

*M. Sarag*

F.R.I. 47

VERSLAG NR. ....

REPORT NO. 40 .....

VAN .....

OF 1978 .....



*UI/E/S*

**BRANDSTOFNAVORSINGSINSTITUUT  
VAN SUID-AFRIKA**

---

**FUEL RESEARCH INSTITUTE  
OF SOUTH AFRICA**

ONDERWERP: THE HYDROPYROLYSIS (DRY HYDROGENATION) OF A  
SUBJECT: .....

SELECTION OF SOUTH AFRICAN COALS

.....

.....

.....

AFDELING: CHEMISTRY  
DIVISION: .....

NAAM VAN AMPTENAAR: G BARRASS  
NAME OF OFFICER: .....

*FRI 40/1978*

AUTHOR : G BARRASS

LEADER OF PROJECT : G BARRASS

TITLE : THE HYDROLYSIS (DRY HYDRO-  
GENATION) OF A SELECTION OF  
SOUTH AFRICAN COALS

CO-WORKERS : K G HERMANIDES AND J BEKKER

ENQUIRIES TO : G BARRASS

DIVISION : CHEMISTRY

FUEL RESEARCH INSTITUTE OF SOUTH AFRICA

REPORT NO. 40 OF 1978

THE HYDROLYSIS (DRY HYDROGENATION) OF A  
SELECTION OF SOUTH AFRICAN COALS

1. Synopsis

A method utilising the "hot-rod" reactor, as described by Hiteshue et al,<sup>(2)</sup> has been employed to study the hydrolysis characteristics of a selection of South African coals. The effects of various operating parameters involved in this process have been investigated such as coal type, particle size, temperature, heating rate, pressure, solid residence time and vapour residence time. This work has shown that the hydrolysis of local coals, under optimum reaction conditions, gave similar yields and product distributions to those obtained with the same reactor concept using Northern Hemisphere coals. This investigation has confirmed the detrimental effect of the agglomeration properties of bituminous coals, and methods have been suggested which may overcome this problem in future work involving a continuous reactor.

2. Introduction

Initially the method of adding hydrogen to coal was carried out by the Berguis Process<sup>(1)</sup> which was a batch process involving high pressure and temperature in the presence of a liquid and gas phase. However, present day technology requires a simpler and less stringent method of liquefying coal in the presence of hydrogen and one method of accomplishing this is by hydrolysis. Several processes using this concept have been described<sup>(2-12)</sup> and they all involve the production of liquid and gaseous hydrocarbons by the rapid and direct hydrolysis, with or without a catalyst, of dry pulverized coal.

The fossil energy reserves of South Africa consist mainly of bituminous coal. This type of coal is amenable to liquefaction,

and as the experimental processes mentioned above can be undertaken on a laboratory scale, it was decided to examine the behaviour of a selection of local coals under these conditions. According to Schroeder and others<sup>(13)</sup> this concept should eventually be applicable to a commercial scale plant.

### 3. Experimental

- 3.1. Early work on the hydrolysis of coal involved the use of autoclaves which required long heating and cooling cycles and thus the conditions pertaining in these experiments, and the products obtained, bore no resemblance to a continuous process. This problem was overcome by Hiteshue et al<sup>(2)</sup> when they began a study of the hydrolysis reaction with coal at high temperatures and pressures, by using the "hot-rod" reactor. This reactor operated in a non-continuous fluidized bed, or a packed bed mode, and it was decided that it would provide a suitable system in which to carry out an initial study of the effect of hydrolysis on local coals.

A diagram of the system used in the experiments described in this report is shown in Figure 1. The apparatus consisted of a high pressure hydrogen cylinder, a tubular reactor and a product recovery system. Hydrogen from the cylinder was passed into the bottom of the reactor tube and then up through a zone containing steel wool, which acted as a preheater, into the bed of coal. The bed of coal was held within the reactor by plugs of steel wool, and after a steady flow of gas was obtained, the reactor was heated by passing a current through the walls of the vessel. The reactor consisted of a 1800 mm long stainless steel tube of 17 mm outside diameter, and 10,6 mm internal diameter. This tube was heated by using a low voltage transformer that was capable of supplying 700 amperes at 8 volts. Temperatures were measured with a digital thermometer via four thermocouples which were strapped onto the outside wall of the reactor. The products evolved during the reaction were carried out of the reactor by the hydrogen stream. The liquids were condensed in receivers immersed in dry ice, and the gases were vented to the atmosphere, or a gas bag, through a back-pressure regulator and a manually operated throttle valve.

3.2. This system was used to study several different parameters with the object of optimizing the operating conditions in order to obtain a maximum oil yield as well as a suitable product for further upgrading.

The parameters studied were as follows:-

- (i) The effect which the chemical and petrographic constituents of the selected coals have on the product distribution and yields from the hydrolysis reaction.
  - (ii) The effect of temperature from 400°C to 700°C, at a constant pressure, on the conversion of the coal in the presence of hydrogen to asphaltene, oil and gas. Two mesh size fractions of coal, i.e. 0,59 mm to 0,25 mm mesh and 0,149 mm to 0,074 mm mesh, were used initially in these experiments.
  - (iii) Solid residence times, at predetermined temperatures, varying between 2½ minutes to 25 minutes using coal, and coal with sand.
  - (iv) A heating rate of 100°C per minute, and 200°C per minute, up to the selected reaction temperature.
  - (v) The yield and quality of the product with an increase in pressure from 5 MPa to 30 MPa over the aforementioned temperature range.
  - (vi) The effect of hydrogen velocity on the product distribution and yields, (i.e. vapour residence time).
- 3.3. The coals used in these experiments were from Landau, Sigma, Spitzkop, Kriel, Matla, New Wakefield and Waterberg collieries. The main criteria for their selection were their hydrogen to carbon ratio, which varied from 0,6 to 0,8, and their volatile matter content which was generally greater than 36 per cent on a dry ash-free basis. These values together with their complete analyses are shown in Table 1.

Stannous chloride was used as the catalyst as previous work had shown that it was one of the most efficient catalysts<sup>(14)</sup>. The amount of catalyst added on a tin basis was equivalent to one per cent of the mass of the coal (25 g) used in these experiments. The catalyst was added to the coal in aqueous solution, which was then evaporated to dryness. This material was either added to the reactor as such, or else mixed with sand (50 g) having a mesh size of 0,420 mm to 0,149 mm. It was found that the addition of sand to the coal helped to prevent agglomeration<sup>(15)</sup>, thus enhancing the diffusion of hydrogen through the coal, and the removal of the hydrolysis products from the coal.

- 3.4. After an experiment was completed the residue and liquid product were removed from the apparatus with ether. The residue was separated by filtration and then extracted in a Soxhlet apparatus with toluene. The residue which remained upon drying was described as the toluene insoluble material. This material was equivalent to the unreacted carbonaceous material after allowances had been made for the catalyst, ash and sand content.

The ether and toluene were removed from each of the liquid extracts with a rotary evaporator and an excess of n-hexane was added to the liquid residues which remained. After standing for twenty-four hours these solutions were filtered to remove the n-hexane insolubles (asphaltenes) and the n-hexane was evaporated to leave the oils. These products were then combined to give the total asphaltene and oil values, which were then calculated on a percentage dry ash-free basis of the mass of coal used in the experiment.

During the removal of the n-hexane from the oil on the rotary evaporator some of the lower boiling fractions of the oil were carried over with the n-hexane. In order to account for these fractions a corrected oil yield was obtained by subtracting the asphaltene concentration of the ether extract from the initial concentration of the oil plus asphaltene residue before the addition of n-hexane.

The total gas figure was obtained by difference, and is thus suspect, for not only does it contain the value for water, but also any inherent error in this method used to obtain the product distribution.

The overall conversion of coal to liquid and gaseous products was obtained from the formula:-

$$\text{Percentage Conversion} = 100 \left\{ 1 - \frac{\text{Organic material in the residue}}{\text{Organic material in the coal}} \right\}$$

- 3.5. Two gas samples were taken for each test, the first sample on reaching the operating temperature and the second sample mid-way through the test. At a later stage in the experimental programme large plastic sample bags were obtained which allowed the collection of the total gas evolved during the experiment. The gas samples were then analysed chromatographically.
- 3.6. The oils were separated into a number of fractions by adsorption chromatography on silica gel. The column was eluted successively with n-hexane (12 fractions) n-hexane/toluene (with increasing proportions of toluene, 5 fractions) toluene, chloroform and methanol.

These fractions were then investigated by using infra-red, ultra-violet and fluorescence spectroscopy. The infra-red spectra were recorded as smears on sodium chloride plates using a Perkin-Elmer 567 grating spectrophotometer. The ultra-violet and fluorescence spectra were recorded as solutions in hexane using a Unicam SP1700 and a Perkin-Elmer 512 instrument respectively.

Some of the aromatic constituents of the as received oil were analysed using a Perkin-Elmer 3920 chromatograph with a flame ionization detector and a 3 m x 3 mm stainless steel column containing 3 per cent SP 2100 methyl silicone oil on 80 - 100 mesh Supelcon AW-DMCS.

- 3.7. The boiling range distribution of some of the oils obtained in these experiments were determined by gas chromatography. The oil sample was introduced into a gas chromatograph and the temperature of the column was raised at a uniform linear rate, thereby separating the hydrocarbons in boiling-point order. The cumulative areas under the chromatogram, at constant time intervals, were recorded throughout the experiment. These results were then compared with a calibration curve for retention time against boiling-point obtained under similar conditions for a known mixture of hydrocarbons. From these results the boiling range distribution of the material eluting from the gas chromatographic column was obtained.
- 3.8. Thermogravimetric analyses were carried out on some of the oils using a Du Pont 990 thermogravimetric analyser. The loss in mass of the oils was measured from 50°C to 400°C, at a programmed heating rate of 5°C per minute, in a stream of nitrogen.
- 3.9. The viscosities of the oils were measured using a Haake Rotovisco RV 3 viscometer with a cone and plate sensor at 20°C.
- 3.10. Average molecular masses were determined on certain oils using vapour pressure osmometry in benzene solutions with a Knauer apparatus.
- 3.11. Carbon, hydrogen and nitrogen analyses were carried out on a limited number of the oils. This work was carried out under contract using a Perkin-Elmer Model 240 Elemented Analyser.

#### 4. Results

- 4.1. The initial selection of the coals for these experiments was based on the hydrogen to carbon ratio and the volatile matter of the coal. These coals were tested with the "hot-rod" reactor and the results confirmed previous work<sup>(16)</sup> carried out in conventional autoclaves,



that the oil yields and conversions increased linearly with the hydrogen to carbon ratio and the volatile matter content, - see Figures 2 and 3. The petrographic analyses of these coals are shown in Table 2 and a linear relationship was obtained between the vitrinite plus exinite content of the coals and their conversions or oil yields, as shown in Figure 4.

A sample of coal from Kriel colliery was subjected to a float and sink separation at relative densities of 1,40 to 1,65. Each of these fractions was tested in the reactor. It can be seen from Figure 5 that the oil yield increased with the ash content of the fraction whilst the gas yield decreased. This phenomenon may be due to the catalytic effect of the ash, and/or its dispersive effect, which would prevent agglomeration and enhance the diffusion mechanism of the hydrogen and products during the hydrolysis reaction.

