A STRUCTURAL INVESTIGATION OF THE EFFECT OF CATALYSIS ON THE LIQUEFACTION PRODUCTS OF A BROWN AND A BITUMINOUS AUSTRALIAN COAL

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INTRODUCTION

The effect of catalysts on the donor solvent hydrogenation of Australian coals, both brown and black, have been investigated by a number of workers (1-5). However, these studies have concentrated mainly on obtaining conversion, oil yield, asphaltene and preasphaltene data, rather than emphasising chemical structural analysis of the resultant products. To solely use the forementioned criteria as a basis for catalyst evaluation can and may be misleading, as the product quality is an unknown parameter, which can give much insight into both the effectiveness and mechanism of catalysis.

The paper reports a study comparing the effects of a single catalyst, Co/Mo, on two Australian coals of different rank at their uncatalyzed optimal oil yield temperatures (4)(8)(9) under donor solvent conditions. It was considered more appropriate to compare the products from the two coals at their respective optimal oil yield temperatures rather than at the same temperature. The former accounts and compensates for differing thermal reactivities with rank, thereby allowing a direct comparison of product qualities to be made.

The coals used for the study were a Victorian brown coal, LY1277, from the Loy Yang Field, a medium-light lithotype, and a N.S.W. high volatile bituminous coal from the Liddell Field. They were chosen because of their known liquefaction potential. They were reacted at 375°C and 425°C respectively, in batch autoclaves using a solvent (tetralin) coal ratio of 2:1, a catalyst concentration of 10% w/w coal and were reacted for 2 hours at temperature.

The total liquid product (TLP) (defined as CH_2Cl_2 solubles) was fractionated by a separation method (6) designed specifically to separate by functionality into chemically defined classes *viz.* acids, bases and neutrals. This method utilizes a sequence of ion-exchange resins and silica adsorption chromatography. A feature of the method is that it does not remove the donor solvent until all the polar material is absent, hence alleviating the risk of thermal alteration of the samples as may occur with an initial dissolution step. The method is very effective in class separation.

The TLP, residues and the resulting fractions have been investigated by a number of analytical and spectroscopic methods in an attempt to use chemical analysis as a probe for investigating the effectiveness, mode of action, and structural dependence of the catalyst. Although the TLP has been fractionated into its component classes the majority of the data reported here concerns mainly the TLP and residue.

RESULTS AND DISCUSSION

The effect of the Co/Mo catalyst on the two coals, as judged by normal liquefaction criteria is shown in Table 1. In both cases conversion increased with catalysis,

however the oil yields for the catalyzed (C) Liddell run was lower than for the uncatalyzed (UC), run, the converse of the Loy Yang case. The oil yield for the uncatalyzed Liddell run was much better than for both the Loy Yang runs, with the catalyzed Liddel run being only slightly lower in yield than the catalyzed Loy Yang run. On a conversion basis the catalyzed Liddell run gave 92% conversion compared to 62% for the uncatalyzed run, and 75% and 60% for the catalyzed and uncatalyzed Loy Yang runs respectively. Hence, on an oil yield/conversion basis the coals exhibit different liquefaction behaviour. Catalytic liquefaction of Liddell markedly increases conversion, but decreases oil yield. The increased conversion is at the expense of increased H_2O production and gasification. The gases being predominantly hydrocarbons. To determine the effect of catalyst, as to whether it primarily increases oil yield and/or conversion, or actually upgrades the products, the ratio of the H_2O and gases to oil yield must be taken. Clearly the ratio of H_2O/oil yield and gas/oil yield is very similar for the Loy Yang runs (Table 1), while it is markedly different between the two Liddell runs. These data indicate that in the Loy Yang runs the catalyst is not removing heteroatoms or upgrading the product, but rather interacting only with the coal and assisting its dissolution. However in the Liddell case the marked increase in the two ratios indicates both cleavage of alkyl side chains and heteroatom removal (i.e. the product is being affected by the catalyst).

