

## EVIDENCE FOR MACERAL SYNERGISM IN CATALYTIC HYDROPYROLYSIS AND HYDROGENATION OF A SUB-BITUMINOUS COAL

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### ABSTRACT

In order to investigate the possible synergistic effect of exinite on vitrinite conversion in both hydropyrolysis and batchwise (solvent-free) hydrogenation, experiments with and without a sulphided molybdenum catalyst have been conducted on maceral concentrates separated by density gradient centrifugation (DGC) from an Indonesian sub-bituminous coal. As anticipated, the conversions achieved with virtually pure exinite in both catalytic hydropyrolysis (520°C, 150 bar) and hydrogenation (400°C, 70 bar) are close to 100% daf coal. Without catalyst, there is no evidence of synergism in hydropyrolysis. However, with catalyst, the conversions achieved in both regimes with the fractions and blends containing between 25 and 50% exinite are higher than the predicted values (both pyridine and dichloromethane-solubles in hydrogenation).

### INTRODUCTION

Although it is now generally recognised that oil yields broadly increase with decreasing rank especially when retrogressive reactions for low-rank coals are avoided by having good contact between coal and solvent (1,2), these ideal circumstances are not realised under other conversion regimes. For example, in hydropyrolysis where there is no vehicle solvent to aid conversion, dispersed catalysts are much less effective for lignites and sub-bituminous coals (3) than for bituminous coals. In such instances, hydrogen transfer within the coal is going to be the crucial factor and, intuitively, this is going to be aided by having a high degree of fluidity and sufficient hydrogen-rich exinite. Indeed, it has been recognised that synergistic effects involving macerals may be evident in coal liquefaction and this has prompted a number of studies on maceral concentrates (4-6). Care is required in interpreting results since fine grinding normally required to prepare high purity maceral concentrates may induce oxidation. Nonetheless, as anticipated, conversions for exinite concentrates are generally much higher than those for vitrinite (4-6), but appreciable conversions to pyridine and THF-soluble material have been found for inertinite fractions, especially those rich in semi-fusinite (4,5). Further, conversions for whole coals have been found to be higher than those predicted from individual maceral yields suggesting that synergism occurs from the maceral associations within the coals (4,5). Indeed, the liquefaction residue from the vitrinite of one of these coals comprised mainly vitroplast which was not evident for the whole coal (4).

Although the above evidence strongly suggests that synergism between macerals can occur at a microscopic scale within coals, there is little information thus far on the influence of liquefaction conditions on the extent to which this phenomenon occurs. However, hydropyrolysis tests on handpicked durain and fusain samples from a UK bituminous coal have indicated that exinite only promotes vitrinite conversion in the presence of catalyst (3). In order to investigate this aspect further in both hydropyrolysis and batchwise (solvent-free) hydrogenation, experiments with and without a sulphided molybdenum (Mo) catalyst have been conducted on maceral concentrates separated by density gradient centrifugation (DGC) from an Eocene sub-bituminous coal from Indonesia. This coal has a high exinite and low inertinite content which facilitated the separation of relatively pure exinite and vitrinite fractions with + 400 mesh particles size required for hydropyrolysis to prevent the fixed-bed reactor plugging.

## EXPERIMENTAL

The Indonesian sub-bituminous coal was obtained from the US Geological Survey. The coal was crushed to -100 mesh, demineralised with hydrofluoric and boric acids (7) and dry screened to + 400 mesh. Maceral separation was based on the density gradient centrifugation (DGC) method developed by Dyrkacz and co-workers (8) with certain modifications (7). Briefly, the DGC separation involves forming a cesium chloride density gradient within a spinning, high capacity (2 dm<sup>3</sup>) centrifuge rotor. A demineralised coal/surfactant slurry is then dispersed across this gradient at forces ranging from 7,000 to 25,000 gravity. The procedure can be repeated numerous times with the corresponding fractions from repeat runs being combined to provide sufficient sample. In this study, two preliminary DGC runs were carried out on 16.2 g of sample. This provided a density profile curve to design a more efficient larger scale separation which was conducted on 225.1 g of coal in a series of 15 DGC runs, the recovery being 98.5%. The rotor effluent was divided into 12 density fractions plus the remaining sink fraction. The results of chemical and petrographic analysis on the initial coal and the fractions actually used in the hydropyrolysis and hydrogenation experiments are listed in Table 1.