4.2. In general the overall conversion increased with the increase in temperature from 400°C to 700°C. The oil yield reached a maximum of about 40 per cent between 500°C and 550°C for the coals such as New Wakefield, Waterberg and Matla which may be regarded as the most suitable for hydrolysis. Above 600°C the oil yield began to decrease and the gas yield increased rapidly. The asphaltenes decreased with temperature and were insignificant above 500°C. The insoluble residues (unconverted carbonaceous materials) showed similar trends and reached a minimum of 15 per cent at 700°C. An example of the product distribution obtained from New Wakefield coal (0,59 mm to 0,25 mm mesh) is shown in Figure 6.

Tests with the 0,59 mm to 0,25 mm mesh coal were carried out with 25 g of coal, whereas, 15 g of coal were used with the 0,149 mm to 0,074 mm mesh coal as greater quantities caused plugging of the reactor. The conversions were less than those obtained with the 0,59 mm to 0,25 mm mesh coal probably due to agglomeration, but the oil yields were similar except that the maximum of 40 per cent was only reached at 600°C - see Figure 7.

4.3. In order to try and reduce the plugging which occurred in the reactor, sand was mixed with the coal. This prevented plugging and also reduced the influence of the diffusion limitations in the hydrolysis reaction. Unfortunately this increase in conversion resulted in improved gas yields rather than oil yields. The oil yields were similar up to 500°C to the oil yields obtained from tests without sand. However, above this temperature the oil yields decreased more rapidly with the addition of sand compared to the tests without sand. It was found that coal (25 g) of 0,59 mm to 0,25 mm mesh size, in conjunction with sand (50 g) of 0,42 mm to 0,149 mm mesh size, gave acceptable results, and this combination of mass and particle size was used in the remaining experiments - see Figures 6 and 8.

4.4. The effect of solid residence time was studied over a period of up to 25 minutes at a selected temperature. The heating rate was 100°C per minute and as the time taken to reach a selected temperature varied, only the time at this selected temperature was considered.

The test with coal only showed that the conversions increased with time up to 15 minutes and then decreased. This was probably caused by agglomeration which would hinder the diffusion of hydrogen to, and the products away from the active sites. The addition of sand to the coal reduced the agglomeration and the conversion increased continuously with time - see Figure 9.

The oil yields increased slightly with time up to 15 minutes after which they decreased, whereas, the gas yield increased continuously with time. The decrease in oil yield with time was probably due to its conversion to gas by the thermal cracking of the oil retained in the coal bed and on the walls of the reactor.

The information obtained in the time studies for coal with and without sand were used to try and obtain rate data from the conversion figures. Arrhenius plots were drawn which showed a change in the sign of the slope at temperatures above 500°C - see

Figure 10. This phenomenon according to Marsh et al<sup>(17)</sup> was due to a diffusion controlled mechanism. Thus the overall rate of the reaction was not totally controlled by the chemical hydrolysis of the coal, but was also influenced by the diffusional restriction within the coal particle and by the agglomeration of the coal. The diffusion restriction caused by agglomeration was reduced above 500°C by the addition of sand resulting in an increase in the rate constant compared to coal alone, but the change in the sign of the slope was still evident. This change in the slope might be reduced further by the addition of more sand, but probably would not be totally eradicated, due to the diffusion restriction within the coal particle itself.

At temperatures below 500°C the rate of reaction for coal only was greater than the mixture of coal and sand. This may be because the sand in the mixture affects the heat transfer characteristics of the reactor bed. Thus the bed temperature containing sand could be lower than the measured wall temperature of the reactor, whereas, with coal the bed temperature would probably approximate to the wall temperature of the reactor. If the coal and sand bed temperature was actually 50°C lower than the temperature measured, then this would give reaction rate constants similar to those obtained from the coal bed below 500°C.

- 4.5. In order to study the effect of heating rate several experiments were carried out using a heating rate of 200°C per minute - see Figure 11. By comparing these results with those obtained at 100°C per minute, i.e. Figures 8 and 11, it can be seen that the conversion and gas yields were lower for the experiments carried out with the higher heating rate, whereas, the oil/yields were similar for both heating rates.

Although the oil yields were almost independent of the heating rates considered, the quality of the oil appeared to improve with the increase in the reaction temperature as well as with the increase in heating rate. This improvement in oil quality was confirmed by

carrying out simulated distillations, thermal gravimetric analyses, molecular mass and viscosity measurements on the oils - see Figures 12 - 17. The oil quality was not as good as that obtained by Steinberg<sup>(8)</sup> or Pelofsky<sup>(9)</sup> using short residence time reactors. The heating rates in these reactors were several orders of magnitude greater than those obtainable with the "hot-rod" reactor, which resulted in a completely different product spectrum, the liquids consisting mainly of benzene, toluene and xylene.

It must be stressed that the simulated distillations and the thermal gravimetric analyses were not absolute boiling range measurements, but only indicated trends which occurred in the variation of oil quality with increasing temperature and heating rate.

In the future it is hoped to determine the true boiling point range of the oil with a semi-micro, or micro, spinning band still. This method should also help to overcome the problem of the loss of the light fractions during the removal of the extraction solvents. This loss of the light fractions during the removal of the extraction solvents with a Büchi Rotavapor (one theoretical plate) may explain the differences obtained with oils prepared under similar experimental conditions - see Figures 12 and 14.

The molecular masses and the viscosities of the oils decreased with the increase in reaction temperature - see Figures 16 and 17. The decrease in viscosity of the oil with increase in reaction temperature may be caused by the breaking of the carbon to heteroatom bond, with the subsequent loss of the heteroatom, thereby reducing hydrogen bonding, which has a marked effect on the viscosity of the oil<sup>(18)</sup>.

- 4.6. The conversion increased with pressure over the range of 5 MPa to 20 MPa - see Figure 18. The oil and gas yields followed a similar trend and any increase in pressure above this level had very little effect on these yields within the temperature range considered (400°C to 700°C).

4.7. The study of the effect of the variation in the flow rate of hydrogen at 500°C, 25 MPa pressure and a reaction time of 15 minutes, showed that the conversion of the coal, asphaltene and oil yield increased, whereas, the gas yield decreased as the hydrogen flow rate was increased. A flow increase from 8 litres per minute to 49 litres per minute of hydrogen increased the conversion of coal from 72 per cent to 87 per cent, the asphaltenes from 0,5 per cent to 5,0 per cent and the oil yield from 16 per cent to 37 per cent. The gas yield decreased from 55 per cent to 40 per cent for the same conditions - see Figure 21.

This would seem to indicate that at slower flow rates some of the oil and asphaltene formed was either coked, cracked or broken down to gas before being carried out of the reactor. However, with increasing flow rates these products were removed from the reactor before they could either coke or break down to form a gaseous product.

The increase in flow rate of the hydrogen also improved the quality of the oil, which was confirmed by carrying out simulated distillations. These distillations indicated that the amount boiling below 200°C was 10 per cent by volume for a hydrogen flow rate of 8 litres per minute and 28 per cent for a hydrogen flow rate of 49 litres per minute - see Figure 22.

4.8. The n-hexane soluble oils were examined by infra-red, ultra-violet and fluorescence spectroscopy, and by gas liquid chromatography. Generally the oils were separated into fractions by silica gel chromatography and these fractions were classified as aliphatic, aromatic and heteroatom containing compounds by their infra-red spectra<sup>(19)</sup>.

The composition of the aliphatic fractions of the oils were measured by gas liquid chromatography and consisted mainly of n-alkanes. The lower-boiling n-alkanes were not detected, probably due to their loss during the extraction procedure, and the fraction

consisted mainly of the compounds  $n$ -C<sub>13</sub> and the higher homologues. The results are shown in Table 3 and it can be seen that there was a decrease in the relative amount of the higher molecular mass  $n$ -alkanes as the temperature was increased. It would seem that hydrocracking of the longer chained  $n$ -alkanes occurred to a significant extent above 500°C. The lighter  $n$ -alkanes were likely, due to their higher volatility, to have been removed from the reactor at a faster rate than their longer chain homologues, and thus were not broken down to the same extent<sup>(18)</sup>.

The simpler aromatics were determined quantitatively by gas liquid chromatography. The original oil and not the fraction separated by silica gel chromatography was used in each case, and the column was incapable of separating compounds of the same carbon number. The lighter aromatics, as with the aforementioned lighter  $n$ -alkanes, were lost to some extent with the separation procedure for the oil. The results are shown in Table 4 and it can be seen that there was an increase in the higher aromatic compounds as the temperature of the reaction was increased.

Ultra-violet and fluorescence analyses of the aromatic fractions were able to identify twelve of the aromatic ring structures in the oil. These were anthracene, chrysene, pyrene, 1-alkylpyrene, 9, 10-dialkyl anthracene, benz(a) anthracene, benzo (a) pyrene, benzo (ghi) perylene, dibenzo (def, mno) chrysene, perylene, coronene and dibenzo (b, def) chrysene<sup>(20)</sup>.

The percentage of heteroatom containing compounds in the oil decreased with increasing temperature - see Figure 23, which resulted in a decrease in the viscosity of the oil as mentioned previously<sup>(18)</sup>.

- 4.9. Generally two gas samples were taken for each test, the first sample on reaching the operating temperature and the second sample mid-way through the test. In later experiments the whole

of the gas make was collected and analysed - see Table 5. The gas composition was calculated on a hydrocarbon basis and these results were then expressed as a percentage of the D.A.F. coal - see Table 6. The other constituents namely oxygen, nitrogen and carbon dioxide, were probably present as a result of the desorption of air from the coal, leakages in the gas sampling systems, the decomposition of carbonates from the mineral matter in the coal and the reaction of some of the oxygen in the coal with carbon to give carbon dioxide.

Methane and ethane, the two major constituents in the hydrocarbon mixtures increased with increase in temperature, pressure time and heating rate. The remaining hydrocarbons decreased with the increase in the aforementioned variables, probably because of the breakdown of these gases to ethane and methane with the increase in the severity of the reaction conditions.

The total gas yields which were obtained by difference, usually increased with the increase in temperature, pressure, time and with the inertinite content of the coal. This increase in gas yield with increasing inertinite content of the coals is shown in Figure 24.

As the heating rate and the flow rate of the hydrogen were increased the total gas yields decreased, thus the quicker the coal reached temperature and the quicker the product was removed from the hot zone the less breakdown to gas occurred.

- 4.10. Ultimate analyses were carried out on the chars which showed that the elimination of sulphur occurred up to  $500^{\circ}\text{C}$ . Between  $500^{\circ}\text{C}$  and  $600^{\circ}\text{C}$  there was no loss of sulphur, but above  $600^{\circ}\text{C}$  the loss of sulphur recurred. The sulphur removed below  $500^{\circ}\text{C}$  was probably organic, whereas, the sulphur eliminated above  $600^{\circ}\text{C}$  was possibly inorganic in origin. The elimination of nitrogen, hydrogen and oxygen were rapid up to  $500^{\circ}\text{C}$ , however, above this temperature their disappearance was more gradual with the exception of oxygen

which had disappeared altogether. However, this complete removal of oxygen above 500°C is questionable as the figure is obtained by difference and thus contains the inherent error in the ultimate analysis.

## 5. Discussion

- 5.1. The conversion data and oil yields obtained in these experiments were correlated against the hydrogen to carbon ratio, volatile matter and the vitrinite plus exinite content of the coals using linear regression analyses. This information was then compared with linear regressions of data from Australian coals<sup>(21)</sup>, which like South African coals are of a Gondwanaland origin, and North American coals<sup>(22,23)</sup> of a Carboniferous, Cretaceous and Tertiary origin. It was hoped that in addition to these correlations helping in the selection of suitable coals for hydrolysis, they may also indicate any differences in the hydrolysis behaviour of coals from different continents and geological ages - see Table 7.

