolysis mechanism.



(a)



(b)

C-N hydrogenolysis of THQ can occur via (a) displacement or (b) elimination reaction (Nelson et al., 1979). Both of these reactions are catalysed by base. The base required can be supplied by a surface oxide or H_2S dissociation reaction. Similarly, OPA undergoes C-N hydrogenolysis.

The activation energy of HDN of quinoline developed at both pressures are different (95 kJ mol^{-1} at 500 psi and 108 kJ mol^{-1} at 1000 psi) can be explained in terms of the hydrogen functionality which has not been considered in the analysis and the fraction of sites occupied by hydrogen will depend more or less on both pressure and

temperature. It is also evident from rate constant measurement that rate of HDN is faster than rate of tetralin hydrogenation.

Lastly, an important feature that was observed in quinoline HDN was the appearance of polymeric N-compounds which cause severe blockage of reactor at long operating times and are thought to be precursor to coke formation. The production of this polymeric compound increases with increasing quinoline concentration. However, at high temperature and pressure, formation of this compound was inhibited. Also at slow feed rate (high contact time) such reaction was increased. At this stage it is difficult to ascertain whether quinoline or one of its intermediate products were responsible for this polymeric compound. Therefore, subsequent experiments involving THQ and OPA resolved these uncertainties and a plausible mechanism by which such polymeric compounds may form is discussed in a later section (6.3.1.).

6.2.2. Influence of quinoline on tetralin hydrogenation

Kinetics of tetralin hydrogenation were dealt with in earlier chapters (Chapters Four and Five). Apparent rate constants of tetralin hydrogenation were obtained from reaction data of Feedstock No. 1 to 3 (Appendix A, D.9. to D.32) by assuming pseudo-first order reaction kinetics. As in previous cases this was justified by the high correlation

of the $-\ell n(1-x)$ vs τ plots and was true for all feedstock reactions with varying quinoline concentrations. Table 6.3 summarises the results of rate constants and activation energy measurements of tetralin hydrogenation under the influence of varying concentrations of quinoline.

Table 6.3 Apparent rate constant and activation energy of tetralin hydrogenation.

Feedstock No.1: Tetralin/Quinoline (0.21 wt %)/CS_2 (0.1 mol %)								
Pressure (psi)	-	500	500	500	500	1000	1000	1000	1000
Temp. (°C)	-	300	315	325	330	301	315	324	330
k_{H_G} (hr^{-1})	-0.12	0.20	0.29	0.32	0.16	0.30	0.46	0.51
$E_{app}(H_G)$	-	96 ±4 kJ mol^{-1}				117 ±5 kJ mol^{-1}		
Feedstock No.2. Tetralin/Quinoline (0.63 wt %)/CS_2 (0.1 mol %)								
Pressure (psi)	-	500	500	500	500	1000	1000	1000	1000
Temp. (°C)	-	300	315	324	331	301	317	324	330
k_{H_G} (hr^{-1})	-0.09	0.19	0.23	0.30	0.14	0.26	0.41	0.47
$E_{app}(H_G)$	-	110 ±3 kJ mol^{-1}				124 ±6 kJ mol^{-1}		
Feedstock No.3. Tetralin/Quinoline (1.34 wt %)/CS_2 (0.1 mol %)								
Pressure (psi)	-	500	500	500	500	1000	1000	1000	1000
Temp(°C)	-	300	320	325	330	300	320	324	331
k_{H_G} (hr^{-1})	-0.07	0.16	0.19	0.28	0.09	0.21	0.31	0.35
$E_{app}(H_G)$	-	126 ±4 kJ mol^{-1}				131 ±7 kJ mol^{-1}		

At this point a graphical representation would be useful to portray the effect of quinoline concentration on tetralin hydrogenation under various experimental conditions (temperature and pressure). Figures 6.3., 6.4. and 6.5 give such a portrayal.

Firstly, from Figures 6.3. and 6.4. it can be seen that increasing quinoline concentration reduces the rate of tetralin hydrogenation and that at low quinoline concentrations a large reduction is observed. Subsequent increases in quinoline concentration do not appear to have that great an effect. This trend was also observed in the preliminary experiments on aged catalysts. Figure 6.5. shows that for both operating pressures (500 and 1000 psi), the apparent activation energy increases with quinoline concentration signifying that in some way poisoning by quinoline has changed the intrinsic activity of the catalyst. For the time being if these figures are left aside,and Table 6.3. and some salient features of experimental data from Appendix A are considered, the effect of poisoning can be looked at from different aspects.

From Table 6.3. it can be seen that the effect of hydrogen pressure on the enhancement of tetralin hydrogenation rate has been reduced when compared with pure tetralin hydrogenation (Chapter Five, Table 5.1.)

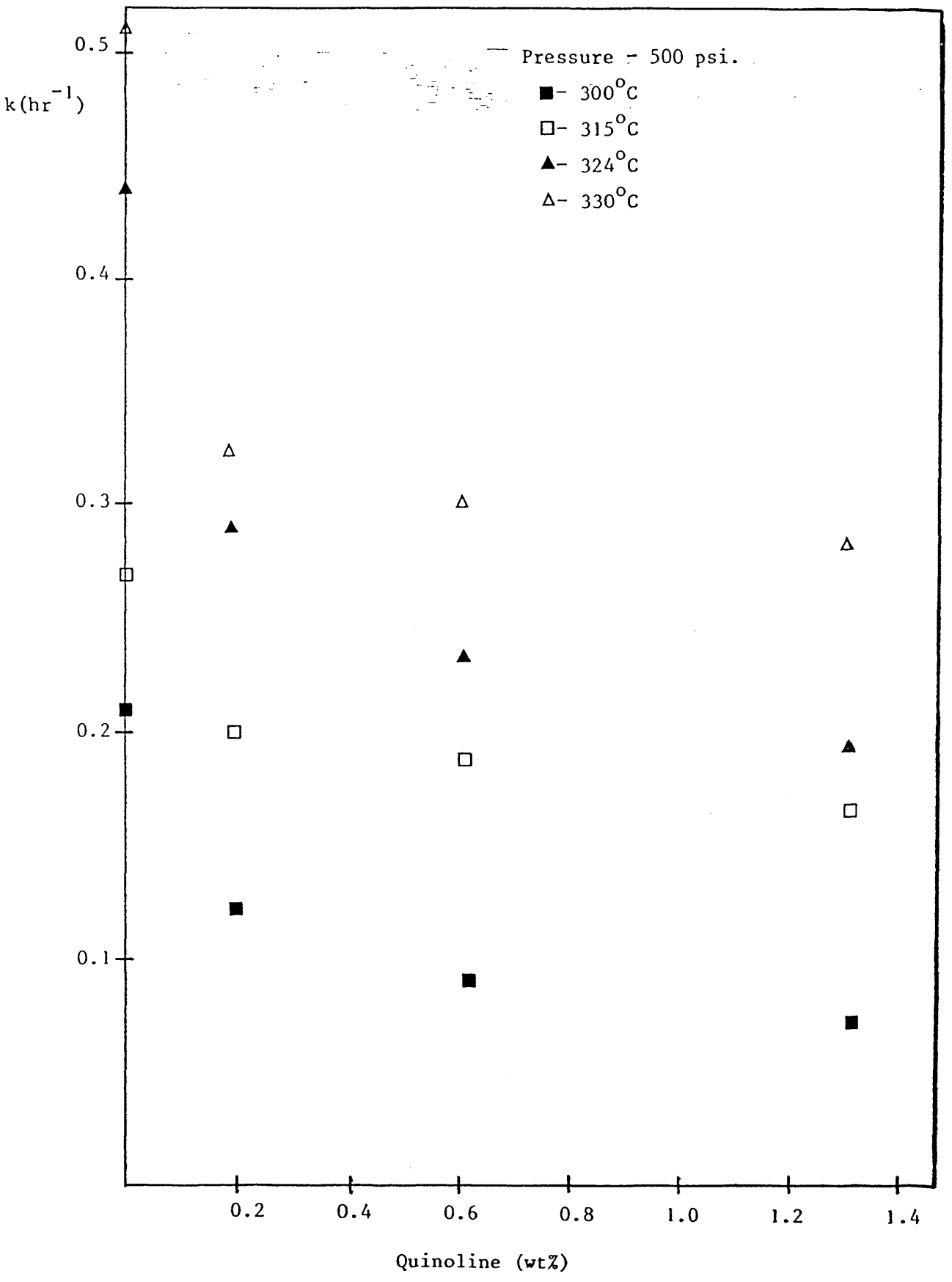


Figure 6.3. Effect of quinoline concentration on apparent rate constant of tetralin hydrogenation

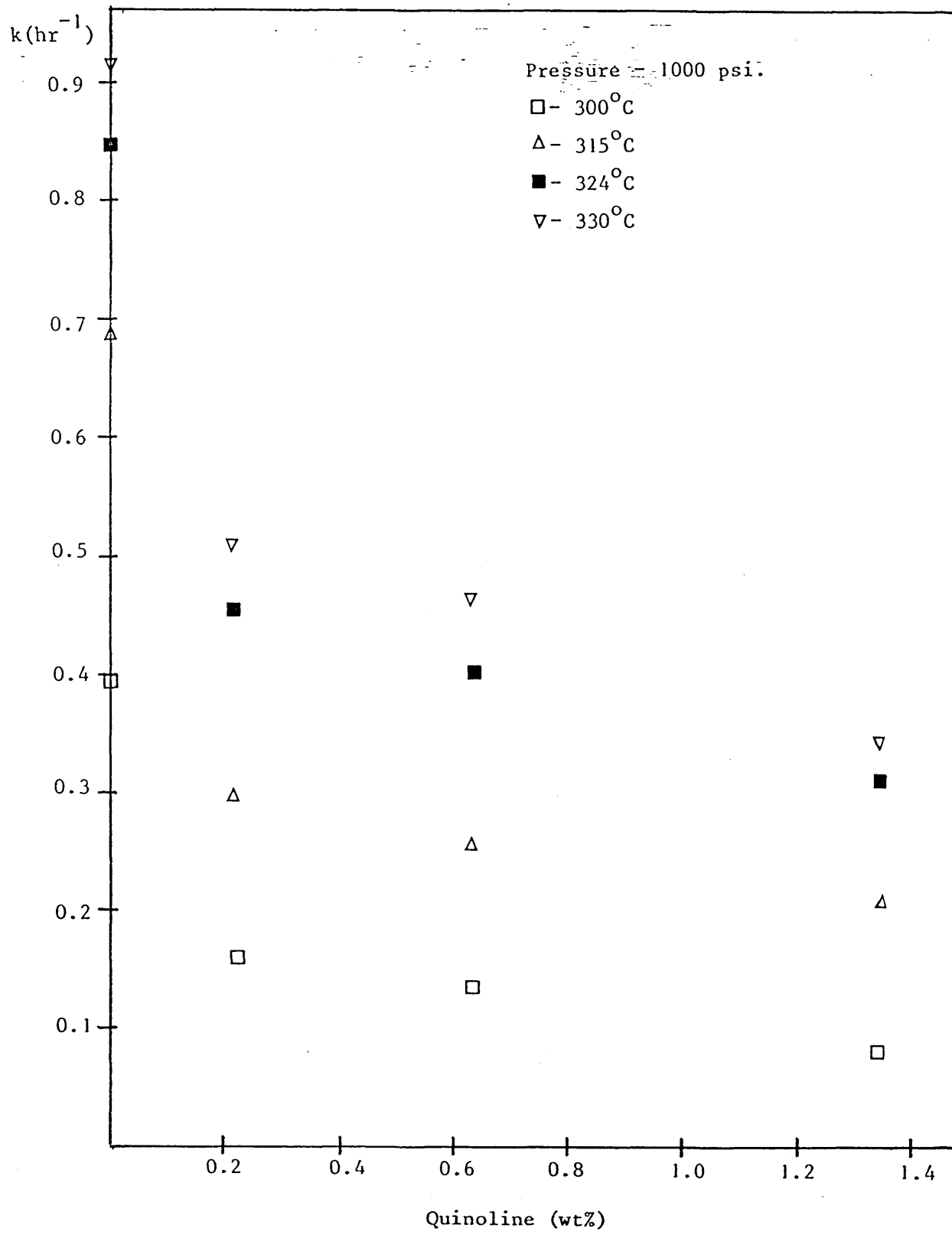


Figure 6.4. Effect of quinoline concentration on apparent rate constant of tetralin hydrogenation

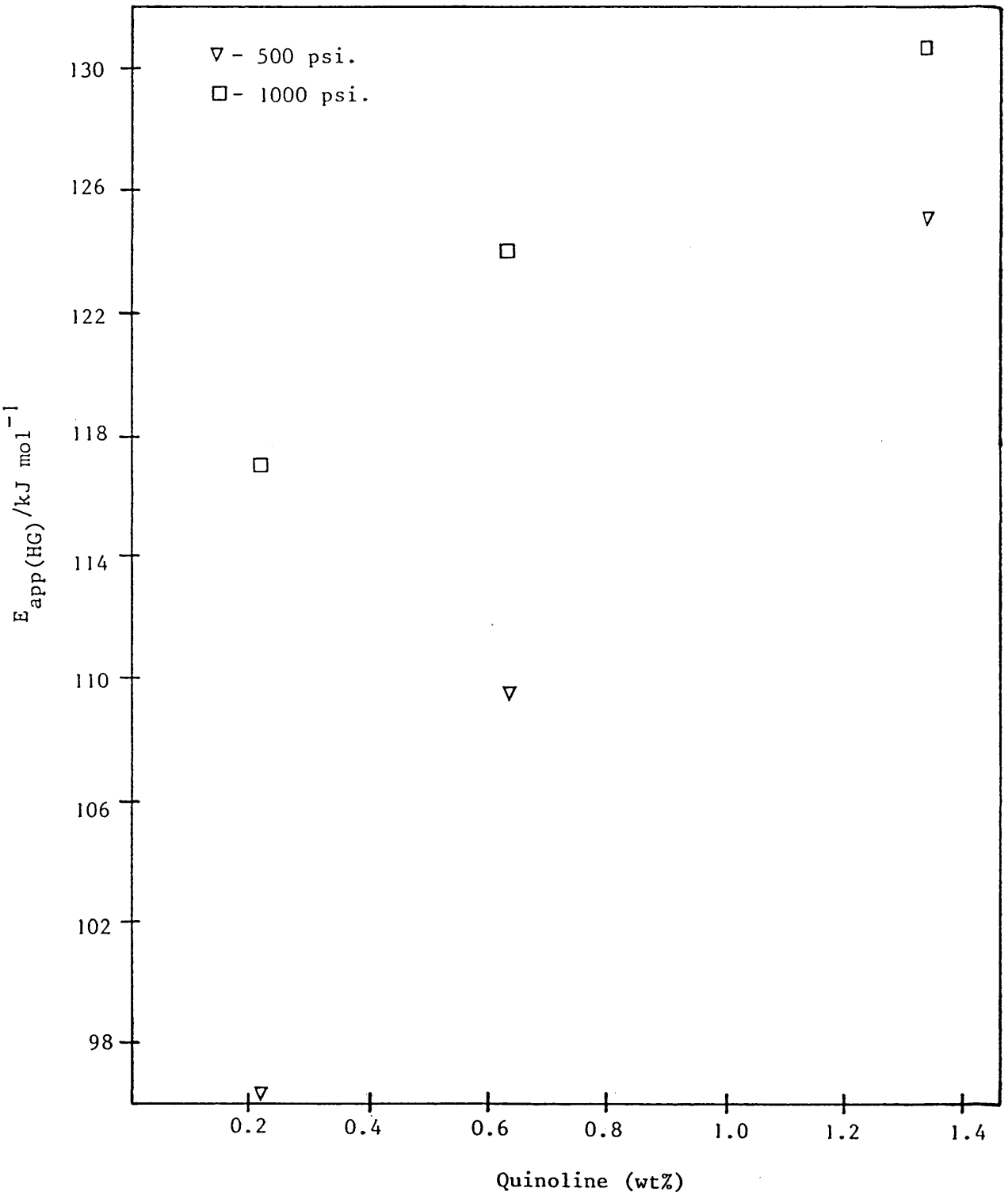


Figure 6.5. Effect of quinoline concentration on apparent activation energy of tetralin hydrogenation

For example, at 300°C, k_{HG} increased by 2 times for pure tetralin hydrogenation indicating that the reaction is first order in hydrogen whereas k_{HG} increased by 1.3 times for tetralin feed containing 0.21 wt% quinoline. If quinoline or THQ are considered to adsorb on a catalyst site, the structures of the molecules are such that they may block adjacent sites completely or partially. These adjacent sites could well be the sites where hydrogen adsorbs and thus reducing its effectiveness even at higher pressure.

The initial drop in rate of tetralin hydrogenation by low concentration of quinoline may be explained in terms of highly active hydrogenation sites. If these highly active sites were small in number and these were to be poisoned first then the reduction in the hydrogenation rate will be severe.

Other observations from experimental data were that selectivity towards trans-decalin was reduced (0.83 to 0.72) by increasing quinoline concentration which has also been found in earlier work (Chapter Four). Quinoline poisoning reduced the hydrogenation activity more than the dehydrogenation activity of the catalyst. For example, at 315°C, selectivity towards dehydrogenation is 0.16 for

pure tetralin feed compared to 0.30 for tetralin/quinoline (0.63 wt%) feed). This could be due to the presence of sites for dehydrogenation reaction or donor-solvent type interactions.

6.2.3. Curve fitting of tetralin hydrogenation under the influence of quinoline poisoning

This would be a convenient point to reconsider the results given in Table 6.3. and give it a further quantitative treatment to ascertain any relation between quinoline concentration, hydrogenation rate constant and activation energy.

A visual observation on the rate constant vs. quinoline wt% graphs (Figures 6.3. and 6.4.)suggests that an exponential decay relationship may exist. To test this, the k_{HG} vs. Q wt% graphs were fitted with the following equation:

$$k = ae^{-bQ}$$

The fitted equations thus obtained are tabulated in Table 6.4.

Table 6.4. Fitted equation of tetralin hydrogenation rate constant versus quinoline concentration.

Fitted equation : $k = ae^{-bQ}$

Press.(psi)	500				1000			
Temp(°C)	300	315	324	330	300	315	324	330
a	0.16	0.24	0.37	0.41	0.28	0.48	0.66	0.73
b	0.70	0.33	0.56	0.35	0.92	0.71	0.63	0.60
Correlation	0.92	0.89	0.91	0.76	0.87	0.81	0.87	0.87

It can be seen that the correlation of such fittings are poor as expected. This is due to the fact that k does not reach a zero value at very high concentration of quinoline. Therefore, the equation was modified to the following.

$$k = ae^{-bQ} + c$$

c is a constant; value of which was inserted arbitrarily until a best correlated-fit curve was obtained. The final fitted equations eventually obtained are given Table 6.5.

Table 6.5. Fitted equation of tetralin hydrogenation rate constant versus quinoline concentration.

Fitted equation : $k = ae^{-bQ} + c$

Press (psi)	500				1000			
Temp.(°C)	300	315	324	330	300	315	324	330
a	0.11	0.10	0.21	0.14	0.25	0.33	0.46	0.49
b	-2.35	-2.05	-1.91	-1.61	-3.20	-3.12	-2.94	-2.81
c	0.065	0.154	0.172	0.260	0.087	0.205	0.302	0.340
Correlation	0.99	0.98	0.99	0.95	0.97	0.98	0.98	0.97

Comparing Table 6.4.with Table 6.5. it is demonstrated that the latter equation is a better relationship between rate constant and quinoline concentration. Figures 6.6. and 6.7. illustrate the difference between the two fits. The

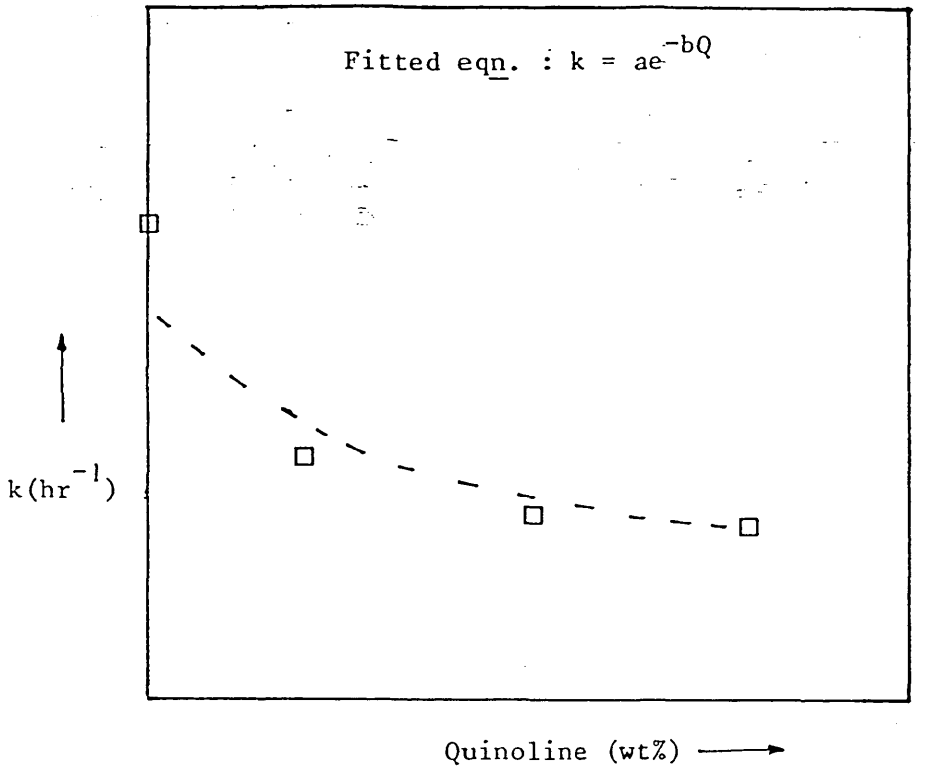


Figure 6.6. Fitted graph of apparent rate constant of tetralin hydrogenation versus quinoline concentration.

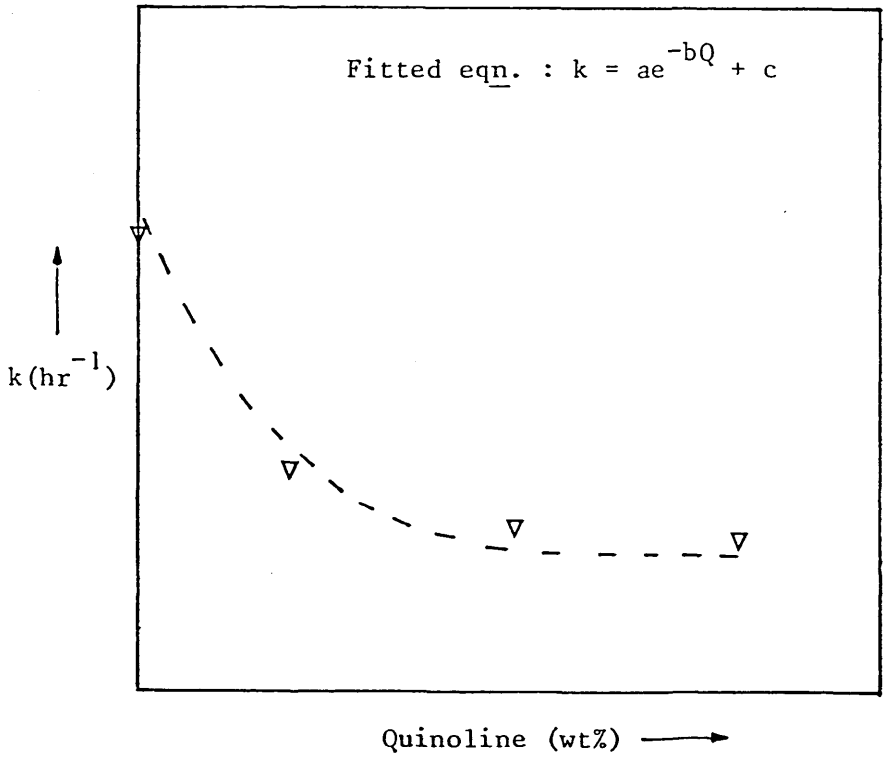


Figure 6.7. Fitted graph of apparent rate constant of tetralin hydrogenation versus quinoline concentration

exponential coefficients, b, developed at both pressures,are also meaningful and show that increasing temperature reduces the exponential decay indicating that poisoning is decreasing comparatively. There are two possibilities for such behaviour. An increase in temperature can increase the desorption rate of quinoline or its intermediate products from active sites or remove intermediates by HDN thereby allowing tetralin molecules to react at those sites. It was noted that as quinoline HDN increased, the poisoning effect decreased. On the other hand the increase in temperature may cause tetralin to react on less reactive sites which are not selectively poisoned by nitrogen compounds. Here another empirical relationship can be deduced. With very high quinoline concentration the term, ae^{-bQ}, will approach zero, when c will be equal to k. c therefore represents a value that indicates the minimum rate of hydrogenation even with very high content of poison. Here, c increases with temperature and pressure which therefore shows that at such elevated reaction conditions poisoning becomes less effective.

