RELATIONSHIPS BETWEEN COAL LIQUEFACTION BEHAVIOUR AND THE COMPOSITION OF SOUTH AFRICAN COALS

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GEOLOGICAL ORIGIN OF SOUTH AFRICAN COALS

The coal deposits of South Africa were formed during the Permian age just after a retreat of glaciation. This makes it almost certain that the climate was temperate rather than subtropical and may explain the differences between the plant life in South Africa at that time and the flora of the North American carboniferous era. The predominance of the inertinite maceral group in South African coals is indicative of drier swamp conditions in which rotting processes as well as peatification played a more dominant role than in the formation of the humic coals of Europe (1). South African coals were thought to be deposited in deltaic or fluvial environments where fluctuations in water level may have caused deposition of large quantities of mineral matter. South African coals generally have not reached a very high rank although in Natal anthracites are found. This rank increase seems to be due to metamorphism brought about by dolerite intrusions rather than by stratigraphic depth.

GEOGRAPHICAL LOCATION AND COAL RESERVES OF SOUTH AFRICA

The main coal fields lie in the Highveld area of the Orange Free State, South-eastern Transvaal and Natal. Other coal fields are located in the Northern part of the country, the Waterberg field on the Botswana border and the Limpopo and Pafuri fields on the borders of Rhodesia and Mocambique.

Table 1 shows the raw bituminous coal reserve figures at various ash contents (2). The total figure of 81,274 million tonnes is for total mineable coal in situ down to 300 meters. About half of the coal reserves contain between 30 to 35% mineral matter, thus by world standards South African coal is of poor quality.

TABLE 1: SUMMARY OF COAL RESERVES : MILLIONS OF TONNES

ASH %	5-10	10-15	15-20	20-25	25-30	30-35	TOTAL
PROVEN	18	794	3,720	6,197	7,912	13,582	32,223
INDICATED	-	645	2,866	5,507	5,224	11,785	26,027
INFERRED	2	60	2,034	3,516	5,429	11,983	23,024
TOTAL	20	1,499	8,620	15,220	18,565	37,350	81,274

LIQUEFACTION BEHAVIOUR OF A VARIETY OF SOUTH AFRICAN COALS

Experimental:

Two experimental procedures were used in this preliminary study of the liquefaction behaviour of South African coals. These were:

(i) dry hydrogenation using the hot-rod reactor (3).
(ii) slurried hydrogenation using a rotating autoclave.

(i) Hot-Rod Method:

This system was very similar to the one used by Hiteshue at the U.S.B.M. except that larger quantities of coal were used. In this method sand (0.42 - 0.15 mm) was mixed with the coal in a 2:1 mass ratio. It was found that the addition of sand to the coal helped to prevent agglomeration (4) thus enhancing the diffusion of hydrogen through the coal and the removal of the liquefaction products from the coal. In experiments using a catalyst an aqueous solution of stannous chloride was added to the coal, evaporated to dryness, and then mixed with the sand. The amount of catalyst added on a tin basis was 1% of the mass of the coal. These mixtures were placed in a hot-rod reactor, pressurized with hydrogen to 25 MPa and heated to 500°C at a heating rate of 200°C per minute. Reaction time at temperature was 15 minutes.

(ii) Rotating Autoclave Method:

The reactor was a 1 liter stainless steel rotating autoclave. In the experiments using anthracene oil, the ratio of oil to coal was 2:1, and the final reaction temperature was 430°C. The autoclave was pressurized with hydrogen to 10 MPa at room temperature. Final pressure at reaction temperature was approximately 25 MPa. The products after liquefaction were filtered while hot, and the residue was soxhlet extracted with toluene for 24 hours.

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

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

The oil is the n-hexane soluble portion of the product, and the asphaltene is the toluene soluble n-hexane insoluble portion.

Analyses of Coals Studied:

The coals used in these experiments were from Landau, Sigma, Spitzkop, Kriel, Matla, New Wakefield and Waterberg collieries. Table 2 shows their proximate and ultimate analyses.