The rate of increase of the conversion with respect to the hydrogen to carbon ratio, volatile matter and the reactive macerals (vitrinite plus exinite) of the coals as shown by the slopes for these equations were as follows:-

Australia > South Africa > North America.

The correlation coefficients for these equations were of a similar order and showed that the results for conversion against hydrogen to carbon ratio and reactive macerals were better than those for conversion against the volatile matter of the coal. These results were obtained using different hydrolysis conditions such as temperature, pressure, residence time, with or without a catalyst, different catalysts and with and without a liquid vehicle. Thus these variations in hydrolysis process conditions may override any variations shown by the nature of the coals themselves.



Linear regression equations were also obtained for the oil yields and oil plus asphaltene yields using these same variables only for experiments carried out without a liquid vehicle. The values for the slopes and the correlation coefficients for the South African coals were generally greater or better than those obtained for the North American coals. It would seem that the hydrogen to carbon ratio and the volatile matter content provide an adequate means of selecting South African coals which will give maximum oil yields via the hydrolysis conditions described in this report.

Recently Given et al<sup>(24,25)</sup> have carried out work using a computer to obtain stepwise multiple regression analyses on a large number of results and have shown that conversion data can be related to variables such as the total sulphur, carbon, reactivities (vitrinite plus exinite) and the phenolic hydroxyl content of the coal. The limited number of results for conversion used in the linear regression analyses described above were reprocessed using stepwise multiple regression analyses and the following expressions were obtained for the conversion values of the coals considered.

$$\begin{aligned} \text{North America:- } \% \text{ CONVERSION} &= -0,33 (\% \text{ S TOTAL}) + 0,90 (\% \text{ REACTIVES}) \\ &+ 0,97 (\% \text{ C}) - 76,02 \end{aligned}$$

$$\begin{aligned} \text{South Africa :- } \% \text{ CONVERSION} &= 3,52 (\% \text{ S TOTAL}) + 0,80 (\% \text{ REACTIVES}) \\ &- 1,42 (\% \text{ C}) + 129,01 \end{aligned}$$

$$\begin{aligned} \text{Australia :- } \% \text{ CONVERSION} &= 8,48 (\% \text{ S TOTAL}) + 0,58 (\% \text{ REACTIVES}) \\ &+ 0,42 (\% \text{ C}) - 8,76 \end{aligned}$$

The multiple correlation coefficients for these expressions were 0,89, 0,85 and 0,96, respectively, which are better than those obtained initially where the conversion was correlated with either the hydrogen to carbon ratio, volatile matter or total reactivities (vitrinite plus exinite) of the different coals. However, a much larger selection of results, obtained under similar experimental conditions would be required before the aforementioned expressions and their multiple correlation coefficients could be calculated and

used to compare the conversions and oil yields from different continental and geological aged coals.

- 5.2. Empirical regressions of hydrolysis yields from several different processes were carried out by Holmes et al<sup>(26)</sup> which showed trends of a similar nature in the product distribution to those obtained in these experiments. They confirmed that very little reaction took place below 400°C, but above this temperature both the oil and gas yields increased as was shown in the experiments described in the present report. A maximum oil yield was obtained between 550°C and 600°C, whereas, the maximum was generally between 500°C and 550°C for the South African coals. As in the experiments with local coals they showed that the gases did not exhibit a maximum, but increased continuously with temperature.

One of the processes which they examined was the work carried out by Clark et al<sup>(27)</sup>. This work consisted of a series of runs covering a hydrogen pressure range up to 6,8 MPa at 500°C and 600°C. From this data the following expressions were correlated for oil, hydrocarbon gases and char.

$$\begin{aligned} \text{OIL} &= 2,227 T^{\frac{1}{2}} + 0,5960 P^{\frac{1}{2}} - 45,189 \\ \text{GAS} &= 1,572 \times 10^{-4} TP + 0,0319 T - 0,0764 P + 0,0940 \theta - 15,014 \\ \text{CHAR} &= 167,201 - 0,1524 T - 1,0166 P^{\frac{1}{2}} \end{aligned}$$

where T = temperature, °C;

P = partial pressure of hydrogen, p.s.i.a.;

θ = solid residence time, min.

These correlations were applied to a set of results from the present experiments carried out with New Wakefield coal at 5,0 MPa and reasonable agreement was obtained for the oil yields within the temperature range of 450°C to 550°C. Above this temperature the predicted oil yields were greater than those obtained in practice as the aforementioned equation for the oil yield made no allowance for the thermal cracking of the oils at temperatures above 600°C.

For the experiments described in the present report the yields for the gases were greater and the chars were less than the predicted results, probably because of the two different types of reactor used. In Clark's work an autoclave was used with its inherent slow heating rate, which would probably permit the repolymerization of some of the product to give a char rather than a breakdown to gas. However, the opposite occurs in the "hot-rod" reactor, which utilizes a faster heating rate, and even more so in the entrained reactor systems where the heating rate is even faster.

The work of Holmes et al<sup>(26)</sup> also showed that the oil and gas yields increased with the increase in the partial pressure of hydrogen up to 40 MPa, however, these results together with those of Hill et al<sup>(28)</sup> showed that there was very little increase in conversion, gas or oil yield above 20 MPa at a temperature of 500<sup>o</sup>C. At higher temperatures the conversion and gas yield increased with increasing pressure probably due to the thermal breakdown of oil to gas, and with the carbon hydrogen reaction, the main product of which is methane.

At a temperature of 500<sup>o</sup>C the oil yield obtained from local coals was found to be a function of the square root of pressure, which confirmed the results of Holmes<sup>(26)</sup>, and it would seem that any increase in pressure above 15 to 20 MPa will only result in a very small increase in the oil yield - see Figure 19.

These experiments, together with the work of Hiteshue et al<sup>(2)-(5)</sup>, have shown that the characteristics of the product oil improved with the increase in temperature and pressure. However, simulated distillations of the oils obtained at lower pressures in this work have shown that the lighter fractions, i.e. boiling below 200<sup>o</sup>C, decreased with the increase in pressure from 5 MPa to 20 MPa. It appears that a sufficient hydrogen partial pressure is required to stabilize the free radicals formed during the pyrolysis reaction, but as the hydrogen pressure was increased it prevented or hindered the removal of these lighter fractions from the reactor bed. This

restriction would in turn enhance the repolymerization of these light fractions to coke or their breakdown to gas. As the hydrogen partial pressure was increased it would continue to breakdown the heavier fractions boiling above 200°C to lighter fractions, thus although a minimum was reached for the -200°C fraction at 20 MPa, it then began to increase with further increase in pressure - see Figure 20.

In general the oils produced at lower temperatures and pressures contained a fairly high asphaltene concentration, whereas, at elevated temperatures and pressures the oil collected was low in asphaltenes but of a high aromatic content.

From this work it would seem that high temperatures (550°C) and pressures (20 MPa) are necessary for the hydrolysis of coal. The optimum temperatures and pressure will have to be determined by an economic assessment between the increased construction and operating costs for these conditions, and the increased oil yields and oil quality which would result.

- 5.3. It was evident from this work and the work of Hiteshue<sup>(2)-(5)</sup> that for a given set of pressure and temperature conditions, solids' residence time had a small effect on the oil yield, but had a direct relationship on the coal conversion and the gas yields. In general after two minutes the oil yield had reached a plateau for both these experiments, and those of Hiteshue, which then increased slightly with time up to 15 minutes. This was the limit for Hiteshue's data, whereas, in this work, experiments were carried out up to a residence time of 25 minutes. At residence times greater than 15 minutes, as discussed in Section 3.4., the oil yields began to decrease with time due to the oil being converted to gas.

A more drastic effect on the product distribution was evident by increasing the hydrogen flow rate, thereby, altering the product residence time. Again the similarities between this work and

that of Hiteshue were evident. An increase in conversion from 71 per cent to 96 per cent, and in the total liquid yield (oil plus asphaltene) from 13 per cent to 51 per cent was obtained with an increase in hydrogen flow rate from 1,2 to 13,5 litres per minute of hydrogen per gram of coal for Hiteshue's work. In the present experiments the conversion increased from 72 per cent to 87 per cent, and the total liquid yield (oil plus asphaltene) from 17,5 per cent to 42 per cent with an increase in hydrogen flow rate from 0,3 to 2,0 litres per minute of hydrogen per gram of coal. It is thought that the increase in conversion with the subsequent increase in oil yield, and decrease in gas yield, can be attributed to a decrease in cracking of the liquids because of the time at which the volatiles were at the reaction temperature.

The increase in flow rate of the hydrogen improved the quality of the oil in both sets of experiments. Hiteshue showed that when the retention time of the volatiles was 5 seconds or longer, the condensed liquids were light in colour, low in viscosity and contained a large quantity of distillable oil. At an exposure time of 2,3 seconds, the liquids were dark in colour, viscous and contained an appreciable amount of asphaltene. This is in reasonable agreement with the simulated distillation data obtained on the oils from these experiments - see Figure 22. In this Figure it can be seen that the distillation curve for the oil plus asphaltene, obtained at a hydrogen flow rate of 62,5 litres per minute, had dropped below the distillation curves obtained for the oil plus asphaltene at 49 and 35,5 litres per minute, this was probably because of the large asphaltene content of this oil - see Figure 21. Thus by increasing the flow rate of the hydrogen the quantity of oil and its quality was improved, but there would appear to be a limit to this improvement as is shown in Figure 21 where the asphaltene increased considerably at 62,5 litres per minute as it probably has insufficient time to breakdown to oil or gas. The decrease in oil yield, and the subsequent rapid increase in the gas yield at this flow rate, was thought to be due to the loss of some of the lighter fraction of the oil which

was not trapped even by having two condensers in series. This problem might be overcome by inserting an activated charcoal trap to adsorb any of the light material carried through the condensers by the faster hydrogen flow rate.

- 5.4. The agglomeration of bituminous coal in hydrogen would appear to be the major problem in the use of high temperature, and high pressure systems, for the continuous production of liquids from the hydrolysis of coal.

As the temperature of the hydrolysis reaction is increased more severe pyrolytic rupture of the coal occurs and produces species of lower average molecular mass, i.e. asphaltenes and heavy oils, which wet the partially hydrogenated coal remaining. Thus the fluidity increases with temperature, but at the same time the increase in temperature speeds up the resolidification reaction or "dry-up time". This resolidification reaction breaks down the aforementioned products to give a coke, hydrocarbon gases and lower boiling oils. In the process of its formation the coke acts as a binder for the partially reacted coal and results in the formation of an agglomerated mass.

High hydrogen partial pressure enhances the plasticity of coal to such an extent that even non-caking low rank coals can display an agglomerating tendency. The high pressure tends to prevent the escape of the lower molecular mass species, thereby, increasing the "dry-up time" which increases the fluidity of the coal. Hydrogen also contributes to the pyrolytic reaction by saturating the double bonds in the coal and by the stabilization of the free radicals formed during the thermal decomposition of the coal. Stabilization of the free radicals retards the repolymerization reactions and contributes additional liquid-like material which would enhance the fluidity of the plastic coal.

Thus it would seem that the agglomerating tendency of a coal is dependent upon the duration of the resolidification reaction, which in turn is dependent upon the reaction conditions which effect the fluidity of the molten coal<sup>(29)</sup>.

