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INTEGRATED COAL CONVERSION
DP/POL/77/102
POLAND

Technical report: Visit to Institute of Chemical
Processing, Zabrze, Poland*

Prepared for the Government of Poland
by the United Nations Industrial Development Organization,
executing agency for the United Nations Development Programme

Based on the work of F.L. Scargill,
consultant in coal pyrolysis

United Nations Industrial Development Organization
Vienna

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I. INTRODUCTION

The project document requires that as Executive Agency UNIDO should organise the visits of Experts to Poland. There are 6 expert posts to be filled, each of 1 month's duration. Following the second meeting of the Technical Committee, 18 - 25th June 1979, it was agreed that shorter missions by more than one expert would be preferable in order to increase the chances of securing the services of high-level experts who are normally reluctant to accept 1 month's assignments. This visit fills one of their posts in Pyrolysis.

II. BRIEFING IN VIENNA

The normal briefing in Vienna took place on 21st and 22nd January. Discussions on the project took place with Mr M. Mauig, Industrial Development Officer, Chemical Industries Section, UNIDO. It was agreed, that in order to allow maximum time for the expert to work in Poland, the de-briefing in Vienna would be dispensed with, and the two days allowed for this be used for this purpose.

III. TECHNICAL VISIT BY EXPERT TO INSTITUTE OF CHEMICAL PROCESSING, ZABRZE
24-1-80 — 8-2-80

The expert travelled to Katowice on the 23rd January, and met Asst. Prof. Doc.
Dr Jadwiga Kulczycka, and Prof. Dr. Eng. O. Zbraniborski on the 24th January.

The programme of the visit was discussed, and it was agreed that lectures on the
following subjects would be given:-

        Pyrolysis in Fluidized Beds

        Hydro-Pyrolysis

        Flash Hydro-Pyrolysis

        Fluidized bed combustion

        Classical Coke-oven control and automation.

In addition, visits to the laboratories and discussion on the equipment of the
Rotary Carbonizer and Fluidized Bed Combustion would be undertaken.

On the 25th January it was agreed that the expert move from Katowice to Zabrze in
order to be closer to the Institute, and therefore be able to spend more time
there. Further detailed discussions on the programme took place with
Professor Dr. Eng. H. Zielinski and Professor Dr. Eng. Zbraniborski. A visit
was then made to the laboratories and the site of the new pilot plant, where
construction was in progress. It was pleasing to note that the Project was to
programme. Subject to Instrumentation, and control equipment being delivered
on time, completion will be as programmed.

Further discussions took place on the fluidized bed section of the project, and the need to have the facility to precisely maintain bed conditions, to maximise output.

A pleasant office has been prepared for the expert and full facilities for typing, duplicating, and preparation of slides have been put at his disposal.

Monday.   28-1-80

Lecture on the Pyrolysis of Coal in a fluidized bed to produce smokeless briquettes.

The lecture commenced at 10.00 a.m., and with the exception of a short break, continued with the discussion period to 3.00 p.m.   (APPENDIX I)

Tuesday.   29-1-80

Meeting with Deputy Director Prof. Dr. Eng. O. Zbraniborski, M.Sc. A. Kubeczka, Research Worker.

The Deputy Director welcomed me, and expressed the hope that there would be a mutual exchange of view on Pyrolysis, Gasification, Liquefaction, Coke-making, both Classical and Formed-Coke and related subjects.   He also expressed the hope that my stay in Poland, for which he thanked the UNIDO, would be a happy and successful one.   He personally was very pleased I had come to Poland.   The expert replied that he too hoped his visit would be of as much help as possible in these subjects.

A discussion on these matters then took place.   (APPENDIX 2).

Wednesday.   30-1-80

Visit to HUTA Katowice Cokeworks.

Persons met,

1.   Director.

2.   Technical Manager.

(APPENDIX 3)

Thursday.   31-1-80

Lecture on Automatic and Computer control of Classic Coke-Ovens.
(APPENDIX 4)

Friday.   1-2-80

Visit to Laboratory, Institute of Chemical Processing of Coal.   Department of
Environmental Protection.   Krakow.
(APPENDIX 5)

Monday.   4-2-80

This day was spent preparing for the major lecture on Hydro-Pyrolysis and
Flash-Hydropyrolysis.

Tuesday.   5-2-80

Lecture of Hydro-Pyrolysis and Flash-Hydropyrolysis.

Tuesday.   5-2-80 (continued)

Arrangements had been made for Scientists from laboratories and Universities
throughout Poland to be present.

(APPENDIX 6).

Wednesday.   6-2-80

The morning was spent with first Professor Doc. Dr. Jadwiga Kulczycka, Director
of the UNDP/UNIDO Project Office Katowice.   We discussed the work the expert had
done in Zabrze.   She had discussed this with the Director of the Institute of
Chemical Processing of Coal at Zabrze.   Professor Dr. Eng. H. Zielinski, and
said both were very pleased and considered the visit had been highly successful.

The afternoon was spent at the Institute further discussing technical details of
the new pilot plant.   This is a relatively simple process, and could have much
value for developing countries with coal reserves, and who should not move directly
to the latest advanced technology.

Friday.   8-2-80

Final discussions took place on the Pilot Plant project, with the Director,
Prof. Zbraniborski and senior staff.

The Director asked the expert his honest views on the project, and whether there
were variations, alterations, or improvements that he would wish to recommend.

Friday. 8-2-80 (continued)

The expert replied that he had been carefully through the philosophy, and design behind the pilot plant, and the specific requirements of the Institute's programme. With all these in mind he considered the pilot-plant was sound in conception.

When it was commissioned there would of course be problems, but these would be overcome and the plant would yield much information. He believed the next stage should be a pressurized fluidized bed. There was general agreement. The philosophy behind the Pilot Plant was, that Poland had large reserves of high ash, high sulphur coals. If some of the volatiles should be used to produce medium B.T.U. gas for domestic and industrial use, the char would then be used for Power generation in e.g. a fluidized bed.

A discussion took place on what was considered a "cut-off" point, where the percentage of ash in the coal made it undesirable, and/or uneconomic for it to be used for this dual purpose of gas production and power generation. Much depended on transport costs, (the cost of transporting ash), - and the ability to dispose of the ash easily and economically. Perhaps 20% ash would be a maximum content in the coal.

A further discussion took place on the equipment being supplied under the Project by UNIDO. It was pleasing to note that the HP.1000 was on order, but disappointing to note that the Gas Chromatograph (Mass Spectrometer MP5992A,) and the Mass Flow System had been deleted due to limitation of funds.

Friday.   8-2-80 (continued)

This would make the control and analysis of performance of the pilot plant impossible to the precise degree required to obtain maximum information.   It was hoped that means may be found to provide this equipment.

That concluded the formal meeting.

The Director again thanked UNIDO for arranging for this expert's visit, which he considered highly successful and useful to the Institute.   The expert thanked the Director and his staff, for all the help and assistance which they had given and which had materially assisted in the visit's success.

IV.   CONCLUSIONS   -   RECOMMENDATIONS

On Wednesday 6th February, 1980 a final meeting was held in Katowice with
Madame Kulczycka when the work carried out by the Consultant was discussed.

Undoubtedly the UNDP/UNIDO project was strengthening and supporting the Government's
own large inputs.   Specifically in Pyrolysis, the project was to schedule,
and the equipment being provided in the UNDP/UNIDO project was a vital part
of this project.   Madame Kulczycka said that they were grateful to UNIDO for
supplying my Services.   She had discussed this with the Director, Professor
Zeilinski, and both agreed that this visit had been very helpful.

On Friday 8th February, 1980 a final meeting was held with the Director of the
Institute of Chemical Processing, Professor Zeilinski.   (Details are separately
recorded).   The project was re-appraised and both the Director and the Consultant
were in agreement that the Project was sound in both philosophy and technical
content and should proceed as planned.   The Consultant noted that two items
of equipment on the original list for the Pilot Plant had been deleted.   Namely
the Gas Chromatograph/Mass Spectrometer and the Mass Flow System.   He considered
this equipment as key equipment for both control and monitoring.

CONCLUSIONS

There is an excellent rapport between the Polish Authorities and UNDP/UNIDO
which will undoubtedly help to bring the project to a successful conclusion.
There are a number of areas where problems may arise on commissioning, but
they can be dealt with when they arise.   The construction of the equipment is
going ahead.   The next major step will be commissioning towards the end of the
year.

RECOMMENDATION

(a)   For Consideration and Action by the Polish Authorities

    I.   To continue the programme as planned.

(b)   For Consideration by UNIDO

    I.   To re-examine the possibility of providing sufficient funds to
    purchase the Gas Chromatograph/Mass Spectrometer MP5992 A, together
    with the Mass flow system originally requested in the equipment for
    the Combuster/Fluidized Bed Pilot Plant.

    2.   To continue to support the programme.

APPENDIX I.   28-1-80

Lecture : The N.C.B. Char Briquetting Process using Fluidized Beds

Short Description of Process

General

The 1956 Clean Air Act made it an offence for smoke to be emitted from a domestic chimney. This stimulated demand for domestic fuel of a smokeless nature, whilst possessing burning properties at least equal to traditional house coal.

Processes existing in the 1950's required coal of special size or quality which limited large scale production. To overcome this the National Coal Board developed the Fluidized Bed Char Briquetting process to convert non-coking, low rank small coal which is produced in large quantities from mechanized coal faces into domestic smokeless briquettes.

The essential requirement of the process is the partial de-volatralisation of the coal in such a manner that the resulting char can be briquetted without the addition of a binder.

Coal Preparations

The coal must have uniform coking properties, minimum and uniform moisture content. Ash content below 4%. This is a requirement of the product, not the process. The coal is crushed, classified, and thermally dried. The coal $(0"-1^a)$ passes through a primary crusher before being fed into the entrained flash dryer unit where gases at $600^{\circ}C$ carry and dry the coal to the cyclones for separation of the coal particles from the gas.

Process

The dried coal is fed via a screw-feeder into the fluidized-bed. It is fluidized in the lower part of the carbonizer by fluidizing gas (normally air/steam mixture) blown through nozzles. The volatile content of the coal is reduced from approximately 38% to 22% which renders it smokeless. The bed temperature is precisely controlled $\pm$ 3% by controlling the air/steam mixture with a suitable control box (During the discussion, the expert agreed to send details of this equipment to Zabrze.

The depth of the bed is again precisely controlled by a level controller operating the screw-feeder charger.

The char leaves the fluidized bed through char-lines, lagged and trace-heated, and falls by gravity to extrusion presses where it is briquetted at pressures between 4 and 8 tons per square inch.

Discussion

A lengthy discussion ensued. (The Zabrze Pilot Plant contains a Fluidized Bed). The following information was given by the expert.

1. The off-gases carry 4.5 gms /SCF of -20 micron fines.

2. The off-gases carry 4.5 gms /SCF of Tar vapour.

3. Each stream produces 580,000 SCF/per hour of off-gas.

4. The C.V. of the off-gases average 290 B.Th.U.

5. The Internal measurements of the Fluidized bed are 13'0" dia x 50'0" depth.

6. Internal cyclones are fitted to catch and return fine particles to the bed.

7. The steel off-gas lines have internal refractory linings and are externally lagged. They are fitted with steam injectors in case of fires.

8. A golden rule for efficient operation of a fluidized bed in constant, steady operating conditions.

9. The off-gas _must_ pass through the off-gas lines with sufficient velocity to avoid deposition. The extraction fans were designed to give a minimum velocity of 20 meters per second.

10. The off-gas was used for steam generation.

11. The process can be adapted to manufacture formed coke.

APPENDIX II.   29.1.80

Meeting in the morning with:

1.   Deputy Director.

2.   Professor O. Zbraniborski.

3.   M.Sc. A. Kabeszka.

The Deputy Director welcomed me, and expressed the hope that there would be a mutual exchange of views on Pyrolysis, Gasification, Liquifaction, Coke-making and related subjects.   He also expressed the hope that my stay in Poland, for which he thanked the UNIDO would be a happy and successful one.

I replied that I too hoped that my visit would be of help to the, and thanked him for the kindness both he and everyone in Poland had shown me.   The first part of the business included arranging a visit to Polands largest coke-ovens, and a visit to Krakov.

The following was then discussed:-

1.   The Institute's Pyrolysis Project

I explained that I would be discussing technical areas of this at a later stage of my visit, - particularly control systems for the Fluidized bed. Concern was expressed about a possible delay in the delivery of the H.P.1000 Computer and associated equipment.   This equipment which it had been agreed to purchase will substantially improve the operating efficiency of the new pilot plant, and will allow a proper evaluation of results obtained.

2. <u>Formed Coke</u>

I had already seen and had examined the model for the new formed coke pilot plant. Coal is dried and pre-heated in two streams. One stream passes to a Rotary Kiln where it is heated and converted to char. The second stream passes to a mixer, where it is joined by the char, as the solid heat carrier. The final mixture (that of char and coal) is briquetted in a roll press, and subsequently cooled. The precise method of cooling has yet to be determined but may be in a bunker.

A discussion on the merits and de-merits of formed coke took place. It was agreed, that the main advantages of a formed coke plant was its ability to use inferior coals.

I pointed out the failures of both Ruhrköle and B.S.C. to get their B.B.F. plants to operate satisfactorily. The B.S.C. plant which was now closed down represented a capital outlay of £30 millions. The consultant would, if asked help them on their new pilot-plant when commissioning begins.

<u>Gasification</u>

After Formed Coke, Gasification is the second priority for the Institute. They have a need for medium CV gas, for Industry and for Domestic use. Production of this from indigenous resources would materially assist the economy. In addition as a chemical feedstock, (and for liquid production) they are working on the Methanol route. They already posses vehicles operating on fuels including methanol.

Liquefaction

The Deputy Director said that liquefaction by the Coal digest route would continue to have extraction problems, e.g. the blocking of Candle Filters, Drum Filters and Centrifuges. I suggested that the N.C.B. Gas extraction and hydrogenation, had I believed, a good chance of success! It uses a novel technique to produce a low ash extract from coal which can be upgraded to premium liquid fuels and chemical feedstocks. Crushed coal is mixed with a light aromatic solvent (e.g. toluene) in a reactor operating at 2900 - 4000 p.s.i.g. and 300 - 400°C. Up to 50% of the coal passes into a gas phase solution leaving an involatile residue. The gas phase, containing the dissolved constituents is transferred to a vessel at atmospheric pressure thereby causing the materials extracted from the coal to precipitate. The solvent is condensed and recycled to the reactor and the extract is hydrogenated to light liquid fuels or chemical feedstocks. The solid residue will be gasified to produce process hydrogen and S.N.G.

