

HIGH PRESSURE TPR APPARATUS TO INVESTIGATE
ORGANIC SULPHUR FORMS IN COALS.

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ABSTRACT

Temperature programmed reduction (TPR) has been used to investigate the distribution of organic sulphur forms in coals. However, the method used thus far suffers from a number of inherent drawbacks including the low proportion of thiophenic sulphur observed directly and the likelihood of secondary reactions converting sulphides into thiophenes. These drawbacks have largely been overcome using a well swept fixed-bed reactor at relatively high hydrogen pressures (~ 150 bar) with an effective dispersed hydrodesulphurisation catalyst, such as sulphided molybdenum. For three high sulphur coals (a Spanish and a Turkish lignite and a US hvc bituminous coal), levels of desulphurisation were in excess of 90% for the organic sulphur. The first results from the high pressure TPR apparatus with a quadrupole mass spectrometer for on-line analysis of hydrogen sulphide is presented.

1.0 INTRODUCTION

The identification and quantification of the various organic sulphur species in coals is of great importance due to their effects, both beneficial and detrimental, on the subsequent devolatilisation and liquefaction of coal and coal-derived products. At present no established method exists for the direct determination of the distribution of organic sulphur in coal and coal-related products. Several novel techniques have been proposed.

Flash pyrolysis studies on the thermal decomposition of sulphur groups in coal showed that aliphatic sulphur containing groups decompose at much lower temperatures than aromatic groups. However resolution between different aliphatic and aromatic groups was poor⁽¹⁾.

X-ray studies, both surface (XPS)^(2,3) and bulk (XANES)⁽⁴⁾ characterisation techniques, have shown that it is possible to distinguish between thiophenic and non-thiophenic sulphur groups, however the narrow absorption energy range observed for sulphur containing model compounds coupled with the known number of forms of organic sulphur present in coals results in poor resolution between groups. A larger range is observed for oxidised sulphur

groups², it is therefore possible that selective oxidation before x-ray analysis may offer improved resolution.

Another method which has been investigated involves the oxidative pyrolysis of the coal which converts the sulphur into SO₂ for subsequent on-line gas analysis, however the resulting resolution between functional groups is generally not as good as that achieved with TPR^{3,4} (see following).

In recent years several researchers have been investigating the use of Temperature Programmed Reduction (TPR) for the identification of organic sulphur forms in coal and related products^{7,8,9,10}. TPR is based on the principle that each form of organic sulphur exhibits a characteristic reduction temperature, which in a hydrogen rich environment, results in the formation of hydrogen sulphide. The ease of reduction of the various sulphur forms have been found to be in the order thiols > aliphatic sulphides > aromatic sulphides > thiophenes¹¹. The current TPR methods generate the hydrogen rich atmosphere by refluxing the coal in a mixture of hydrogen donor solvents¹². The evolved hydrogen sulphide is swept from the reaction pot by a stream of inert carrier gas at atmospheric pressure. The original method used lead acetate impregnated paper as the H₂S detector^{7,8}, later workers have used a potentiometric system to measure the evolved H₂S as the sulphide ion, giving a greater degree of quantitation⁹. Sulphur sensitive Flame Photometric Detection (FPD) has also been used however flame stability was found to influence overall sensitivity to a large extent¹⁰.

The TPR method has been the most widely used technique, however at present it contains several limitations which reduce its effectiveness as an analytical technique. The solvent mixture used to generate the hydrogen atmosphere has a relatively low boiling point (< 400°C), consequently complex thiophenes are not detected and must be estimated by difference¹⁰. Overall sulphur balances are poor, with sulphur of all functionalities remaining in the char after analysis, possibly due to mass transfer limitations inherent to the reaction pot, which could result in retrogressive reactions including transformation of aliphatic sulphides to thiophenes^{11,12}. Finally, the overall contribution of pyrite to the evolved H₂S signal, particularly the transformation of pyrite to pyrrhotite and to iron with the subsequent evolution of H₂S appears to have been overlooked or considered negligible by previous researchers.

This paper presents results obtained for three high sulphur coals from a high pressure fixed bed hydrolysis reactor which is relatively unaffected by any mass transfer effects and any associated retrogressive reactions resulting in effective desulphurisation, including the removal of complex thiophenes. This reactor has been modified through the fitting of a suitable gas analysis system to form a TPR reactor.