Elemental analysis (Table 2) gives credence to these initial conclusions with H/C and O/C ratios being marginally higher for the uncatalyzed Loy Yang oil than the catalyzed oil, but still very similar. Whereas, the Liddell runs show the converse *viz.*, increased H/C and much decreased O/C for the catalyzed compared to the uncatalyzed oil. Data on the oils (Table 3) shows the composition (% w/w oil) of the LY1277 oils to be very similar (similar percentages of the various acidic, basic and neutral materials). This adds further to the hypothesis that the catalyst is primarily increasing the yield of product rather than upgrading it. If the catalyst had acted on the oil it would not be unreasonable to expect differences in the composition of the oils. This is indeed shown with the Liddell oils, where the uncatalyzed oil has 75% of its material as acids and bases (25% and 50% respectively), whereas in the catalyzed oil over 75% of the material is neutral, with less than 16% being basic. It is observed that nearly 70% of the oil exists as nonpolar neutrals which are predominantly aliphatic and aromatic hydrocarbons (7), whereas in the uncatalyzed oil this fraction represents only 14%. This is in marked contrast to the LY1277 oils where their respective percentages of nonpolar neutrals is very similar, as is the percentage of polar neutrals. Obviously this data shows quite markedly that for the Liddell oils the catalyst is acting not only on the coal but also on the resultant product, upgrading it via loss of functionalities to produce hydrocarbon neutral material. This data reaffirms the trends shown by H_2O/oil yield and gas/oil yield ratios.

Spectroscopic and molecular weight data further confirms these trends. A comparison of IR spectra (Figs. 1, 2), using semi-quantitative methods reveals only a minor decrease in the -OH absorption for the catalyzed LY1277 oil, whilst there is a marked reduction in the same absorption in the catalyzed Liddell oil. This is reinforced by the analogous reduction in the H_{OH} as shown by ^1H nmr. The aromaticities as determined by ^{13}C nmr (Fig. 3) of both catalyzed oils increased marginally over their uncatalyzed counterparts, with both the Liddell oils being much more aromatic than the LY1277 oils.

^1H nmr has shown there to be a reduction in the amount of aromatic protons (Har) for the catalyzed compared to the uncatalyzed LY1277 oil, the converse occurred for the Liddell oils (Table 4). Similarly, the percentage of methylene protons (Ho) and hence average side chain length increased for the catalyzed LY1277 oil compared to the uncatalyzed oil, whereas there was a marked reduction in both for the catalyzed Liddell oil. This is not surprising considering the high yield of

hydrocarbon gases from the latter, most probably formed from side chain cleavage. This view is further substantiated by the increase in the percentage of protons or carbons α to aromatic rings ($H\alpha$) compared to the uncatalyzed Liddell oil. However, with the catalyzed LY1277 oil there is a marked reduction in the percentage of $H\alpha$. This observation and the increase in Ho suggests that the catalyst may be operating in either of two ways: (a) hydrogenating aromatic rings or (b) enhancing the cleavage and hence ring opening of naphthenic rings in the coal structure. It is more likely the latter is occurring as the former was not observed for the Liddell oil, which also contains aromatic rings, and the structure of brown coal is suggested as having a large proportion of naphthenic rings and arene systems (10). This mode of action of the catalyst is more consistent with the other data, suggesting it is operating on the decomposition and dissolution of the coal rather than upgrading the oil. Modified Brown-Ladner equations (11) showed the LY1277 oils to both have a similar degree of substitution, whereas the Liddell oils were much lower in value with the catalyzed oil being substantially lower than that for the uncatalyzed oil. This trend is also shown by the Har/Car ratio, from both the modified Brown-Ladner method and directly from ^{1}H and ^{13}C nmr, (cf. Table 4) where the degree of condensation is much reduced for the uncatalyzed compared to the catalyzed Liddell oil, which in turn is similar in value to the LY1277 oils

This is suggestive of the catalyzed Liddell oil having a smaller average ring size and hence molecular weight than the other oils. Molecular weight data proves this to be the case, with the catalyzed Liddell oil having a MW less than half that of the uncatalyzed oil (169 and 379 respectively). The latter is slightly less than that found for the LY1277 oils which in turn have similar MWs (498 for the uncatalyzed and 512 for the catalyzed oil).