Coke-Ovens

Present and proposed practices were discussed, as "classical" coke production in Coke-ovens.

1. ### Pre-heating and Drying

   This allowed lower quality cokes to be used and in theory had much to commend it.

2. ### Pipe-Line Charging

   The Consultant pointed out that both in the U.S.A. and the United Kingdom (British Steel) this method of supplying dried and pre-heated coal to the ovens had been unsuccessful. There are several reasons.

(a) Difficulties using steam as a transporter.

(b) A heavy carry-over of fines into the hydraulic main, with loss of coke-product and degradation of the tar.

(c) Heavy carbon build-up on the walls and roof of the ovens.

(d) Inability to fill the ovens,with heavy carry-over.

(e) Excessive top-heats in the battery.

3. Pre-Carbon Charging

The Deputy Director said they had a test rig using this process. The Consultant considered it an improvement on pipe-line charging, but had reservations on its efficiency.

4. Anti-Pollution Methods

The Consultant outlined the methods currently being adopted in the U.K. and the U.S.A.

(a) Smokeless Charging - in the U.K. this was effected by on-line "sequential" charging, with steam injection in the ascension pipes.

(b) Smokeless discharging with a hood, and fume extraction via a pipe to a wet-scrubber and/or electrostatic precipitator.

(c) Great attention to detail in the cleaning of doors. Experiments with water jet cleaning of doors offered very good possibilities.

Further discussions took place on the possible effect of emissions from Coke-ovens (with Benz Pyrenes) on the health of Coke-oven workers. The Consultant described mortality studies carried out in the USA and UK.

Finally the Deputy Director stated that by the year 2000 Poland would be producing 29 million tons of Coke a year in Coke-ovens. Direct reduction of iron-ore for the production of ovens was many years away.

The meeting then concluded.

APPENDIX 3. 30.1.80

Visit to the Coke Works - Huta Katowice

Persons met:

1. Director

2. Technical Manager.

This is a vast Coke-Works producing 5.000 Tons of Coke per day. Production includes coke for the Steel Industry (Blast Furnaces), the Foundry Industry, (Cupolas) and Domestic and Industrial. It has a full by-product plant including the Production of Sulphuric Acid and through to Sulphate of Ammonia.

It contains standard 5.5 meter ovens together with stamp charged ovens.

1. Quality of Coals

All coals were blends. It is interesting to note, that performances in the stamp charged ovens were similar to the one set in the U.K. The quality of coke is improved by the use of stamp charging. On this event it allowed the works to use cheaper coals and still maintain quality. Further cheaper coals were used for the production of domestic coke.

2. Quality of Coke

The Metallurgical coke averaged Micum +40 at 1. and Micum -10 at 6 - 7. These are good figures. A subsequent examination of the coke at site confirmed it was good and consistent in size and texture.

3. Battery Operators.

The batteries were being well operated. The doors were tight and well cleaned. With the exception of the oldest battery, chimney stacks were good.

On the most modern battery there was automatic lid-lifting mechanism, but it was out of commission in this visit. At this stage, anti-pollution equipment, inthe form of smokeless charging, and smokeless discharging, was not fitted.

General Discussion

A general discussion took place with the Director,

Initially, the consultant at the request of the Director, described the current thinking in the U.K. on liquefaction and gasification from coals. He described the N.C.B. Vapour Phase route for liquefaction. On gasification, the main effort was in the U.S.A. where, with 2nd generation processes, it is becoming clear that the S.N.G. programme favours the Slagging Lurgi, Cogas and Hygas.

On third generation processes, many of the fluidized bed and entrained flow processes have the advantage of operation under pressure and, unlike the Winkler System, are designed for good carbon utilization.

Returning to Coke-oven practice, which is a very important part of Pyrolysis, best practices were discussed. The Director has a very important question:- "How can you make better coke, faster, in present equipment.

The Consultant described his experiences with Drying, Preheating, and Pipe-line charging. The theory of supplying dried and preheated coal to coke-ovens would enable them to increase throughput by up to 40% and would allow cheaper coals to be used, and still maintain current quality.

In practice no commercial installation had been successful. The problems encountered included:-

1. Mal-functioning of the Drying and Preheating system.

2. Blockages in the coal transport lines.

3. The inability to fill the ovens without excessive carry-over of fire coal into the hydraulic main.

4. High top heats.

5. Excessive carbon build-up on the walls and roof.

6. Blockages of the ascension pipes.

Most of these can be overcome, but excessive carry-over, carbon build-up and blockages in the ascension pipes, (partly caused by carry-over) could prove intractable. It was his recommendation that this process should not be installed on a commercial battery.

The Director described their experimental drying and preheating plant (17 tons per hour). It was intended initially to use a larry-can for feeding the ovens. After discussion when the Consultant described his experiences with using dried coal (not preheated) in a larry-can, he suggested that care must be taken in charging, and the hoppers and system purged with either nitrogen or another inert gas.

That concluded the discussion.

APPENDIX 4.   31.1.80

Lecture on Automatic and Computer Control of Classic Coke-Ovens

The Consultant said that Automatic and Computer Control of Conventional (Classic)

coke-ovens was quite feasible.   It was obviously easier to build in equipment

for Computer Control while new batteries were being built, but obviously much

could be done with existing batteries.

The reasons and need for Computer control were that it was becoming increasingly

difficult to obtain manpower to operate Coke-ovens, particularly men of the right

calibre.   The operation of the Coke-ovens would suffer because of this, their

life would be shortened, and even more important, the quality of the coke would

suffer.

The Steps to Computer Control

1.   The Battery Heating

   (a) In a new battery, Thermo-couples (2) are built into each wall.   These,

        through tranducers to the Computer, control the main gas inlet valves

        (2) to the battery heating system.   Because the battery is a large

        "heat-sink", the control must allow for time-lapses in temperature

        changes.

   (b) On an existing battery the Consultant suggested that an Optical Pyrometer

        could be located on the Ram machine, perhaps in the cabin, and this

        could locate on the oven walls after pushing a charge.   The temperature

        differential between the oven wall and the flue could be correlated.

        The signals from the Pyrometer could then be passed to the Computer,

        and control effected.

2. Coke-Oven Machinery

All the machinery, i.e. the Charge-car, the Ram machine, the Coke guide, and the Coke-car can be computer controlled. This means, the precise quantity of coal can be charged·to the charge-car, every time, which in turn means the ovens can be completely filled every time.

This discharging is carried out on a precise time control, which means the coal is correctly carboned and is discharged as coke from the ovens at precisely the correct time. The coke-car, (after correct positioning of the coke guide) is automatically located in the correct position before the oven is allowed to be discharged. It moves forward (by winches) at precisely the correct speed, thus filling evenly. Similarly, automatic guiding allowed all coke to be guided to the same degree.

The computer control can be expanded to automatic door clearing, coal fluidizing, screening by-products and virtually every feature of coke-oven operation.

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APPENDIX 5.   1.2.1980

Visit to Laboratory

Institute of Chemical Processing of Coal, Department of Environmental Protection,
Krakow.

Present:

Professor O. Braniborsky

Doctor Julian Grudzien

F.L. Scargill.   (Consultant).

The meeting discussed the questions of Environmental Protection.   For example,
the beautiful city of Krakow, where its beautiful stone-work was being attacked
and eroded by Carbon-Dioxide and Fluorides and Chlorines from adjacent industry.

Poland had recently passed new Environmental Protection Laws which were very
strict, and which would help to safeguard the environment.   Industry will have
to comply.

This laboratory discovered the route to manufacture activated carbon from Coal.
This is a most important substance in the purification of gases and liquids.

It is now being manufactured in large quantities in the U.K. where it is used
for both aqueous and gaseous purification.

The methods of Anti-Pollution for Classic Coke-Ovens were discussed, together
with the methods used in the U.K. to monitor Benzine insolubles on the top of
Coke-oven batteries.

This consisted of operators carrying personal samplers. The products remaining in the filters were recovered and analysed for the quantity of Benzine insolubles.

At the same time, mortality studies were carried out for the previous 15 years. Final results of this latter study indicated only a marginal increase in the incidence of lung cancer amongst coke-oven workers over the general public.

APPENDIX 6.   5.2.80

Hydro-Pyrolysis and Flash Hydro-Pyrolysis of Coal

References

1.   The Hydro-Pyrolysis of Coal to B.T.X.

G. Fyres.   W.R. Ladner and J.O.H. Newman

National Coal Board.   Coal Research Establishment.   U.K.

2.   Flash Hydro-Pyrolysis of Coal.   (APPENDIX 1(a))

M. Steinberg and P. Fallan

Brookhaven National Laboratory. U.S.A.

3.   The Formation of B.T.X. by the Hydro-Pyrolysis of Coals.

M.J. Finn,   G. Fyres,   W.R. Ladner & J.O.H. Newman.

U.K.   (APPENCIX 2(a))

Introduction

Ladies and Gentlemen,

I am very pleased to be here, and I am honoured that such a distinguished gathering
is present today.   In the experiments in Complex Coal Conversion, this Institute
is specialising in Pyrolysis.   The new experimental equipment being constructed
here now will add to the knowledge this Institute already possesses.   I now want
to describe work which has been and is being carried out in the U.S.A. and the U.K.
on that form of Pyrolysis known as Hydro-Pyrolysis and Flash Hydro-Pyrolysis.

I want to make it perfectly clear, that this work in no way supersedes the work
on Pyrolysis being carried out at this Institute.   It may well be a logical ex-
tension of it at a later date.

The hydropyrolysis of coal is defined broadly as the reaction between coal and
hydrogen at elevated temperatures and pressures.   As the nature of the products
depends to a large extent on the operating conditions it is convenien to distin-
guish between different types of hydropyrolysis.   The term "hydrogasification"
is used when methane is the desired product, and "hydropyrolysis" is used when the
principal products are liquids and gas.   "Flash hydropyrolysis" is a more recent
development of hydropyrolysis which uses very high heating rates (1000 Ks^{-1}) with
the object of producing benzene, toluene and zylenes (BTX).

The main aim of the early hydropyrolysis studies in the U.K. and later in 1972
at the United States Bureau of Mines was to make methane.   More recently, interest
has been directed to the production of liquid products, particularly BTX, by flash
hydropyrolysis.   This review is mainly confined to work on flash hydropyrolysis:
emphasis is on non-catalytic studies, although some work on catalytic hydropyrolysis
is discussed.

Until the 1960's, nearly all BTX was a byproduct of coal carbonisation but since then the proportion of BTX derived from petroleum (see Table 1) has steadily increased. However, the cost of petroleum has risen steeply since 1973 and if this trend continues the production of aromatics from coal may again become economic. In the long term, as oil reserves are depleted, it will be necessary to use coal as a chemical feedstock.

A number of different laboratories in the U.S.A. and one in the U.K. have been involved in hydropyrolysis research with the objective of making either oil or BTX from coal. For convenience, the work has been reviewed according to the various laboratories concerned. The highest oil and BTX yields obtained and the conditions used to achieve these yields are summarised in Table 2. The term "oil" which is used widely by American workers can cover all liquid products from water to tars and sometimes even includes material solvent-extracted from the char.

United States Bureau of Mines

The United States Bureau of Mines has undertaken a number of studies on the hydropyrolysis of coals with various objectives. Hiteshue and co-workers developed a simple apparatus: the essential feature was the containment of 8 g of coal in a steel tube through which pressurised hydrogen was flowing; the tube could be rapidly heated (up to 20 Ks^{-1}) to a definite temperature by passing a large electric current through it. The residence time of the coal in the hot zone was controlled by the duration of heating, and that of the volatile products by the hydrogen flow rate. The effects of various parameters on the yield and composition of the products were determined. Although many of the experiments were carried out using a catalyst (1% molybdenum), it was only effective when the coal residence time at the final temperature was as short as 1 min; for a coal residence time of 15 min, the same yields were obtained whether the catalyst was present or not.

Using a sub-bituminous New Mexico coal, the effects of coal residence time (0 to 15 mins), pressure (35 to 415 bar) and temperature (873 to 1173 K) on the yield and composition of the liquid and gaseous products were investigated systematically. In general, the conversion of the coal to gas increased as each of these parameters was increased, but the yield of oil was independent of the coal residence time, showing that its formation was confined to the initial stages of decomposition. At 873 K, the oil yield was also independent of pressure but, at 1173 K, it decreased with increasing pressure and was lower than the corresponding yield at 873 K. This decrease in yield at the higher temperature was probably due to thermal cracking of the oil to carbon, methane and other products.

The maximum yield of oil obtained was about 40% of the coal and the yields of single-ring aromatics (including phenols) ranged from 2 to 6% of coal. Although it was not possible to correlate the composition of the oil with all the operating conditions, it was observed that, at 1073 K, the residence time of the volatile products had a marked effect on both the yield and composition. When the residence time of the volatiles was 5 s or longer, the condensed liquids were light coloured, had a low viscosity and contained a large quantity of distillable oil. In contrast a residence time of 2.3 s gave a dark, viscous oil containing an appreciable amount of asphaltene. This difference was attributed to hydrocracking of the volatile products at the longer residence times.

Brookhaven National Laboratory (Appendix (a))

The costs of the production of petrol and substitute natural gas were estimated assuming 13% yields of benzene and light oil, and a 28% yield of hydrocarbon gases. It was concluded that the economics came close to favouring investment under U.S.A. conditions.

In addition, an independent analysis of experimental data (part provided by Brookhaven) found that the economics of production of substitute natural gas (with BTX as a byproduct) by flash hydropyrolysis appeared to be superior to other conversion processes such as Hygas, Lurgi and Fischer-Tropsch.

Cities Service R & D

Rosen et al patented the hydropyrolysis of coal in disperse phase. Coal was rapidly heated for a predetermined time by injecting into preheated hydrogen and the products were rapidly quenched with cold hydrogen. Very high yields, up to 46% benzene, were claimed (but not proved) using a sub-bituminous coal at 200 bar and 1063 K.

In a later publication Pelofsky et al when describing work carried out on a $0.28g \ s^{-1}$ scale, gave the yield of light oil (which contained 94% benzene) as only 16%.

