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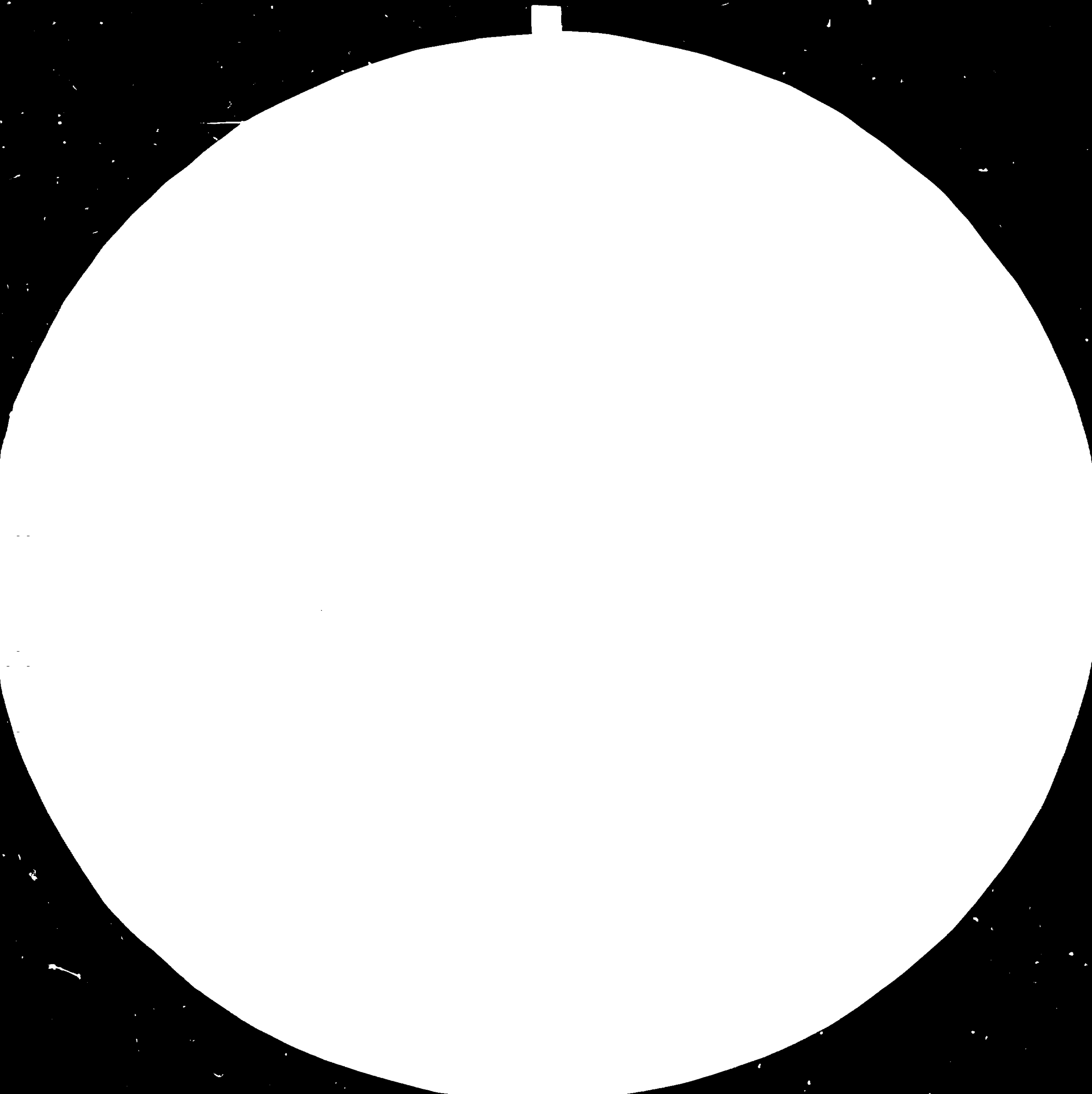
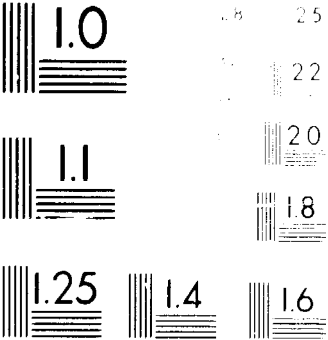
UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

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UNITED NATIONS INDUSTRIAL
DEVELOPMENT ORGANIZATION

August 1984
English

China.

TECHNOLOGIES OF DIRECT COAL LIQUEFACTION

DP/CPR/80/048

Technical Report*

Prepared for the Government of the People's Republic of China
by the United Nations Industrial Development Organization,
acting as executing agency for the United Nations Development Programme

Based on the work of

R. Staker, Consultant in Coal Conversion Technologies

and

M.J. Oliver, Consultant in Liquid Analysis

March 10 - 27, 1984

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1. NOTES BY ROBER STAKER

1.1. Chinese liquefaction program

The Chinese coal liquefaction program is part of an overall program designed to ensure adequate supplies of energy for all parts of the rapidly expanding Chinese economy. This program is set in terms of some years.

Presently known oil resources are considered relatively small, compared to the potential demand for liquid fuels. However, coal resources are known to be large and these offer an alternative source of liquid fuels via liquefaction.

The present coal utilisation plans contain the following activities which relate to coal liquefaction:

exploration and resource measurement,
evaluation of coal characteristics,
batch autoclave testing of selected coals,
continuous reactor testing of preferred coals,
upgrading of coal-derived liquids to specification fuels,
preparation of plant design and feasibility study.

This plan provides for an orderly progression of work. Each successive stage involves more complex technology which requires a bigger investment in equipment, methods and trained personnel. The gradual implementation of this plan will ensure wise use of people and equipment.

The program at CCMRI has now reached the stage of continuous reactor testing, four short runs having been completed. The batch autoclave work is well advanced and some 30-40 coals have been tested. No work has yet been done on liquid upgrading; this needs an adequate supply of coal-derived liquids from the continuous reactor. The design of a commercial-sized plant and the preparation of a feasibility study must await the successful completion of all the preceding stages of research.

12. Lectures and discussions

I presented four sessions of lectures, which were followed by a time of questions and answers, from 9.00 to 11.30. The following topics were presented:

Coal liquefaction research in Australia,
Coal liquefaction research at ACIRL,
Planning, running and interpretation.

These lectures were based on my knowledge and understanding of the aims and work of the various programs within Australia. Particular emphasis was placed on experience at ACIRL. Each lecture was attended by about 40 chemists and engineers. The lectures and discussions on general and detailed chemistry by Mr. Oliver provided a wider background to the chemical engineering presentations and alerted engineers to the vital importance of chemistry in understanding and evaluating liquefaction processes. Many topics were raised during the question sessions.

Two further discussion sessions were held with 15-20 engineers who asked many questions related to the details of the ACIRL experimental methods and equipment. The topics raised and discussed were wide-ranging and revealed much interest in practical matters. Temperature control, brown coal drying, red mud analysis, hydrogen consumption determination, slurry pump operations, and the comparison of CO-Steam and hydrogenation processes were some of the topics discussed.

The engineers revealed a clear understanding of the importance of recycle operation and the proper attainment of process and chemical stability. This was discussed at length - covering the sequential achievement of stable process conditions (temperature, pressure, solids concentration in reactor, etc.), stable production of recycle solvent production, stable recycle solvent quality (and indices of quality), and stable product oil yield and quality. Suitable analytical parameters were also discussed. Interest was expressed in several fundamental chemical engineering problems - gas and liquid flow in the reactor, and solids accumulation in the reactor - but ACIRL has virtually no experience in these matters because they are not included in the experimental program.

The lectures and discussions were concluded by two additional morning sessions of combined questions and answers in which the CCMRI program was outlined and final topics discussed.

Three volumes of Abstracts from recent Australian Workshops on Coal Liquefaction (6th, 7th and 8th) were presented to the Institute. These volumes record many of the major activities of the various liquefaction researchers with Australia. Three reports on work done at ACIRL will be sent from Australia; these discuss aspects of continuous reactor design, semi-continuous autoclave tests, and product oil analysis.

1.3. Comments on Chinese program

The general aims of the CCMRI program are most soundly based. The logical progression in the program is being put into effect.

The batch autoclave program has provided a good basis for the selection of coals for continuous reactor testing. The continuous reactor has only been used in once-through mode and the distillation equipment has not been commissioned yet. However, the practical experience gained to date is a good foundation for future work.

The following major steps by the Institute are required to allow the overall program to reach a successful conclusion. It is most probable that most of these steps are included in the Institute's forward planning.

1. Full commissioning of the continuous reactor.

2. Extended operation of the reactor under recycle conditions with recovery of product and recycle oils by distillation.

3. Development of fully experienced engineers and technicians able to understand, operate and maintain the continuous reactor.

4. Gradual improvement of the reactor facilities as limitations become obvious or are required to meet the special objectives of China's research priorities. One possible improvement is the installation of a plug-flow, long-tube, reactor vessel.

5. Training and development of a selected group of engineers to handle reactor dynamics, reaction kinetics, heat transfer calculations and other relevant chemical engineering topics. Such skills are essential if the data from the current small-scale experiments are to be used in commercial-scale designs.

6. Additional training of staff in the selection and use of catalysts for liquid upgrading to standard grade fuels (e.g. gasoline or diesel).

7. Commissioning and operation of the smaller (Xytel) reactor for liquid upgrading, using liquids produced by the larger coal-conversion reactor. This may require some plant changes such as the design and installation of a trickle-bed reactor.

8. Development of close co-operation with those groups within the Institute who are studying coal preparation and coal gasification. These are most important in determining the quality of coal fed to the conversion plant, the overall energy efficiency, and the supply of hydrogen and gaseous process fuels. It may be necessary to second a coal preparation engineer to the liquefaction team to facilitate the integration of coal preparation into the overall program.

9. Inclusion of design engineers and project planners in the liquefaction team (at an appropriate time) to assist in the plant design and project feasibility study.

1.4. Recommendations for future action

The long-term implementation will require specific action to ensure adequate staff training. Firstly, access to scientific literature (journals and text books) is necessary to enable staff members to gain the theoretical background which will be necessary to conduct studies on reactor dynamics etc. Such studies form a valid basis for the design of larger scale equipment from the results obtained in the present experimental units.

Secondly, provision should be made for overseas travel so that Chinese engineers (chemists) can attend selected conferences and especially visit and work in laboratories which use techniques relevant to the Chinese programs and needs. One or two months practical experience in an overseas laboratory would be more valuable than a similar time spent in visiting a large number of institutions.

Thirdly, the invitation of overseas workers to lecture, discuss and possibly work in the laboratories would enable expertise to be imparted to a large number of CMMRI staff under conditions most directly related to their work and needs. A four or five week visit, during an experimental run and the evaluation of the results, would be most valuable to both the Institute and the visitor who would learn details of the methods used at the Institute.

Lastly, some financial assistance may be needed to purchase additional equipment to supplement that now available. All such proposed purchases should be most carefully reviewed to ensure relevance and to avoid the proliferation of desirable but not necessarily essential equipment. Non-essential equipment can dilute the work effort of staff and cause neglect of essential items within the program. The purchase of additional equipment with internal Chinese funds should also be subject to vigorous review for the same reasons.

Careful adherence to the general principles which form the basis of the CCMRI program, gradual expansion of the skills of the various members of the liquefaction team, and adoption of the recommendations presented in this report will ensure that China develops an independent liquefaction technology capability. Provided that China builds up a general industrial capacity which is able to produce large compressors and pumps, large pressure vessels, high pressure valves and process control systems, the design, construction and operation of a complete coal liquefaction plant (with only limited involvement by overseas interests) will be a realistic goal. This may be 10-15 years in the future.

2. NOTES BY M.J. CLIVER

2.1. Introduction

I gave a series of lectures and discussions as required by the terms of my job description. My four formal lectures covered a variety of subjects covering the chemical analysis of products derived from coal hydrogenation experiments, and also some introductions to the kinds of chemical changes which occur during hydrogenation processes. The texts of these lectures are appended to this report.

Most of my topics were derived from personal experience with "continuous" reactor products, although the CCMRI has only recently started their research program with their two continuous reactor systems. Most of their work to date has been with "batch" reactor experiments.

Continuous reactor products have a more "advanced" chemical character than those derived from batch reactors. I attempted to show how chemical changes occur when a continuous reactor proceeds from a start-up condition to a stable physical and chemcial process. Some of my concepts appeared to be new to the CCMRI workers, particularly with reference to the accumulation of phenolic and saturated chemical species, and the typical changes in hydroaromatic species. Although some of my subjects involved sophisticated methods of analysis, I also showed how I have used quite simple techniques to estimate some important chemical parameters.

The question sessions following each lecture were vigorous, revealing a high degree of interest, intellect, and understanding. The sessions were attended by about forty key chemists and engineers.

Two days of discussion followed, where I gave short ad-lib addresses on invited topics, to mainly an audience of chemists. The subjects were essentially amplifications of the formal lecture subjects.

A further two days were spent with the combined audience, where myself and Dr. Staker exchanged a variety of technical data.

2.2. Conclusions

- I feel that I have stimulated interest in some new, but simple, methods of analysis which will help the CCMRI workers to understand the chemistry of their experimentation more fully.

- Great interest was shown in Simulated Distillation, but their work was not yet far advanced, so that I was not able to give them proper advice on the interpretation of their own results.

- The analysis of gases created much discussion, but I was ill-prepared to give necessary detailed information because it was not one of my lecture topics.

- GC and GCMS techniques generated many questions, especially with respect to the analysis of hydroaromatic compounds. The acquisition of a GCMS system would allow the CCMRI to study this subject in addition to having at hand a powerful tool for studying many other important chemical classes unique to coal-derived liquids.

- Considerable attention was paid to explanations of the physical and chemical changes leading to stable operation of continuous reactor systems. This should prepare the CCMRI chemists to decide what type of chemical analyses to perform, and when to select samples.

On-the-spot assessment of the CCMRI's chemistry resources and needs has obligated me to send further detailed practical information when I return to Australia, particularly with respect to the identification of compound classes by GCMS, and to Simulated Distillation Software specifically for the brand of instrumentation used at CCMRI.

2.3. Recommendations

The CCMRI should be given suitable financial assistance for:

(i) The acquisition of proprietary software and factory manufactured columns for Simulated Distillation analysis. This technique will become more useful when the CCMRI commission their distillation equipment.

(ii) The acquisition of suitable accessories for the improvement of gas analysis techniques.

(iii) The acquisition of a suitable GCMS system, and the proper training of one or more system operators. Attention should be paid to the relatively high cost of maintenance of such a system, and the convenient availability of service facilities.

(iv) International travel, to allow attendance of CCMRI personnel at pertinent conferences, or to visit relevant co-operative installations, or to bring suitably skilled experts to Beijing.

3. Acknowledgement

Both UNIDO and CCMRI personnel gave the utmost assistance and consideration at all times. Their efforts made our visit to Beijing both technically valuable and personally enjoyable.

ANNEX I

SUMMARY OF LECTURES BY R. STAKER

COPIES OF OVERHEAD TRANSPARENCIES

COAL LIQUEFACTION RESEARCH IN AUSTRALIA

Research may be divided into three different levels - fundamental, applied and pilot-plant. This division will be clearly seen when the coal liquefaction activities of individual centres of study are reviewed. The funding of such work may be classified as either government or company sponsored.

Government sponsored work is sometimes conducted within government controlled laboratories. Often, it is conducted in outside laboratories under programs which either support the utilization of the coal resources of a state or study the production of liquid fuels via particular processes from selected coals.

The Federal government of Australia supports coal liquefaction in two different ways. Firstly, the government supports the whole system of CSIRO laboratories which have been in operation for many years and have consistently included the characterization and origin of coals in their fundamental research programs (in addition to agriculture, animal husbandry, mineral resources and processing etc). Current CSIRO programs now include many within the energy area.

Secondly, the government has introduced a program for the support of energy based programs, covering such diverse activities as coal mining, coal liquefaction, shale oil production, ethanol production from sugar cane and cassava, solar energy utilization, conservation and the manufacture of metallurgical coke. This program (known as the National Energy Research, Development and Demonstration Program) provides money for CSIRO, universities and private organizations which contract to carry out specific agreed programs which are seen to be relevant to the needs of Australia.

The separate state governments within Australia, which may be considered to be similar to the provinces of China, also support liquefaction research. The largest single research program involved three states (Victoria, New South Wales and Queensland), the Federal government and a number of separate groups from West Germany in a joint venture, often called the Imhausen Study. Each state carefully selected a coal which represented coal reserves which were considered to be suitable for conversion to liquid fuels. The coals chosen were a brown coal from Victoria (Morwell); a high-volatile bituminous coal from New South Wales (Upper Hunter) and a per-hydrous, sub-bituminous coal from Queensland (Wandoan). Samples were sent to West Germany for liquefaction testing and the results were incorporated into a complete design and economic evaluation. This is the most comprehensive study that has been reported in Australia. Unfortunately, Australian participation was limited to observer status.

Two states also support liquefaction research through various departments, organization or committees. These organizations may carry out their own programs or may provide money for other institutions, such as universities.

The various centres of study are conveniently divided into those which report their work openly, although some details may be held in confidence, and those that release virtually no technical results although they are known to be interested in the conversion of coal to liquid fuels. These latter include the major overseas-based oil companies.

The most active organization is CSIRO, which has coal liquefaction programs in three laboratories. ACIRL has a substantial program and two universities have a number of staff and students working on aspects of liquefaction. One private company (BHP, a coal, iron-and-steel, and oil producer) also has a substantial program.

CSIRO - DIVISION OF FOSSIL FUELS (Mr J Smith)

PO Box 136, North Ryde, NSW, 2113

Coal characterization: routine analysis, trace elements, petrography, pyrolysis GC
Liquefaction mechanisms: petrography, deuterium tracer exchange, oil chemistry by NMR etc, hydrogenation modelling
Liquefaction processes: flash pyrolysis (1 g/h and 20 kg/h), batch and continuous hydrogenation, flash pyrolysis tar processing
Other activities: electrode coke, economics of liquefaction processes

CSIRO - PHYSICAL TECHNOLOGY UNIT (Dr L Lynch)

338 Blaxland Rd, Ryde, NSW, 2112

Coal characterization by NMR: brown coal drying, heating black coal

CSIRO - DIVISION OF APPLIED ORGANIC CHEMISTRY (Dr P Wailes)

GPO Box 433, Melbourne, Victoria, 3001

Analytical methods: ion exchange chromatography, fluorescence spectroscopy, gas chromatography
Pyrolysis tar processing: primary and secondary hydrogenation
Other processes: supercritical extraction, gas pyrolysis

AUSTRALIAN COAL INDUSTRY RESEARCH LABORATORIES (ACIRL) (Dr N Kelvin)

PO Box83, North Ryde, NSW, 21 3

Coal characterization: routine analysis, oxygen functional groups, ash analysis, petrography, small autoclave tests
Liquefaction reactors: 1-2 kg/h continuous reactor, 4 L semi-continuous reactor, 57 L batch reactor, twin 50 mL shaking reactors
Oil analysis: gas chromatograpny, high pressure liquid chromatography, gas chromatography-mass spectrometry, elemental analysis

BHP - MELBOURNE RESEARCH LABORATORIES (Dr B Smith)

PO Box 264, Clayton, Victoria, 3168

Processes: first stage continuous coal hydrogenation reactor, second stage liquid product hydrogenator, micro-autoclave, gasoline reformer
Analytical methods: routine methods for coals and oils, NMR for liquefaction products and upgraded liquids, oil industry methods

BHP - CENTRAL RESEARCH LABORATORIES (Dr P Fredericks)
PO Box 188, Wallsend, NSW, 2287

Solvent refined coal: analysis, utilization, methods of manufacture
Coal analyses: routine, direct oxygen, low temperature ashing, Fourier transform infra-red

UNIVERSITY OF MELBOURNE (Mr R Yost)
Parkville, Victoria, 3052

Processes: CO-Steam, aqueous solvent extraction with carbon monoxide, hydrogenation, brown coal
Analytical methods: ion-exchange chromatography

MONASH UNIVERSITY (Prof R Jackson)
Clayton, Victoria, 3168

Equipment: small autoclaves, research continuous reactor
Methods: wide range analyses, hydrogenation of brown coal,reaction mechanisms, reactor dynamics, Mossbauer spectroscopy

CSR CO LTD (Mr R Hutchison)
GPO Box 483, Sydney, NSW, 2001

Methods: hydrogenation, batch autoclaves, disposable Fe catalysts

AMPOL RESEARCH LABORATORY (Dr A Clark)
PO Box 40, Wynnum Central, Queensland, 4178

Methods: oil-industry analyses, hydro-treating coal-derived liquids, production of standard quality liquid fuels

STATE ELECTRICITY COMMISSION OF VICTORIA (Mr R Higgins)
Howard Street, Richmond, Victoria, 3121

Methods: detailed brown coal analysis, brown coal petrography, scanning electron microscope, coal survey, oil charactization

NEW SOUTH WALES DEPARTMENT OF MINERAL RESOURCES (Mr J Hobbs)
PO Box 76, Lidcombe, NSW, 2141

Methods: coal resource survey, batch autoclave

ROYAL MELBOURNE INSTITUTE OF TECHNOLOGY (Dr S Bhattacharya)
GPO Box 2476V, Melbourne, Victoria, 3001

Methods: rheology, brown coal-oil slurries

UNIVERSITY OF NEW SOUTH WALES (Prof D Trimm)
PO Box 1, Kensington, NSW, 2033

Methods: catalyst design, catalyst characterization, oil upgrading, gasification

UNIVERSITY OF TASMANIA (Prof F Larkins)
GPO Box 252C, Hobart, Tasmania, 7001

Methods: coal characterization

BROWN COAL LIQUEFACTION VICTORIA PTY LTD (Mr J Owen-Smith)
33rd Floor, 459 Collins Street, Melbourne, Victoria, 3000

Methods: construction of pilot-plant for liquefaction of brown coal, analytical laboratory

The list of laboratories and activities is not complete, but it covers the most active groups that are working in Australia. Some groups may have reduced their work effort or may have changed the emphasis of their programs.

In general, the work undertaken in programs within Australia is not aimed at the development of totally new technology, but is directed towards the improvement of existing methods and the application of such methods to selected Australian coals.

COAL LIQUEFACTION RESEARCH AT ACIRL

ACIRL is an independent institute which works almost exclusivley with coal and immediately related topics. Routine analysis, sample evaluation, research and methods of coal utilization are the major work areas.

ACIRL first became interested in coal liquefaction processes in 1965 and a number of Australian coals were shown to be suitable for conversion to SRC (solvent refined coal). This work was done in small batch autoclaves using tetralin as the solvent. The SRC was useful as a pitch for carbon electrode binder and could also be converted to a high purity coke for use in such electrodes. However, petroleum coke and coal-tar pitches were cheap and in good supply and so further experimental work could not be justified.

ACIRL recommenced liquefaction research in 1973 after the sudden increases in the price of crude oil, but the work was now directed to the production of liquid fuels. A large number of coals from many parts of Australia were tested in a 4 litre batch autoclave, using the well-established tetralin method. This series of tests identified a number of coals as potential supplies for conversion to liquid fuels. Some of these coals have since been used in the ACIRL program and have also been studied by other workers.

It soon became obvious that the data obtained from batch autoclave tests are of limited value, most especially with respect to the nature of the liquids produced. Considering this point, some workers have tried to develop batch-recycle methods in which the solvent is generally an hydrogenated anthracene oil which is recovered and used in the next test on the same coal. ACIRL decided that a far better approach to the problem was to design and build a small reactor (known as Mark I) which would produce small quantities of oil and provide valuable experience for any further work. The new German technology was used as the basis of design, being chosen for the apparent effectiveness of the simple, abundant and cheap red mud-sulphur catalyst and the claimed simplicity of vacuum distillation to recover recycle solvent and product oils. The reactor system was commissioned in late 1977. It was operated for more than 4000 hours and handled in excess of 1300 kg coal before being radically modified and upgraded.

This unit was rated at 0.3 kg coal per hour at 435 C and 21 MPa. The actual reactor vessel was a four litre stirred autoclave, product slurry was discharged intermittently, and recycle solvent plus net product oils were recovered solely by distillation-in-glass, with a final cut point of 450 C and 20 mm. One brown, three sub-bituminous and three high-volatile bituminous coals were tested using red mud and sulphur as catalyst.

The small scale of operation, tendency to leak at the stirrer gland of the reactor vessel, the reactor configuration and manual distillation methods all caused some problems but many useful results were obtained. In fact, the results were supported by the findings of independent workers using much larger scale experimental equipment. It was clearly demonstrated that those Australian coals which had previously been identified as suitable for conversion in the batch autoclave program gave good yields of liquid products in the small continuous reactor. Red mud and sulphur catalyst increased yields by about 35% and caused a marked increase in the hydrogen content of light product oils. Experience with a sub-bituminous coal during some 400 hours of operations (in three consecutive runs) showed that red mud-sulphur catalyst improved the quality of recycle solvent as indicated by the hydro-aromatic : aromatic ratio. The accumulation of both phenolic compounds and long straight-chain saturates in the recycle solvent was also observed. The improvement in solvent hydro-aromatic content and increase in oil yield were observed almost immediately, with the solvent quality stabilizing after 3 - 5 passes. On the other hand, the accumulation of saturates was still occuring at the end of the third run.

Some typical results are shown, with the results expressed as % on dry ash-free coal (daf).

	OIL	GAS	WATER
MORWELL brown	47	28	17
WANDOAN sub-bituminous	46	12	10
UPPER HUNTER high-volatile bituminous	43	12	3

TABLE 1 415 C, 21MPa, 3% RED MUD + 1% SULPHUR, Mark I reactor

The upgraded reactor system (Mark II) is currently rated at 1 kg coal per hour but this will be doubled when larger slurry pumps are installed. Process conditions are normally in the range 400-465 C and 20-30 MPa. The reactor vessel is a long-tube vertical (58mm diameter, 2m long) design with three separately controlled heating zones and a nominal slurry retention time of 2 hours. We believe that this is excessive for many of the more reactive Australian coals (brown and sub-bituminous) and changes are being made so that the retention time can be as low as 0.6 hours. The system uses a hot separator to remove the lighter oils and a continuous distillation unit to recover the heavier oils for recycle solvent.

One high-volatile bituminous, one brown, and two sub-bituminous coals have been tested to date. The reactor has been used successfully with both hydrogen and carbon monoxide-hydrogen mixture to process brown coal. A total of 2400 hours operation on coal has been reached and about 1800 kg coal has been processed. The longest unbroken experimental run has been 150 hours; such truly continuous operation is most important since any interruptions in an otherwise long run are normally marked by the addition of flushing solvents, prolonged retention of slurry with the added risk of settling of coal and catalyst, cooling and subsequent reheating of slurry, and general departure from the intended process conditions. True continuous operation and the achievement of equilibrium conditions (with respect to oil yield, solvent quality and product oil characteristics) are made much more difficult by unplanned stoppages.

Our operating experience suggests that each shift team requires a shift leader (frequently a chemical engineer), a chemical technician and a mechanical tradesman. It is possible to operate without an experienced tradesman on shift but only at the expense of equipment reliability and process control as the shift leader becomes overloaded with problems and must give low priority to some aspects of his task. The two most important factors in successful operation are adequate maintenance by skilled persons and carefully prepared operating instructions for all aspects of the work.

The results obtained in the new reactor generally support those from the original unit. Oil yields from the various black coals are a little higher but the relative ranking of the coals tested remains the same. In addition, the rapid increase in gas production with temperature has been clearly confirmed and some evidence is now available that the more reactive coals do not need temperatures as high as the high-volatile bituminous coals. The preheat stage before the main reactor is most important and its removal will reduce oil yields by about 25%.