Finally, in Figure 6.5.the apparent activation energy of tetralin hydrogenation and concentration of quinoline are related. A linear relationship seems to exist. The fitted equation is of the type: $E = bQ + c$. From the fitted graph (Figure 6.8), the slope b shows that at higher pressure the

Fitted eqn. : $E = bQ + c$

□ - b = 26.03, c = 91.75, corr. = 0.99

▽ - b = 11.79, c = 115.39, corr. = 0.98

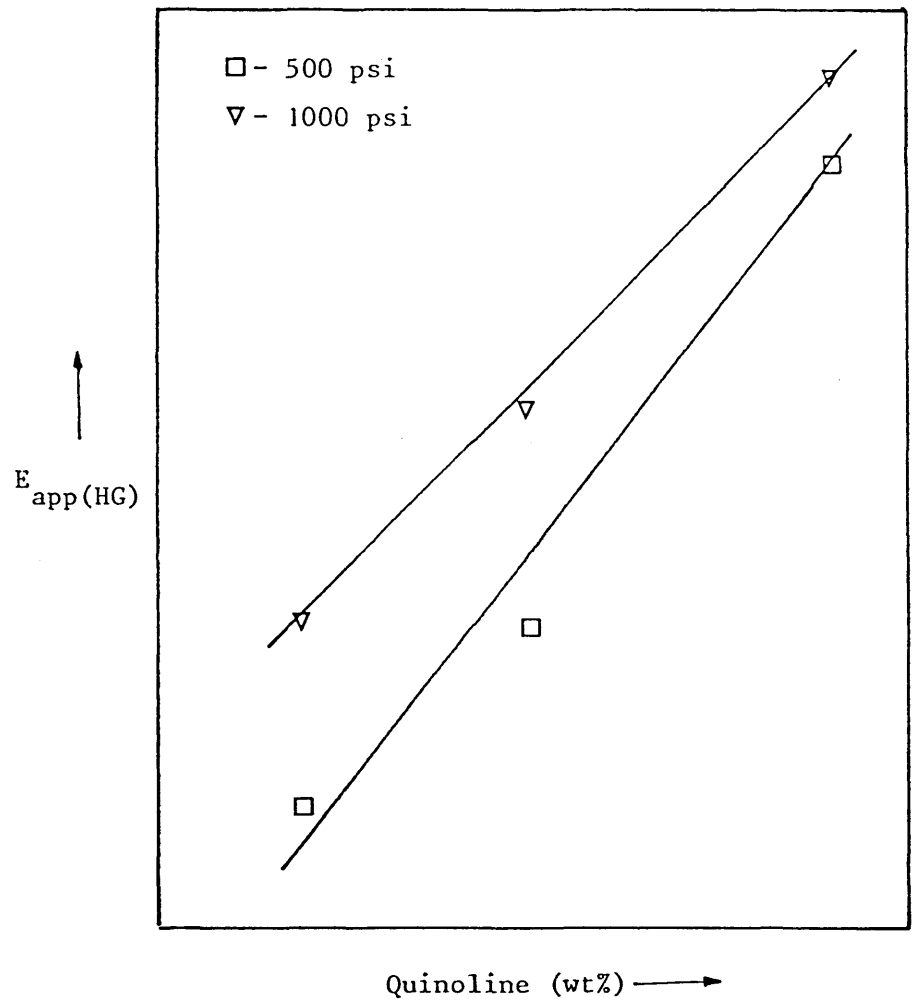


Figure 6.8. Fitted graph of apparent activation energy of tetralin hydrogenation versus quinoline concentration

increase in apparent activation energy is less compared to lower pressure. If the activation energy change is an indication of some change in the intrinsic activity of the catalyst due to poisoning, then it appears that at higher pressures quinoline has less effect on such changes in activity. This would be expected from the increased HDN rate at the higher pressure. Earlier it was observed that at two different pressures the activation energy varied for the same reaction (quinoline HDN). This was explained in terms of hydrogen functionality which may vary with pressure. Now, a similar explanation can be drawn whereby it indicates that quinoline poisoning has less effect on the hydrogen functionality at higher pressure compared to lower pressure.

6.3. TETRALIN/1,2,3,4-TETRAHYDROQUINOLINE (THQ) AND TETRALIN /O-PROPYLANILINE (OPA) HYDROGENATION

6.3.1. 1,2,3,4-tetrahydroquinoline and o-propylaniline hydrodenitrogenation (HDN)

The major products of 1,2,3,4-tetrahydroquinoline HDN were o-propylaniline and n-propylbenzene. Side products detected were polymeric nitrogen compounds. The major product of o-propylaniline HDN was n-propylbenzene only.

Kinetics of quinoline HDN has been reviewed in Section 6.2.1. The same design equation has been used to calculate (data used from Appendix A, D.41 to d.48 and D.57 to D.64).

the apparent rate constant of THQ and OPA HDN reactions.

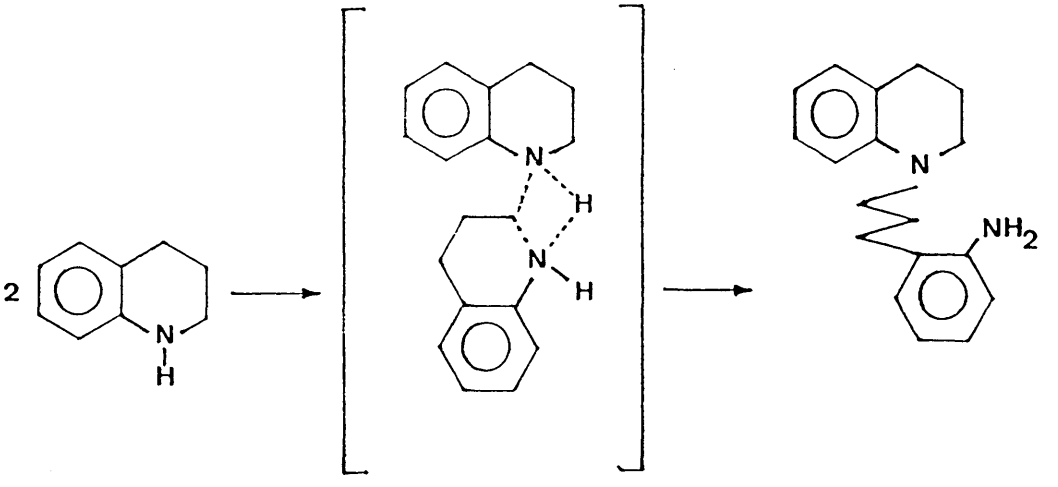
The high correlations of the plots of $-\ell n\ (1-x)$ vs τ and log plots of $k_{HDN} = Ae^{-\frac{E}{RT}}$, confirmed that the assumptions of psuedo-first order reaction kinetics taking place with plug-flow pattern in a fixed bed reactor were valid. Table 6.6 summarises the results of THQ and OPA hydrodenitrogenation rate constant and apparent activation energy.

Table 6.6. Apparent rate constant and activation energy of THQ and OPA HDN

Feedstock No.4. Tetralin/THQ (0.5 wt %)/CS_2 (0.1 mol %)								
Press.(psi)	500	500	500	500	1000	1000	1000	1000
Temp.(°C)	300	315	325	330	301	315	324	330
$k_{HDN}(hr^{-1})$	0.31	0.51	0.69	0.86	0.50	0.88	1.25	1.61
E_{app}(HDN)	-	95 ± 2 kJ mol^{-1}				108 ± 3 kJ mol^{-1}		
Feedstock No.5. Tetralin/OPA (0.47 wt %)/CS_2 (0.1 mol %)								
Press.(psi)	500	500	500	500	1000	1000	1000	1000
Temp.(°C)	300	315	324	330	300	315	325	331
$k_{HDN}(hr^{-1})$	0.32	0.50	0.68	0.85	0.51	0.88	1.26	1.63
E_{app}(HDN)		93 ± 3 kJ mol^{-1}				111 ± 3 kJ mol^{-1}		

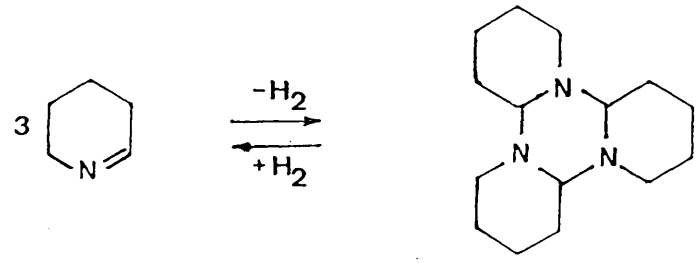
Rate of HDN of OPA is similar but slightly faster than THQ (e.g. k_{HDN}, OPA = 0.32 hr^{-1}; k_{HDN}, THQ = 0.31 hr^{-1}). Rate data (Satterfield and Yang, 1984) also confirm these findings and suggested that the hydrogenolysis of THQ was rate determining. From the composition data (Appendix A) it was established that THQ is responsible for the polymeric compound. There are two plausible mechanism for such a reaction.

An alkyl transfer reaction can occur by cleavage of C-N bond between two THQ molecules :

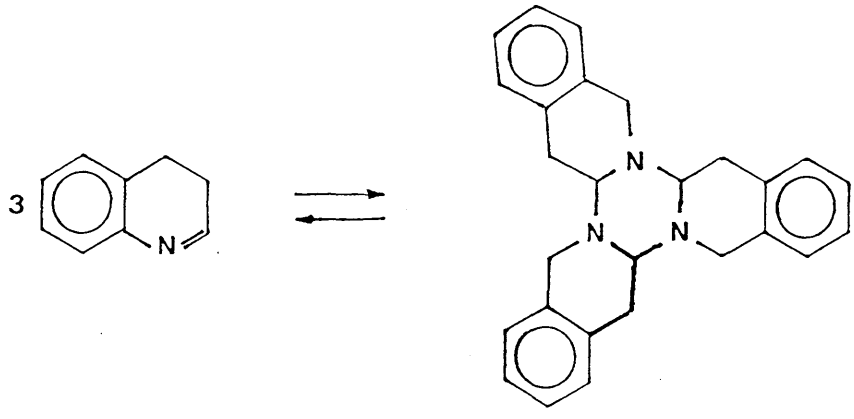


Eichorn et al.,(1980) did detect such alkyl N-compounds in the product of quinoline HDN.

The imine, Δ'-piperidiene, exists in both monomeric and trimeric form (Schopf et al., 1948)



A similar reaction could occur if the nitrogen containing ring of quinoline was partially hydrogenated and a solid trimer could result:



Reactions with 5,6,7,8-tetrahydroquinoline (Yang and Satterfield,1984) caused plugging of reactors where such similar trimers were formed. There are other examples where imine compounds form similar trimers (Luttringhaus et al., 1959). Such trimeric compound when formed on the surface of a catalyst can lead to coke formation and therefore as a general case it could be a problem encountered when coal liquids or heavy oils are hydroprocessed.

6.3.2. Influence of THQ and OPA on tetralin hydrogenation

Apparent rate constants of tetralin hydrogenations were obtained from reaction data of Feedstock No.4 and 5 (Appendix A, D.41 to D.48 and D.57 to D.64) by assuming pseudo-first order reaction mechanism. As in previous cases the rate constants were obtained from $-\ell n(1-x)$ vs τ plots. Activation energies were obtained from the log plots of the Arrhenius equation, $k = Ae^{-\frac{E}{RT}}$. Table 6.7 summarises the results of apparent rate constant and activation energy measurements of tetralin hydrogenation under the influence of THQ and OPA:

Table 6.7. Apparent rate constant and activation energy of tetralin hydrogenation.

Feedstock No.4. Tetralin/THQ (0.5 wt %)/CS_2 (0.1 mol %)								
Press.(psi) -	500	500	500	500	1000	1000	1000	1000
Temp.(°C) -	300	315	325	330	301	315	324	330
$k_{HG}(hr^{-1})$ -	0.09	0.19	0.23	0.30	0.14	0.26	0.41	0.47
$E_{app}(HG)$ -		110 ±3 kJ mol^{-1}				124 ±6 kJ mol^{-1}		
Feedstock No.5. Tetralin/OPA (0.47 wt %)/CS_2 (0.1 mol %)								
Press.(psi) -	500	500	500	500	1000	1000	1000	1000
Temp.(°C) -	300	315	324	330	300	315	325	331
$k_{HG}(hr^{-1})$ -	0.11	0.19	0.27	0.31	0.16	0.30	0.46	0.50
$E_{app}(HG)$ -		102 ±4 kJ mol^{-1}				114 ±6 kJ mol^{-1}		

Now, turning the attention towards the effect of THQ and OPA on the rate of tetralin hydrogenation, it can be deduced from Table 6.7. that THQ reduces the rate fractionally more than OPA. Although their basicities are more or less comparable, their molecule size may play a vital role in poisoning. The fused benzene ring of THQ can occupy an adjacent site, whereas the smaller molecule, OPA, may not. However, it must be remembered that OPA is an intermediate product of THQ HDN. Therefore for THQ poisoning occurs both by THQ and OPA.

An important observation to note from the composition data is that THQ has affected the selectivity of tetralin to trans-decalins from an unpoisoned value of 0.83 to 0.78, whereas the effect of OPA is negligible. This could be a consequence of size (see above) or it may be that ring opening of THQ may take place on an isomerisation site.

Since concentration of THQ and OPA are different from concentration of quinoline used a direct comparison may be erroneous when ascertaining their order of poisoning. Here the fitted data in Section 6.2.1. can be utilised to bring all these three nitrogen compounds under an iso-concentration value and deduce their poisoning effect. To this effect the unknown values of hydrogenation rate constant (k_{HG}) due to quinoline (Q) poisoning are tabulated in Table 6.8. This can then be compared with experimental values of THQ and OPA poisoning (Table 6.9.)

Table 6.8. Interpolated tetralin hydrogenation rate constant under influence of unknown quinoline concentration

Press.(psi) -	500	500	500	500	1000	1000	1000	1000
Temp.(°C) -	300	315	324	330	300	315	324	330
*k_{HG}(0.47%Q)-0.10	0.19	0.24	0.29	0.14	0.27	0.42	0.47	
*k_{HG}(0.50%Q)-0.10	0.19	0.23	0.29	0.14	0.26	0.41	0.47	
*k_{HG}(0.74%Q)-0.08	0.17	0.20	0.27	0.11	0.23	0.35	0.40	

* predicted from Table 6.5. (Fitted data)

Table 6.9. Apparent rate constants of tetralin hydrogenation under the influence of THQ and OPA

Press.(psi) -	500	500	500	500	1000	1000	1000	1000
Temp.(°C) -	300	315	324	330	300	315	324	330
k_{HG}(0.47%OPA)0.11	0.19	0.27	0.31	0.16	0.30	0.46	0.50	
k_{HG}(0.50%THQ)0.09	0.19	0.23	0.30	0.14	0.26	0.41	0.47	

With some exceptions the values indicate a similar poisoning by THQ, Q and OPA with OPA having slightly less effect. Clearly, since Q and THQ tend towards equilibrium it would be expected that the poisoning effect for these would be similar. Also, OPA is an intermediate of Q and THQ HDN and, therefore, for these molecules poisoning occurs by Q, THQ and OPA.

6.4. 1,6-DIMETHYLNAPTHALENE (DMN)/QUINOLINE HYDROGENATION

Table 6.10 summarises the results of DMN/quinoline (feedstock No.6.) hydrogenation reactions (data used from Appendix A, D.77 to D.80)

Table 6.10. Apparent rate constant and activation energy of DMN hydrogenation and quinoline HDN

Feedstock No.6. 1,6-Dimethylnapthalene/quinoline (0.5 wt %)/CS_2 (0.1 mol %)

Press.(psi)	-	500	500	500	500
Temp.(°C)	-	300	315	324	330
$k_{HG}(hr^{-1})$	-	2.65	4.60	6.37	7.85
$E_{app}(HG)$	-		104 ±2 kJ mol^{-1}		
$k_{HDN}(hr^{-1})$	-	0.30	0.49	0.68	0.81
$E_{app}(HDN)$	-		96 ±3 kJ mol^{-1}		

These hydrogenation rate constants (k_{HG}) and activation energy ($E_{app}(HG)$) values obtained will be meaningful if compared to values from reaction of pure DMN. Similarly, HDN rate constant and activation energy values can be compared with values from tetralin/quinoline reactions.

It can be deduced from Table 5.2. (Section 5.3). and Table 6.10. that 0.5 wt% quinoline has reduced the hydrogenation rate constant between 4.8% to 7.4%. The higher reduction is at lower temperature. Here it also

shows (c.f. tetralin/quinoline reactions) that at higher temperatures poisoning becomes less pronounced. But the important feature is that the effect of quinoline poisoning on DMN hydrogenation is substantially less than on tetralin hydrogenation (reduction of tetralin rate constant was between 40% to 52% under same experimental conditions). This can be rationalised on the basis that molecules of fast reactions can be hydrogenated on both highly to moderately active sites and if quinoline molecules or its intermediate products were to poison the highly active sites preferentially, the overall result would be a mild effect on the rate. From the experimental evidence of both tetralin and DMN hydrogenation this argument appears to hold. Other features of interest to note from experimental data are that selectivity towards isomers of dimethyltetralins are unaffected by quinoline poisoning, whereas in the case of tetralin to decalins the selectivity was reduced. The inference then put forward was an interference of quinoline on an isomerisation site or effect of some nature on the activated π-complex of tetralin. Here it is more likely that for fast reactions, quinoline poisoning has little effect on the activated π-complex of DMN, although there may be an argument to suggest that an isomerisation site may vary in its type with respect

to its activity, some of which is unaffected by quinoline poisoning. Another observation made was that poisoning by quinoline completely suppressed the hydrodealkylation reaction of DMN. It was mentioned earlier that both thermal or catalytic dealkylation (Wiseman, 1972) can occur but the present observation infers that it is a catalytic process and that competitive adsorption by a poison (quinoline) can retard or suppress it. However, it is useful to note that this dealkylation reaction was a minor one and therefore its importance is to be given on that context.

The apparent activation energy of DMN hydrogenation has increased with quinoline poisoning. Such an increase was thought to be due to a change in the intrinsic activity of the catalyst. Once again, comparing this with E_{app} of tetralin hydrogenation, the increase has been less. For DMN, it was from 101 kJ mol^{-1} to 104 kJ mol^{-1} but for tetralin it was 93 kJ mol^{-1} to*105 kJ mol^{-1} *(predicted from fitted data for a 0.5 wt% quinoline concentration). Therefore it would appear that the extent of change on the intrinsic activity by quinoline poisoning is less in DMN hydrogenation than in

tetralin, although the catalyst was the same as well as the amount of quinoline (0.5 wt%). Thus, DMN seems to interfere with quinoline poisoning thereby affecting its effect on the change in intrinsic activity of the catalyst. This notion can be taken further when comparing the k_{HDN} values here with k_{HDN} from tetralin/quinoline reactions. It is seen that k_{HDN} has been slightly suppressed by DMN hydrogenation thereby reducing the effect of quinoline poisoning on the intrinsic activity of the catalyst.

6.5. SUMMARY

Rate of hydroprocessing reactions are in the order: 1,6-dimethylnapthalene hydrogenation $\rangle$ HDN of quinoline, THQ and OPA $\rangle$ tetralin hydrogenation.

Tetralin, a partially hydrogenated aromatic, is subject to severe poisoning by heterocyclic nitrogen compounds (quinoline and THQ) compared to DMN an unsaturated 2-ring aromatic. Therefore, as a general case the problem encountered in hydroprocessing mid-distillates from coal extract will not be the 2 to 3 ring unsaturated aromatics present in such fractions but of its intermediate products formed during such reactions.

Poisoning by nitrogen compounds on the hydrogenation rate of tetralin are similar: THQ ~ quinoline $\gtrsim$ OPA.

Trimeric compounds formed from partially hydrogenated heterocyclic nitrogen molecules could be a problem encountered in the hydroprocessing of coal extract or heavy oils. These solid trimers cause blockage of reactors and lead to the formation of coke, which deactivates the catalyst. At high pressures and temperatures formation of such compounds are retarded.

Interaction between HDN and hydrogenation (HG) exists. HDN appears to retard HG of unsaturated and partially hydrogenated aromatics whereas HG of unsaturated aromatics retards HDN but the severity is less in the latter case. These interactions can be generally identified to be responsible for change in intrinsic activity of catalyst, interference with activated π-complex and blockage of catalyst site of different types.

An empirical relationship has been established between concentration of quinoline with the rate constant of tetralin hydrogenation and its activation energy. The two relationships are as follows:

(a) $k = ae^{-bQ} + c$

where, k = rate constant of tetralin hydrogenation, and

(b) $E = bQ + c$

where, E = apparent activation energy of tetralin hydrogenation. Q is the concentration of quinoline in wt%.

CHAPTER SEVEN : HYDROGENATION OF TETRALIN/NITROGEN/OXYGEN AND 1,6-DIMETHYLNAPTHALENE/NITROGEN/OXYGEN COMPOUND MODEL FEEDSTOCKS

7.1. INTRODUCTION

In the preliminary experiments (Chapter Four), the effect of a representative oxygen compound, dibenzofuran, present in mid-distillates on tetralin hydrogenation was studied. The influence of dibenzofuran was demonstrated only on the hydrogenation reaction. However, the main focus of the thesis was mid-distillate hydrogenation which contains nitrogen compounds. Therefore, it naturally followed that effects of an oxygen compound should be investigated on a feedstock that contained both hydrocarbon and a nitrogen compound.

The choice of the hydrocarbon compounds, namely, tetralin and 1,6-dimethylnapthalene were already established which were discussed in earlier chapters. Quinoline was also established as the choice of the nitrogen compound but intermediate nitrogen compounds from quinoline reaction itself had to be taken into account in mid-distillate reaction. Thus the effect of the oxygen compound, dibenzofuran, on reaction of feedstock that contained 1,2,3,4-tetrahydroquinoline and o-propylaniline along with tetralin were also studied.

In the case of 1,6-dimethylnapthalene hydrogenation, the effect of dibenzofuran was investigated with quinoline as the only nitrogen

compound. Two factors were considered here for the design of the experimental programme. Firstly, 1,6-dimethylnapthalene was in short supply and, secondly, there was a practical limit to the number of experiments that could be carried out in a reasonable time. However, investigation with quinoline as the only common nitrogen compound feed component did not handicap the research undertaken as one of the main aims of studying 1,6-dimethylnapthalene hydrogenation was for better understanding and a comparison with tetralin hydrogenation which was the main focus of this thesis. It was not necessary to study the reaction of pure dibenzofuran as was also the case for the pure nitrogen compounds (quinoline, THQ and OPA) because the main aim of the thesis was to investigate competitive reaction conditions which would be the actual situation in case of mid-distillate hydrogenation.

For the purpose of this thesis it was adequate to investigate a single concentration of dibenzofuran in the model feedstock. However, the choice of the single concentration (approx - 1.25 wt %) was not arbitrary, it was established from experimental findings from preliminary experiments which showed that at this concentration DBF begins to have an effect on tetralin

hydrogenation.

Hydrogenation of four model feedstocks were carried out on the same charge of AKZO-153 catalyst used for the pure tetralin and 1,6-dimethylnapthalene feeds. These experiments enabled the establishment of the effect of a representative oxygen compound (dibenzofuran) present in mid-distillates of coal extracts on other hydroprocessing reaction : hydrogenation (HG) and hydrodenitrogenation (HDN). The study of these feedstocks also demonstrated the relative rate of different hydroprocessing i.e. HG, HDN and hydrodeoxygenation (HDO), under competitive reaction condition.

The standard experimental conditions for each feed were as follows:

weight of catalyst	- 8 g
particle size of catalyst	- 0.3 to 0.6mm
weight hour space velocity (WHSV)	- 1.75-4.09ghr^{-1} g-cat^{-1}
Hydrogen pressure	- 500 and *1000 psi
Hydrogen flow-rate	- 490 cm^3/min(STP)
Reaction temperature	- 300 - 330°C

*tetralin containing feed only

7.2. TETRALIN/Q/DBF, TETRALIN/THQ/DBF AND TETRALIN/OPA/DBF HYDROGENATION

7.2.1. Kinetic Results

Kinetics of hydrogenation of tetralin and HDN of quinoline has been discussed in earlier chapters. Hydrodeoxygenation of DBF is an irreversible reaction. The same design equation used for HG and HDN has been utilised for calculating apparent rate constants of dibenzofuran HDO. These pseudo-first order kinetics for HDO were also assumed by other researchers (Rollman, 1977; Schuit et al., 1973; Flinn et al., 1963). Figure 7.1 illustrates the accuracy of the assumption in terms of fractional conversion versus contact time plots. Activation energies were determined from an Arrhenius plot and a typical example is shown in Figure 7.2.

