

EXTRACTION OF AUSTRALIAN COALS WITH SUPERCRITICAL WATER

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INTRODUCTION

The extraction of coals with supercritical fluids is a promising route for the production of liquid fuels and chemical feedstocks from coal. Generally, hydrocarbon solvents, notably toluene, have been used as the supercritical fluid. Supercritical water extraction has not received the same attention and only recently the first detailed study was reported. In that work, Holder et al. (1) obtained high conversion for extraction of a German brown coal and a Bruceston bituminous coal with supercritical water at ca. 375°C and 23 MPa. They reported conversions of 70-75% for the brown coal and ca 58% for the bituminous coal, when the coal was injected into the reactor. However, the conversion was lower (ca 58% for the brown coal) when the coal was present during the heating-up period. These high yields contrast with the work of Scarrah (2), who obtained a conversion of approximately 35% and a liquid yield of only about 10% for the extraction of a North Dakota lignite at 400°C and 28 MPa, while Holder et al. also obtained very low conversion with a high sodium lignite (1). In other brief reports (3-5) on the extraction of bituminous coals with supercritical water, conversions were considerably less than produced with the Bruceston coal (1). However, the conditions used in at least one of these studies (4) were not ideal for supercritical water extraction as the solvent density was relatively low. Nevertheless, there appears to be considerable variation in the extractive power of supercritical water with different coals. None of the above reports discussed in any detail the chemical nature of the products, nor how the products compare with those obtained from more conventional solvents.

The potential use of supercritical water appears especially attractive for the extraction of brown coals with their high water content, 50-70% for Victorian brown coals, thus removing the need for a coal-drying stage. The drying and extraction of these low rank coals would occur in a single process. The purpose of the present study was to investigate the feasibility of the extraction of Australian black and brown coals with supercritical water. The chemical nature of the products is discussed together with a comparison with toluene extraction of the same coals.

EXPERIMENTAL

The analyses of the coals used are given in Table 1.

Supercritical gas extractions

Method A Extractions were carried out for 1 h at temperature in a 1 l semi-continuous reactor (6). The reactor was charged with coal (50 g dry basis) and solvent (600 ml) and heated. When the temperature reached 300°C, solvent (1 l h⁻¹) was pumped via a dip tube, which acts as a pre-heater, into the bottom of the reactor and through the coal bed. The pressure was controlled by adjusting throttling valves and the gaseous phase was condensed by a water-cooled condenser.

For the toluene extractions, the work-up procedure was as described previously (6). For the water extractions, most of the extract is insoluble in water, after cooling and lowering of the pressure, and precipitates out in the condenser and receiver. The product adhering to the sides of the condenser and receiver was collected by washing with acetone and then THF. The aqueous suspension was evaporated to dryness on a rotary evaporator and the residue extracted with acetone and THF. The solvents were removed under reduced pressure from the combined acetone and THF solutions to give the total extract (liquid product). In calculating the conversion figures, any product which was insoluble in THF was assumed to be unreacted coal, which had been carried over. The liquid product was extracted with hot toluene and the cooled solution filtered to give the pre-asphaltene fraction. After the toluene was removed under reduced pressure from the filtrate, the residue was re-dissolved in a small volume of toluene and a 20 fold excess of pentane added to precipitate the asphaltene which was filtered off. The pentane and toluene were then removed from the filtrate under reduced pressure to give the oil. For the NaOH extractions, the NaOH solutions were neutralised with HCl. The insoluble extract was washed with water and then extracted with THF.

Method B Extractions were carried out in a 500 ml rocking autoclave fitted with a stainless steel liner. The internal volume of the autoclave with liner was 420 ml. The autoclave was charged with coal and solvent, heated to 380°C and maintained at that temperature for 1 h. The residue was washed out of the cooled reactor with acetone, filtered, washed with pyridine and then acetone and dried under vacuum. In some cases, g.c. analyses of the gases in the cooled reactor were carried out.

Analytical procedures for the products were as described previously (7).