PREHEATER	25	420	420	420	420	420
REACTOR	430	430	430	430	450	465
GAS	15	15	15	15	25	29
WATER	10	12	12	12	14	7
OIL	44	58	56	56	52	38
RESIDUE	32	27	22	22	17	33
TOTAL	101	112	105	105	108	107
HYDROGEN	1	13	5	5	12	8
REACTOR RECOVERY	94.6	95.4	99.2	98.0	94.5	92.5
ASH RECOVERY	110	100	110	90	100	110

TABLE 2 : WANDOAN COAL, 3%RM + 1%S, 3kg/h slurry, 30MPa, Mark II reactor

	73	74	75A	75B
PREHEATER	420	420	25	25
REACTOR	430	430	430	450
GAS	16	15	15	25
WATER	10	12	5	7
OIL	46	46	37	46
RESIDUE	28	30	46	25
TOTAL	100	103	103	103
HYDROGEN	-	3	3	4
REACTOR RECOVERY	95.8	98.3	94.5	88.8
ASH RECOVERY	60	90	90	50

TABLE 3 : UPPER HUNTER COAL, 3%RM + 1%S, 3kg/h slurry, 30MPa, Mark II

	OLD	NEW SAMPLE	
	79A	79B	81B
GAS	16	18	15
WATER	9	13	10
OIL	60	68	59
RESIDUE	20	10	22
TOTAL	105	109	106
HYDROGEN	5	7	6
REACTOR RECOVERY	98.9	97.0	98.4
ASH RECOVERY	80	60	90

TABLE 4 : TAROOM COAL, 3%RM + 1%S, 3kg/h slurry, 30MPa, Mark II, preheater 420 C, reactor 430 C

	WANDOAN	UPPER HUNTER	OLD TAROOM	NEW TAROOM	MORWELL
CARBON	77.6	81.4	77.5	76.4	67.7
HYDROGEN	6.0	5.2	6.0	6.4	4.8
NITROGEN	1.0	2.0	1.1	1.1	0.6
SULPHUR	0.3	0.5	0.3	0.3	0.4
OXYGEN	15.1	10.9	15.1	15.8	26.5

TABLE 5 : COAL ANALYSES (Ultimate, daf)

One of the major problems faced by any liquefaction program is the testing of a wide range of process conditions within a sensible time. The use of the conventional batch autoclave test is apparently easy but the results are open to doubt because the test conditions are so far removed from those that would be used in a continuous reactor. This is particularly so for rate of heating, concentration of hydrogen in the vapour phase, and retention time of the more volatile products. There is also a major problem in the selection of a realistic solvent. ACIRL has designed and constructed a semi-continuous reactor, based on a standard four litre autoclave, which incorporates a continuous flow of hydrogen to maintain a high partial pressure of hydrogen in the reactor at all times and remove the light oils as they are formed whilst returning the solvent vapours to the reaction zones as condensate. A limited number of tests on black coals strongly suggests that the semi-continuous reactor (SCR) does achieve similar results to those obtained on the continuous unit. In addition, tests have shown that recycle solvent from the continuous reactor can be used in the SCR and that hydrogenated anthracene oils can also be used with considerable success.

TEMPERATURE, C PRESSURE, MPa TIME, h	430 22 3	430 30 2	430 30 2	430 30 2	450 30 2
COAL	W	W	T/old	T/new	W
GAS semi	25	16	18	19	23
cont	(25)	15	16	15	23
WATER semi	11	12	8	9	11
cont	7	12	9	10	14
OIL semi	46	57	58	63	50
cont	50	56	60	59	50
RESIDUE semi	25	20	23	20	18
cont	23	22	20	22	19

TABLE 6 COMPARISON OF SEMI-CONTINUOUS REACTOR AND CONTINUOUS REACTOR MARK II (W = Wandoan, T/old = old Taroom, T/new = new Taroom)

The semi-continuous reactor is able to give information on the yield of oil that can be obtained under the set of conditions that have been chosen for evaluation, with the solvent that is being used. However, the test can not give data on the equilibrium operation of a reactor system unless the semi-continuous reactor is operated in such a way that the solvent can reach equilibrium. Probably four or five recycles are the minimum number needed. This requirement to approach equilibrium may not be very important in some cases because the composition of the starting solvent will be very similar to that expected at equilibrium; this can easily occur if the process conditions are reasonably severe and there is considerable catalytic activity to rehydrogenate the solvent. On the other hand, if the process conditions are mild or catalytic activity is low, there may be very considerable change in solvent characteristics in a single experiment.

There is another related problem to equilibrium - the conversion of solvent species to lower boiling range product oils which may seem to enhance the yield of oil. This problem can be guarded against by achieving a good recovery of both liquids and solids at all stages of the test program (say, 99%+) and checking the boiling point distribution of the recovered solvent.

Many investigators have tried to predict oil yields and oil characteristics from simple tests. There has been only limited success in such efforts to date. There are some extremely simple tests that can be used most effectively to identify those coals that are good prospects for conversion to liquid fuels. The proximate analysis, especially the dry ash-free volatile matter, and the ultimate analysis, expressed in terms of the atomic hydrogen to carbon ratio, are reliable indicators of the liquefaction potential of a coal. The petrographic analysis of the coal can be used to support the routine chemical analyses. Vitrinite plus exinite content and vitrinite reflectance are useful indicators.

ASH	< 10% dry basis, after washing
VOLATILE MATTER	> 40% daf
CARBON	< 82% daf
HYDROGEN	> 5% daf
SULPHUR	low
NITROGEN	low
VITRINITE + EXINITE	> 60%
VITRINITE REFLECTANCE	< 0.7%
PROVED RESERVES	> 100 million tonnes

TABLE 7 DESIRABLE COAL PROPERTIES

The different properties which are listed as desirable must all be considered in different ways. Thus, a high carbon coal is not conducive to conversion to liquid fuels but a high ash content does not necessarily reduce conversion but it does have a considerable effect on the expected size of the reactor and the rate of wear of the various mechanical items of equipment. The sulphur level is important in two ways - high sulphur will generally have a beneficial catalytic effect but will present a practical problem with sulphur removal from the liquid products and the gaseous streams. Nitrogen will have no real effect on conversion but will cause considerable trouble in the liquid upgrading stages as nitrogen removal is both essential and chemicallly difficult.

The Australian coals which are the preferred coals for conversion can be compared with the above criteria. By way of contrast, two coals of possible interest are listed. Collie coal, from the rapidly developing state of Western Australia, would be a useful source of liquid fuels if the coal were suitable because the state is remote from the main cities of Australia - but the coal is not satisfactory for conversion by direct hydrogenation. The Oaklands coal is a most substantial resource, located in a rural area with some major settlements that could assist in the development of a large project - but the coal characteristics are considered to be much more suitable for gasification.

	M	W	T	UH	C	O
ASH	2-3	8-12	6-10	8-12	3	18
VOLATILES	54	51	54	42	39	36
CARBON	68	77	78	81	77	74
HYDROGEN	4.8	6.0	6.3	5.2	3.9	4.0
ATOMIC H/C	0.85	0.91	0.95	0.77	0.61	0.65
SULPHUR	0.4	0.4	0.3	0.5	0.2	0.4
NITROGEN	1.1	1.0	1.0	2.0		
VIT + EX	98*	88	95	68	46	36
VIT REFLECTANCE		0.38	0.44	0.59	0.38	0.36

M = MORWELL
W = WANDOAN
T = TAROOM
UH = UPPER HUNTER
C = COLLIE
O = OAKLANDS
* = huminite + liptinite

TABLE 8 ANALYSIS OF SOME AUSTRALIAN COALS

ACIRL has demonstrated the suitability of a number of Australian coals for direct conversion to liquid fuels using the new German technology. This method of hydrogenation makes deliberate use of cheap, disposable iron-sulphur catalyst to improve yields and recovers all liquid products and recycle solvent by vacuum distillation. However, we believe that oil yields obtained with the German technology will be closely related to those that would be obtained by the various other direct liquefaction processes such as Exxon donor solvent or H-Coal. In particular, the ranking of a number of coals should be the same for each of the various direct processes since we believe that the essential step in each of the liquefaction processes is the interaction of a donor solvent with the thermally-derived breakdown products of the coal. The exact response of a coal to a specific process is best measured by a test program using the coal and the process under a range of process conditions but good estimates can be made by using, say, the German process as a standard test and then allowing for the particular characteristics of the selected process.

One major requirement of any program is the study of the effect of the primary process conditions of temperature, pressure and retention time. Some coals are more reactive than others and can be thermally disrupted at lower temperatures than some other coals. Having achieved the primary disruption and the production of reactive fragments, the next task is to stabilize such fragments by the supply of hydrogen from a donor solvent. The alternative to the supply of hydrogen is the interaction of these fragments to produce stable high molecular weight materials which may be less conducive to conversion to liquid products than the original coal. In such a case, the most probable products become gases, tars and cokes. A most important reason for choosing temperatures to suit coal reactivity is that gas production, especially the production of the low molecular weight hydrocarbons such as methane and ethane, increases rapidly with temperature and so consumes hydrogen and carbon to make relatively low value products.

Process optimization is also related to equipment design and capital cost because high operating pressures require physically stronger vessels and more powerful pumps and compressors. In addition, retention time determines the size and consequently the cost of a reactor, and temperature determines the safe working stress for the materials of construction. Such considerations may not seem important when planning a program to determine the oil yield of a coal but are critical when designing the equipment to be used in a full-scale plant.

Coal preparation is not a topic normally considered to be part of a program to measure the oil yield of a coal. The ash content of a coal has several important effects on the design and operation of a reactor. Firstly, the ash content of the coal determines the volume of coal to be handled per unit weight of organic matter - ash is non-reactive and only takes up space in process vessels. Secondly, ash causes severe abrasion and erosion in the various items of plant such as pumps, process lines and most especially high pressure slurry let-down valves. And thirdly, some workers believe that the presence of ash in the feed to a distillation unit requires the presence of a similar amount of coal liquids in the residue stream to maintain fluidity of the residue; this then means a loss of potential liquid products. If these considerations have any validity, the removal of mineral matter during coal preparation is a vital part of a coal liquefaction process and deserves the full attention of the chemical engineer.

Coal preparation methods always produce a waste stream to complement the clean stream and this often leads to the loss of a significant proportion of the carbon in the feed stream. This problem is particularly severe for many Australian coals which give poor yields of coal when ash levels of 8-10% are reached. The alternative is to produce a middlings stream with about 20-30% ash and thus reduce the overall carbon loss to as little as 5-10%. This solution requires the utilization of the high-ash middlings and the most sensible uses in a coal liquefaction plant are combustion to produce heat and electricty and gasification to produce fuel gases and hydrogen for the conversion stage and the liquid upgrading stages. A natural consequence of the efficient use of middlings is that there is less demand for the "waste" streams from the liquefaction process: light hydrocarbon gases and residues from distillation. This suggest that gas production should be as low as possible, consistent with excellent conversion of coal to oil and minimization of residues. The efficient use of the total energy content of the coal is a challenge for the whole team involved in process development and plant design.

ACIRL has watched the development of a number of liquefaction processes over the last ten years. We still believe that the new German technology is as good as any of the competing processes but we also see that there are positive gains to be made by studying each of the individual processes. Thus, we are interesed in the concept of bottoms recycle as a means of returning some of the high molecular weight polycyclic aromatics (claimed to be good potential hydrogen donors) to the reactor as solvent. Similarly, we believe that solvent extraction of residues could be a useful way of recovering these polycyclic aromatics for inclusion in the solvent phase. Such topics are included in our long-range research program.

PLANNING, RUNNING AND INTERPRETATION

The planning and execution of an experimental run in a continuous reactor are only the preliminaries in the overall process of gaining a parcel of experimental data from a reactor run. And yet each of these preliminary stages is as important as the final calculations and interpretation.

The prime aim of an experiment should be very easy to establish but it is generally quite difficult to come to a clear statement of the run objectives. Some objectives that may be considered are

1 demonstration of long-term operation of equipment,
2 determination of oil yield,
3 achievement of stable operation with recycle balance,
4 production of a sample of product oil,
5 comparison of two catalysts or process conditions,

All the comments that follow are based on my experience which has been gained on the ACIRL continuous reactors but I believe that there is a sound theoretical basis to all observations which are recorded. I also believe that there is a sound reason why particular run and interpretive methods should be used and so I am confident that the general principles can be applied to any reactor program.

The requirements of several of these different objectives could be included in a single, long run but the achievement of such objectives requires extremely careful planning. The demonstration of equipment reliability is perhaps the easiest test to formulate and plan because the chemistry of the liquefaction reactions are not involved in the operations except to the extent that they determine the viscosity of fluids to be pumped and the corrosion problems that may be experienced. Such a run would only need to use a sensible set of process conditions that produced products with properties that were generally similar to those that were expected in the full-sized plant. Similarly, the choice of coal and starting solvent would not be critical. However, it must be recognized that the ability to sustain long-term reactor operation is, in fact, the key to the achievement of every other aim. Short runs with unscheduled stoppages or unplanned variations in process conditions yield only numbers, not data.

The ability to maintain stable operation for long periods (in our case, 10-15 days) depends on the training of the staff and the thoroughness of the maintenance that was carried out before the run commenced. In addition, the success of a long run also depends on the equipment design, especially the features that enable on-shift maintenance procedures to be carried out safely. One key requirement in on-shift maintenance is the employment of appropriate skilled persons on shift so that the quality of the work that is done is as high as possible at all times. This is particularly important whilst running because an error in judgement can have very serious consequences, leading to an unscheduled shutdown. Our experience is that three persons are needed on our reactor system to handle all the tasks that arise during routine operations. The staff would need to be increased if there were less automatic controls or if the number of feed slurries and product discharges were increased above the present level of four per day. Our shift team consists of a shift leader, a technician and a mechanical tradesman. The shift leader is often a chemical engineer, but the position has been most ably taken by chemists and well practised mechanical technicians. The most important qualification for a shift leader is experience, and we believe that nine months is the minimum time that is needed to acquire a good background in practical operating methods. Since the shift leader must make decisions about on-shift maintenance of both mechanical and electical systems (including power, data gathering and control circuits), a wide knowledge of the individual plant items is necessary and this is most easily acquired during the routine maintenance periods between runs. The training of a shift leader is not a formal program but is based on sharing the knowledge that has been accumulated by other shift leaders, and this knowledge is shared by watching the shift leader in action and by discussing problems and possible solutions as they arise. The latter stages of a new shift leader's training consist of taking charge of the shift while a skilled shift leader acts as technician and is immediately available to give advice or to watch the method that is being used to solve an operating problem.

The duties of the technician are virtually as important as those of the shift leader as he is primarily responsible for the collection and labelling of all samples - and our experience shows that there are almost as many problems in this area as there are in actual plant operation. The technician is also responsible for the crushing of coal and the preparation of feed slurries in accordance with the run plans. The technician is also the right hand of the shift leader and must gradually learn to read all the outputs of the control system and to be able to understand the significance of the information. This is especially important when the equipment is not operating properly or the leader is away from the control centre to attend to other things. Since the shift leader is responsible for all the mechanical equipment like air compressors, hydrogen compressors and high pressure slurry pumps (all of which require routine checking), the technician must learn some of the essential skills of a leader if he is to be really useful on shift.

The mechanical technician also has a vital contribution to make to the success of a run and our most recent experience has made us reconsider our old rule of using only two persons per shift. When we did some experimental work with carbon monoxide-hydrogen mixtures during a study of the CO-Steam process, we considered that it was necessary to have three persons on shift for safety reasons and the only additional persons available were the mechanical technicians. We found that they were able to make a large contribution to the success of the runs and enabled the shift leader to devote more effort to supervision of the program and process conditions. Our most recent practice has been to include a person with mechanical skills on almost every shift. This has enabled us to adjust control valves, replace blocked piping, adjust leaking fittings, service vacuum pumps and repack stirrer or pump packed glands without shutting down or running the risk that the job may not be done properly. If there are no problems with the equipment, the mechanical technician is able to work on outstanding jobs. Thus, it is possible to keep a supply of properly maintained high pressure valves ready to replace any valve in use in the equipment that needs to be replaced due to wear. The mechanical technicians have also shown that they bring a considerable degree of skill and initiative to the on-shift maintenance problems whilst also gaining a good basic knowledge of the equipment and its operation.

The measurement of oil yield is frequently seen to be a relatively simple procedure that needs few special precautions. This is not so, although the measurement of product quality is considerably more difficult. My own observations suggest that product yield can be stabilized as soon as recycle solvent balance has been reached and the solvent quality, as defined by the hydro-aromatic content, has come close to its equilibrium value. Thus, the achievement of recycle balance is necessary before the measurement of oil yield can be made with any real degree of confidence.

The achievement of stable operation with recycle balance is a rather demanding objective for a run and requires that the process conditions be carefully chosen so that they reflect the conditions desired. In particular, the temperature cut between net product oil and recycle oil must be continually monitored so that a proper distribution of distillable oil between product and solvent can be made. It is most probable that the temperature cut points for the various distillation stages will have to be reviewed as the test progresses. Even if exact balance is achieved, there will be a net loss of solvent from the system because samples will be withdrawn and this can be significant in small-scale operations. Our current sampling practice removes about 1% of the recycle solvent per discharge, but earlier procedures on the smaller Mark I reactor probably used 5% per discharge. Thus, there must be a clearly defined method to replace the amount of solvent that is taken as samples. It will also be necessary to keep the overall process severity under review so that the solvent does not become excessively light or heavy, even though remaining in balance. The consequences of running with light solvent are rapid settling of coal and catalyst in the feed slurry and excessive evaporation of solvent in the preheater and reactor, leading to blockages and coking. Heavy solvent may well cause serious pumping problems due to high viscosity.

The masses of all materials entering and leaving the reactor system must be carefully recorded. This must include all spillages of feed slurry and all feed slurry that remains in the feed preparation vessels. All leaks from high pressure slurry pumps must be taken into account. Flushing solvent that may be used to clear a blocked process line, prime a faulty pump or prevent a preheater blockage must be fully accounted for. This may seem most elementary but it is still a source of constant concern within our own program at ACIRL. The process of recording all masses should provide an opportunity to detect operating problems before they become serious. Thus, a gradual decrease in the amount of slurry being pumped to the reactor may point to a problem with mass measurement (weighing device or flow meter) or the pumping system. If the pumps are delivering less than intended, the retention time in the reactor will be greater than intended and there will have been an unintentional change in process conditions. Similarly, the recording of gas flows can give an indication of the development of leaks, not only in the gas lines but also in the hot zones where vapour-gas mixtures are being handled. The early detection of vapour leaks, which represent the more volatile oils, is essential because a simple calculation will show the following:

100 coal as fed
85 dry ash-free coal
200 recycle solvent
40 product oil from a good coal
240 total distillable oils at exit of reactor
2% loss of distillable oil = 4.8 parts which is equivalent to 12% of the yield of product oil (now 40 - 5 = 35)

It must always remain a prime aim of any experimental run to detect any deviation from the run plan as early as possible during the run so that corrective action can be taken before the objectives of the run are so severely compromised that the information that is being sought can no longer be obtained.

The accounting for mass should extend to ash balance around the reactor, as can be determined by the ash contained in the vacuum distillation residues compared to that in the feed to the reactor. Loss of ash probably indicates an accumulation of ash in the reactor and there will probably also be an accumulation of unreacted coal. Such an accumulation of solids in the reactor will correspond to a displacement of oils from the reactor and, although the effect may be relatively small, this will cause an apparent increase in the recovery of recycle and product oils. In addition, the accumulation of ash will mean an accumulation of catalyst and a possible increase in coal conversion or light product yield. The analysis of vacuum residues for ash whilst the run is continuing requires that a chemical technician is available at least once a day for such duties, and it may be useful to have such assistance available on every shift. If a chemist is available, addition analyses can be conducted to determine the quality of the recycle solvent and the light oils; both these analyses can be done by gas chromatograph.

The time taken to achieve recycle balance will depend on the rate of production of coal-derived solvent, the ratio of coal to solvent, and the quantity of solvent in the whole process. Our experience shows that the quality of the solvent (hydro-aromatic content) can reach an equilibrium before specific starting-solvent components are diluted out or new coal-derived components build up to their final levels. It is desirable to conduct tests with as high a ratio of coal to solvent as is practical, both because this represents the anticipated commercial practice and because it helps to minimize the time taken for solvent characteristics to reach equilibrium. Similarly, the stock of solvent and slurry held in process should be kept to the minimum value consistent with reliable operation. Slurry feed tanks should not be so large that large quantities of solvent are held but they should not be so small that a minor process upset will cause the feed pumps to run out of slurry. The same arguments apply to the amount of solvent held in stock between the distillation stage and the preparation of new slurry batches.

The measurement of oil yield requires all the care demanded by the attainment of recycle balance because oil yield is the excess oil recovered over that required for recycle balance. This is elementary but sometimes forgotten. Since the extent of coal conversion and oil production is generally considered to be a function of solvent quality (availability of donor hydrogen or hydro-aromatic content), oil yield can be determined as soon as the solvent quality stabilizes.

The production of a sample of product oil will require stable operation, the achievement of process equilibrium and the collection of the oil sample after the above objectives have been met. If the aim is to collect only a small sample, the product oils collected in the last stage of the run when process stability was demonstrated will be sufficient. But if the aim is to accumulate sufficient coal-derived liquids for the production of standard grade fuels or the study of upgrading methods, then there will be a need to either extend the run significantly or conduct subsequent runs using the same process conditions and the same stock of recycle solvent.

The requirement that the quality of the recycle solvent should stabilize before product oils are collected is generally neglected in small-scale studies because it is inconvenient to run the equipment long enough to ensure solvent stability. Some recent results showed that the composition of the recycle solvent, as indicated by hydro-aromatics, came to equilibrium with about 36 hours. But the product oils showed a strong influence of the starting solvent, as evidenced by an abnormally high toluene and indan content, for several more days. And the composition of the recycle solvent was still not what we expected because there was virtually no accumulation of phenolics or long-chain saturates. A period of about ten days operation is probably necessary before there are clear indications of the chemical composition of the recycle solvent. Although it is possible to obtain oil samples fairly early in a long run, the only way that equilibrium can be demonstrated is by gathering enough data points to show that oil compositions are not changing.

Catalyst comparisons are a further complication of the above discussions. Catalysts may be tested to determine the effect on coal conversion, oil yield, or product quality. Each of these three tasks is more difficult that the previous. If the catalyst does not make a large difference to the recycle oil composition or the degree of product oil cracking, it is practical to make the comparison in a short trial but all the above points on system and solvent stabilty are just as relevant.

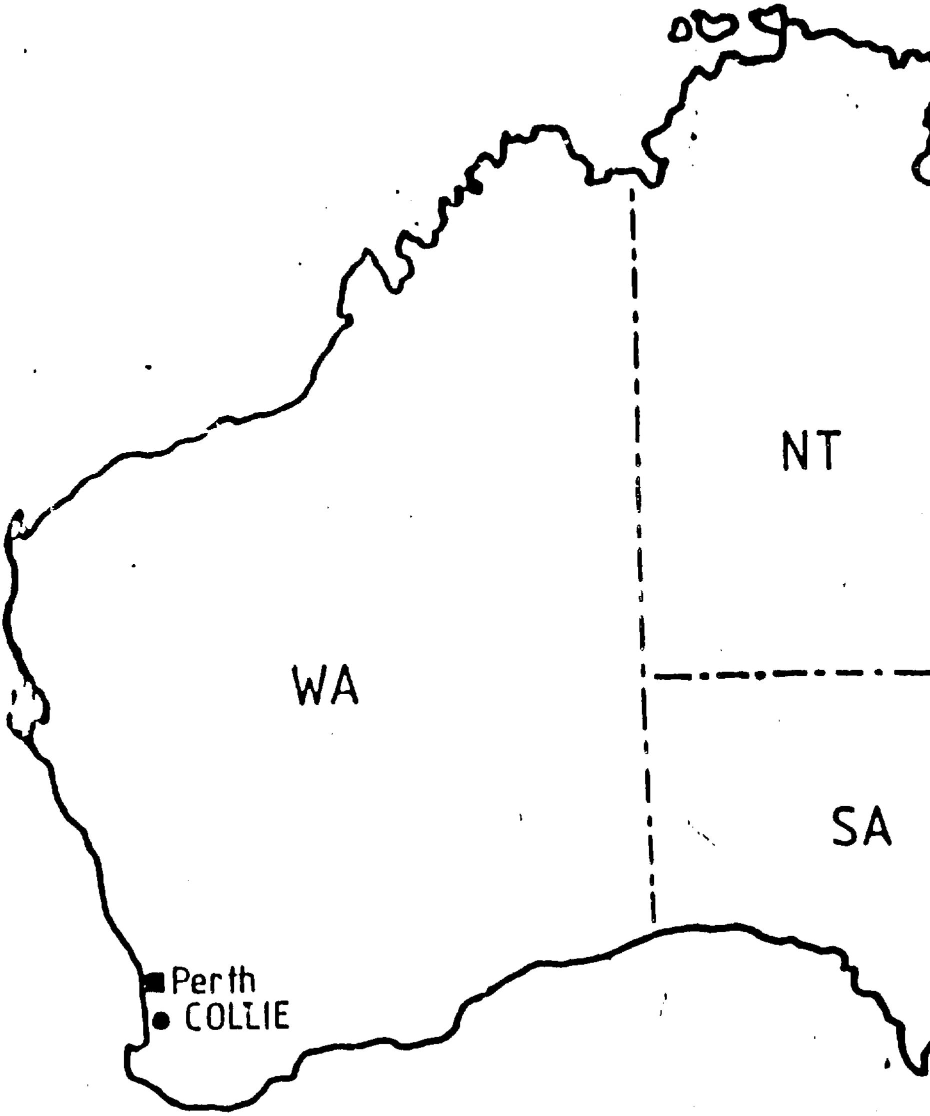
Having successfully planned and conducted a run, the next major task is to evaluate the results and discover the experimental truth, removing as many of the uncertainties as possible. The first step is to examine the various mass balances - in our case to conduct a balance around the reactor and another around the light oil distillation unit. Such balances will be perturbed by items such as spills of slurry, leaks of vapour and gases, loss of highly volatile liquids (butanes, pentanes) and dissolved gases, errors in metering, and errors in the recording of data. We have discovered incorrect recording of weights and mistakes in simple arithmetic; systematic checking of the work sheets is absolutely necessary.

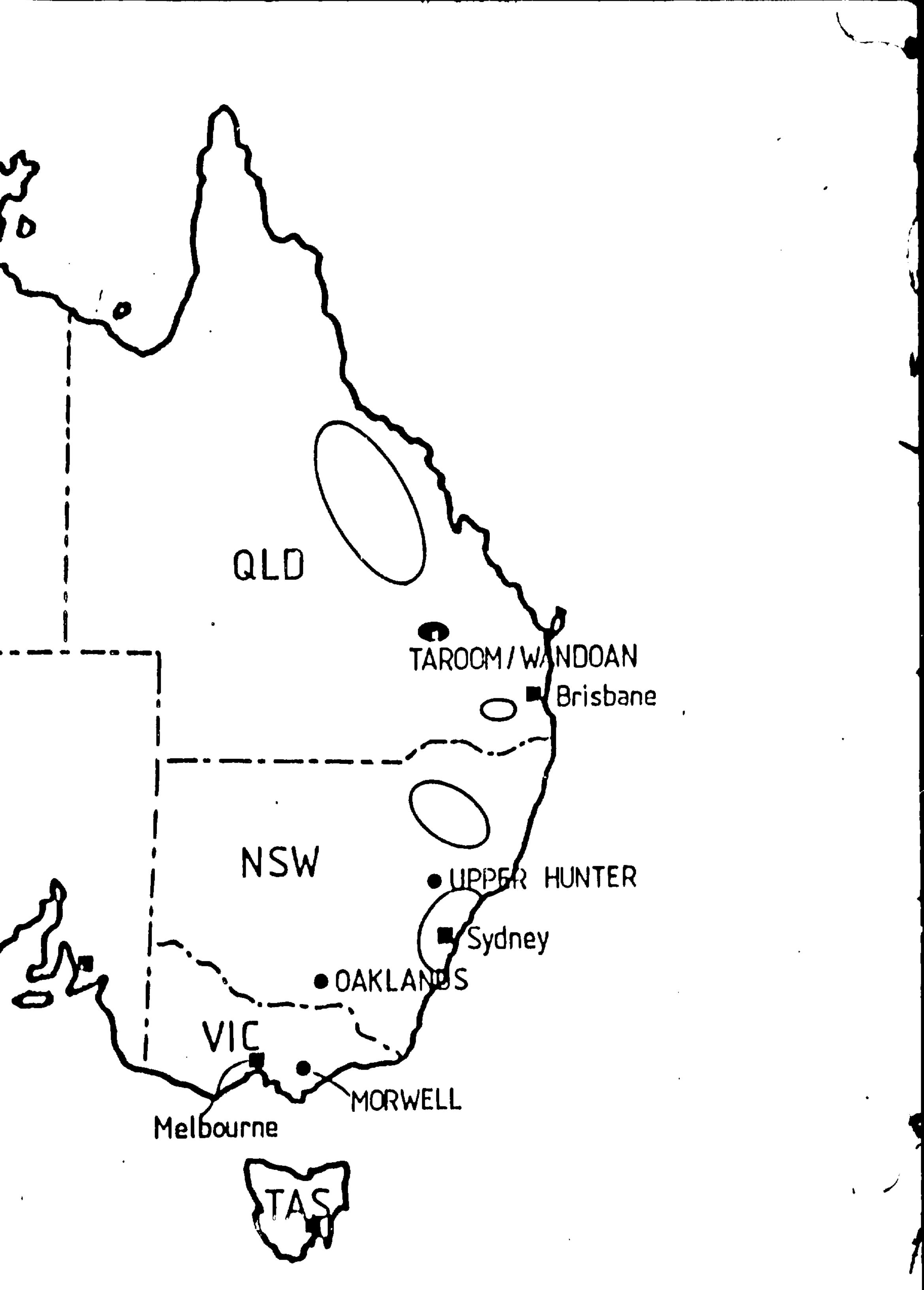
The calibration of balances, flow meters, gas meters, thermocouples, and pressure transducers and gauges is an annoying job that can not be neglected. Losses of vapour and gases can often be observed at fittings and valves and the best way to solve this problem is to remove the leak before any significant amount is lost. However, if there is evidence to demonstrate that such a loss occurred during a run, the application of sound chemical engineering principles will enable an estimate to be made of the composition of the leak. Our experience suggests that a leak in the hot, high pressure area is mainly volatile oil - perhaps as much as 60% of the leak. If the mass loss is only 1-2% of the total mass flow, any correction for losses can be reasonably reliable but this is not so if the loss rises to 5%. Data from one series of tests on the Mark I reactor showed that a loss of 1% of the total mass corresponded to a 2.8%daf loss of oil yield. This figure does not apply to the new reactor but it is indicative of the scale of losses that can occur.