In order to overcome this problem of the agglomeration behaviour of bituminous coals during hydrolysis several methods have been investigated:-

- (i) The coal was preoxidized before passing it into the reactor, which reduced the agglomeration, but also exacted penalties in the product yields, thus reducing the process efficiency. This method of pretreating the coal would complicate a major process by making it less amenable to applications where close control of load variations would be required.
- (ii) Dilute the coal feed with an inert material such as char or sand as was necessary in these preliminary investigations using the "hot-rod" reactor. This external mixing of the coal with an inert, dried and sized diluent would certainly prove to be uneconomic when applied to a large scale process.
- (iii) A mechanical stirrer has been used in small bench-scale reactors but the problem of providing seals and bearings for a large rotating shaft in a commercial size reactor bed working at high pressures would be formidable.
- (iv) The bed-recirculation method appears to be one of the most promising ways of preventing agglomeration. It would seem that the rapid recirculation of the reactor bed into which fresh coal is fed at high velocities would prevent the coal particles from sticking to each other long enough for the coal to be devolatilized and thus become non-agglomerating. This could be accomplished by installing a draft tube in the centre of the fluidized bed. The coal would be fed into the draft tube, along with the recycled char from the bed, and would then be carried upward to the main bed in light phase fluidization at relatively high superficial gas velocity. Recirculation would be accomplished by the descent of the char in an annular down comer that would be in dense phase fluidization at a lower superficial velocity.

(v) Another method of preventing agglomeration would be to carry out the hydrolysis of the coal in a dilute phase free fall reactor. It has been established that the diameter of the reactor must be at least 7 - 8 cms and the wall temperatures must be above 700°C to prevent agglomeration occurring on the walls of the reactor and between the coal particles.

(vi) The process being developed by the Rocketdyne Division of Rockwell International has overcome the agglomeration problem by using a short residence time reactor system followed by a rapid product quench. The coal is transported into the high pressure reactor in a very dense phase and a rocket-engine type injector system is used for rapid coal and gas mixing. Reaction times of 10 - 1000 milliseconds are typical at temperatures of 800°C to 1000°C and pressures of 3,5 MPa to 10 MPa.

5.5. The oils produced in these experiments closely resembled those obtained in Hiteshue's work. There was very little difference in the elemental composition of the oils from the two sets of experiments and it could be seen that the hydrogen to carbon ratio remained almost constant at ca. 1,0 as one would expect for a highly aromatic product over a temperature range of 400°C to 800°C - see Table 8. In both experiments the aromatic content increased as the temperature was raised. Hiteshue obtained about 80 per cent aromatics at 800°C, whereas, these results gave about 70 per cent at 700°C. The benzene content was higher in Hiteshue's results (36 per cent) compared to these results (4 per cent). This difference was probably due to the temperature and it would seem that we were losing some of the lighter aromatics when the hexane was removed with the rotavapor after the separation of the asphaltenes.

The hydrocarbon gases showed similar trends in both the groups of experiments and consisted mainly of methane, ethane and propane at the lower temperature, whereas, at temperatures of 700°C to 800°C



the main constituent was methane. The hydrocarbon gases were probably a product of the hydrolysis reaction and the cracking of the lower molecular mass oils, but at the higher temperatures the gaseous products were undoubtedly derived in part from the carbon hydrogen reaction.

The ultimate analyses of the chars from Hiteshue's work showed similar trends to this work. The sulphur removal with increase in temperature indicated the same temperature regions for the removal of organic and inorganic sulphur, and similar rate of removal of the sulphur from the coal. The elimination of nitrogen, oxygen and hydrogen showed similar trends and rates of disappearance. The nitrogen would have reacted to form ammonia, or was present in the oil as complex organic compounds, the oxygen would have been converted to water and carbon dioxide and the hydrogen would have been used in the production of gaseous and liquid products.

## 6. Conclusion

- 6.1. From this work it would seem that the hydrogen to carbon ratio and the volatile matter content provide an adequate means for the initial selection of South African coals for the hydrolysis reaction. There are many other factors relating to the selected coals' properties which effect the product distribution one of the more important ones mentioned in this report being its petrographic composition. It would appear that an increase in the vitrinite plus exinite content improves the oil yield, whereas, an increase in inertinite content tends to favour an increase in the gas plus water yield. Other properties such as mineral matter and the heteroatom content obviously play a part in this reaction, but to what extent is still uncertain. It is felt that further work could be carried out with the "hot-rod" reactor to screen additional coals from the Southern and Northern Hemisphere coalfields. These results could be processed in a statistical manner as described by Given<sup>(24)(25)</sup> and would hopefully indicate any differences in the hydrolysis reaction which may be due to the composition of the coal. The advantage of carrying out this work with one type of reactor would be to remove any process variables which have a considerable effect on the product distribution from the hydrolysis reaction with coal.

6.2. Comparison of this work with that of Hiteshue's (2)-(5) using similar reactor concepts and experimental conditions has shown that the South African coals are as amenable to hydrolysis as are the North American coals. Maximum oil yields were obtained at similar temperatures ( $550^{\circ}\text{C}$ ) and pressures (15 - 20 MPa). Any increase in temperature at the solid and vapour residence time pertaining in these experiments resulted in the breakdown of the oil to give a gas. The threshold value for pressure was because only a sufficient hydrogen partial pressure was required to capture and stabilize the free radicals formed in the initial pyrolysis reaction<sup>(30)</sup>. If the hydrogen partial pressure were increased further it would apparently affect the lighter fraction of the oil (see Section 5.2.) and the carbon hydrogen reaction which is insignificant at this temperature. The more severe the operating conditions were, the better was the quality of the oil as shown by its molecular mass, viscosity and boiling range. The aromaticity of the oil also increased with the increase in temperature.

The hydrocarbon gases produced in these experiments were rich in methane, ethane and propane at the lower temperatures. As the temperatures were increased to between  $700^{\circ}\text{C}$  and  $800^{\circ}\text{C}$  the main constituent was methane which was probably derived in considerable part from the carbon hydrogen reaction.

The yield of char decreased with the increase in the operating temperature. In a commercial process an economic assessment would have to be undertaken to determine whether it would be more economic to obtain the process hydrogen from the char or whether it would be better to convert as much of the char to methane and steam reform this product to give the hydrogen.

6.3. It would seem from this work that the most important factor which has to be considered in the hydrolysis reaction is the agglomeration behaviour of the coal. This problem, which is more severe in bituminous coal, must be overcome to enable the coal to be processed continuously in a dry state.

The most likely way of overcoming this problem is by selecting the correct reactor configuration which in turn will influence the product distribution and quality. There are three types of reactor configurations which may overcome this problem:-

- (i) The free fall dilute phase reactor which would enable one to feed coal into a reactor of a minimum diameter of 7 - 8 cms. and having a wall temperature of at least 700°C to prevent agglomeration occurring on the walls of the reactor and between the coal particles<sup>(6)-(9)</sup>.
- (ii) The fast fluidized-bed<sup>(29)</sup> which would be continuous, entrained, have a high turbulence and a longer solid residence time than the free fall dilute phase reactor.
- (iii) The entrained, continuous high turbulence system as exemplified by the Rocketdyne reactor of Rockwell International<sup>(31)</sup>.

From a commercial aspect this latter process is the most advanced having a throughput of 160,000 kg/h/m<sup>3</sup> whilst preventing agglomeration by the use of high temperature and high turbulent coal and gas mixing procedures. However, for laboratory rather than plant investigations it is felt that the first two types of reactor configurations would be more applicable to our requirements. Thus it is hoped to continue this work using the free fall dilute phase reactor and eventually to also use this same reactor in a fluidized bed mode to investigate the concept of a fast fluidized bed, where the rapid internal recycling of char and high turbulence conditions may prevent agglomeration and give maximum oil yields.

7. Acknowledgements

The author wishes to express his thanks to the personnel of the Coal Survey Laboratory for the coal and petrographic analyses, to Dr. J.R. Kershaw for the analyses of the liquids, and to the latter in conjunction with Dr. D. Gray for the helpful discussions during the execution of this work.

G BARRASS  
PRINCIPAL RESEARCH OFFICER

PRETORIA  
1978/09/07  
GB/ug

8. References

- (1) W.R.K. Wu and H.H. Storch. Hydrogenation of Coal and Tar. US Bureau of Mines. Bulletin 633, 1968.
- (2) R.W. Hiteshue, S. Friedman and R. Madden. Hydrogenation of Coal to Gaseous Hydrocarbons. US Bureau of Mines. Report of Investigations 6027, 1962.
- (3) R.W. Hiteshue, S. Friedman and R. Madden. Hydrogenation of Bituminous Coals, Lignite, Anthracite and Char. US Bureau of Mines. Report of Investigations 6125, 1962.
- (4) R.W. Hiteshue, S. Friedman and R. Madden. Hydrogasification of High-Volatile A Bituminous Coal. US Bureau of Mines. Report of Investigations 6376, 1964.
- (5) S. Friedman, R.W. Hiteshue and M.D. Schlesinger. Hydrogenation of New Mexico Coal at Short Residence Time and High Temperature. US Bureau of Mines. Report of Investigations 6470, 1964.
- (6) S.A. Qader and G.R. Hill. Fuels by Hydrocracking Oil from Coal. Hydrocarbon Processing. March 1969, Vol. 48 141.
- (7) S.A. Qader, R.A. Haddadin, L.L. Anderson and G.R. Hill. Coal can also Yield Liquid Fuels. Hydrocarbon Processing. September, 1969 Vol. 48 147.
- (8) M. Steinberg and P. Fallon. Coal Liquefaction by Rapid Gas Phase Hydrogenation. Hydrocracking and Hydrotreating. ACS Symposium Series 20.
- (9) A.H. Pelofsky, M.I. Greene and C.J. Sadella. Short Residence Time (SRT) Coal Hydrolysis. ACS Div. of Fuel Chem. Vol. 21 No. 5 August 1976 154.

- (10) P.S. Lewis and R.W. Hiteshue. Hydrogenating Coal in the Entrained State. Ind. Eng. Chem. Vol. 52 No. 11 November 1960 919.
- (11) R.E. Wood and W.H. Wiser. Coal Liquefaction in Coiled Tube Reactors. Ind. Eng. Chem. Process Des. Dev. Vol. 15 No. 1 1976 144.
- (12) W.C. Schroeder (assigned to Fossil Fuels, Inc.), US Pat. 3,030,298 (April 17, 1962) and US Pat. 3,152,063 (October 6, 1964).
- (13) W.C. Schroeder. Solid Phase Hydrogenation Cuts Costs. Hydrocarbon Processing. January 1976 131.
- (14) G. Barrass and J.R. Kershaw. High Pressure Hydrogenation of Coal - Part 2. The Effect of Certain Catalysts. FRI Report 10, 1977.
- (15) D. Gray. Inherent Mineral Matter in Coal and its Effect Upon Hydrogenation. Fuel Vol. 57. April 1978 213.
- (16) G. Barrass. A Preliminary Study of the Hydrogenation Characteristics of South African Coals. FRI Report 25, 1976.
- (17) D.W. Taylor and H. Marsh. Carbon Gasification in the Presence of Metal Catalysts. Fuel Vol. 54 July, 1975 219.
- (18) J.R. Kershaw and G. Barrass. Changes in the Chemical Composition of the Oil Formed with Variations in Hydrogenation Conditions. FRI Report 30, 1978.
- (19) J.R. Kershaw. Chemical Nature of the Oil Formed by Hydrogenation, Supercritical Gas Extraction and Soxhlet Extraction of The Same Coal. S. Afri. J. Chem. 1977 Vol. XXX 205.
- (20) J.R. Kershaw. Fluorescence Spectroscopy in the Characterization of Coal Derived Liquids. Fuel Vol. 57 May 1978 299.