RESULTS AND DISCUSSION

Good conversions were obtained for extraction of a number of Victorian brown coals at conditions (380°C and 22 MPa) close to the critical temperature (374°C) and pressure (22 MPa) of water (see Table 2). The conversion increased as the volatile matter content of these coals increased (see Fig. 1). Similar trends were also obtained for toluene and 5% tetralin/toluene extraction. The highest conversions were obtained for the two pale lithotypes (F and G). These were slightly lower than obtained by Holder et al. (1) for extraction of a high volatile German brown coal and may be due to differences in the extraction procedure. Except for the low ash Loy Yang coal, data for the brown coals are given on a dry mineral and inorganic free (dmif) basis which is the preferred basis for recording data on these coals (8). The conversions were not as high for Millmerran (sub-bituminous) and Liddell (bituminous) coals (see Table 2). Holder et al (1) only obtained high conversions for extraction of Bruceton coal with high reactor stirrer speeds which were not possible with our reactor. The conversion and liquid yield data in Table 2 are the average of duplicate determinations. Average variation between the duplicates was 1.8%. The asphaltene and pre-asphaltene contents of the liquids are high (see Table 2), as is the case with supercritical gas extraction using hydrocarbon solvents. Two of the coals, Morwell and Yallourn were as-mined samples that had not been dried and were broken into small pieces for the extraction. The promising results obtained with these coals indicates the feasibility of extracting 'wet' brown coals with supercritical water.

Extractions of two of the coals, Loy Yang and Coolungoolun, were also

carried out in a rocking autoclave (method B) mainly to allow analysis of the gases to be carried out. The results of these extractions are shown in Table 3. The high carbon dioxide yields obtained, especially from Loy Yang coal, were indicative of the high carboxylic content of the brown coals. The hydrocarbon gas make was low as was the yield of carbon monoxide. Studies of the pyrolysis of Victorian brown coals have shown that significant quantities of water are evolved together with the carbon dioxide (9). The loss of water (and also hydrogen sulphide in the case of Coolungoolun coal) presumably accounts for some of the difference between the conversion figures and the sum of the extract yield and the gas figures in Table 3. The carbon dioxide yield was noticeably lower on extraction of Coolungoolun coal, which has the lowest oxygen content of the seven brown coals, than for extraction of Loy Yang coal.

Chemical Nature of the Product

Analytical data for the oils, asphaltenes and pre-asphaltenes from the various extractions are summarised in Table 4. There appeared to be little difference between the liquids produced from the coals A-E under the same conditions (380°C, 22 MPa). This is not surprising considering the similarity between the coals (see Table 1). The liquids have a high oxygen and hydroxyl content, especially in the asphaltene and pre-asphaltene fractions, in keeping with the high oxygen content of these coals. The H/C atomic ratio of the oils, asphaltenes and pre-asphaltenes are higher than for most coal liquids.

¹³C-NMR spectra showed the presence of substantial amounts of unsubstituted alkyl chains, with a chain length of more than eight carbon atoms, in both the oils and asphaltenes by strong signals at ca 14, 23, 32, 29 and 29.5 ppm, which are due to the respective α , β , γ , δ and ϵ carbons (10). Weak signals at ca 178 ppm indicated the presence of COOH groups in the oils and asphaltenes.

Analytical data on the residues from four extractions are given in Table 5. The high calorific value of the extraction residues indicates that they should be attractive materials for combustion.

¹³C CP-MAS NMR spectra were recorded for Coolungoolun coal and for the residue from extraction of this coal with supercritical water. The major difference between the two spectra was a much more intense aliphatic peak centered at 30 ppm in the spectrum of the starting coal. The decrease in the intensity of the aliphatic signal on processing is in agreement with the aliphatic nature of the liquid product especially the presence of long methylene chains in the oil and asphaltene. These methylene chains contribute significantly to the peak at 30 ppm in the starting coal (11).

The extraction of Coolungoolun coal with supercritical water can be summarised as:-

Coal H/C=0.87 $f_a = 0.62$	H ₂ O 380°C ⁺ 22 MPa	Char, 57.6%, H/C=0.60, $f_a=0.84$
		+
		Pre-asphaltene, 7.6%, H/C=0.96, $f_a=0.79$
		+
		Asphaltene, 5.3%, H/C=0.99, $f_a=0.66$
		+
Oil, 13.2%, H/C=1.35, $f_a=0.47$		
+		
CO ₂ , 9.7%		

(This shows the major products. The amount of CO₂ produced was assumed to be the same using the semi-continuous reactor (method A) as using the rocking autoclave (method B).)