Table 7.1. summaries the results of hydrogenation of model feedstock Nos.1 to 3. (Data used from Appendix A, D.33 to D.40, D.49 to D.56 and D.65 to D.72).

From Table 7.1. it can be concluded that under competitive reaction conditions the order of rates of hydroprocessing are as follows : HDN $>$ HDO $>$ HG of hydroaromatics (tetralin).

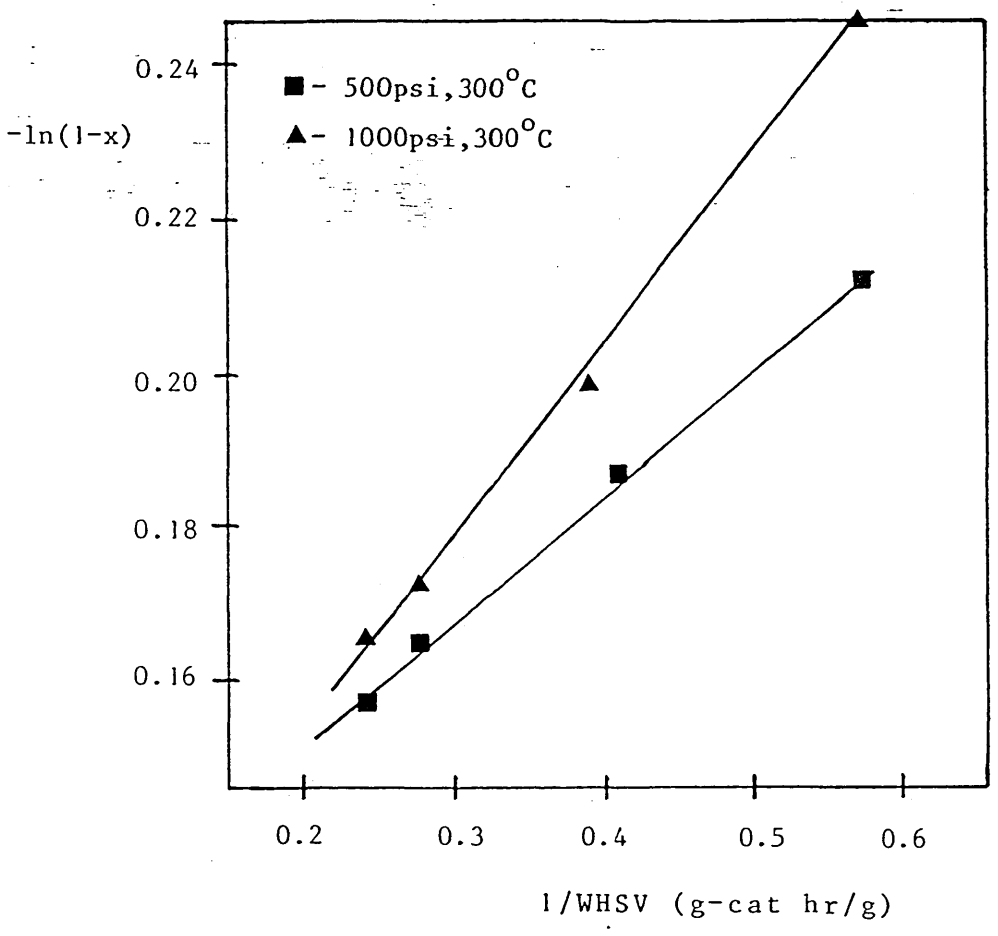


Figure 7.1. Pseudo-first order kinetics of dibenzofuran HDO

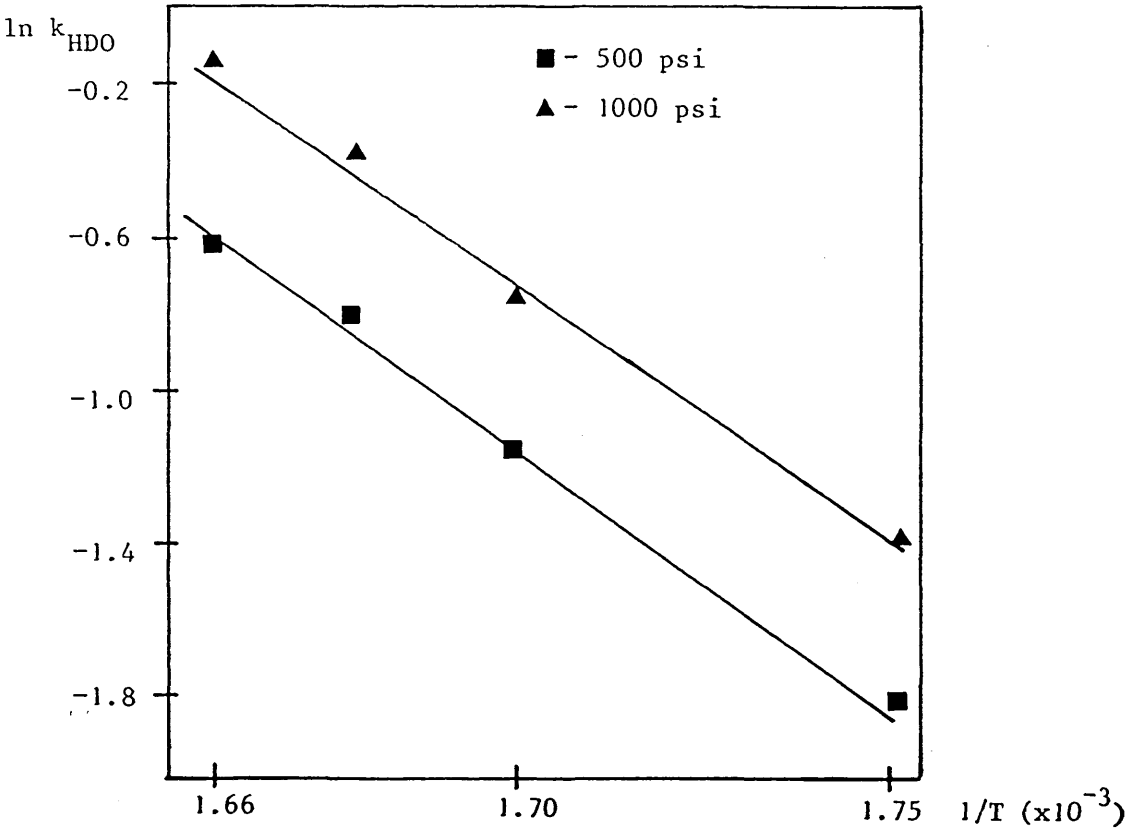


Figure 7.2. Arrhenius plot of the apparent rate constant of dibenzofuran HDO

TABLE 7.1 Apparent rate constant and activation energy of hydrogenation, hydrodenitrogenation and hydrodeoxygenation reactions.

Feedstock No.1: Tetralin/quinoline (0.74 wt %)/ dibenzofuran (1.23 wt %)

Press.(psi)	-	500	500	500	500	1000	1000	1000	1000
Temp(°C)	-	300	315	325	330	300	315	324	330
$k_{HG}(hr^{-1})$	-0.11	0.19	0.28	0.33	0.26	0.49	0.66	0.71	
$E_{app}(HG)$	-	106 ±4 kJ mol^{-1}				98 ±4 kJ mol^{-1}			
$k_{HDN}(hr^{-1})$	-0.34	0.57	0.76	0.95	0.54	0.95	1.36	1.72	
$E_{app}(HDN)$	-	96 ±2 kJ mol^{-1}				109 ±3 kJ mol^{-1}			
$k_{HDO}(hr^{-1})$	-0.17	0.30	0.48	0.59	0.24	0.46	0.68	0.85	
$E_{app}(HDO)$	-	121 ±6 kJ mol^{-1}				122 ±3 kJ mol^{-1}			

Feedstock No.2: Tetralin/1,2,3,4-tetrahydroquinoline (0.50 wt%)/dibenzofuran (1.25 wt %)

Press.(psi)	-	500	500	500	500	1000	1000	1000	1000
Temp(°C)	-	300	315	324	330	301	315	324	330
$k_{HG}(hr^{-1})$	-0.12	0.20	0.29	0.36	0.24	0.40	0.55	0.67	
$E_{app}(HG)$	-	106 ±4 kJ mol^{-1}				99 ±2 kJ mol^{-1}			
$k_{HDN}(hr^{-1})$	-0.34	0.57	0.76	0.95	0.54	0.95	1.36	1.72	
$E_{app}(HDN)$	-	96 ±2 kJ mol^{-1}				109 ±3 kJ mol^{-1}			
$k_{HDO}(hr^{-1})$	-0.17	0.30	0.48	0.59	0.24	0.46	0.68	0.85	
$E_{app}(HDO)$	-	121 ±6 kJ mol^{-1}				122 ±3 kJ mol^{-1}			

Table 7.1. (Cont'd)

Feedstock No.3. Tetralin/o-propylaniline (0.47 wt %)/ dibenzofuran (1.25 wt %)

Press.(psi)	-	500	500	500	500	1000	1000	1000	1000
Temp.(°C)	-	300	315	324	330	300	315	325	330
$k_{HG}(hr^{-1})$	-0.13	0.22	0.30	0.35	0.25	0.40	0.56	0.66
$E_{app}(HG)$	-	97 ±2 kJ mol^{-1}				94 ±3 kJ mol^{-1}		
$k_{HDN}(hr^{-1})$	-0.34	0.57	0.76	0.95	0.54	0.95	1.36	1.72
$E_{app}(HDN)$	-	96 ±2 kJ mol^{-1}				109 ±3 kJ mol^{-1}		
$k_{HDO}(hr^{-1})$	-0.17	0.30	0.48	0.54	0.24	0.46	0.68	0.85
$E_{app}(HDO)$	-	121 ±6 kJ mol^{-1}				122 ±3 kJ mol^{-1}		

7.3. INTERACTION OF DIFFERENT HYDROPROCESSING REACTION UNDER COMPETITIVE CONDITIONS

To illustrate the interaction of hydroprocessing reactions, a convenient approach is to demonstrate the effect of dibenzofuran on other hydroprocessing reactions individually where the results in Table 7.1. need to be compared with earlier findings. These effects can be broadly categorised into three groups:

(a) Effect of DBF on hydrogenation rate constant of tetralin,

(b) effect of DBF on HDN reaction rate,

(c) effect of DBF on apparent activation energy of tetralin hydrogenation.

7.3.1. Effect of DBF on hydrogenation rate constant of tetralin.

To illustrate the effect in (a)above, Table 7.2. shown will be useful. From Table 7.2. it can be seen that the presence of DBF has enhanced the rate of hydrogenation. At first sight it appears to be in contradiction with earlier findings (Chapter Four) where DBF (1.5 wt%) had slightly reduced the rate. But here the enhancement is with respect to a value under the influence of a poison. Therefore, what it infers is that the poisoning effect of nitrogen compounds has been reduced by dibenzofuran. Here, it must be noted

TABLE 7.2. Tetralin hydrogenation rate constant under the influence of nitrogen and oxygen compounds.

Press.(psi)	-	500	500	500	500	1000	1000	1000	1000
Temp.(°C)	-	300	315	324	330	300	315	324	330
*k_{HG}(0.74% Q)	-	0.08	0.17	0.20	0.27	0.11	0.23	0.35	0.40
K_{HG}(0.74% Q/DBF)		0.11	0.19	0.28	0.33	0.26	0.49	0.66	0.71
k_{HG}(0.50% THQ)	-	0.09	0.19	0.23	0.30	0.14	0.26	0.41	0.47
k_{HG}(0.50% THQ/DBF)		0.12	0.20	0.29	0.36	0.24	0.40	0.55	0.67
k_{HG}(0.47% OPA)	-	0.11	0.19	0.27	0.31	0.16	0.30	0.46	0.50
k_{HG}(0.47% OPA/DBF)	-	0.13	0.22	0.30	0.35	0.25	0.40	0.56	0.66

*Interpolated values from Table 6.8 (Chapter Six)

that all three hydroprocessing reactions (HG, HDO and HDN) are taking place. Satterfield and Carter (1981) observed that water (a product of HDO) slightly increased the saturation of hydrocarbon products. This was also found in the present work which is a reflection of the enhancement of the hydrogenation rate. Other observations from Table 7.2. show that dibenzofuran HDO has a similar effect on tetralin hydrogenation for all three feedstocks which contained different nitrogen compounds. Table 7.2. also shows that at higher pressures dibenzofuran HDO has greater interaction in reducing the effect of poisoning due to nitrogen compounds. This may be a combination of two factors. Firstly, the increased HDO rate and therefore increased water production leading to a reduction in the severity of poisoning. Secondly, at higher pressures the higher HDN rate will result in a reduced degree of poisoning (see Chapter 6).

7.3.2. Effect of DBF on HDN reaction rate.

To qualify the effect in category (b), Table 7.1. and 6.2. (Chapter Six) need to be compared. It can be gathered from both these tables that dibenzofuran HDO has enhanced the rate of HDN. This finding is in broad agreement with other researchers (Satterfield and Carter, 1981). In their case they found that water vapour (a

product of HDO) moderately accelerates certain reactions in the catalytic HDN of quinoline on Ni-Mo/Al_2O_3 catalysts and at the same time with similar degree it inhibits others, resulting in a little net effect on the overall HDN rate. But in the present work, enhancement of rate was observed for all three nitrogen compounds, two of which are intermediates in the quinoline HDN network. Enhancement of rate was between 6.3% to 11.8% (500 psi) depending upon the reaction temperature. However, at higher pressure (1000 psi) dibenzofuran HDO effect on HDN rate remains the same as that at lower pressures except that the temperature has negligible effect on the enhancement of the rate. This is an interesting feature as HDO appears to interact in a different mode towards HG and HDN. There has been so little work on HDO under competitive reaction conditions that a plausible explanaton of such behaviour is difficult. In any case water vapour appears to play the vital role although only two relevant publications (Satterfield and Carter, 1981; Goudriaan, 1974) cover such investigations.

Finally, an important observation made from experimental data is that HDO of DBF suppresses the formation of polymeric N-compounds. The formation of

these compounds are thought to take place on Bronsted acid sites (Yang and Satterfield, 1984). Thus it is likely that H_2O interferes with this process on such sites by either preferential adsorption or in situ regeneration. HDN reaction which also takes place on such sites should have been retarded by preferential adsorption, but it was not. Therefore, a selective adsorption mechanism infers that a stronger acidic form of Bronsted sites may exist for polymerisation reactions only. This notion was also suggested by Yang and Satterfield (1984). If such reactions are suppressed, a method for in-situ regeneration of catalyst or avoidance of coke lay down are a possibility which needs further investigation. Although this is beyond the scope of this thesis, it sets the experimental design for future research into this subject.

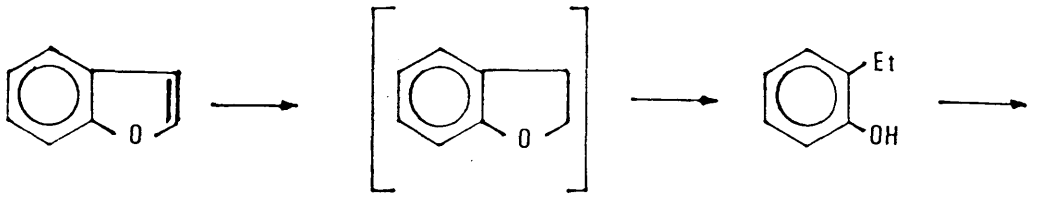
7.3.3. Effect of DBF on apparent activation energy of tetralin hydrogenation

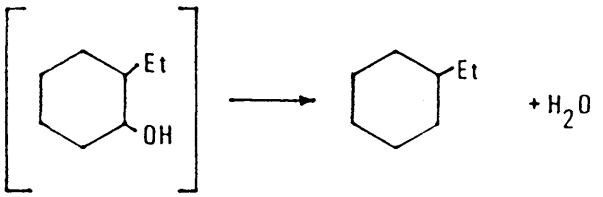
Once again if Table 7.1. and 6.3. (Chapter Six) are compared, it shows that addition of DBF in the feed has decreased the apparent activation energy of tetralin hydrogenation with respect to its poisoned value. It is interesting to note that earlier findings showed that poisoning had increased the activation energy. Therefore the mode of action either by a poison or one which

enhances a reaction are in the same manner but in the opposite direction. Such change in activation energy is thought to occur due to a change in the intrinsic activity of the catalyst or an interaction with the activated π-complex of tetralin. Whichever the case is, HDO of DBF affects either or both of them. It is most likely that water is responsible. This argument can be drawn parallel to that of effect by H_2S in HDN reaction (Satterfield and Gultekin, 1981; Yang and Satterfield, 1984). These researchers found that H_2S decreased the activation energy of hydrogenolysis reaction of quinoline. The explanation of such behaviour was attributed to an increase in Bronsted acid sites which were suggested to be more active than sulphur vacant sites. However, in the present research the concentration of H_2S was kept constant and therefore the behaviour observed can only be attributed to action of H_2O formed during HDO of DBF. Therefore an increase in Bronsted acid sites as suggested by the above researchers cannot be the contributing factor.

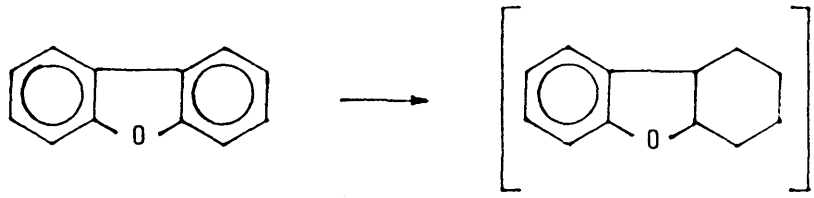
7.3.4. Mechanism of HDO

At this point a discussion on mechanism of HDO will be useful in further rationalisation of the effects of DBF on other hydroprocessing reactions. To begin with, Weisser and Landa (1973) illustrate several reaction routes for HDO reaction of DBF on MoS_2. One of the routes is via cyclohexylphenol and a proposed mechanism via this path is considered here. Rollman (1977) proposed a reaction scheme for benzofuran HDO analogous to that of N-removal.

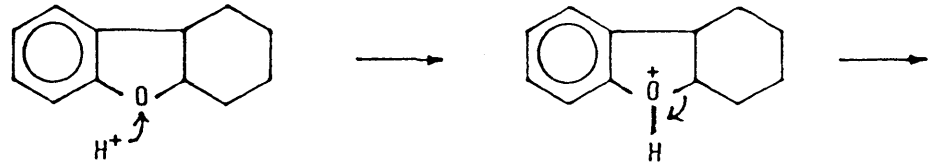




Therefore to form the phenolic intermediate, prior ring saturation is necessary. Considering DBF reaction the first step would be hydrogenation of one of the ring:

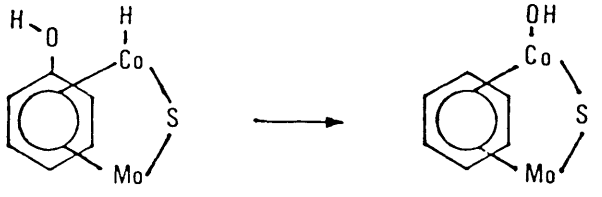


This hydrogenated intermediate complex can be protonated by an acid to form the cyclohexylphenol intermediate:



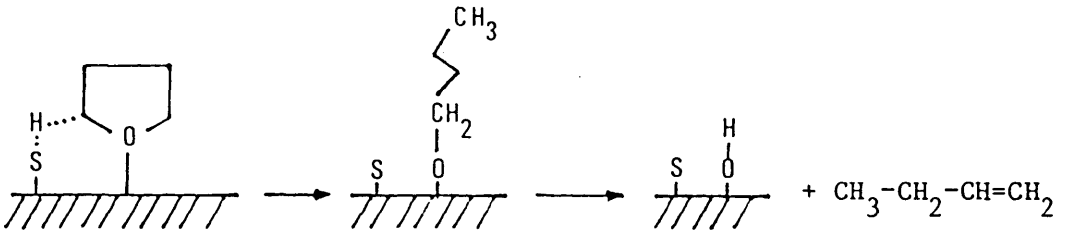


According to Rollman's (1977) scheme further hydrogenation of the phenolic ring is required for the final C-O hydrogenolysis. But in the present research cyclohexylbenzene was the only product observed in most cases. Thus it would appear that the phenolic intermediate (not detected in the reaction) had undergone direct C-O hydrogenolysis. A proposed mechanism by Weigold (1982) showed that deoxygenation of phenols in the presence of Co-Mo/Al_2O_3 catalyst at 300°C proceeds almost exclusively by the direct C-O hydrogenolysis route:

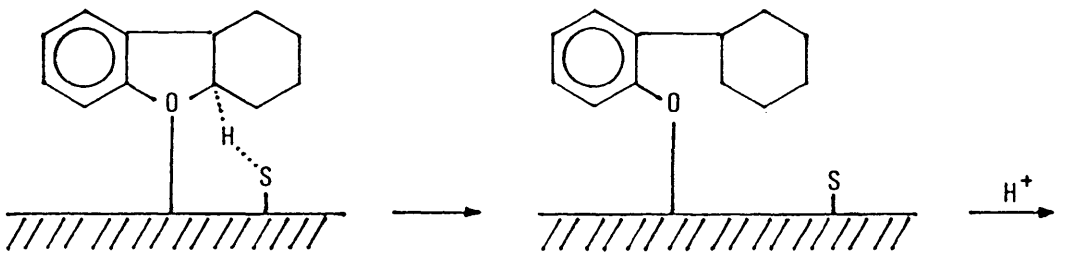


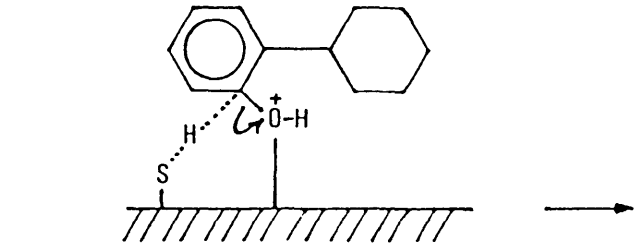
Thus it is quite possible that the phenolic intermediate of DBF reaction proceeds via such a mechanistic path in the presence of Ni-Mo/Al_2O_3 catalyst.

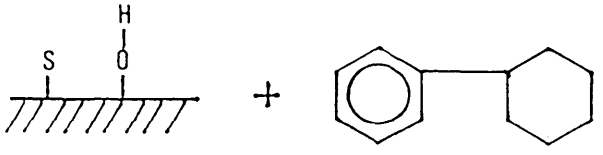
A second plausible mechanism for HDO of DBF is considered here from the viewpoint of a proposed mechanism by Furimsky (1983a) on tetrahydrofuran reaction over a sulphide catalyst.



A slight variance of the above mechanism is proposed for DBF reaction in consideration of the absence of an olefin product in the present research:



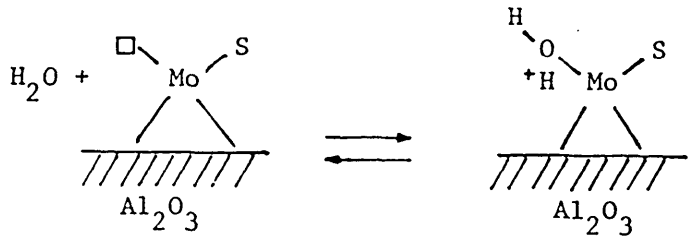




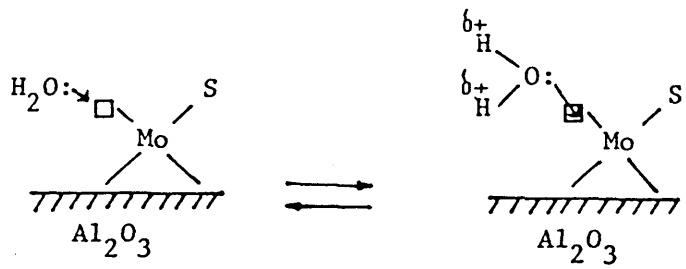
Under conditions of higher temperature and pressure, dicyclohexyl was observed, which can be attributed to further hydrogenation of cyclohexylbenzene and not necessarily the reaction product formed via Rollman's (1977) reaction scheme. The second mechanism proposed here may also explain the absence of 2-cyclohexylphenol in the HDO products.