2.0 EXPERIMENTAL

Table 1 lists the ultimate analyses and sulphur distributions of the coal samples studied.

The hydropyrolysis reactor has been described previously⁽¹⁾. The desulphurisation experiments were conducted on a 5g scale at 520°C using a gas velocity of $\sim 0.2 \text{ m s}^{-1}$ to virtually overcome mass transfer limitations to volatile release. For each coal (75-200 μm), three tests were conducted using a pressure of (i) 150 bar nitrogen and (ii) 150 bar hydrogen with and without a sulphided molybdenum (Mo) catalyst (1% loading prepared from ammonium dioxodithiomolybdate⁽²⁾). In addition, the thermal desulphurisation of the three coals was also investigated in the temperature range 250-500°C using the BS volatile matter test (BS1016).

For the TPR runs, a smaller but otherwise identical reactor system was used. 2g of coal was heated from ambient to 570°C at 2°Cmin^{-1} . The hydrogen pressure was again 150 bar and the gas velocity $\sim 0.2 \text{ m s}^{-1}$. On line analysis of the gas stream for H_2S and other gaseous products is performed using a quadrupole mass spectrometer in multiple ion monitoring mode. The atmospheric pressure side of the exit stream from the reactor was connected to the mass spectrometer by a 1.8 m length of heated capillary tubing sampling at a rate of 25 ml min^{-1} . The reactor thermocouple signal is also fed to the mass spectrometer allowing direct plots of evolved gas concentration against bed temperature to be generated.

Concentrations of pyritic and pyrrhotitic sulphur in the chars were determined. FTIR was used to compare the relative amounts of sulphatic sulphur in the chars and corresponding low temperature ash samples, sulphate absorbances occurring in the range 1110-1150 cm^{-1} . Gas chromatography (GC) with mass spectrometric (MS) and flame photometric detection (FPD) were carried out to compare the distribution of thiophenic compounds in the tars.

3.0 RESULTS AND DISCUSSION

3.1 DESULPHURISATION

Table 1 lists the distribution of sulphur forms in the original coals and Table 2 summarises the char and tar yields for the desulphurisation tests as well as the sulphur distributions in the pyrolysis products. The two lignites gave broadly comparable tar yields and total conversions in corresponding tests, but these were slightly higher than those obtained for Bevier-Wheeler coal. As anticipated, the total conversions increased in going from pyrolysis to high pressure hydropyrolysis and catalytic hydropyrolysis (Table 2). The extent of desulphurisation (sulphur in gas plus tar as a percentage of that in the original coal) increased with increasing conversion (Table 2) but a number of marked differences were found for the coals investigated.

In Table 2 it has been assumed that sulphatic sulphur remains in the chars and is unaffected by pyrolysis. Indeed, only small differences were found in the absorbances of the characteristic IR sulphatic bands at 1110-1150 cm^{-1} between the chars and the corresponding low temperature ashes when the spectra were normalised to 1mg cm^{-2} of mineral matter. For all three coals, significantly more pyrite is reduced during high pressure hydrolysis than in pyrolysis (Table 2). The ease of pyrite reduction to pyrrhotite and iron is greatest for Bevier-Wheeler coal and optical microscopy has shown that it would appear to correlate with the size of pyrite particles in the coal. For the lignites, much of the pyrite occurs as fine grains dispersed in both the organic and mineral matter. In Bevier-Wheeler coal, the pyrite is mainly present as relatively large particles which are presumed to be more accessible to hydrogen than fine grains.

The three coals display completely different trends for the removal of organic sulphur (Table 2). For Cayirhan lignite, nearly all of the organic sulphur is eliminated as tar and gas in pyrolysis compared with ~75% for Mequinenza lignite. The implication is clearly that little of the organic sulphur exists in condensed thiophenic structures for Cayirhan lignite. Indeed, nearly all the organic sulphur is also removed in the standard volatile matter test at 500°C with ~ 20% being eliminated below 250°C (Figure 1). The fact that much more of the sulphur is released from the Cayirhan lignite below 250°C (Figure 1) implies that this lignite contains a greater proportion of aliphatic sulphides/thiols than Mequinenza lignite. However there is the strong possibility that some thiophenic sulphur results from cyclisation and aromatisation of non-thiophenic forms during pyrolysis^(11,12). As anticipated, the extent of organic sulphur removal is low for Bevier-Wheeler coal with only ~ 20% being eliminated in pyrolysis and also at 500°C in the volatile matter test (Table 2 and Figure 1). However, in catalytic hydrolysis the proportion eliminated is ~ 90%.