The loss of gases may occur in the low pressure or hydrogen feed lines and this can be revealed by a careful examination of the elemental balances for carbon and hydrogen. If the loss is from the high pressure zone, there will be a loss of both carbon and hydrogen and this should be apparent from the elemental balances. If the loss is from the gas lines, considerably more hydrogen should be lost than carbon and this fact will assist in the correct allocation of losses. Gas meters are a regular source of trouble, especially when small amounts of coal-derived liquid are carried over into the meter. Suitable traps will help to reduce this problem but will not necessarily eliminate it. A more sreious problem is the loss of dissolved gases from the light oil products that are sent to distillation. Experience with the Mark I reactor suggested that 0.6% of the total product slurry weight was lost on refluxing; this represents about 1.5-2.0% on coal. Our present reactor removes the gases from the heavy product slurry before it is vacuum distilled by degassing the slurry at about 250 C at 300-500 kPa. However the light oils do seem to consistently lose about 2% by mass on distillation, presumably as dissolved gases which would represent about 1% on coal. Such losses are not large but they must be properly taken into account.

Another very important source of loss is the retention of volatile oils in the residues from the vacuum distillation. We routinely test the vacuum residues by thermogravimetric analysis to measure ash and volatiles. Not all the volatiles can be recovered by a careful, small-scale laboratory vacuum distillation, but substantial quantities of recycle solvent can easily be lost in the residues if the distillation performance is poor. Analysis can estimate the amount of recoverable solvent in the residues and this data can be used to determine the oil yield. However, the recycle solvent quality will be incorrect if these high boiling oils are not returned to process and any correction to the yield data will not be able to take the effect of solvent quality in account. This example is a perfect illustration of the need to ensure that all stages of the process operate at the desired set point if reliable information is to be gathered.

Interpretation of data is one of the more demanding tasks of the chemical engineer engaged on coal liquefaction research because it is both tedious and necessary. Some additional pointers to interpretation are the comparison of data from consecutive discharge periods to search for figures that are inconsistent and the association of minor (or major) plant upsets with fluctuations in plant performance. But the most challenging problems are to sort out the effects of such things as preheater purges which cause rather indeterminate losses of slurry, unintentional use of flushing solvent to prevent serious equipment problems which grossly upsets all simple flow and mass balance calculations, and unexplained departures from the carefully planned run schedule. The other, even greater, challenge is to devise procedures to prevent such problems. I can not give any real help in that area as we are still trying do to this ourselves.


NT
WA
SA
Perth
COLLIE


QLD
TAROOM / WANDOAN
Brisbane
NSW
UPPER HUNTER
Sydney
OAKLANDS
VIC
MORWELL
Melbourne
TAS

DESIRABLE COAL PROPERTIES

Ash	< 10% db
Volatile Matter	> 40% daf
Carbon	< 82% daf
Hydrogen	> 5.0% daf
Sulphur	0 – 10%
Vitrinite + Exinite	> 60 vol %
Vitrinite Reflectance	< 0.7%
Recoverable Reserves	> 100 million t

BROWN COAL

MORWELL, VICTORIA

3-4

54

68

4.8

0.4

98.6*

*Huminite + liptinite

SUBBITUMINOUS

WANDOAN, QLD

(WASHED)

8-9

50-51

77

6.0

0.4

88

0.39

BITUMINOUS

DENMAN-SCONE, N.S.W.

(WASHED)

10-11

42

81

5.2

0.5

68

0.59

SUBBITUMINOUS

COLLIE, W.A.

2.6

39

77

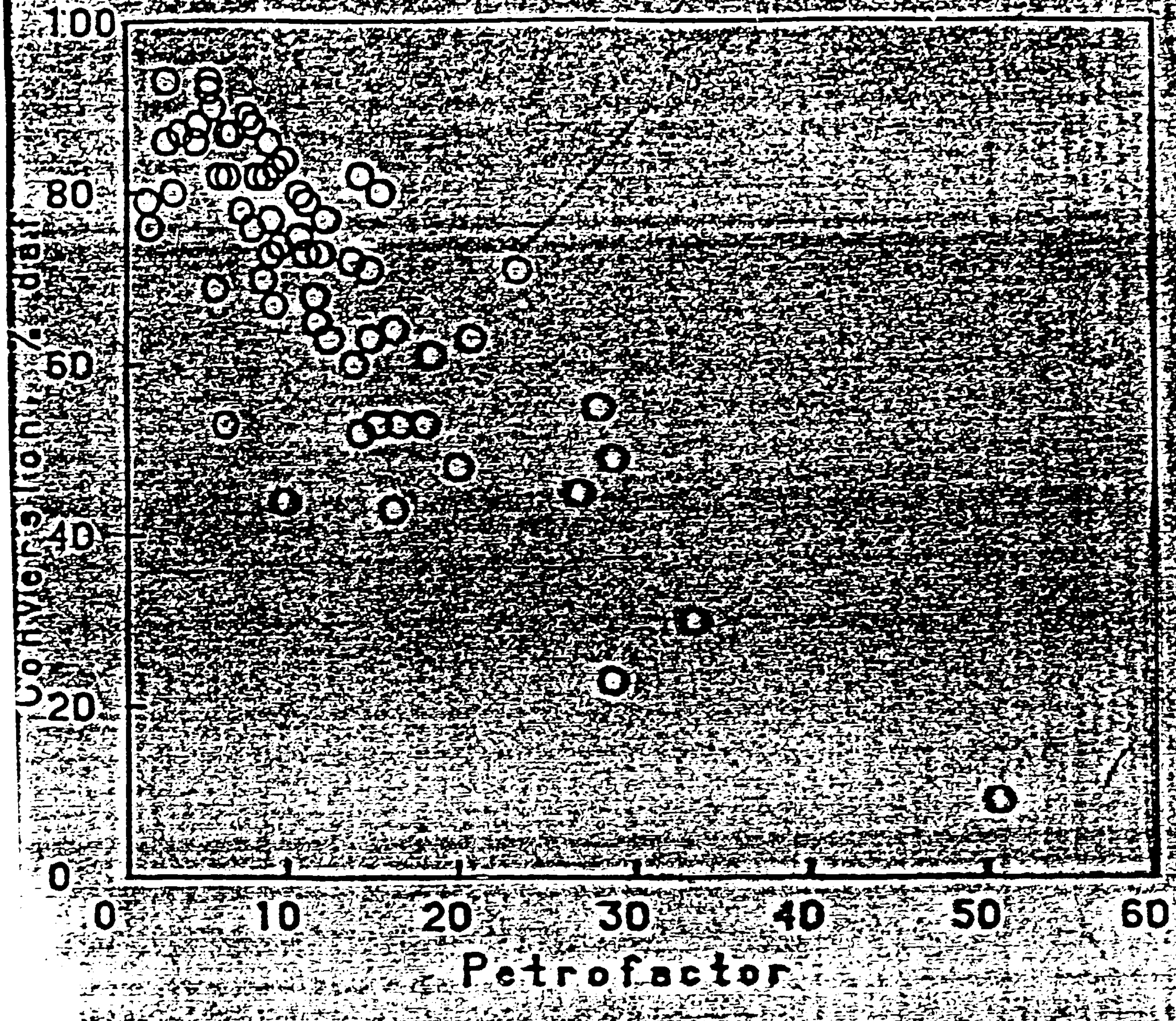
3.9

0.2

46

0.38


Batch autoclave
○ Continuous reactor (non-catalytic)
● Continuous reactor (with red mud)
Oil yield, % daf
0
10
20
30
40
50
60
70
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
(H+O+N+S)/C atomic ratio

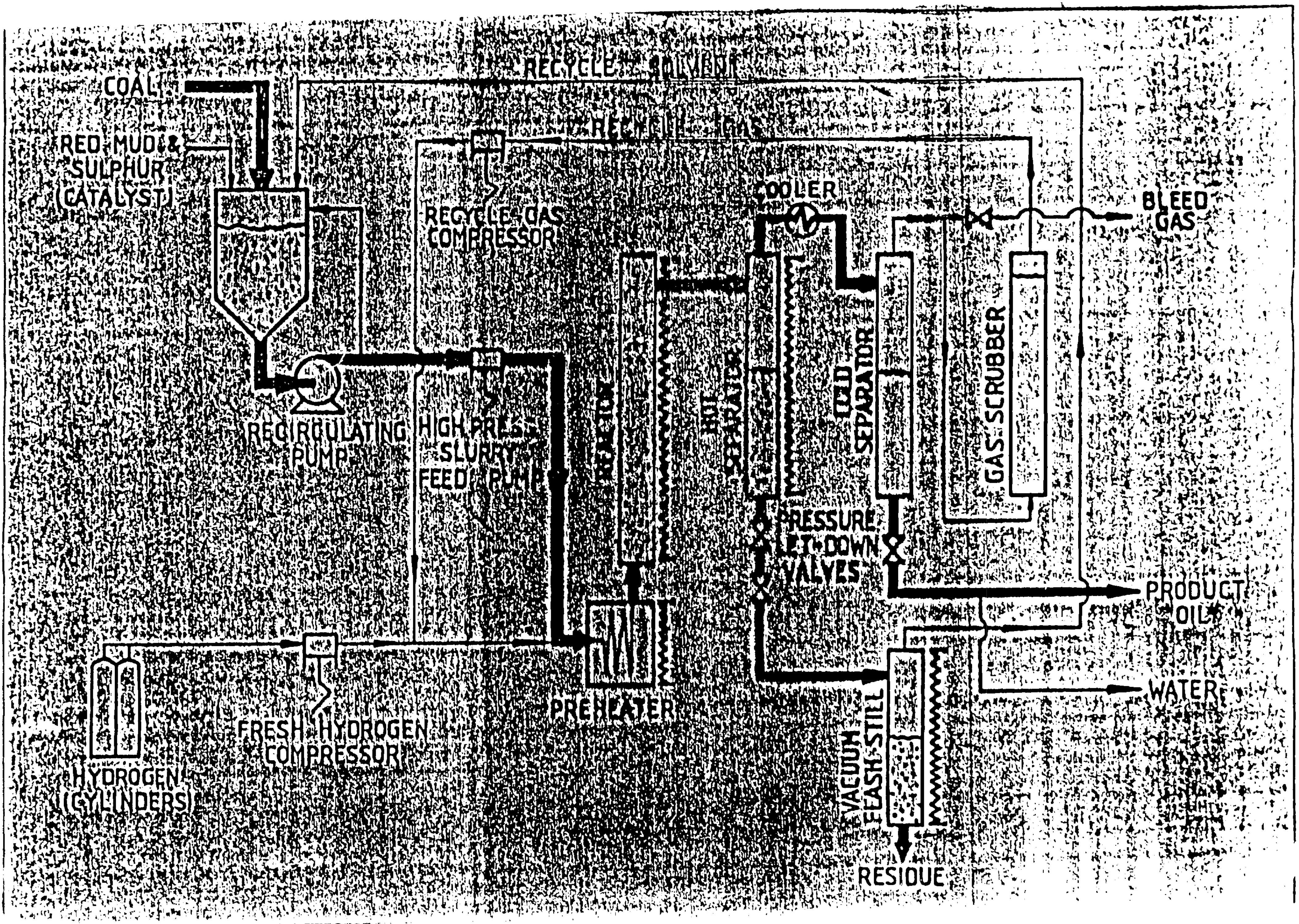


$$\text{PETROFACTOR} = \frac{1000 \bullet \text{R}_o\text{MAX}}{\text{VITRINITE} + \text{EXINITE, VOL\%}}$$

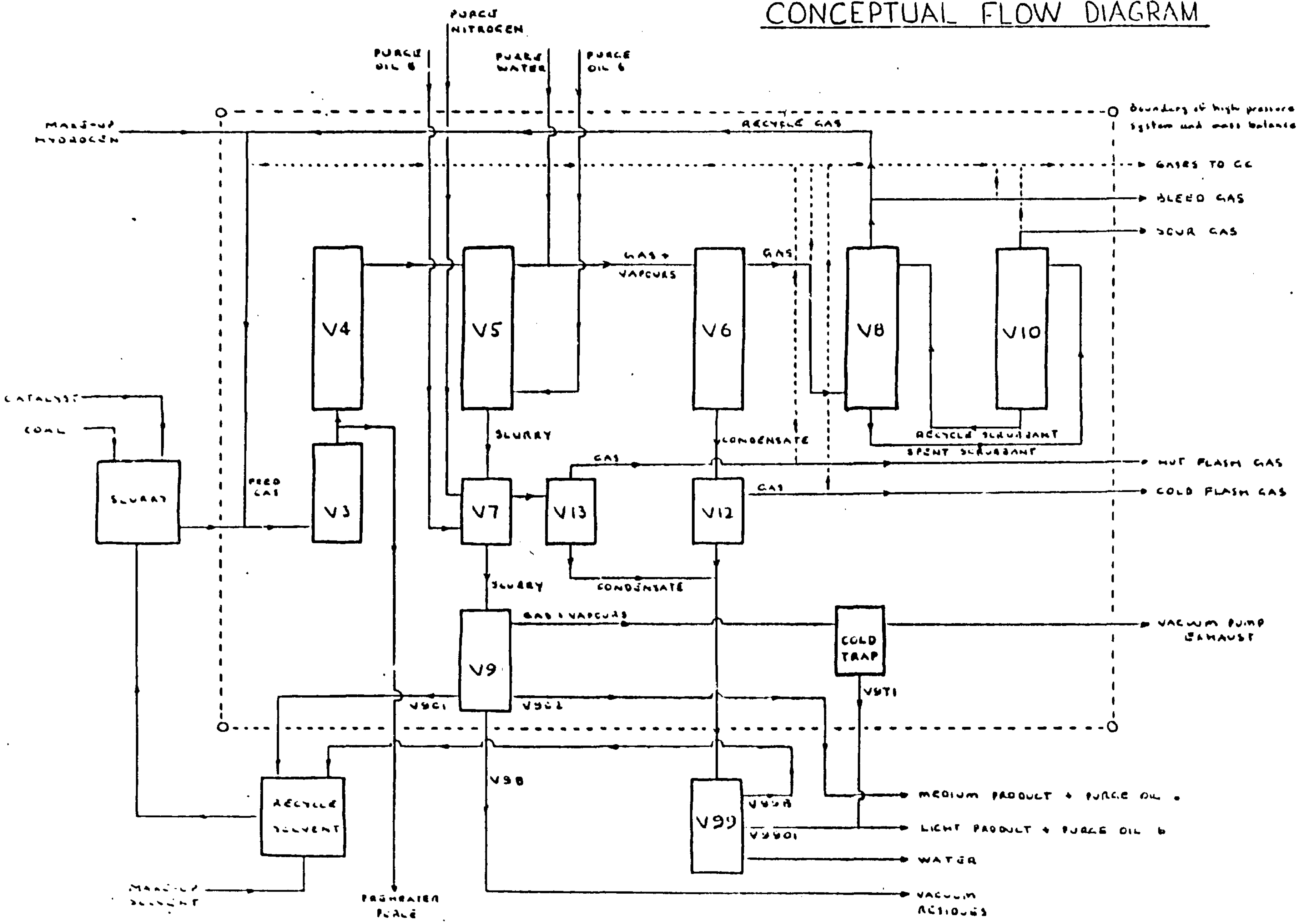
CONTINUOUS REACTOR

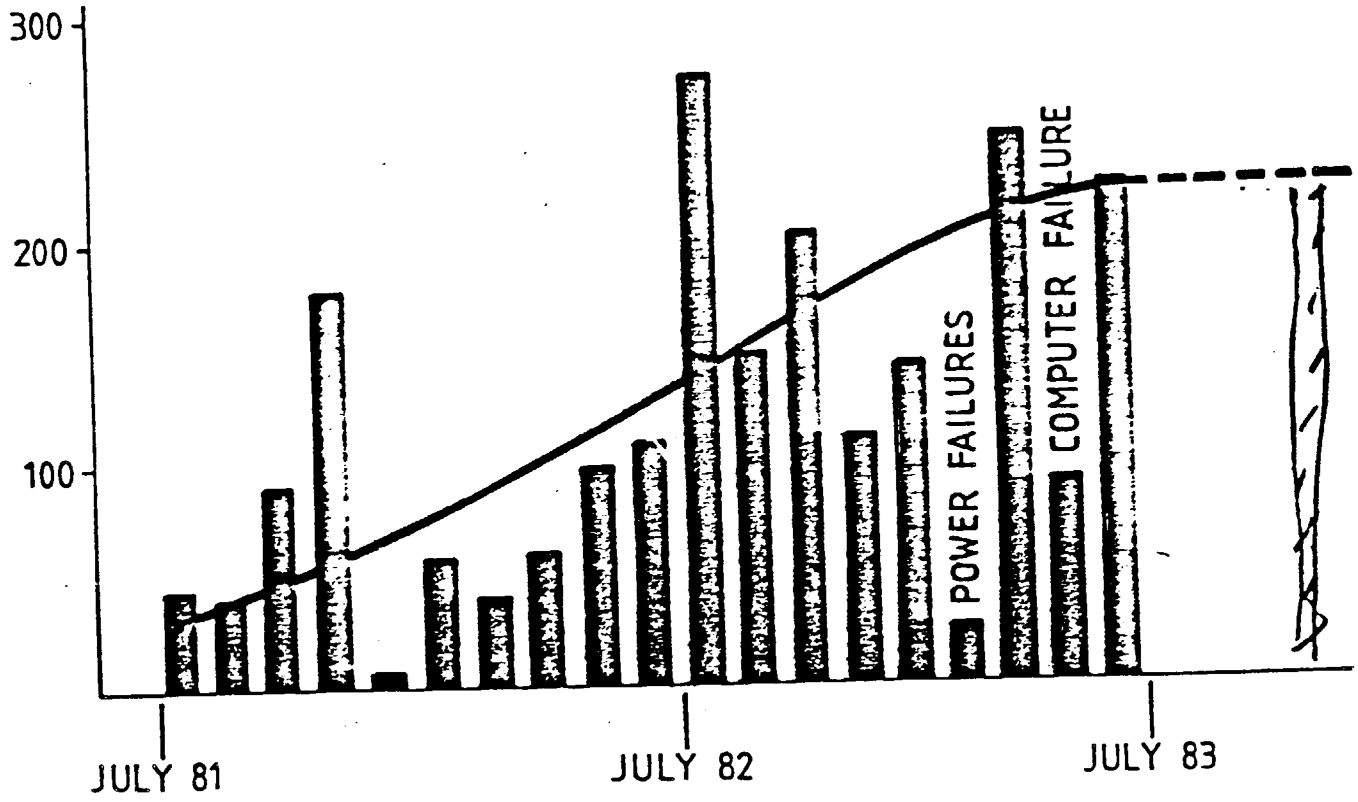
MARK II

DESIGN FEED RATES	20-50 KG/D COAL 50-120 KG/D SLURRY 200 L/MIN H_2
DESIGN OIL OUTPUT	[illegible]
REACTOR VOLUME	[illegible]
RATED TEMPERATURE	[illegible]
RATED PRESSURE	[illegible]

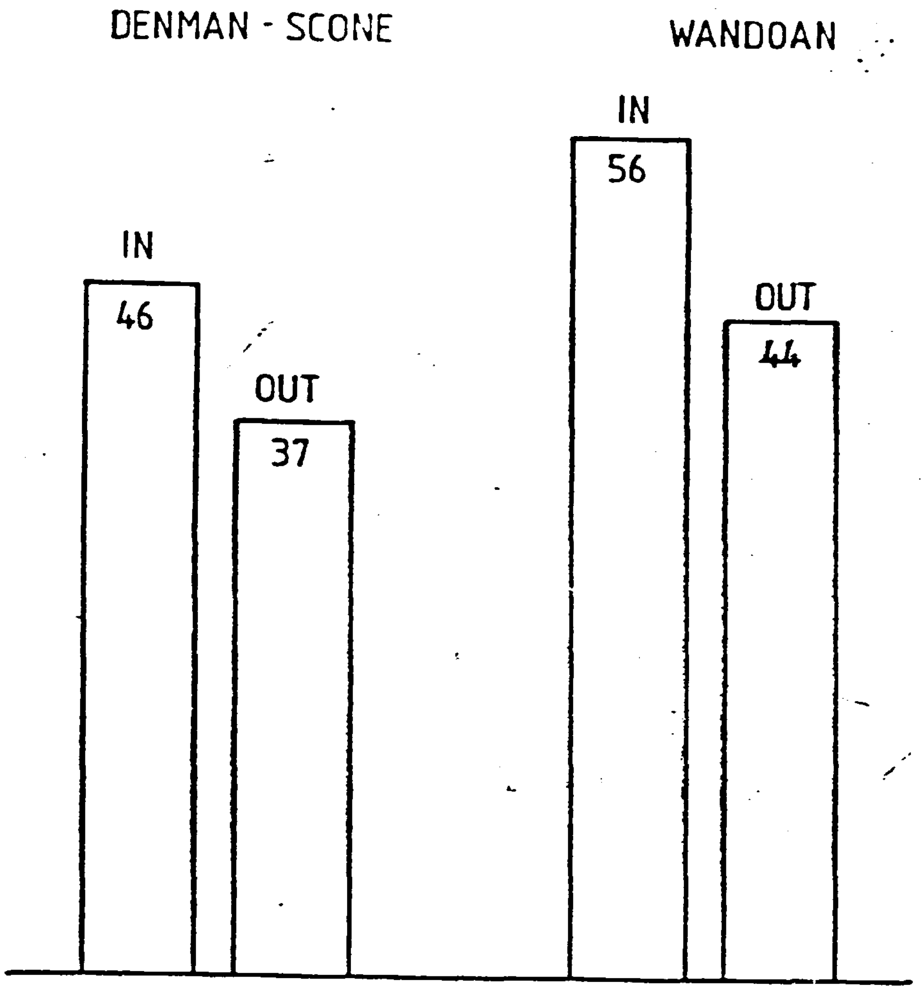

RECYCLE SOLVENT
COAL
RED MUD & SULPHUR (CATALYST)
RECYCLE GAS
RECYCLE GAS COMPRESSOR
COOLER
BLEED GAS
RECIRCULATING PUMP
HIGH PRESS SLURRY FEED PUMP
REACTOR
HOT SEPARATOR
COLD SEPARATOR
GAS SCRUBBER
PRESSURE LET-DOWN VALVES
PRODUCT OIL
WATER
PREHEATER
FRESH HYDROGEN COMPRESSOR
HYDROGEN (CYLINDERS)
VACUUM FLASH STILL
RESIDUE

CONCEPTUAL FLOW DIAGRAM





ON STREAM TIME FOR MARK II



EFFECT OF PREHEATER

R. STAKER. P. BENNETT. N.V. DUNG.

TABLE 1 : WANDOAN COAL, 3% RM + 1% S, 3 KG/H SLURRY, 30 MPA

	75C	76	78	81A	77A	77B
PREHEATER	25	420	420	420	420	420
REACTOR	430	430	430	430	450	465
GAS	15	15	15	15	25	29
WATER	10	12	12	12	14	7
OIL	44	58	56	56	52	38
RESIDUE	32	27	22	22	17	33
TOTAL	101	112	105	105	108	107
HYDROGEN	1	13	5	5	12	8
REACTOR RECOVERY	94.6	95.4	99.2	98.0	94.5	92.5
ASH RECOVERY	110	100	110	90	100	110

TABLE 2: UPPER HUNTER COAL, 3% RM + 1% S, 3 KG/H SLURRY, 30 MPA

	73	74	75A	75B
PREHEATER	420	420	25	25
REACTOR	430	430	430	450
GAS	16	15	15	25
WATER	10	12	5	7
OIL	46	46	37	46
RESIDUE	28	30	46	25
TOTAL	100	103	103	103
HYDROGEN	-	3	3	4
REACTOR RECOVERY	95.8	98.3	94.5	88.8
ASH RECOVERY	60	90	90	50

TABLE 3 : TAROOM COAL, 3% RM + 1% S, 3 KG/H SLURRY, 30 MPA,
PREHEATER 420 DEG.C, REACTOR 430 DEG. C.

	OLD	NEW SAMPLE	
	79A	79B	81B
GAS	16	18	15
WATER	9	13	10
OIL	60	68	59
RESIDUE	20	10	22
TOTAL	105	109	106
HYDROGEN	5	7	6
REACTOR RECOVERY	98.9	97.0	98.4
ASH RECOVERY	80	60	90

TABLE 4 : COAL ANALYSES (ULTIMATE, DAF)

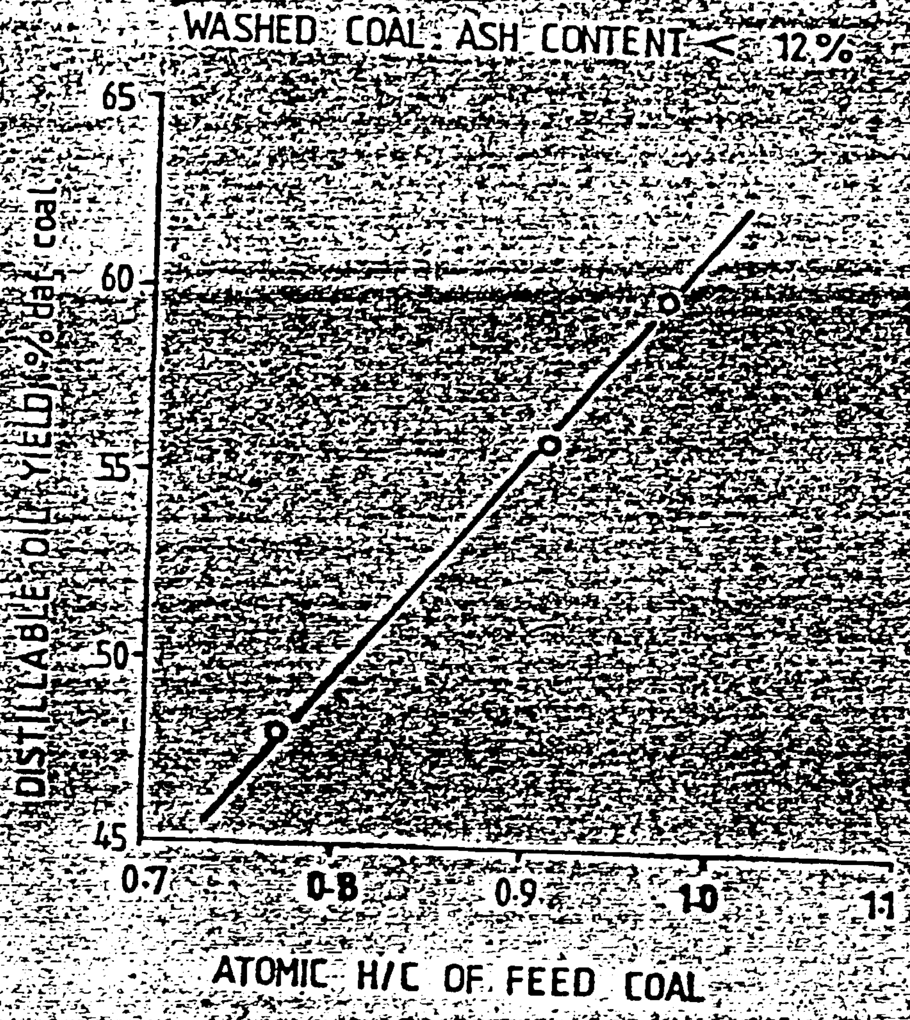
	WANDOAN	UPPER HUNTER	OLD TAROOM	NEW TAROOM
CARBON	77·6	81·4	77·5	76·4
HYDROGEN	6·0	5·2	6·0	6·4
NITROGEN	1·0	2·0	1·1	1·1
SULPHUR	0·3	0·5	0·3	0·3
OXYGEN	15·1	10·9	15·1	15·8