The mode in which DBF reaction interacts with HG, HDN and polymerisation reaction can be postulated on the

basis of mechanisms discussed above. Dissociative adsorption of H_2O onto a zeolite or alumina are known to take place. A similar reaction can occur as shown below where the monolayer model has been assumed, although the scheme would be equally valid for all the models proposed for sulphide catalysts.

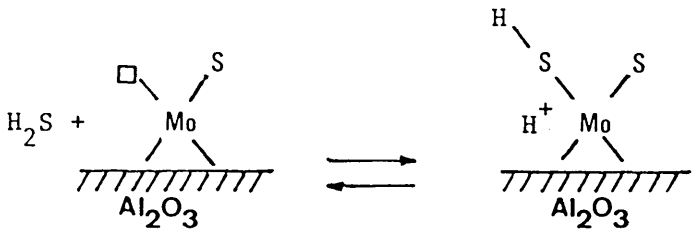


The Bronsted acid site thus formed is a hydrogenolysis site and can take part in enhancing HDN. This may be at the expense of weaker sulphur vacant sites thereby allowing tetralin hydrogenation to take place on other highly active vacant sites, where nitrogen compound would have otherwise adsorbed. These may be the primary reasons for the increase in HDN as well as HG rate. Also vacant sites may well be transformed into semi-Bronsted acid sites by interaction of oxygen lone pair of H_2O :

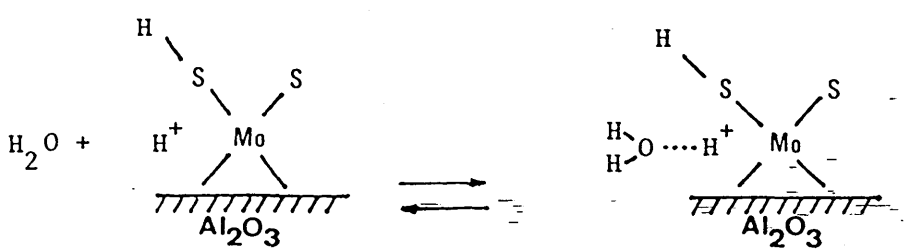


The OH group shown in HDO mechanism on a catalyst surface may preferentially adsorb on hydrogenation site in place of a nitrogen compound. Protonated OH groups are good leaving groups which then may allow further reaction of tetralin hydrogenation. In this way, the effect of nitrogen compound poisoning may be reduced.

Yang and Satterfield (1984) postulated a similar (c.f.H_2O) interaction of H_2S with a catalyst where vacant sites are transformed into Bronsted acid site:



Formation of Bronsted acid sites via this interaction is more facile than H_2O interaction. Nevertheless, some of these sites are believed to be responsible for the polymerisation reaction. A mechanism by which H_2O may suppress this reaction would be hydration of these acid sites:



7.4. 1,6-DIMETHYLNAPTHALENE/QUINOLINE/DIBENZOFURAN HYDROGENATION.

Table 7.3. summarises the results of hydrogenation of model feedstock No.4. (data used from Appendix A, D.81 to D.84) :

TABLE 7.3. Apparent rate constant and activation energy of HG, HDN and HDO reactions.

Feedstock No.4: 1,6 dimethylnapthalene/quinoline (0.50 wt %)/dibenzofuran (1.25 wt %)

Press(psi)	- 500	500	500	500
Temp(°C)	- 300	317	324	330
$k_{HG}(hr^{-1})$	- 2.70	5.00	6.41	7.85
$E_{app}(HG)$	-	102 ±1 kJ mol^{-1}		
$k_{HDN}(hr^{-1})$	- 0.32	0.58	0.73	0.90
$E_{app}(HDN)$	-	99 ±1 kJ mol^{-1}		
$k_{HDO}(hr^{-1})$	- 0.16	0.33	0.44	0.57
$E_{app}(HDO)$	-	122 ±1 kJ mol^{-1}		

From the above table it can be concluded that under competitive reaction conditions the order of rate of hydroprocessing is as follows: HG of 1,6-dimethylnapthalene $\rangle$ HDN $\rangle$ HDO. Similar trends, in terms of HDO interaction were observed as in the case for feedstock containing tetralin. Here also, DBF increased HDN rate but enhancement of HG rate (compare Table 7.3. and 6.10) is negligible. This is reasonable as the

actual reduction of hydrogenation rate due to quinoline poisoning was very little and HDO of DBF itself does not enhance HG reaction. Enhancement is mainly reflected when the effect of poisoning is reduced.

Formation of polymeric N-compounds were also suppressed by interaction of DBF reaction.

7.5. SUMMARY

Rate of hydroprocessing reactions are in the order : 1,6-dimethylnapthalene HG $\rangle$ HDN of quinoline, THQ and OPA $\rangle$ HDO $\rangle$ tetralin HG.

Interaction of HDO of DBF causes reduction of nitrogen compound poisoning which is reflected in the enhancement of HDN and HG rate under competitive reaction conditions.

Rate determining step of HDO of DBF reaction is thought to be the formation of a phenolic intermediate. This is supported by the fact that HDO of a phenol is faster than benzofuran (Rollman, 1977) which in itself is faster than DBF.

H_2O, a product of HDO, acts as a substrate which can suppress the formation of polymeric N-compounds and thus reduce coke lay down on catalyst. A mechanism of such interaction has been postulated where H_2O blocks Bronsted acid sites responsible for polymerisation reaction.

CHAPTER EIGHT : PREPARATION AND ACTIVITY OF UNSUPPORTED CATALYST.

8.1. INTRODUCTION

Preparations of unsupported catalyst of nickel and cobalt molybdenum were carried out which were described in the experimental chapter (Chapter Three). The preparation method adopted was homogenous sulphide precipitation (HSP). The experimentally pre-determined ratios of cobalt and nickel were confirmed by scanning electron microscopy, analysed results of which are given in Appendix C. Hydrogenation of dibenzothiophene were carried out on two samples of unsupported cobalt-molybdenum catalysts supplied by Institut de Recherches sur la Catalyse, Villeurbanne, France. These samples were prepared by two methods. One of them was by HSP and the other by co-maceration (CM) method. The atomic ratios of cobalt to molybdenum were confirmed by scanning electron microscopy (Appendix C). It was useful to carry out the reaction on the catalysts supplied by the Institut rather than those prepared for this thesis as the aim was to compare unsupported catalysts prepared by different methods and in different reactors. Structural characterisation had also been carried out at the Institut.

It has been established (Farragher et al., 1973; Candia et al., 1982; Hagenbach et al.,1973; Delmon,1977) that hydrodesulphurisation (HDS) activity on both supported and unsupported catalyst behaves quite similarly. The inference is that, although the support is of importance, the active phase is essentially the determining factor. The support appears to play little direct role but influences the creation of the active phase by improving dispersion. It has been demonstrated (Breysse et al.,1981; Candia et al.,1981) that for both supported and unsupported catalyst, adaptation of different preparation method results in formation of different proportions of the active phase, which in turn promotes varying catalytic activity.

The experiments thus undertaken here, at conditions close to industrial processing, will illustrate such differences in the activities of catalysts prepared by different methods.

8.2. TRIAL CATALYST PREPARATION AND ELECTRON MICROSCOPY RESULTS

The HSP method adopted for preparation of the catalysts was quite successful. The experimentally pre-determined loading of metals in terms of atomic ratios (r=Ni/Ni+Mo and Co/Co+Mo of approximately 0.3) were reproducible. This was confirmed by the analysed

results (Appendix C) of scanning electron microscopy and are given below:

Ni-Mo catalyst, batch A r=0.31

batch B r=0.32

Co-Mo catalyst, batch A r=0.35

batch B r=0.33

The catalysts supplied by the Institut had atomic ratios (r) of 0.33 (HSP Method) and 0.32 (CM method).

8.3. HYDROGENATON OF DIBENZOTHIOPHENE

Hydrogenation of dibenzothiophene was carried out in the Trickle-bed reactor by dissolving the solid compound in n-octane used as the carrier solvent. The internal standard used was n-decane. Carbondisulphide was not required as the in-situ sulphiding agent since DBT reaction itself produces hydrogen sulphide. Reactants and products were analysed by gas chromatography using Carbowax-400/Porasil-F as the column.

The initial product of dibenzothiophene hydrogenation is biphenyl which arises due to direct hydrogenolysis(hydrodesulphurisation) reaction. The biphenyl further hydrogenates to produce cyclohexylbenzene. In the present study biphenyl and cyclohexylbenzene were the only products of dibenzothiophene hydrodesulphurisation (HDS) reaction. No product (dicyclohexyl) of deep hydrogenation was

observed. The apparent rate constants of dibenzothiophene hydrodesulphurisation were obtained by assuming a pseudo-first order reaction (c.f. hydrogenation, HDN and HDO rate constants). Figure 8.1 illustrates the pseudo-first order kinetics of HDS in the trickle-bed reactor. The high correlation of the plots justified the model.

Table 8.1 shows the experimental conditions and summarises the results obtained for dibenzothiophene HDS.

From Table 8.1 it can be seen that the catalyst prepared by HSP method has higher HDS activity compared to the catalyst prepared by the CM method. Other features to note is that selectivity towards hydrogenation is the opposite. The CM catalyst has better hydrogenating activity than the HSP catalyst. The hydrogenation selectivity remained essentially constant over the range of space velocities studied. The rate of HDS increased approximately by one and a half times by doubling the hydrogen pressure on both catalysts. The apparent activation energy of HDS reaction lies between 81-83 kJ/mol over both catalysts.

The results are in broad agreement with other researchers (Candia et al., 1981) and particularly with that of Breysse et al., (1982), where the same catalysts have been used in a high pressure flow microreactor

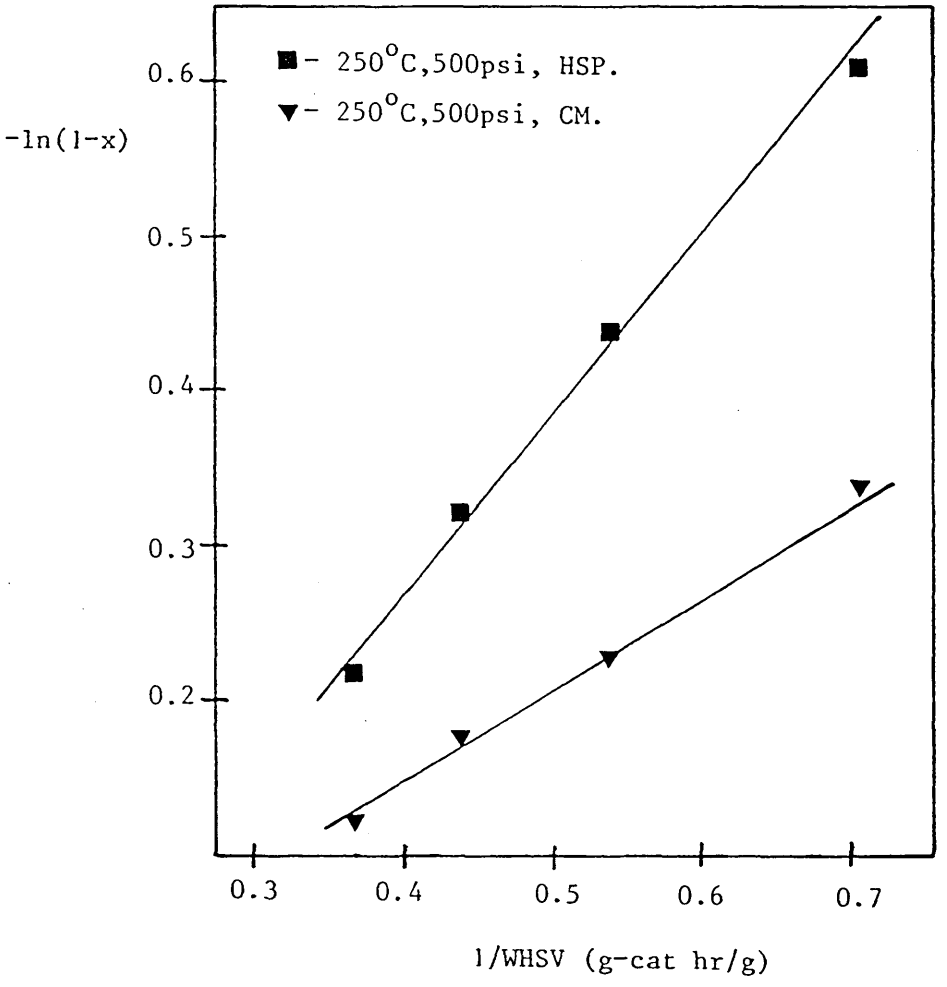


Figure 8.1 pseudo-first order kinetics of dibenzothiophene HDS.

Table 8.1 Experimental conditions and kinetic results of dibenzothiophene HDS

Conditions: Temperature - 250°C and 275°C

Pressure - 500 psi and 1000 psi

WHSV - 1.40 - 2.72 hr^{-1}

Catalysts: (a) Co-Mo HSP, r=0.33, A=35 $m^2\ g^{-1}$

(b) Co-Mo CM, r=0.32, A=27 $m^2\ g^{-1}$

Results:

Catalyst	HSP				CM			
T/°C	250	250	275	275	250	250	250	250
P/Psi	500	1000	500	1000	500	1000	500	1000
k_s/hr^{-1}	1.15	1.76	2.81	4.24	0.59	0.98	1.45	2.41
$k_i/m^{-2}g\ hr^{-1}$ ($x10^{-2}$)	3.29	5.03	8.02	12.11	2.19	3.64	5.37	8.93
Hydrogenation(%)	12.6	13	14	14	26	27	27	27.5

k_s = apparent specific rate constant

k_i = apparent intrinsic rate constant

working in the vapour phase. The results can be rationalised from a viewpoint of different active phases in the catalysts.

Firstly, both samples of catalysts had similar atomic ratios of metals, thus the difference in activity is attributed to the extent of promotional effect. Delmon (1977) and Hagenbach et al., (1971) showed that cobalt-molybdenum (CM) catalysts are composed of a mixture of MoS_2 and Co_9S_8. The presence of Co_9S_8 was considered to be associated in promoting the catalytic activity.

In the case of cobalt-molybdenum (HSP) catalyst Candia et al., (1981) have identified a unique phase (Co-Mo-S) by emission mossbauer spectroscopy. The presence of this phase is related to high HDS activity. This single phase structure consists of several stacked but highly folded and disordered MoS_2. The most likely location of the cobalt atom is as a substituent for Mo at the edges. The active site (Clausen et al., 1983) may also be due to vacancies created from the removal of sulphur atoms coordinated to both Co and neighbouring Mo atoms.

Therefore the results obtained in this thesis are in agreement, that HSP catalyst which contains the Co-Mo-S phase are more active in HDS activity compared to CM

catalyst. However the hydrogenation activity is opposite and therefore the CoMoS phase has little influence on hydrogenation activity. This is further reflected by the absence of deep hydrogenation on HSP catalyst. But in the case of CM-catalyst the absence of deep hydrogenation was unusual from a viewpoint of it possessing better hydrogenating activity. This is slightly in variance with results obtained on the same catalysts by Breysse et al., (1982), where some deep hydrogenation were observed. However this difference in experimental results may arise from the different reactor used or because of a more sensitive analytical method.

Overall, the results agree with other researchers and it can be established that hydrogenolysis sites particularly related to hydrodesulphurisation are different than hydrogenation sites.

Unsupported Ni-Mo catalysts prepared for this thesis were not studied,as the powdery catalyst was unsuitable for prolonged investigation in the trickle-bed reactor due to reactor blockages and destruction of valve seats. The original experimental programme also included studying these catalysts in a spinning basket autoclave but was not possible as the manufacturer of the autoclave did not deliver it on time.

8.4. SUMMARY

Unsupported cobalt-molybdenum (HSP) catalyst is approximately one and a half times more active than its corresponding CM catalyst with respect to HDS activity. CM catalyst has better hydrogenating activity than HSP catalyst.

Activation energy of both catalysts lies between 81-83 kJ/Mol. Hydrodesulphurisation reaction takes place at a different site than that of hydrogenation reaction.

CHAPTER NINE : CONCLUSIONS

This study was undertaken in order to elucidate the behaviour of different hydroprocessing reactions that take place during the hydrogenation of model coal extract mid-distillates on a commercial nickel-molybdenum sulphide catalyst. Especial emphasis was given in studying these hydroprocessing reactions under competitive reaction conditions. A preliminary study on unsupported cobalt-molybdenum catalysts containing a different proportion of active phases was used to establish the hydrodesulphurisation activity in a trickle-bed reactor.

The main conclusions which can be drawn from this present thesis can be summarised as follows:

1. Hydrogenation of tetralin and 1,6-dimethylnapthalene

(i) At conditions close to industrial processing (1000 psi), the hydrogenation of tetralin produced only trans and cis decalins of which trans-decalin was favoured. The pseudo-first order hydrogenation rate constants were between 0.4 to 0.92 hr^{-1} and the activation energy was 84 kJ mol^{-1} in the temperature range of 300 to 330°C.

(ii) Hydrogenation of tetralin was first order with respect to hydrogen.

(iii) The major products of 1,6-dimethylnapthalene

hydrogenation were dimethyl tetralins, which further reacted slowly to dimethyl decalins. Small quantities of 1-methylnapthalene was produced as a side product due to catalytic hydrodealkylation reaction.

(iv) Hydrogenation of 1,6-dimethylnapthalene preferentially takes place at the meta-substituted ring.

(v) 1,6-dimethylnapthalene reacts approximately 16 times faster than tetralin under comparable conditions.

2. HDN of nitrogen compounds and their influence on tetralin and 1,6-dimethylnapthalene hydrogenation.

(i) Rate of HDN were in the order: quinoline $\simeq$ THQ $\lesssim$ OPA.

(ii) The products of quinoline hydrogenation were THQ, OPA and n-propyl benzene.

(iii) The hydrogenolysis steps were the slowest in quinoline hydrogenation.

(iv) The extent of hydrogenation of the quinoline ring was found to be a function of the inherent activity of the catalyst.

(v) In the range of concentration studied, quinoline was not self inhibiting towards HDN.

(vi) THQ was responsible for producing trimeric nitrogen compounds which are precursors to coke.

(vii) Poisoning by nitrogen compounds on the hydrogenation rate of tetralin were in the order: quinoline ~ THQ $\gtrsim$ OPA.

(viii) Poisoning by quinoline on the hydrogenation rate of tetralin showed an exponential decay with no apparent threshold.

(ix) Activation energy of tetralin hydrogenation were increased due to poisoning by nitrogen compounds.

(x) Selectivity towards trans-decalin decreased with increasing quinoline concentration. Presence of THQ also decreased selectivity but OPA had a negligible effect.

(xi) Influence of quinoline in reducing the rate of 1,6-dimethylnapthalene hydrogenation was not severe.

(xii) Selectivity towards dimethyl tetralins was unaffected by quinoline poisoning.

(xiii) Activation energy of 1,6-dimethylnapthalene hydrogenation was only slightly increased due to quinoline poisoning.

(xiv) Increasing temperature and pressures of hydroprocessing reaction caused reduction in the poisoning effect due to nitrogen compounds.

3. HDO of dibenzofuran and interaction of different hydroprocessing reactions.

(i) The major product of dibenzofuran HDO was cyclohexylbenzene.

(ii) It appeared that initial ring saturation of dibenzofuran and subsequent oxygen atom removal takes

place at the same site or the initial ring saturation was a slower step with C-O hydrogenolysis being rapid.

(iii) Rate of hydroprocessing reactions were in the order: 1,6-dimethylnapthalene HG $\rangle$ HDN of quinoline, THQ and OPA $\rangle$ HDO $\rangle$ tetralin HG.

(iv) Under the influence of dibenzofuran HDO, the effect of nitrogen compound poisoning on the hydrogenation rates of tetralin and 1,6-dimethylnapthalene were reduced.

(v) Dibenzofuran reduced the extent of increase in the activation energy of tetralin hydrogenation due to nitrogen compounds. This effect appeared to be due to water, a product of dibenzofuran HDO.

4. HDS of dibenzothiophene over unsupported catalysts.

(i) The products of dibenzothiophene hydrogenation were biphenyl and cyclohexylbenzene.

(ii) Catalyst containing higher proportion of the Co-Mo-S phase had higher HDS activity but its hydrogenation activity was opposite which inferred that hydrogenation and hydrogenolysis sites are different.

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APPENDICES

APPENDIX A

FEED AND PRODUCT COMPOSITION OF MAIN REACTIONS

tr = trace

* = chromatographic separation poor for the purpose of quantitative analysis.

Notes: feed and product composition are in moles unless otherwise stated.

compositions based on 0.5 µl sample.

REACTION: D.1.

PURE TETRALIN HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 300°C

Feed composition:

tetralin - 35.48×10^{-6} mols

n-decane - 1.11×10^{-6} mols

carbon disulphide - 0.1 mol%

impurities - tr

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	:	32.92	32.89	32.33	31.05
trans-decaline ($\times 10^{-6}$)	:	1.53	1.83	2.30	3.35
cis-decalin ($\times 10^{-6}$)	:	0.43	0.46	0.56	0.73
napthalène ($\times 10^{-6}$)	:	tr	-	-	-
n-decane ($\times 10^{-6}$)	:	1.10	1.10	1.11	1.10

REACTION: D.2.

PURE TETRALIN HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 315°C

Feed composition:

tetralin - 35.17 x 10^{-6}mols

n-decane - 1.40 x 10^{-6}mols

carbon disulphide - 0.1 mol%

impurities - tr

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin (x10^{-6})	:	30.91	30.72	30.57	29.16
trans-decalin (x10^{-6})	:	1.70	2.07	2.51	3.91
cis-decalin (x10^{-6})	:	0.45	0.53	0.70	1.08
napthalene (x10^{-6})	:	2.08	1.82	1.39	0.95
n-decane (x10^{-6})	:	1.39	1.40	1.39	1.40

REACTION: D.3.

PURE TETRALIN HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 324°C

Feed composition:

tetralin - 35.34 x 10^{-6}mols

n-decane - 1.24 x 10^{-6}mols

carbon disulphide - 0.1 mol%

impurities - tr

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($x10^{-6}$)	:	26.69	25.74	25.29	23.84
trans-decalin ($x10^{-6}$)	:	3.32	4.90	5.39	7.29
cis-decalin ($x10^{-6}$)	:	0.75	1.02	1.11	1.46
napthalene ($x10^{-6}$)	:	4.58	3.65	3.35	2.34
n-decane ($x10^{-6}$)	:	1.23	1.24	1.24	1.24

REACTION: D.4.

PURE TETRALIN HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 330°C

Feed composition:

tetralin - 35.48×10^{-6} mols

n-decane - 1.11×10^{-6} mols

carbon disulphide - 0.1 mol%

impurities - tr

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	:	25.67	25.18	24.68	22.74
trans-decalin ($\times 10^{-6}$)	:	3.03	4.69	5.36	7.56
cis-decalin ($\times 10^{-6}$)	:	0.72	1.00	1.17	1.57
napthalene ($\times 10^{-6}$)	:	6.04	4.61	4.26	3.59
n-decane ($\times 10^{-6}$)	:	1.11	1.10	1.11	1.11

REACTION: D.5.

PURE TETRALIN HYDROGENATION

REACTION CONDITION:

Pressure - 1000 psi

Temperature - 300°C

Feed composition:

tetralin - 34.61×10^{-6} mols

n-decane - 1.72×10^{-6} mols

carbon disulphide - 0.1 mol%

impurities - tr

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	:	28.37	27.94	26.82	24.89
trans-decalin ($\times 10^{-6}$)	:	5.10	5.45	6.44	8.05
cis-decalin ($\times 10^{-6}$)	:	1.13	1.22	1.32	1.65
napthalene ($\times 10^{-6}$)	:	-	-	-	-
n-decane ($\times 10^{-6}$)	:	1.71	1.72	1.70	1.71

REACTION: D.6.

PURE TETRALIN HYDROGENATION

REACTION CONDITION:

Pressure - 1000 psi

Temperature - 315°C

Feed composition:

tetralin - 34.61×10^{-6} mols

n-decane - 1.92×10^{-6} mols

carbon disulphide - 0.1 mol%

impurities - tr

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	:	27.51	26.34	23.90	21.77
trans-decalin ($\times 10^{-6}$)	:	5.89	6.86	8.86	10.40
cis-decalin ($\times 10^{-6}$)	:	1.20	1.41	1.84	2.41
napthalene ($\times 10^{-6}$)	:	-	-	-	-
n-decane ($\times 10^{-6}$)	:	1.91	1.90	1.91	1.90

REACTION: D.7.

