TRACE ELEMENT REDUCTION IN FILTERED COAL EXTRACT SOLUTIONS USING SOLVENT PRECIPITATION

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INTRODUCTION

In two-stage coal liquefaction processes the coal is digested in a solvent in the first stage and then hydrocracked in the second stage in order to increase the hydrogen to carbon ratio and the yield of distillate material. At some point in the process mineral matter and undissolved residual material must be removed, and the processes used for this step are usually filtration or solvent deashing, with the latter taking the form of anti-solvent or critical solvent deashing. The deashing step can occur either between the first and second stages or after the second stage [1]. The major advantage of deashing before the second stage is that it reduces catalyst deactivation during hydrocracking due to both carbon deposition and trace element deposition as reported by Stohl and Stephens[1]. However, even when deashing occurs before the second stage, deactivation of the catalyst still occurs due to both carbon and trace element deposition [1-6]. In the case of carbon deposition the cause is not known, although there is some evidence linking high molecular weight species to carbon deposition [1,7]. With trace elements none of the deashing processes in use is completely effective and, therefore, some trace elements go forward to the hydrocracking stage.

The British Coal process is a two-stage process with filtration as the deashing step occuring between the digestion and hydrocracking stages [8]. Previous work in this laboratory using Point of Ayr and Calverton coals [9,10] has shown that increasing the digestion pressure considerably reduces the ash level in the extract solution after filtration, and that where this effect is modified by the use of different coals or hydrogen-donating solutions, then this can be overcome by reducing the filtration temperature. It was also shown that the distribution of trace elements in the original coal ash was different from that in the extract solution ash. For example, the proportions of manganese and titanium increased twenty-fold and ten-fold respectively, and the proportions of calcium and magnesium also increased. These elements, which show an increase in proportion, have also been found to be catalyst deactivators [11-16] and were also found to deposit most readily on the hydrocracking catalyst [2]. Thus, it is important that the level of these trace elements is as low as possible if their deposition on the hydrocracking catalyst is to be reduced.

Previous work [17,18] studying the form of the trace elements remaining in the filtered coal extract solution shows that their removal is no easy matter. They pass through fine filters and are

not easily removed by guard beds [17]. Increasing the digestion pressure, as described above, has been successful, but efforts to reproduce this effect at low digestion pressures, by the addition of low-boiling material prior to filtration, were unsuccessful [10]. However, it has been shown [18] that the insoluble portion of solvent extractions, used to characterise the filtered coal extract solution, contain a high proportion of the trace elements present in the original extract. The solvents used were pentane, toluene and THF, and with toluene, for example, about 80% of the trace element content precipitated out with the insolubles. Thus, it may be possible to carry out a solvent precipitation on coal extract solution which has already been filtered, in order to reduce the trace element concentration to a very low level.

In this paper work carried out using toluene and THF to remove trace elements from filtered coal extract solutions will be described. The effect of extract to solvent ratio was studied as well as the temperature of extraction. Trace element concentrations have been measured both before and after precipitation, and the nature of the extract solution after solvent precipitation, compared to that of the original extract solution, has been examined.

EXPERIMENTAL

Materials

The coal used was Point of Ayr , supplied by British Coal, preground to -200 µm. An analysis of the coal is given in Table 1. The solvent used in the digestion was process-derived hydrogenated anthracene oil (HAO), again supplied by British Coal.

Procedures

Liquefaction was carried out by heating a mixture of the coal and HAO to a temperature of 400-420°C in a 2 litre autoclave. The pressure was controlled by venting vapours, as required, to a condensing trap. At the end of the digestion period, which was 45 minutes above 400°C, the contents were cooled to the filtration temperature and vapours vented to reduce the pressure to the filtration pressure. The mixture in the autoclave was then filtered through a pressure filter containing a "Nomex" cloth using the residual pressure in the autoclave. A solvent-to-coal ratio of 2:1 was used. The procedure has been described previously [9].

Solvent precipitation experiments were carried out on the filtered extract solution, produced as described above, using a stirred 0.2 litre autoclave. The extract and solvent were mixed together cold, in the autoclave, and then heated to the extraction temperature in a fluidised sand bath. The mixture was agitated at the extraction temperature for 20 minutes and then filtered, using the pressure in the autoclave or an applied nitrogen pressure, into a pressure filter containining a "Nomex" cloth at the extraction temperature. Some experiments were also carried out where the solvent was injected, using an applied nitrogen pressure, into the autoclave

containing the extract at the required temperature.

Analysis

Ash yields of the liquid products were determined by evaporating a sample (≈25 g) in a platinum crucible until coke formed. The ashing was completed in a muffle furnace set at 850°C.

Trace element analysis was carried out on the ash by carrying out a fusion with lithium metaborate followed by dissolution in 10% hydrochloric acid. The resulting solution was analysed using atomic emission and absorption spectrometry (AA). The method has been described previuosly [7].