The effect of pressure and temperature

The conversion and liquid yield both increase considerably as the pressure increases (see Fig. 2). The asphaltene and pre-asphaltene content of the liquids also increase with pressure (compare 5,6 and 7 in Table 2). The H/C atomic ratios of the oil and asphaltene fractions decrease, while the hydrogen and carbon (for the oil) aromaticities increase (see Table 4) with increasing pressure. This presumably indicates that the more aliphatic products are extracted preferentially.

Extractions of Gelliondale coal were carried out at 380°C, 420°C and 460°C. There were only small differences between the conversions, liquid yields and nature of the products at these various temperatures (compare 2, 3 and 4 in Tables 2 and 4). This is somewhat surprising as it was expected, especially in light of the recent work of Holder et al. (1), that the highest conversion would occur at the highest water density, namely at 380°C. However, this was not the case. Possibly, increased thermal fragmentation of the coal compensates for the decrease in the extractive powers of the supercritical water as the temperature is increased.

Generally, raising the temperature increases the aromaticity of coal liquefaction products. However, there were no significant changes in either the H/C atomic ratios or the hydrogen aromaticities (see Table 4) of the oils, asphaltenes or pre-asphaltenes with temperature. The most noticeable change in the liquid product with temperature was a slight decrease in the pre-asphaltene content. The results in Table 6 do, however, suggest that there is a trend towards decreasing H/C ratio of the extraction residue with temperature.

Comparison between toluene and water extractions

At 380°C and 22 MPa, the conversions for the brown coals were considerably higher but for black coals slightly lower for extraction with water than with toluene (see Table 2 and Fig. 2). The difference between coals of various rank is further shown by extraction with water/toluene mixtures of a brown, a sub-bituminous and a bituminous coal at a constant gas density in a rocking autoclave. The presence of water was more advantageous for the extraction of the brown coal than for the higher rank coals (see Fig. 3), though in all cases the presence of water increased conversion. The highest conversions were obtained for mixtures of the two solvents. The difference between the liquid yields from water and toluene extractions was less pronounced than between the conversions. Extraction with water is more pressure dependent than with toluene (see Fig. 2).

Although the oils are similar, there are significant differences in the composition of the toluene and water extracts of Gelliondale coal at 380°C and 22 MPa (compare 1 with 2 in Tables 2 and 4). The oxygen content of both the asphaltene and the pre-asphaltene as well as the pre-asphaltene content are significantly higher in the water extract than in the toluene extract. It is also noticeable that the asphaltene from the water extraction has a lower H/C atomic ratio and molecular weight but a higher hydroxyl content and

aromaticity than the asphaltene from the toluene extraction. This work is unable to explain whether the differences between the water and toluene extracts are due to the supercritical water extracting more polar substances from the coal, or whether reactions occur between the coal fragments and supercritical water which give rise to the high oxygen content of the extract.

Extraction with alkali and tetralin/water mixtures

A considerable increase in conversion of Morwell brown coal occurs when dilute sodium hydroxide was used in place of water (see Table 6 and Fig. 4). Dilute sodium carbonate and formate had a similar effect (see Table 6). The conversion and liquid yield increases with the molarity of the sodium hydroxide (Fig. 4). The dissolution of low rank coals by sodium (or potassium) hydroxide solutions has been previously documented (11-13) and; therefore, an increase in conversion was expected. It is noticeable that the increase in liquid yield is mainly due to an increase in the pre-asphaltene fraction (Fig. 4). The composition of the oils and asphaltenes from the sodium hydroxide extractions appear similar to those obtained from water extraction but the pre-asphaltenes from the alkali extractions have lower H/C ratios and high hydrogen aromaticities than from water extraction.

Increase in conversion is also obtained with tetralin/water mixtures (see Table 6) in an analogous manner to the increased conversion with the addition of small amounts of tetralin to toluene (6 and Fig.1).

CONCLUSIONS

This study indicates that extraction with supercritical water could be an attractive route for liquefaction of Victorian brown coals. The low cost and ready availability of the solvent (water), the relatively high H/C ratio of the extracts, and also as neither hydrogen nor a coal-drying stage are required, are positive factors.