- (21) R.E. Guyot and J.F. Cudmore. Production of Synthetic Oil and Chemicals from Coal. Batch Autoclave Hydrogenation Studies Part 1. Australian Coal Industry Research Laboratories Ltd. June 1975.
- (22) P.H. Given, D.C. Cronauer, W. Spackman, H.L. Lovell, A. Davis and B. Biswas. Dependence of Coal Liquefaction Behaviour on Coal Characteristics. 1. Vitrinite - rich Samples. Fuel Vol. 54 January, 1975 34.
- (23) P.H. Given, D.C. Cronauer, W. Spackman, H.L. Lovell, A. Davis and B. Biswas. Dependence of Coal Liquefaction Behaviour on Coal Characteristics. 2. Role of Petrographic Composition. Fuel Vol. 54 January, 1975 40.
- (24) M.B. Abdel-Baset, R.F. Yarzab and P.H. Given. Dependence of Coal Liquefaction Behaviour on Coal Characteristics. 3. Statistical **Correlations** of Conversion in Coal-Tetralin Interactions. Fuel Vol. 57 February 1978 89.
- (25) Z. Abdel-Baset, P.H. Given and R.F. Yarzab. Re-examination of the Phenolic Hydroxyl Contents of Coals. Fuel Vol. 57 February, 1978 95.
- (26) J.M. Holmes, H.D. Cochran, M.S. Edwards, D.S. Joy and P.M. Lantz. Hydrocarbonization Research Phase I Report. Review and Evaluation of Hydrocarbonization Data. Oak Ridge National Laboratory August, 1975 ORNL-TM-4835.
- (27) E.L. Clark et al. Hydrogenation of Coal in a Fluidized-Bed. Ind. Eng. Chem. 42, 861 May, 1950.
- (28) G.R. Hill et al. Project Western Coal: Conversion of Coal into Liquids. University of Utah May, 1970 PB-234 748.
- (29) J. Yerushalmi. Fluid Bed Processing of Agglomerating Coals. Coal Processing Technology Vol. 3. 156.

- (30) D.B. Anthony, J.B. Howard, H.C. Hottel and H.P. Meissner.  
Rapid Devolatilization and Hydrogasification of Bituminous Coal.  
Fuel Vol. 55 April, 1976 121.
  
- (31) J.A. Gray and K.M. Sprouse. Hydrogasifier Development for the  
Hydrane Process. US Dept. of Energy. Report No. FE-2518-4.



TABLE 1

PROXIMATE AND ULTIMATE ANALYSES OF COALS USED IN THE HYDRO-  
PYROLYSIS EXPERIMENTS

COAL	PROXIMATE ANALYSES (AIR DRIED BASIS)				ULTIMATE ANALYSES (DRY ASH-FREE BASIS)					% VOL. MAT. (DAF)	H/C RATIO
	% H <sub>2</sub> O	% ASH	% VOL. MAT.	% FIX. CARB.	% C	% H	% N	% S	% O		
MATLA	6,0	10,9	35,3	47,6	78,84	5,48	2,03	0,53	13,12	42,5	0,83
WATERBERG	3,4	12,7	34,8	49,1	80,68	5,47	1,47	1,04	11,34	41,5	0,81
NEW WAKEFIELD	4,9	14,9	32,8	47,4	79,15	5,41	2,11	2,28	11,05	40,9	0,82
KRIEL	3,8	20,2	30,3	45,7	79,13	5,28	2,04	2,88	10,67	39,9	0,80
SPITZKOP	3,2	12,7	32,7	51,4	81,68	5,33	2,07	1,31	9,61	38,9	0,78
SIGMA	6,6	29,6	21,9	41,9	76,71	4,42	1,55	1,08	16,24	34,3	0,69
LANDAU	2,5	14,3	23,3	59,9	84,10	4,41	1,91	0,64	8,94	28,0	0,63

TABLE 2

PETROGRAPHIC ANALYSES OF COALS USED IN THE  
HYDROPYROLYSIS EXPERIMENTS

COAL	MACERAL ANALYSES					RATIO REACTIVES /INERTS
	% VITRINITE	% EXINITE	% INERTINITE	% VISIBLE MINERALS		
MATLA	75,9	82,1	6,2	15,6	1,0	5,0:1
WATERBERG	83,2	87,4	4,2	5,7	6,9	6,9:1
NEW WAKEFIELD	72,2	77,2	5,0	13,2	9,6	3,4:1
KRIEL	50,8	62,9	12,1	21,5	15,6	1,7:1
SPITZKOP	55,0	61,3	6,3	35,9	2,8	1,6:1
SIGMA *	63,5	68,2	4,7	17,3	14,5	2,1:1
LANDAU **	57,2	63,2	6,0	28,4	8,4	1,7:1

\* This analysis is very far from a normal petrographic analysis of Sigma coal. *As with the  
u. with  
microcell  
analyses*

\*\* " " " also definitely suspect.

TABLE 3

VARIATION OF ALIPHATIC HYDROCARBONS WITH TEMPERATURE FOR NEW WAKEFIELD COAL (18)

ALKANE	% OF TOTAL ALKANES						
	400°C	450°C	500°C	550°C	600°C	650°C	700°C
<u>n</u> - C <sub>13</sub>	5,9	7,1	5,6	6,7	7,9	9,2	11,0
<u>n</u> - C <sub>14</sub>	6,7	7,3	7,3	8,4	9,5	13,9	11,2
<u>n</u> - C <sub>15</sub>	6,3	6,0	9,5	10,1	11,4	12,1	9,7
<u>n</u> - C <sub>16</sub>	7,4	7,0	10,0	10,8	11,3	9,8	9,9
<u>n</u> - C <sub>17</sub> (AND PRISTANE)	6,2	5,9	8,0	9,6	10,9	10,3	9,8
<u>n</u> - C <sub>18</sub> (AND PHYTANE)	6,3	7,1	8,6	9,0	9,3	8,4	8,5
<u>n</u> - C <sub>19</sub>	6,1	7,4	8,6	8,3	7,8	7,1	7,5
<u>n</u> - C <sub>20</sub>	7,1	7,4	8,3	7,4	6,1	5,6	6,3
<u>n</u> - C <sub>21</sub>	7,6	7,3	6,6	5,8	4,6	4,3	5,2
<u>n</u> - C <sub>22</sub>	8,8	7,6	5,7	5,2	3,6	3,3	4,2
<u>n</u> - C <sub>23</sub>	8,3	7,7	5,2	4,6	3,1	2,9	3,5
<u>n</u> - C <sub>24</sub>	7,1	6,2	3,7	3,1	1,9	1,9	2,2
<u>n</u> - C <sub>25</sub>	5,6	5,1	3,0	2,5	1,8	1,4	1,5
<u>n</u> - C <sub>26</sub>	3,3	3,0	1,4	1,0	0,7	0,6	0,5

TABLE 4

VARIATION OF AROMATIC HYDROCARBONS WITH TEMPERA-  
TURE FOR NEW WAKEFIELD COAL

AROMATIC	% AROMATICS						
COMPOUND	400°C	450°C	500°C	550°C	600°C	650°C	700°C
BENZENE/CYCLOHEXANE	8,2	5,4	11,3	-	1,8	9,8	3,8
TOLUENE	2,1	1,5	2,7	0,4	1,1	3,2	1,8
XYLENES/ETHYL BENZENE	1,6	1,4	2,2	1,4	1,6	4,3	3,9
TRI METHYL BENZENE/ ETHYL TOLUENE	2,0	2,3	3,7	4,6	5,6	8,2	10,7
NAPHTHALENE	1,2	1,3	3,4	4,8	7,1	9,9	23,0
2 Me - NAPHTHALENE	1,8	2,4	6,3	6,9	8,4	8,1	10,1
PHENANTHRENE/ ANTHRACENE	0,3	0,2	1,3	2,9	7,7	4,1	8,3
PYRENE	0,9	0,9	1,0	1,5	6,7	3,2	5,3

TABLE 5

## VARIATION IN GAS ANALYSES RESULTS (FOR THE WHOLE SAMPLE) WITH INCREASE IN TEMPERATURE

COAL	TEMPERATURE °C	% OXYGEN	% NITROGEN	% CARBON MONOXIDE	% CARBON DIOXIDE	% HYDROGEN (BALANCE)	% METHANE	% ETHYLENE	% ETHANE	% PROPYLENE	% PROPANE	% I-BUTANE	% N-BUTANE
NEW WAKEFIELD	400	1,15	6,05	N.D.	0,04	92,64	0,08	0,003	0,026	0,004	0,012	0,001	0,003
	450	1,53	7,97	N.D.	0,04	90,14	0,21	0,006	0,070	0,008	0,031	0,002	0,003
	600	2,34	11,56	N.D.	0,10	84,58	0,85	0,024	0,335	0,014	0,115	0,066	0,022
	650	0,94	4,76	N.D.	0,04	92,70	1,03	0,011	0,398	0,010	0,094	0,007	0,005
	700	0,91	4,88	N.D.	0,02	92,65	1,12	0,010	0,350	0,007	0,045	0,002	0,003
SIGMA	400	0,86	4,48	N.D.	0,06	94,01	0,41	0,010	0,122	0,006	0,035	0,001	N.D.
	450	0,82	4,24	N.D.	0,09	94,00	0,58	0,015	0,193	0,008	0,050	0,006	0,004
	500	0,62	3,03	N.D.	0,11	95,41	0,54	0,025	0,177	0,015	0,073	0,005	0,005
	550	1,62	8,58	N.D.	0,06	89,60	0,10	0,001	0,038	0,001	0,009	N.D.	N.D.
	600	1,64	8,07	N.D.	0,03	89,51	0,66	0,001	0,094	0,001	0,006	N.D.	N.D.
	650	1,50	8,03	N.D.	0,03	89,52	0,82	0,001	0,096	0,001	0,006	0,001	N.D.

N.D. = NOT DETECTED

TABLE 6

VARIATION IN HYDROCARBON GAS CONCENTRATIONS WITH THE INCREASE IN TEMPERATURE  
 (HYDROCARBON CONCENTRATIONS CALCULATED ON A AIR/CO<sub>2</sub> FREE BASIS AND EXPRESSED  
 AS A PERCENTAGE OF THE D.A.F. COAL)

COAL	TEMPERATURE °C	% METHANE	% ETHYLENE	% ETHANE	% PROPYLENE	% PROPANE	% I-BUTANE	% N-BUTANE
NEW WAKEFIELD	400	1,07	0,07	0,69	0,15	0,46	0,05	0,15
	450	3,06	0,16	1,93	0,32	1,25	0,10	0,14
	600	14,02	0,69	10,34	0,60	5,22	3,95	1,33
	650	16,21	0,30	11,72	0,43	4,07	0,37	0,27
	700	18,07	0,29	10,64	0,28	2,01	0,11	0,17
SIGMA	400	7,61	0,33	4,21	0,27	1,77	0,06	N.D.
	450	10,23	0,47	6,37	0,35	2,44	0,36	0,24
	500	9,30	0,76	5,71	0,70	3,47	0,30	0,30
	550	1,96	0,03	1,39	0,04	0,48	N.D.	N.D.
	600	13,27	0,13	3,56	0,05	0,35	N.D.	N.D.
	650	17,05	0,03	3,72	0,04	0,36	0,06	N.D.