The semi-quantitative IR data agrees very well with that from ^{1}H nmr. The aromatic C-H bending region in the IR increases only marginally for the catalyzed Loy Yang oil (Fig. 1) but is markedly increased for the catalyzed Liddell oil (Fig. 2). The differences in the relative amounts of -OH stretchings are also reaffirmed by the amount of -C-O- IR spectral intensity, with the Liddell oils being less than the LY1277 oils, and the catalyzed Liddell oil being markedly reduced in the amount of -C-O- stretching while the LY1277 is only marginally reduced. Similarly the ^{13}C nmr also agreed with the ^{1}H nmr data, indicating that the $C_{aliphatic}/C_{aromatic}$ ratio decreases quite markedly between the LY1277 and Liddell oils (Fig. 3), but only slightly between the uncatalyzed and catalyzed oil from the same coal.

IR investigations of the residues revealed that the contribution of aliphatic $-CH_2-$, $-CH_3$ bending regions were greater in the catalyzed than in the uncatalyzed residues. CP-MASS ^{13}C nmr of LY1277 catalyzed residue (Fig. 4) showed it to have a lower aromaticity than the uncatalyzed residue, but still higher than the parent coal. For the Liddell case, hower, both residues had the same aromaticity which again were higher than the parent coal. The data from the LY1277 residues indicates that the catalyst, may in fact be hydrogenating aromatic rings whilst dissolving the coal. Why this occurs only for LY1277 and not for Liddell may be due to the selectivity of the catalyst, displaying structural dependence for the chemically very different starting materials. The result is surprising considering the previous data on the oils and the similar aromaticities, but not if the differing structures of the two coals are taken into account.

Pyrolysis-Gas Chromatography of the residues and the parent coals reaffirms previous observations that the catalyst does alter the organic structure of the residues. A main observation is the loss of the alkane/alkenes in the catalyzed Liddell residue, while they are present in the uncatalyzed residue. This agrees with the marked increase in hydrocarbon gas production in the former. The pyrograms of the Loy Yang residues, although differing in some components between

uncatalyzed and catalyzed residues, are not dissimilar, differing mainly in relative quantities of components.

This paper has attempted to show that there are definite advantages and disadvantages associated with the catalytic/non catalytic liquefaction behaviour of coals possessing a wide variation in rank. The use of catalyst, while appearing to only increase the oil yield/conversion for Loy Yang coal, markedly upgraded the product from Liddell coal - thereby indicating a quite different mode of action (reflecting a structural dependence) in each case. The possibility that the mode of action and reactivity of the catalyst may be temperature dependent (as the oils were produced at two different temperatures) cannot be overlooked. It was not the purpose of this paper to investigate such a possible phenomena. Rather it was to show, and it clearly has, the problems that may arise in product quality and upgrading if the only criteria for liquefaction are oil yield and conversion based.

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TABLE 1: PRODUCT DISTRIBUTION

Sample	Conversion %	Oil[A] yield	H_2O[A] yield	Residue	Gas[A]	H_2O/oil yield	gas/oil yield
LY1277 (uncat.)	60.30	45.92	6.52	40.72	6.84	0.14	0.15
LY1277 (cat.)	74.63	55.89	8.02	25.37	10.37	0.14	0.19
Liddell (uncat.)	62.22	59.57	1.48	37.78	1.17	0.03	0.02
Liddell (cat.)	91.75	54.71	8.25	8.25	29.53	0.15	0.54