PURE TETRALIN HYDROGENATION

REACTION CONDITION:

Pressure - 1000 psi

Temperature - 324°C

Feed composition:

tetralin - 34.49×10^{-6} mols

n-decane - 1.72×10^{-6} mols

carbon disulphide - 0.1 mol%

impurities - tr

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	:	24.63	23.55	21.19	18.55
trans-decalin ($\times 10^{-6}$)	:	8.10	8.93	10.69	12.26
cis-decalin ($\times 10^{-6}$)	:	1.75	2.01	2.59	3.65
napthalene ($\times 10^{-6}$)	:	-	-	-	-
n-decane ($\times 10^{-6}$)	:	1.70	1.71	1.71	1.72

REACTION: D.8.

PURE TETRALIN HYDROGENATION

REACTION CONDITION:

Pressure - 1000 psi

Temperature - 329°C

Feed composition:

tetralin - 34.49×10^{-6} mols

n-decane - 1.72×10^{-6} mols

carbon disulphide - 0.1 mol%

impurities - tr

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	:	24.48	23.32	20.84	17.94
trans-decalin ($\times 10^{-6}$)	:	8.23	9.24	11.26	12.72
cis-decalin ($\times 10^{-6}$)	:	1.76	1.92	2.39	3.82
napthalene ($\times 10^{-6}$)	:	-	-	-	-
n-decane ($\times 10^{-6}$)	:	1.72	1.71	1.72	1.71

REACTION: D.9.

TETRALIN/QUINOLINE (0.21 wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 300°C

Feed composition:

tetralin - 35.30×10^{-6} mols

quinoline - 78.88×10^{-9} mols

impurities - 0.24 wt %

n-decane - 1.13×10^{-6} mols.

carbon-disulphide - 0.1 mol%

Product composition:

WHSV	:	4.09	3.63	2.62	1.74
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($x10^{-6}$)	:	33.70	33.50	33.18	32.38
trans-decalin ($x10^{-6}$)	:	1.28	1.44	1.72	2.36
cis-decalin ($x10^{-6}$)	:	0.32	0.36	0.40	0.55
napthalene ($x10^{-6}$)	:	-	-	-	-
quinoline ($x10^{-9}$)	:	9.47	9.07	7.89	6.31
1,2,3,4-tetrahydro-quinoline($x10^{-9}$)	:	40.43	38.89	33.10	27.60
o-propylaniline($x10^{-9}$)	:	17.32	18.30	23.97	26.51
n-propylbenzene($x10^{-9}$)	:	11.63	12.42	13.02	18.36
polymeric N-compound	:	-	tr	tr	tr
n-decane ($x10^{-6}$)	:	1.13	1.12	1.13	1.12

REACTION: D.10.

TETRALIN/QUINOLINE (0.21 wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 315°C

Feed composition:

tetralin - 35.30×10^{-6} mols

quinoline - 78.88×10^{-9} mols

impurities - 0.24 wt %

n-decane - 1.13×10^{-6} mols.

carbon-disulphide - 0.1 mol%

Product composition:

WHSV	:	4.09	3.63	2.62	1.74
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($x10^{-6}$)	:	30.70	30.59	30.51	29.53
trans-decalin ($x10^{-6}$)	:	1.62	1.88	2.32	3.35
cis-decalin ($x10^{-6}$)	:	0.40	0.47	0.55	0.79
napthalene ($x10^{-6}$)	:	2.57	2.35	1.91	1.61
quinoline ($x10^{-9}$)	:	10.25	9.47	8.68	7.10
1,2,3,4-tetrahydro-quinoline($x10^{-9}$)	:	32.57	28.40	25.06	20.99
o-propylaniline($x10^{-9}$)	:	17.53	20.57	20.52	22.74
n-propylbenzene($x10^{-9}$)	:	18.53	20.43	24.44	28.05
polymeric N-compound	:	-	-	tr	tr
n-decane ($x10^{-6}$)	:	1.13	1.12	1.13	1.13

REACTION: D.11.

TETRALIN/QUINOLINE (0.21 wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 325°C

Feed composition:

tetralin - 35.30×10^{-6} mols

quinoline - 78.88×10^{-9} mols

impurities - 0.24 wt %

n-decane - 1.13×10^{-6} mols.

carbon-disulphide - 0.1 mol%

Product composition:

WHSV	4.09	3.63	2.62	1.74
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	29.22	28.68	28.03	27.59
trans-decalin ($\times 10^{-6}$)	1.85	2.25	3.01	4.31
cis-decalin ($\times 10^{-6}$)	0.46	0.53	0.70	1.01
napthalene ($\times 10^{-6}$)	3.77	3.84	3.56	2.39
quinoline ($\times 10^{-9}$)	11.04	10.65	9.47	7.10
1,2,3,4-tetrahydro-quinoline ($\times 10^{-9}$)	29.63	25.74	22.53	18.11
o-propylaniline ($\times 10^{-9}$)	16.66	19.41	19.98	20.43
n-propylbenzene ($\times 10^{-9}$)	21.55	23.08	26.90	33.22
polymeric N-compound	-	-	-	tr
n-decane ($\times 10^{-6}$)	1.13	1.12	1.13	1.13

REACTION: D.12.

TETRALIN/QUINOLINE (0.21 wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 330°C

Feed composition:

tetralin - 35.30×10^{-6} mols

quinoline - 78.88×10^{-9} mols

impurities - 0.24 wt %

n-decane - 1.13×10^{-6} mols.

carbon-disulphide - 0.1 mol%

Product composition:

WHSV	4.09	3.63	2.62	1.74
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	28.58	28.02	27.87	27.12
trans-decalin ($\times 10^{-6}$)	2.12	2.54	3.33	4.77
cis-decalin ($\times 10^{-6}$)	0.50	0.59	0.83	1.12
napthalene ($\times 10^{-6}$)	4.10	4.15	3.27	2.29
quinoline ($\times 10^{-9}$)	12.62	11.04	10.65	8.68
1,2,3,4-tetrahydro-quinoline ($\times 10^{-9}$)	27.56	23.55	19.69	14.84
o-propylaniline ($\times 10^{-9}$)	16.18	19.27	18.17	18.13
n-propylbenzene ($\times 10^{-9}$)	22.52	25.02	30.37	37.23
polymeric N-compound	-	-	-	-
n-decane ($\times 10^{-6}$)	1.13	1.12	1.12	1.12

REACTION: D.13.

TETRALIN/QUINOLINE (0.21 wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 1000psi

Temperature - 301°C

Feed composition:

tetralin - 35.30×10^{-6} mols

quinoline - 78.88×10^{-9} mols

impurities - 0.24 wt %

n-decane - 1.13×10^{-6} mols.

carbon-disulphide - 0.1 mol%

Product composition:

WHSV	:	4.09	3.63	2.62	1.74
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	:	29.98	29.81	29.36	28.44
trans-decalin ($\times 10^{-6}$)	:	4.25	4.38	4.80	5.55
cis-decalin ($\times 10^{-6}$)	:	1.06	1.09	1.13	1.30
napthalene ($\times 10^{-6}$)	:	-	-	-	-
quinoline ($\times 10^{-9}$)	:	9.45	9.06	7.71	6.29
1,2,3,4-tetrahydro-quinoline ($\times 10^{-9}$)	:	39.20	36.84	29.01	24.89
o-propylaniline ($\times 10^{-9}$)	:	16.80	17.34	21.89	23.92
n-propylbenzene ($\times 10^{-9}$)	:	13.43	15.63	20.19	23.70
polymeric N-compound	:	-	-	tr	tr
n-decane ($\times 10^{-6}$)	:	1.13	1.13	1.12	1.13

REACTION: D.14.

TETRALIN/QUINOLINE (0.21 wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 1000 psi

Temperature - 315°C

Feed composition:

tetralin - 35.30×10^{-6} mols

quinoline - 78.88×10^{-9} mols

impurities - 0.24 wt %

n-decane - 1.13×10^{-6} mols.

carbon-disulphide - 0.1 mol%

Product composition:

WHSV	:	4.09	3.63	2.62	1.74
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($x10^{-6}$)	:	28.88	28.62	27.65	26.15
trans-decalin ($x10^{-6}$)	:	5.14	5.34	6.20	7.41
cis-decalin ($x10^{-6}$)	:	1.28	1.34	1.45	1.74
napthalene ($x10^{-6}$)	:	-	-	-	-
quinoline ($x10^{-9}$)	:	10.11	9.46	8.63	7.01
1,2,3,4-tetrahydro-quinoline($x10^{-9}$)	:	34.38	29.83	25.88	19.26
o-propylaniline($x10^{-9}$)	:	18.51	21.60	21.18	20.86
n-propylbenzene($x10^{-9}$)	:	15.88	17.99	23.19	31.75
polymeric N-compound	:	-	-	-	tr
n-decane ($x10^{-6}$)	:	1.13	1.13	1.13	1.12

REACTION: D.15.

TETRALIN/QUINOLINE (0.21 wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 1000 psi

Temperature - 324°C

Feed composition:

tetralin - 35.30×10^{-6} mols

quinoline - 78.88×10^{-9} mols

impurities - 0.24 wt %

n-decane - 1.13×10^{-6} mols.

carbon-disulphide - 0.1 mol%

Product composition:

WHSV	:	4.09	3.63	2.62	1.74
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	:	26.00	25.71	24.34	22.40
trans-decalin ($\times 10^{-6}$)	:	7.52	7.77	8.87	10.44
cis-decalin ($\times 10^{-6}$)	:	1.77	1.82	2.08	2.45
napthalene ($\times 10^{-6}$)	:	-	-	-	-
quinoline ($\times 10^{-9}$)	:	11.01	10.63	9.45	7.08
1,2,3,4-tetrahydro-quinoline ($\times 10^{-9}$)	:	30.47	25.74	21.07	14.91
o-propylaniline ($\times 10^{-9}$)	:	17.14	19.41	18.68	16.82
n-propylbenzene ($\times 10^{-9}$)	:	20.26	23.10	29.68	40.07
polymeric N-compound	:	-	-	-	-
n-decane ($\times 10^{-6}$)	:	1.13	1.12	1.12	1.13

REACTION: D.16.

TETRALIN/QUINOLINE (0.21 wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 1000 psi

Temperature - 330°C

Feed composition:

tetralin - 35.30×10^{-6} mols

quinoline - 78.88×10^{-9} mols

impurities - 0.24 wt %

n-decane - 1.13×10^{-6} mols.

carbon-disulphide - 0.1 mol%

Product composition:

WHSV	:	4.09	3.63	2.62	1.74
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($x10^{-6}$)	:	25.95	25.56	24.11	21.99
trans-decalin ($x10^{-6}$)	:	7.48	7.79	9.06	10.77
cis-decalin ($x10^{-6}$)	:	1.87	1.95	2.13	2.53
napthalene ($x10^{-6}$)	:	-	-	-	-
quinoline ($x10^{-9}$)	:	12.53	11.01	10.62	8.60
1,2,3,4-tetrahydro-quinoline($x10^{-9}$)	:	27.39	22.83	17.75	10.94
o-propylaniline($x10^{-9}$)	:	16.08	18.68	16.39	13.37
n-propylbenzene($x10^{-9}$)	:	22.88	26.37	34.12	45.97
polymeric N-compound	:	-	-	-	-
n-decane ($x10^{-6}$)	:	1.13	1.13	1.13	1.12

REACTION: D.17.

TETRALIN/QUINOLINE (0.63 wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 300°C

Feed composition:

tetralin - 35.32×10^{-6} mols

quinoline - 23.66×10^{-8} mols

impurities - 0.33 wt%

n-decane - 0.93×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	33.92	33.78	33.49	32.85
trans-decalin ($\times 10^{-6}$)	1.08	1.19	1.45	1.94
cis-decalin ($\times 10^{-6}$)	0.31	0.33	0.38	0.51
napthalene ($\times 10^{-6}$)	-	-	-	-
quinoline ($\times 10^{-8}$)	2.84	2.72	2.37	1.89
1,2,3,4-tetrahydro-quinoline ($\times 10^{-8}$)	12.04	11.70	9.89	8.26
o-propylaniline ($\times 10^{-8}$)	5.16	5.51	7.46	7.94
n-propylbenzene ($\times 10^{-8}$)	3.49	3.73	3.91	5.51
polymeric N-compound	tr	tr	tr	tr
n-decane ($\times 10^{-6}$)	0.93	0.92	0.93	0.93

REACTION: D.18.

TETRALIN/QUINOLINE (0.63 wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 315°C

Feed composition:

tetralin - 35.32×10^{-6} mols

quinoline - 23.66×10^{-8} mols

impurities - 0.33 wt%

n-decane - 0.93×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	:	31.37	31.33	31.13	30.33
trans-decalin ($\times 10^{-6}$)	:	1.34	1.56	2.07	2.99
cis-decalin ($\times 10^{-6}$)	:	0.40	0.43	0.55	0.80
napthalene ($\times 10^{-6}$)	:	2.20	2.00	1.57	1.19
quinoline ($\times 10^{-8}$)	:	3.08	2.84	2.60	2.13
1,2,3,4-tetrahydro-quinoline ($\times 10^{-8}$)	:	9.72	8.52	7.55	6.30
o-propylaniline ($\times 10^{-8}$)	:	5.23	6.16	6.18	6.82
n-propylbenzene ($\times 10^{-8}$)	:	5.56	6.13	7.33	8.41
polymeric N-compound	:	tr	tr	tr	tr
n-decane ($\times 10^{-6}$)	:	0.93	0.93	0.93	0.92

REACTION: D.19.

TETRALIN/QUINOLINE (0.63 wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 324°C

Feed composition:

tetralin - 35.32×10^{-6} mols

quinoline - 23.66×10^{-8} mols

impurities - 0.33 wt%

n-decane - 0.93×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($x10^{-6}$)	:	29.90	29.84	29.33	28.84
trans-decalin ($x10^{-6}$)	:	1.50	1.74	2.33	3.39
cis-decalin ($x10^{-6}$)	:	0.45	0.50	0.66	0.96
napthalene ($x10^{-6}$)	:	3.47	3.24	3.00	2.13
quinoline ($x10^{-8}$)	:	3.31	3.19	2.84	2.37
1,2,3,4-tetrahydro-quinoline ($x10^{-8}$)	:	8.89	7.70	6.73	5.29
o-propylaniline ($x10^{-8}$)	:	5.00	5.80	5.97	5.96
n-propylbenzene ($x10^{-8}$)	:	6.46	6.92	8.07	9.97
polymeric N-compound	:	-	tr	tr	tr
n-decane ($x10^{-6}$)	:	0.92	0.93	0.93	0.93

REACTION: D.20.

TETRALIN/QUINOLINE (0.63 wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 331°C

Feed composition:

tetralin - 35.32×10^{-6} mols

quinoline - 23.66×10^{-8} mols

impurities - 0.33 wt%

n-decane - 0.93×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	:	28.93	28.89	28.78	28.01
trans-decalin ($\times 10^{-6}$)	:	1.65	2.13	3.14	4.19
cis-decalin ($\times 10^{-6}$)	:	0.49	0.60	0.89	1.18
napthalene ($\times 10^{-6}$)	:	4.25	3.70	2.51	1.93
quinoline ($\times 10^{-8}$)	:	3.79	3.31	3.19	2.60
1,2,3,4-tetrahydro-quinoline ($\times 10^{-8}$)	:	8.27	7.07	5.88	4.41
o-propylaniline ($\times 10^{-8}$)	:	4.85	5.78	5.42	5.39
n-propylbenzene ($\times 10^{-8}$)	:	6.75	7.50	9.11	11.17
polymeric N-compound	:	-	-	tr	tr
n-decane ($\times 10^{-6}$)	:	0.93	0.93	0.92	0.93

REACTION: D.21.

TETRALIN/QUINOLINE (0.63 wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 1000 psi

Temperature - 301°C

Feed composition:

tetralin - 35.32×10^{-6} mols

quinoline - 23.66×10^{-8} mols

impurities - 0.33 wt%

n-decane - 0.93×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	30.72	30.54	30.11	29.33
trans-decalin ($\times 10^{-6}$)	3.59	3.72	4.11	4.73
cis-decalin ($\times 10^{-6}$)	1.01	1.05	1.09	1.26
napthalene ($\times 10^{-6}$)	-	-	-	-
quinoline ($\times 10^{-8}$)	2.79	2.68	2.32	1.85
1,2,3,4-tetrahydro-quinoline ($\times 10^{-8}$)	11.79	11.05	8.68	7.45
o-propylaniline ($\times 10^{-8}$)	5.05	5.20	6.54	7.15
n-propylbenzene ($\times 10^{-8}$)	4.03	4.69	6.05	7.11
polymeric N-compound	-	tr	tr	tr
n-decane ($\times 10^{-6}$)	0.93	0.93	0.92	0.93

REACTION: D.22.

TETRALIN/QUINOLINE (0.63 wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 1000 psi

Temperature - 317°C

Feed composition:

tetralin - 35.32×10^{-6} mols

quinoline - 23.66×10^{-8} mols

impurities - 0.33 wt%

n-decane - 0.93×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	:	29.60	29.33	28.51	27.17
trans-decalin ($\times 10^{-6}$)	:	4.40	4.61	5.37	6.44
cis-decalin ($\times 10^{-6}$)	:	1.32	1.38	1.44	1.71
napthalene ($\times 10^{-6}$)	:	-	-	-	-
quinoline ($\times 10^{-8}$)	:	3.01	2.72	2.57	2.10
1,2,3,4-tetrahydro-quinoline ($\times 10^{-8}$)	:	10.33	9.01	7.74	5.74
o-propylaniline ($\times 10^{-8}$)	:	5.56	6.53	6.34	6.21
n-propylbenzene ($\times 10^{-8}$)	:	4.76	5.40	6.96	9.52
polymeric N-compound	:	-	-	tr	tr
n-decane ($\times 10^{-6}$)	:	0.93	0.93	0.92	0.93

REACTION: D.23.

TETRALIN/QUINOLINE (0.63 wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 1000 psi

Temperature - 324°C

Feed composition:

tetralin - 35.32×10^{-6} mols

quinoline - 23.66×10^{-8} mols

impurities - 0.33 wt%

n-decane - 0.93×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	:	26.79	26.35	25.31	23.42
trans-decalin ($\times 10^{-6}$)	:	6.55	6.91	7.88	9.28
cis-decalin ($\times 10^{-6}$)	:	1.96	2.06	2.13	2.62
napthalene ($\times 10^{-6}$)	:	-	-	-	-
quinoline ($\times 10^{-8}$)	:	3.29	3.17	2.80	2.30
1,2,3,4-tetrahydro-quinoline ($\times 10^{-8}$)	:	9.15	7.73	6.34	4.37
o-propylaniline ($\times 10^{-8}$)	:	4.15	5.83	5.62	4.93
n-propylbenzene ($\times 10^{-8}$)	:	6.08	6.93	8.90	12.02
polymeric N-compound	:	-	-	-	tr
n-decane ($\times 10^{-6}$)	:	0.93	0.93	0.93	0.92

REACTION: D.24.

TETRALIN/QUINOLINE (0.63 wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 1000 psi

Temperature - 330°C

Feed composition:

tetralin - 35.32×10^{-6} mols

quinoline - 23.66×10^{-8} mols

impurities - 0.33 wt%

n-decane - 0.93×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($x10^{-6}$)	26.72	26.31	25.40	22.90
trans-decalin ($x10^{-6}$)	6.61	6.94	7.74	9.69
cis-decalin ($x10^{-6}$)	1.97	2.07	2.18	2.73
napthalene ($x10^{-6}$)	-	-	-	-
quinoline ($x10^{-8}$)	3.70	3.25	3.10	2.56
1,2,3,4-tetrahydro-quinoline ($x10^{-8}$)	8.25	6.88	5.37	3.29
o-propylaniline ($x10^{-8}$)	4.85	5.62	4.95	4.02
n-propylbenzene ($x10^{-8}$)	6.86	7.91	10.24	13.79
polymeric N-compound	-	-	-	-
n-decane ($x10^{-6}$)	0.93	0.92	0.93	0.92

REACTION: D.25.

TETRALIN/QUINOLINE (1.34 wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 300°C

Feed composition:

tetralin - 34.11×10^{-6} mols

quinoline - 50.33×10^{-8} mols

impurities - 0.33 wt %

n-decane - 1.82×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	32.80	32.74	32.49	32.06
trans-decalin ($\times 10^{-6}$)	0.91	0.96	1.14	1.46
cis-decalin ($\times 10^{-6}$)	0.39	0.41	0.47	0.59
napthalene ($\times 10^{-6}$)	-	-	-	-
quinoline ($\times 10^{-8}$)	6.04	5.79	5.03	4.02
1,2,3,4-tetrahydro-quinoline ($\times 10^{-8}$)	25.76	24.31	20.57	17.14
o-propylaniline ($\times 10^{-8}$)	10.31	11.44	15.52	16.46
n-propylbenzene ($\times 10^{-8}$)	7.42	7.93	8.31	11.71
polymeric N-compound	0.04wt%	0.07wt%	0.10wt%	0.12wt%
n-decane ($\times 10^{-6}$)	1.82	1.82	1.81	1.81

REACTION: D.26.

TETRALIN/QUINOLINE (1.34 wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 320°C

Feed composition:

tetralin - 34.11×10^{-6} mols

quinoline - 50.33×10^{-8} mols

impurities - 0.33 wt %

n-decane - 1.82×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	:	30.41	30.34	30.11	29.32
trans-decalin ($\times 10^{-6}$)	:	1.13	1.24	1.58	2.31
cis-decalin ($\times 10^{-6}$)	:	0.46	0.50	0.65	0.95
napthalene ($\times 10^{-6}$)	:	2.11	2.03	1.77	1.53
quinoline ($\times 10^{-8}$)	:	6.54	6.04	5.54	4.53
1,2,3,4-tetrahydro-quinoline ($\times 10^{-8}$)	:	20.16	17.81	15.95	12.50
o-propylaniline ($\times 10^{-8}$)	:	10.86	12.89	13.05	13.55
n-propylbenzene ($\times 10^{-8}$)	:	12.57	13.24	15.34	19.25
polymeric N-compound	:	0.03wt%	0.06wt%	0.08wt%	0.10wt%
n-decane ($\times 10^{-6}$)	:	1.82	1.81	1.82	1.82

REACTION: D.27.

TETRALIN/QUINOLINE (1.34 wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 325°C

Feed composition:

tetralin - 34.11×10^{-6} mols

quinoline - 50.33×10^{-8} mols

impurities - 0.33 wt %

n-decane - 1.82×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($x10^{-6}$)	:	29.22	2912	28.69	28.45
trans-decalin ($x10^{-6}$)	:	1.21	1.34	1.78	2.65
cis-decalin ($x10^{-6}$)	:	0.50	0.55	0.69	1.03
napthalene ($x10^{-6}$)	:	3.18	3.10	2.95	1.98
quinoline ($x10^{-8}$)	:	7.05	6.79	6.04	5.03
1,2,3,4-tetrahydro-quinoline ($x10^{-8}$)	:	18.84	16.33	14.27	11.21
o-propylaniline ($x10^{-8}$)	:	10.59	12.32	12.66	12.64
n-propylbenzene ($x10^{-8}$)	:	13.75	14.73	17.16	21.20
polymeric N-compound	:	0.01wt%	0.04wt%	0.07wt%	0.08wt%
n-decane ($x10^{-6}$)	:	1.82	1.81	1.82	1.82

REACTION: D.28

TETRALIN/QUINOLINE (1.34 wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 330°C

Feed composition:

tetralin - 34.11×10^{-6} mols

quinoline - 50.33×10^{-8} mols

impurities - 0.33 wt %

n-decane - 1.82×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	: 4.09	3.63	2.62	1.75
1/WHSV	: 0.24	0.28	0.38	0.57
tetralin ($x10^{-6}$)	: 27.50	27.34	26.95	26.24
trans-decalin ($x10^{-6}$)	: 1.48	1.66	2.31	3.56
cis-decalin ($x10^{-6}$)	: 0.57	0.65	0.85	1.32
napthalene ($x10^{-6}$)	: 4.56	4.46	4.00	2.99
quinoline ($x10^{-8}$)	: 8.05	7.05	6.79	5.54
1,2,3,4-tetrahydro-quinoline ($x10^{-8}$)	: 17.58	14.97	12.48	9.37
o-propylaniline ($x10^{-8}$)	: 10.32	12.25	11.52	11.46
n-propylbenzene ($x10^{-8}$)	: 14.37	15.96	19.38	23.76
polymeric N-compound	: tr	0.02wt%	0.04wt%	0.06wt%
n-decane ($x10^{-6}$)	: 1.81	1.82	1.82	1.82

REACTION: D.29.