N.D. = NOT DETECTED

TABLE 7

COMPARISON OF THE REGRESSION ANALYSES FOR THE COAL PROPERTIES USED IN THE SELECTION OF A COAL  
FOR HYDROLYSIS

CONDITIONS OF EXPERIMENTS FROM WHICH RESULTS OBTAINED	H/C RATIO		VOLATILE MATTER		VITRINITE PLUS EXINITE	
	REGRESSION EQUATION	CORRELATION COEFF.	REGRESSION EQUATION	CORRELATION COEFF.	REGRESSION EQUATION	CORRELATION COEFF.
CONVERSION						
SOUTH AFRICAN COALS AT 25 MPa, 500°C CATALYST Sn	$y = 0,46 + 0,004 x$	0,61	$y = 16,50 + 0,28 x$	0,62	$y = 20,65 + 0,66 x$	0,73
NORTH AMERICAN COALS AT 18 MPa, 400°C, CATALYST Mo	$y = 1,06 - 0,003 x$	-0,71	$y = 53,23 - 0,15 x$	-0,42	$y = 42,85 + 0,57 x$	0,84
AUSTRALIAN COALS AT 20 MPa, 400°C, SOLVENT	$y = 0,43 + 0,005 x$	0,69	$y = 16,52 + 0,29 x$	0,49	$y = -25,28 + 1,30 x$	0,91
OIL YIELD						
SOUTH AFRICAN COALS AT 25 MPa, 500°C, CATALYST Sn	$y = 0,57 + 0,006 x$	0,91	$y = 24,52 + 0,42 x$	0,91	$y = 47,73 + 0,75 x$	0,80
NORTH AMERICAN COALS AT 18 MPa, 400°C, CATALYST Mo	$y = 1,16 - 0,012 x$	-0,79	$y = 28,59 + 0,42 x$	0,47	$y = 78,49 + 0,42 x$	0,36
OIL + ASPHALTENE						
SOUTH AFRICAN COALS AT 25 MPa, 500°C, CATALYST Sn	$y = 0,57 + 0,005 x$	1,00	$y = 23,29 + 0,38 x$	0,95	$y = 51,77 + 0,51 x$	0,63
NORTH AMERICAN COALS AT 18 MPa, 400°C, CATALYST Mo	$y = 1,10 - 0,004 x$	-0,62	$y = 27,06 + 0,19 x$	0,41	$y = 71,18 + 0,27 x$	0,46

TABLE 8

COMPARISON OF THE ELEMENTAL COMPOSITION OF OILS  
FROM SOUTH AFRICAN AND NORTH AMERICAN COALS  
USING THE "HOT-ROD" REACTOR

COAL	TEMPERATURE °C	PRESSURE MPa	% C	% H	% N	H/ C RATIO
NEW WAKEFIELD (SOUTH AFRICA)	400	25	82,65	7,85	< 0,3	1,14
	500	25	86,44	8,06	1,25	1,12
	600	25	85,02	7,91	0,81	1,12
	700	25	86,14	7,67	1,38	1,07
ROCK SPRINGS Wyo (NORTH AMERICA)	480	40	88,9	8,0	1,2	1,08
	525	40	85,1	8,2	-	1,16
	600	40	87,9	7,0	-	0,96
	800	40	85,9	7,7	-	1,08



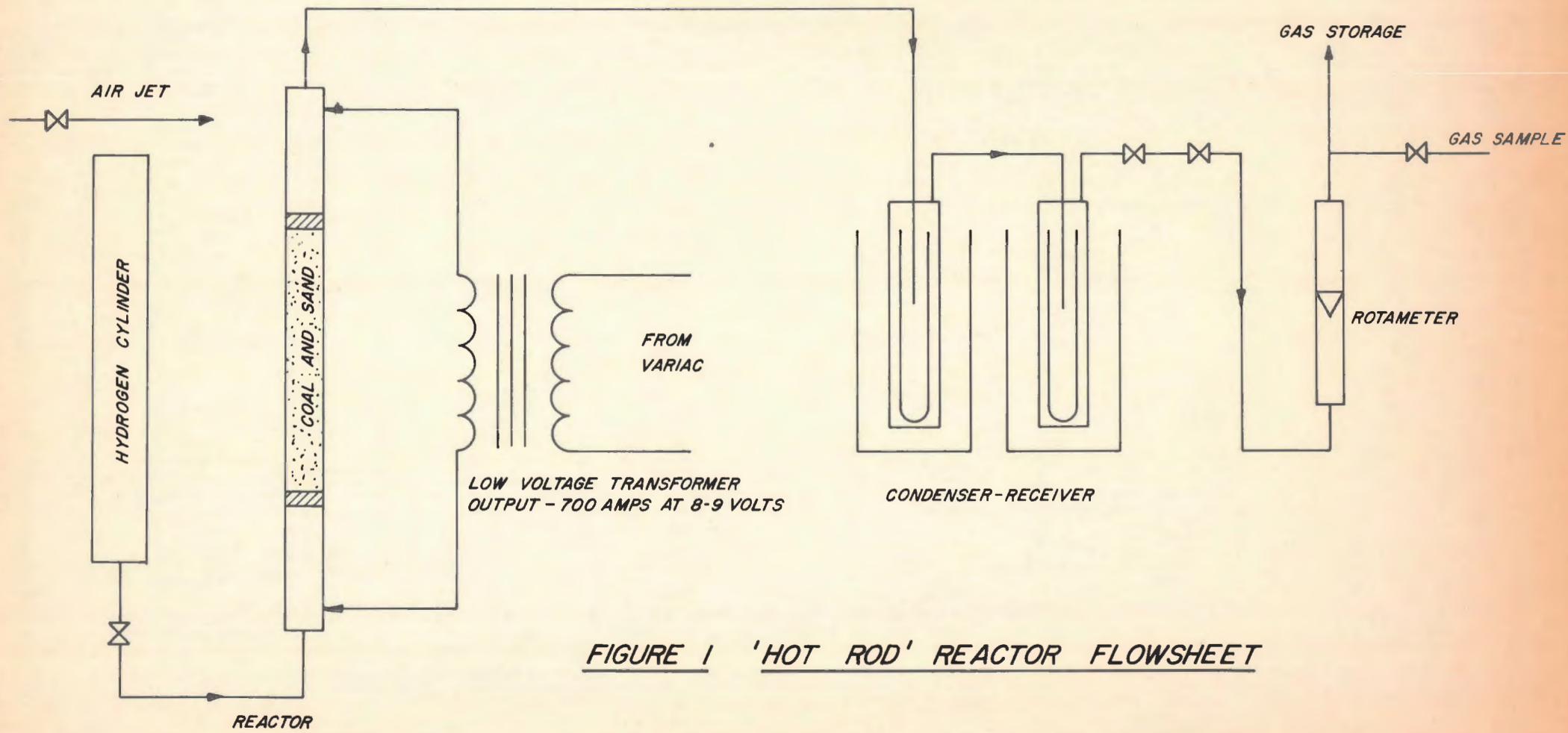


FIGURE 1 'HOT ROD' REACTOR FLOWSHEET

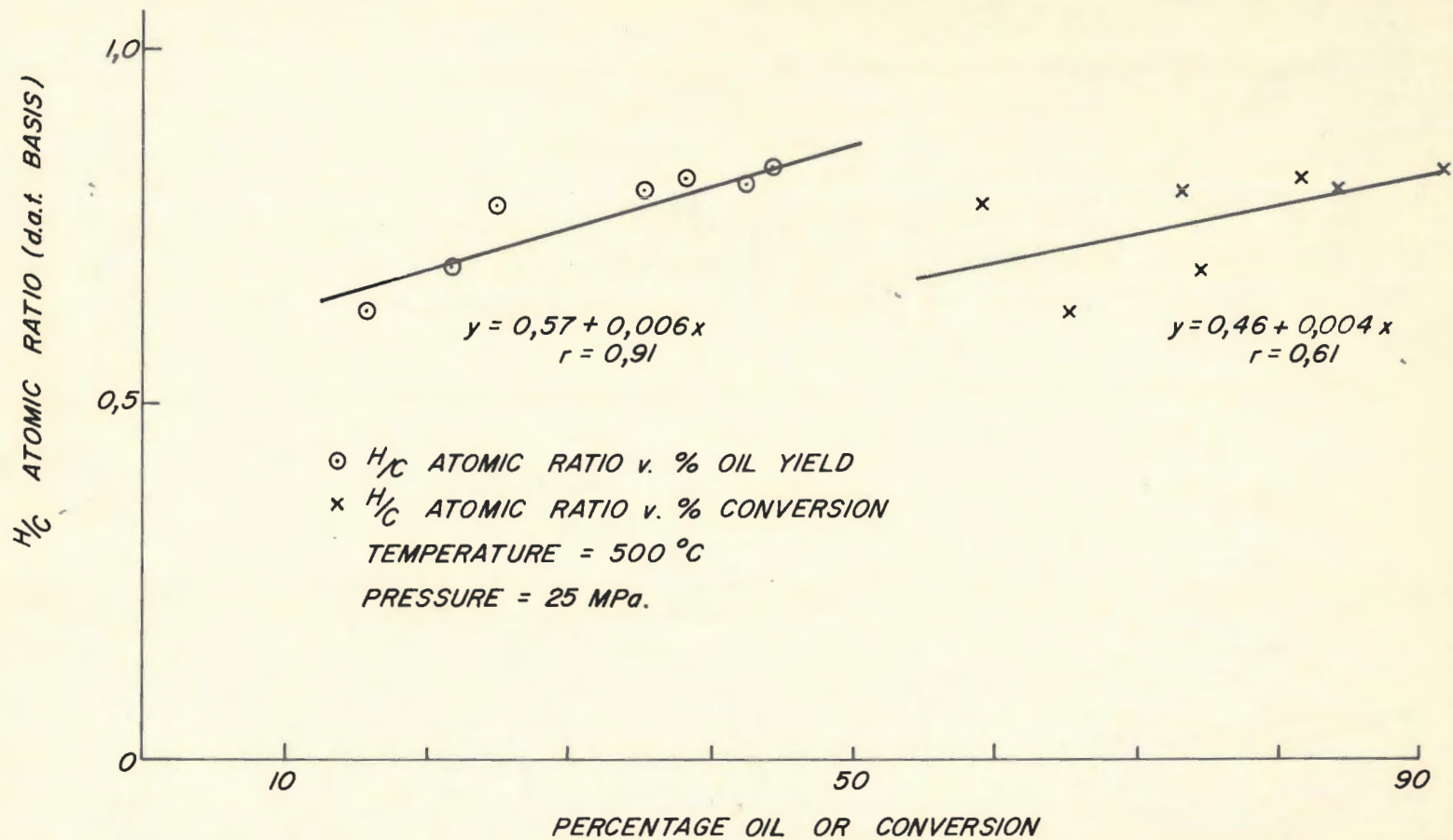


FIGURE 2 VARIATION OF THE PERCENTAGE CONVERSION AND OIL YIELD WITH THE  
 $H/C$  ATOMIC RATIO OF THE COAL (d.a.f. BASIS)