By 1977 Cities Service had built and tested thefollowing reactors: a 1.2 m by 28 mm ID free fall type, a 6 to 18 m by 6 mm ID entrained flow type and a 1.2 m long, vertical, entrained flow type. A range of coals, oil shale, tar sand and coal tar was hydropyrolysed, although few results have been published. Most of the tests were with North Dakota Lignite which was crushed, dried and pulverised in nitrogen before final drying in vacuum. Solids residence time of 0.5 to 4 s with vapour residence time of 4 to 40 s were obtained in the free-fall reactor, whereas the entrained flow systems gave solids residence time of 0.08 to 30 s with vapour residence times of 0.08 to 8.6 s; the 1.2 m upward, entrained flow reactor gave the shortest residence time. Hydropyrolysis of lignite for 2 s at 973 K and 153 bar gave 4.7% BTX plus 13% light oil and 12.5% methane; the light oil was said to be easily and economically hydrocracked to benzene.

The coal heating rate was estimated as $5 \times 10^4 \, k \, s^{-1}$ and the hydrogen consumption was 5% w/w on lignite. Rapid heating of coal in the presence of high pressure hydrogen was said to lead to high yields of volatiles because the vaporised tar was stabilised. The quality of the secondary products could be controlled by altering the pyrolysis conditions, low severity pyrolysis yielding a light oil containing polynuclear aromatics whereas high severity pyrolysis (up to 1300 K) gave little light oil but mainly benzene, methane and ethane. A sequential reaction mechanism was proposed to explain the results, coal pyrolysing to tar which reacted with hydrogen to give benzene; gas was produced at each stage. Overcracking of the products yeilded gas (methane and ethane) and coke, the latter by catalytic decomposition of benzene by hot char. Only after the coal had been devolatilised was there significant reaction between char and hydrogen to form methane, the rate of hydrogenation then being dependent on pressure.

Means of scaling-up the Cities Services process to produce BTX and byproduct substitute natural gas (SNG) have been described; lignite could be dried by distilling a benzene-water azeotrope from a benzene-lignite slurry, which would be pumped up to pressure before flashing off the excess benzene. The coal would be fed through separate injectors into a 36 - tube reactor through which it would be transported upwards under fast fluidisation in hot hydrogen, part of which would be combusted with oxygen to raise its temperature further. The exothermic heat of reaction would be removed from the tubes by a high pressure water boiler around the tubes and molten metal would be used to quench the products and recover useful heat.

An evaluation of the economics of SNG production by Cities Service and the Foster Wheeler Energy Corporation concluded that flash hydropyrolysis SNG (BTX was a major byproduct) could cost 80% of Lurgi-produced SNG. The major difference between plants designed for SNG and BTX production was the higher temperature reactor used to form SNG and the use of molten metal cooling of the reactor tubes.

An independent study of the economics of the Cities Service process by Oak Ridge National Laboratory concluded that the cost of flash hydropyrolysis technology is comparable with, if not better than, the cost of other coal conversion processes. Sufficient data for a firm process design were required before a detailed engineering evaluation of the process could be undertaken to determine where further development was required.

Rockwell International, Rocketdyne Division

Oberg et al described the initial trials of a hydropyrolysis reactor based on a rocket motor injector. Hydrogen was preheated and further heated by partial combustion with oxygen before being rapidly mixed with coal and injected into a disperse-phase reactor. The reactor was used at pressures of 35 to 104 bar with a coal feed rate of 50 g s^{-1}.

The products were quenched with water sprays. Adhesion of the coal to the walls of the reactor was reduced by heating them to above 1144 K. Reaction times of 0.01 to 1 s at temperatures up to 1420 K were employed and tar yields of up to 33% were deduced by difference from the yields of gas and char.

Later reports described the scale-up of this technique and the rapid pyrolysis of up to 270 g s^{-1} of caking, bituminous Kentucky coal. About one third of the coal could be converted into liquids by injecting coal into hydrogen preheated in a fired heater followed by partial combustion with oxygen to 1340 K. Up to 9% BTX was obtained by hydropyrolysis of 70 to 104 bar for 0.08 s at 1255 K. The BTX was recovered by quenching the reaction with water sprays, removing the char at 811 K, cooling to 311 K to condense the water and tar and removing the light aromatics on activated carbon. Hydrogen equivalent to 3% w/w of the coal was calculated to have reacted with the coal. Increasing the reaction time and temperature increased the methane yield at the expense of the liquids.

Institute of Gas Technology

The hydropyrolysis of lignite or non-caking coals in entrained flow through a heated tube with high pressure hydrogen was described by Duncan et al. The aim was to convert coal to high yields of gasoline; the process is known as the Riser Cracking of coal. A bench-scale reactor transported 0.2 to 0.5 g.s.$^{-1}$ of -7- m lignite in hydrogen at up to 139 bar through a 21m x 3 mm ID helix heated to 1200 K. The reactants were heated to reaction temperature in the first 15 m of the helix in 1.7 s. The char was separated and tar mist removed before the pressure was reduced. At a pressure of 139 bar and a residence time of approximately 3 s, 0.35 g s^{-1} of lignite were transported by 11 g min^{-1} of hydrogen to yield 10.6% oil which contained 3.1% BTX. The benzene content of the oil increased to 60% as the coal outlet temperature and the hydrogen coal ratio were increased. Generally, 50% of the carbon in the coal was converted to gaseous and liquid products, the liquid yield increasing with total conversion.

The mechanism of reaction was defined as the pyrolysis of lignite to volatiles which, on entering the bulk gaseous phase, were fragmented to free radicals which then reacted with the hydrogen to form stable species.

University of Utah

With the objective of producing a liquid fuel of low sulphur content, Wood and Wiser and Anderson et al investigated the catalytic hydropyrolysis of a bituminous Utah coal. Zinc chloride (5.5% by weight of coal) was used as the catalyst. A disperse phase reactor consisting of coiled narrow tubes (3 to 13 mm ID) and heated externally was used. The carrier gas was pressurised hydrogen and, by using high gas velocities, turbulent flow and rapid heat exchange were achieved. The catalyst coating the coal particles melted and, consequently, a liquid annulus was driven through the tube much more slowly (2 to 6 s duration) than the gas (0.6 s). To find theoptimum conditions for high liquid yields, the effects of pressure up to 173 bar and of temperature up to 973 K were investigated.

The oil yield, which included material extracted from the char by toluene, approached a limit of 50% with increasing temperature. The oil contained, typically 20% water, 20% benzene insolubles, 15% asphaltenes and 40% light oils. The latter contained 60% neutral oil, 20% bases and 20% tar acids. The zinc chloride which appeared in the char and oil was difficult to recover. According to the authors further work was necessary on the recovery and recycling of the catalyst and to find a method to prevent agglomeration of the char to make the process viable.

The results obtained and the techniques used by the University of Utah were reviewed by Oak Ridge National Laboratory with the conclusion that catalyst recovery must be solved if the process is to become economically viable.

National Coal Board   (Appendix 2(a))

Discussion

Most hydropyrolysis studies have been carried out with low-rank coals. The amount used per experiment varied from a single charge of 10mg or less (Growcock and Mackenzie ; Graff et al) to 293 g s^{-1} in the Rocketdyne reactor. Rapid heating in hydrogen causes even low-rank coals to agglomerate, although the effect is less pronounced with lignite than with bituminous coal. Dilution with inert material and preoxidation have been used to reduce this problem.

The Yields of Oil and BTX

The yields of oil, BTX and benzene obtained by hydropyrolysis are summarised in Table 2. Although oil yields of up to 40% w/w on dry ash-free coal have been achieved, those of BTX aremuch lower (3-15%) except for one unsubstantiated, and perhaps rather optimistic, patent claim of 46% by Rosen et al. However, most of these BTX yields are appreciably greater than the 1% obtained by conventional carbonisation at atmospheric pressure in an inert atmosphere.

Effect of reaction Conditions

The important variables affecting the hydropyrolysis of a particular coal are (i) the rate at which the coal is heated, (ii) the temperature and time histories of both the coal and the volatiles and (iii) the hydrogen pressure. Although the main findings on the effects of these variables are discussed under the headings in the rest of this Section, it must be remembered that variables are often inter-related in a set of experimental data; for example in an alteration of vapour residence time by a change in hydrogen flow will also change the ratio of coal to hydrogen. Consequently, the following remarks present an over simplified picture.

Heating Rate

The effect of rapid heating in an inert atmosphere at atmospheric pressure is well known. Weight losses can be at least 30% greater than in the BS method for volatiles; moreover the tar yield can be markedly increased by rapid heating. Most of the best yields of benzene obtained have been achieved at very high heating rates as shown (see Table 2). Squires has shown, however, that for BTX formation no advantage is gained by increasing the heating rate beyond about 650 K s^{-1}.

Temperature and Vapour Residence Time

As might be expected, negligible reaction occurs when coal is hydropyrolysed below 600K but, with increasing temperature, both the benzene and oil yields go through a maxima in the range 1000-1100 K. From the point of view of BTX and oil formation, the residence time of the solid appears to be relatively unimportant provided that it is adequate to allow the release of the volatiles, after which the main reaction is hydrogenation of the residual char. However, there is some evidence that the char can catalyse the decomposition of benzene to coke.

On the other hand, the vapour residence time can have a marked effect on the yield and composition of the oil. Friedman et al found that vapour residence times less than 3 s resulted in the production of dark, viscous liquids whereas longer residence times resulted in light distillable oils. The results of Squires and co-workers showed that there is an optimum residence time (depending on temperature) for maximum BTX yields, which in their apparatus was 3 s at 973 K. Pelofsky et al, operating a disperse-phase system, have claimed high benzene yields (15%) using vapour residence times of up to 14 s.

Pressure

The effect of hydrogen pressure on the yields of BTX and oil in hydropyrolysis is complex. Application of pressure alone suppresses the release of volatiles, while the presence of hydrogen is likely to reduce polymerisation and increase liquefaction. The overall effect is that gas yields and, under certain conditions, BTX and liquid yields all increase with increase in hydrogen pressure, as has been shown by Growcock and Mackenzie. However, the exact form of the relationship between yield and hydrogen pressure is uncertain. Holmes and colleagues, who have attempted to correlate the data of other workers on hydrogen pressure, found that oil yields can be either linear or square-root functions of the pressure. For example, their correlation of the data of Albright and Davis gave a linear function while that of the data of Kawa and Eddinger et al revealed square-root functions. As the oil yield is also dependent on several other parameters, it is perhaps not surprising that the pressure relationship may vary from one apparatus to another.

Mechanism of Hydropyrolysis

Although the main features of the kinetics of coal pyrolysis (Fitzgerald, Chermin and van Krevelen, Pitt) and also of hydrogasification have been established, it has not yet been possible to resolve in detail the chemistry of the complex reactions involved in the formation of BTX and tar.

Early work on the hydrogasification of coal showed that, although the rate was initially high, it decayed rapidly to a low value. Some workers considered that the initally high rate corresponded to the hydrogenation of the volatiles and the lower rate to that of fixed carbon. Other workers such as Moseley and Paterson concluded that, at sufficiently high pressures, the hydrogenation of the volatiles and the fixed carbon could not be treated separately. In a more detailed mathematical analysis of the kinetics of hydrogasification of a bituminous coal, Feldman et al postulated that the coal contained three types of carbon of different reactivities; the most reactive was the side chains which were readily split off.

These kinetic studies of hydrogasification, apart from showing different regions of reactivity in the carbon matrix, do not contribute to our understanding of the formation of liquid products by hydropyrolysis. In fact, the later stages of gasification are probably not associated with the formation of liquid products. However, papers by Anthony and his co-workers on rapid devolatilisation consider the interaction of hydrogen with the coal during the initial stages of pyrolysis. They used an apparatus similar to that of Squires but with an electrically heated wire mesh, whereby a thin layer of coal was extremely rapidly heated. After maintenance of the coal at a definite temperature for a specified time, it was rapidly cooled and, from the weight of the residual char, the extent of devolatilisation was determined. The composition of the volatiles was not investigated.

They found that, for extremely high heating rates (750 to 10,000 K s^{-1}) and a temperature of 1173 K, most of the volatile loss occurred during the first second and was the same whether the atmosphere was hydrogen of helium. Thus, under these conditions, the hydrogen had little effect on the initial rapid devolatilisation of the coal. After this initial stage, however, devolatilisation continued in a hydrogen atmosphere but not in helium. Moreover, the effect of pressure on the extent of devolatilisation depended on the atmosphere.

In helium, the extent of devolatilisation decreased with increasing pressure, whereas in hydrogen it increased with pressure after passing through an initial minimum.

Anthony and his co-workers, on the basis of their experimental results, developed a theory of the kinetics of primary devolatilisation of the coal in an inert atmosphere. Their theoretical treatment, which was similar to that of Pitt, postulated a set of independent first-order parallel reactions covering a range of activation energies. As Fitzgerald and, independently, Chermin and van Krevelen had proposed earlier, they postulated that the primary pyrolysis products formed initially within the coal particles consisted of two types. These were (i) unreactive products which escaped readily into the surrounding atmosphere and (ii) reactive products, including free radicals, which could either polymerise within the coal particle to form coke, or crack on the hot internal surfaces thereby depositing solid within the particle and releasing volatiles into the atmosphere. Consequently, factors such as a high heating rate and small particle size would reduce the residence time of the reactive decomposition products within the coal particle and enhance the yield of volatile products. Conversely, in an inert atmosphere, high pressure, by delaying the escape of the reactive molecules from the particles, would lead to cracking to coke and reduce the volatile yield. According to their view, hydrogen, by reacting with the reactive decomposition products within the coal would inhibit polymerisation and so increase the volatile yield. The extent to which this occurred would increase with hydrogen pressure. It should be stressed that their theory only applies to the initial devolatilisation, i.e. to short residence times of the coal. For longer residence times, the residual carbon will be partly gasified and, although the extent will increase with pressure, the type of reaction involved will be different.

However, Greene suggested that the rapid, initial release of volatiles from within coal particles undergoing flash hydropyrolysis reduces ingress of hydrogen. Thus hydrogen is not available for reaction with volatiles until they have entered the bulk, gaseous phase, where the larger, volatile organic molecules crack to free radicals which are stabilised by the hydrogen and cannot polymerise to tar and coke. Cracking is progressive and sequential via the most stable molecules such as polynuclear aromatics, substituted benzenes, benzene and ethane to methane. Only after the main devolatilisation processes have occurred is there hydrogen counter diffusion into the porous char structure to give increased reaction between hydrogen and carbon: higher hydrogen pressures strongly influence this counter diffusion.

Anthony and his co-workers investigated the effect of temperature on the devolatilisation of coal heated in various atmospheres for short residence times (5 to 20 s). The extent of devolatilisation, as measured by the weight loss, increased with increasing temperature and, above 870 K, was greater in hydrogen than in helium. They concluded that this effect could not be explained in terms of kinetics (i.e. that the pyrolysis and hydrogenation reactions had markedly different activation energies), but rather that the proportion of volatile products from the hydrogenation reactions greatly exceeded that from pyrolysis.