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Table 1 Analyses of coal used

	(A)	(B)	(C)	(D)	E	F	(G)	(H)	(I)
	Loy Yang	Gelliondale	Coolungoolun	Morwell	Yallourn	Morwell	Yallourn	Millmerran	Liddell
Moisture	10.8 ^a	7.3 ^a	11.5 ^a	52.6 ^a	65.0 ^a	56.5 ^a	57.2 ^a	4.9 ^a	3.3 ^a
Ash	0.6 ^b	4.5 ^b	2.2 ^b	2.7 ^b	1.3 ^b	3.7 ^b	1.6 ^b	18.1 ^b	29.0 ^b
Minerals and inorganics		1.8 ^b	2.0 ^b	1.6 ^b	1.0 ^b	2.0 ^b	1.3 ^b		
Volatile matter	48.3 ^c	51.4 ^d	48.9 ^d	50.2 ^d	51.7 ^d	56.0 ^d	61.2 ^d	50.7 ^c	44.6 ^c
C	71.0 ^c	66.5 ^d	70.7 ^d	69.6 ^d	67.3 ^d	71.5 ^d	71.2 ^d	79.0 ^c	80.6 ^c
H	4.8 ^c	4.7 ^d	5.1 ^d	5.0 ^d	4.7 ^d	5.8 ^d	6.2 ^d	6.3 ^c	6.0 ^c
N	0.6 ^c	0.6 ^d	0.5 ^d	1.2 ^c	2.1 ^c				
S	0.3 ^c	0.8 ^d	4.1 ^d	0.3 ^d	0.2 ^d	0.7 ^d	0.2 ^d	0.7 ^c	0.4 ^c
O (by difference)	23.3 ^c	27.4 ^d	19.5 ^d	24.5 ^d	27.2 ^d	21.4 ^d	21.9 ^d	12.8 ^c	10.9 ^c
H/C atom. ratio	0.81	0.85	0.87	0.86	0.84	0.97	1.04	0.96 ^c	0.89

^a wt%; ^b wt% dry basis; ^c wt% dry ash free basis; ^d wt% dry mineral and inorganic free (dmif) basis.

Table 2 Conditions, conversions, liquid yields and product distribution for extraction of Australian coals using a semi-continuous reactor (method A)

Extraction No.	Coal	Solvent	Temperature (°C)	Pressure (MPa)	Conversion	Liquid Yield	Oil	Asphaltene	Pre-asphaltene
1	Gelliondale	Toluene	380	22	33.6	17.5 ^b	7.9 ^b	5.8	3.8
2	Gelliondale	Water	380	22	52.7	22.6	9.0	6.5	7.1
3	Gelliondale	Water	420	22	56.7	23.1	10.7	6.4	6.0
4	Gelliondale	Water	460	22	57.2	20.5	9.4	6.3	4.8
5	Loy Yang	Water	380	7	22.8 ^a	5.7 ^a	3.7 ^a	1.2 ^a	0.8 ^a
6	Loy Yang	Water	380	15	38.6 ^a	13.7 ^a	8.1 ^a	3.0 ^a	2.6 ^a
7	Loy Yang	Water	380	22	51.1 ^a	25.5 ^a	11.3 ^a	6.5 ^a	7.7 ^a
8	Coolungoolun	Water	380	22	42.4	26.1	13.2	5.3	7.6
9	Morwell	Water	380	22	51.7	22.7	9.8	5.7	7.1
10	Yallourn	Water	380	22	54.4	25.1	9.4	5.6	9.8
11	Morwell Pale	Water	380	22	57.6	32.0	13.5	8.8	9.7
12	Yallourn Pale	Water	380	22	67.3	44.0	16.9	11.1	16.0
13	Millmerran	Toluene	380	22	38.8 ^a				
14	Millmerran	Water	380	22	34.7 ^a				
15	Liddell	Toluene	380	22	30.4 ^a				
16	Liddell	Water	380	22	25.5 ^a				

(wt% coal dmif)

^a daf basis not dmif; ^b corrected for bibenzyl formed on toluene pyrolysis

Table 3 Conversions and products from extraction of Victorian brown coals (25 g) with water (137 g) in a rocking autoclave (method B) at 380°C.

Coal	Pressure	Conversion	Liquid Yield	CO ₂	CO/air	CH ₄ /C ₂ H ₆ /C ₃ H ₈
(wt% coal)						
Loy Yang	24	45.6 ^a	21.7 ^a	16.9 ^a	0.3 ^a	0.4 ^a
Coolungoolun ^c	23	39.8 ^b	21.3 ^b	9.7 ^b	0.9 ^b	0.7 ^b

^a daf; ^b dmif; ^c phenols (0.19%), acetone (0.23%), methanol (0.05%) and ethyl methyl ketone (0.05%) were also formed.