The petrographic analyses of the coals are shown in Table 3. One-third of the semi-fusinite, the largest component of the inertinite in Sigma coal, is considered reactive and is included in the total reactive maceral content.

TABLE 2: PROXIMATE AND ULTIMATE ANALYSES OF COALS USED IN THE LIQUEFACTION EXPERIMENTS

COAL	PROXIMATE ANALYSES (AIR DRIED BASIS)				ULTIMATE ANALYSES (D.A.F. BASIS)					% VOL. MAT. (DAF)	H/C RATIO
	% H_2O	% ASH	% VOL. MAT.	% FIX. CARB.	% C	% H	% N	% S	% O		
MATLA	6.0	10.9	35.3	47.8	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 3: PETROGRAPHIC ANALYSES OF COALS USED IN THE LIQUEFACTION EXPERIMENTS

COAL	MACERAL ANALYSES			
	% VITRINITE	% EXINITE	% INERTINITE	% VISIBLE MINERALS
MATLA	75.9	6.2	15.6	1.0
WATERBERG	83.2	4.2	5.7	6.9
NEW WAKEFIELD	72.2	5.0	13.2	9.6
KRIEL	50.8	12.1	21.5	15.6
SPITZKOP	55.0	6.3	35.9	2.8
SIGMA	27.9	3.1	58.9	10.1
LANDAU	57.2	6.0	28.4	8.4

Results of the Preliminary Investigation:

The effect of the following parameters was studied in relation to liquid yields and conversions during coal liquefaction:

1) volatile matter content
2) H/C atomic ratio
3) reactive maceral content
4) mineral matter constituents
5) process parameters

Emphasis in this paper is placed on the coal parameters 1 - 4, and only brief mention is made concerning the process parameters.

Figures 1 and 2 show the percentage conversion (d.a.f. basis) of the coals plotted against the H/C ratio, the volatile matter and the reactive maceral content for the anthracene oil runs.
Figures 3 and 4 show the percentage conversion and the oil yield plotted against the H/C ratio, volatile matter and reactive macerals. These results were obtained from dry hydrogenation runs using the hot-rod reactor.
Figures 5 and 6 show the total liquid product obtained (oil plus asphaltene) plotted against the H/C ratio, volatile matter and reactive maceral content of the coals.

The effect of the inorganic constituents in the coal was studied in two ways. Firstly, a sample of coal from Kriel colliery was subjected to a float and sink separation. The analyses of the float and sink fractions is shown in Table 4.

TABLE 4: ANALYSES OF FLOAT/SINK FRACTIONS

Relative Density	Vitrinite	Exinite	Inertinite	Visible Minerals	Ash
1.4 float	80.6	7.5	6.5	5.4	6.7
1.4 - 1.5	78.3	8.3	9.1	4.3	7.0
1.5 - 1.65	65.5	9.1	15.9	9.7	16.0
1.65 sink	66.6		33.4		45.3

Figure 7 shows the product distribution obtained from dry hydrogenation of these float/sink fractions.

The second procedure studied the particular effects of the pyrite content of the coals during hydrogenation. Unwashed coals were selected so that the only parameter to show significant variation was the total sulfur content. Of this total sulfur, approximately 1% was organic, and the rest was pyritic. Since total mineral matter was also known to affect conversion, it was kept as constant as possible.
Table 5 shows the analyses of the coals used to study the effect of pyrite.

TABLE 5: ANALYSES OF UNWASHED COALS USED TO DETERMINE THE EFFECT OF PYRITES

NUMBER	V+E	TOTAL ASH %	MOISTURE %	SULFUR %	VM
555 O	83.0	24	2.4	6.5	31.9
524 K	83.8	22	3.0	5.7	29.1
651 J	83.7	26	2.3	5.0	32.2
553 H	82.0	22	2.8	4.1	32.5
524 B	82.0	22	2.7	2.2	32.1
554 C	83.2	24	2.5	1.9	30.2
555 A	80.0	22	2.4	1.3	32.5

V+E = Vitrinite + Exinite VM = Volatile Matter

Reaction conditions used in the hot-rod reactor for the pyrite experiments were 25 MPa, 450°C and a 2:1 sand:coal ratio.
A process temperature study was conducted using Waterberg, New Wakefield, Sigma and Landau coals, and at 650°C the conversions for these coals were 89, 87, 90 and 88% respectively. Within experimental error the conversions had all converged to the same value regardless of the characteristics of the individual coals. The product distribution of oil and gas, however, was different, the higher temperature resulting in higher gas make and lower oil yield. If, however, the vapor residence times are shortened it may be possible to quench the vapors before extensive cracking to gas occurs.