Although these detailed investigations provided some insight into the way hydrogen affects the devolatilisation of coal during the initial stages of hydropyrolysis, they were not concerned with the proportion and composition of liquid products obtained. These must to some extent be dependent on the hydrocracking of the volatile products, including polynuclear aromatics, after they have escaped from the coal. According to Korosi, Woebcke and Virk, polynuclear aromatic compounds present in oils produced from coal must be hydrogenated to their fully alicyclic analogues in order to provide desirable pyrolysis products.

The extent of hydrocracking will depend on the temperature and residence time of the vapour, parameters which Squires has found markedly influence BTX formation. The combination of temperature and vapour residence time should be such as to promote the maximum hydrocracking to BTX and avoid any subsequent hydrocracking to carbon.

Apart from the possible formation of BTX by hydrocracking of the volatile products, there are two other possible mechanisms of formation. The first is by synthesis from smaller molecules or radicals. The other possibility is that single benzene rings chemically bound to the coal matrix are split off by pyrolysis as benzene radicals and are immediately converted to benzene by the addition of hydrogen. It is probable that all three types of reaction contribute to the formation of BTX.

Studies show that the evolution of volatiles from high-volatile British coals and their cracking to benzene during hydropyrolysis are sequential reactions. This was confirmed using a two-stage reactor in which the coal was heated at a controlled rate (5 K s^{-1}) and the volatiles cracked in a separate zone at constant temperature. Hydropyrolysis of model compounds showed that benzene was a major product for the cracking of polynuclear aromatics under hydrogen pressure.
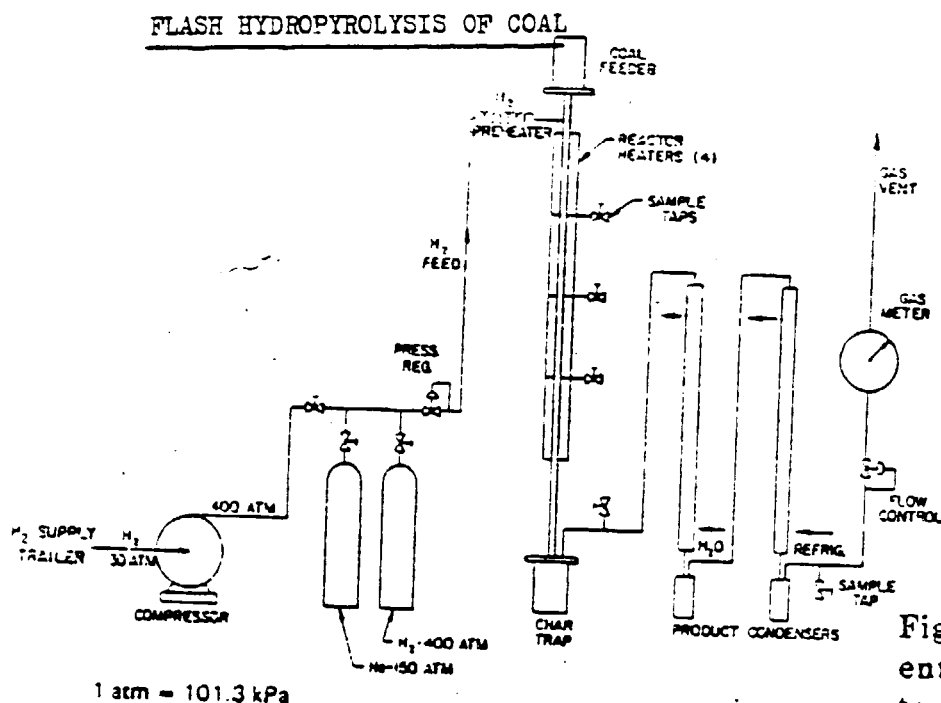
FLASH HYDROPYROLYSIS OF COAL
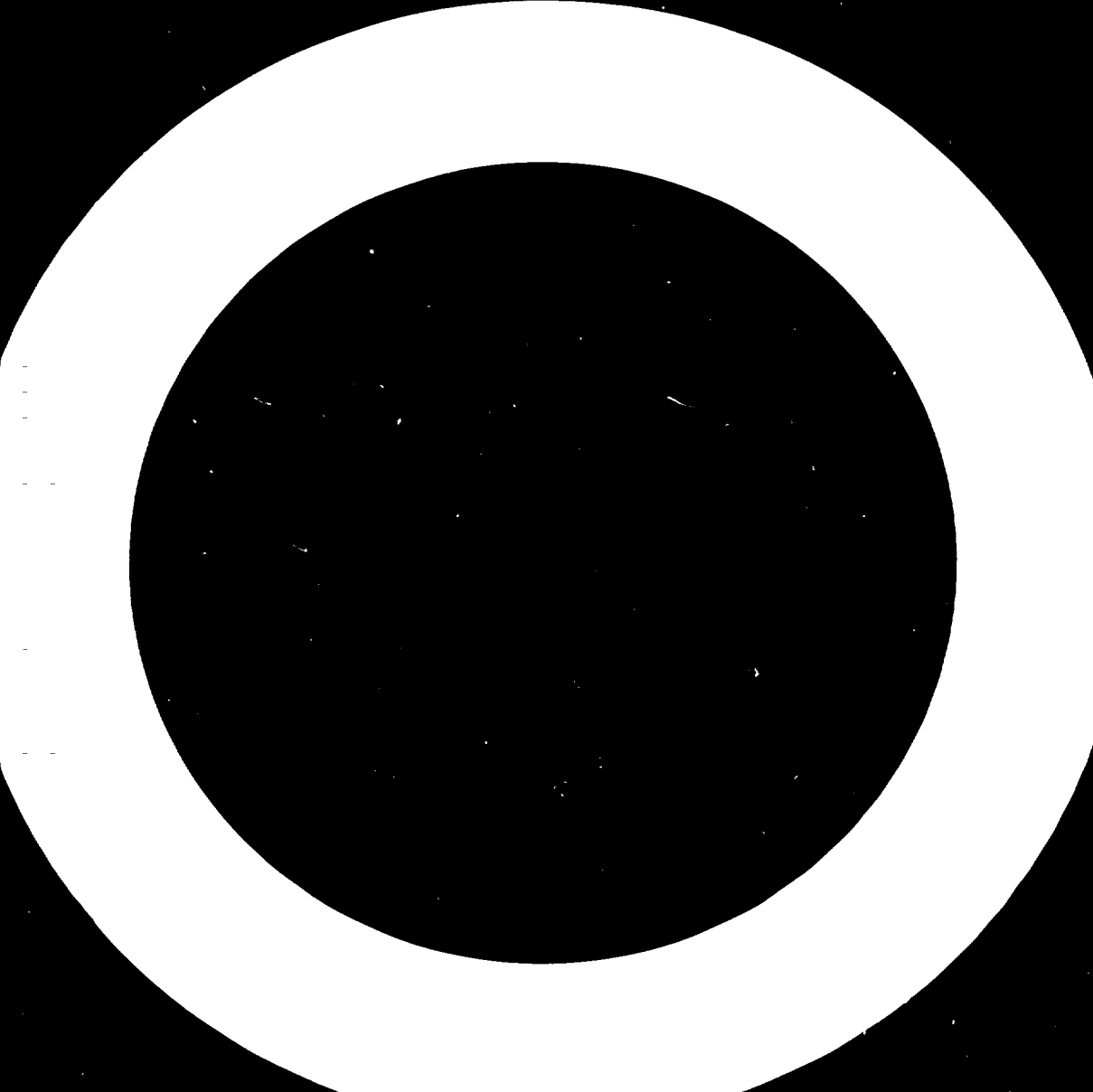
Figure 1. Flowsheet of entrained tubular reactor experiment for flash hydropyrolysis of coaL

1 atm = 101.3 kPa

COAL PROCESSING TECHNOLOGY:

Flash Hydropyrolysis of Coal

Experimental results indicate that the principal liquid yields are benzene and aromatic oil; gaseous yields are methane and ethane.

M. Steinberg and P. Fallon
Brookhaven National Laboratory, Upton, N.Y.

Following early work in the 1960s on the rapid gas-phase hydrogenation of coal for the synthesis of liquid hydrocar-

bons, preliminary bench-scale experiments in a 19-mm diameter x 2.4-m long downflow reactor was undertaken at Brookhaven National Laboratory in 1974. [1] When hydrogenating lignite at temperatures and pressures up to 700°C and 1,500 psi (10,343 kPa), the results indicated significant yields of liquids, especially benzene, and gaseous hydrocarbons, particularly methane and ethane. The liquid yields increased for reaction residence times less than 30 seconds.

Figure 2.
BTX vs. temperature.

1 lb/sq in gauge = 6.895 kPa
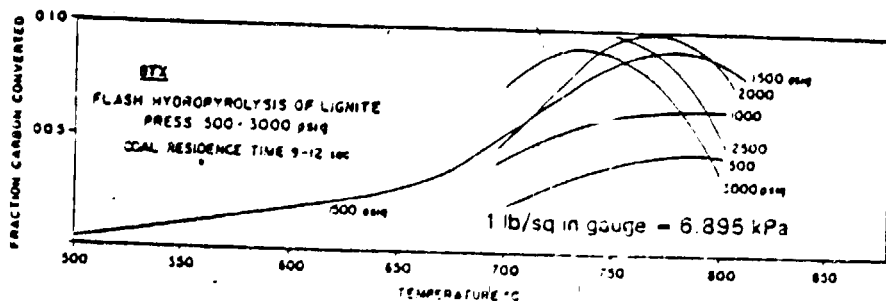
Figure 3.
Total HC gas vs. pressure.

Figure 4.
Yield vs. residence time.

Preliminary process design and economic evaluation of a flash hydropyrolysis process (2) indicated a reasonable return on capital investment, especially for chemical feedstock production. This gave encouragement to the further investigation and development of a flash hydrop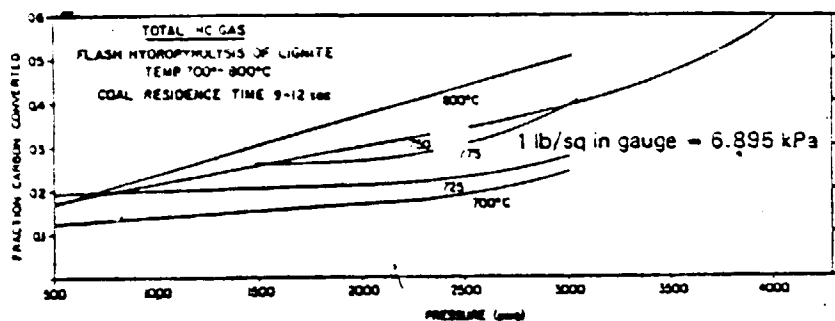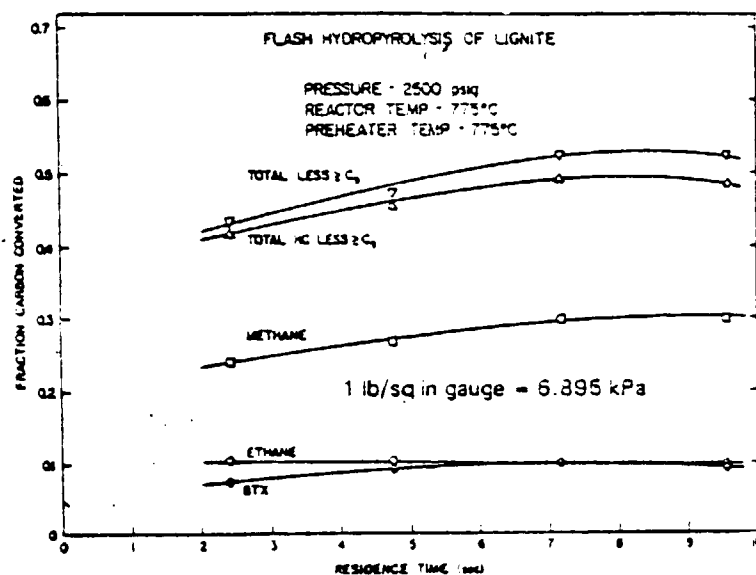yrolysis process (FHP) that featured a one step, non-catalytic, rapid, deep hydrogenation system for coversion of coal to synthetic liquids and gaseous fuels. In late 1976, a larger, versatile, and highly instrumented, entrained downflow tubular reactor was constructed and placed into operation. (3, 4)

During this period, several university research laboratories have contributed to an understanding of the rapid coal hydrogenation reaction, notably, R. Graff et al. (5) at City University of New York, and J. B. Howard et al. (6) at MIT. In addition, three federally-supported industrial programs have been undertaken at Cities Service Research and Development Co. on a short residence time (CS-SRT) hydrogenation process, (7) at the Institute of Gas Technology on a high-speed riser cracking process using a coil reactor (8) and at Rocketdyne Corp. on a rocket type reactor system. (9) Other private industrial oil and chemical companies also appear to be actively interested in the FHP system.

Experimental apparatus

The 25.4 mm dia tubular reactor, 2.4-m long, equipped with four sectional clam-shell electric heaters, followed by 1.2 m of cooling section, is constructed of Inconel 617, a high Cr-Ni alloy. A 1.5-kg capacity, pressurized, coal feed hopper mounted on top of the reactor tube can feed coal up to 2

lb/hr (908 g/h) downflow to the reactor. Hydrogen can be supplied up to 5 lb/hr (2.27 kg/h) and preheated to a maximum of 1900°C in a 6.4-mm diameter, electrical resistance-heated, hairpin tube. Reactor tube maximum operating conditions are 4,000 psi (27.6 MPa) and 800°C, or 2,500 psi (17.24 MPa) and 900°C. An on-line process gas chromatograph can analyze 10 chemical components every eight minutes with sample taps every two feet along the length of the reactor and in the traps and vent lines. A char trap maintained at 300°C separates out the char and avoids condensation of liquid hydrocarbons. This is followed by a water-cooled trap that separates the oils ($\geq C_5$), and a low-temperature trap (−40°C) for separating the condensable BTX ($\leq C_4$). The remaining gases are vented up a stack. A schematic of the apparatus is shown in Figure 1.