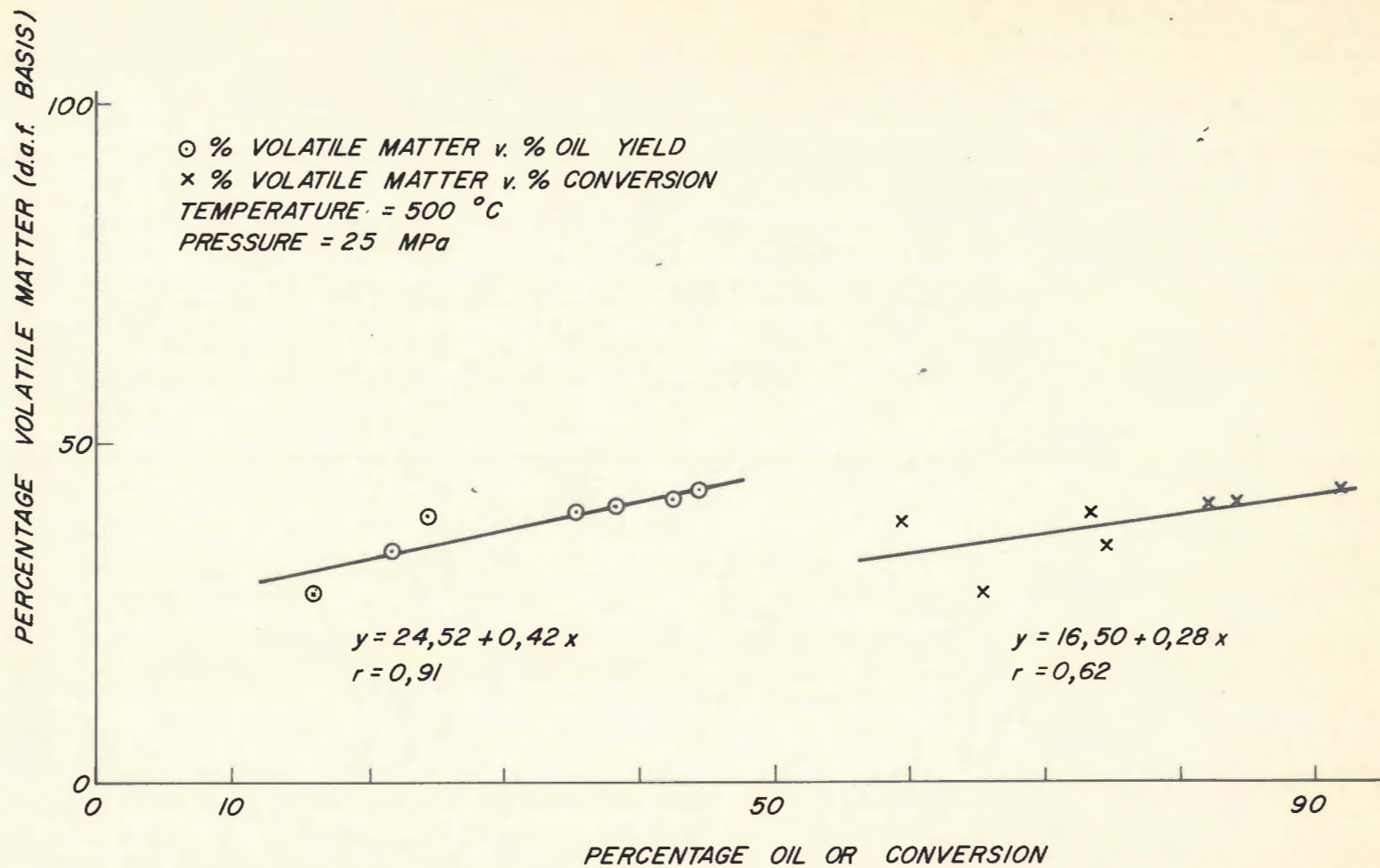


FIGURE 3 VARIATION OF THE PERCENTAGE CONVERSION AND OIL YIELD WITH THE VOLATILE MATTER OF THE COAL (d.a.f. BASIS)

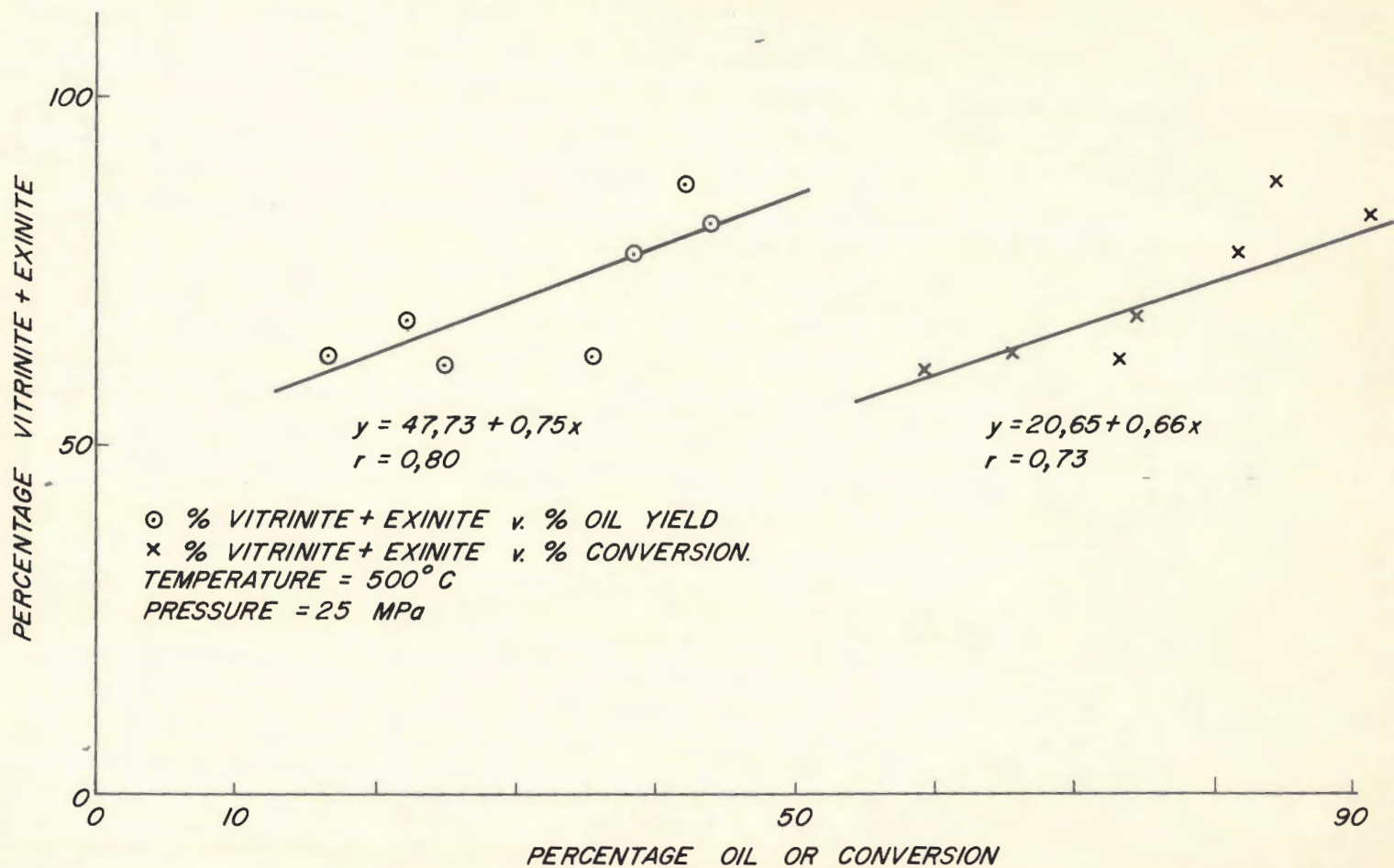


FIGURE 4 VARIATION OF THE PERCENTAGE CONVERSION AND OIL YIELD WITH THE PERCENTAGE VITRINITE + EXINITE CONTENT OF THE COAL.

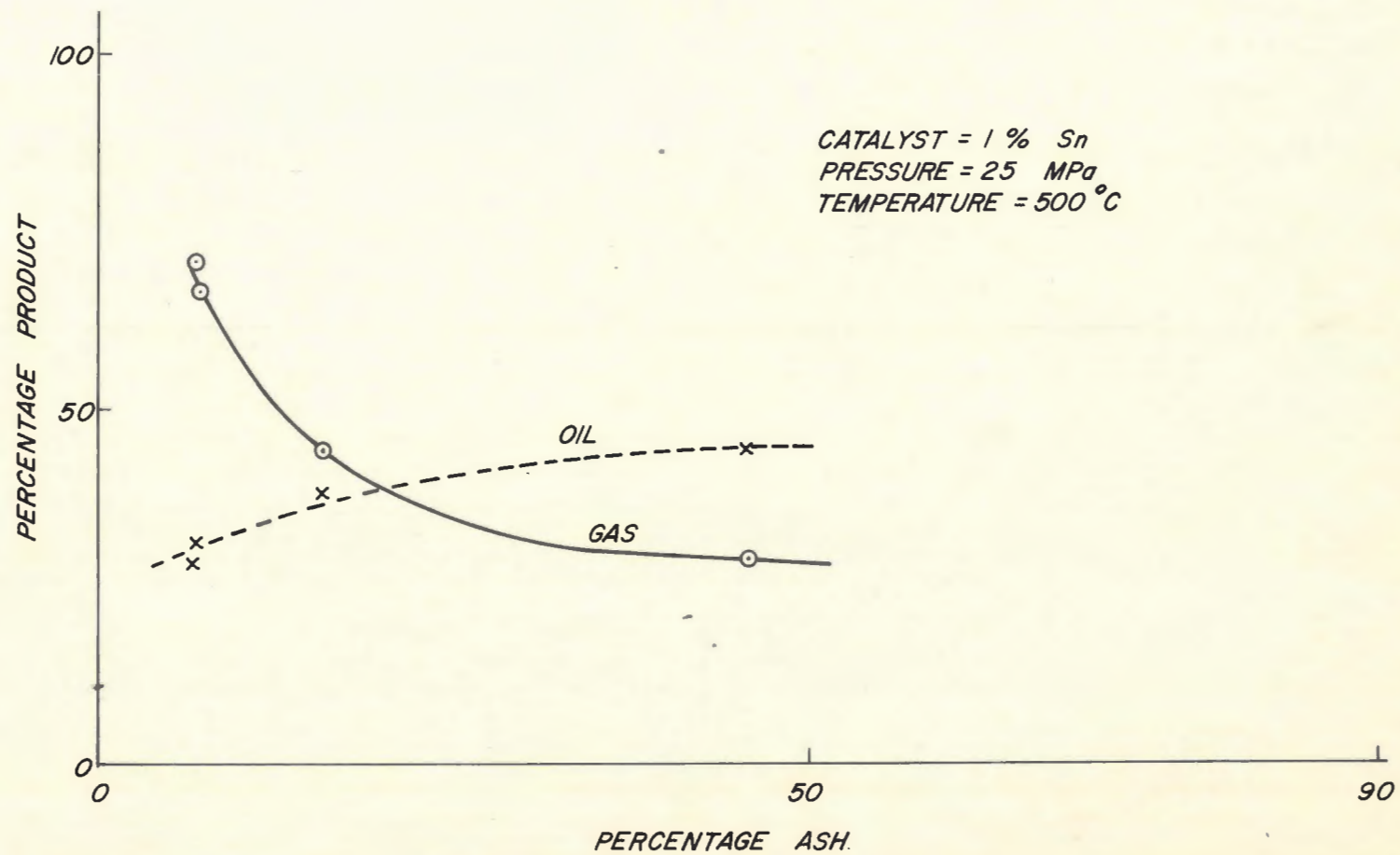


FIGURE 5 VARIATION IN PRODUCT DISTRIBUTION WITH ASH CONTENT FOR KRIEL COAL  
(0,149mm / 0,074 mm)