Relationships Between Liquefaction Behaviour and the Coal Composition

Organic coal properties

The results of liquefaction using anthracene oil shown in figures 1 and 2 indicate a good correlation between conversion and the H/C atomic ratio, volatile matter and reactive maceral content of the coals. Comparison of these anthracene oil results with results from dry hydrogenation in the absence of anthracene oil (figures 3 and 4) shows that the slopes of the linear correlations are very similar. In the case of conversion against volatile matter, the slopes are identical. The significance of this is not clear as a different mechanism is probably operative in the two techniques. The anthracene oil most certainly acts as a hydrogen donor solvent, and the molecular hydrogen rehydrogenates the solvent. In the case of dry hydrogenation radical stabilization occurs directly by reaction with molecular hydrogen.

No oil yield data are available from the anthracene oil experiments because of the complications in separating product oil, which results from coal liquefaction, and anthracene oil. In the case of dry hydrogenation this complication does not exist, and very reliable oil and oil plus asphaltene yield data are available. Excellent correlations are obtained by plotting oil plus asphaltene yield against H/C ratio and volatile matter content of the coals with correlation coefficients of 0.96 and 0.95, respectively (Figure 5).

It must be stressed that there is an intercorrelation between the coal properties themselves. The correlation between the volatile matter and the H/C ratio for the South African coals studied is extremely high, the correlation coefficient being 0.99. Thus a good correlation of yield with one of these properties obviously implies a similarly good correlation with the other. However, the correlations between the volatile matter and the reactive maceral content and between the reactive maceral content and the H/C ratio were not statistically significant for the coals studied.

The correlation against the concentration of reactive macerals present (Figure 6) is not as good as for the H/C ratio and the volatile matter. A partial explanation of this may be that for South African coals, portions of the inertinite content seem to be definitely reactive to liquefaction. The semi-fusinite, often very high in these coals, is particularly reactive to hydrogenation, and also other maceral constituents of the inertinite group show some reactivity in this regard.

The correlation of conversion against the coal parameters is consistently not as good as with the oil and oil plus asphaltene data. This may be explained by the very high mineral matter contents of South African coals. At conversion conditions, the chemical composition of this mineral matter may undergo considerable change. For example, decarboxylation of carbonates and dehydroxylation of clay minerals

could occur, resulting in a higher measured weight loss of the coal. When calculating conversions, the mineral matter is considered to be unchanged after the hydrogenation reaction, but this is not necessarily the case.

Conversion data from South African coals were compared to data from a selection of Australian coals, also of Gondwanaland origin. These coals were hydrogenated in the presence of a tar derived solvent at 400°C, 11 - 20 MPa and in a ratio 5:1 oil : coal (5). This selection of coals used by the A.C.I.R.L. included three non-Australian coals, and these were omitted in the correlations reported here. An excellent correlation was found between the conversion and the reactive maceral content of the coals. In addition a correlation existed between the conversion and the $H/_C$ atomic ratio.

Table 6 shows the linear regression analyses and the correlation coefficients for the conversion data from South African and Australian coals.