The general trend of yields for the FHP conversion of coal (lignite) to products collected at the exit of the tubular reactor are shown for the light liquid product, BTX ($\leq C$, mainly benzene), in Figure 2, and the main gaseous hydrocarbon products methane and ethane in Figure 3. It appears that the yield (in terms of fraction of carbon converted) of liquid remains at a relatively low level at any given pressure until temperatures on the order of 650°C are reached. The BTX yield tends to rise and reach a maximum in the order of 10% at temperatures ranging from 725°C to 800°C after which the yield declines. Thus, a dynamic equilibrium appears to be established between the formation and the decomposition of the liquid hydrocarbons. In the case of the gaseous hydrocarbons, the yield appears to continually rise both as a function of pressure and temperature reaching values as high as 50 to 60%. However, these are not maximum yields because they have been measured

at the reactor exit, which is across the entire length of the reactor for coal residence times ranging from about 9 to 12 seconds. The yields have been found to vary along the length of the reactor going through a maximum in a number of cases.

Concerning the flash hydropyrolysis operation, it is calculated that the average coal particle heat-up from ambient feed temperature to reactor temperature is approximately 50,000 °C/sec when mixed at the entrance to the reactor with 750°C preheated hydrogen. The average cool-down or quench rate of the reaction mixture from the heated reaction zone, through the air-cooled quench zone, to the 300°C char trap is approximately 200°C/sec. The initial cool-down rate at the exit of the reaction zone may be higher, however. Maximum yields were determined from the highest measured value along the length of the reactor using the sample taps. One example of the product yield as a function of coal particle residence times is given in Figure 4 at 2,500 psi (17.24 MPa) and 775°C.

In the temperature range of 750° to 800°C and pressure range of 2,000 to 2,500 psi (13.79 to 17.24 MPa), the maximum yield for BTX peaks out at residence times in the reactor varying from 2 to 7 seconds with the shorter residence times at the higher temperatures.

Because of the higher boiling range of the heavier oils ($\geq C_9$) these are determined only by collection at the end of the reactor. As shown in Figure 5 for North Dakota lignite at temperatures in the range of 725° to 750°C and 2,000 psi (13.79 MPa), the maximum yield of the heavier liquid hydrocarbons ($\geq C_9$), is approximately equal to that of the BTX yield. Above 750°C, however, the $\geq C_9$'s decrease much more rapidly with increasing temperature than the BTX. Since one of the probable products of decomposition or hydrocracking of the heavier liquids is BTX, there appears to be a relationship between the measured yields of these two liquid products. At even higher temperatures, (>775°C) the heavier liquids ($\geq C_9$'s) decrease rapidly due primarily to hydrogenation and rapid formation of gaseous hydrocarbons.

As reactor temperatures increase to above 875°C, the principal product remaining is methane with smaller amounts of ethane. The maximum gaseous hydrocarbon yield occurs between 2.4 and 7 seconds coal particle residence time over a range of pressures, as given in Figure 6. The almost linear nature of the curves shows a yield increase of from 2.3 to 3.8% per 100 lb/sq in (689.5 kPa) of total system pressure. This pressure effect is thermodynamically in agreement with that predicted for the hydrogen-carbon reaction producing CH_4 and C_2H_4.

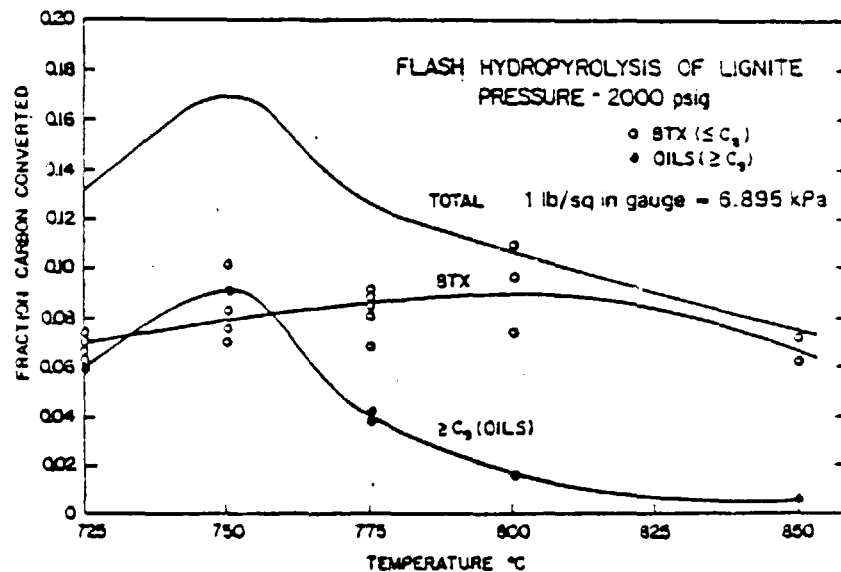Since the feed ratio of hydrogen to coal is usually in the

Figure 5.
Liquid yield
vs. temperature.
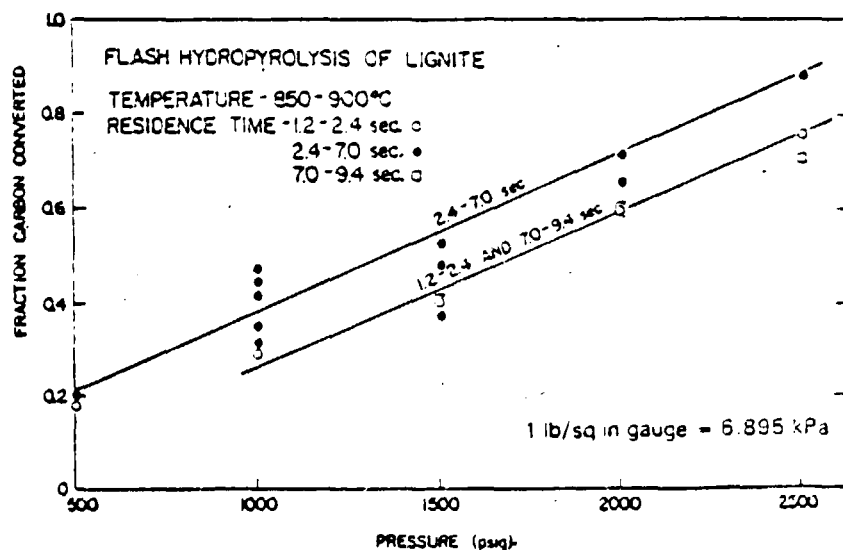

Figure 6.
Gaseous HC
vs. pressure.

Table 1. Flash hydropyrolysis of North Dakota lignite.

(Maximum liquid and maximum gas yield runs)

	Max. Liquid Run	Max. Gas Run
Reactor Temperature, °C	775	875
Reactor Pressure, lb/sq in gauge	2,000	2,500
H_2 Feed Rate, lb/hr	0.82	0.88
Coal Feed Rate, lb/hr	0.98	0.95
Residence Time, sec.	7.1	4.7
Product Yields (% Carbon)		
CO	3.4	1.3
CH_4	30.9	88.0
C_2H_6	10.3	0.5
Total HC Gas	41.2	88.5
BTX	10.2	0.7
$\geq C_9$	9.7	0.0
Total Liquid	19.9	0.7
Total	64.5	90.5
Heat of Reaction, kcal/gm coal	−0.70	−1.3
Hydrogen Consumption, lb/lb coal	0.077	0.20
Effective Carbon Conversion, %	58.3	62.4
Effective Energy Efficiency, %	75.9	100.0

Metric conversions:
1 lb/sq in gauge = 6.895 kPa
1 lb/hr = 454 g/h
1 kcal/gm = 4.187 kJ/g

order of 1 kg of hydrogen to 1 kg of coal, the product concentration in the process gas stream are far below thermodynamic equilibrium values. Due to this dilute phase, the methane gas usually is below 5 mol % concentration in the equipment while the equilibrium concentration is 34% at 700°C and 4,000 psig (27.6 MPa gauge), and 32% at 900°C and 500 psig (3.45 MPa gauge). By decreasing the hydrogen-to-coal feed ratio in the reactor to 0.2 at 2,500 psig (17.24 MPa gauge) and 875°C, a methane concentration as high as 33% was observed. The thermodynamic equilibrium concentration under these conditions is 61%; thus, the methane reached 54% of the equilibrium value.

Two maximum yield runs are shown in Table 1. One run listed is the highest liquid yield run (19.9% liquid and 64.5% total conversion) and the other is the highest gaseous yield run (88.5% gaseous HC and 90.5% total conversion).

The nitrogen and sulfur distribution and balances were measured. The lignite is a relatively low sulfur content coal (0.5% S). With FHP the major portion, 48 to 77% of initial S remains in the char. The oil is found to contain <0.1% S. For the nitrogen (initial N content is 0.9%), less than half remains in the char and the oil contains <0.2% N.

Mixing recycled char with the lignite feed and addition of iron oxide to the lignite improved the yield of BTX and ethane.

Reactor model

A three-step reaction model has been developed in an attempt to obtain generalized expressions for the hydrocarbon component yields as a function of pressure, temperature, and residence time. (*10*) The experimental data have been fitted to Arrhenius-type rate equations taking into account formation and decomposition of major products. Activation energies indicate mainly a chemical reaction controlled mechanism. The use of these rate equations in conjunction with heat balance expressions are applied to the design of a hydropyrolysis reaction vessel. Additional experimental, design, and analysis work is needed to obtain a much more detailed understanding of the reactor engineering.

Process design and preliminary economic estimates were made for three versions of the FHP process system (*10*): 1) producing only liquid products for motor gasoline fuel; 2) producing both liquid and gaseous hydrocarbon products for motor gasoline and pipeline gas; and 3) producing only gaseous products for pipeline gas. For comparable overall values of coal conversions (62%), the minimum production cost is obtained for the combined production of motor gasoline and pipeline gas.

The largest factor (~35%) in the capital cost of the FHP plant is the equipment needed for recycling and conditioning the hydrogen process, gas. The FHP process has the advantage of allowing effective gas-solid and gas-liquid separation operations for producing hydrocarbon products from the unconverted char, oils, and process gas. In addition, the FHP system has the distinct advantage of versatility and process flexibility. The product slate and the production rate of gaseous and liquid hydrocarbon fuel products can be altered in the same reactor, depending on reactor operating conditions. #

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APPENDIX 2 (a)

THE HYDRO-PYROLYSIS OF COAL TO BTX

M.J. FINN, G. FYNES, W.R. LADNER, J.O. NEWMAN — NATIONAL COAL BOARD

ABSTRACT
        The pyrolysis of British coals has been studied at hydrogen pressures of 50
to 150 bar in single- and two-stage, tube reactors at heating rates of up to
30 K s^{-1}. In the single stage reactor, hydropyrolysis of a high-volatile coal
gave up to 4.5% single-ring aromatics; the results suggested that the evolution
of volatiles and their cracking to benzene were sequential reactions. This was
confirmed using a two-stage reactor in which the coal was heated at a controlled
rate and the volatiles cracked in a separate zone at constant temperature.
Yields of up to 12% benzene were obtained from a high volatile coal in hydrogen
(similar to the yields obtained by various workers from American coals by flash
pyrolysis) without very rapid heating of the coal. Hydropyrolysis of model
compounds showed that benzene was a major product of the cracking of polynuclear
aromatics under hydrogen pressure.

1. INTRODUCTION

        The carbonisation of coal under hydrogen pressure is known as 'hydro-
pyrolysis'. A review of published work[1] showed that flash hydropyrolysis of
coal, which involves heating rates of hundreds of K s^{-1}, can give appreciable
yields of light aromatic hydrocarbons such as benzene, toluene and xylenes
(BTX). The present paper is concerned with studies of both single-stage and
two-stage hydropyrolysis of coals aimed at producing single-ring aromatics,
especially benzene, from coal. In the single-stage reactor the carbonisation
and cracking zones are heated by the same source, while in the two-stage reactor
there is independent control of the carbonisation and cracking zones.

2. MATERIALS

2.1. Coals

        The analyses of the coals used for hydropyrolysis are given in Table 1.
The coals were ground, sized +251 -500 μm and dried at 373 K in vacuum.

2.2. Model Compounds

        Hydropyrolysis experiments were also carried out on six aromatic
hydrocarbons: benzene, toluene, p-xylene, naphthalene, anthracene and
phenanthrene. Where possible, 'ANALAR' grade chemicals were used without further
purification. As the hydropyrolysis reactor was only suitable for solids, 1g of
compound was either absorbed on or mixed with 9g of active carbon (NC3
Anthrasorb).

3. SINGLE-STAGE HYDROPYROLYSIS

3.1. Experimental

        The design of the reactor is based on that used by Hiteshue and co-
workers at the USBM[2]. A 1830 mm long x 8 mm ID stainless steel, pressure tube
in which about 10g of coal were secured between degreased wire wool plugs was
heated by passing a large current (up to 1600A) through its wall. The heating
rate was controlled by switching tappings on a transformer. The pyrolysis

vapours were swept out of the reaction zone by pressurised hydrogen at up to
150 bar, some of the liquid products collecting in the ice-cooled trap. The
remaining liquid products and gases were reduced to atmospheric pressure through
a needle valve, which was also used to control the flow rate, before being
collected for analysis. The products in the trap were weighed and then washed
from the trap and adjoining tubing with chloroform. The residual char in the
reactor was weighed and analysed.

3.2. Product Analysis

Both gaseous and liquid products were analysed by chromatography. The
hydrocarbon gases were measured on an alumina column with a flame ionisation
detector, and the permanent gases on a molecular sieve 5A column with a
katharometer detector. The liquids were measured using a silicone SCOT column
with a flame ionisation detector. Water was estimated by titration with Karl
Fisher reagent. Proximate and ultimate analyses were carried out on selected
char samples.

3.3. Results

The effect of variations in the final heat-treatment temperature and
in the vapour residence time on the yields of single-ring aromatics formed by
hydropyrolysis of high-volatile Linby coal was investigated using heating rates
in the range 7 to 30 K s^{-1}, a pressure of 150 bar and zero solids residence
time at maximum temperature.

3.3.1 The effect of final heat-treatment temperature

The effect of the final carbonisation temperature on the yields of
benzene, toluene and xylenes (BTX) and phenol, cresols and xylenols (PCX) is
shown in Figure 1, where it can be seen that for a vapour residence time of
approximately 10 s the yields of both BTX and PCX passed through a maximum at
a temperature of about 1000 K. The maximum yield of single-ring aromatics was
approximately 4.5%, being composed of about equivalent amounts of BTX and
phenolics.

3.3.2 The effect of vapour residence time

The effect of vapour residence on the yields of BTX and PCX at heating
rates of 10, 20 and 30 K s^{-1} to a final heat-treatment temperature of 1000 K
is shown in Figures 2a and b. The yield of BTX increased steadily over the
range of residence times investigated and was little affected by the heating
rate. In contrast, the yield of PCX passed through a maximum at a residence
time of 3 s and was markedly affected by the heating rate, at the two higher
heating rates the PCX being almost completely destroyed after 9 s.
Dehydroxylation of the PCX to BTX at the longer residence times only partly
explains the fate of the PCX since the decrease in PCX is considerably
greater than the increase in BTX.