Table 5 Analytical data for extraction residues

Extraction No.	2	3	4	8
Moisture (wt%)	10.8	10.6	9.8	6.0
Ash (wt% dry basis)	8.9	9.2	9.4	3.6
Volatile Matter (wt% dry basis)	31.7	27.1	21.6	26.6
C (wt% dry basis)	71.8	73.9	76.2	76.3
H (wt% dry basis)	3.6	3.5	3.2	3.8
N (wt% dry basis)	0.7	0.7	0.7	0.7
S (wt% dry basis)	0.9	0.9	0.8	3.7
H/C atom. ratio	0.60	0.57	0.50	0.60
Specific energy (MJ/kg, dry basis)	27.5	28.1	28.9	30.4
Aromatic carbon (% C)				84

Table 6 Conversions for extraction of Morwell coal (15 g dry) in a rocking autoclave (method B) with aqueous solvents (150 g) at 380°C

Solvent	Conversion (wt% coal dmif)
Water	48.7
0.5 M NaOH	66.6
0.25 M Na ₂ CO ₃	63.8
0.5 M HCOONa	67.0
10% Tetralin/Water	55.3
20% Tetralin/Water	59.8

Table 4 Analyses of Liquid Products

Extraction No.	1	2	3	4	5	6	7	8	9	10
<u>Oil</u>										
H/C	1.40 ^b	1.41	1.40	1.38	1.48	1.45	1.41	1.33	1.34	1.37
O (wt%) ^a	9.2 ^b	9.5	10.0	10.8	9.5	7.2	7.2	(9.3)	7.7	9.3
OH (wt%)	4.1 ^b	5.1	4.4	4.8	4.2	3.4	2.6	3.7	4.4	4.7
Mol. Wt.	285 ^b	271	295	287	287	263	243	314	291	287
Aromatic H (%)	16 ^b	17	18	18	13	15	17	17	18	17
Aromatic C (%)	40 ^b	44				41	44	47		
<u>Asphaltene</u>										
H/C	1.23	1.07	1.09	1.08	1.26	1.13	1.07	0.99	1.02	1.11
O (wt%)	13.5	19.4	16.4	17.9	17.4	19.4	16.9	(18.3)	14.9	18.5
OH (wt%)	7.2	10.3	10.0	11.6				9.3	9.2	10.1
Mol. Wt.	470	374	349	350	332	368	393	415	369	323
Aromatic H (%)	28	36	35	36	27	33	36	34	32	33
Aromatic C (%)	53	69						66		
<u>Pre-asphaltene</u>										
H/C	0.88	1.03	0.99	0.97				0.96	0.93	0.93
O (wt%)	14.8	19.6	17.1	16.9				(21.1)	17.1	19.7
OH (wt%)								8.3		
Mol. Wt.								469		
Aromatic H (%)								45	42	43
Aromatic C (%)								79		

^a oxygen figures are by direct determination except for those in parenthesis which are by difference; ^b corrected for bibenzyl

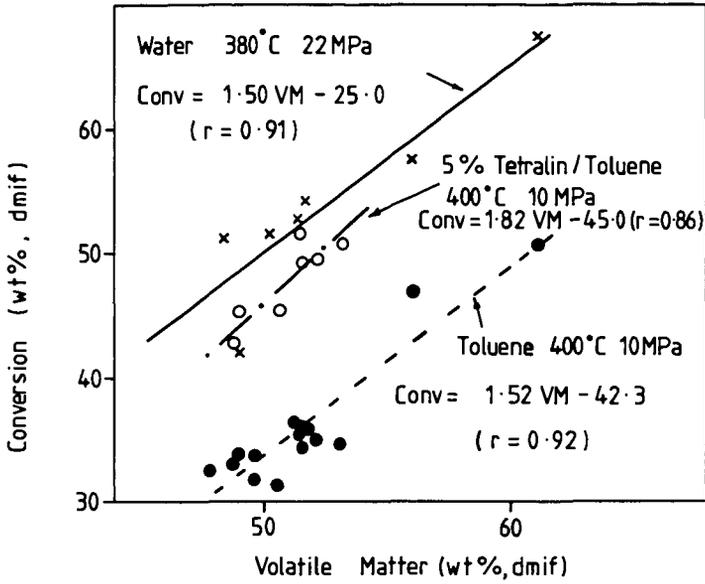


Fig.1 Variation in Conversion with Volatile Matter Content of Victorian Brown Coals