TABLE 6 : REGRESSION EQUATIONS FOR SOUTH AFRICAN AND AUSTRALIAN COALS

COUNTRY	REGRESSION EQUATION	CORRELATION COEF.	CONDITIONS
SOUTH AFRICA	$C = 0.56\ R + 39.0$	0.63	DRY (Sn)
	$C = 1.4\ (VM) + 25.0$	0.63	DRY (Sn)
	$C = 91.8\ \{H/C\} + 7.2$	0.61	DRY (Sn)
	$C = 0.47\ R + 48.0$	0.92	ANTHRACENE OIL
	$C = 1.4\ (VM) + 40.0$	0.89	ANTHRACENE OIL
	$C = 106.6\{H/C\} + 1.0$	0.96	ANTHRACENE OIL
AUSTRALIA	$C = 0.65\ R + 26.0$	0.92	TAR OIL
	$C = 83.5\ \{H/C\} + 1.6$	0.70	TAR OIL

C = CONVERSION, R = REACTIVE MACERALS, VM = (D.A.F.) VOLATILE MATTER

Inorganic Coal Properties:

There is positive evidence that mineral matter behaves beneficially during coal conversion. It has been demonstrated that certain coal minerals, particularly iron compounds, catalyze the hydrogenation of coal-derived solvents (6). Mukherjee et al (7) hydrogenated float/sink fractions of an Indian coal and found that the conversion increased continuously with the amount of mineral matter present in the fraction. It is difficult to assess the effect of the mineral matter in the coal on liquefaction. When using float/sink fractions of the same coal, the petrographic constitution of the coal fractions usually changes significantly with more inertinite being found in the higher density fractions. Also the mineral matter distribution changes from fraction to fraction, and the physical distribution of the mineral phases causes considerable variation in the surface areas available for possible catalysis. In addition, the combination of the effects of increased mineral matter and decreased reactive maceral content in increasing density fractions decreases the tendency of the coal to agglomerate. This allows more effective diffusion in the system (4).

To try to overcome these difficulties, a series of unwashed coals was chosen so that the only parameter to change significantly was the total sulfur content. Table 5 shows the analysis of the coals, and Figure 8 clearly shows the effect

of pyrite content of the coal on conversions and liquid product yields during liquefaction. Conversions increased from about 50 to 70% using the hot-rod reactor with no added catalyst. Thus it would appear that pyrite can act catalytically in the dry hydrogenation reaction as well as in slurried reactions.

The results from the float/sink fractions (Figure 7) are more difficult to interpret because of the simultaneous variation of mineral matter and petrography (see Table 4). It could be that the increase in oil yield obtained with the higher mineral matter fractions is due to the increase in sulfur that varies from 0.5% in the 1.4 float to 9% in the 1.65 sink fraction. The significance as far as South African coals are concerned is that mineral matter does not necessarily mean poor performance during coal liquefaction. Evidence so far suggests that the mineral matter can be beneficial in increasing conversion and liquid product yields. From a processing viewpoint, high mineral matter can create other problems, and a trade off between possible catalytic benefits and engineering process difficulties must be arrived at.

SUMMARY:

For the South African bituminous coals studied so far the following conclusions can be made:

(i) Conversion data obtained from coal liquefaction under dry hydrogenation conditions and in the presence of anthracene oil show good correlations with the $^{H}/_{C}$ ratio, the volatile matter and the reactive maceral content of the coals.
(ii) For dry hydrogenation, excellent correlations are obtained between total liquid product and oil yield with the $^{H}/_{C}$ ratio and the volatile matter of the coals. The correlation of liquid product yield with reactive maceral content is not as good, but liquid product increases with an increase in reactive maceral content.
(iii) The pyrite in the coal, as estimated from the total sulfur, appears to act catalytically in the dry hydrogenation reaction and enhances the overall liquid yield.
(iv) It appears that as the severity of processing is increased, the importance of the coal characteristics themselves become less significant when considering overall conversion.

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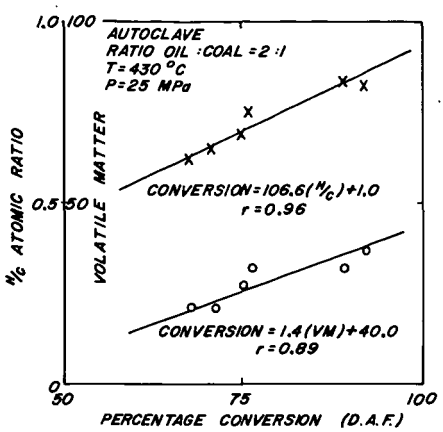

FIGURE 1 VARIATION OF THE PERCENTAGE CONVERSION (D.A.F.) WITH THE H/C RATIO AND VOLATILE MATTER OF THE COAL.