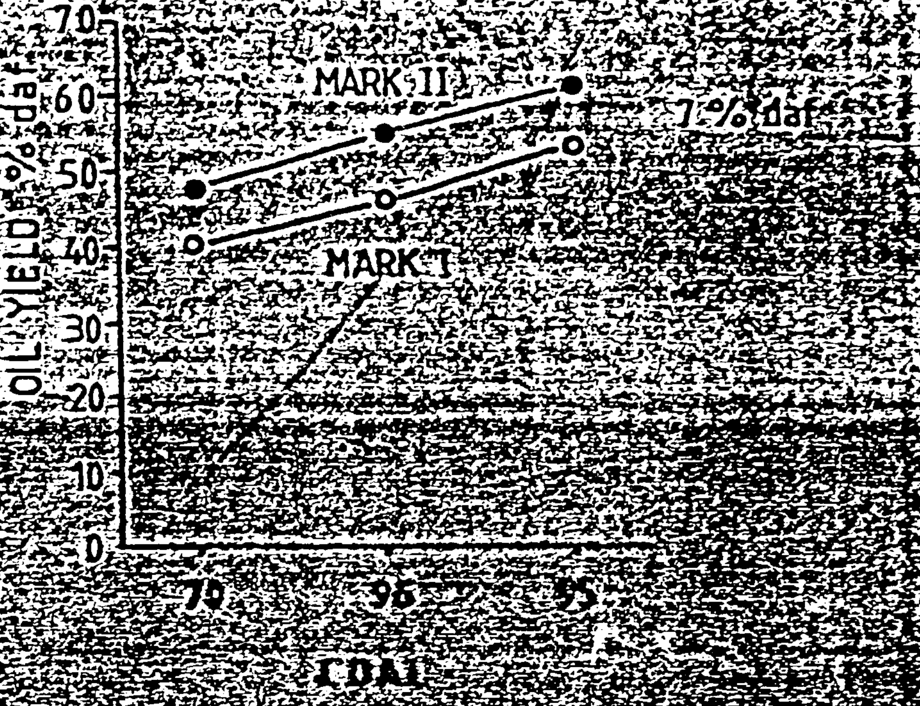
SCR vs. MARK II

T, °C		430	430	430	430	450
P, MPa		22	30	30	30	30
t, h		3	2	2	2	2
COAL		96	96	95	104	96
GAS	SCR	25	16	18	19	23
	MARK II	(25)	15	16	15	23
WATER	SCR	11	12	8	9	11
	MARK II	7	12	9	10	14
OIL	SCR	46	57	58	63	50
	MARK II	50	56	60	59	50
RESIDUE	SCR	25	20	23	20	18
	MARK II	23	22	20	22	19

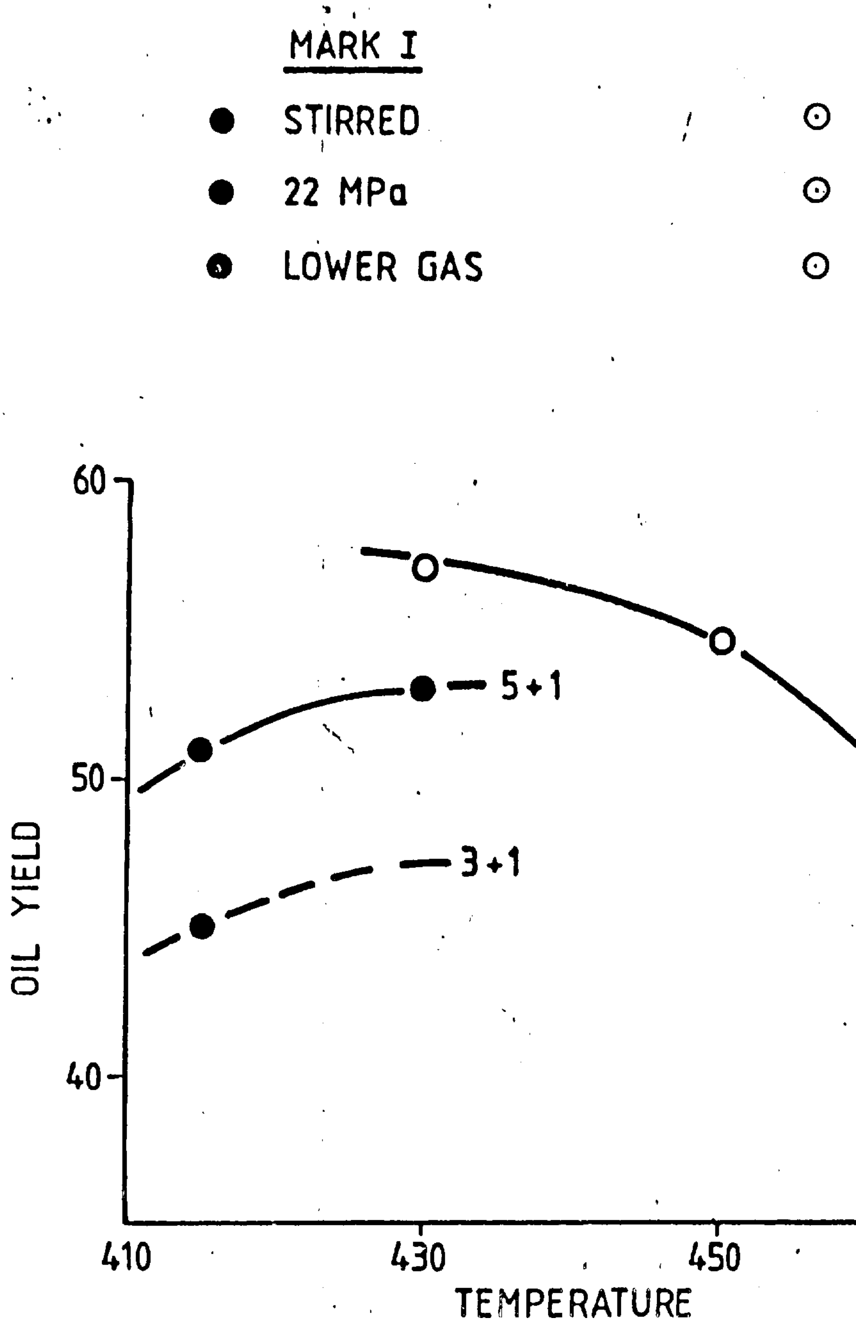
TYPICAL DISTILLABLE OIL YIELDS

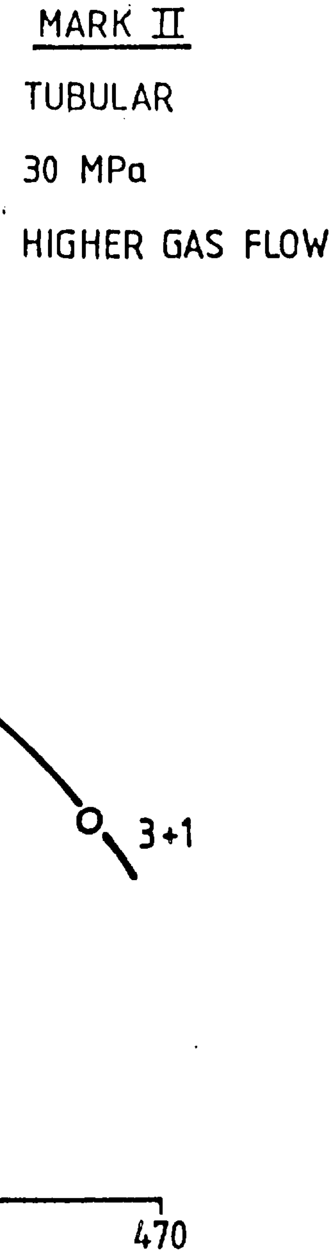
	LITRES/TONNE DAF
BROWN COAL, VIC.	500+
WANDOAN, QLD.	550
TAROOM, QLD.	600
UPPER HUNTER, N.S.W.	460

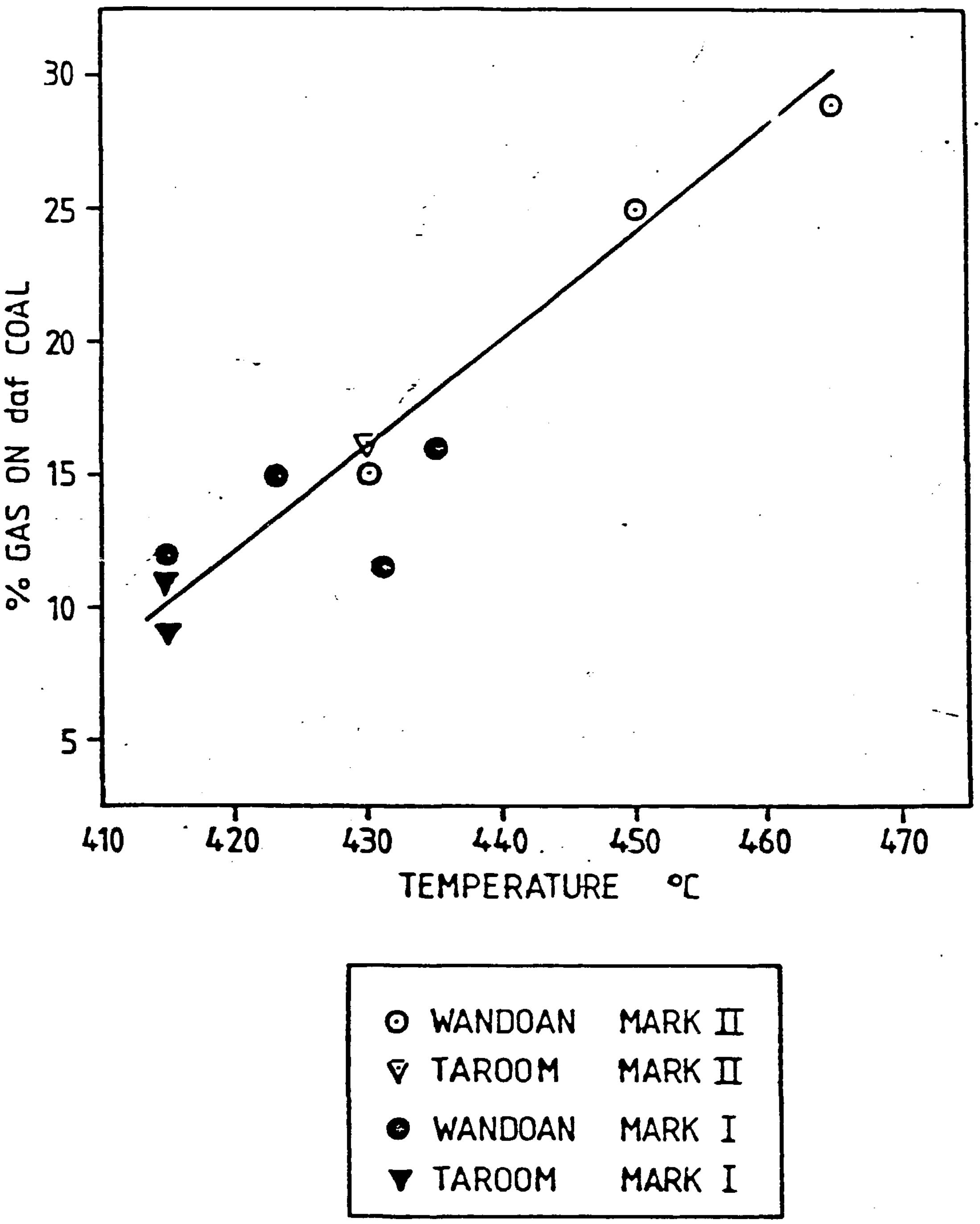

WASHED COAL ASH CONTENT < 12%
DISTILLABLE OIL YIELD % daf coal
65
60
55
50
45
0·7
0·8
0·9
1·0
1·1
ATOMIC H/C OF FEED COAL

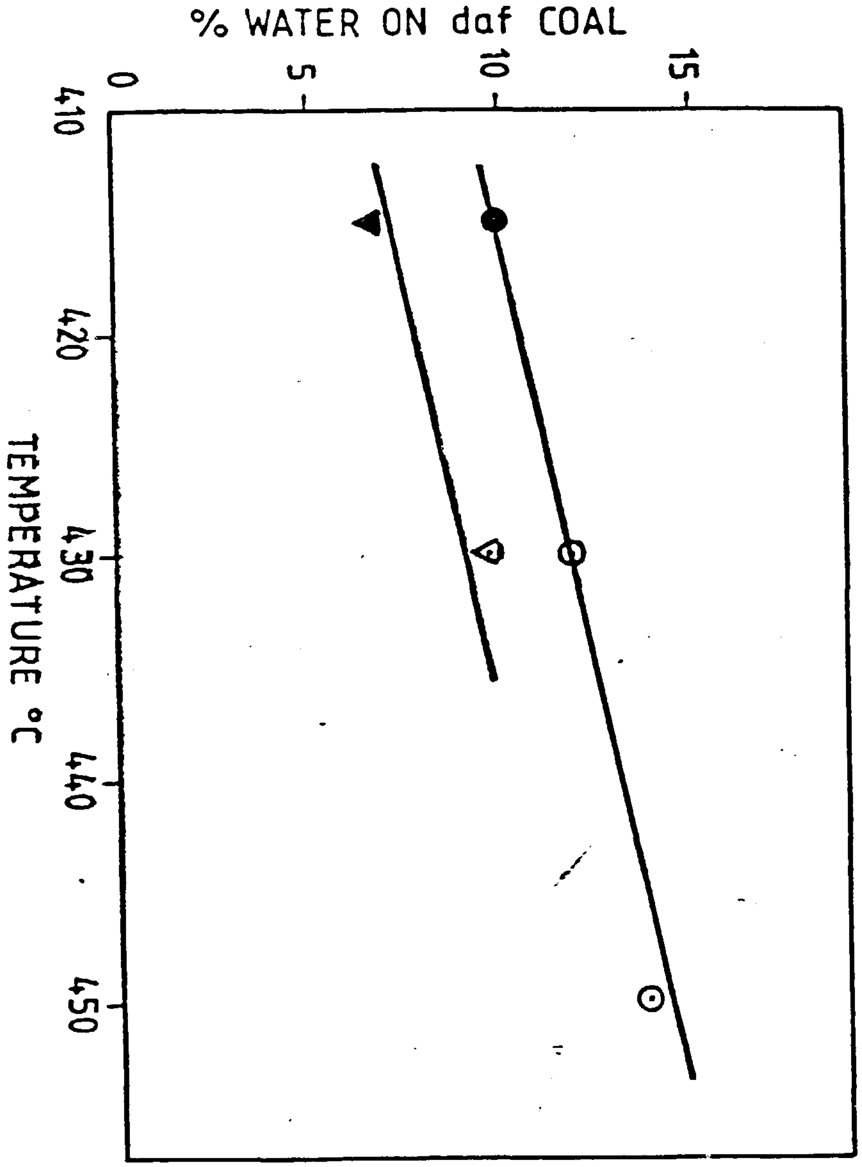


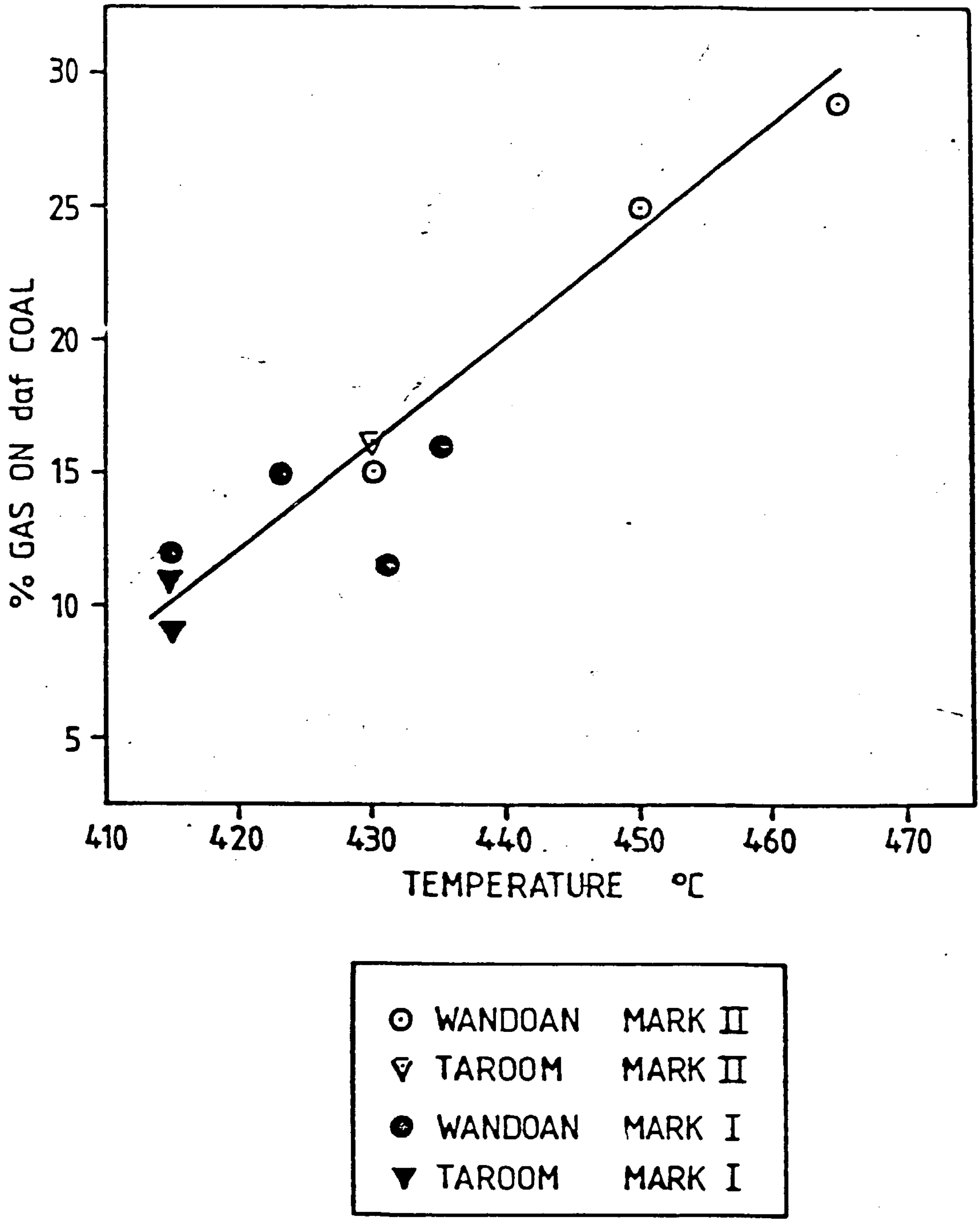
	MARK I vs MARK II	
TEMPERATURE, °C	415	430
PRESSURE, MPa	21	30
RESIDENCE TIME, h	2	2
GAS FLOW/COAL, m^3/kg	2.2	5.6
FLOW REGIME	MIXED	PLUG FLOW


MARK I
STIRRED
22 MPa
LOWER GAS
60
50
40
OIL YIELD
5+1
3+1
410
430
450
TEMPERATURE

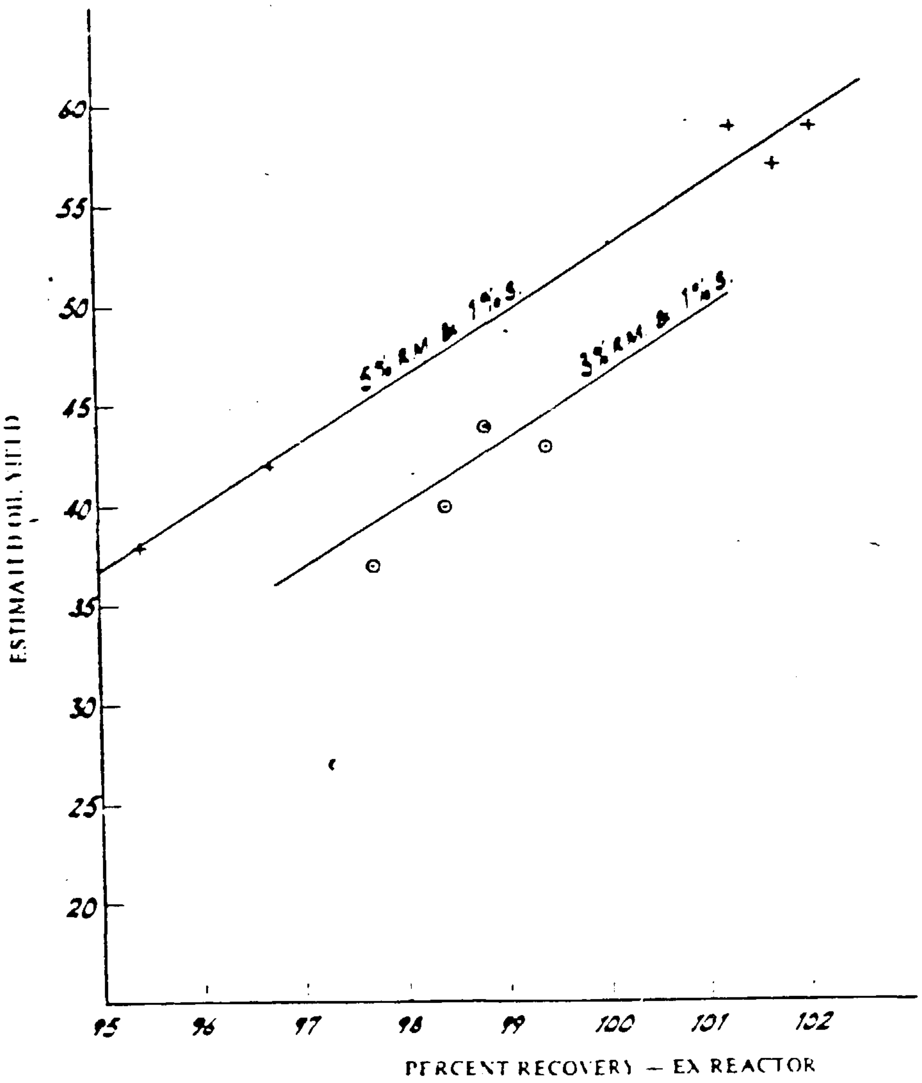

MARK II
TUBULAR
30 MPa
HIGHER GAS FLOW
3+1
470


% GAS ON daf COAL
30
25
20
15
10
5
410
420
430
440
450
460
470
TEMPERATURE °C
○ WANDOAN MARK II
▽ TAROOM MARK II
● WANDOAN MARK I
▼ TAROOM MARK I


% WATER ON daf COAL
0
5
10
15
410
420
430
440
450
TEMPERATURE °C



% GAS ON daf COAL
30
25
20
15
10
5
410
420
430
440
450
460
470
TEMPERATURE °C
⊙ WANDOAN MARK II
▽ TAROOM MARK II
● WANDOAN MARK I
▼ TAROOM MARK I


5% RM & 1% S.
3% RM & 1% S.
ESTIMATED OIL YIELD
60
55
50
45
40
35
30
25
20
95
96
97
98
99
100
101
102
PERCENT RECOVERY — EX REACTOR

ANNEX II

SUMMARY OF LECTURES BY M. J. OLIVER

1. INTRODUCTORY LECTURE

- General statements about the techniques of analysis of coal derived liquids.
- The products from our continuous reactor unit (CRU).
- The types of analysis that we perform regularly on those products.
- The major chemical changes which occur in the products as the reactor system comes to equilibrium.

2. USEFUL GENERAL METHODS

- Phenolics. Direct titration and extraction.
- Saturates. Liquid chromatography, gas chromatography, and sulphonation.
- Aromatics. Liquid and gas chromatograohy, Infra-Red.
- Resioues. Thermogravimetric analysis.
- Basic Nitrogen.
- Solvent extraction.

3. GAS CHROMATOGRAPHY AND GCMS.

- Description of ACIRL's system.
- Applications. Fractions from chromatography.
  Hydroaromatics.
  Distribution of species.
  Reactor dynamics.
- Quantitation problems.
- Interpretation of GCMS.
- Direct MS of "heavy" materials.

4. SIMULATED DISTILLATION.

- Reproducibility.
- Quantitation.
- Applications. Evaluation of distillation.
  Evaluation of process "Chemistry".
  Prediction of other analytical parameters.
- Dependence of analytical results on boiling point distribution. (Saturates, phenolics.)

1. INTRODUCTORY LECTURE.

We have attempted to examine the products of our CRU using all of the techniques available at our laboratory. We have used Infra-Red absorption, elution chromatography, high pressure liquid chromatography, capillary gas chromatography, gas chromatography-mass spectrometry, wet chemical methods, elemental analysis, thermogravimetric analysis, solvent extraction and distillation.

- General Statements About the Techniques of Analysis of Coal Derived Liquids.

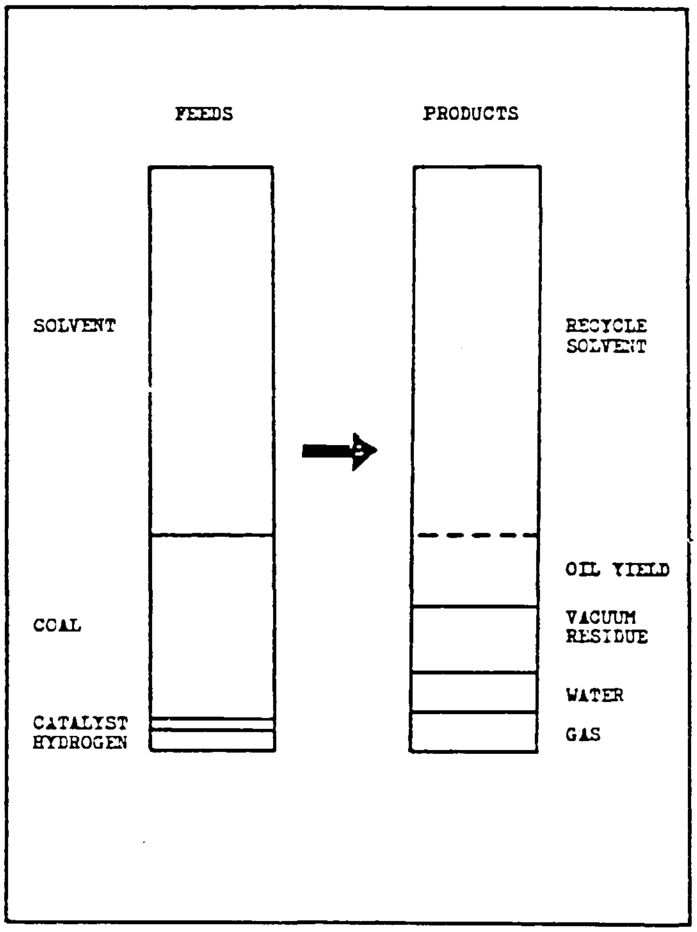
We have found that many simple techniques like I-R absorption can give useful information, but that this information is better interpreted with knowledge gained from other techniques. In practice, many techniques have major and minor disadvantages. The interpretation of results from a single technique can often be misleading if the limitations of the method are not properly understood. Furthermore, the type of sample being analysed must be understood also. For example, it is important to make sure that the boiling range of two samples are identical before other analysed parameters are compared. Some classes of compounds are very sensitive to changes in boiling range. As another example, the distinction between oils and ashphaltenes by sovent extraction is usually considered to be a simple matter, but the results can depend on the exact procedure used, and the molecular weight range of the sample.
Sophisticated methods are also not free from problems. GCMS is an extremely powerful tool for the investigation of coal derived liquids, but suffers from major quantitation problems. We can characterise a class of compounds very well using GCMS, but must rely on alternative methods to quantify that class.

The results obtained from a single analytical technique must always be carefully interpreted, bearing in mind the disadvantages of that particular method.

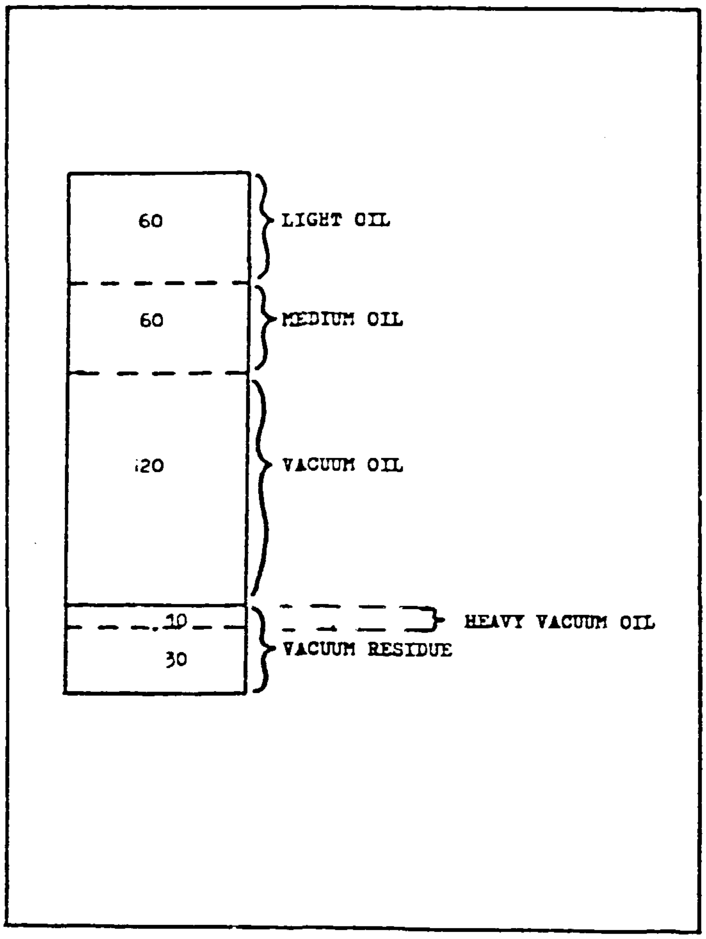
- The Products from our Continuous Reactor.

My colleague, Dr. Staker, will describe the engineering configuration of our CRU, so I will not present those details here.

Most of my experience has been involved with the analysis of the products of our CRU, so I will firstly describe a typical product "slate" from the hydrogenation of Wandoan coal. (Queensland sub-bituninous). The following diagram typically represents our process.



The following diagram illustrates the oil and residue streams in more detail. Naturally, process temperatures in the reactor and the distillation unit can significantly alter the relative proportions of each stream. There is normally a large overlap of boiling range characteristics of each product stream.