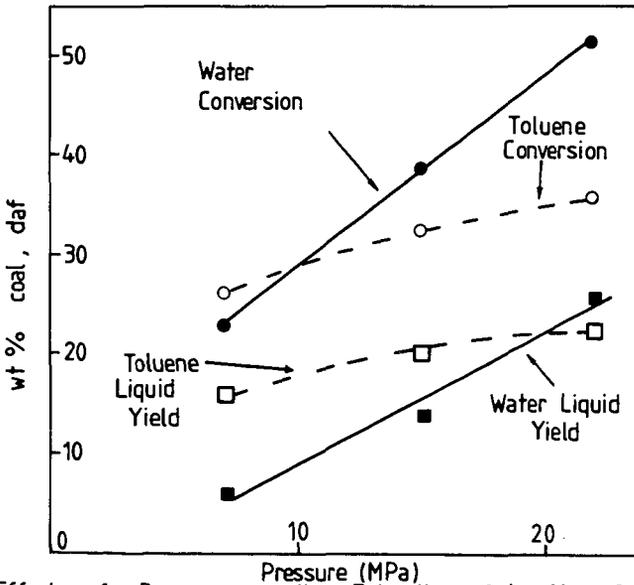


Fig. 2 Effect of Pressure on the Extraction of Loy Yang Coal at 380°C

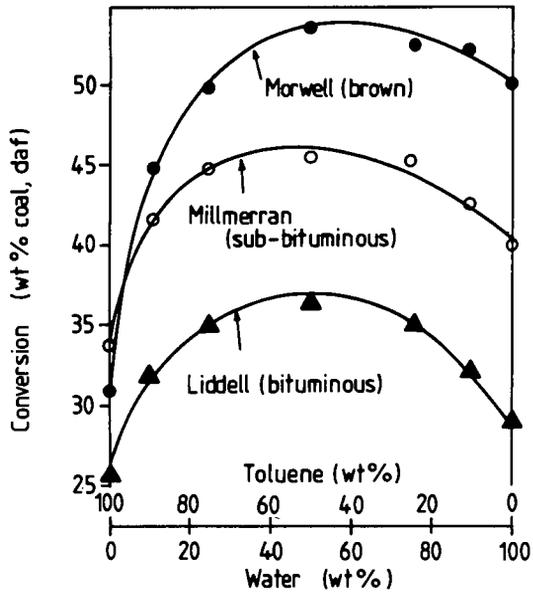


Fig. 3 Extraction with Toluene / Water Mixtures in a Rocking Autoclave at 380°C and a Gas Density of 0.44g/ml.

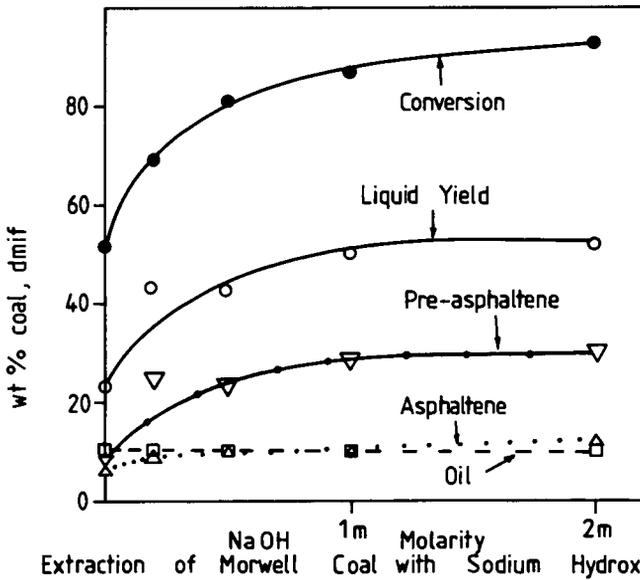


Fig. 4 Extraction of Morwell Coal with Sodium Hydroxide