TETRALIN/QUINOLINE (1.34 wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 1000 psi

Temperature - 300°C

Feed composition:

tetralin - 34.11×10^{-6} mols

quinoline - 50.33×10^{-8} mols

impurities - 0.33 wt %

n-decane - 1.82×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($x10^{-6}$)	:	30.35	30.25	29.96	29.46
trans-decalin ($x10^{-6}$)	:	2.63	2.70	2.95	3.29
cis-decalin ($x10^{-6}$)	:	1.13	1.15	1.20	1.35
napthalene ($x10^{-6}$)	:	-	-	-	-
quinoline ($x10^{-8}$)	:	6.00	5.71	5.01	3.98
1,2,3,4-tetrahydro-quinoline ($x10^{-8}$)	:	24.99	23.49	18.41	15.83
o-propylaniline ($x10^{-8}$)	:	10.71	11.05	13.88	15.20
n-propylbenzene ($x10^{-8}$)	:	8.57	9.38	12.88	15.12
polymeric N-compound	:	tr	tr	tr	0.02wt%
n-decane ($x10^{-6}$)	:	1.82	1.82	1.82	1.81

REACTION: D.30.

TETRALIN/QUINOLINE (1.34 wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 1000 psi

Temperature - 320°C

Feed composition:

tetralin - 34.11×10^{-6} mols

quinoline - 50.33×10^{-8} mols

impurities - 0.33 wt %

n-decane - 1.82×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	:	28.91	28.72	28.13	27.19
trans-decalin ($\times 10^{-6}$)	:	3.69	3.82	4.25	4.91
cis-decalin ($\times 10^{-6}$)	:	1.51	1.56	1.73	2.01
napthalene ($\times 10^{-6}$)	:	-	-	-	-
quinoline ($\times 10^{-8}$)	:	6.50	6.01	5.49	4.48
1,2,3,4-tetrahydro-quinoline ($\times 10^{-8}$)	:	21.19	18.45	15.66	10.92
o-propylaniline ($\times 10^{-8}$)	:	11.41	13.36	12.81	11.82
n-propylbenzene ($\times 10^{-8}$)	:	11.16	12.41	16.22	22.91
polymeric N-compound	:	tr	tr	tr	tr
n-decane ($\times 10^{-6}$)	:	1.82	1.82	1.82	1.82

REACTION: D.31.

TETRALIN/QUINOLINE (1.34 wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 1000 psi

Temperature - 324°C

Feed composition:

tetralin - 34.11×10^{-6} mols

quinoline - 50.33×10^{-8} mols

impurities - 0.33 wt %

n-decane - 1.82×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($x10^{-6}$)	:	26.26	26.02	25.24	23.71
trans-decalin ($x10^{-6}$)	:	5.57	5.74	6.39	7.49
cis-decalin ($x10^{-6}$)	:	2.28	2.35	2.48	2.91
napthalene ($x10^{-6}$)	:	-	-	-	-
quinoline ($x10^{-8}$)	:	6.99	6.70	6.00	4.98
1,2,3,4-tetrahydro-quinoline ($x10^{-8}$)	:	19.46	16.42	13.40	9.23
o-propylaniline ($x10^{-8}$)	:	10.95	12.38	11.89	10.40
n-propylbenzene ($x10^{-8}$)	:	12.93	14.74	18.94	25.57
polymeric N-compound	:	-	tr	tr	tr
n-decane ($x10^{-6}$)	:	1.82	1.82	1.81	1.82

REACTION: D.32.

TETRALIN/QUINOLINE (1.34 wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 1000 psi

Temperature - 331°C

Feed composition:

tetralin - 34.11×10^{-6} mols

quinoline - 50.33×10^{-8} mols

impurities - 0.33 wt %

n-decane - 1.82×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	:	26.23	25.98	25.07	23.37
trans-decalin ($\times 10^{-6}$)	:	5.67	5.85	6.60	7.84
cis-decalin ($\times 10^{-6}$)	:	2.21	2.28	2.44	2.90
napthalene ($\times 10^{-6}$)	:	-	-	-	-
quinoline ($\times 10^{-8}$)	:	8.01	6.98	6.70	5.47
1,2,3,4-tetrahydro-quinoline ($\times 10^{-8}$)	:	17.46	14.59	11.34	6.94
o-propylaniline ($\times 10^{-8}$)	:	10.26	11.93	10.46	8.49
n-propylbenzene ($\times 10^{-8}$)	:	14.60	16.83	21.77	29.33
polymeric N-compound	:	-	-	tr	tr
n-decane ($\times 10^{-6}$)	:	1.82	1.82	1.82	1.81

REACTION: D.33.

TETRALIN/QUINOLINE (0.74 wt%)/DIBENZOFURAN (1.23 wt%) HYDROGENATION.

REACTION CONDITION:

Pressure - 500 psi

Temperature - 300°C

Feed composition:

tetralin - 33.78×10^{-6} mols

quinoline - 27.79×10^{-8} mols

dibenzofuran- 35.46×10^{-8} mols

n-decane - 1.91×10^{-6} mols

impurities - 0.33 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($x10^{-6}$)	32.34	32.17	31.00	31.19
trans-decalin ($x10^{-6}$)	1.11	1.24	1.48	2.02
cis-decalin ($x10^{-6}$)	0.33	0.37	0.42	0.57
napthalene ($x10^{-6}$)	-	-	-	-
quinoline ($x10^{-8}$)	3.33	3.20	2.78	2.22
1,2,3,4-tetrahydro-quinoline ($x10^{-8}$)	13.96	13.49	11.11	9.48
o-propylaniline ($x10^{-8}$)	5.98	6.35	8.38	9.10
n-propylbenzene ($x10^{-8}$)	4.52	4.75	5.52	6.99
dibenzofuran ($x10^{-8}$)	30.27	30.12	29.51	28.62
cyclohexylbenzene ($x10^{-8}$)	5.19	5.34	5.95	6.84
dicyclohexyl ($x10^{-8}$)	-	-	-	-
polymeric N-compound	-	-	-	-
n-decane ($x10^{-6}$)	1.90	1.91	1.91	1.91

REACTION: D.34.

TETRALIN/QUINOLINE (0.74 wt%)/DIBENZOFURAN (1.23 wt%) HYDROGENATION.

REACTION CONDITION:

Pressure - 500 psi

Temperature - 315°C

Feed composition:

tetralin - 33.78×10^{-6} mols

quinoline - 27.79×10^{-8} mols

dibenzofuran- 35.46×10^{-8} mols

n-decane - 1.91×10^{-6} mols

impurities - 0.33 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	:	29.64	29.52	29.46	28.41
trans-decalin ($\times 10^{-6}$)	:	1.40	1.64	2.02	2.93
cis-decalin ($\times 10^{-6}$)	:	0.42	0.49	0.57	0.83
napthalene ($\times 10^{-6}$)	:	2.32	2.13	1.73	1.61
quinoline ($\times 10^{-8}$)	:	3.61	3.33	3.06	2.50
1,2,3,4-tetrahydro-quinoline ($\times 10^{-8}$)	:	11.26	10.02	9.03	7.15
o-propylaniline ($\times 10^{-8}$)	:	6.06	7.26	7.38	7.75
n-propylbenzene ($\times 10^{-8}$)	:	6.86	7.18	8.32	10.39
dibenzofuran ($\times 10^{-8}$)	:	29.36	29.10	28.05	26.59
cyclohexylbenzene ($\times 10^{-8}$)		6.10	6.36	7.41	8.87
dicyclohexyl ($\times 10^{-8}$)	:	-	-	-	-
polymeric N-compound	:	-	-	-	-
n-decane ($\times 10^{-6}$)	:	1.91	1.91	1.91	1.90

REACTION: D.35.

TETRALIN/QUINOLINE (0.74 wt%)/DIBENZOFURAN (1.23 wt%) HYDROGENATION.

REACTION CONDITION:

Pressure - 500 psi

Temperature - 325°C

Feed composition:

tetralin - 33.78×10^{-6} mols

quinoline - 27.79×10^{-8} mols

dibenzofuran- 35.46×10^{-8} mols

n-decane - 1.91×10^{-6} mols

impurities - 0.33 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV :	4.09	3.63	2.62	1.75
1/WHSV :	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$) :	27.97	27.80	27.36	26.24
trans-decalin ($\times 10^{-6}$) :	1.61	2.07	2.50	3.81
cis-decalin ($\times 10^{-6}$) :	0.48	0.62	0.71	1.08
napthalene ($\times 10^{-6}$) :	3.72	3.29	3.21	2.65
quinoline ($\times 10^{-8}$) :	3.89	3.75	3.33	2.78
1,2,3,4-tetrahydro-quinoline ($\times 10^{-8}$) :	10.30	8.99	17.84	6.02
o-propylaniline ($\times 10^{-8}$):	5.79	6.79	6.95	6.80
n-propylbenzene ($\times 10^{-8}$):	7.81	8.26	9.67	12.19
dibenzofuran ($\times 10^{-8}$):	28.39	27.99	26.44	24.31
cyclohexylbenzene ($\times 10^{-8}$)	7.07	7.47	9.02	11.15
dicyclohexyl ($\times 10^{-8}$):	-	-	-	-
polymeric N-compound :	-	-	-	-
n-decane ($\times 10^{-6}$):	1.91	1.90	1.91	1.91

REACTION: D.36.

TETRALIN/QUINOLINE (0.74 wt%)/DIBENZOFURAN (1.23 wt%) HYDROGENATION.

REACTION CONDITION:

Pressure - 500 psi

Temperature - 330°C

Feed composition:

tetralin - 33.78×10^{-6} mols

quinoline - 27.79×10^{-8} mols

dibenzofuran- 35.46×10^{-8} mols

n-decane - 1.91×10^{-6} mols

impurities - 0.33 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($x10^{-6}$)	:	26.39	26.03	25.97	24.36
trans-decalin ($x10^{-6}$)	:	1.88	2.27	2.93	4.48
cis-decalin ($x10^{-6}$)	:	0.56	0.68	0.82	1.19
napthalene ($x10^{-6}$)	:	4.95	4.80	4.06	3.75
quinoline ($x10^{-8}$)	:	4.45	3.89	3.75	3.06
1,2,3,4-tetrahydro-quinoline ($x10^{-8}$)	:	9.51	8.31	7.06	5.07
o-propylaniline ($x10^{-8}$)	:	5.58	6.80	6.51	6.20
n-propylbenzene ($x10^{-8}$)	:	8.25	8.80	10.47	13.46
dibenzofuran ($x10^{-8}$)	:	27.39	26.93	25.11	22.62
cyclohexylbenzene ($x10^{-8}$)	:	8.07	8.53	10.35	12.84
dicyclohexyl ($x10^{-8}$)	:	-	-	-	-
polymeric N-compound	:	-	-	-	-
n-decane ($x10^{-6}$)	:	1.91	1.91	1.91	1.90

REACTION: D.37.

TETRALIN/QUINOLINE (0.74 wt%)/DIBENZOFURAN (1.23 wt%) HYDROGENATION.

REACTION CONDITION:

Pressure - 1000psi

Temperature - 300°C

Feed composition:

tetralin - 33.78×10^{-6} mols

quinoline - 27.79×10^{-8} mols

dibenzofuran- 35.46×10^{-8} mols

n-decane - 1.91×10^{-6} mols

impurities - 0.33 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	28.71	28.48	27.75	25.98
trans-decalin ($\times 10^{-6}$)	3.90	4.08	4.70	5.80
cis-decalin ($\times 10^{-6}$)	1.17	1.22	1.33	1.64
napthalene ($\times 10^{-6}$)	-	-	-	-
quinoline ($\times 10^{-8}$)	3.28	3.17	2.70	2.17
1,2,3,4-tetrahydro-quinoline ($\times 10^{-8}$)	13.52	13.11	10.47	8.39
o-propylaniline ($\times 10^{-8}$)	5.80	6.17	7.89	8.07
n-propylbenzene ($\times 10^{-8}$)	5.19	5.34	6.73	9.16
dibenzofuran ($\times 10^{-8}$)	30.06	29.84	29.00	27.77
cyclohexylbenzene ($\times 10^{-8}$)	5.40	5.62	6.46	7.69
dicyclohexyl ($\times 10^{-8}$)	-	-	-	-
polymeric N-compound	-	-	-	-
n-decane ($\times 10^{-6}$)	1.90	1.91	1.91	1.90

REACTION: D.38.

TETRALIN/QUINOLINE (0.74 wt%)/DIBENZOFURAN (1.23 wt%) HYDROGENATION.

REACTION CONDITION:

Pressure - 1000psi

Temperature - 315°C

Feed composition:

tetralin - 33.78×10^{-6} mols

quinoline - 27.79×10^{-8} mols

dibenzofuran- 35.46×10^{-8} mols

n-decane - 1.91×10^{-6} mols

impurities - 0.33 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($x10^{-6}$)	27.72	27.32	26.02	23.58
trans-decalin ($x10^{-6}$)	4.67	4.97	6.05	7.96
cis-decalin ($x10^{-6}$)	1.39	1.49	1.71	2.24
napthalene ($x10^{-6}$)	-	-	-	-
quinoline ($x10^{-8}$)	3.57	3.28	3.01	2.45
1,2,3,4-tetrahydro-quinoline($x10^{-8}$)	11.23	9.85	8.50	6.16
o-propylaniline($x10^{-8}$)	6.04	7.13	6.96	6.67
n-propylbenzene($x10^{-8}$)	6.95	7.53	9.32	12.51
dibenzofuran ($x10^{-8}$)	29.07	28.70	27.18	25.06
cyclohexylbenzene($x10^{-8}$)	6.39	6.76	8.28	10.00
dicyclohexyl ($x10^{-8}$)	tr	tr	tr	0.40
polymeric N-compound	-	-	-	-
n-decane ($x10^{-6}$)	1.91	1.91	1.90	1.91

REACTION: D.39.

TETRALIN/QUINOLINE (0.74 wt%)/DIBENZOFURAN (1.23 wt%) HYDROGENATION.

REACTION CONDITION:

Pressure - 1000psi

Temperature - 324°C

Feed composition:

tetralin - 33.78×10^{-6} mols

quinoline - 27.79×10^{-8} mols

dibenzofuran- 35.46×10^{-8} mols

n-decane - 1.91×10^{-6} mols

impurities - 0.33 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	24.99	24.51	22.67	20.17
trans-decalin ($\times 10^{-6}$)	6.77	7.14	8.67	10.75
cis-decalin ($\times 10^{-6}$)	2.02	2.13	2.44	2.86
napthalene ($\times 10^{-6}$)	-	-	-	-
quinoline ($\times 10^{-8}$)	3.79	3.68	3.26	2.70
1,2,3,4-tetrahydro-quinoline ($\times 10^{-8}$)	10.16	8.67	7.03	4.67
o-propylaniline ($\times 10^{-8}$)	5.72	6.54	6.23	5.27
n-propylbenzene ($\times 10^{-8}$)	8.12	8.90	11.27	15.15
dibenzofuran ($\times 10^{-8}$)	28.18	27.62	25.47	22.59
cyclohexylbenzene ($\times 10^{-8}$)	7.28	7.84	9.59	12.35
dicyclohexyl ($\times 10^{-8}$)	tr	tr	0.40	0.52
polymeric N-compound	-	-	-	-
n-decane ($\times 10^{-6}$)	1.91	1.91	1.91	1.90

REACTION: D.40.

TETRALIN/QUINOLINE (0.74 wt%)/DIBENZOFURAN (1.23 wt%) HYDROGENATION.

REACTION CONDITION:

Pressure - 1000psi

Temperature - 330°C

Feed composition:

tetralin - 33.78×10^{-6} mols

quinoline - 27.79×10^{-8} mols

dibenzofuran- 35.46×10^{-8} mols

n-decane - 1.91×10^{-6} mols

impurities - 0.33 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($x10^{-6}$)	:	24.63	24.15	22.24	2.67 19.55
trans-decalin ($x10^{-6}$)	:	7.05	7.42	9.00	11.24
cis-decalin ($x10^{-6}$)	:	2.10	2.21	2.54	2.99
napthalene ($x10^{-6}$)	:	-	-	-	-
quinoline ($x10^{-8}$)	:	4.40	3.82	3.70	3.00
1,2,3,4-tetrahydro-quinoline ($x10^{-8}$)	:	9.23	7.89	6.06	3.54
o-propylaniline ($x10^{-8}$)	:	5.42	6.45	5.59	4.33
n-propylbenzene ($x10^{-8}$)	:	8.74	9.63	12.44	16.92
dibenzofuran ($x10^{-8}$)	:	27.27	26.62	24.04	20.67
cyclohexylbenzene ($x10^{-8}$)		8.19	8.49	10.96	14.20
dicyclohexyl ($x10^{-8}$)	:	tr	0.35	0.46	0.59
polymeric N-compound	:	-	-	-	-
n-decane ($x10^{-6}$)	:	1.90	1.91	1.91	1.91

REACTION: D.41.

TETRALIN/1,2,3,4-TETRAHYDROQUINOLINE (0.50 wt %)

HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 300°C

Feed composition:

tetralin - 35.21×10^{-6} mols

1,2,3,4-tetrahydroquinoline - 18.21×10^{-8} mols.

n-decane - 1.19×10^{-6} mols

impurities - 0.01 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	33.82	33.70	33.38	32.77
trans-decalin ($\times 10^{-6}$)	1.08	1.18	1.45	1.94
cis-decalin ($\times 10^{-6}$)	0.31	0.33	0.38	0.50
napthalene ($\times 10^{-6}$)	-	-	-	-
1,2,3,4-tetrahydro-quinoline ($\times 10^{-8}$)	10.86	10.43	8.66	7.13
o-propylaniline ($\times 10^{-8}$)	4.66	4.91	6.54	6.84
n-propylbenzene ($\times 10^{-8}$)	2.69	2.87	3.01	4.24
polymeric N-compound	tr	tr	tr	tr
n-decane ($\times 10^{-6}$)	1.19	1.19	1.18	1.19

REACTION: D.42.

TETRALIN/1,2,3,4-TETRAHYDROQUINOLINE (0.50 wt %)

HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 315°C

Feed composition:

tetralin - 35.21×10^{-6} mols

1,2,3,4-tetrahydroquinoline - 18.21×10^{-8} mols.

n-decane - 1.19×10^{-6} mols

impurities - 0.01 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	31.27	31.22	31.03	30.24
trans-decalin ($\times 10^{-6}$)	1.35	1.56	2.06	2.98
cis-decalin ($\times 10^{-6}$)	0.39	0.43	0.55	0.80
napthalene ($\times 10^{-6}$)	2.20	2.00	1.57	1.19
1,2,3,4-tetrahydro-quinoline ($\times 10^{-8}$)	9.06	7.82	6.91	5.63
o-propylaniline ($\times 10^{-8}$)	4.87	5.67	5.66	6.10
n-propylbenzene ($\times 10^{-8}$)	4.28	4.72	5.64	6.48
polymeric N-compound	tr	tr	tr	tr
n-decane ($\times 10^{-6}$)	1.19	1.18	1.19	1.19

REACTION: D.43.

TETRALIN/1,2,3,4-TETRAHYDROQUINOLINE (0.50 wt %)

HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 324°C

Feed composition:

tetralin - 35.21×10^{-6} mols

1,2,3,4-tetrahydroquinoline - 18.21×10^{-8} mols.

n-decane - 1.19×10^{-6} mols

impurities - 0.01 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	:	29.81	29.74	29.21	28.74
trans-decalin ($\times 10^{-6}$)	:	1.51	1.74	2.36	3.43
cis-decalin ($\times 10^{-6}$)	:	0.43	0.49	0.63	0.91
napthalene ($\times 10^{-6}$)	:	3.46	3.24	3.01	2.13
1,2,3,4-tetrahydro-quinoline ($\times 10^{-8}$)	:	8.47	7.34	6.36	4.95
o-propylaniline ($\times 10^{-8}$)	:	4.77	5.54	5.64	5.59
n-propylbenzene ($\times 10^{-8}$)	:	4.97	5.33	6.21	7.67
polymeric N-compound	:	-	tr	tr	tr
n-decane ($\times 10^{-6}$)	:	1.19	1.19	1.19	1.19

REACTION: D.44

TETRALIN/1,2,3,4-TETRAHYDROQUINOLINE (0.50 wt %)

HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 330°C

Feed composition:

tetralin - 35.21×10^{-6} mols

1,2,3,4-tetrahydroquinoline - 18.21×10^{-8} mols.

n-decane - 1.19×10^{-6} mols

impurities - 0.01 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	28.87	28.80	28.69	27.95
trans-decalin ($\times 10^{-6}$)	1.66	2.12	3.18	4.23
cis-decalin ($\times 10^{-6}$)	0.47	0.60	0.84	1.12
napthalene ($\times 10^{-6}$)	4.21	3.69	2.50	1.91
1,2,3,4-tetrahydro-quinoline ($\times 10^{-8}$)	8.20	6.84	5.82	4.33
o-propylaniline ($\times 10^{-8}$)	4.81	5.59	5.38	5.28
n-propylbenzene ($\times 10^{-8}$)	5.20	5.78	7.01	8.60
polymeric N-compound	-	-	tr	tr
n-decane ($\times 10^{-6}$)	1.19	1.19	1.19	1.18

REACTION: D.45.

TETRALIN/1,2,3,4-TETRAHYDROQUINOLINE (0.50 wt %)

HYDROGENATION

REACTION CONDITION:

Pressure - 1000psi

Temperature - 300°C

Feed composition:

tetralin - 35.21×10^{-6} mols

1,2,3,4-tetrahydroquinoline - 18.21×10^{-8} mols.

n-decane - 1.19×10^{-6} mols

impurities - 0.01 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	30.63	30.46	30.03	29.24
trans-decalin ($\times 10^{-6}$)	3.56	3.71	4.09	4.72
cis-decalin ($\times 10^{-6}$)	1.02	1.04	1.09	1.25
napthalene ($\times 10^{-6}$)	-	-	-	-
1,2,3,4-tetrahydro-quinoline ($\times 10^{-8}$)	10.58	9.93	7.72	6.50
o-propylaniline ($\times 10^{-8}$)	4.53	4.67	5.83	6.24
n-propylbenzene ($\times 10^{-8}$)	3.10	3.61	4.66	5.47
polymeric N-compound	-	tr	tr	tr
n-decane ($\times 10^{-6}$)	1.19	1.19	1.19	1.19

REACTION: D.46.m

TETRALIN/1,2,3,4-TETRAHYDROQUINOLINE (0.50 wt %)

HYDROGENATION

REACTION CONDITION:

Pressure - 1000psi

Temperature - 315°C

Feed composition:

tetralin - 35.21×10^{-6} mols

1,2,3,4-tetrahydroquinoline - 18.21×10^{-8} mols.

n-decane - 1.19×10^{-6} mols

impurities - 0.01 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	29.51	29.24	28.42	27.08
trans-decalin ($\times 10^{-6}$)	4.45	4.66	5.36	6.42
cis-decalin ($\times 10^{-6}$)	1.25	1.31	1.43	1.71
napthalene ($\times 10^{-6}$)	-	-	-	-
1,2,3,4-tetrahydro-quinoline ($\times 10^{-8}$)	9.45	8.15	7.07	5.22
o-propylaniline ($\times 10^{-8}$)	5.09	5.91	5.79	5.66
n-propylbenzene ($\times 10^{-8}$)	3.67	4.15	5.35	7.33
polymeric N-compound	-	-	tr	tr
n-decane ($\times 10^{-6}$)	1.19	1.18	1.19	1.19

REACTION: D.47.

TETRALIN/1,2,3,4-TETRAHYDROQUINOLINE (0.50 wt %)

HYDROGENATION

REACTION CONDITION:

Pressure - 1000psi

Temperature - 324°C

Feed composition:

tetralin - 35.21×10^{-6} mols

1,2,3,4-tetrahydroquinoline - 18.21×10^{-8} mols.

n-decane - 1.19×10^{-6} mols

impurities - 0.01 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($x10^{-6}$)	:	26.73	26.27	25.23	23.34
trans-decalin ($x10^{-6}$)	:	6.61	6.97	7.88	9.50
cis-decalin ($x10^{-6}$)	:	1.87	1.97	2.10	2.37
napthalene ($x10^{-6}$)	:	-	-	-	-
1,2,3,4-tetrahydro-quinoline($x10^{-8}$)	:	8.66	7.34	6.02	4.21
o-propylaniline($x10^{-8}$)	:	4.87	5.54	5.34	4.75
n-propylbenzene($x10^{-8}$)	:	4.68	5.33	6.85	9.25
polymeric N-compound	:	-	-	-	tr
n-decane ($x10^{-6}$)	:	1.19	1.19	1.19	1.19

REACTION: D.48.