Since our continuous vacuum distillation unit is run at conditions to prevent gasification or coking, the vacuum residue stream contains between 15% and 35% of oil recoverable by further batch vacuum distillation, and is useful as recycle solvent. Usually however, the recycle solvent is made from the vacuum oil, medium oil, and the heavy ends of light oil after flash distillation.

[illegible] Types of Analysis that we Perform Regularly on Those Products.

(i[illegible]es. Various gas streams are continuously selected and analysed by our process gas analyser for H_2, CH_4, CO_2, CO, H_2S and C_2-C_5 hydrocarbons. The major requirement is to determine the molecular weight of each stream to enable mass balance calculations, but also to check on the gas scrubber performance.

(ii) Process Water. Process water and light oil are discharged together from the hot separator stream, and are manually separated. The foul water would be a disposal problem on an industrial scale, and is analysed for ammonia, sulphide, pH, and occasionally carbonate. The water also contains about 1% organic matter, mainly phenol and cresols.

(iii) Oils and Residues. The following table demonstrates the usual analyses performed on the oils and residues.

	LIGHT OIL	MEDIUM OIL	VACUUM OIL	VACUUM RESIDUE	HEAVY VAC.OIL
C,H,N	*	*	*	*	*
basic N	*	*	*	X	*
acidic OH	*	*	*	*	*
S	*	*	*	*	*
Density	*	*	*	X	X
Saturates	*	*	*	X	X
Infra-Red	*	*	*		*
Sim.Dist.	*	*	*		*
Toluene Insol.				*	
Hexane Insol.			*	X	*
Proximate				*	

* Regular analysis

X Occassional analysis, or special conditions apply.

When unusual situations develop, or when the above list does not fully explain any changes in product characteristics, GC and/or GCMS is used as a further analytical tool. For example, we recently processed a Victorian Brown coal using synthesis gas. Many of the regular analyses were unusual, and so we conducted

GCMS analysis on the recycle solvent. We found that the hydroaromatics content was much lower than we have found with sub-bituminous coals, and therefore the "donor" property of the solvent was considered to be poor. Later evidence suggested that this abnormal property was most likely due to a combination of low gas feed rate, faulty mechanical agitation, and solids accumulation in the reactor.

The light and medium oils are usually straw coloured when freshly distilled, but turn black on exposure to air and light. Sometimes these products have a red tinge, especially when phenolics content has accumulated to equilibrium levels. The vacuum and heavy vacuum oils are initially yellow to light brown in colour, but these also darken on exposure to air. Recycle solvent is subjected to the same analysis procedures as vacuum oils.

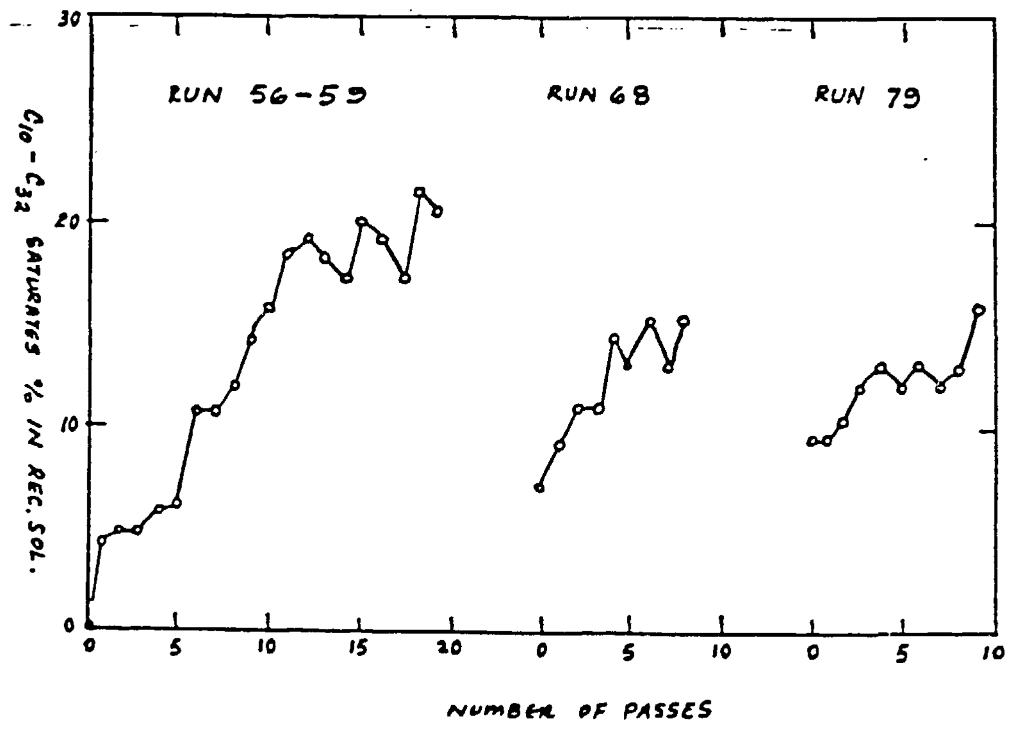
The sampling and analysis scheme that I have presented is actually a simplification. During a run, new feed slurry is prepared, and discharges are made every six hours. Fourteen samples of feeds and products are taken at this time. Therefore, at the end of a run I can be given up to 700 samples to analyse. My first step is to decide when the process has physically and chemically reached a steady state, and select or composite samples to represent the most steady period of operation. Careful study of the recorded details of the run can eliminate a few samples because of obvious problems such as leaks, blockages in the preheater or feed line, and agitator malfunction. Conferences with the CRU operators sometimes reveal problems which were not recorded, and so a post-run conference can be an important source of information for the supervisor of chemical analysis. But the major question, "When has the process reached a steady state ?" is the subject of the next section.

- The Major Chemical Changes Which Occur in the Products as the Reactor System Comes to Equilibrium.

Many hydrogenation experiments use tetralin, creosote oil, hydrogenated creosote oil, anthracene oil, and hydrogenated anthracene oil as the solvent. In most cases, the conversion to toluene solubles is the same as that obtained with a continuous reactor using stedy state solvent and the same conditions. Even conversion to oils based on hexane solubility may be similar, although a continuous reactor will generally have a slightly higher oil yield at steady state. However, if the products of a single pass experiment are characterised, they will exhibit major differences when compared to the products of a highly recycled, continuous reactor operation.

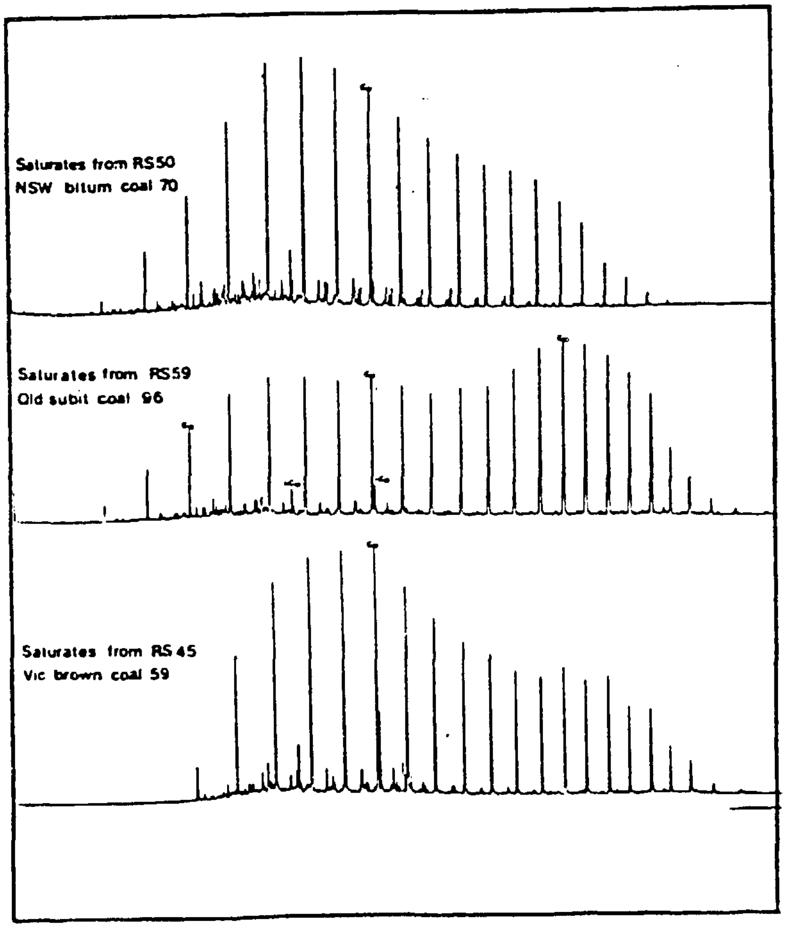
Three major chemical changes take place in the composition of the oils recycling in a continuous reactor. These changes are most noticeable if athermal solvent like creosote or anthracene oil has been used to start up the process.

(i) Saturates, which are usually not present in starting solvent, may accumulate to about 20% in recycle solvent. This process can take up to 10 passes to stabilise.

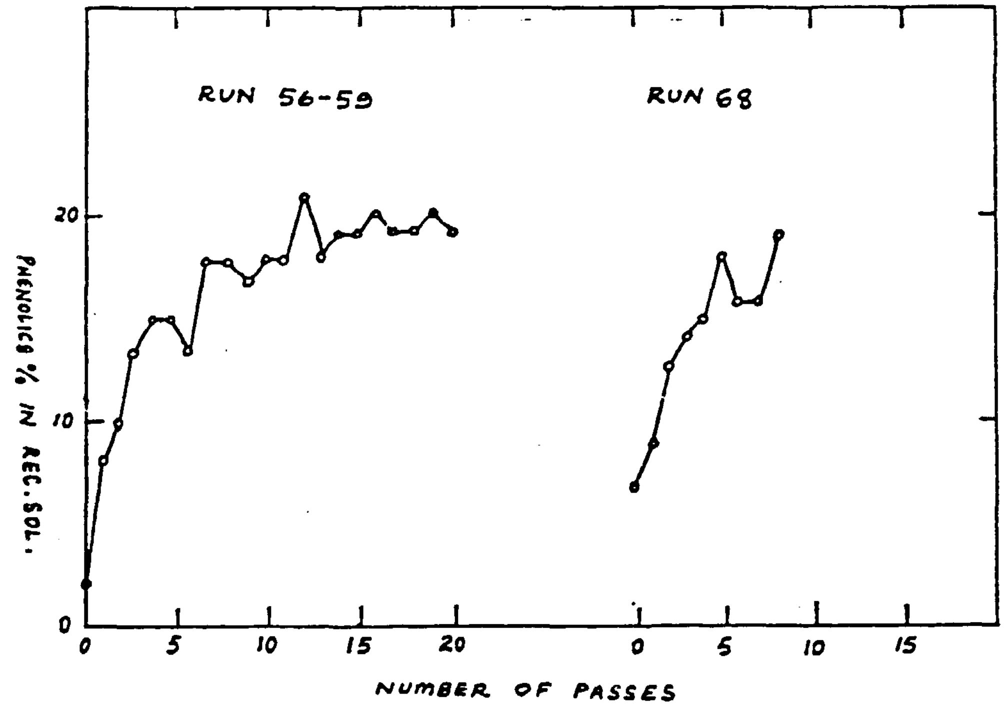


Presumably, this accumulation is is an equilibrium between the rate of generation of saturates from the coal, and the rate of conversion to lighter saturates which are withdrawn as light oil product. The proportion of light oil product withdrawn from the system, and the process severity will obviously affect the equilibrium level of saturates. Also, it is likely that the lightest saturates are produced directly from the coal, rather than from a series of intermediate reactions. By lightest saturates I mean C_1-C_3 hydrocarbon gases, which are not normally included as product oil. However, we have not been able to devise any satisfactory experiments to prove or disprove these statements.

We have found that the Queensland sub-bituminous coals, Wandoan and Taroom, tend to reach higher steady state saturate levels than other coals. The New South Wales coal, Denman-Scone, accumulates lower levels of saturates, but the distribution of saturate species is noticeably different.



(ii) Phenolic compounds also accumulate to levels of about 20% in recycle solvent. However, phenolics are not evenly distributed, and occur mainly in the boiling ranges 175-250°C and 450°+ . This means that the distillation cut used to discriminate between light oil product and recycle solvent, very often 175-250°C, can readily cause fluctuations in the level of phenolics in recycle oil, even though other conditions and/or chemistry has reached steady state. Our best information shows that phenolics require about 5-7 passes to stabilise.

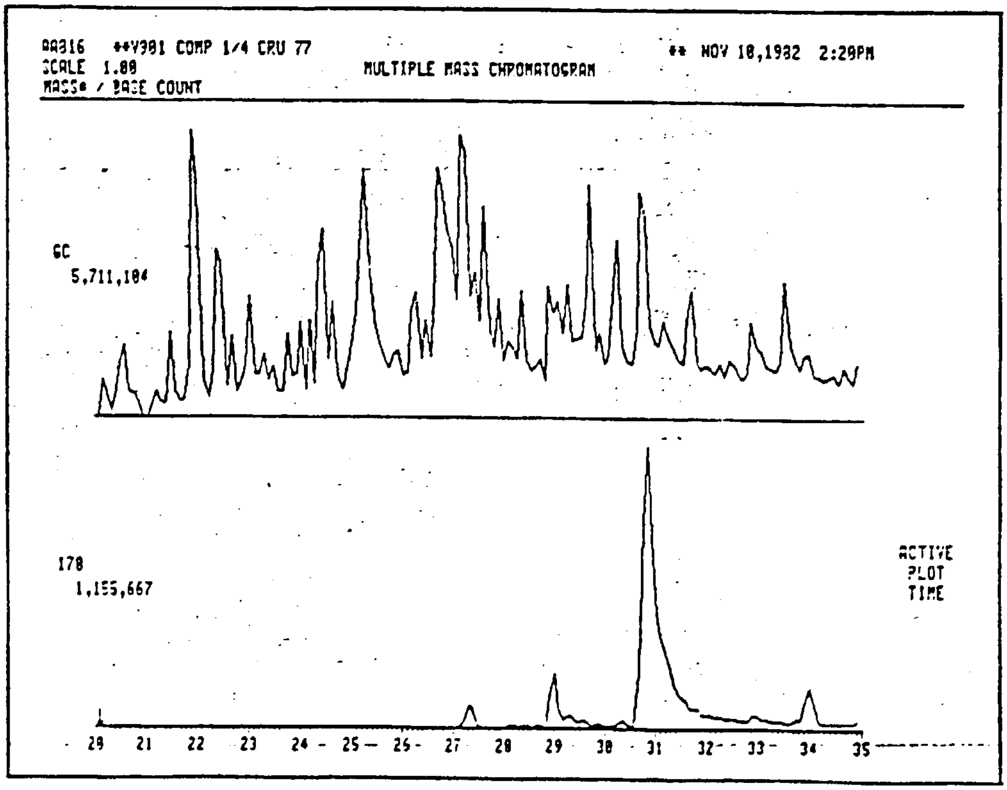


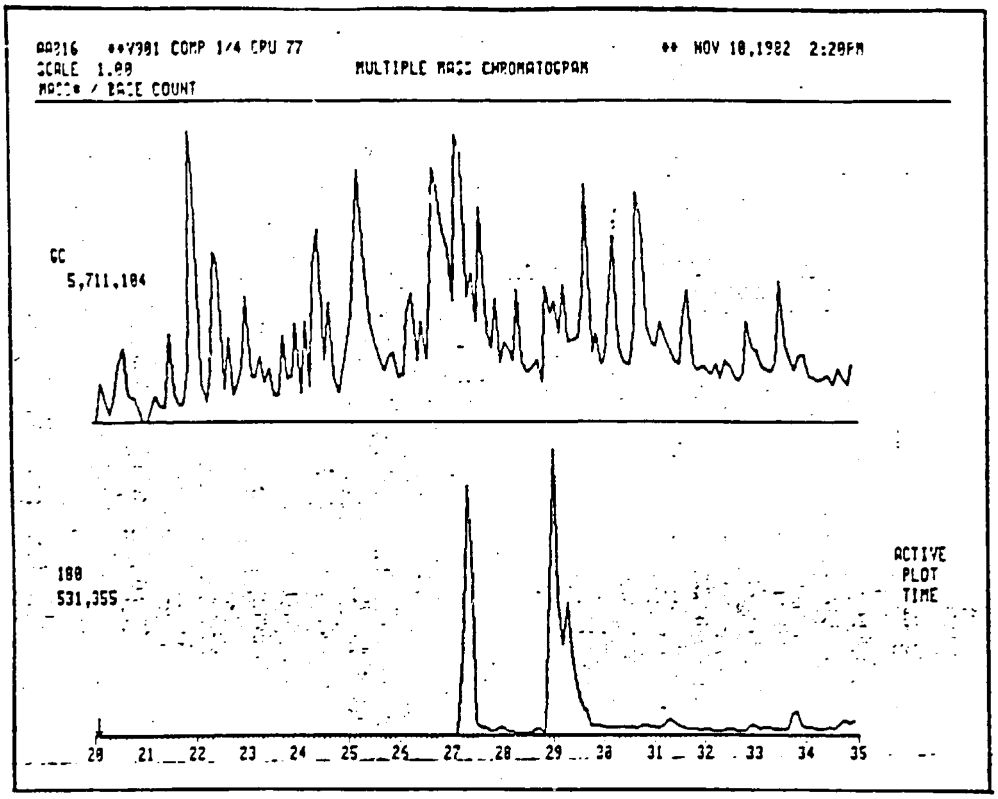
Our studies of the composition of phenolics show that they are mainly phenol, cresols, and diminishing concentrations of C_2 - C_6 substituted phenols. However , we have found phenolic species in heavy vacuum distillate containing up to about C_{20} substituent chains. Mass balance studies have shown that about 2% coal oxygen is converted to phenolics, about half resides in the vacuum residue, and the other half resides in the oils. We are studying the matter further using micro-autoclave reactions.

OH MASS BALANCE RUN 77B

	MASS KG	OH %	MASS OH KG			
COAL IN	100.0	4.82			4.82	
OIL IN	188.5	2.17	4.09	4.09	4.09	
			4.09	4.09	8.91	IN
LIGHT OIL OUT	65.4	2.63	1.72	1.72	1.72	
MEDIUM OIL OUT	48.7	2.61	1.27	1.27	1.27	
VACUUM OIL OUT	99.5	1.88	1.87	1.87	1.87	
VACUUM RESIDUE OUT	59.6	1.56		.93	.93	
			4.86	5.79	5.79	OUT
			+.77	+1.70	-3.12	YIELD

(iii) Hydroaromatics are an important class of components if the donor property of the recycle solvent is considered. Hydroaromatics cannot be separated as a class by chemical methods but can be readily identified in GCMS chromatograms.




AA216 **V381 COMP 1/4 CPU 77
** NOV 18,1982 2:29PM
SCALE 1.00
MULTIPLE MASS CHROMATOGRAM
MASS# / BASE COUNT
GC
5,711,104
180
531,355
ACTIVE
PLOT
TIME
20
21
22
23
24
25
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31
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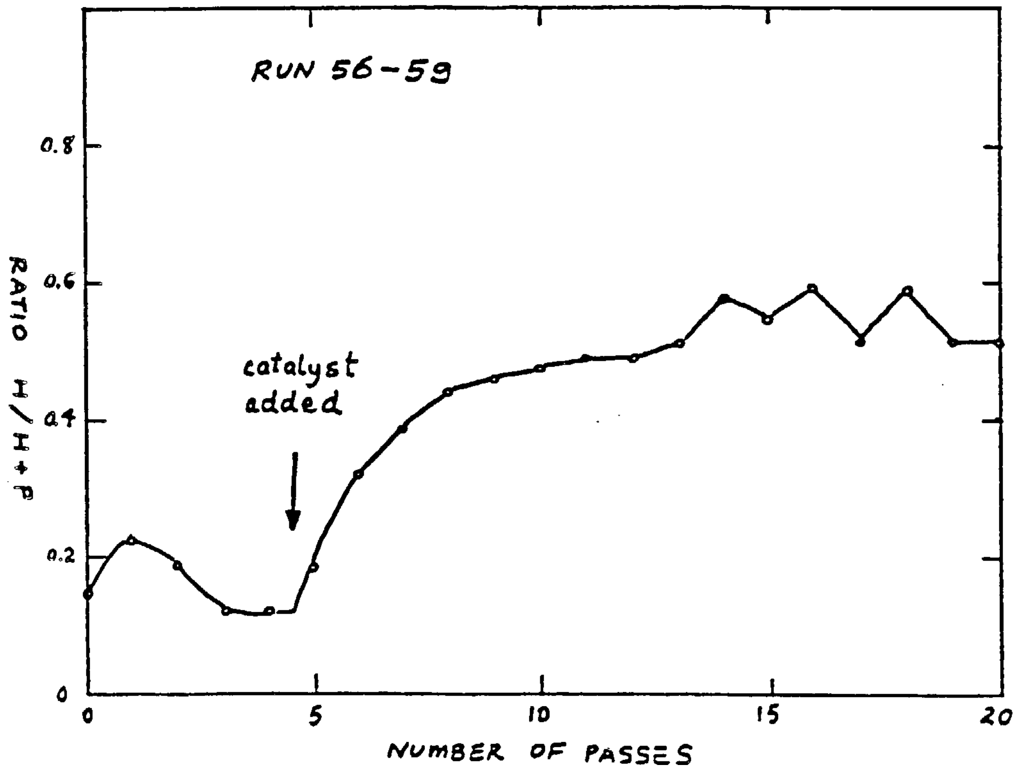
33
34
35

We have noticed that hydroaromatics are more dependent on the presence of catalyst than phenolics or saturates, and follow different behaviour. However , their presence in higher concentrations would be expected to modify the behaviour of the other classes. We studied their behaviour during a run in which no catalyst was added to the feed slurry. The starting solvent was moderately hydrogenated creosote containing an hydroaromatic ratio of 0.15. This ratio reduced to 0.10 after 5 passes, during which time the phenolics and saturates accumulated to about 50% of their later steady state value. Catalyst was then added to the slurry, and hydroaromatics rose to a ratio of .5 - .6 within a further 3-5 passes.



The quantity of hydrogen needed to raise a solvent from a ratio of .1 to .5 is quite small, about 0.1-0.3%, depending of course on the most abundant isomers present in the solvent. Therefore, this type of change is not often noticed in elemental analysis, and so other techniques, especially if the major changes in hydrogen content are caused by accumulation of saturates.
Some of our microautoclave studies tend to confirm that hydroaromatics are most important in the initial rapid stage of conversion , and may take up to one hour's residence time to regenerate. We have lately seen that hydroaromatics behave differently with brown coal, and may be more difficult to maintain at high levels than with sub-bituminous coals. However , this unexpected property may be due to our limited experience with brown coals, and the selection of proper processing conditions.

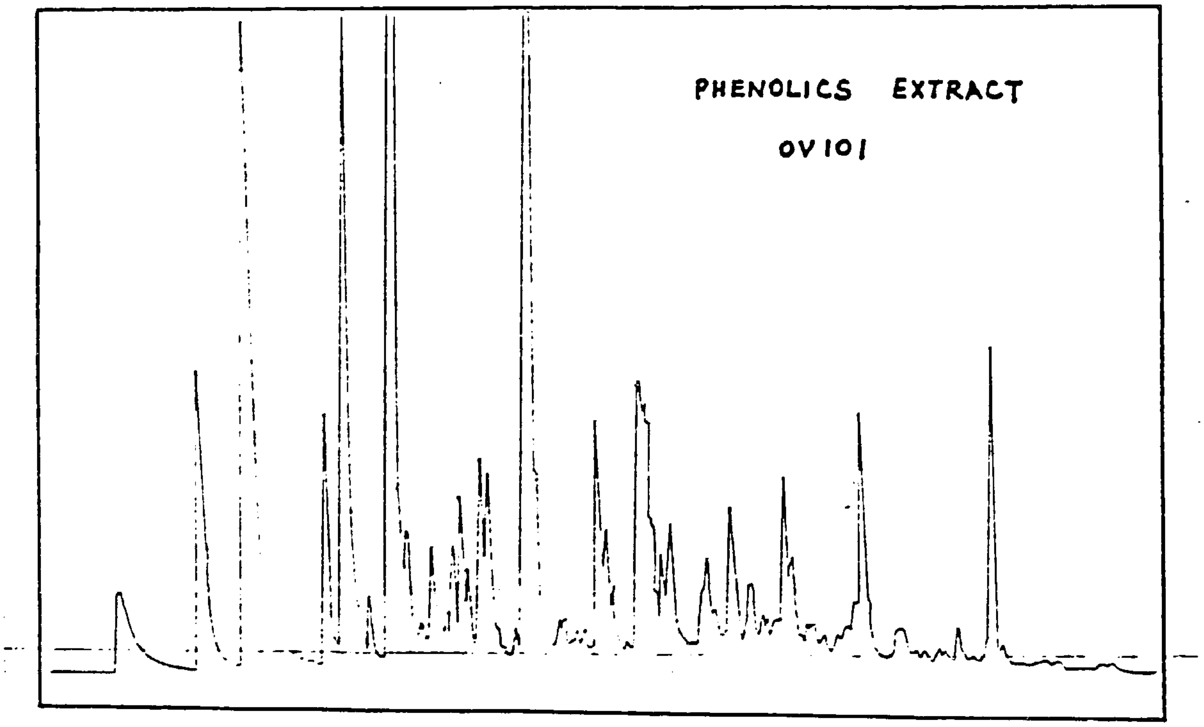
COMMENTS. A wide variety of analytical techniques can be useful in the study of coal hydrogenation. No single technique is perfect. No single technique is best.

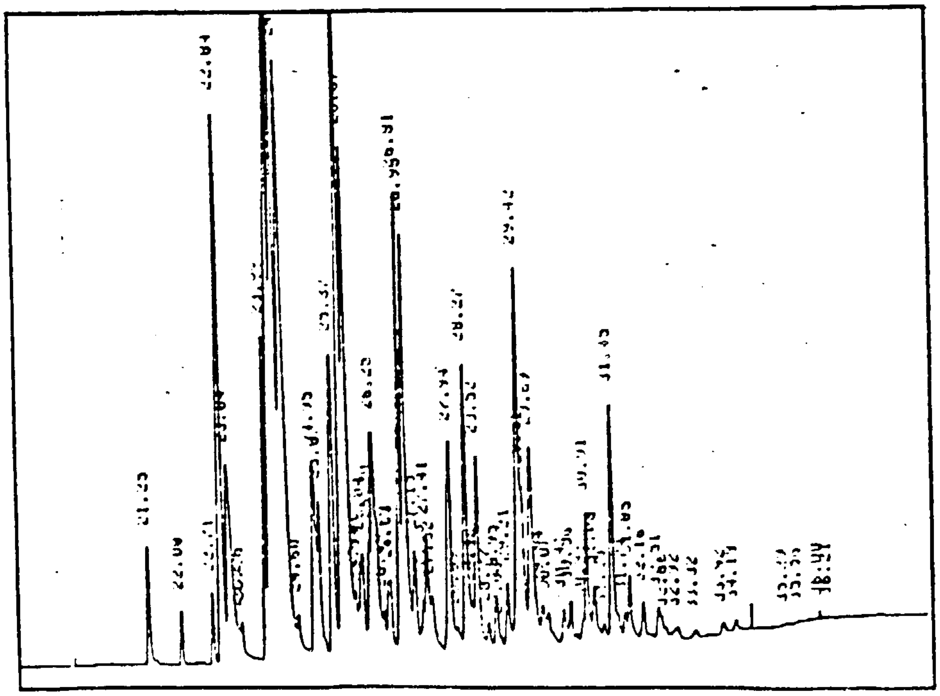
Interpretation of results should only be attempted when the process has reached a steady state. This steady state is achieved when the levels of saturates and phenolics have stabilised mainly in the recycle solvent, and when beneficial levels of hydroaromatics are achieved and stabilised. The steady state requires at least ten recycle operations.

2. USEFUL GENERAL METHODS.

- Phenolics.

Phenolics are a major component of continuous reactor products and account for almost all of their oxygen content. Phenolics can be relatively efficiently extracted from lighter oils using aqueous alkalies.