Analysis was carried out on the fractions which boiled below 350°C of the extract and the filtrate produced after solvent precipitation, using a Perkin Elmer model 8500 GC fitted with a wide-bore, OV-1 capillary column 25 m long and 0.53 µm diameter. The oven temperature was 40°C for 1 minute followed by a temperature ramp at 4°C per minute to 250°C where the temperature was held. Carrier gas was helium at a flow of 6 cm^3/min. There was no split on the sample injected into the column and a FID detector was used. Initial fractionation of the samples was carried out by vacuum distillation.

RESULTS AND DISCUSSION

Reduction in ash levels

In the first series of experiments toluene was used as the solvent and the extractions were carried out at a temperature of 110°C. The ratio of extract to toluene was varied and a blank run was also carried out with no toluene added. This was to make certain that no precipitation was occurring as a result of cooling and reheating the filtered extract solution. These results are shown in Table 2.

From the results in Table 2 it can be seen that by increasing the quantity of toluene used then the amount of material precipitated is increased and the ash level of the filtrate decreases. It is clear, from the filtrate mass, that there is still a significant quantity of toluene remaining. At the temperature used this might be expected. To allow for this an equivalent extract ash is calculated as shown in Table 2. This figure also shows a steady decrease as the mass of toluene used increases. The mass of cake obtained shows that there would be a significant loss of product, by precipitation, if this method were to be used to remove trace elements. The extract solution used in this series of experiments had a "high" ash value of 0.056%. In the next set of experiments an extract solution with a lower ash value of 0.018% was used and the effect of varying the extract temperature was studied.

Table 3 shows that as the temperature of extraction is increased, then the mass of cake decreases, but the equivalent extract ash increases. However, it would seem that a significant reduction in the amount of material precipitated can be obtained without a large

increase in the ash level of the filtrate. This is especially seen in the increase in temperature from 100 to 138°C.

All the above experiments were carried out by mixing the extract and toluene together cold in the autoclave and then heating to the extraction temperature. In a commercial operation, the solvent would probably be added to a hot extract. This was simulated by injecting toluene into heated extract at the required temperature. The results obtained were similar to those shown in Tables 2 and 3.

Table 4 shows the results obtained when THF is used as the solvent. The reason THF was tried was that the normal value of the THF insolubles is about 2-4%, but it was noted [10] that over 60% of the trace elements precipitated out with the insolubles. Thus, it may be possible to reduce the trace element concentration with only a small amount of material precipitated. However, the results obtained from these experiments show that THF gave little, if any, reduction in ash level in the extract solution.

The results for toluene show that it is possible to reduce the trace element concentration in filtered extract solutions using this method. There is a price to pay, however, and that is loss of product as precipitated material. This can be reduced by increasing the extraction temperature to an optimum level. However, the value of this lost product is questionable, since it will be mainly preasphaltenic, difficult to convert to useful products in the hydrocracking stage and could be responsible for much of the carbon deposition on the hydrocracking catalyst.

Trace element concentrations

Not only is the overall ash level important in the coal extract solution, which is fed to the hydrocracking stage, but also the concentration of the individual trace elements. Table 5 shows the concentration of trace elements in the ash from the original extract and the filtrate produced after toluene extraction. This was for an extract with an ash level of 0.035%, extracted with toluene at 165°C to give a filtrate with an ash level of 0.01%. The results show that there are some differences, with calcium reducing and iron and titanium increasing their proportions. However, the changes are not great and it would be expected that if the filtrate were fed to the hydrocracker it would deposit trace elements as observed previously [2], except, of course, there would be a smaller quantity overall.

Nature of the extract solution after precipitation

When toluene extractions were carried out at 110°C it was clear that toluene remained in the filtrate from the mass obtained. With the higher temperature extractions the filtration was also carried out at the same temperature and the mass of filtrate was accordingly lower as most of the toluene was boiled off from the filtrate. However, examination of the filtrate showed that it was much more fluid than the original extract and it appeared that some toluene remained in it. Analysis of the extract and filtrate were

carried out using an initial vacuum distillation and GC analysis as described previously. The aim being to find how much toluene remained. However, no toluene was seen in the chromatogram.

Table 6 shows some results obtained for the simulated distillation of extract and filtrate after toluene extraction. It can be seen that the fraction boiling up to 150°C is reduced after extraction, contrary to expectations, and that the fraction from 200-300°C increases, mainly in the 250-300°C range. Examination of the chromatogram shows no difference in the actual components present, only differences in their quantity. With the low boiling material the reduction is probably a consequence of the heating at elevated temperatures during filtration coupled with the stripping of the toluene. The reason for the increase in the other ranges is not known and more extensive analysis is required to answer this problem.