For the hydrogenation and hydropyrolysis experiments with the sulphided Mo catalyst, the maceral concentrates and their blends were impregnated with ammonium dioxodithiomolybdate in methanol solution to give a Mo loading of 1%. The fixed-bed hydropyrolysis apparatus in which the reactor tube is heated resistively has been described previously (3,9). A temperature of 520°C and a pressure of 150 bar were chosen as the standard test conditions to optimise both the tar yield and selectivity (% tar/% gas) in catalytic hydropyrolysis (3,9). To simplify the mass balances, dried coals were used (50°C *in vacuo* for 1 hr.). Tests were carried out on 2-5 g of sample which was mixed with of sand (1:2 mass ratio) to prevent blockages and to enable the reactor tube to be emptied easily. The reactor were heated at 5°C s<sup>-1</sup> and held at 520°C for 10 minutes with a hydrogen flow rate of 10 dm<sup>3</sup> min<sup>-1</sup> (measured at atmospheric pressure and ambient temperature) which was sufficient to overcome mass transfer. Char yields were determined from the weight loss of the reactor tube and tar yields from the weight gain of the dry-ice cooled trap. Tar was recovered for analysis by washing the trap thoroughly with dichloromethane (DCM).

The hydrogenation experiments were carried out in a 9/16" O.D. microautoclaves (*ca* 10 cm<sup>3</sup> internal volume) constructed of Autoclave Engineer high pressure fittings. 0.3 g of sample was loaded into the microautoclave which was pressurised to 70 bar with hydrogen. The sandbath at 400°C was raised to fully submerge the microautoclave for 60 min., the heat-up period being *ca* 5

min. After reaction, the microreactor was cooled in dry-ice before de-pressurising. The reactor contents were then recovered by filling the microreactor with dichloromethane (DCM) and placing it in an ultrasonic bath. The DCM washings were refluxed for *ca* 5 hours, filtered through phase separating paper and then the DCM-solubles were recovered by evaporating the filtrate to dryness. The DCM-insolubles were weighed after drying *in vacuo* and were then refluxed in pyridine for *ca* 5 hours and filtered to determine the yield of pyridine-insolubles.

## RESULTS AND DISCUSSION

### Hydropyrolysis

Figure 1 shows the effect of exinite concentration on conversion in hydropyrolysis with and without catalyst for the maceral concentrates and one of their blends. As anticipated, the conversion achieved with virtually pure exinite (fraction 1) in catalytic hydropyrolysis is close to 100% daf coal. Without catalyst, there is no evidence of synergism with the conversions lying close to the predicted values from those obtained with virtually pure exinite and the concentrates containing 90% vitrinite (fractions 5 and 6, Figure 1). However, with catalyst, the conversions achieved with the fractions containing between 25 and 50% exinite generally appear to be higher than the predicted values; above 50% exinite, the experimental error of  $\pm 1-2\%$  is greater than the differences anticipated making synergistic effects more difficult to identify. Since the two fractions, 5 and 6 which both contain *ca* 90% vitrinite give conversions differing by 5% daf coal, it is difficult to deduce a baseline conversion for vitrinite. Further, synergism may be evident within these fractions as they contain 10% exinite (Table 1). However, the fact that the conversion with catalyst for the 50:50 blend of fractions 1 and 6 is higher by 5% daf coal than that predicted from the individual conversions confirms that the effect is real.

### Hydrogenation

Figure 2 presents the yields of DCM-soluble product and pyridine-insolubles obtained in catalytic hydrogenation using essentially the same fractions and, again, there is clear evidence of synergism. The fact that it is evident in both the yields of DCM-soluble oil and pyridine-insolubles indicates that both the initial dissolution process and subsequent hydrocracking of the primary dissolution product are affected. Indeed, the synergistic effect is somewhat more pronounced than in catalytic hydropyrolysis possibly due to the longer residence time and the more effective contact between exinite and vitrinite in catalytic hydrogenation.