For Mequinenza lignite, GC has shown that thiophenes are the dominant species over benzo- and dibenzothiophenes in the pyrolysis tar. However, in the high pressure hydrolysis tars, thiophenes are present in trace amounts which is consistent with the greater ease of hydrodesulphurisation of single ring thiophenes. For Cayirhan lignite, benzothiophenes are the major thiophene class present in the pyrolysis tar but in going to catalytic hydrolysis, dibenzothiophenes and other high molecular weight thiophenes become the dominant species.

3.2 HIGH PRESSURE TEMPERATURE PROGRAMMED REDUCTION

Figure 2 shows the H_2S evolution trace for Mequinenza lignite (A) untreated and (B) impregnated with the molybdenum catalyst. The higher resolution trace obtained without catalyst shows seven distinct peaks which can be assigned to various functional groups based on characteristic reduction temperatures identified in earlier studies⁽¹⁾. At present, studies are under way to confirm

the reduction temperatures of various model compounds in the swept bed TPR reactor.

The trace for the catalyst impregnated sample shows a loss of fine resolution, but more thiophenic sulphur is detected around 300-400°C, and over a smaller temperature range than for the untreated sample. The loss of resolution may be as a result of a continual adsorption/desorption of H₂S on the hot catalyst surface. Different catalyst compositions and loadings will be investigated in order to improve the resolution observed for catalyst impregnated coals.

4.0 CONCLUSIONS

The use of a fixed bed pyrolysis reactor swept with high velocity hydrogen has been shown to effectively desulphurise high sulphur coals. The reactor is relatively unaffected by any mass transport limitations and as a result, retrogressive sulphur transformations are avoided. The reactor system has been adapted to enable the characterisation of organic sulphur species within the coals via high pressure temperature programmed reduction and initial results have shown a high degree of resolution between functional groups.

5.0 ACKNOWLEDGEMENTS

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Table 1. Ultimate and Sulphur Analyses of Coal Samples

		Lignites		hvc Bituminous
		Mequinenza (Spain)	Cayirhan (Turkey)	PSOC 1409 Bevier-Wheeler (N th America)
(% daf)	C	66.4	64.3	76.9
	H	5.8	5.1	5.5
	N	1.6	2.3	1.8
Sulphur (% db)	Total	9.0	4.8	6.8
	Pyritic	0.5	1.0	4.0
	Sulphate	0.5	0.9	0.3
	Organic	8.0	2.9	2.5

Table 2. Distribution of Sulphur in Pyrolysis Products
(% Original Sulphur in Coal)

	% Yield		Char					Tar	Gas*	%DS
	Char	Tar	S _T	S _p	S ⁻	S _{SO4}	S _o *			
Mequinenza			100	6	<1	6	88			
Py	53	33	38	4	1	6	27	25	37	62
Hypy	27	50	13	1	2	6	4	18	69	87
C.Hypy	13	63	10	1	2	6	1	23	67	90
Cayirhan			100	21	<2	19	54			
Py	49	39	45	16	5	19	<1	20	35	55
Hypy	25	57	27	1	6	19	<1	11	62	73
C.Hypy	16	63	22	1	1	19	<1	12	66	78
Bevier Wheeler			100	59	<1	5	36			
Py	63	25	61	10	16	5	30	7	32	39
Hypy	39	48	27	2	9	5	11	9	64	73
C.Hypy	30	56	20	1	11	5	3	6	74	80

* := by difference
 S_T := Total sulphur
 S_p := Pyritic sulphur
 %DS := % Desulphurisation
 S⁻ := Pyrrhotitic sulphur
 S_{SO4} := Sulphatic sulphur
 S_o := Organic sulphur