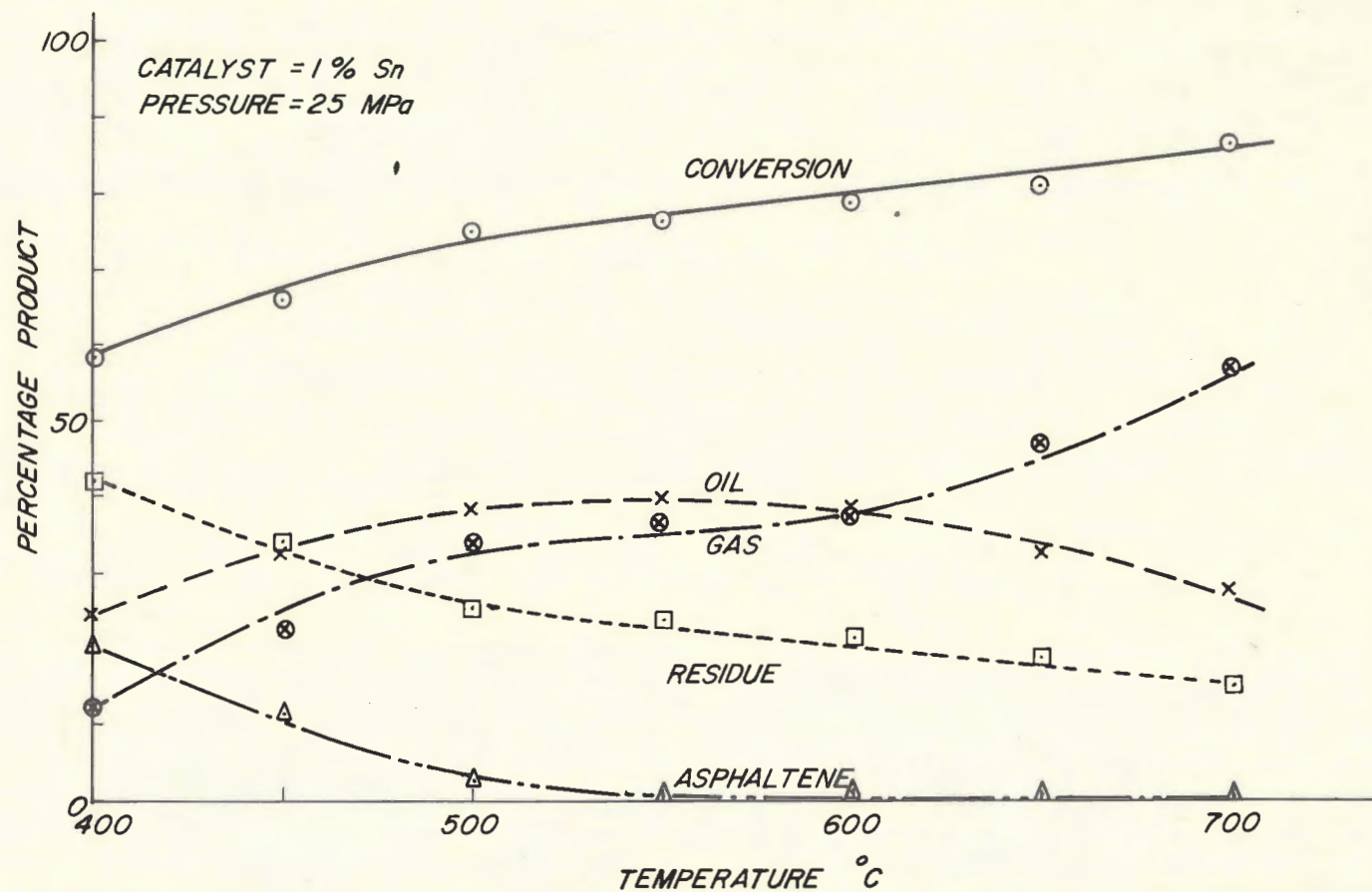


FIGURE 6 VARIATION IN PRODUCT DISTRIBUTION WITH TEMPERATURE FOR NEW WAKEFIELD COAL (0,59 mm - 0,25 mm)

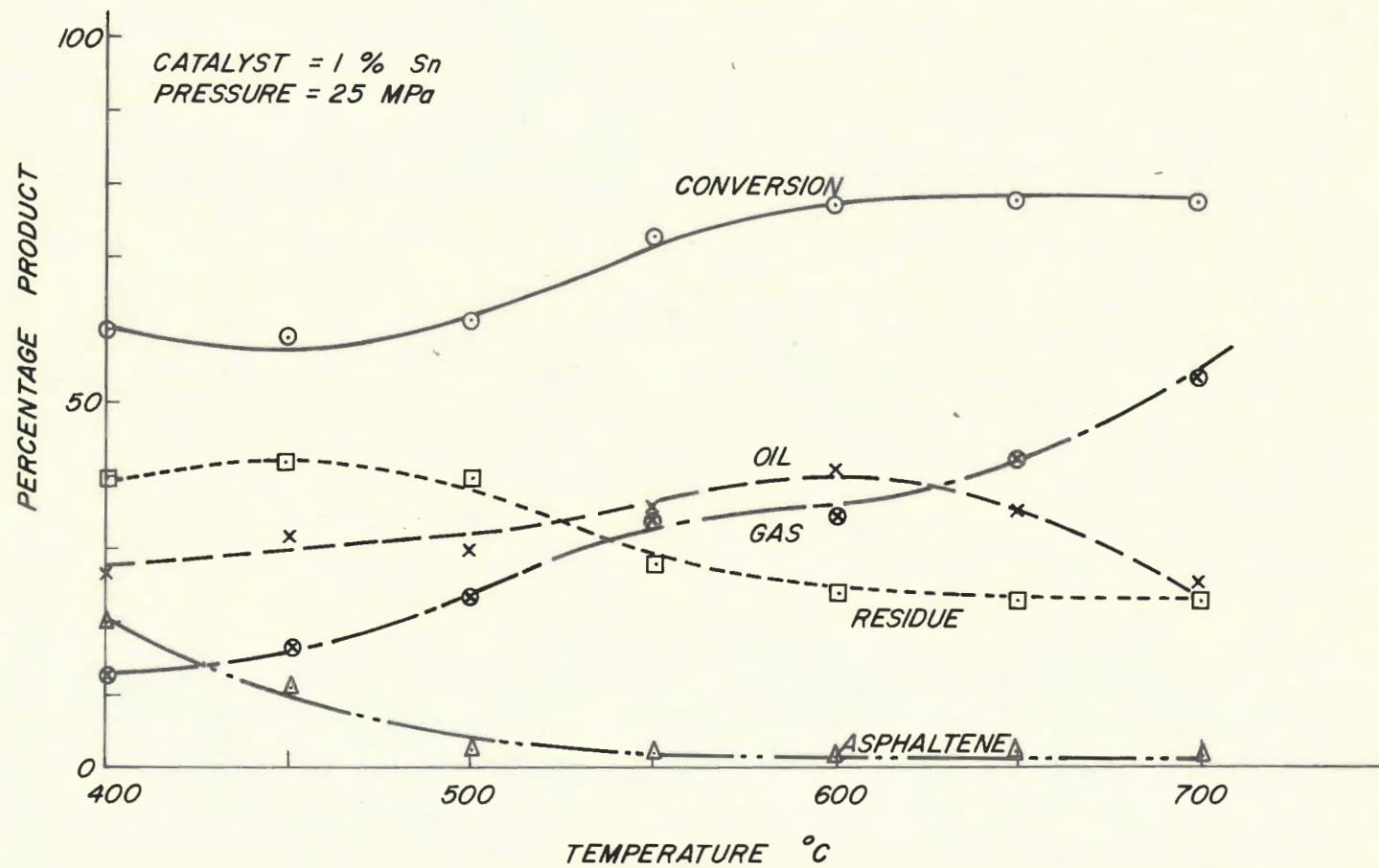
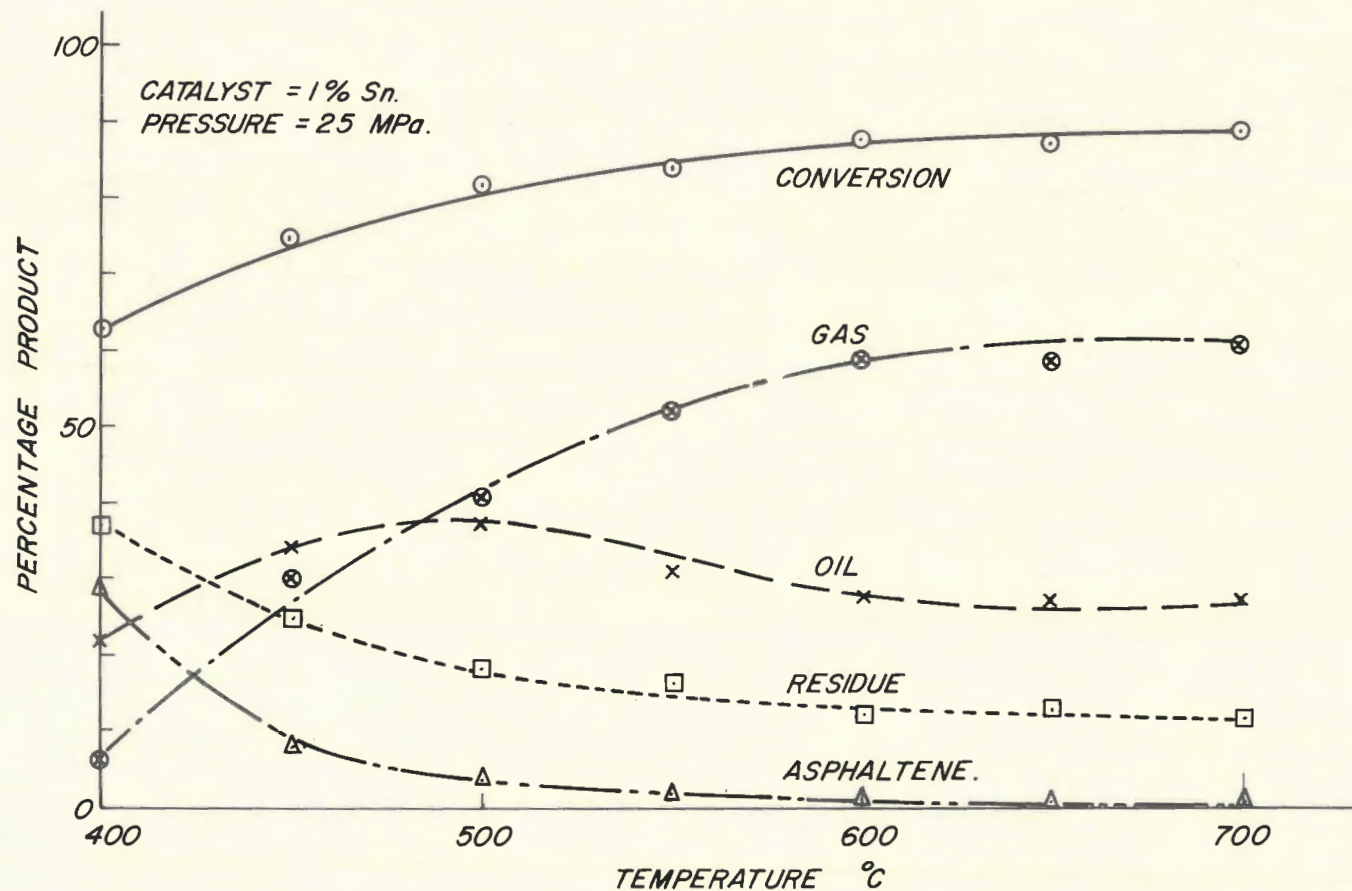


FIGURE 7 VARIATION IN PRODUCT DISTRIBUTION WITH TEMPERATURE FOR NEW WAKEFIELD COAL (0,149mm - 0,074 mm)



**FIGURE 8** VARIATION IN PRODUCT DISTRIBUTION WITH TEMPERATURE FOR NEW WAKEFIELD COAL (0,59 mm - 0,25 mm) WITH SAND. (HEATING RATE 100 °C/min.)