ACKNOWLEDGEMENTS

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Table 1 Analysis of Point of Ayr Coal

Proximate analysis			Elementary Analysis				
VM	Ash	Moisture	C	H	N	O	S
(wt% db)		%	(wt% dmmf)				
31.6	13.1	3.5	82.7	5.2	1.8	7.5	2.8

Table 2 Extraction of coal extract solution with toluene
- effect of toluene to extract ratio

Temperature of extraction : 110°C
Ash of original coal extract solution : 0.056%

Mass Extract		(g)	56	55	61.3	55	55
Mass Toluene		(g)	56	32	24.5	11	0
Ratio Extract/Tol			1:1	1.7:1	2.5:1	5:1	BLANK
Filtrate	- Mass	(g)	81.3	66.1	79.0	62.3	
	- Ash	(%)	0.007	0.014	0.038	0.047	0.055
Cake	- Mass	(g)	18.7	15.4	3.0	1.5	
	- Ash	(%)	0.255	0.185	0.19	0.285	NO EFFECT
Equivalent Extract Ash		(%)	0.011	0.016	0.049	0.053	

Note: Equivalent Extract Ash = $\frac{\text{Mass Filtrate} * \text{Filtrate Ash}}{\text{Mass Extract}}$

Table 3 Extraction of coal extract solution with toluene
- effect of temperature

Ratio extract/toluene : 1.67:1
Ash of original coal extract solution : 0.018%

Extraction Temp		(°C)	100	138	175	200
Mass Extract		(g)	50	50	46.5	50
Filtrate	- Mass	(g)	51.6	59.1	55.7	50.1
	Ash	(%)	0.006	0.007	0.008	0.014
Cake	- Mass	(g)	20.4	10.0	6.9	3.4
	Ash	(%)	0.205	0.16	0.44	2.2
Equivalent Extract Ash		(%)	0.006	0.007	0.01	0.014

Table 4 Extraction of coal extract solution with THF

Ash of original coal extract solution : 0.018%

Extraction Temp	(°C)	122	103	66	66
Mass Extract	(g)	50	50	50	50
Mass THF	(g)	30	30	30	50
Ratio Extract/THF		1.67:1	1.67:1	1.67:1	1:1
Filtrate - Mass	(g)	55.1	59.3	69.6	81.5
- Ash	(%)	0.012	0.013	0.016	0.011
Cake - Mass	(g)	4.1	4.8	4.8	9.5
Equivalent Extract Ash	(%)	0.013	0.015	0.022	0.018

Table 5 Trace element analysis

Proportion of Element in Ash (%)	Original Extract	Filtrate after Toluene extraction
Al	5.5	6.3
Ti	1.8	4.0
Si	4.0	2.8
Ca	25.6	15.2
Mn	3.0	4.5
Fe	3.8	8.2
Mg	5.4	5.4
Na	1.5	2.4
K	0.5	0

Table 6 Simulated distillation of extract and filtrate after extraction with toluene at 165°C

	Original Extract	Filtrate 1	Filtrate 2	Filtrate 3
		(%)		
0-100°C	0.47	0.05	0.04	0.06
0-150°C	1.21	0.10	0.08	0.09
0-200°C	6.97	5.11	4.28	4.18
0-250°C	19.3	32.9	20.0	21.1
0-300°C	54.6	78.5	64.1	67.5
0-350°C	100	100	100	100

Extracts prepared with an extract:toluene ratio of:
1: 1.6/1
2: 2.5/1
3: 3.3/1

Fig.1. A comparison of the plastometry curves for coal H1 at 0.5 and 5 MPa (Heating Rate 3 °C min $^{-1}$)

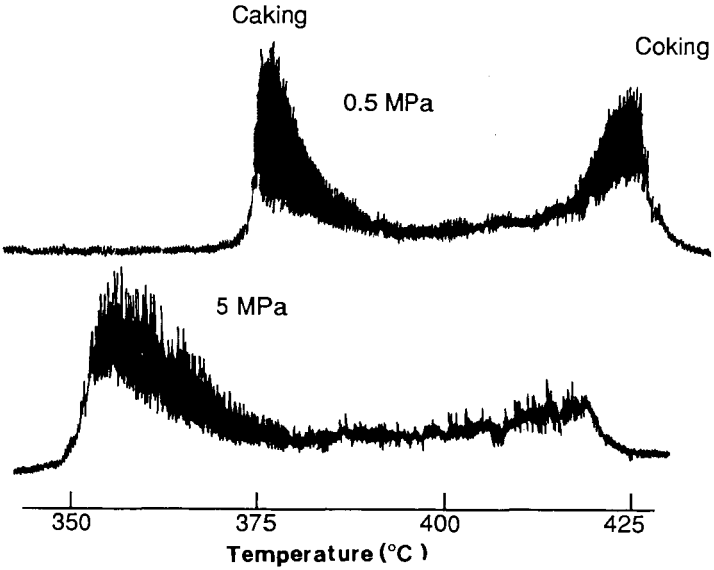

Fig. 1. A comparison of the plastometry curves for coal HI at 0·5 and 5MPa(heating rate 3°C min^{-1})