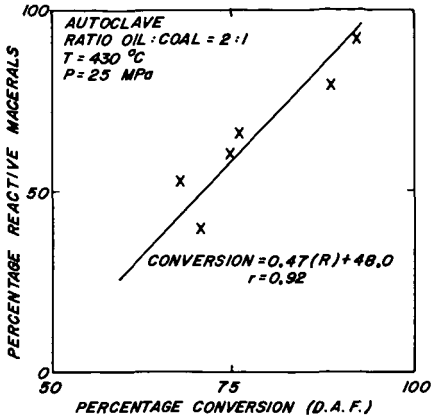

FIGURE 2 VARIATION OF THE PERCENTAGE CONVERSION (D.A.F) WITH THE REACTIVE MACERAL CONTENT OF THE COAL.

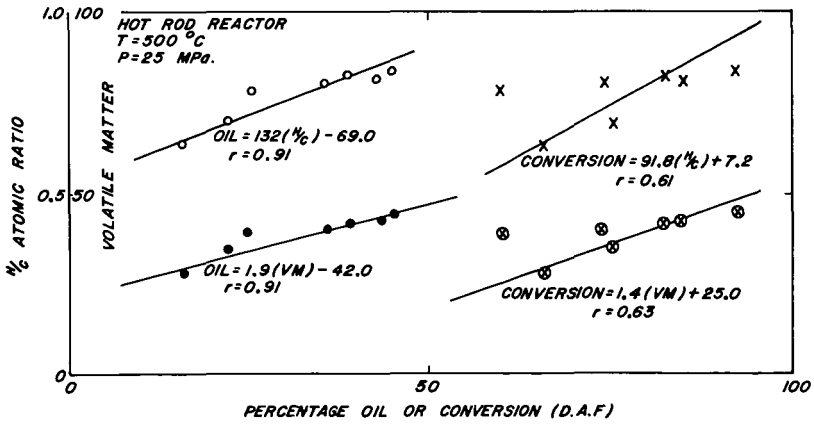

FIGURE 3 VARIATION OF THE PERCENTAGE CONVERSION AND OIL YIELD WITH THE VOLATILE MATTER AND THE H/C ATOMIC RATIO OF THE COAL.

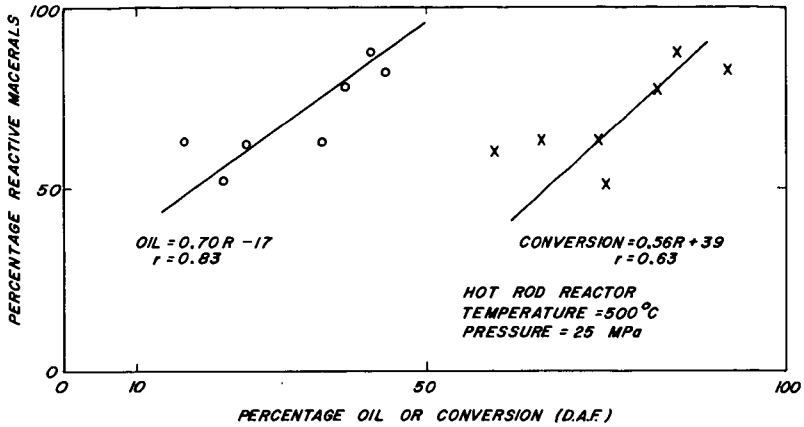

FIGURE 4 VARIATION OF THE PERCENTAGE CONVERSION AND OIL YIELD WITH THE REACTIVE MACERAL CONTENT.