TETRALIN/1,2,3,4-TETRAHYDROQUINOLINE (0.50 wt %)

HYDROGENATION

REACTION CONDITION:

Pressure - 1000psi

Temperature - 330°C

Feed composition:

tetralin - 35.21×10^{-6} mols

1,2,3,4-tetrahydroquinoline - 18.21×10^{-8} mols.

n-decane - 1.19×10^{-6} mols

impurities - 0.01 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($x10^{-6}$)	26.66	26.23	25.32	22.83
trans-decalin ($x10^{-6}$)	6.67	7.00	7.81	9.90
cis-decalin ($x10^{-6}$)	1.88	1.98	2.08	2.48
napthalene ($x10^{-6}$)	-	-	-	-
1,2,3,4-tetrahydro-quinoline($x10^{-8}$)	8.15	6.67	5.37	3.42
o-propylaniline($x10^{-8}$)	4.78	5.45	4.96	4.18
n-propylbenzene($x10^{-8}$)	5.28	6.09	7.88	10.61
polymeric N-compound	-	-	-	-
n-decane ($x10^{-6}$)	1.18	1.19	1.19	1.19

REACTION: D.49.

TETRALIN/1,2,3,4-TETRAHYDROQUINOLINE (0.50 wt %) /DIBENZOFURAN (1.25 wt %) HYDROGENATION.

REACTION CONDITION:

Pressure - 500 psi

Temperature - 300°C

Feed composition:

tetralin - 34.71×10^{-6} mols

1,2,3,4-tetrahydroquinoline - 18.21×10^{-8} mols

dibenzofuran - 36.04×10^{-8} mols

n-decane - 1.23×10^{-6} mols

impurities - 0.02 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($x10^{-6}$)	33.28	33.10	32.74	32.74
trans-decalin ($x10^{-6}$)	1.12	1.26	1.56	2.15
cis-decalin ($x10^{-6}$)	0.31	0.35	0.41	0.57
napthalene ($x10^{-6}$)	-	-	-	-
1,2,3,4-tetrahydro-quinoline ($x10^{-8}$)	10.68	10.27	8.32	6.95
o-propylaniline($x10^{-8}$)	4.57	4.83	6.27	6.68
n-propylbenzene($x10^{-8}$)	2.96	3.11	3.62	4.58
dibenzofuran ($x10^{-8}$)	30.76	30.61	29.98	29.08
cyclohexylbenzene($x10^{-8}$)	5.27	5.43	6.05	6.95
dicyclohexyl ($x10^{-8}$)	-	-	-	-
polymeric N-compound	-	-	-	-
n-decane ($x10^{-6}$)	1.23	1.23	1.22	1.23

REACTION: D.50.

TETRALIN/1,2,3,4-TETRAHYDROQUINOLINE (0.50 wt %) /DIBENZOFURAN (1.25 wt %) HYDROGENATION.

REACTION CONDITION:

Pressure - 500 psi

Temperature - 315°C

Feed composition:

tetralin - 34.71×10^{-6} mols

1,2,3,4-tetrahydroquinoline - 18.21×10^{-8} mols

dibenzofuran - 36.04×10^{-8} mols

n-decane - 1.23×10^{-6} mols

impurities - 0.02 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	30.75	30.55	30.10	29.59
trans-decalin ($\times 10^{-6}$)	1.42	1.65	2.14	3.10
cis-decalin ($\times 10^{-6}$)	0.40	0.46	0.57	0.82
napthalene ($\times 10^{-6}$)	2.14	2.05	1.90	1.20
1,2,3,4-tetrahydro-quinoline ($\times 10^{-8}$)	8.92	7.83	7.02	5.47
o-propylaniline ($\times 10^{-8}$)	4.80	5.67	5.74	5.93
n-propylbenzene ($\times 10^{-8}$)	4.49	4.71	5.45	6.81
dibenzofuran ($\times 10^{-8}$)	30.06	29.80	28.51	27.35
cyclohexylbenzene ($\times 10^{-8}$)	5.98	6.24	7.53	8.69
dicyclohexyl ($\times 10^{-8}$)	-	-	-	-
polymeric N-compound	-	-	-	-
n-decane ($\times 10^{-6}$)	1.23	1.23	1.23	1.23

REACTION: D.51.

TETRALIN/1,2,3,4-TETRAHYDROQUINOLINE (0.50 wt %) /DIBENZOFURAN (1.25 wt %) HYDROGENATION.

REACTION CONDITION:

Pressure - 500 psi

Temperature - 324°C

Feed composition:

tetralin - 34.71×10^{-6} mols

1,2,3,4-tetrahydroquinoline - 18.21×10^{-8} mols

dibenzofuran - 36.04×10^{-8} mols

n-decane - 1.23×10^{-6} mols

impurities - 0.02 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	28.82	28.69	28.21	27.44
trans-decalin ($\times 10^{-6}$)	1.65	1.97	2.67	4.07
cis-decalin ($\times 10^{-6}$)	0.47	0.56	0.71	1.01
napthalene ($\times 10^{-6}$)	3.77	3.49	3.12	2.18
1,2,3,4-tetrahydro-quinoline ($\times 10^{-8}$)	8.38	7.30	6.29	4.80
o-propylaniline($\times 10^{-8}$)	4.71	5.50	5.58	5.42
n-propylbenzene($\times 10^{-8}$)	5.12	5.41	6.34	7.99
dibenzofuran ($\times 10^{-8}$)	28.85	28.45	26.88	24.71
cyclohexylbenzene($\times 10^{-8}$)	7.19	7.59	9.17	11.33
dicyclohexyl ($\times 10^{-8}$)	-	-	-	-
polymeric N-compound	-	-	-	-
n-decane ($\times 10^{-6}$)	1.23	1.22	1.23	1.23

REACTION: D.52.

TETRALIN/1,2,3,4-TETRAHYDROQUINOLINE (0.50 wt %) /DIBENZOFURAN (1.25 wt %) HYDROGENATION.

REACTION CONDITION:

Pressure - 500 psi

Temperature - 330°C

Feed composition:

tetralin - 34.71×10^{-6} mols

1,2,3,4-tetrahydroquinoline - 18.21×10^{-8} mols

dibenzofuran - 36.04×10^{-8} mols

n-decane - 1.23×10^{-6} mols

impurities - 0.02 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($x10^{-6}$)	27.85	27.79	27.49	26.10
trans-decalin ($x10^{-6}$)	1.88	2.28	3.137	4.82
cis-decalin ($x10^{-6}$)	0.53	0.64	0.83	1.21
napthalene ($x10^{-6}$)	4.45	4.00	3.26	2.58
1,2,3,4-tetrahydro-quinoline ($x10^{-8}$)	8.06	6.85	5.90	4.23
o-propylaniline($x10^{-8}$)	4.74	5.60	5.45	5.16
n-propylbenzene($x10^{-8}$)	5.41	5.76	6.86	8.82
dibenzofuran ($x10^{-8}$)	27.84	27.37	25.52	22.99
cyclohexylbenzene($x10^{-8}$)	8.20	8.67	10.52	13.05
dicyclohexyl ($x10^{-8}$)	-	-	-	-
polymeric N-compound	-	-	-	-
n-decane ($x10^{-6}$)	1.23	1.23	1.23	1.22

REACTION: D.53.

TETRALIN/1,2,3,4-TETRAHYDROQUINOLINE (0.50 wt %) /DIBENZOFURAN (1.25 wt %) HYDROGENATION.

REACTION CONDITION:

Pressure - 1000psi

Temperature - 301°C

Feed composition:

tetralin - 34.71×10^{-6} mols

1,2,3,4-tetrahydroquinoline - 18.21×10^{-8} mols

dibenzofuran - 36.04×10^{-8} mols

n-decane - 1.23×10^{-6} mols

impurities - 0.02 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($x10^{-6}$)	29.97	29.66	29.00	27.69
trans-decalin ($x10^{-6}$)	3.70	3.94	4.51	5.55
cis-decalin ($x10^{-6}$)	1.04	1.11	1.20	1.47
napthalene ($x10^{-6}$)	-	-	-	-
1,2,3,4-tetrahydro-quinoline ($x10^{-8}$)	10.37	10.00	7.87	6.23
o-propylaniline($x10^{-8}$)	4.44	4.71	5.93	5.98
n-propylbenzene($x10^{-8}$)	3.40	3.50	4.41	6.00
dibenzofuran ($x10^{-8}$)	30.55	30.33	29.47	28.23
cyclohexylbenzene($x10^{-8}$)	5.49	5.71	6.57	7.81
dicyclohexyl ($x10^{-8}$)	-	-	-	tr
polymeric N-compound	-	-	-	-
n-decane ($x10^{-6}$)	1.23	1.23	1.22	1.23

REACTION: D.54.

TETRALIN/1,2,3,4-TETRAHYDROQUINOLINE (0.50 wt %) /DIBENZOFURAN (1.25 wt %) HYDROGENATION.

REACTION CONDITION:

Pressure - 1000psi

Temperature - 315°C

Feed composition:

tetralin - 34.71×10^{-6} mols

1,2,3,4-tetrahydroquinoline - 18.21×10^{-8} mols

dibenzofuran - 36.04×10^{-8} mols

n-decane - 1.23×10^{-6} mols

impurities - 0.02 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($x10^{-6}$)	28.84	28.34	27.31	25.28
trans-decalin ($x10^{-6}$)	4.58	4.97	5.85	7.45
cis-decalin ($x10^{-6}$)	1.29	1.40	1.55	1.98
napthalene ($x10^{-6}$)	-	-	-	-
1,2,3,4-tetrahydro-quinoline ($x10^{-8}$)	8.87	7.70	6.66	4.80
o-propylaniline($x10^{-8}$)	4.78	5.58	5.45	5.21
n-propylbenzene($x10^{-8}$)	4.56	4.93	6.10	8.20
dibenzofuran ($x10^{-8}$)	29.55	29.17	27.62	25.47
cyclohexylbenzene($x10^{-8}$)	6.49	6.87	8.42	10.15
dicyclohexyl ($x10^{-8}$)	tr	tr	tr	0.42
polymeric N-compound	-	-	-	-
n-decane ($x10^{-6}$)	1.23	1.23	1.23	1.22

REACTION: D.55.

TETRALIN/1,2,3,4-TETRAHYDROQUINOLINE (0.50 wt %) /DIBENZOFURAN (1.25 wt %) HYDROGENATION.

REACTION CONDITION:

Pressure - 1000psi

Temperature - 324°C

Feed composition:

tetralin - 34.71×10^{-6} mols

1,2,3,4-tetrahydroquinoline - 18.21×10^{-8} mols

dibenzofuran - 36.04×10^{-8} mols

n-decane - 1.23×10^{-6} mols

impurities - 0.02 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($x10^{-6}$)	25.99	25.37	24.11	21.68
trans-decalin ($x10^{-6}$)	6.80	7.29	8.37	10.42
cis-decalin ($x10^{-6}$)	1.92	2.05	2.23	2.61
napthalene ($x10^{-6}$)	-	-	-	-
1,2,3,4-tetrahydro-quinoline ($x10^{-8}$)	8.25	7.06	5.74	3.89
o-propylaniline($x10^{-8}$)	4.64	5.32	5.09	4.39
n-propylbenzene($x10^{-8}$)	5.32	5.83	7.38	9.93
dibenzofuran ($x10^{-8}$)	28.64	28.07	25.88	22.96
cyclohexylbenzene($x10^{-8}$)	7.40	7.97	9.75	12.56
dicyclohexyl ($x10^{-8}$)	tr	tr	0.41	0.52
polymeric N-compound	-	-	-	-
n-decane ($x10^{-6}$)	1.23	1.22	1.23	1.23

REACTION: D.56.

TETRALIN/1,2,3,4-TETRAHYDROQUINOLINE (0.50 wt %) /DIBENZOFURAN (1.25 wt %) HYDROGENATION.

REACTION CONDITION:

Pressure - 1000psi

Temperature - 330°C

Feed composition:

tetralin - 34.71×10^{-6} mols

1,2,3,4-tetrahydroquinoline - 18.21×10^{-8} mols

dibenzofuran - 36.04×10^{-8} mols

n-decane - 1.23×10^{-6} mols

impurities - 0.02 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($x10^{-6}$)	25.81	25.06	23.55	20.69
trans-decalin ($x10^{-6}$)	6.94	7.53	8.82	11.22
cis-decalin ($x10^{-6}$)	1.96	2.12	2.34	2.80
napthalene ($x10^{-6}$)	-	-	-	-
1,2,3,4-tetrahydro-quinoline ($x10^{-8}$)	7.86	6.55	5.23	3.20
o-propylaniline($x10^{-8}$)	4.62	5.35	4.83	3.92
n-propylbenzene($x10^{-8}$)	5.73	6.31	8.15	11.09
dibenzofuran ($x10^{-8}$)	27.72	27.05	24.44	21.01
cyclohexylbenzene($x10^{-8}$)	8.32	8.63	11.19	14.43
dicyclohexyl ($x10^{-8}$)	tr	0.36	0.41	0.60
polymeric N-compound	-	-	-	-
n-decane ($x10^{-6}$)	1.23	1.23	1.23	1.23

REACTION: D.57.

TETRALIN/o-PROPYLANILINE (0.47 wt %) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 300°C

Feed composition:

tetralin - 35.22×10^{-6} mols

o-propylaniline - 16.87×10^{-8} mols

impurities - 0.01 wt.%

n-decane - 1.19×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	33.64	33.53	33.09	32.44
trans-decalin ($\times 10^{-6}$)	1.26	1.35	1.73	2.25
cis-decalin ($\times 10^{-6}$)	0.32	0.34	0.40	0.53
napthalene ($\times 10^{-6}$)	-	-	-	-
o-propylaniline ($\times 10^{-8}$)	14.13	13.91	13.55	12.71
n-propylbenzene ($\times 10^{-8}$)	2.73	2.96	3.31	4.15
polymeric N-compound	-	-	-	-
n-decane ($\times 10^{-6}$)	1.19	1.19	1.19	1.18

REACTION: D.58.

TETRALIN/o-PROPYLANILINE (0.47 wt %) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 315°C

Feed composition:

tetralin - 35.22×10^{-6} mols

o-propylaniline - 16.87×10^{-8} mols

impurities - 0.01 wt.%

n-decane - 1.19×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	:	30.75	30.66	30.32	29.60
trans-decalin ($\times 10^{-6}$)	:	1.61	1.75	2.34	3.18
cis-decalin ($\times 10^{-6}$)	:	0.40	0.44	0.55	0.82
napthalene ($\times 10^{-6}$)	:	2.46	2.36	2.00	1.68
o-propylaniline ($\times 10^{-8}$)	:	12.60	12.28	11.80	10.66
n-propylbenzene ($\times 10^{-8}$)	:	4.26	4.58	5.06	6.21
polymeric N-compound	:	-	-	-	-
n-decane ($\times 10^{-6}$)	:	1.19	1.19	1.18	1.19

REACTION: D.59.

TETRALIN/o-PROPYLANILINE (0.47 wt %) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 324°C

Feed composition:

tetralin - 35.22×10^{-6} mols

o-propylaniline - 16.87×10^{-8} mols

impurities - 0.01 wt.%

n-decane - 1.19×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	:	29.49	29.30	28.61	27.93
trans-decalin ($\times 10^{-6}$)	:	1.83	2.05	2.92	4.13
cis-decalin ($\times 10^{-6}$)	:	0.46	0.51	0.78	0.97
napthalene ($\times 10^{-6}$)	:	3.44	3.36	3.01	2.18
o-propylaniline ($\times 10^{-8}$)	:	11.94	11.54	10.85	9.51
n-propylbenzene ($\times 10^{-8}$)	:	4.93	5.33	6.01	7.36
polymeric N-compound	:	-	-	-	-
n-decane ($\times 10^{-6}$)	:	1.19	1.18	1.19	1.19

REACTION: D.60.

TETRALIN/o-PROPYLANILINE (0.47 wt %) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 330°C

Feed composition:

tetralin - 35.22×10^{-6} mols

o-propylaniline - 16.87×10^{-8} mols

impurities - 0.01 wt.%

n-decane - 1.19×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	: 4.09	3.63	2.62	1.75
1/WHSV	: 0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	: 32.62	32.15	30.98	29.30
trans-decalin ($\times 10^{-6}$)	: 2.08	2.45	3.43	4.79
cis-decalin ($\times 10^{-6}$)	: 0.58	0.61	0.80	1.12
napthalene ($\times 10^{-6}$)	: 4.82	4.56	4.13	2.91
o-propylaniline ($\times 10^{-8}$)	: 11.64	11.10	10.33	8.72
n-propylbenzene ($\times 10^{-8}$)	: 5.23	5.76	6.52	8.14
polymeric N-compound	: -	-	-	-
n-decane ($\times 10^{-6}$)	: 1.18	1.19	1.19	1.19

REACTION: D.61.

TETRALIN/o-PROPYLANILINE (0.47 wt %) HYDROGENATION

REACTION CONDITION:

Pressure - 1000psi

Temperature - 300°C

Feed composition:

tetralin - 35.22×10^{-6} mols

o-propylaniline - 16.87×10^{-8} mols

impurities - 0.01 wt.%

n-decane - 1.19×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	:	30.28	30.14	29.56	28.72
trans-decalin ($\times 10^{-6}$)	:	3.94	4.06	4.52	5.26
cis-decalin ($\times 10^{-6}$)	:	0.99	1.02	1.13	1.23
napthalene ($\times 10^{-6}$)	:	-	-	-	-
o-propylaniline ($\times 10^{-8}$)	:	13.78	13.51	12.80	11.63
n-propylbenzene ($\times 10^{-8}$)	:	3.09	3.35	4.07	5.22
polymeric N-compound	:	-	-	-	-
n-decane ($\times 10^{-6}$)	:	1.19	1.19	1.19	1.19

REACTION: D.62.

TETRALIN/o-PROPYLANILINE (0.47 wt %) HYDROGENATION

REACTION CONDITION:

Pressure - 1000psi

Temperature - 315°C

Feed composition:

tetralin - 35.22×10^{-6} mols

o-propylaniline - 16.87×10^{-8} mols

impurities - 0.01 wt.%

n-decane - 1.19×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	:	28.80	28.54	27.55	26.08
trans-decalin ($\times 10^{-6}$)	:	5.13	5.34	6.21	7.39
cis-decalin ($\times 10^{-6}$)	:	1.28	1.33	1.46	1.73
napthalene ($\times 10^{-6}$)	:	-	-	-	-
o-propylaniline ($\times 10^{-8}$)	:	12.43	12.0L7	10.96	9.32
n-propylbenzene ($\times 10^{-8}$)	:	4.43	4.80	5.90	7.53
polymeric N-compound	:	-	-	-	-
n-decane ($\times 10^{-6}$)	:	1.19	1.19	1.19	1.19

REACTION: D.63.

TETRALIN/o-PROPYLANILINE (0.47 wt %) HYDROGENATION

REACTION CONDITION:

Pressure - 1000psi

Temperature - 325°C

Feed composition:

tetralin - 35.22×10^{-6} mols

o-propylaniline - 16.87×10^{-8} mols

impurities - 0.01 wt.%

n-decane - 1.19×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	: 4.09	3.63	2.62	1.75
1/WHSV	: 0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	: 26.05	25.64	24.45	22.38
trans-decalin ($\times 10^{-6}$)	: 7.33	7.66	8.72	10.39
cis-decalin ($\times 10^{-6}$)	: 1.83	1.92	2.04	2.44
napthalene ($\times 10^{-6}$)	: -	-	-	-
o-propylaniline ($\times 10^{-8}$)	: 11.56	11.01	9.67	7.63
n-propylbenzene ($\times 10^{-8}$)	: 5.31	5.85	7.20	9.24
polymeric N-compound	: -	-	-	-
n-decane ($\times 10^{-6}$)	: 1.19	1.19	1.19	1.19

REACTION: D.64.

TETRALIN/o-PROPYLANILINE (0.47 wt %) HYDROGENATION

REACTION CONDITION:

Pressure - 1000psi

Temperature - 331°C

Feed composition:

tetralin - 35.22×10^{-6} mols

o-propylaniline - 16.87×10^{-8} mols

impurities - 0.01 wt.%

n-decane - 1.19×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	:	4.09	3.63	2.62	1.75
1/WHSV	:	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	:	25.89	25.23	24.24	21.88
trans-decalin ($\times 10^{-6}$)	:	7.46	7.98	8.89	10.80
cis-decalin ($\times 10^{-6}$)	:	1.86	1.99	2.09	2.53
napthalene ($\times 10^{-6}$)	:	-	-	-	-
o-propylaniline ($\times 10^{-8}$)	:	11.16	10.51	8.87	6.55
n-propylbenzene ($\times 10^{-8}$)	:	5.70	6.36	8.00	10.32
polymeric N-compound	:	-	-	-	-
n-decane ($\times 10^{-6}$)	:	1.19	1.18	1.19	1.19

REACTION: D.65.

TETRALIN/o-PROPYLANILINE (0.47 wt %)/DIBENZOFURAN(1.25wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 300°C

Feed composition:

tetralin - 34.76×10^{-6} mols

o-propylaniline - 16.87×10^{-8} mols

dibenzofuran- 36.04×10^{-8} mols

impurities - 0.02 wt.%

n-decane - 1.19×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	33.12	32.98	32.51	31.73
trans-decalin ($\times 10^{-6}$)	1.30	1.42	1.82	2.45
cis-decalin ($\times 10^{-6}$)	0.33	0.36	0.43	0.57
napthalene ($\times 10^{-6}$)	-	-	-	-
o-propylaniline ($\times 10^{-8}$)	14.12	13.98	13.52	12.63
n-propylbenzene ($\times 10^{-8}$)	2.74	2.88	3.35	4.24
dibenzofuran ($\times 10^{-8}$)	30.76	30.61	29.98	29.08
cyclohexylbenzene (10^{-8})	5.27	5.43	6.05	6.95
dicyclohexyl ($\times 10^{-8}$)	-	-	-	-
polymeric N-compound	-	-	-	-
n-decane ($\times 10^{-6}$)	1.19	1.19	1.18	1.19

REACTION: D.66.

TETRALIN/o-PROPYLANILINE (0.47 wt %)/DIBENZOFURAN(1.25wt%)-HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 315°C

Feed composition:

tetralin - 34.76×10^{-6} mols

o-propylaniline - 16.87×10^{-8} mols

dibenzofuran- 36.04×10^{-8} mols

impurities - 0.02 wt.%

n-decane - 1.19×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	30.29	30.10	29.63	28.62
trans-decalin ($\times 10^{-6}$)	1.61	1.81	2.45	3.48
cis-decalin ($\times 10^{-6}$)	0.40	0.45	0.58	0.82
napthalene ($\times 10^{-6}$)	2.46	2.40	2.10	1.84
o-propylaniline ($\times 10^{-8}$)	12.70	12.50	11.82	10.56
n-propylbenzene ($\times 10^{-8}$)	4.16	4.36	5.05	6.31
dibenzofuran ($\times 10^{-8}$)	30.06	29.80	28.51	27.35
cyclohexylbenzene (10^{-8})	5.98	6.24	7.53	8.69
dicyclohexyl ($\times 10^{-8}$)	-	-	-	-
polymeric N-compound	-	-	-	-
n-decane ($\times 10^{-6}$)	1.19	1.19	1.19	1.18

REACTION: D.67.

TETRALIN/o-PROPYLANILINE (0.47 wt %)/DIBENZOFURAN(1.25wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 324°C

Feed composition:

tetralin - 34.76×10^{-6} mols

o-propylaniline - 16.87×10^{-8} mols

dibenzofuran- 36.04×10^{-8} mols

impurities - 0.02 wt.%

n-decane - 1.19×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	28.88	28.70	28.02	27.08
trans-decalin ($\times 10^{-6}$)	1.86	2.13	3.01	4.36
cis-decalin ($\times 10^{-6}$)	0.47	0.53	0.70	1.02
napthalene ($\times 10^{-6}$)	3.50	3.40	3.03	2.30
o-propylaniline($\times 10^{-8}$)	12.13	11.86	10.99	9.47
n-propylbenzene($\times 10^{-8}$)	4.74	5.01	5.87	7.40
dibenzofuran ($\times 10^{-8}$)	28.85	28.45	26.88	24.71
cyclohexylbenzene(10^{-8})	7.19	7.59	9.17	11.33
dicyclohexyl ($\times 10^{-8}$)	-	-	-	-
polymeric N-compound	-	-	-	-
n-decane ($\times 10^{-6}$)	1.19	1.18	1.19	1.19

REACTION: D.68.