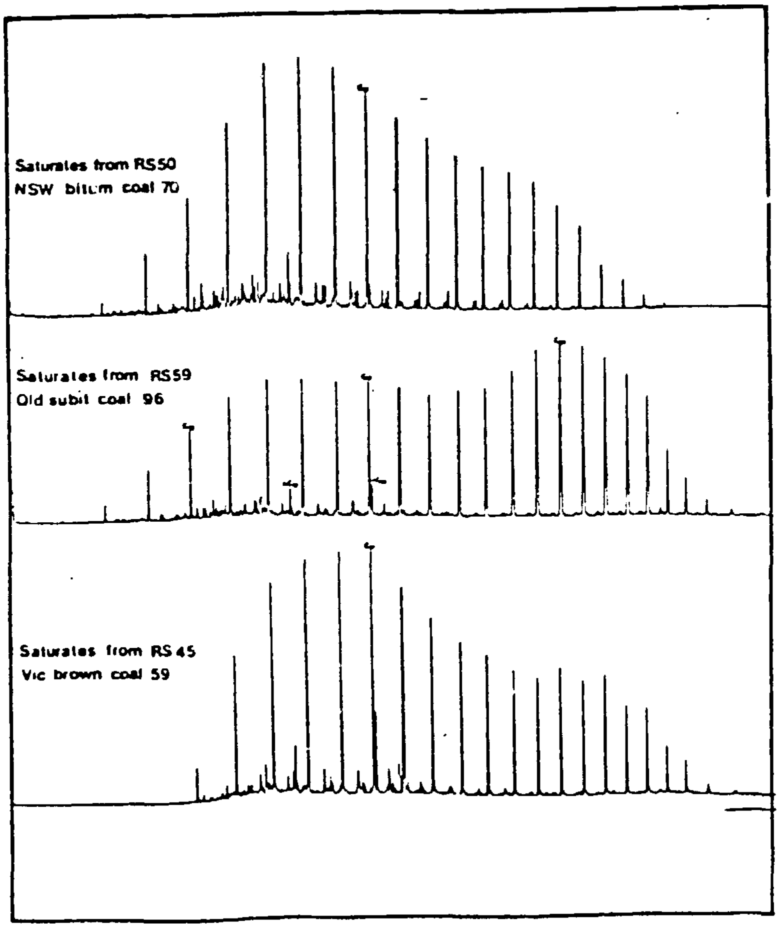
During our earliest runs we used a primitive method to estimate phenolics. The method involved extraction, precipitation, and measurement of the precipitate's volume. When we saw 20 vol.% phenolics in some products, we were inclined to disbelieve the results. But later work has shown that these early results were essentially correct.

We now prefer to measure the functional group, Aromatic OH, directly using enthalpimetric titration. The technique is relatively simple and economic, and has been used by coke-oven tar analysts for many years. The particular advantage of this method is that it is applicable to almost any material that can be suspended in acetone, even coal with special treatment. However, under the best conditions, not better than 5% inaccuracy must be expected.

If we wish to calculate the % phenolics from %OH, we use an estimate of likely molecular weight using simulated distillation results and knowledge acquired from GCMS.

Saturates.

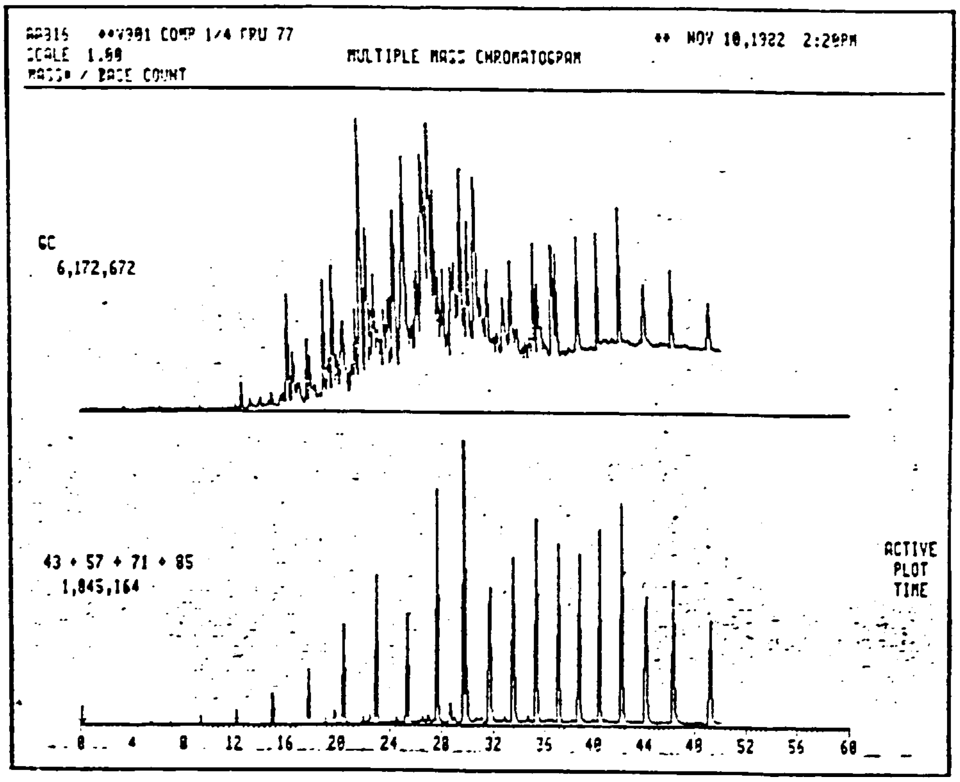
Saturates can be effectively determined by a variety of methods. Elution chromatography, normally using silica gel or silica gel and alumina as adsorbent, generally yields a clean fraction of saturates which can be weighed after removal of solvent.



Light oils may contain major quantities of volatile saturates, and in this case a better method is to use the Fluorescent Indicator Absorbtion (FIA) test. The method yields a value for saturates, olefins, and aromatics. Polar compounds interfere and must be removed before the test is carried out.
Volume % saturates can be quickly and economically determined using sulphonation to remove all other components. Samples are sulphonated using H_2SO_4/P_2O_5 praferably at 0^oC, the products are carefully centrifuged, and saturate collect in an upper layer. Samples containing saturates bigger than about $C_{16}H_{34}$ tend to crystallise in an unsuitable state, but a controlled quantity of a liquid paraffin such as dodecane can be added to the reaction.

The method can be modified to yield a value of mass% saturates with the help of gas chromatography. Samples can be sulphonated in the presence of a known quantity of internal standard, dodecane is satisfactory, and the saturate layer injected into a GC. Mass% saturates can then be calculated with respect to the internal standard.
Very heavy oils sometimes produce very viscous sulphonation products from which it is difficult to seperate the saturates. Reduction of sample size normally corrects the problem.

Saturates can be seen in GC chromatograms of whole oils, but many major and most minor species are obscured by other major aromatic components etc., and quantitative estimates are difficult. However saturates can easily be seen in GCMS chromatograms by the use of selected ion display. Quantitation by GCMS is most difficult, but the distribution of saturate species gained is practically identical to that gained from sulphonation/GC.

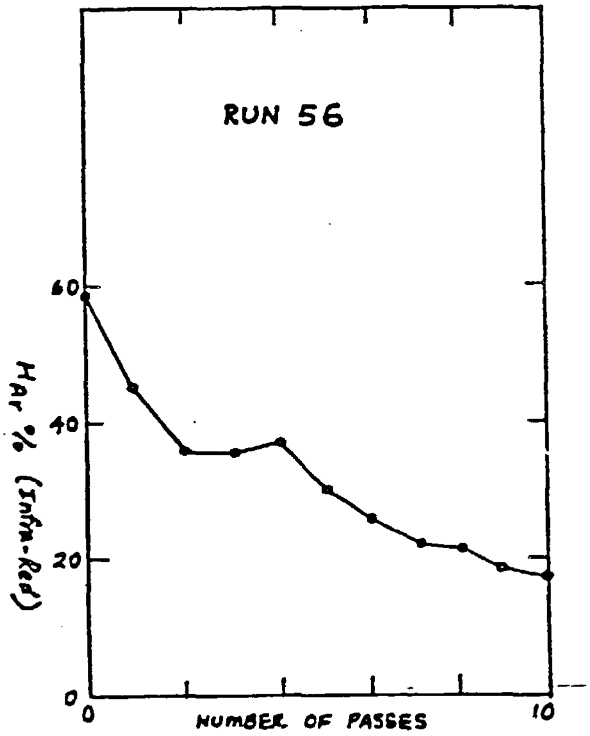


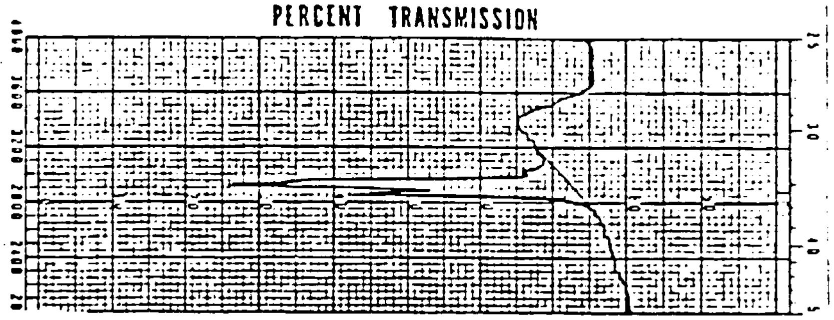
- Aromatics.

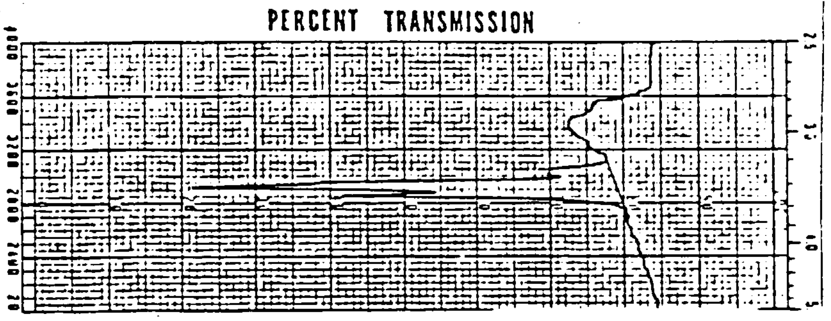
Detailed study of aromatics and hydroaromatics is most conveniently made using GC and GCMS methods. Aromatics of molecular weight higher than pyrene are normally not efficiently eluted by high resolution columns , although this factor is usually due to injector od detector design, Of course, the use of short or packed columns allow more heavy components to be eluted, but there is a corresponding loss of resolution.

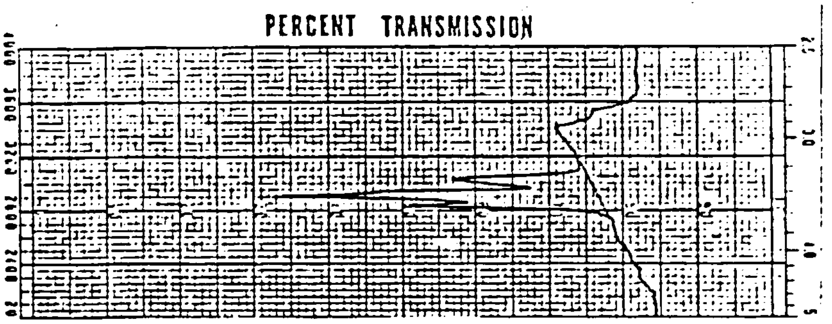
We have used elution chromatography to separate oil into fractions yielding saturates, monoaromatics, polyaromatics and polars. We found that there were problems of recovery, sometimes due to evaporation losses of volatile components, and sometimes due to irreversible adsorption of polar materials on alumina. We have also used HPLC to study changes in aromatic components, but the UV detector was generally unsatisfactory for resolving hydroaromatics in the prescence of aromatics. Nevertheless, there has been major advances in HPLC technology, particularly columns and detectors, and the problem may not be so apparent today.

During most CRU runs we follow changes in most streams using Infra-Red absorption. We calculate the % aromatic CH stretching and aliphatic CH stretching absorptions. Although many factors contribute to this value, the method is the simplest tool which indicates the approach to equilibrium of the reactor system. It is not possible to discriminate between changes in hydroaromatics and accumulation of saturates using this method. Accumulation of phenolics to high levels interferes with the analysis due to the nearby broad OH stretching absorptions, although the effect is partly reduced by the use of non-polar diluents.



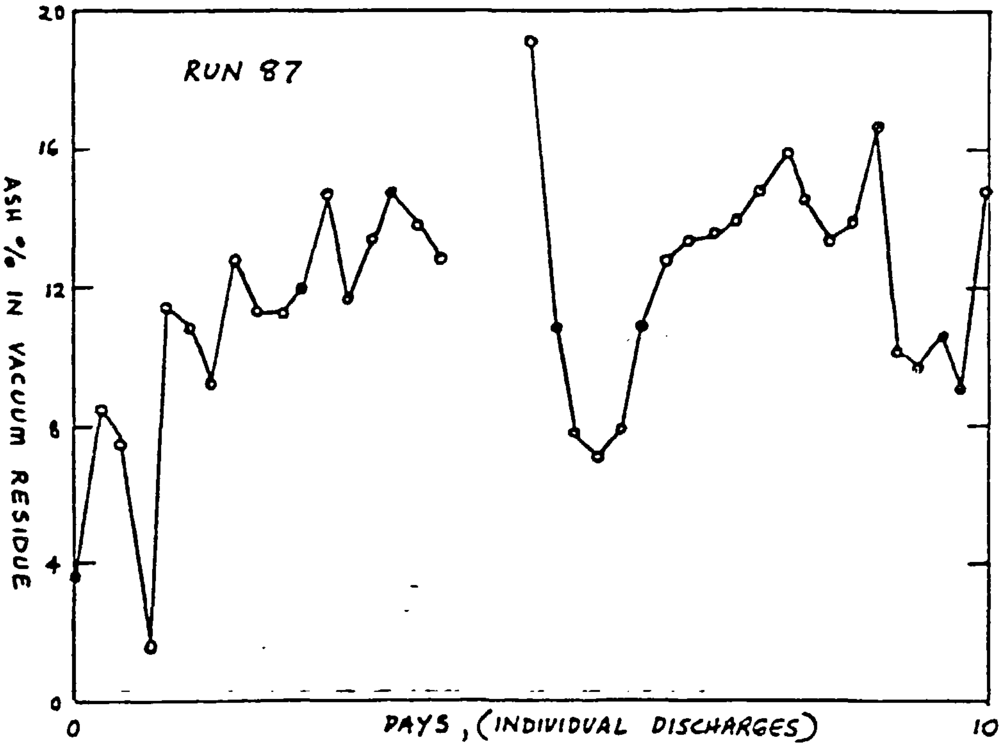






- <u>Residues.</u>

If possible, we try to monitor the proximate analysis of the vacuum residue stream as soon as it is discharged from the reactor. We determine the volatile matter, fixed carbon, and ash content using a thermogravimetric analyser. Naturally we could also use conventional furnace methods, but the TGA also gives us a crude volatility profile of the material.
The ash content is the most important, because it tells us when the in-line distillation unit has achieved stable operation, and also indicates when solids may be separating in the reactor system.



- <u>Basic Nitrogen.</u>

We determine total C,H, and N in all products using an automated micro elemental analyser. Considerable operator experience is necessary to ensure that the N value is accurate. We also determine the basic N in most products using non-aqueous titration. This method is relatively fast, and is more accurate than the micro method for total N. We find that basic N and total N are the same in light oils, and that basic N becomes a progressively smaller fraction of total N as the boiling range of the sample increases. The basic N ratio also tends to increase as the prosess moves towards a steady state, this phenomenon being more noticeable in the heavier products.

- Solvent Extraction.

many low severity hydrogenation experiments use solvent extraction to estimate oil yield, ashphaltenes, etc. In these cases, the molecular weight differences between oils and ashphaltenes are sufficiently great to justify the effectiveness and reliability of the extraction solvents and method. However, high severity experiments, and particularly continuous reactor systems, tend to produce materials of an intermediate molecular weight. The distinction between oils and ashphaltenes is now not so clear, and solvent extraction methods can give variable results, affected by the exact procedure used, and the physical condition of the sample.

3. GAS CHROMATOGRAPHY AND GCMS.

- Description of System.

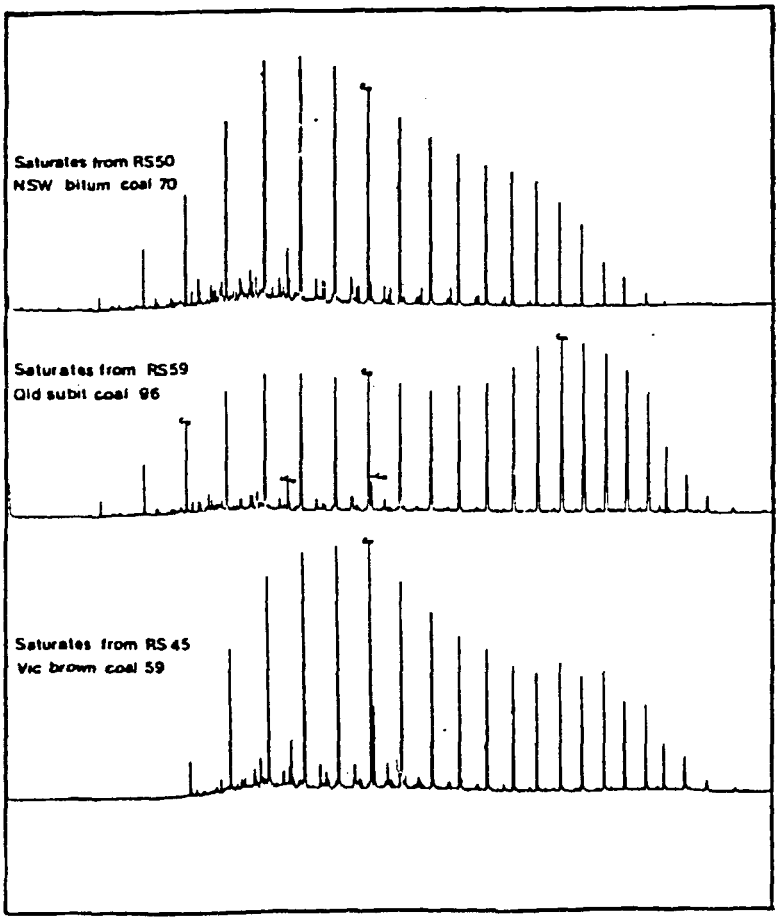
We have two microprocessor based gas chromatographs. One is dedicated to gas analysis, and the other is free to carry out a wide variety of functions, such as capillary GC and simulated distillation.

In addition we have a DuPont DP-1 GCMS system which contains a fully programmable capillary GC. The mass spectrometer is a low resolution, magnetic sector, accelerating voltage scanning type, with a programmable direct inlet probe attachment. The instrument is able to switch from electron ionisation to chemical ionisation in a few seconds, and up to three reagent gases can be selected from the instrument console. The instrument is not equipped to carry out low voltage ionisation work. The GC.MS interface is a heated jet separator.

- Applications.

- Fractions from chromatography.

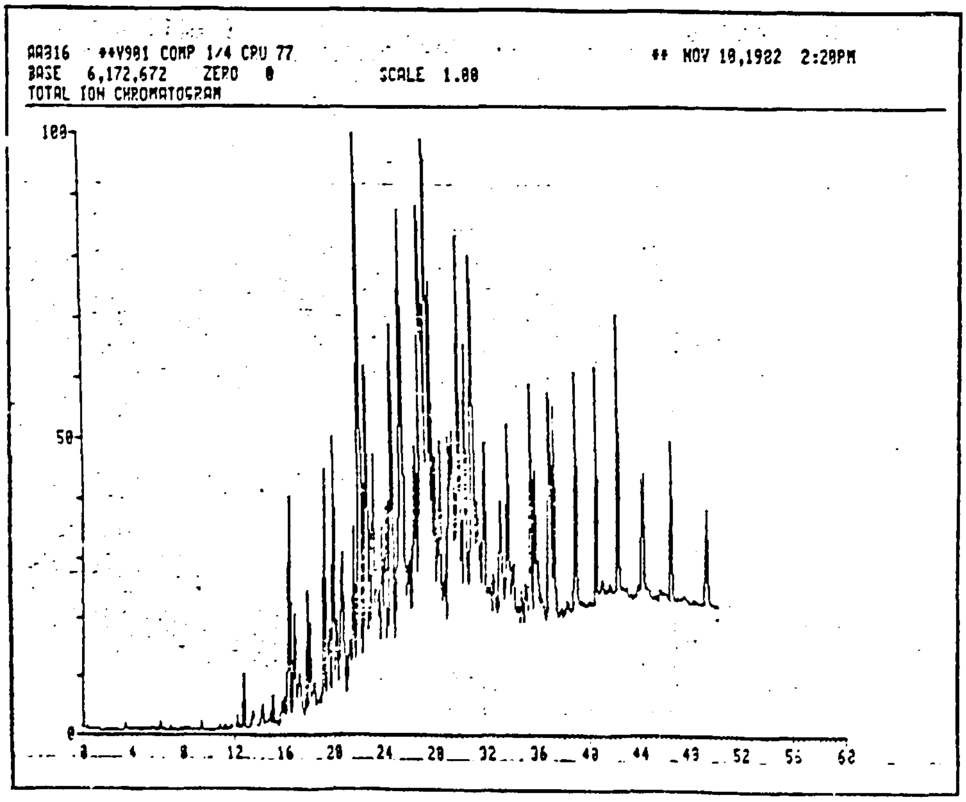
Our first application of GCMS was to inspect the fractions obtained from elution chromatograohy.

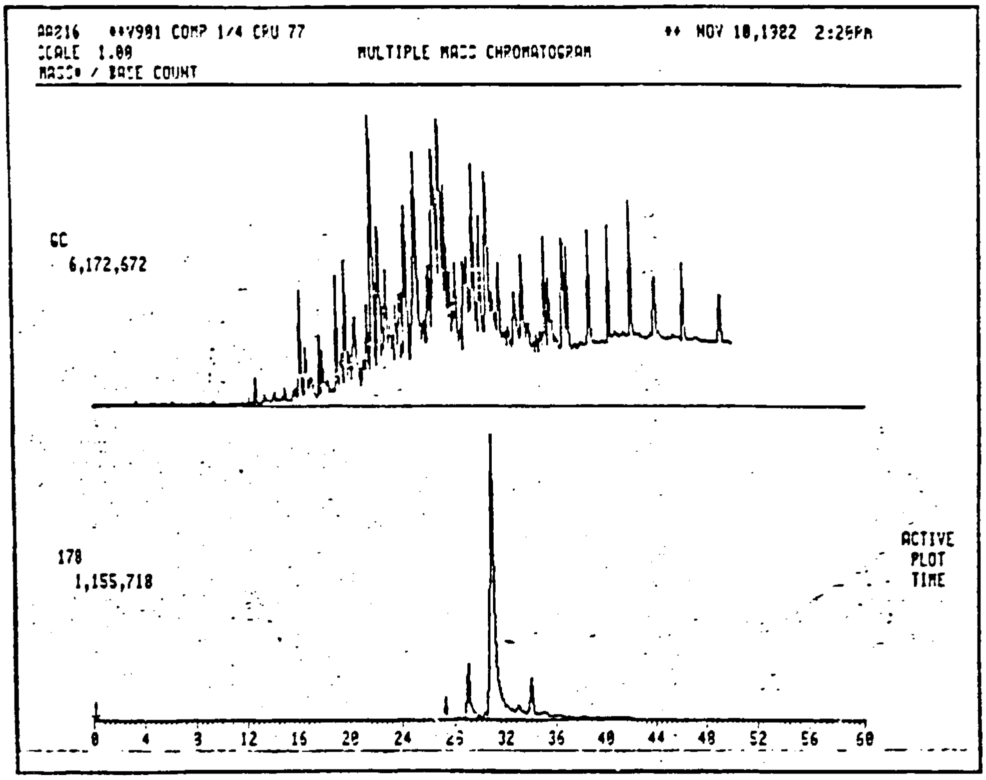


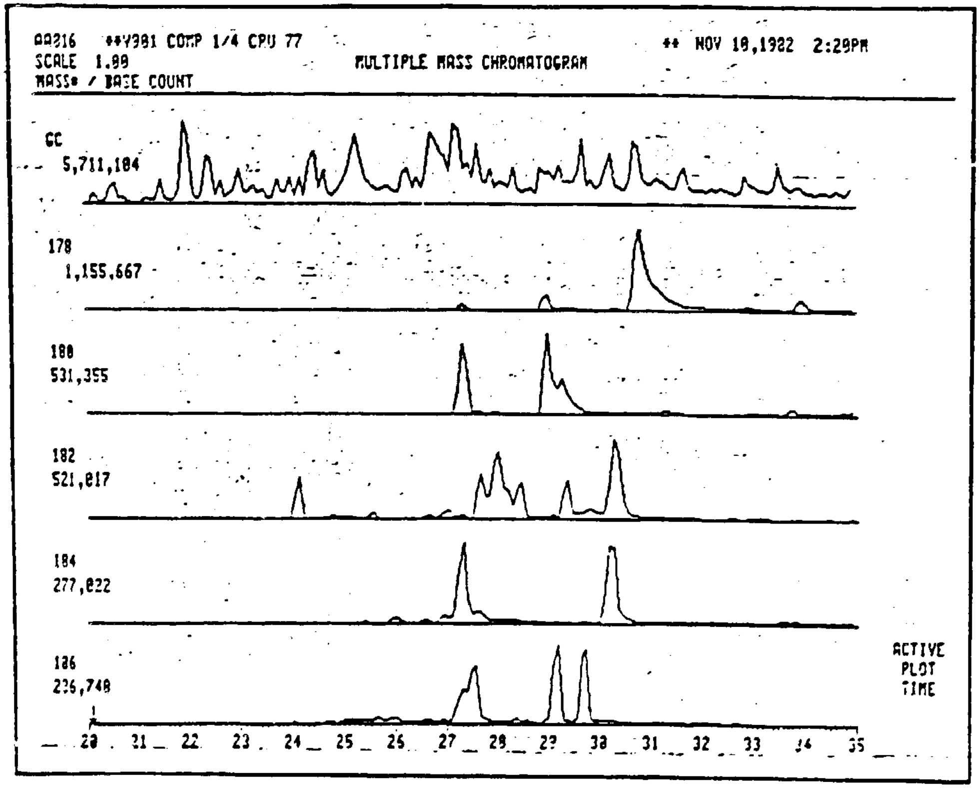
Saturate fractions invariably contained only saturates, but we found that our separation scheme for mono-aromatics and polyaromatics was somewhat variable. The quantity of toluene eluted was critical, as was the source of the silica and alumina. In fact, the capillary GCMS was able to characterise the whole aromatic fraction perfectly well, without needing separation into two fractions. Polar fractions proved to be difficult materials, because the GCMS indicated that they were mainly nitrogen compounds with lesser amounts of phenolic components. Of course we already knew that phenolics were major components and nitrogen components were relatively minor. Obviously the phenolics were being irreversibly adsorbed, and mainly accounted for the generally low recoveries from the column.

- Hydroaromatics.

As I have mentioned before, GCMS is very effective at characterising hydroaromatics. We are accustomed to expressing the hydroaromatics content as a ratio, H / H + P , where H is the sum of hydroaromatic species, and P is the sum of their precursors. We consider that a ratio of 0.4 -0.6 indicates that the hydrogenation reaction is proceeding very well. However, if the ratio is less than 0.3, then either the system has not reached equilibrium, or some abnormal event has occurred.