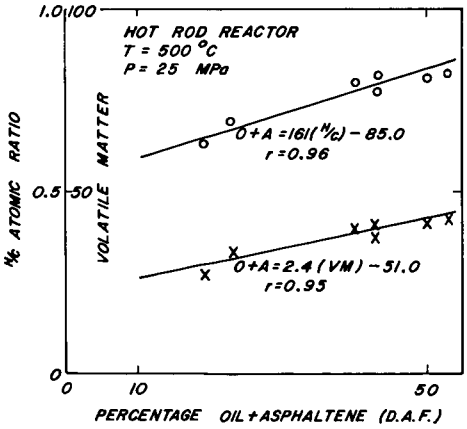

FIGURE 5. VARIATION IN THE OIL + ASPHALTENE YIELD WITH THE H/C RATIO AND VOLATILE MATTER OF THE COAL.

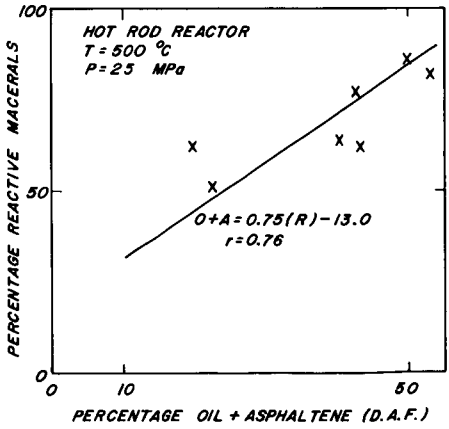

FIGURE 6 VARIATION IN OIL + ASPHALTENE YIELD WITH THE REACTIVE MACERAL CONTENT OF THE COAL.

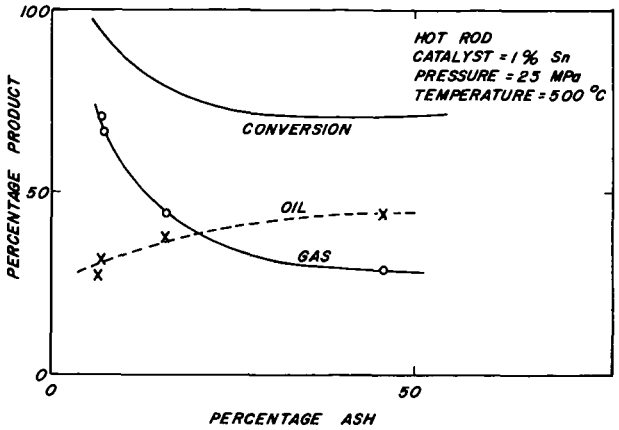

FIGURE 7 VARIATION IN PRODUCT DISTRIBUTION WITH ASH CONTENT FOR KRIEL COAL (0.149 mm / 0.074 mm)

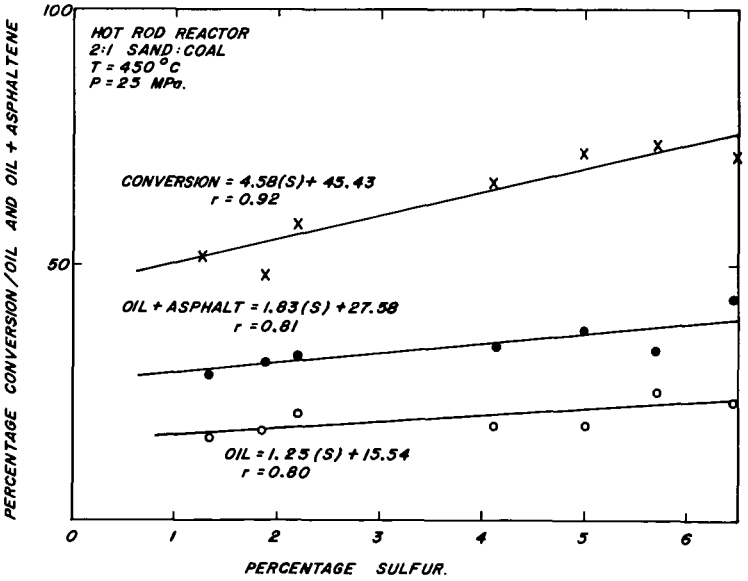

FIGURE 8 VARIATION IN CONVERSION, OIL AND OIL PLUS ASPHALTENE YIELD WITH SULFUR CONTENT.