A - g/100 g DAF coal

TABLE 2: ELEMENTAL ANALYSES

Sample	C	H	O*	N	S	H/C	O/C	N/C	ASH
		(DAF)							
LY1277	65.66	4.48	31.34	0.80	0.20	0.819	0.358	0.010	<1.0
Liddell	80.1	5.9	10.90	2.03	1.0	0.883	0.102	0.022	28.1
Total Oils									
LY1277 (uncat.)	81.72	7.49	9.79	1.00	-	1.10	0.089	0.010	
LY1277 (cat.)	85.08	6.85	7.83	0.24	-	0.966	0.069	0.002	
Liddell (uncat.)	87.80	6.15	3.94	2.11	-	0.841	0.033	0.021	
Liddell (cat.)	90.71	6.53	1.53	1.23	-	0.863	0.013	0.015	
Residues									
LY1277 (uncat.)	80.13	4.98	16.93	1.05	-	0.746	0.159	0.011	3.0
LY1277 (cat.)	69.66	4.95	24.51	0.889	-	0.853	0.264	0.011	17.9
Liddell (uncat.)	82.73	4.85	9.97	2.45	-	0.704	0.090	0.025	25.6
Liddell (cat.)	63.18	4.64	29.38	2.81	-	0.881	0.349	0.038	72.6

*By difference

TABLE 3: CHEMICAL CLASS COMPOSITION OF TOTAL LIQUID PRODUCT (w/w % of oil)

Fraction*	LY1277		Liddell	
	Uncatalyzed	Catalyzed	Uncatalyzed	Catalyzed
A1	22.09	23.51	11.63	1.69
A2	0.86	0.68	2.72	1.91
A3	1.03	1.36	2.48	0.42
A4	6.72	5.62	2.48	0.84
A5	1.55	1.19	0.01	2.12
A6	1.38	1.87	2.72	1.06
B1	2.80	4.77	2.97	0.21
B2	9.00	9.03	50.50	15.25
TN	54.50	51.97	24.49	76.50
NPN	31.07	34.76	14.45	69.84
PN	23.43	17.21	10.04	6.66

A series - acidic fractions from resins
B series - basic fractions from resins
TN = Total neutrals, i.e., NPN + PN: NPN = Nonpolar neutrals;
PN = Polar neutrals.
*See Ref. 6.

TABLE 4: ^{1}H-NMR DATA ON TOTAL LIQUID PRODUCTS

	^{1}H nmr Data											Mw Data[b]	
Sample	H_O	H_α	H_{ar}	H_{OH}	$\frac{H_{ali}}{H_{ar}}$	$\frac{H_{ali}}{C_{ali}}$	$\frac{H_{ar}}{C_{ar}}$	f_a†	δG†	$\frac{H_{aru}}{C_{ar}}$†	n†	$\bar{Mn}$	$\bar{Mw}$
LY1277 (uncat.)	29.0	32.9	27.1	11.0	2.3	1.71	0.45	0.66	0.74	1.75[c]	1.88	498	1049
LY1277 (cat.)	39.6	28.1	22.6	9.6	3.0	2.24	0.35	0.67	0.74	1.23	2.41	512	997
Liddell (uncat.)	35.7	23.4	31.2	9.6	1.9	2.49	0.43	0.75	0.54	0.58	2.52	379	758
Liddell (cat.)	21.3	29.3	45.1	4.3	1.1	2.27	0.60	0.78	0.35	0.76	1.73	169	240

† - Brown Ladner Method of ^{1}H nmr data analysis
b - GPC-HPLC method for molecular weight determination
c - High values due to high O/H ratio