AA216 **V981 COMP 1/4 CPU 77
SCALE 1.00
MASS# / BASE COUNT
MULTIPLE MASS CHROMATOGRAM
** NOV 10,1982 2:26PM
GC
6,172,672
178
1,155,718
ACTIVE
PLOT
TIME
0
4
8
12
16
20
24
28
32
36
40
44
48
52
56
60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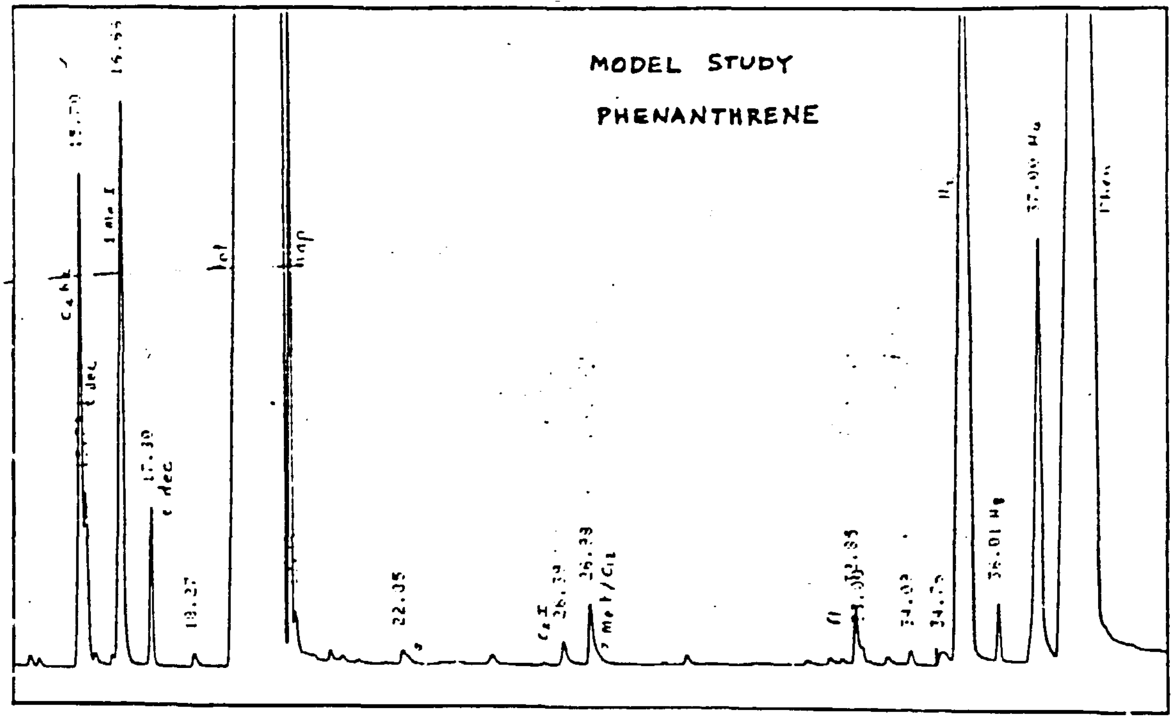
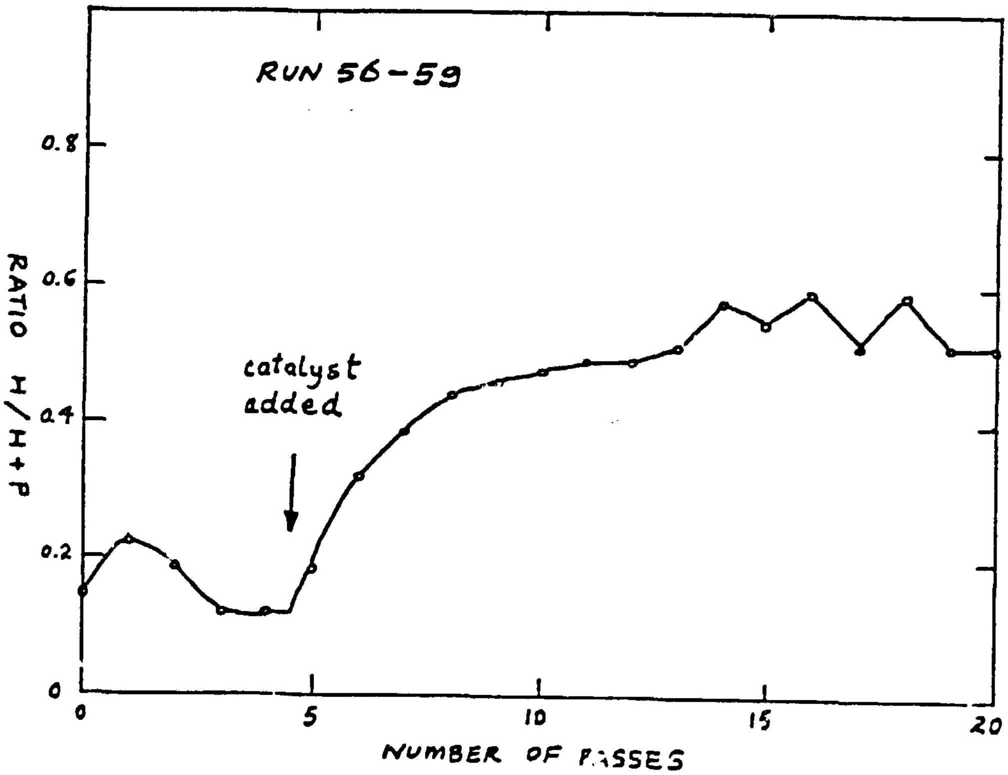
SCALE 1.00
MASS# / BASE COUNT
MULTIPLE MASS CHROMATOGRAM
** NOV 10,1982 2:29PM
GC
5,711,104
178
1,155,667
180
531,355
182
521,017
184
277,022
186
236,740
ACTIVE
PLOT
TIME
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35

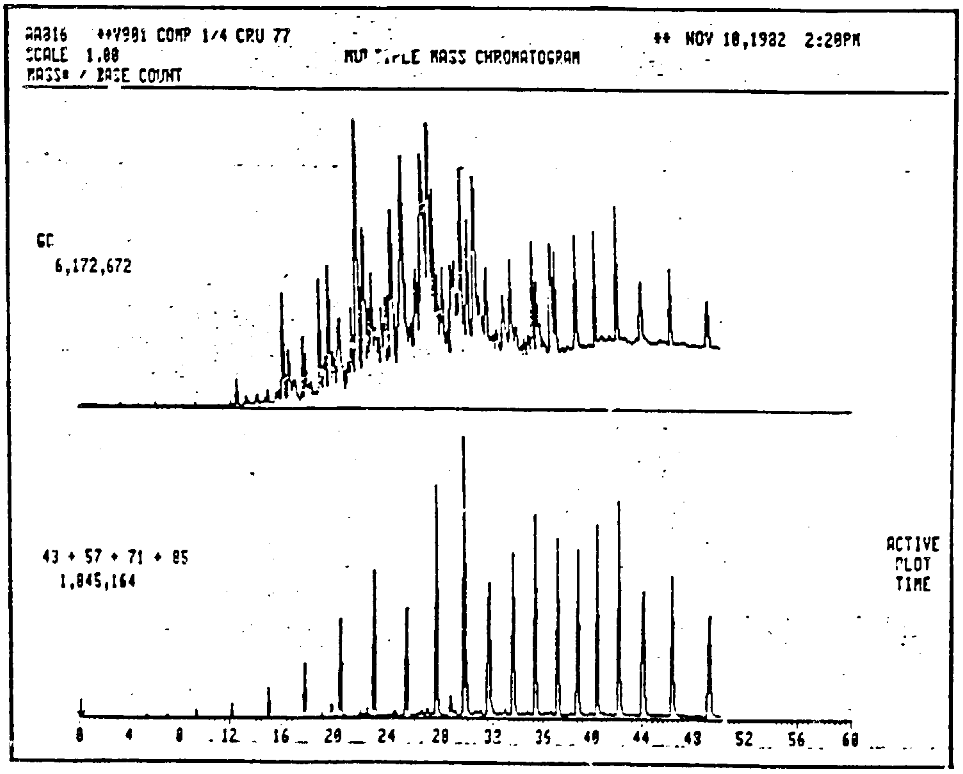

MODEL STUDY
PHENANTHRENE
16.55
17.30
c dec
18.27
Tet
Nap
22.35
26.33
36.01 H8
Phen


RUN 56-59
RATIO H/H+P
0
0.2
0.4
0.6
0.8
catalyst added
0
5
10
15
20
NUMBER OF PASSES

We have noticed that when an event such as abnormal accumulation of solids in the reactor occurs, the hydroaromatics dissappear and the corresponding aromatics increase usually by the same amount. That is, a dehydrogenation reaction occurs. The heaviest hydroaromatics dissappear first, but the lightest hydroaromatics do not change by a large amount. Some authorities declare that recycling of heavy aromatics is beneficial, and so the H/H+P ratio of the heavy aromatics may be the most important factor influencing hydrogen donor ability. More experimental work in this field is indicated.

- Distribution of species.

GCMS is a very powerful technique, especially its ability to locate a particular compound or group of related compounds, in a very complex chromatogram containing many hundreds of components. Saturates are often obscured by other components in a GC chromatogram. But with a GCMS chromatogram it is an easy matter to select only those ions characteristic for saturates, and display a clear picture of the relative distribution of saturate isomers.

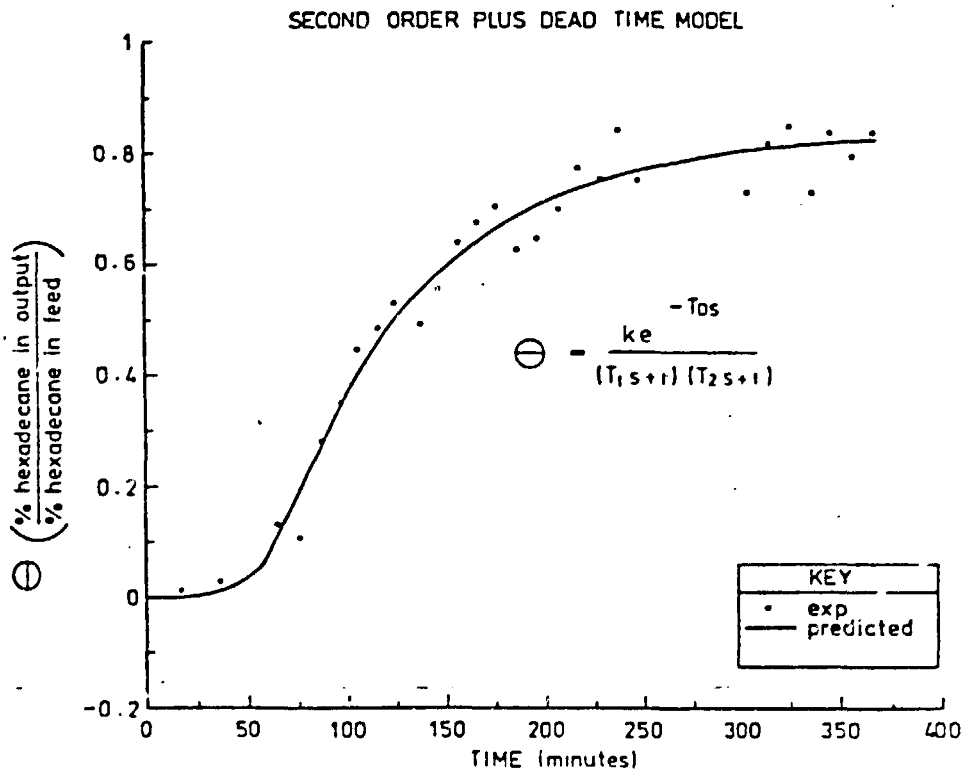


When chromatograms of whole oils are produced using non-polar columns, the peaks due to phenolics are usually broad, and hard to see. But the GCMS can easily locate phenolics by plotting characteristic molecular ions. Other homologous series can be located in the same way.

The GCMS suffers from problems of reliable quantitation, but a single GCMS chromatogram contains a tremendous amount of specific information, and its usefulness is only limited by the skill and experience of the operator.

- Reactor dynamics.

GC techniques were used to examine the flow characteristics of our continuous reactor system. A pure compound , hexadecane, was chosen because it had a boiling point near the middle of our recycle solvent. The hexadecane was added to a batch of feed slurry, and the product slurry was monitored for changes in concentration of that chemical every 10 or 20 minutes. After much work, a reasonable picture of the process liquid flow characteristic was obtained.



- Quantitation Problems.

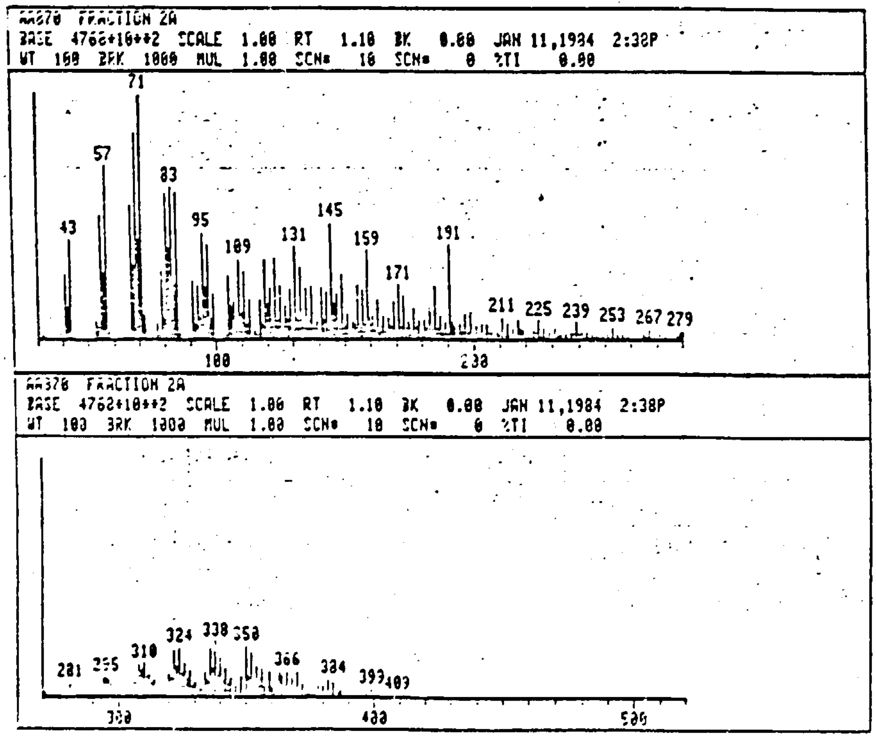
Gas chromatography using a flame ionisation detector is a reasonable quantitative tool. That is, the "Area%" of a component is normally close to the mass% of that component. However if the sample contains a significant concentration of non-volatile matter then the Area% will not be close to the mass%. Unfortunately, the GC does not speak, and cannot tell the analyst that non-volatile matter is present, unless the analyst has used an internal standard. The choice of internal standard is often difficult if the sample has a wide boiling range.
Oxygen and nitrogen compounds have lower sensitivities than carbon and hydrogen only compounds, so some quantitative errors are likely if polar materials are major components. Nevertheless, for distillate oils, GC yields satisfactory quantitative data, especially for comparative work.

GCMS is a different matter. Most compounds have unique sensitivities due to their unique fragmentation patterns. That sensitivity can vary from day to day depending on the internal "cleanliness" of the instrument, or its degree of "tuning". Within a class of compounds, individuals may have quite similar sensitivities, but differences between classes of compounds can vary by a factor of 10. Various techniques, such as low voltage EI, chemical ionisation, and Field Ionisation tend to improve the quantitative ability of GCMS, but the simplest approach that we use is to refer the identifications from GCMS to Area% measurements from a GC trace.

- Direct MS of Heavy Materials.

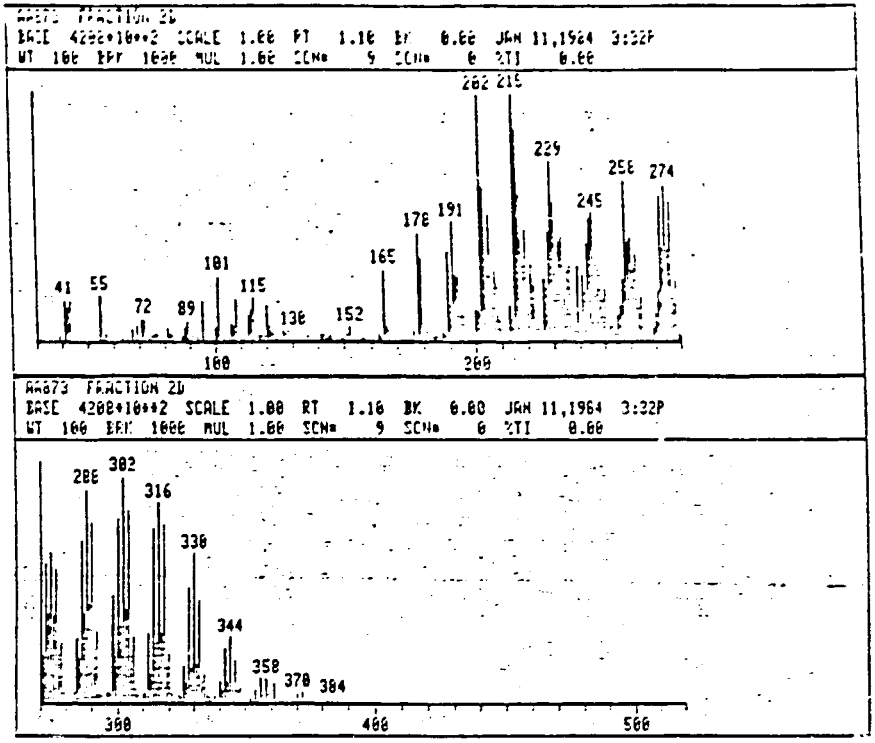
We have lately made considerable use of our MS to study the volatile components of vacuum residue from our CRU. This material is derived from batch vacuum distillation of the residues, and has a high boiling point. It is not well handled by capillary columns, although it elutes efficiently from short simulated distillation columns.

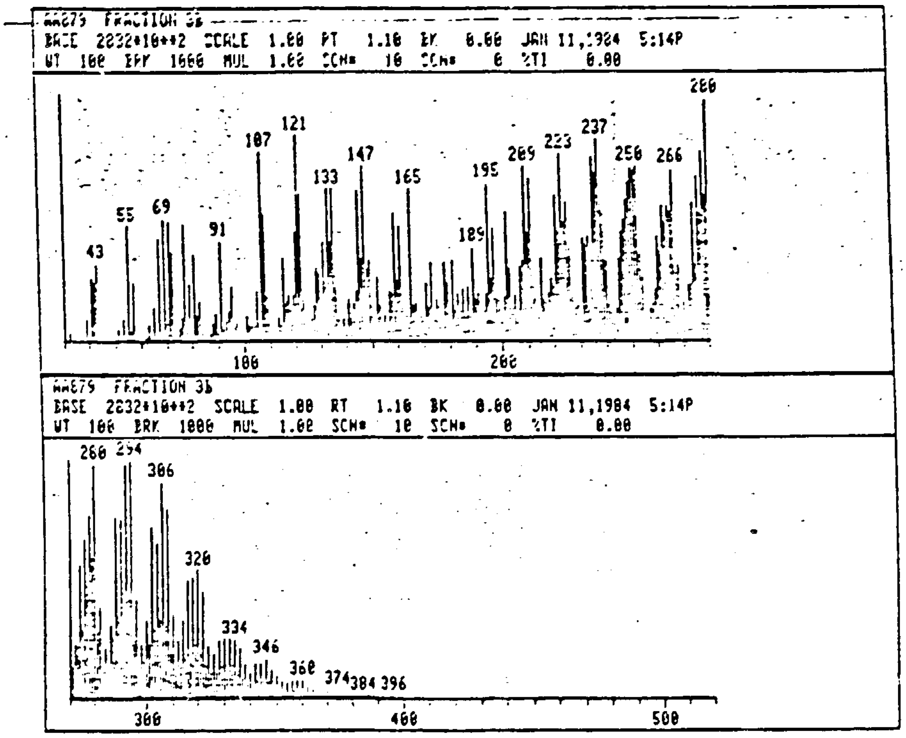
Small samples are placed on the tip of a direct insertion probe which can be inserted directly into the source of the mass spectrometer. The probe is then temperature programmed and results in a crude seperation. The mass spectra are very complex due to the large number of components present, and we have revived the use of elution chromatography in order to fractionate and simplify samples before MS measurements. Naturally, better instrumentation is available for this particular purpose at high cost, but we try to utilise existing equipment to the utmost.



```
AA370  FRACTION 2A
BASE  4762*10**2  SCALE  1.00  RT  1.10  BK  0.00  JAN 11,1984  2:38P
WT  100  BRK  1000  MUL  1.00  SCN#  10  SCN#  0  %TI  0.00
```

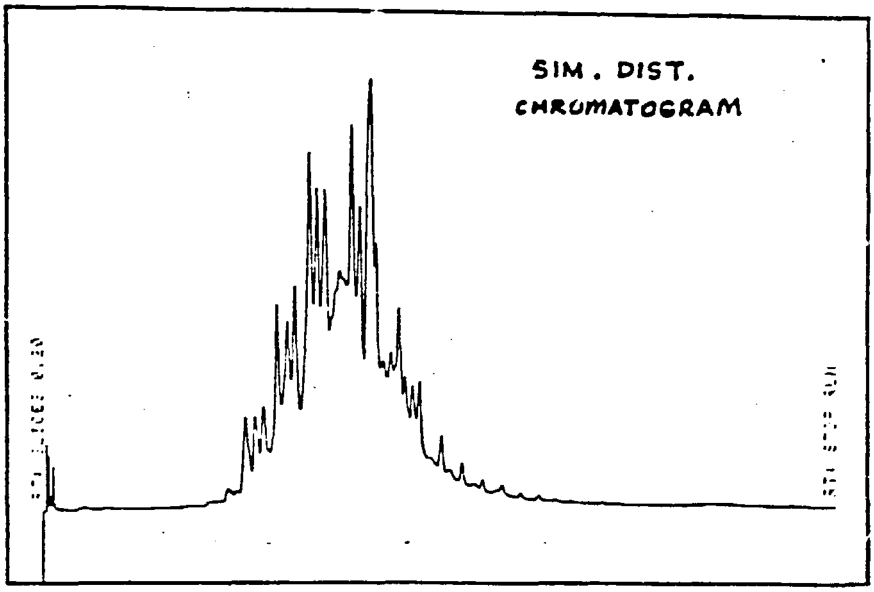
```
AA370  FRACTION 2A
BASE  4762*10**2  SCALE  1.00  RT  1.10  BK  0.00  JAN 11,1984  2:38P
WT  100  BRK  1000  MUL  1.00  SCN#  10  SCN#  0  %TI  0.00
```


AA673 FRACTION 2D
BASE 4208*10**2 SCALE 1.00 RT 1.16 BK 0.00 JAN 11,1984 3:32P
WT 100 BRK 1000 MUL 1.00 SCN# 9 SCN# 0 %TI 0.00
41
55
72
89
101
115
130
152
165
178
191
202
215
229
245
258
274
100
200
AA673 FRACTION 2D
BASE 4208*10**2 SCALE 1.00 RT 1.16 BK 0.00 JAN 11,1984 3:32P
WT 100 BRK 1000 MUL 1.00 SCN# 9 SCN# 0 %TI 0.00
288
302
316
330
344
358
370
384
300
400
500

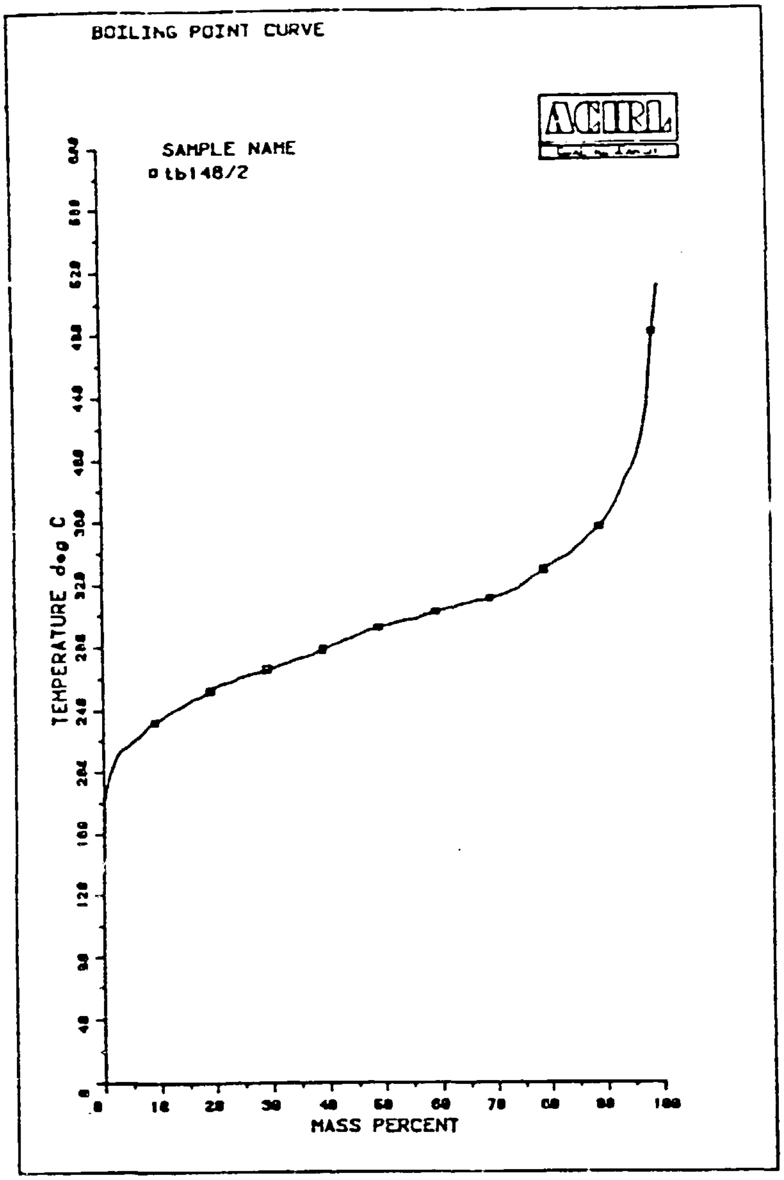

AA673 FRACTION 3D
BASE 2232*10**2 SCALE 1.00 RT 1.16 BK 0.00 JAN 11,1984 5:14P
WT 100 BRK 1000 MUL 1.00 SCN# 10 SCN# 0 %TI 0.00
43
55
69
91
107
121
133
147
165
189
195
209
223
237
250
266
280
100
200
AA673 FRACTION 3D
BASE 2232*10**2 SCALE 1.00 RT 1.16 BK 0.00 JAN 11,1984 5:14P
WT 100 BRK 1000 MUL 1.00 SCN# 10 SCN# 0 %TI 0.00
280
294
306
320
334
346
360
374
384
396
300
400
500

4. SIMULATED DISTILLATION.

Widely conflicting views can be found in the literature regarding the application of simulated distillation to coal derived oils. Nevertheless, we make considerable internal use of the technique, and it has helped to solve a few problems.



```
          SIMULATED DISTILLATION    SAMPLE-     tb148/2

          INITIAL BOILING POINT      181.95
MASS %     TEMP. C
 •   1       199.[illegible]   •    26         261.7   •     51        293.6   •     76        320.5   •
 •   2       210.1   •    27         262.9   •     52        294.5   •     77        322.9   •
 •   3       213.2   •    28         264.0   •     53        295.3   •     78        325.4   •
 •   4       216.7   •    29         265.0   •     54        296.1   •     79        327.8   •
 •   5       219.7   •    30         266.1   •     55        296.9   •     80        330.2   •
 •   6       222.3   •    31         267.2   •     56        297.9   •     81        332.6   •
 •   7       225.8   •    32         268.4   •     57        299.0   •     82        334.6   •
 •   8       230.2   •    33         269.6   •     56        300.1   •     83        337.1   •
 •   9       232.1   •    34         271.2   •     59        301.2   •     84        339.7   •
 •  10       234.1   •    35         272.3   •     60        302.3   •     85        342.5   •
 •  11       236.5   •    36         273.4   •     61        303.3   •     86        345.6   •
 •  12       233.6   •    37         274.6   •     62        304.4   •     87        349.3   •
 •  13       240.6   •    38         276.0   •     63        305.5   •     88        352.4   •
 •  14       242.6   •    39         277.7   •     64        306.6   •     89        355.4   •
 •  15       244.5   •    40         279.3   •     65        307.4   •     90        358.8   •
 •  16       246.1   •    41         280.8   •     66        308.0   •     91        364.5   •
 •  17       247.7   •    42         282.3   •     67        308.7   •     92        371.6   •
 •  16       249.5   •    43         283.8   •     68        309.3   •     93        377.8   •
 •  19       251.8   •    44         285.1   •     69        309.9   •     94        396.8   •
 •  20       254.0   •    45         286.5   •     70        310.7   •     95        393.1   •
 •  21       256.2   •    46         287.9   •     71        311.9   •     96        402.0   •
 •  22       257.2   •    47         289.3   •     72        313.1   •     97        413.8   •
 •  23       258.3   •    48         290.5   •     73        314.3   •     98        435.4   •
 •  24       259.4   •    49         291.6   •     74        316.1   •     99        490.2   •
 •  25       260.5   •    50         292.6   •     75        316.2   •    100        507.8   •
```



- Reproducibility.

The technique can be very reproducible if the correct conditions are carefully met, and rivals the reproducibility of most manual distillation techniques. An added advantage is that the method only consumes tiny amounts of sample.

Variations in instrument conditions can affect the reproducibility but this problem is rarely met with modern instruments. We have found that manual injection can suffer large variations, especially when analysing very light samples, so we prefer to use an automatic injection device with a sample carousel.

- Quantitation.

All column packings discriminate between saturate and aromatic components when boiling points versus retention times are inspected. The best columns show little discrimination for components boiling below about 170°C. However, components in coal derived oils boiling over 170°C are usually 80% aromatic, and the ramifications of standardising the temperature scale with a completely saturated standard must be considered.

- Applications.

- Evaluation of Distillation.

The merits of this application are obvious. We have used SIM.DIST. to examine improvements in the continuous distillation unit in our reactor system before we started another run with coal. We concluded that the improvements were justified and were able to continue with normal experimentation.