SULPHUR REMOVAL IN VOLATILE MATTER TESTS

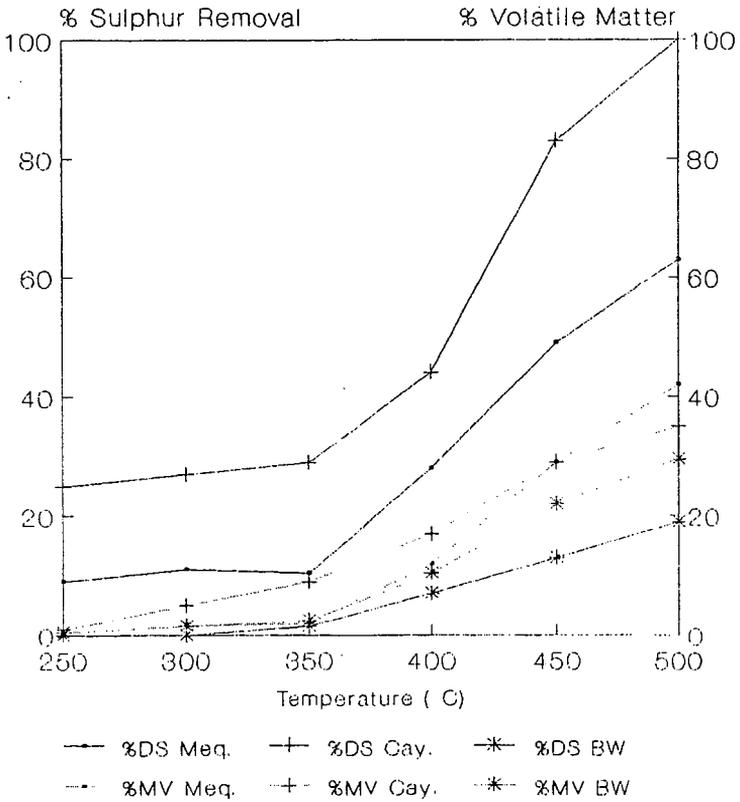
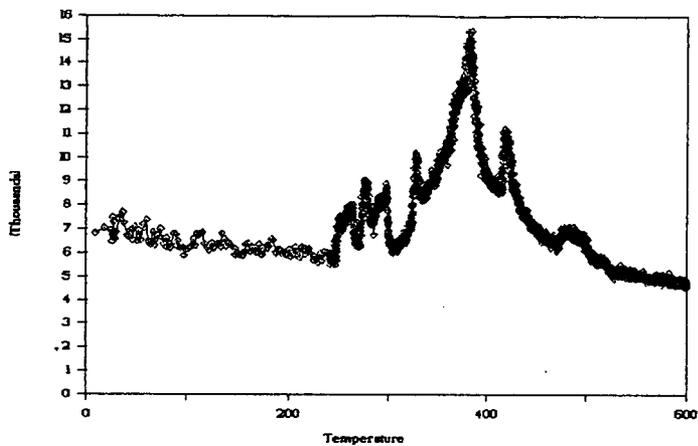


Fig.1. Desulphurisation and Volatile Matter Yields.

(A) Mequinenza No Catalyst



(B) Mequinenza 1% Mo Catalyst

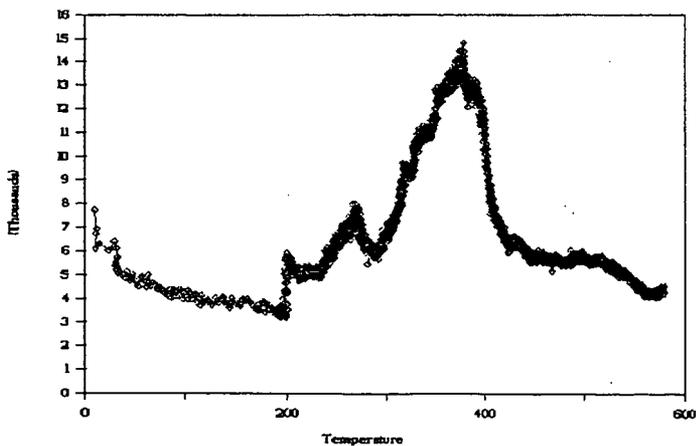


Fig. 2. TPR Traces for Mequinenza Lignite