4. TWO-STAGE HYDROPYROLYSIS

4.1 Modification to Apparatus

The modification to the hydropyrolysis apparatus to enable the
carbonisation and cracking zones to be separated is shown in Figure 3. The
upper portion of the stainless steel tube reactor, which served as the cracking
zone, was thermostatically controlled at temperatures up to 1273 K using two
muffle furnaces; the lower portion which contained the coal was electrically
heated as previously.

4.2   Experimental

The samples (coals, coking coals plus coke and model compounds on active carbon) to be pyrolysed were placed, as before, in the lower section of the tube. The flow of hydrogen through the reactor was established to give the required vapour residence time with the upper section maintained at the cracking temperature. Current was then passed through the lower section to heat it and the sample to the carbonisation temperature. The products were collected and analysed in the same way as with the single-stage reactor.

4.3.   Results

4.3.1   Effect of carbonisation time, temperature and heating rate

The effect of varying the carbonisation time is shown in Figure 4. The methane increases monotonically with time and the benzene yield reaches a limit of about 11% w/w on d.a.f. coal at 9 minutes. Thus, to achieve optimum benzene yield with minimum methane formation, the residence time of the coal should be controlled.

Varying the final carbonisation temperature from 843 to 973 K (at a carbonisation time of 9 minutes) while cracking the products at 1123 K gave the results plotted in Figure 5. Methane increases monotonically with increase in final carbonisation temperature whereas ethane and benzene pass through broad maxima at about 923 K, the benzene yield peaking at 12% w/w on d.a.f. coal (13.4% C on C). The lower benzene yield at 973 K suggests that, at this temperature, some of the benzene is destroyed during the carbonisation stage. The volatile matter content of the char decreased from about 16% at a carbonisation temperature of 750 K to 5.5% at 923 K.

The results of tests on the effect of heating rate show that, at a carbonisation temperature of 750 K, increasing the heating rate of the coal from 1 to 25 K s^{-1} has no significant effect on benzene yields, although the methane and ethane yields are reduced by the higher heating rate.

4.3.2   Effect of cracking temperature and residence time

The yields of gases and liquids were determined after cracking at temperatures from 773 to 1223 K using the relatively low carbonisation temperature of 750 K and a carbonisation time of 15 minutes.

The yields of methane, ethane, benzene and tar are given in Figure 6. Above 900 K, increasingly severe cracking of the carbonisation vapours gives continuously increasing yields of methane, whereas the ethane and benzene pass through broad maxima. The yield of tar decreases with increasing temperature, suggesting that tar vapours are the precursors of much of the ethane and benzene, themselves being hydrogenated to methane under more extreme conditions.

The effect of varying the hydrogen flow rate and hence the gaseous residence time was also investigated. The carbonisation temperature was 873 K and the pressure was 150 bar. The results are summarised in Figure 7 and show that, as the hydrogen flow was increased, the yields of ethane and benzene increased and the benzene passed through a broad maximum. At the lower hydrogen rates, the volatiles were overcracked to give high methane yields. The lowest hydrogen rate of 0.85g min^{-1} (equivalent to a flow of 0.01 m^3 min^{-1} at room temperature and pressure) gave a gaseous residence time of about 7 s in the cracking zone at 150 bar and 1123 K.

4.3.3 Effect of pressure

Tests at 50, 100 and 150 bar in which the vapour residence time was maintained constant by using a constant linear hydrogen velocity gave the results shown in Figure 8. Methane and ethane yields increased linearly with pressure but the benzene yield increased less than proportionally to pressure.

4.3.4 Effect of coal-rank

The results on the effect of coal-rank are summarised as yields versus carbon content of coal in Figure 9 and suggest that the maximum ethane and benzene yields are obtained from the CRC 800 coals. Anthracite, as expected, gave less volatile hydrocarbons, and the coking coals tended to cake in the carboniser and would therefore be difficult to process continuously. The high volatile brown coal contained 24.8% oxygen and the oxygen appeared mainly as water rather than carbon oxides. The Lady Victoria coal gave comparatively low benzene and high methane yields, probably reflecting the high aliphatic content of this coal.

4.3.5 Model compounds

Table 2 gives the results of the hydropyrolysis of the aromatic compounds listed in Section 2.2.; only the aromatic products are listed. The cracking temperature was varied from 823 to 1173 K at a constant vapour residence time of about 5 s. As might be expected, the extent of decomposition increased with increasing temperature, and the percentage remaining undecomposed at 973 K was taken as a measure of thermal stability. The stability sequence in order of decreasing stability was as follows: benzene = naphthalene > phenanthrene toluene > p-xylene > anthracene. It should however be stressed that the order depends on the temperature. Thus, at 1073 K toluene and p-xylene are less stable than anthracene.

The yield of benzene at three temperatures (973, 1073, 1173 K) from the model compounds is shown as a bar chart in Figure 10. Benzene survives both as a feedstock and as a product of the cracking of toluene, p-xylene and polynuclear hydrocarbons. It is interesting that naphthalene, anthracene and phenanthrene give benzene as a major product at the two higher cracking temperatures.

5. DISCUSSION

In line with the various groups of American workers[2-5] who have studied hydropyrolysis, the carbonisation of coal under hydrogen pressure has been shown to give much higher yields of light aromatics, in particular benzene, than are obtained by conventional carbonisation, i.e. at atmospheric pressure in an inert atmosphere.

The results of the experiments carried out in a single-stage reactor similar to that used by Hiteshue, Anderson and Schlesinger[2] are in good agreement with their published data. With this apparatus which employs relatively slow heating rates (up to 30 K s^{-1}) a maximum yield of 4.5% single-ring aromatics can be expected from a low-rank coal.

In these single-stage reactors the temperature cycle of the reactor together with the hydrogen flow rate through it determine the conditions for both the pyrolysis of coal and the hydrocracking of the volatiles produced Thus, it is impossible to optimise simultaneously both the carbonising and cracking conditions. However, in the two-stage hydropyrolysis reactor, the carbonisation and cracking processes have to a large extent been separated and it is therefore possible to optimise separately the conditions for each.

The present work with the two-stage reactor shows that yields of over 10% benzene can be obtained from a low-rank coal without the need for heating at very high rates (up to 1000 K s^{-1}). From the point of view of the design of a hydropyrolysis plant, a process employing a moderate heating rate should be preferable since it is likely to be difficult to achieve very fast heating on an industrial scale.

6. CONCLUSIONS

The present study has:

(i) confirmed that hydropyrolysis of coal produces appreciable yields of single-ring aromatics, especially benzene, and has shown that a benzene yield in excess of 10% can be obtained without heating the coal very rapidly;

(ii) shown that the benzene yield depends on the temperature of the cracking zone and the residence times of the volatiles in this zone;

(iii) demonstrated the potential of a two-stage reactor whereby the pyrolysis and cracking stages can be independently controlled, and which should make it simpler to optimise the yields of desired products.

FIGURE 10. YIELDS OF BENZENE AT VARIOUS TEMPERATURES - FROM MODEL COMPOUNDS

FIGURE 9. THE EFFECT OF COAL RANK ON HYDROPYROLYSIS YIELDS

CONDITIONS: HEATING RATE 5Ks⁻¹, FINAL CARBONISATION TEMPERATURE 873K, CARBONISATION TIME 15min, CRACKING TEMPERATURE 1123K, HYDROGEN 1·44g min⁻¹, PRESSURE 150 BAR, 10g FEEDSTOCK, 8mm ID CARBONISER AND CRACKER.

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FIGURE 7. THE EFFECT OF HYDROGEN RATE ON HYDROPYROLYSIS YIELDS

CONDITIONS: HEATING RATE 5Ks⁻¹ FINAL CARBONISATION TEMPERATURE 873K. CARBONISATION TIME 15min, CRACKING TEMPERATURE 1123K, PRESSURE 150 BAR, 10g OF 251 TO 500μm LINBY COAL, 8mm ID CARBONISER AND CRACKER.
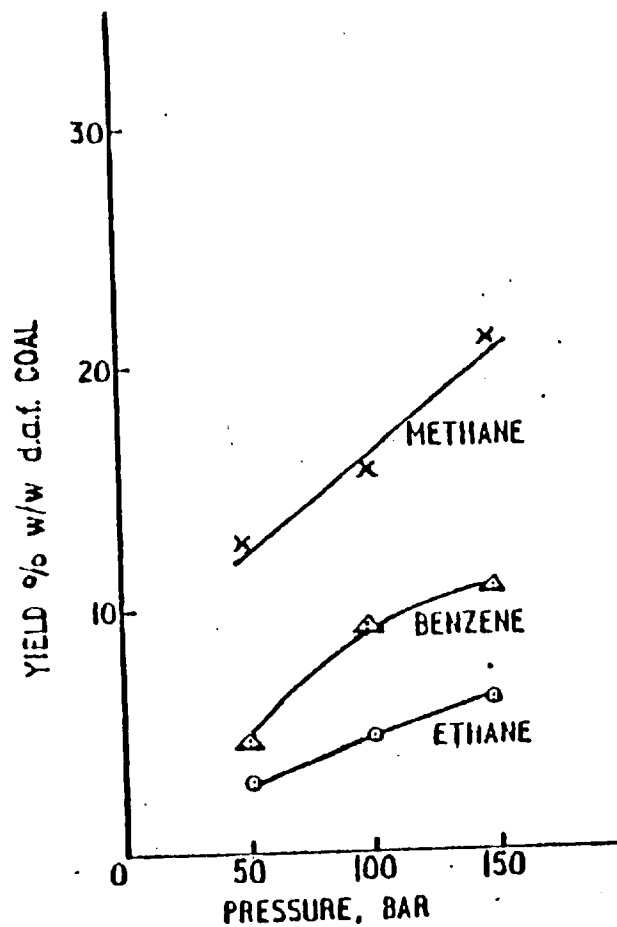
FIGURE 8! THE EFFECT OF PRESSURE ON HYDROPYROLYSIS YIELDS

CONDITIONS: HEATING RATE 5Ks⁻¹, CARBONISATION TEMPERATURE 873K, CARBONISATION TIME 15min, CRACKING TEMPERATURE 1123K, 10g OF 251 TO 500μm LINBY COAL, 8mm ID CARBONISER AND CRACKER.