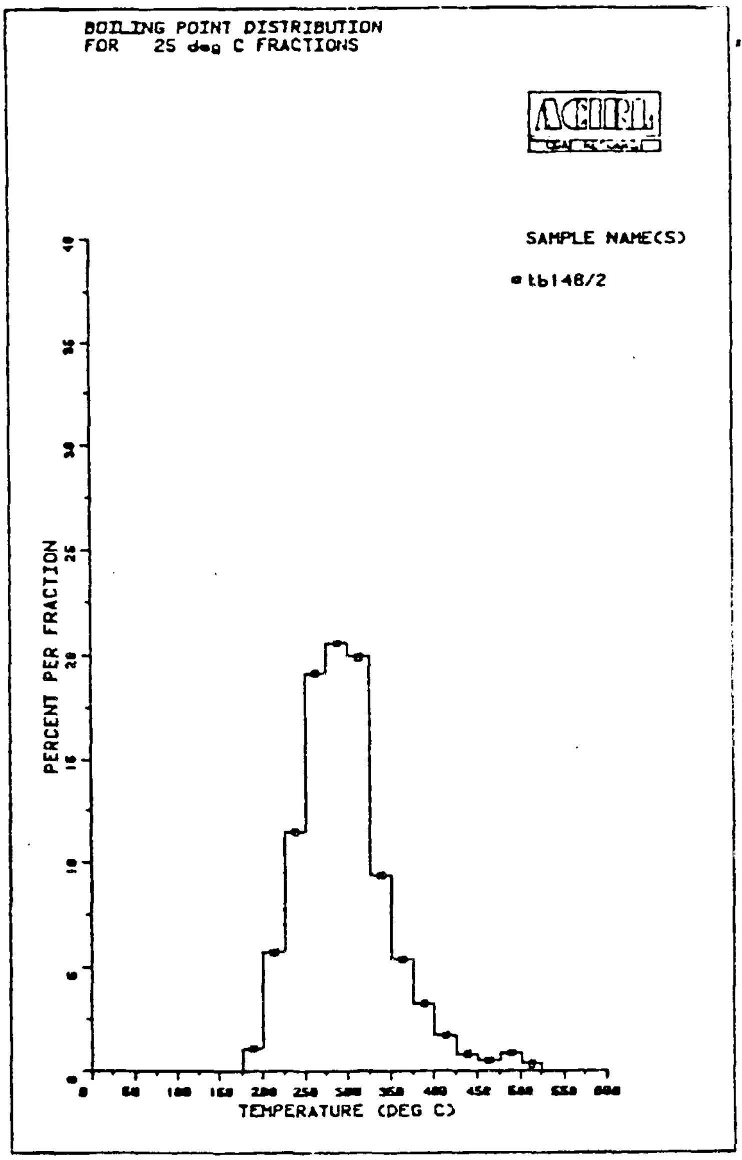
- Evaluation of Process " Chemistry".

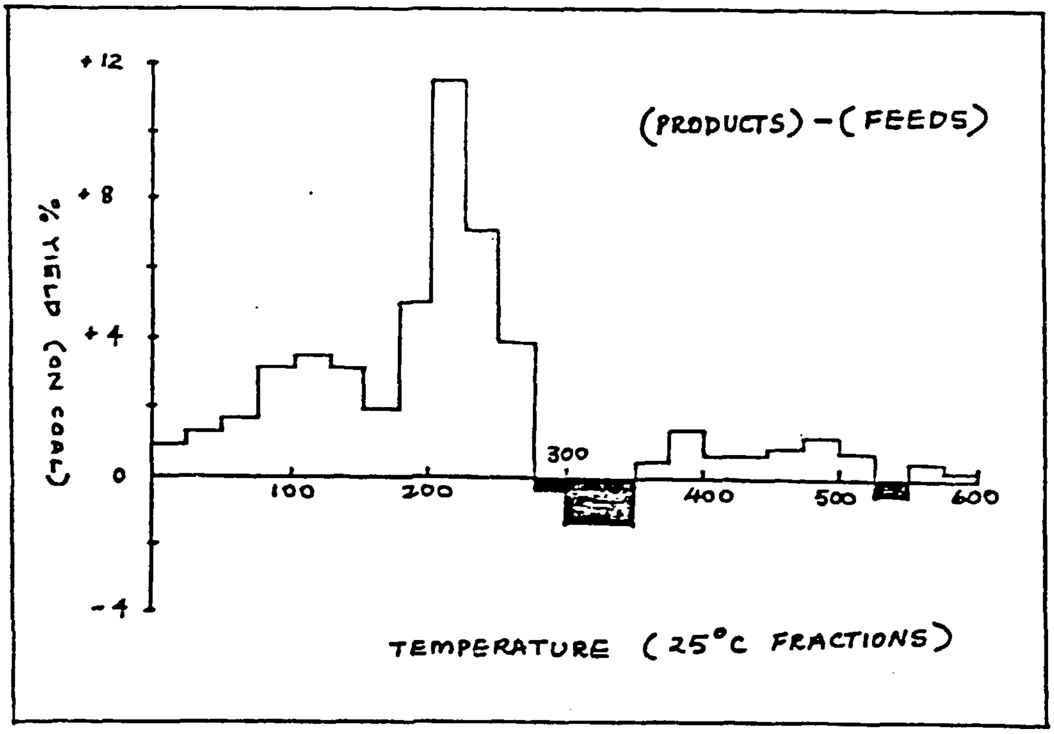
Continuous reactor product streams are numerous and complex. We have been using SIM.DIST. to examine the difference in boiling range between products and feeds. Manual distillation was not possible because the number of samples was large, and the sample size was small.(Our reactor is only small, 1-2 Kg coal per hour, and if our sampling size is too large, we encounter problems with maintaining recycle solvent balance.) The initial requirements are that the mass balance has been determined, and that the correct sets of samples have been chosen, especially feed solvent. The conventional SIM.DIST reports are broken up into 25° ranges and the mass% calculated for each range. The weighted sum of all feeds is subtracted from the weighted sum of all products, and the difference is the boiling point distribution of the real product, that is, the actual product manufactured during the term of the reaction. In practice, there is no single product stream which represents this distribution, since the real product can be spread over the whole boiling range, depending of course on the processing conditions and degree of recycling. SIM.DIST. is the only practical technique which can reveal this type of information.

BOILING POINT DISTRIBUTION

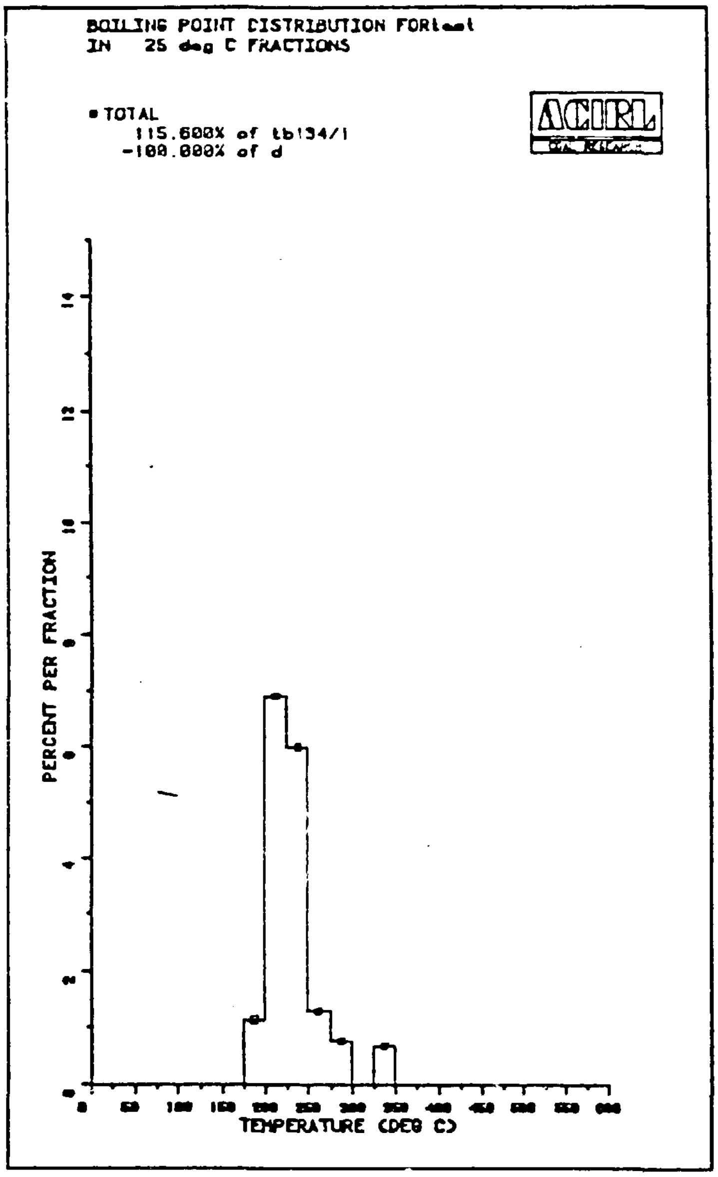
BOILING FRACTION		SAMPLE NAME(S) tb148/2	
0 - 25	*	0.00	*
25 - 50	*	0.00	*
50 - 75	*	0.00	*
75 - 100	*	0.00	*
100 - 125	*	0.00	*
125 - 150	*	0.00	*
150 - 175	*	0.00	*
175 - 200	*	1.07	*
200 - 225	*	5.71	*
225 - 250	*	11.44	*
250 - 275	*	19.13	*
275 - 300	*	20.53	*
300 - 325	*	19.91	*
325 - 350	*	9.37	*
350 - 375	*	5.33	*
375 - 400	*	3.23	*
400 - 425	*	1.75	*
425 - 450	*	0.81	*
450 - 475	*	0.50	*
475 - 500	*	0.84	*
500 - 525	*	0.33	*
525 - 550	*	0.00	*
550 - 575	*	0.00	*
575 - 600	*	0.00	*
TOTAL	*	100.00	*

SPECIFIC GRAVITY	1.007
ATOMIC H/C	1.234



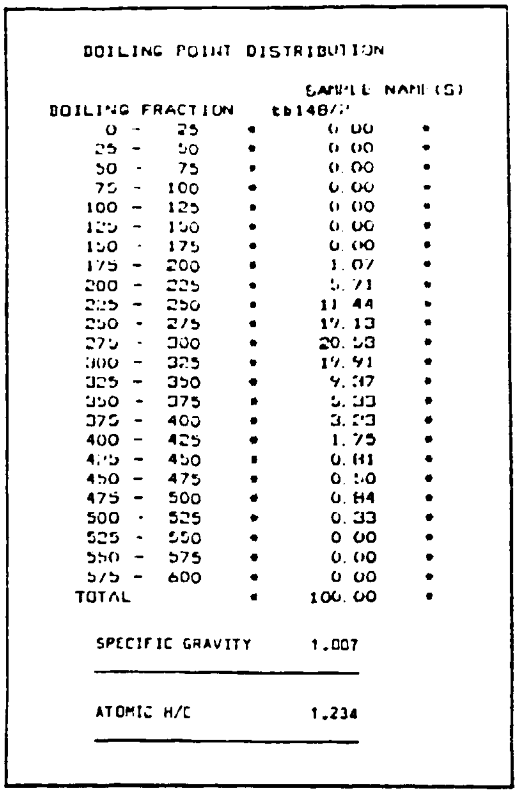


At present, we are stuJying the effect of solvents of different narrow boiling ranges on the nature of the products. This research involves about 200 micro autoclave experiments, and the amount of products from each reaction is naturally small. We hope to find useful fundamental information using a variety of analyses, of which SIM.DIST. will hopefully reveal some kinetics or mechanisms.

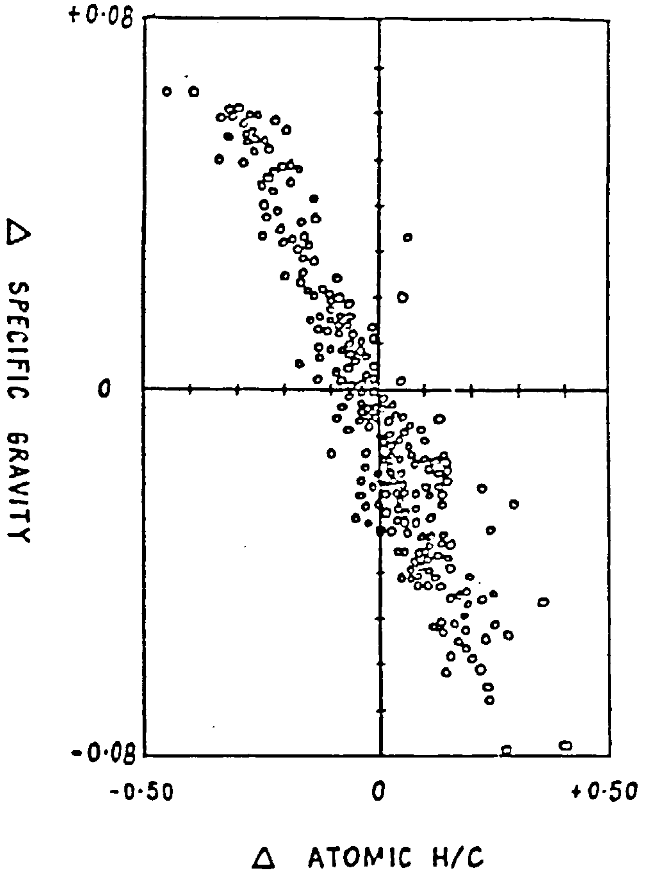


- Prediction of other Analytical Parameters.

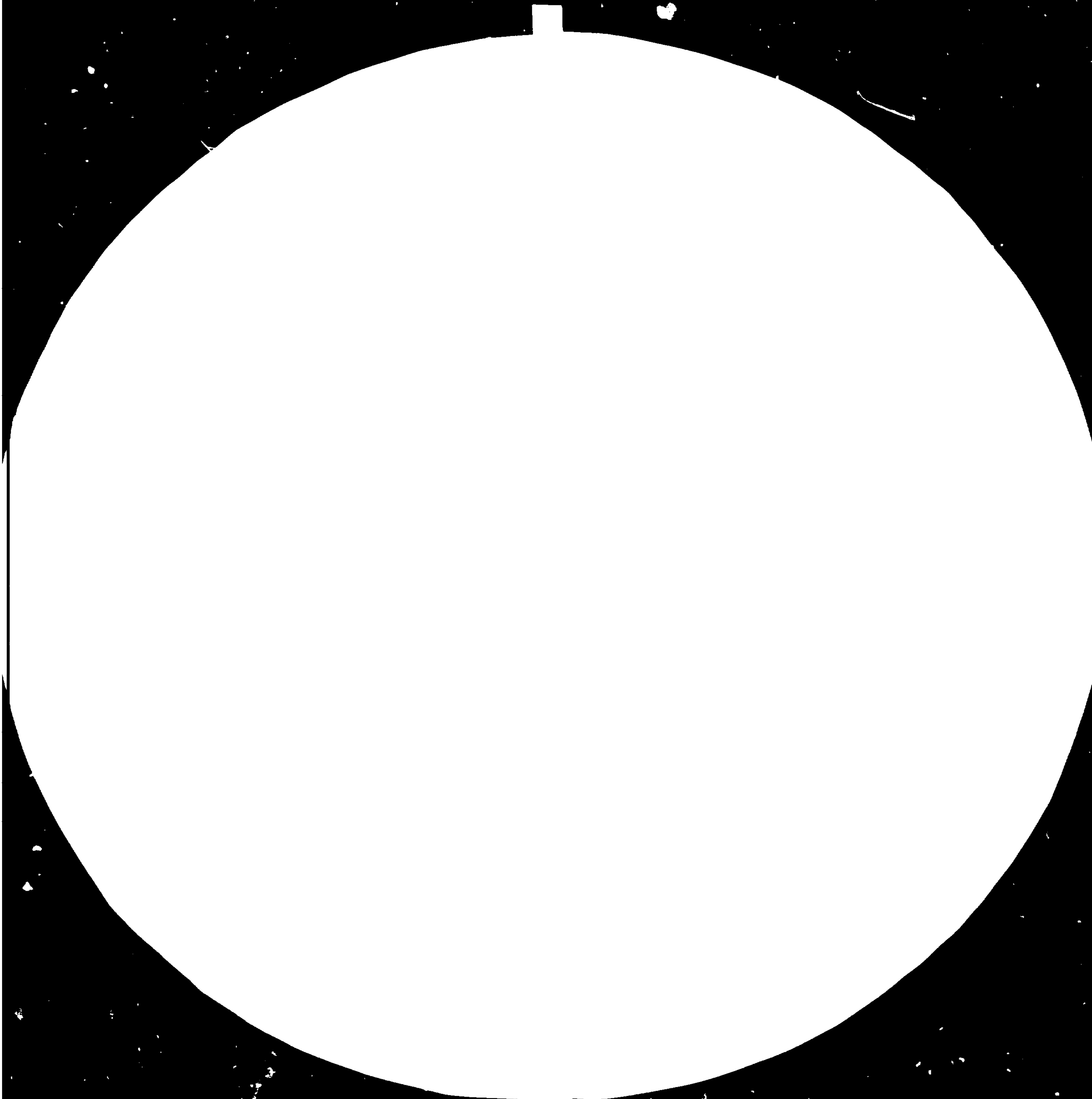
Many analysed parametrs can be highly influenced by the boiling range of the sample. An obvious example is that light oils always have the lowest density and the highest atomic H/C of all products. We were able to prepare, with the help of the literature, two sets of factors with which we could predict the density and H/C of any distillate, using the SIM.DIST. boiling range distribution. Most products from steady state CRU runs showed good agreement between predicted and analysed values. However considerable variations were noticed for many other samples.

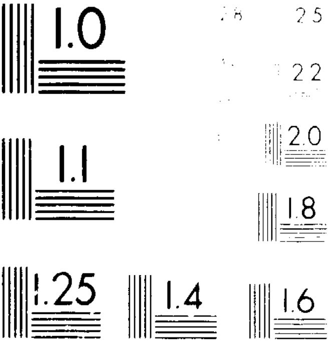


```
BOILING POINT DISTRIBUTION

                                 SAMPLE NAME(S)
BOILING FRACTION      EB148/[illegible]
      0 -   25   *        0.00     *
     25 -   50   *        0.00     *
     50 -   75   *        0.00     *
     75 -  100   *        0.00     *
    100 -  125   *        0.00     *
    125 -  150   *        0.00     *
    150 -  175   *        0.00     *
    175 -  200   *        1.07     *
    200 -  225   *        5.71     *
    225 -  250   *       11.44     *
    250 -  275   *       19.13     *
    275 -  300   *       20.53     *
    300 -  325   *       19.91     *
    325 -  350   *        9.37     *
    350 -  375   *        5.33     *
    375 -  400   *        3.23     *
    400 -  425   *        1.75     *
    425 -  450   *        0.81     *
    450 -  475   *        0.50     *
    475 -  500   *        0.84     *
    500 -  525   *        0.33     *
    525 -  550   *        0.00     *
    550 -  575   *        0.00     *
    575 -  600   *        0.00     *
  TOTAL          *      100.00     *

     SPECIFIC GRAVITY        1.007
     ____________________________

     ATOMIC H/C              1.234
     ____________________________
```



Δ = PREDICTED − OBSERVED



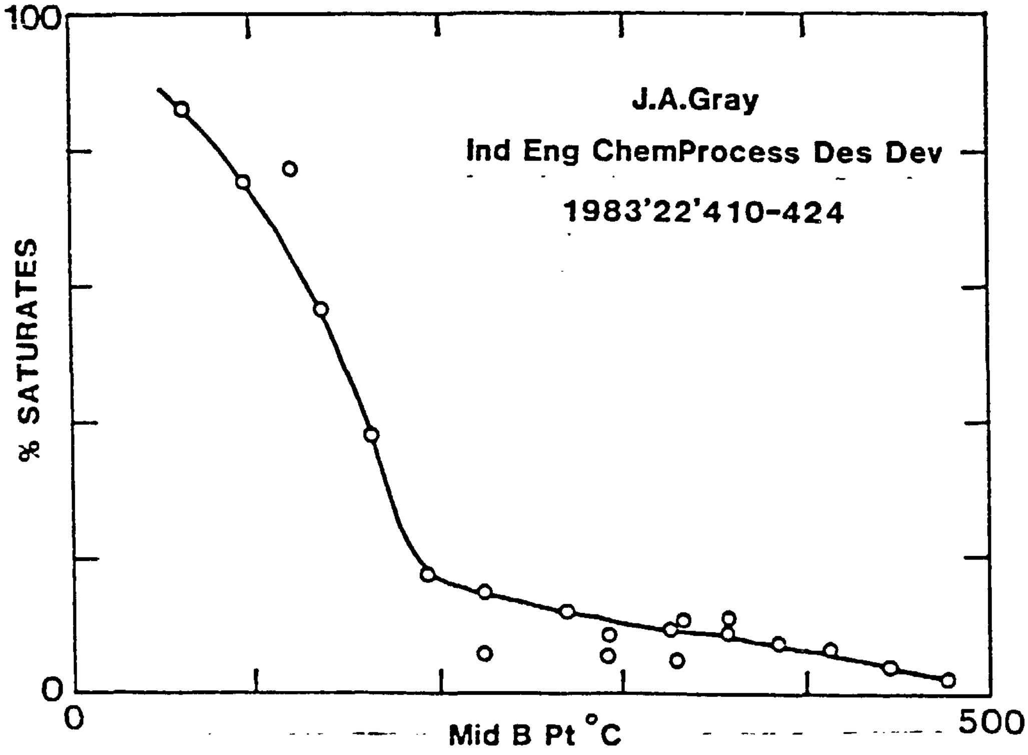

2.5
2.2
2.0
1.8
1.0
1.1
1.25
1.4
1.6

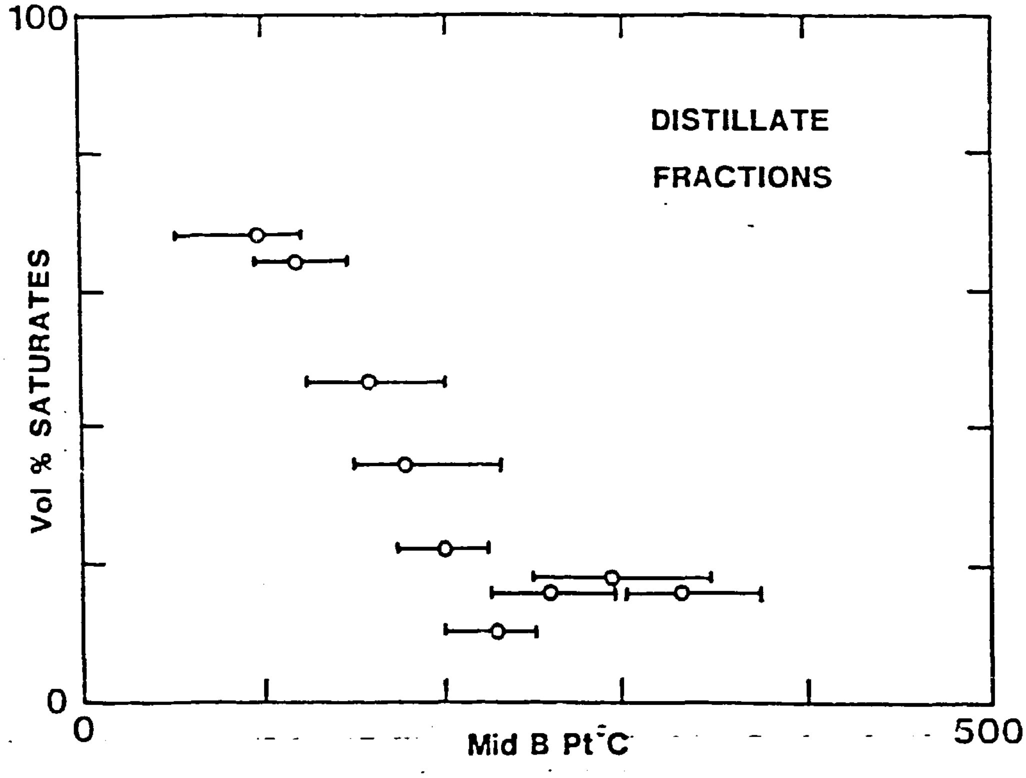
We were able to explain these variations when we realised that both the density and H/C were being influenced mainly by the accumulation of saturates. A very good correlation was then found between the deviation of density and the deviation of H/C. We are now able to make very reasonable predictions of density and H/C for almost any sample of distillate oil from coal conversion experiments.

Unfortunately, we cannot predict the total C+H from the SIM.DIST., so we must continue with tedious elemental analyses. The value of C+H depends largely on the phenolics content which can vary quite widely. We also have sets of factors for predicting N ans S, but we have much less confidence in their usefulness.

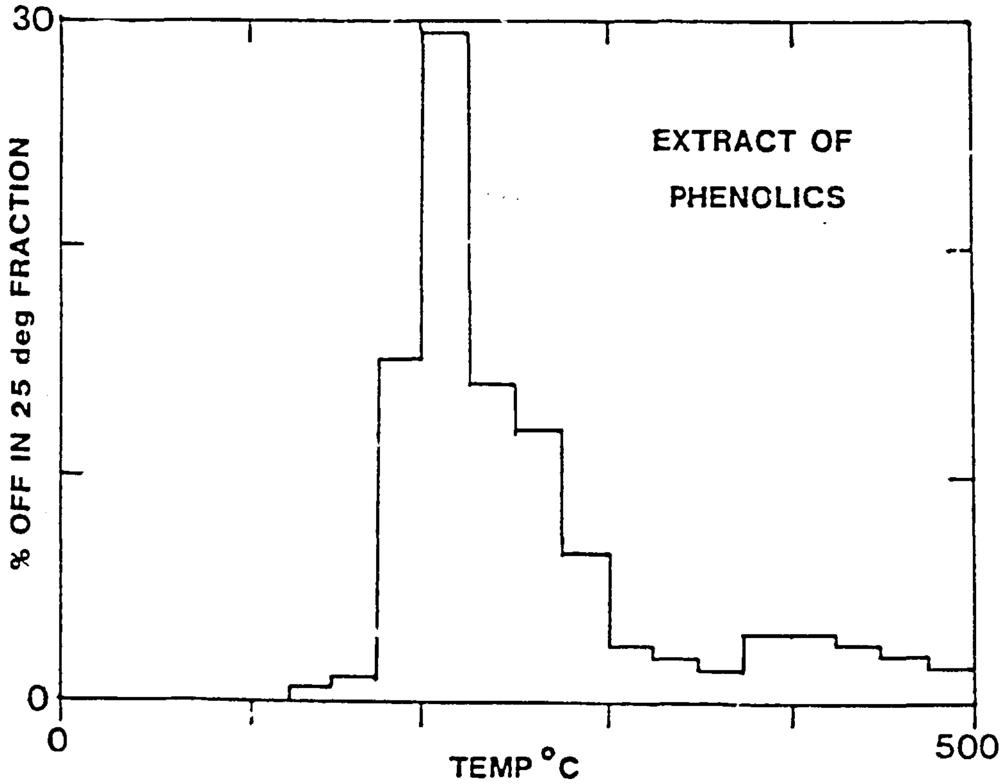
- Dependence of Analytical Results on Boiling Point Distribution.

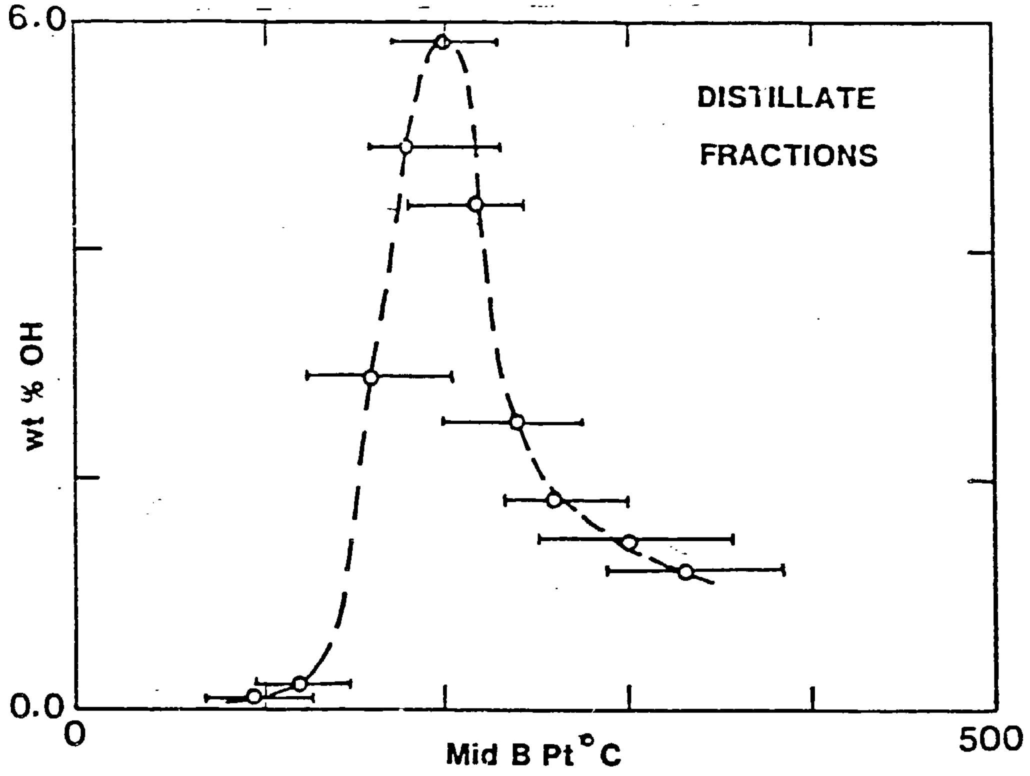
Saturates content is highly dependent on the boiling range profile of the sample. Saturates may account for 80% of some lower narrow boiling ranges, and yet down to a few % in others. Therefore it is possible to mis-interpret the results of comparative experiments if the boiling range profile of the sample is ignored.





Phenolics are also sensitive to boiling range, but not in the same way as saturates. Phenolics occur in greatest abundance in the range 175 - 250°C, and so relative proportions of this boiling range in the sample can decide the phenolics content. Phenolics also tend to increase in +400°C materials.




6.0
0.0
wt % OH
DISTILLATE
FRACTIONS
0
500
Mid B Pt °C