TETRALIN/o-PROPYLANILINE (0.47 wt %)/DIBENZOFURAN(1.25wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 330°C

Feed composition:

tetralin - 34.76×10^{-6} mols

o-propylaniline - 16.87×10^{-8} mols

dibenzofuran- 36.04×10^{-8} mols

impurities - 0.02 wt.%

n-decane - 1.19×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV :	4.09	3.63	2.62	1.75
1/WHSV :	0.24	0.28	0.38	0.57
tetralin ($x10^{-6}$) :	27.34	27.27	26.55	25.64
trans-decalin ($x10^{-6}$) :	2.08	2.39	3.39	4.95
cis-decalin ($x10^{-6}$) :	0.52	0.60	0.80	1.16
napthalene ($x10^{-6}$) :	4.82	4.50	4.02	3.01
o-propylaniline($x10^{-8}$):	11.86	11.53	10.52	8.70
n-propylbenzene($x10^{-8}$):	5.01	5.34	6.35	8.17
dibenzofuran ($x10^{-8}$) :	27.84	27.37	25.52	22.99
cyclohexylbenzene(10^{-8}):	8.20	8.67	10.52	13.05
dicyclohexyl ($x10^{-8}$) :	-	-	-	-
polymeric N-compound :	-	-	-	-
n-decane ($x10^{-6}$) :	1.19	1.19	1.19	1.18

REACTION: D.69.

TETRALIN/o-PROPYLANILINE (0.47 wt %)/DIBENZOFURAN(1.25wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 1000psi

Temperature - 300°C

Feed composition:

tetralin - 34.76×10^{-6} mols

o-propylaniline - 16.87×10^{-8} mols

dibenzofuran- 36.04×10^{-8} mols

impurities - 0.02 wt.%

n-decane - 1.19×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	29.82	29.62	29.01	28.01
trans-decalin ($\times 10^{-6}$)	3.95	4.21	4.76	5.91
cis-decalin ($\times 10^{-6}$)	0.99	1.05	1.19	1.39
napthalene ($\times 10^{-6}$)	-	-	-	-
o-propylaniline ($\times 10^{-8}$)	13.72	13.63	12.79	11.31
n-propylbenzene ($\times 10^{-8}$)	3.15	3.24	4.08	5.56
dibenzofuran ($\times 10^{-8}$)	30.55	30.33	29.47	28.23
cyclohexylbenzene (10^{-8})	5.49	5.71	6.57	7.81
dicyclohexyl ($\times 10^{-8}$)	-	-	-	-
polymeric N-compound	-	-	-	-
n-decane ($\times 10^{-6}$)	1.19	1.19	1.19	1.19

REACTION: D.70.

TETRALIN/o-PROPYLANILINE (0.47 wt %)/DIBENZOFURAN(1.25wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 1000psi

Temperature - 315°C

Feed composition:

tetralin - 34.76×10^{-6} mols

o-propylaniline - 16.87×10^{-8} mols

dibenzofuran- 36.04×10^{-8} mols

impurities - 0.02 wt.%

n-decane - 1.19×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	28.37	28.04	27.04	25.44
trans-decalin ($\times 10^{-6}$)	5.11	5.51	6.40	8.02
cis-decalin ($\times 10^{-6}$)	1.28	1.38	1.50	1.88
napthalene ($\times 10^{-6}$)	-	-	-	-
o-propylaniline($\times 10^{-8}$)	12.65	12.30	11.22	9.28
n-propylbenzene($\times 10^{-8}$)	4.22	4.57	5.65	7.59
dibenzofuran ($\times 10^{-8}$)	29.55	29.17	27.62	25.47
cyclohexylbenzene(10^{-8})	6.49	6.87	8.42	9.51
dicyclohexyl ($\times 10^{-8}$)	tr	tr	tr	1.06
polymeric N-compound	-	-	-	-
n-decane ($\times 10^{-6}$)	1.18	1.19	1.19	1.19

REACTION: D.71.

TETRALIN/o-PROPYLANILINE (0.47 wt %)/DIBENZOFURAN(1.25wt%) HYDROGENATION

REACTION CONDITION:

Pressure - 1000psi

Temperature - 325°C

Feed composition:

tetralin - 34.76×10^{-6} mols

o-propylaniline - 16.87×10^{-8} mols

dibenzofuran- 36.04×10^{-8} mols

impurities - 0.02 wt.%

n-decane - 1.19×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	25.65	25.23	23.96	21.97
trans-decalin ($\times 10^{-6}$)	7.29	7.78	8.91	10.88
cis-decalin ($\times 10^{-6}$)	1.82	1.95	2.09	2.55
napthalene ($\times 10^{-6}$)	-	-	-	-
o-propylaniline($\times 10^{-8}$)	11.94	11.47	10.05	7.67
n-propylbenzene($\times 10^{-8}$)	4.93	5.40	6.82	9.20
dibenzofuran ($\times 10^{-8}$)	28.64	28.07	25.88	22.96
cyclohexylbenzene(10^{-8})	7.40	7.97	9.14	11.77
dicyclohexyl ($\times 10^{-8}$)	tr	tr	1.02	1.31
polymeric N-compound	-	-	-	-
n-decane ($\times 10^{-6}$)	1.19	1.19	1.19	1.19

REACTION: D.72.

TETRALIN/o-PROPYLANILINE (0.47 wt %)/DIBENZOFURAN(1.25wt%)
HYDROGENATION

REACTION CONDITION:

Pressure - 1000psi

Temperature - 330°C

Feed composition:

tetralin - 34.76×10^{-6} mols

o-propylaniline - 16.87×10^{-8} mols

dibenzofuran- 36.04×10^{-8} mols

impurities - 0.02 wt.%

n-decane - 1.19×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
tetralin ($\times 10^{-6}$)	25.51	25.00	23.48	21.13
trans-decalin ($\times 10^{-6}$)	7.40	7.98	9.28	11.53
cis-decalin ($\times 10^{-6}$)	1.85	2.00	2.18	2.71
napthalene ($\times 10^{-6}$)	-	-	-	-
o-propylaniline($\times 10^{-8}$)	11.56	11.03	9.32	6.60
n-propylbenzene($\times 10^{-8}$)	5.31	5.84	7.55	10.27
dibenzofuran ($\times 10^{-8}$)	27.72	27.05	24.44	21.01
cyclohexylbenzene(10^{-8})	8.32	8.09	10.44	13.53
dicyclohexyl ($\times 10^{-8}$)	tr	0.90	1.16	1.50
polymeric N-compound	-	-	-	-
n-decane ($\times 10^{-6}$)	1.18	1.19	1.19	1.18

REACTION: D.73.

PURE 1,6-DIMETHYLNAPTHALENE HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 300°C

Feed composition:

1,6-dimethylnapthalene - 23.55×10^{-6} mols

n-decane - 8.19×10^{-6} mols

impurities - 0.12 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
1,6-dimethylnapthalene: ($\times 10^{-6}$)	19.16	16.95	12.93	7.48
1,6-dimethyl-(1,2,3,4-tetralin) ($\times 10^{-6}$)	1.59	2.31	3.73	5.53
1,6-dimethyl-(5,6,7,8-tetralin) ($\times 10^{-6}$)	2.42	3.76	5.83	8.29
1-methylnapthalene	-	-	-	-
dimethyldecalins($\times 10^{-6}$)	0.31	0.53	1.06	2.25
n-decane ($\times 10^{-6}$)	8.18	8.19	8.19	8.19

REACTION: D.74.

PURE 1,6-DIMETHYLNAPTHALENE HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 315°C

Feed composition:

1,6-dimethylnapthalene - 23.55×10^{-6} mols

n-decane - 8.19×10^{-6} mols

impurities - 0.12 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
1,6-dimethylnapthalene: ($\times 10^{-6}$)	18.78	15.21	9.55	3.73
1,6-dimethyl-(1,2,3,4-tetralin) ($\times 10^{-6}$)	1.71	2.88	4.86	6.33
1,6-dimethyl-(5,6,7,8-tetralin) ($\times 10^{-6}$)	2.68	4.71	7.60	10.32
1-methylnapthalene	-	-	-	-
dimethyldecalins($\times 10^{-6}$)	0.38	0.75	1.54	3.17
n-decane ($\times 10^{-6}$)	8.19	8.19	8.19	8.18

REACTION: D.75.

PURE 1,6-DIMETHYLNAPTHALENE HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 324°C

Feed composition:

1,6-dimethylnapthalene - 23.55×10^{-6} mols

n-decane - 8.19×10^{-6} mols

impurities - 0.12 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
1,6-dimethylnapthalene: ($x10^{-6}$)	17.90	13.39	7.06	1.94
1,6-dimethyl-(1,2,3,4-tetralin) ($x10^{-6}$)	2.00	3.66	5.61	6.32
1,6-dimethyl-(5,6,7,8-tetralin) ($x10^{-6}$)	3.14	5.48	8.41	9.89
1-methylnapthalene	-	-	-	tr
dimethyldecalins($x10^{-6}$)	0.51	1.02	2.47	5.40
n-decane ($x10^{-6}$)	8.19	8.18	8.19	8.19

REACTION: D.76.

PURE 1,6-DIMETHYLNAPTHALENE HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 330°C

Feed composition:

1,6-dimethylnapthalene - 23.55×10^{-6} mols

n-decane - 8.19×10^{-6} mols

impurities - 0.12 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
1,6-dimethylnapthalene: ($\times 10^{-6}$)	16.60	11.63	5.30	1.08
1,6-dimethyl-(1,2,3,4-tetralin) ($\times 10^{-6}$)	2.45	3.95	5.91	5.98
1,6-dimethyl-(5,6,7,8-tetralin) ($\times 10^{-6}$)	3.67	6.18	9.24	9.75
1-methylnapthalene	tr	tr	tr	tr
dimethyldecalins ($\times 10^{-6}$)	0.83	1.79	3.10	6.74
n-decane ($\times 10^{-6}$)	8.19	8.19	8.19	8.18

REACTION: D.77.

1,6-DIMETHYLNAPTHALENE/QUINOLINE (0.50 wt %) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 300°C

Feed composition:

1,6-dimethylnapthalene - 23.71×10^{-6} mols

quinoline - 18.78×10^{-8} mols

n-decane - 7.84×10^{-6} mols

impurities - 0.12 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
1,6-dimethylnapthalene: ($\times 10^{-6}$)	19.63	17.52	13.62	8.19
1,6-dimethyl-(1,2,3,4-tetralin) ($\times 10^{-6}$)	1.48	2.16	3.54	5.21
1,6-dimethyl-(5,6,7,8-tetralin) ($\times 10^{-6}$)	2.31	3.53	5.54	8.14
1-methylnapthalene	-	-	-	-
*dimethyldecalins				
*quinoline				
*1,2,3,4-tetrahydro-quinoline				
*o-propylaniline				
n-propylbenzene($\times 10^{-8}$)	2.76	2.97	3.41	4.27
polymeric N-compound	tr	tr	tr	tr
n-decane ($\times 10^{-6}$)	7.84	7.84	7.83	7.84

REACTION: D.78.

1,6-DIMETHYLNAPTHALENE/QUINOLINE (0.50 wt %) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 315°C

Feed composition:

1,6-dimethylnapthalene - 23.71×10^{-6} mols

quinoline - 18.78×10^{-8} mols

n-decane - 7.84×10^{-6} mols

impurities - 0.12 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
1,6-dimethylnapthalene: ($\times 10^{-6}$)	19.05	15.63	10.10	4.18
1,6-dimethyl-(1,2,3,4-tetralin) ($\times 10^{-6}$)	1.63	2.90	4.72	6.23
1,6-dimethyl-(5,6,7,8-tetralin) ($\times 10^{-6}$)	2.66	4.53	7.39	10.17
1-methylnapthalene	-	-	-	-
*dimethyldecalins				
*quinoline				
*1,2,3,4-tetrahydro-quinoline				
*o-propylaniline				
n-propylbenzene($\times 10^{-8}$)	4.38	4.69	5.33	6.53
polymeric N-compound	tr	tr	tr	tr
n-decane ($\times 10^{-6}$)	7.83	7.84	7.84	7.83

REACTION: D.79.

1,6-DIMETHYLNAPTHALENE/QUINOLINE (0.50 wt %) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 324°C

Feed composition:

1,6-dimethylnapthalene - 23.71×10^{-6} mols

quinoline - 18.78×10^{-8} mols

n-decane - 7.84×10^{-6} mols

impurities - 0.12 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
1,6-dimethylnapthalene: ($x10^{-6}$)	18.20	13.84	7.56	2.22
1,6-dimethyl-(1,2,3,4-tetralin) ($x10^{-6}$)	2.00	3.44	5.22	6.29
1,6-dimethyl-(5,6,7,8-tetralin) ($x10^{-6}$)	3.01	5.39	8.51	9.83
1-methylnapthalene	-	-	-	-
*dimethyldecalins				
*quinoline				
*1,2,3,4-tetrahydro-quinoline				
*o-propylaniline				
n-propylbenzene($x10^{-8}$)	5.12	5.52	6.34	7.86
polymeric N-compound	-	tr	tr	tr
n-decane ($x10^{-6}$)	7.84	7.84	7.84	7.83

REACTION: D.80.

1,6-DIMETHYLNAPTHALENE/QUINOLINE (0.50 wt %) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 330°C

Feed composition:

1,6-dimethylnapthalene - 23.71×10^{-6} mols

quinoline - 18.78×10^{-8} mols

n-decane - 7.84×10^{-6} mols

impurities - 0.12 wt %

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
1,6-dimethylnapthalene: ($\times 10^{-6}$)	16.93	12.08	5.73	1.27
1,6-dimethyl-(1,2,3,4-tetralin) ($\times 10^{-6}$)	2.33	3.76	5.82	5.97
1,6-dimethyl-(5,6,7,8-tetralin) ($\times 10^{-6}$)	3.64	6.13	9.10	9.74
1-methylnapthalene	-	-	-	-
*dimethyldecalins				
*quinoline				
*1,2,3,4-tetrahydro-quinoline				
*o-propylaniline				
n-propylbenzene($\times 10^{-8}$)	5.30	5.75	6.72	8.46
polymeric N-compound	-	tr	tr	tr
n-decane ($\times 10^{-6}$)	7.84	7.83	7.84	7.84

REACTION: D.81.

1,6-DIMETHYLNAPTHALENE/QUINOLINE (0.50 wt %)
DIBENZOFURAN (1.25 wt %) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 300°C

Feed composition:

1,6-dimethylnapthalene - 23.32×10^{-6} mols

quinoline - 18.78×10^{-8} mols

dibenzofuran - 36.04×10^{-8} mols

n-decane - 7.84×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
1,6-dimethylnapthalene: ($x10^{-6}$)	19.24	17.13	13.25	7.89
1,6-dimethyl-(1,2,3,4-tetralin) ($x10^{-6}$)	1.50	2.16	3.53	5.18
1,6-dimethyl-(5,6,7,8-tetralin) ($x10^{-6}$)	2.29	3.53	5.53	8.09
1-methylnapthalene	-	-	-	-
*dimethyldecalins				
*quinoline				
*1,2,3,4-tetrahydro-quinoline				
*o-propylaniline				
n-propylbenzene($x10^{-8}$)	2.81	3.03	3.50	4.41
dibenzofuran ($x10^{-8}$)	30.85	30.64	30.18	29.26
*cyclohexylbenzene				
*dicyclohexyl				
polymeric N-compound	-	-	-	-
n-decane ($x10^{-6}$)	7.84	7.84	7.83	7.84

REACTION: D.82.

1,6-DIMETHYLNAPTHALENE/QUINOLINE (0.50 wt %)
DIBENZOFURAN (1.25 wt %) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 317°C

Feed composition:

1,6-dimethylnapthalene - 23.32×10^{-6} mols

quinoline - 18.78×10^{-8} mols

dibenzofuran - 36.04×10^{-8} mols

n-decane - 7.84×10^{-6} mols

carbon-disulphide - 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
1,6-dimethylnapthalene ($\times 10^{-6}$)	18.68	15.19	9.37	3.59
1,6-dimethyl-(1,2,3,4-tetralin) ($\times 10^{-6}$)	1.67	2.92	4.84	6.47
1,6-dimethyl-(5,6,7,8-tetralin) ($\times 10^{-6}$)	2.60	4.57	7.58	10.11
1-methylnapthalene	-	-	-	-
*dimethyldecalins				
*quinoline				
*1,2,3,4-tetrahydro-quinoline				
*o-propylaniline				
n-propylbenzene ($\times 10^{-8}$)	4.56	4.91	5.65	7.03
dibenzofuran ($\times 10^{-8}$)	29.88	29.46	28.55	26.80
*cyclohexylbenzene				
*dicyclohexyl				
polymeric N-compound	-	-	-	-
n-decane ($\times 10^{-6}$)	7.84	7.84	7.83	7.84

REACTION: D.83.

1,6-DIMETHYLNAPTHALENE/QUINOLINE (0.50 wt %)
DIBENZOFURAN (1.25 wt %) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 324°C

Feed composition:

1,6-dimethylnapthalene	- 23.32×10^{-6} mols
quinoline	- 18.78×10^{-8} mols
dibenzofuran	- 36.04×10^{-8} mols
n-decane	- 7.84×10^{-6} mols
carbon-disulphide	- 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
1,6-dimethylnapthalene: ($x10^{-6}$)	17.84	13.54	7.37	2.15
1,6-dimethyl-(1,2,3,4-tetralin) ($x10^{-6}$)	1.95	3.50	5.29	6.03
1,6-dimethyl-(5,6,7,8-tetralin) ($x10^{-6}$)	3.04	5.25	8.27	9.84
1-methylnapthalene	-	-	-	-
*dimethyldecalins				
*quinoline				
*1,2,3,4-tetrahydro-quinoline				
*o-propylaniline				
n-propylbenzene($x10^{-8}$)	5.22	5.64	6.52	8.12
dibenzofuran ($x10^{-8}$)	28.98	28.43	27.27	25.06
*cyclohexylbenzene				
*dicyclohexyl				
polymeric N-compound	-	-	-	-
n-decane ($x10^{-6}$)	7.83	7.84	7.84	7.83

REACTION: D.84.

1,6-DIMETHYLNAPTHALENE/QUINOLINE (0.50 wt %)
DIBENZOFURAN (1.25 wt %) HYDROGENATION

REACTION CONDITION:

Pressure - 500 psi

Temperature - 330°C

Feed composition:

1,6-dimethylnapthalene	- 23.32×10^{-6} mols
quinoline	- 18.78×10^{-8} mols
dibenzofuran	- 36.04×10^{-8} mols
n-decane	- 7.84×10^{-6} mols
carbon-disulphide	- 0.1 mol %

Product composition:

WHSV	4.09	3.63	2.62	1.75
1/WHSV	0.24	0.28	0.38	0.57
1,6-dimethylnapthalene: ($\times 10^{-6}$)	16.58	11.83	5.61	1.24
1,6-dimethyl-(1,2,3,4-tetralin) ($\times 10^{-6}$)	2.31	3.91	5.73	6.03
1,6-dimethyl-(5,6,7,8-tetralin) ($\times 10^{-6}$)	3.62	5.68	8.97	9.43
1-methylnapthalene	-	-	-	-
*dimethyldecalins				
*quinoline				
*1,2,3,4-tetrahydro-quinoline				
*o-propylaniline				
n-propylbenzene ($\times 10^{-8}$)	5.44	5.94	7.00	8.87
dibenzofuran ($\times 10^{-8}$)	27.93	27.25	25.82	23.14
*cyclohexylbenzene				
*dicyclohexyl				
polymeric N-compound	-	-	-	-
n-decane ($\times 10^{-6}$)	7.84	7.84	7.83	7.84

APPENDIX B

ELEMENTAL ANALYSIS (C, H AND N) OF CATALYST SAMPLES

Notes

(i) Standard used: Cyclohexanone-2,4-dinitrophenylhydrazone,

m.wt. -278.27, $C_6H_{10}.N.NH.C_6H_3(NO_2)_2$.

C - 51.79%

H - 5.07%

N - 20.14%

(ii) Catalyst washing procedures:

(a) Washed with tetrahydrofuran and dried at 100°C.

(b) Washed with xylene/toluene and dried at 100°C.

Catalyst sample	C%	H%	N%	Washing procedure
(i) Unused	0	0	0	(a) and (b)
(ii) Aged - after high content of N_2 compound used	10	2.1	2.2	(a)
(iii) as in (ii)	4.5	0.2	0.1	(a) and (b)
(iv) New batch-150 hrs in operation	0.5	0.2	0	(a)
(v) New batch-700 hrs in operation and THQ feed used	2.3	0.6	0.5	(a)
(vi) as in (v)	1.2	0.1	trace	(a) and (b)
(vii) New batch-1000 hrs in operation	1.3	0.2	trace	(a) and (b)
(viii) New batch-1500 hrs in operation	1.35	0.2	trace	(a) and (b)

APPENDIX C

ANALYSED RESULTS FROM SCANNING ELECTRON MICROSCOPY

INCORPORATING AN X-RAY ENERGY DISPERSIVE ANALYTICAL SYSTEM

```
 ENERGY     RES      AREA
-   5.7  120.43     80597
TOTAL AREA=    121861
......

FIT INDEX= 3.08

ELMT  APP.CONC    ERROR(WT%)
 Ni     11.058       .264
 Ni     12.826      1.281 not used for ZAF
 Mo     33.606       .399
[ 1 2 3 4 5 ZAF'S]

20.00 kV  TILT=   .00 ELEV=35.00 AZIM=   .00 COSINE=1.000

Spectrum:  Ni-Mo (HSP), Thesis sample, batch A

All elmts analysed,NORMALISED

ELMT      ZAF     %ELMT      ATOM.%
NiK: 1 1.065     21.872     31.387
MoL: 1  .906     78.135     68.613
TOTAL            100.007    100.000
```

```
[ 1 2 3 4 5 ZAF'S]

20.00 kV  TILT=   .00 ELEV=35.00 AZIM=   .00 COSINE=1.000

Spectrum: Ni-Mo (HSP) Thesis sample, batch B

All elmts analysed,NORMALISED

ELMT      ZAF     %ELMT      ATOM.%
NiK: 1 1.064     22.607     32.309
MoL: 1  .903     77.400     67.691
TOTAL            100.006    100.000
```

```
-------------------------------------------------------------

                                        LIVETIME(spec.)=   100
 ENERGY     RES      AREA
-   5.8  120.33     81431
TOTAL AREA=    122804
......

FIT INDEX= 8.03

ELMT  APP.CONC    ERROR(WT%)
 Co     13.114       .254
 Mo     35.445       .396
[ 1 2 3 4 ZAF'S]

20.00 kV  TILT=   .00 ELEV=35.00 AZIM=   .00 COSINE=1.000

Spectrum:  Co-Mo (HSP), Thesis sample, batch A

All elmts analysed,NORMALISED

ELMT      ZAF     %ELMT      ATOM.%
CoK: 1 1.020     24.944     35.104
MoL: 1  .916     75.073     64.896
TOTAL           100.017    100.000
-------------------------------------------------------------

[ 1 2 ZAF'S]

20.00 kV  TILT=   .00 ELEV=35.00 AZIM=   .00 COSINE=1.000

Spectrum:  Co-Mo (HSP), Thesis sample, batch B

All elmts analysed

ELMT      ZAF     %ELMT      ATOM.%
CoK: 1 1.021     12.812     32.723
MoL: 1  .922     42.885     67.277
TOTAL            55.698    100.000
-------------------------------------------------------------
```

```
                                                LIVETIME(spec.)=    100
 ENERGY    RES      AREA
-   5.7  120.72    .79307
TOTAL AREA=    252295
......
Peak at     .88 keV omitted?
Peak at   13.80 keV omitted?

FIT INDEX= 1.52

ELMT  APP.CONC    ERROR(WT%)
 Co     11.250       .248
 Mo     37.347      1.871
 S      38.761       .980
[ 1 2 ZAF'S]

20.00 kV  TILT=   .00 ELEV=35.00 AZIM=   .00 COSINE=1.000

Spectrum:  Co-Mo (HSP), Institut sample

All elmts analysed

ELMT      ZAF     %ELMT      ATOM.%
CoK: 1   .915     12.310     11.970
MoL: 1   .906     41.556     24.820
S K: 1 1.099     35.366     63.210
TOTAL              89.233    100.000
-------------------------------------------------------------------

                                                LIVETIME(spec.)=    100
 ENERGY    RES      AREA
-   5.8  121.68    80136
TOTAL AREA=    246068
......
Peak at     .86 keV omitted?

FIT INDEX= 1.31

ELMT  APP.CONC    ERROR(WT%)
 Co     10.799       .245
 Mo     36.705      1.851
 S      37.992       .969
[ 1 2 ZAF'S]

20.00 kV  TILT=   .00 ELEV=35.00 AZIM=   .00 COSINE=1.000

Spectrum:  Co-Mo (CM), Institut sample

All elmts analysed

ELMT      ZAF     %ELMT      ATOM.%
CoK: 1   .915     11.820     11.747
MoL: 1   .907     40.869     24.950
S K: 1 1.100     34.651     63.303
TOTAL              87.340    100.000
-------------------------------------------------------------------
```