FIGURE 5. THE EFFECT OF CARBONISATION TEMPERATURE ON
HYDROPYROLYSIS YIELDS

CONDITIONS: HEATING RATE 5Ks⁻¹, CARBONISATION TIME 9min,
CRACKING TEMPERATURE 1123K, HYDROGEN 1·44g min⁻¹, PRESSURE
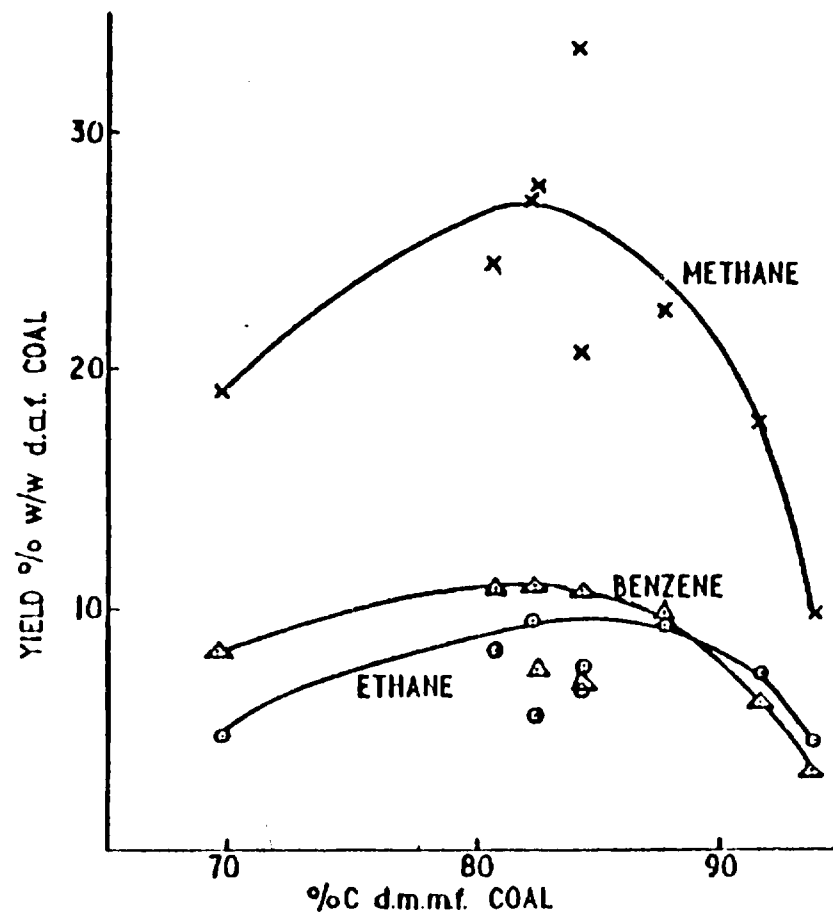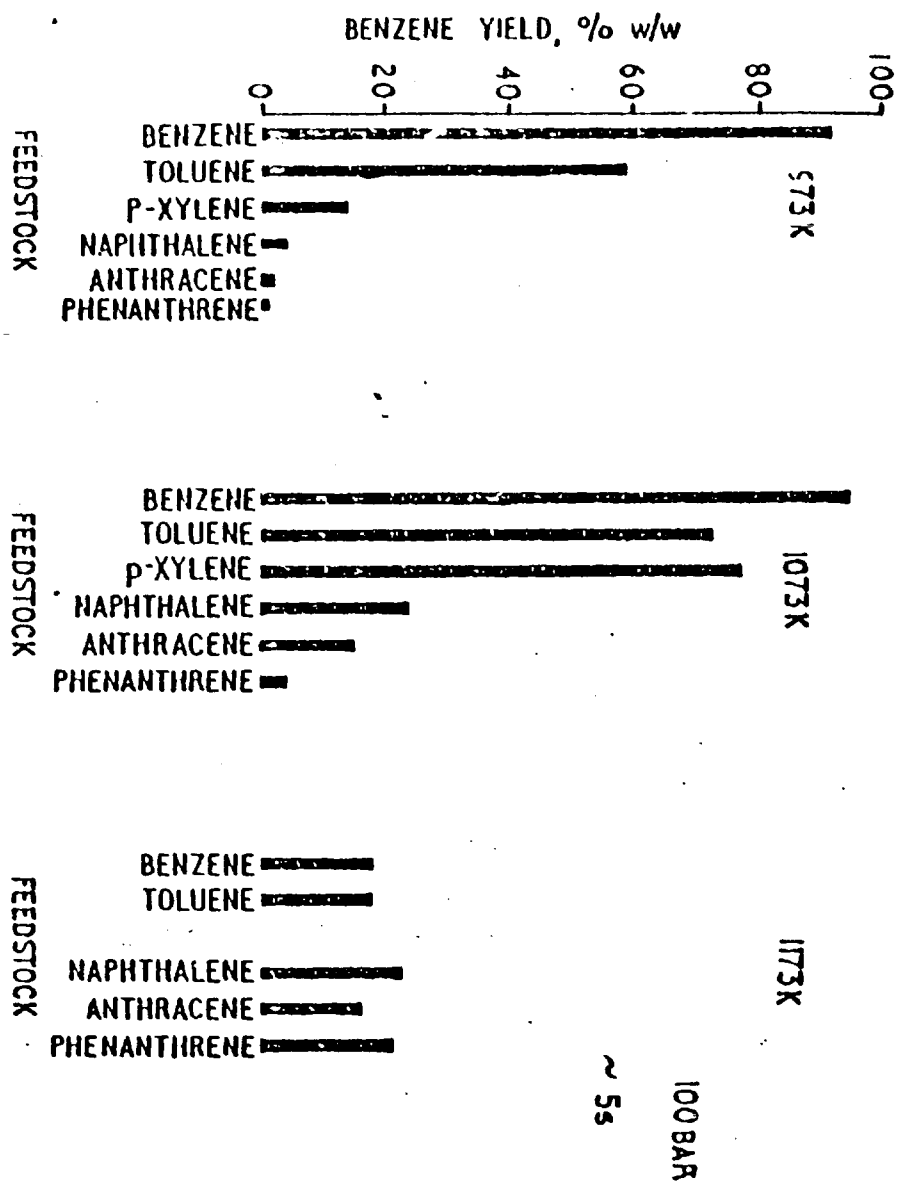150 BAR, 10g LINBY COAL 8mm ID CARBONISER AND CRACKER.
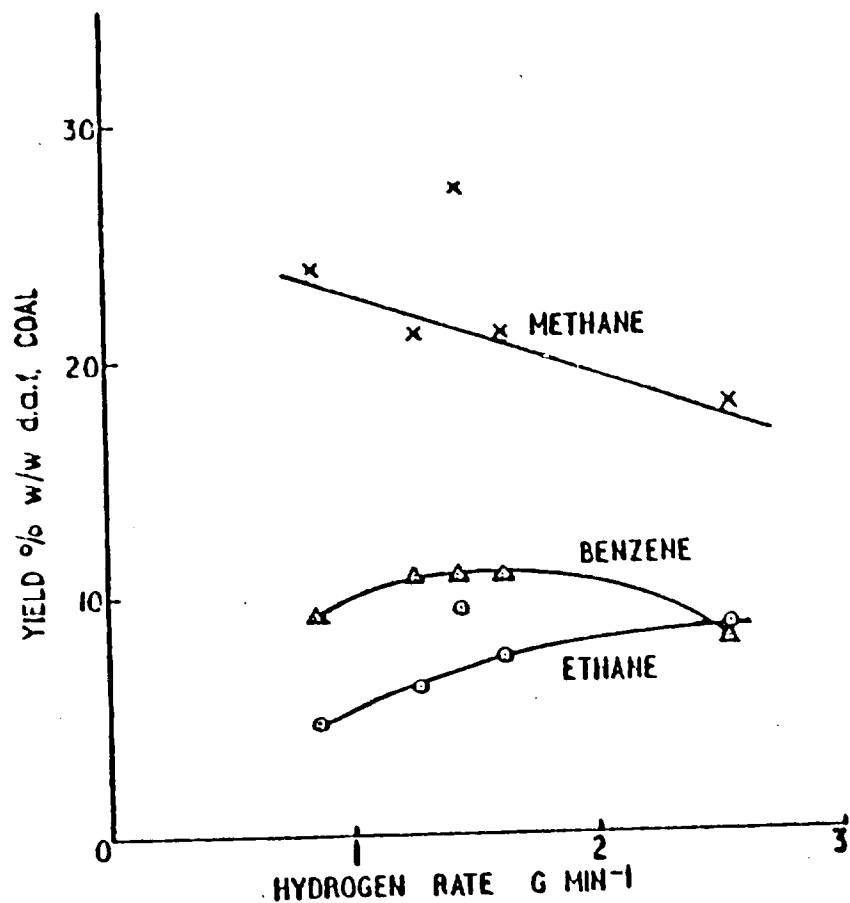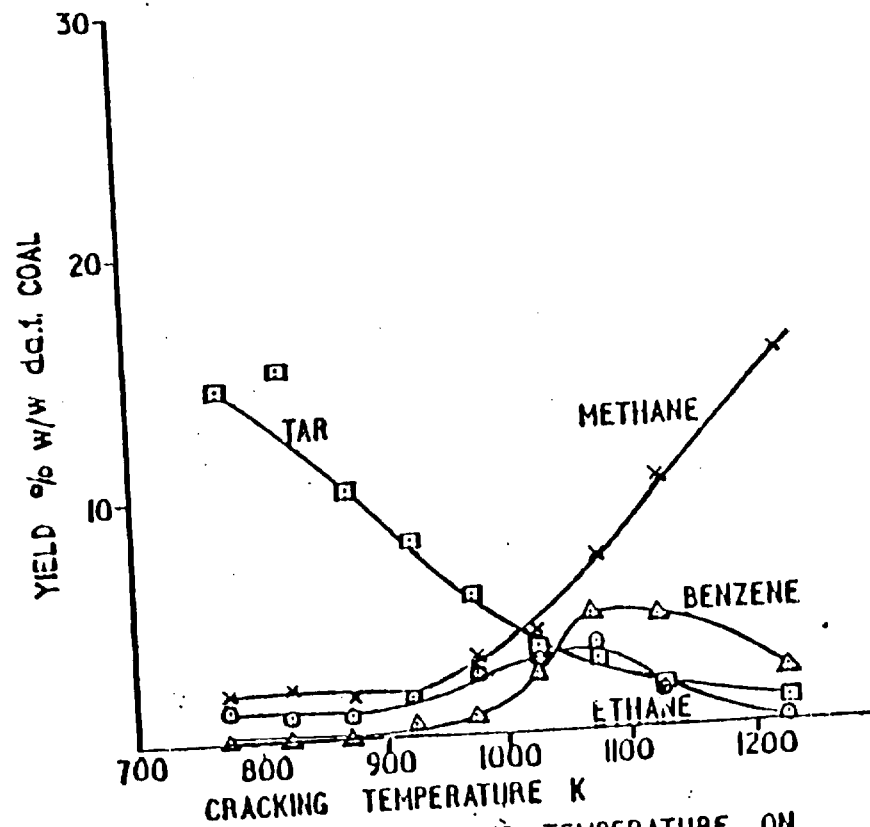

FIGURE 6. THE EFFECT OF CRACKING TEMPERATURE ON
HYDROPYROLYSIS YIELDS

CONDITIONS: HEATING RATE 1Ks⁻¹, FINAL CARBONISATION
TEMPERATURE 750K, CARBONISATION TIME 15min, HYDROGEN
RATE 0·85g min⁻¹, PRESSURE 100 BAR, 10g OF 251 TO 500μm
LINBY COAL, 8mm ID CARBONISER AND CRACKER.

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TC = THERMOCOUPLE
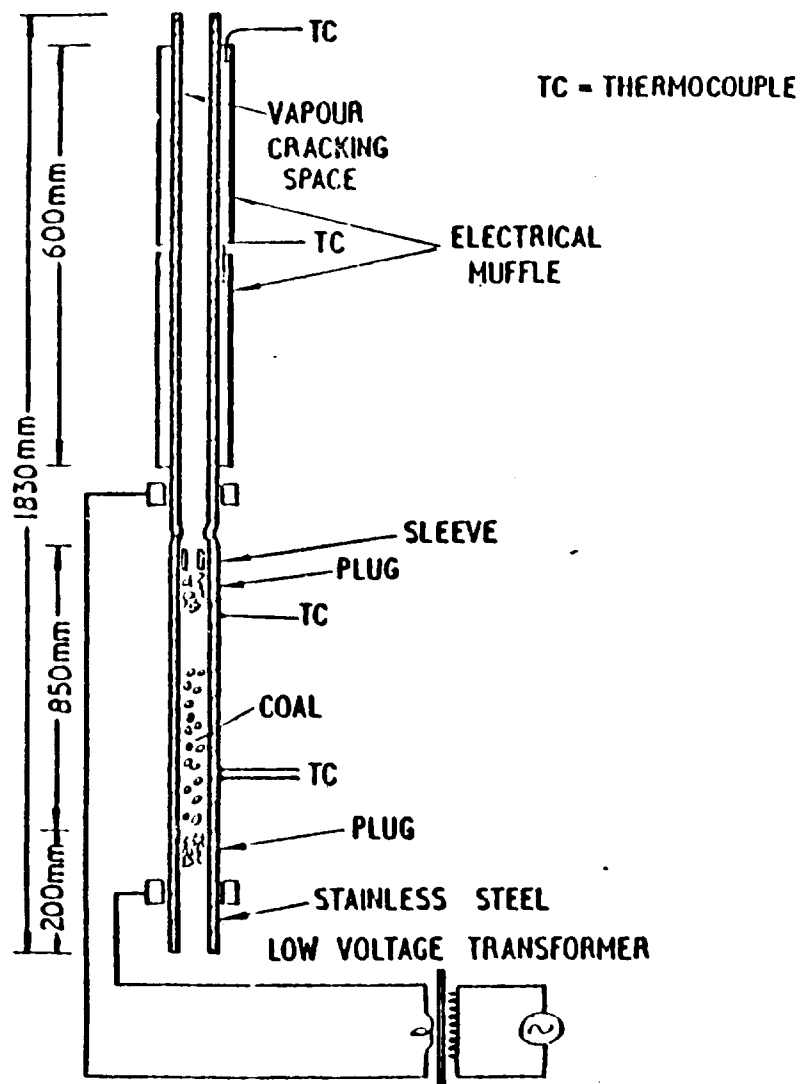
FIGURE 3. DETAILS OF C.R.E. TWO-STAGE REACTOR WITH
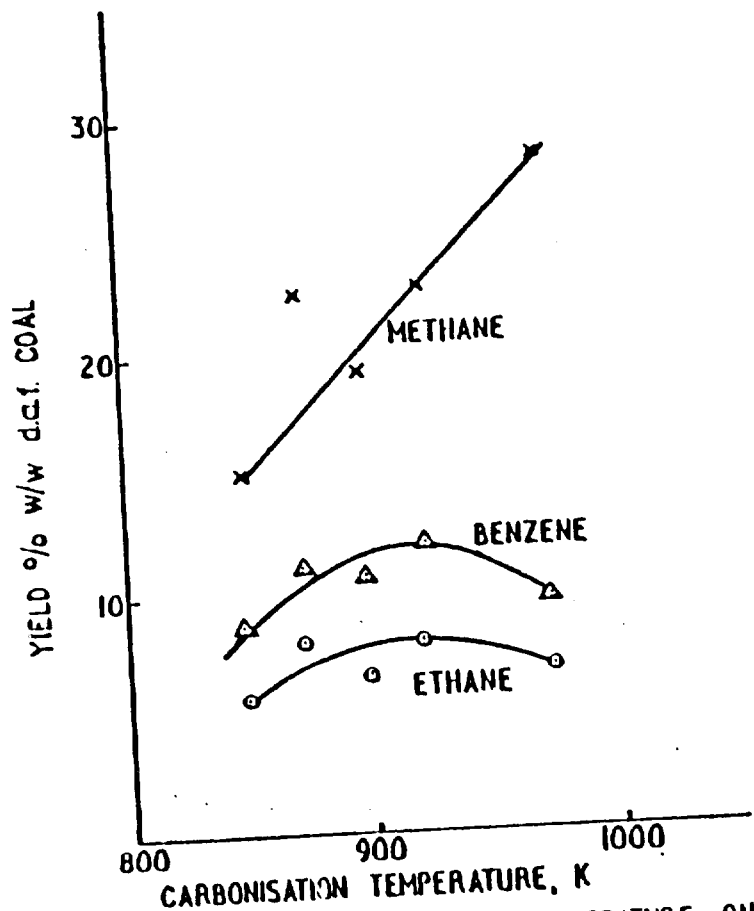TEMPERATURE CONTROL OF VAPOUR SPACE
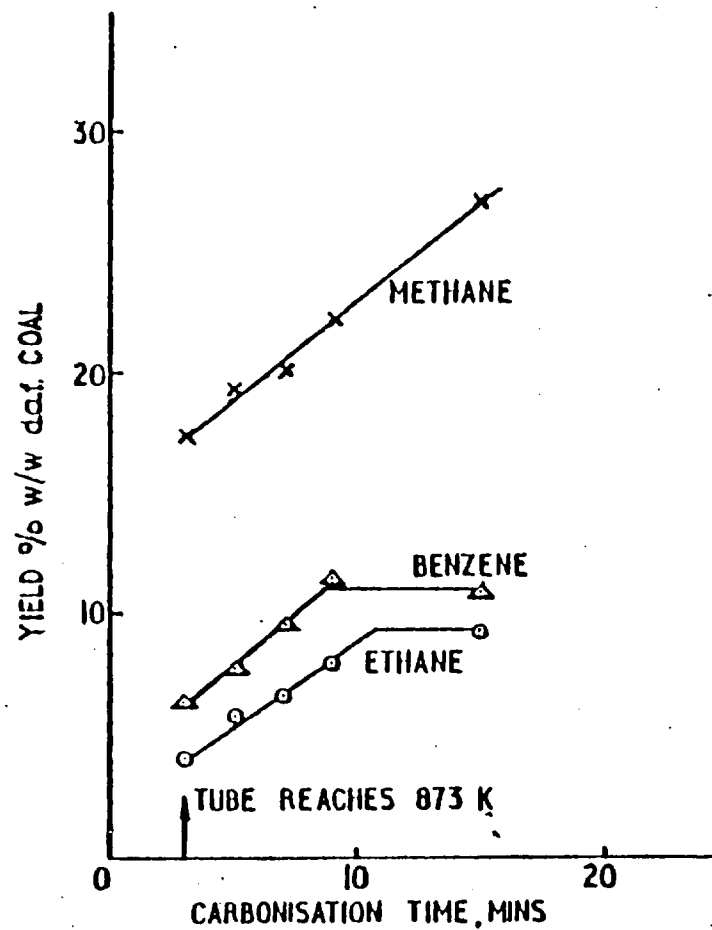
FIGURE 4. THE EFFECT OF CARBONISATION TIME ON HYDROPYROLYSIS
YIELDS

CONDITIONS: HEATING RATE $5Ks^{-1}$, CARBONISATION TEMPERATURE
873K, CRACKING TEMPERATURE 1123K, HYDROGEN $1.44g$ min^{-1},
PRESSURE 150 BAR, 10g LINBY COAL 251 TO 500µm, 8mm ID
CARBONISER AND CRACKER.