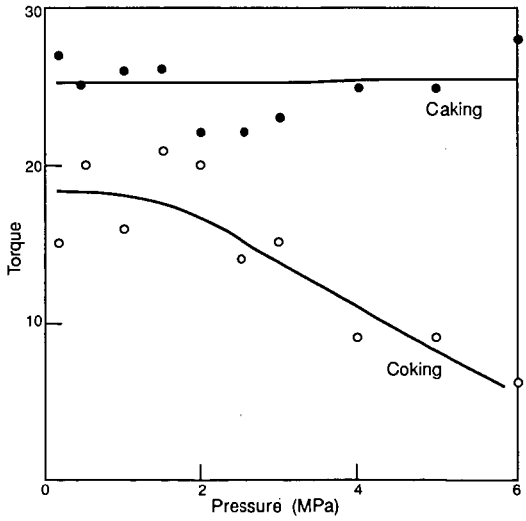

Fig.2. The variation of plastometry torque parameters with pressure for Coal H1 (Heating Rate 3°C min^{-1})

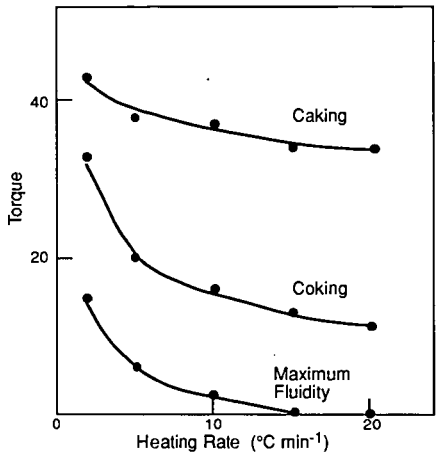

Fig.3. The variation of plastometry torque parameters with heating rate for coal H1 (Pressure 2 MPa)

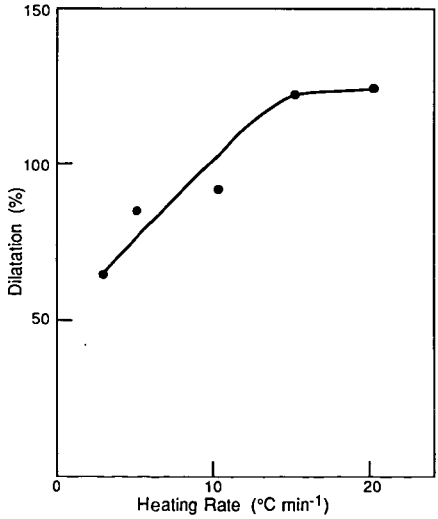

Fig.4. The effect of heating rate on the dilatation of coal Oa (Gauge pressure - 2 MPa)

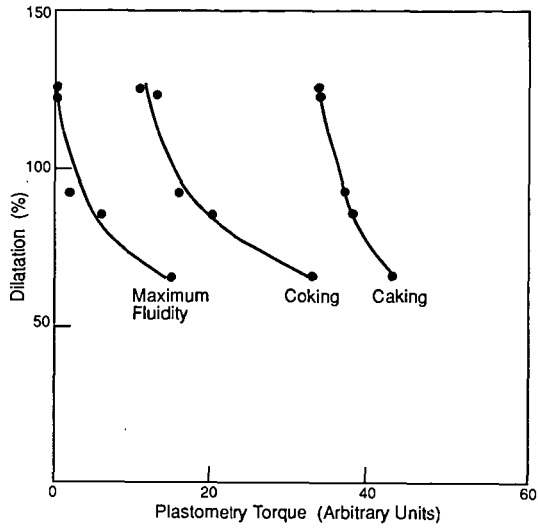

Fig.5. The variation of dilatation with plastometry torque parameters at 2 MPa pressure for coal Oa

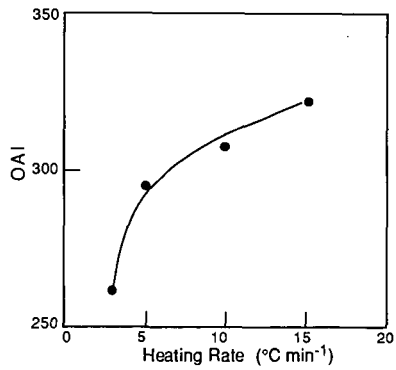

Fig.6. The variation of optical anisotropy index (OAI) with heating rate for coal Oa (Pressure 2 MPa)