### General discussion

The synergistic effects reported here are perhaps more evident than in hydroliquefaction where the presence of a vehicle solvent aids hydrogen transfer. Clearly, in both batchwise hydrogenation and hydropyrolysis, the exinite plays a crucial role in transferring hydrogen atoms from the catalyst sites to the depolymerising coal probably because it forms a fluid pyrobitumen in the early stages of conversion. For hydropyrolysis, the general trends found here are the same as those reported previously for a UK bituminous coal containing 87% dmmf C<sup>(3)</sup>. However, the reasons why lower conversions than anticipated are obtained in catalytic hydropyrolysis for the higher rank bituminous coals and most of the low-rank coals investigated thus far<sup>(3)</sup> are somewhat different. The low-rank coals do not soften to an appreciable extent and there is probably insufficient pyrobitumen generated in the early stages of conversion to prevent retrogressive reactions occurring which probably involve dihydric phenolic moieties. For the bituminous coals containing more than *ca* 84% dmmf C, the hydrogen requirement required for hydrogenating the aromatic structures is likely to be higher than for their lower rank counterparts and, despite the development

of plasticity at some stage during conversion, there is still insufficient hydrogen transfer capability to prevent retrogressive condensation reactions occurring.

### ACKNOWLEDGEMENTS

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**Table 1** Elemental, proximate and petrographic analysis of maceral concentrates

	Parent coal	Maceral fraction						
		1	2	3	4	5	6	
Density range, g cm <sup>-3</sup>		1.12- 1.15	1.15- 1.18	1.20- 1.25	1.25- 1.26	1.26 1.27	1.27- 1.28	
% moisture		1.5	0.6	0.9	1.5	1.8	2.3	1.9
% ash, dry basis		0.4	1.4	1.2	0.7	1.0	0.6	1.3
% V.M., daf basis		58.9	67.0	65.0	55.9	51.0	49.6	48.3
% dmmf	C	79.2	80.1	80.2	78.5	77.0	76.5	76.6
	H	7.2	8.2	7.9	6.8	6.4	6.1	6.0
	N	0.6	0.6	0.9	0.6	0.7	0.7	0.7
% dmmf	Exinite	39.8	97.8	95.2	52.6	22.4	10.0	9.8
	Vitrinite	54.4	1.8	3.4	46.8	77.2	89.4	89.0
	Inertinite	5.6	0.4	1.2	0.6	0.4	0.6	1.2

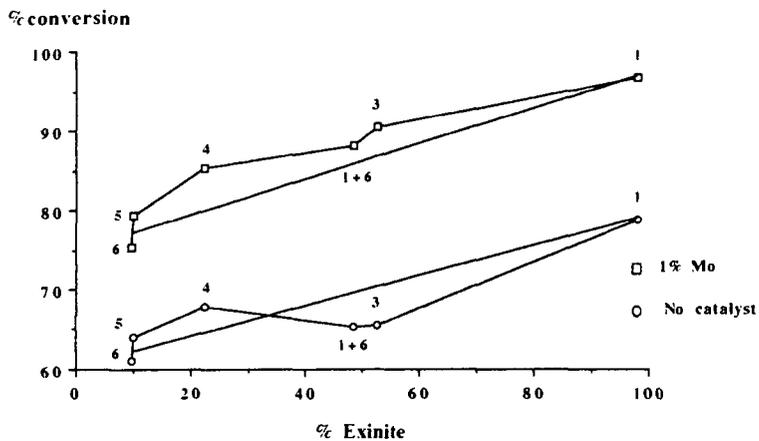


Figure 1. Effect of exinite concentration on hydrolysis conversions using maceral concentrates

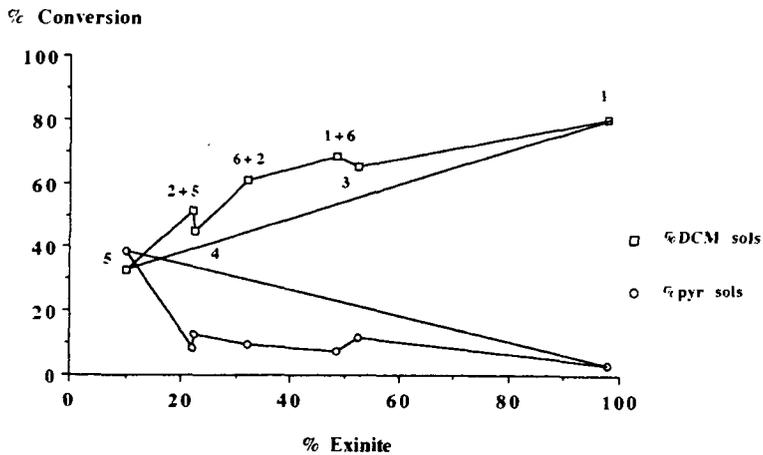


Figure 2. Effect of exinite on catalytic hydrogenation yields using maceral concentrates