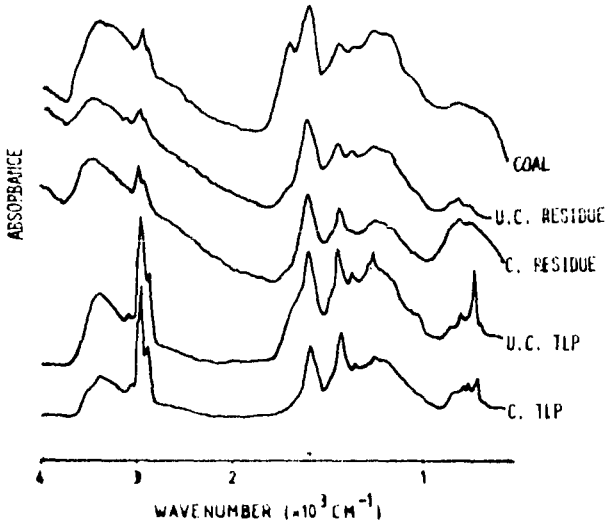

FIG. 1 I.R. SPECTRA OF LY1277 AND ITS LIQUEFACTION PRODUCTS

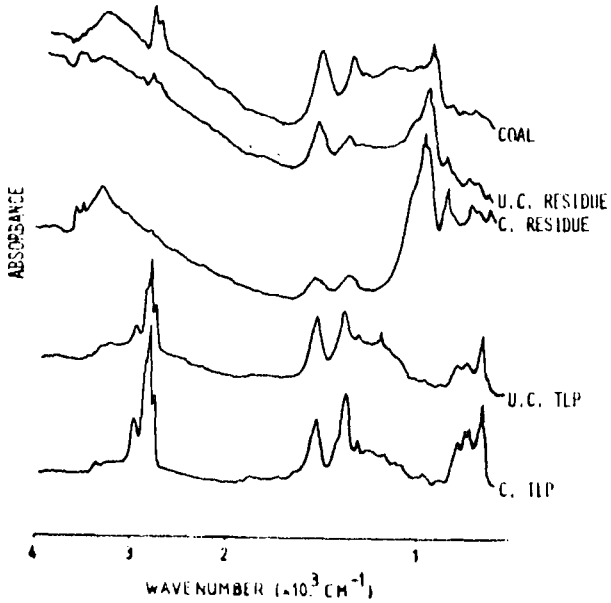

FIG. 2 I.R. SPECTRA OF LIDDELL AND ITS LIQUEFACTION PRODUCTS

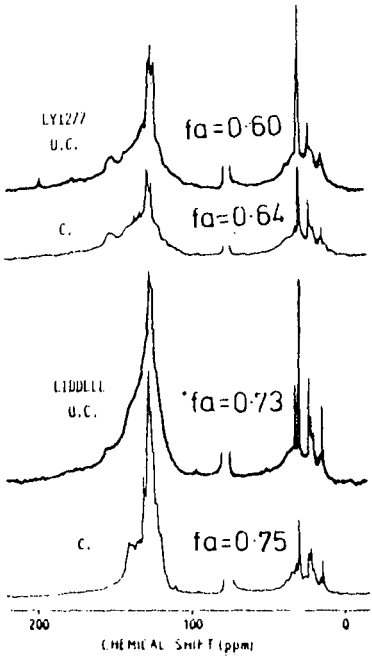

FIG. 3 25.0 MHz ^{13}C NMR OF TOTAL LIQUID PRODUCTS

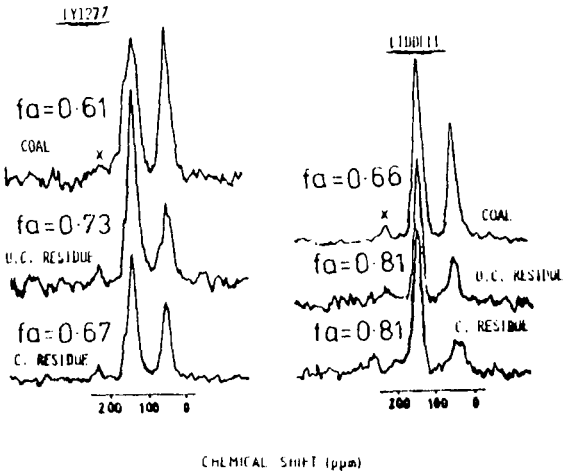

FIG. 4 SOLID STATE ^{13}C NMR OF COALS AND THEIR LIQUEFACTION RESIDUES