FIGURE 1. Left graph — axes: YIELD OF AROMATIC PRODUCTS, % w/w DRY COAL (vertical, 1–5); FINAL TEMPERATURE, K (horizontal, 800–1200). Curve labels: TOTAL SINGLE RING AROMATICS, PHENOLIC COMPOUNDS, TOTAL BTX, BENZENE.
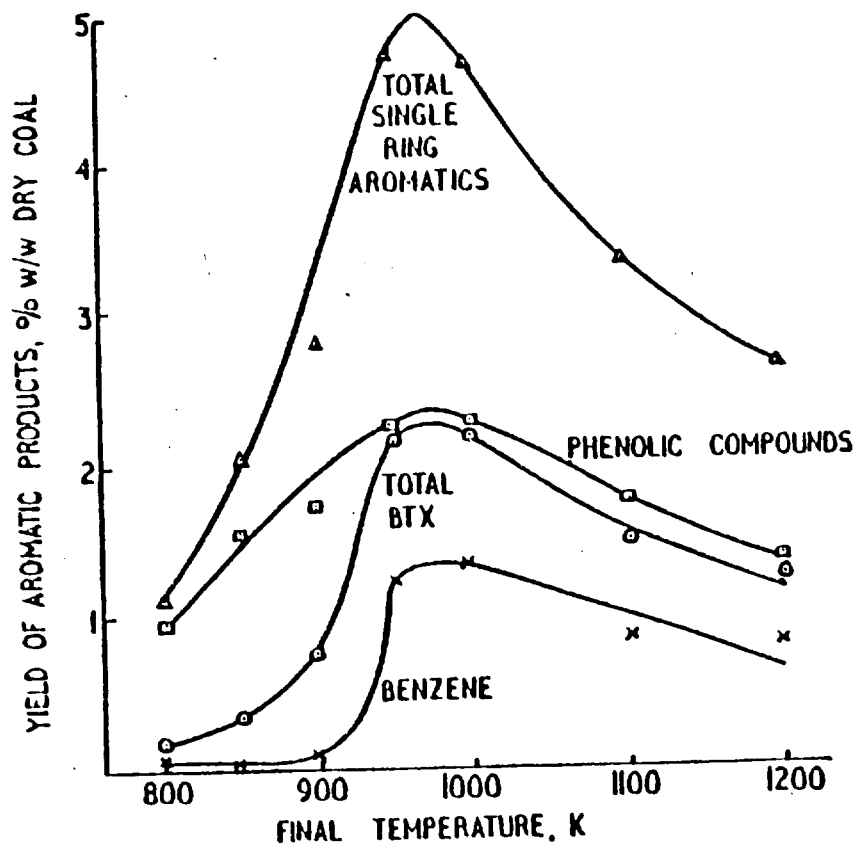
FIGURE 1. EFFECT OF FINAL TEMPERATURE ON YIELD OF PRODUCTS

HEATING RATE 7Ks⁻¹, PRESSURE 150 BAR, SOLIDS RESIDENCE TIME 0s, VAPOUR RESIDENCE TIME 11s, 10g OF 251 TO 500μm LINBY COAL, 8mm ID SINGLE-STAGE REACTOR.

FIGURE 2. Right graphs — (a) YIELD OF PCX, % w/w OF DRY COAL (vertical, 1.0–2.0); (b) YIELD OF BTX, % w/w OF DRY COAL (vertical, 1.0–3.0). Horizontal axis: VAPOUR RESIDENCE TIME, s, AT FINAL TEMPERATURE (2–12).

SYMBOL	HEATING RATE
⊙	10 Ks⁻¹
△	20 Ks⁻¹
⊡	30 Ks⁻¹

FIGURE 2. EFFECT OF VAPOUR RESIDENCE TIME AND HEATING RATE ON YIELDS OF (a) PHENOL, CRESOLS AND XYLENOLS (PCX) AND (b) BENZENE, TOLUENE AND XYLENES (BTX)

FINAL TEMPERATURE 1000K, HEATING RATE 7Ks⁻¹, PRESSURE 150BAR, SOLIDS RESIDENCE TIME 0s, 10g 251 TO 500μm LINBY COAL, 8mm ID SINGLE-STAGE REACTOR.

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Table 2: Yields of Aromatics from Two-stage Hydropyrolysis
of Aromatics

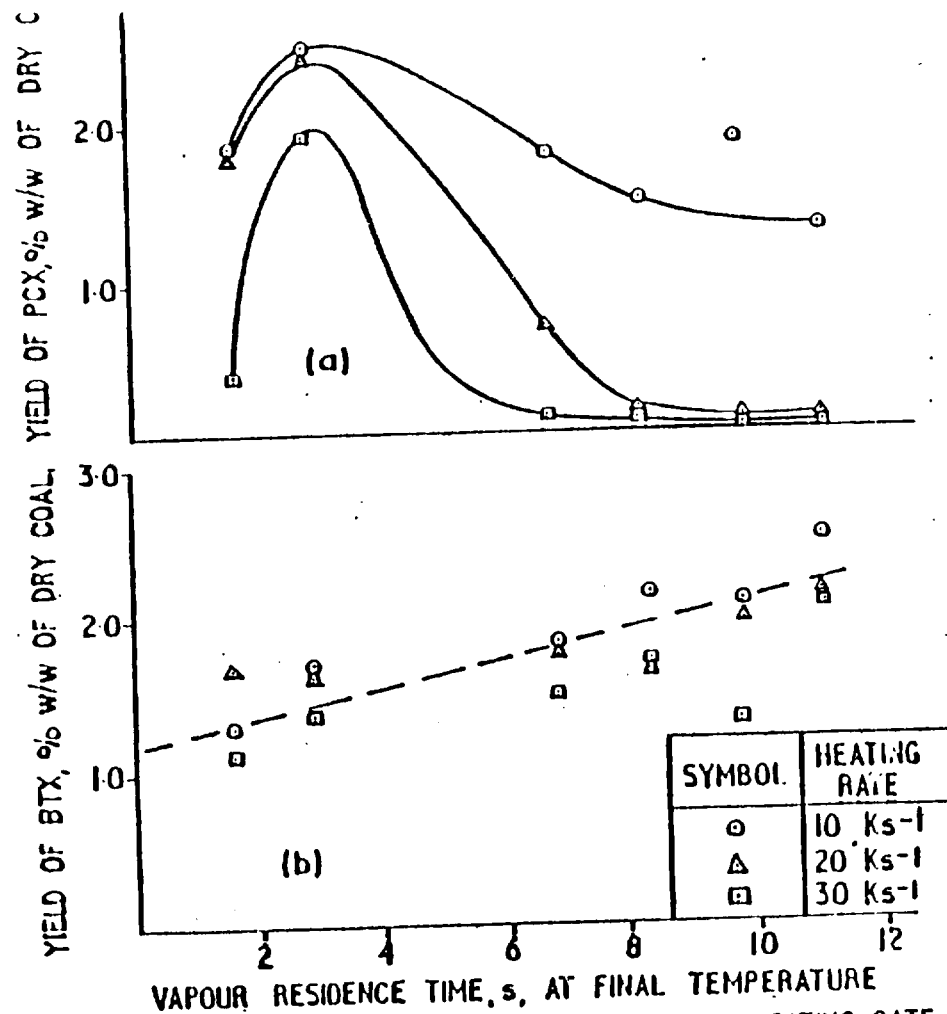| Feedstock	Cracking Temperature, K	Calc. vapour residence time, s	Yield % w/w on feed					
			Benzene	Toluene	Xylenes	Naphthalene	Anthracene	Phenanthrene
Benzene	973	5.2	92					
	1023	4.9	101					
	1073	4.6	95					
	1123	4.4	71					
	1173	4.3	18					
Toluene	823	6.1	20	66				
	873	5.7	21	42				
	973	5.2	59	32				
	1023	4.9	54	1				
	1073	4.6	73	0				
	1123	4.4	61	0				
	1173	4.3	18	0				
p-xylene	773	6.5	4	21	97			
	873	5.7	4	6	76			
	973	5.2	14	23	21			
	1023	4.9	56	7	8			
	1073	4.6	67	0	0			
Naphthalene	773	6.5	1	0.2	0	99		
	973	5.2	4	0.8	0	93		
	1023	4.9	5	2	0	80		
	1073	4.6	24	1	0	52		
	1123	4.4	41	0.4	0	8		
	1173	4.3	23	0.3	0	0.2		
Anthracene	773	6.5	0.5	0.4	0	3	16	
	873	5.5	0.5	0.4	0	2	14	
	973	5.2	2	0.7	0	8	9	
	1073	4.6	15	0.4	0	20	7	
	1173	4.3	16	0.1	0	0.6	2	
Phenanthrene	773	6.5	0.4	0	0	0	0	37
	873	5.7	0.5	0	0	0	0	36
	973	5.2	0.9	0	0	0.9	0	42
	1073	4.6	4	0.1	0	2	0	18
	1173	4.3	21	0	0	0.1	0	0.7

Condition: 1g of feedstock with 9g of active carbon
Carbonised at 750K with 15 min. solids residence time
Heating rate 1 K s^{-1}
8 mm ID carboniser and cracker
Hydrogen 0.85 g min^{-1} at 100 bar.

Table 1: Analyses of Coals

Colliery or Coal Type	NCB CRC No.	Grade	Proximate analysis			Ultimate analysis						Maceral analysis % v/v			Coking test	
			Moisture a.r.	Ash d.b.	V.M. d.a.f.	C	H	N	O	Total S	Cl	Vitrinite	Exinite	Inertinite	Gray King Coke Type	Swelling No.
						d.m.m.f.				a.r.						
Coed Bach	101	Washed duff	2.5	5.6	5.7	93.9	3.1	1.25	0.9	0.8	0.08	62	0	38	A	0
Carw	203	Washed smalls	0.8	10.1	17.9	91.6	4.7	1.55	1.6	0.8	0.01	71	Tr.	29	F	7
Derwent-haugh	301b	Washed smalls	0.5	5.3	29.7	87.6	5.5	1.75	4.3	0.8	0.04	N.D.	N.D.	N.D.	G_9	8½
Bersham	402	Washed + 2 in.	1.9	2.0	38.3	85.9	5.6	1.75	6.8	1.0	0.39	87	3	10	G_9	8½
Annesley	602	Washed doubles	4.5	2.4	38.6	84.3	5.5	1.9	7.2	0.8	0.49	73	9	18	G_4	6½
Linby	802	Washed doubles	8.3	5.8	39.1	82.4	5.3	1.95	9.0	1.0	0.46	79	6	15	G	1
Daw Mill	802	Smalls	9.3	11.7	39.7	80.6	4.9	1.4	11.9	1.65	0.23	63	11	26	C	1
Cotgrave	902	Blend A	8.5	14.2	41.5	82.5	5.7	1.85	9.2	0.65	0.26	N.D.	N.D.	N.D.	A	½
Lady Victoria	—	Cannel	2.0	2.9	52.2	84.4	6.8	1.5	5.8	1.3	0.19	26	21	53	E	1
German brown	—	—	13.5	7.6	52.8	69.7	4.6	0.9	24.8	0.25	0.01	N.D.	N.D.	N.D.	A	0

N.D. — Not determined.

TABLE 2 A Summary of Hydropyrolysis Results

Type of Reactor	Type of Coal	Heating Rate K s⁻¹	Temperature K	Pressure bar	Yield % w/w d.a.f. coal			Reference
					Oil	BTX	Benzene	
Entrained Tube	Lignite	Rapid	973	104	7		10	27
	Lignite	Rapid	998	139	7	7.5	7	29 Rosen
	Sub-bituminous	0.5×10^4	1063	200			46[a]	35
	Lignite	$2.7–8.3 \times 10^4$	894-1130	340-207		16	15	36
	Lignite	$> 5 \times 10^4$	973	153	13	5		39
	Bituminous	Rapid	1255	104	25	9		43,44
	Lignite	315-470	1061	139	7.5	3		45
	Bituminous	650	973	173	20[b]			48
	Sub-bituminous	> 7	773	139	30			55
Fluidised Bed	Bituminous	0.1	873	70	27			15
	Bituminous	Rapid	> 873	> 22	32[c]			25
	Lignite	1×10^4	1023	103			7	26
	Sub-bituminous	Rapid	840	66	29	0.03	0.02	51
Tube	Sub-bituminous	Rapid	813	346	26			1
	Bituminous	7	1073	415	9	3.5	3.2	10
	Bituminous	20	753	415	36	2		11
	Bituminous (Eastern USA)	7	1073	415	19			)
	Bituminous (Western USA)	7	1073	415	26			)12
	Lignite	7	1073	415	33			)
	Bituminous	7	1273	70	19			13
	Sub-bituminous	7	1073	415	40	< 6[d]		14
	Bituminous	650	1073	100		11	10	22
	Bituminous (UK)	5	1123	150		12	12	56

a – Postulated

b – Benzene-soluble oil

c – Postulated

d – Total single-ring aromatics

Note: a typical BTX yield by high temperature carbonisation is about 1%

CONCLUSIONS

(i) Rapid carbonisation of coal in hydrogen at pressures above 70 bar can yield up to 40% of oil w/w on coal.

(ii) Suitable cracking conditions under hydrogen pressure, about 1100 K with vapour residence times of the order of 1 s, convert part of the volatiles to BTX, up to 16% w/w on coal, 94% of which is benzene.

(iii) The greater part of the benzene is formed by the fragmentation of larger volatile molecules in the gas phase to free radicals, which are stabilised by hydrogen addition.

(iv) Low-rank coals give the highest BTX yields.

(v) Methane, a major product is formed by:

  (a) initial carbonisation of coal

  (b) hydrogenation of volatiles in bulk hydrogen

  (c) hydrogenation of devolatilised char.