

CHANGES IN THE CHEMICAL STRUCTURE OF LOW RANK COAL AFTER LOW TEMPERATURE OXIDATION OR DEMINERALISATION BY ACID TREATMENT . ANALYSIS BY FTIR AND UV FLUORESCENCE .

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The studies have been conducted on low rank coal: Flambant de Provence, France, PRV=0.44

FTIR and UV synchronous fluorescence spectroscopy are used to study structural changes in low rank coal after natural oxidation or acid ( HCl/HF ) demineralization.

The observed variations deal mainly with a decrease in aliphatic structures and an increase in the oxygenated species.

A quantitative oxidation study of the effect of temperature, time, mineral matter and oxygen concentrations has been conducted by FTIR.

An attempt to describe the oxygenated species by FTIR and to compare their evolution has been conducted. Various oxidation mechanisms are proposed according to the results.

The UV Fluorescence allows to show in these conditions a change in the polyaromatic ring absorptions , mainly in the 2, 3 range. This correspond to an oxidation or even loss of some aliphatic substituents.

The results are compared to those obtained by C13 NMR of solid coal, and also to the coking and caking values of oxidized coals.

## INTRODUCTION

This study investigates the utility of Fourier Transform InfraRed spectroscopy(FTIR) and synchronous excitation-emission UV fluorescence as a means of measuring increases in the degree of coal oxidation with exposure time in an air atmosphere at various temperatures and for various particle sizes . This multitechnique approach shows much promise in identifying specific changes during coal oxidation or demineralization (1).

These chemical structural changes occurring in a laboratory aerial oxidation experiment are observed on French Gardanne coal , "flambant de Provence" (Subbituminous A) .

It is well known that coal weathering at various temperatures is accompanied by changes in the chemical and physical properties and therefore significantly alters the utilization potential of coals (2-7) .

## EXPERIMENTAL

The coal used was from the "ETOILE N°9" seam of the Gardanne mine located in Provence , near Marseille FRANCE and was sampled directly just before these studies . Characteristics are presented in table 1

The coal used was crushed and sieved in a IKA-VERK A 10 and a IKA-VIBRAX-VXR under controlled atmosphere .

At various temperatures ( from 20°C to 200°C ) , samples were taken at regular intervals and stored in Nitrogen flushed vials to prevent further oxidation before analysis .

TABLE 1.  
Characteristics of "Gardanne coal"

Ultimate Analysis/DFB	%wt	Proximate Analysis	%wt	Petrographic Analysis	%wt
Carbon	60,20	Moisture	7,99	Vitrinite	60,06
Hydrogen	4,30	Ash	20,10	Exinite	6,73
Nitrogen	1,63	Volatile		Inertinite	14,86
Sulphur	4,57	matter /DFB	44,80	_Inertodetrinite	6,40
Oxygen	10,55	FSI (ASTM)	0,50	_Semifusinite	6,13
Ash	18,32	.....	.....	_Fusinite	2,33
.....	.....	.....	.....	Mineral matter	18,32

Coals demineralized by acid treatment (HCl/HF) (8) were studied and we observed the structural modifications which induced disturbances in maceral separations (9,10). FTIR spectra were measured on 5DX and 20SX NICOLET spectrometers using the classical halide pellet IR transmission method (11-13). UV fluorescence spectra were measured on a PERKIN 3000 and synchronous excitation-emission technique was used to study solid coals and coal extracts  $\Delta\lambda=23\text{mm}$  (14).

#### FTIR STUDIES

In a recent work in our laboratory, we noted the high reactivity of "Gardanne coal" in weathering and oxidation reactions and the capacity of FTIR spectroscopy to follow quantitatively the small changes in carbonyl and aliphatic ranges (12). It is possible that coal oxidized by exposure for long time periods at the edge of a seam differs in structure from a coal oxidized at various temperatures in the laboratory (15). In a preliminary work, we observed the similar reaction of coal in natural oxidation of a stockpiled coal and in a laboratory aerial oxidation experiment ( $T_p < 60^\circ\text{C}$ ) (12). Demineralized coals were studied but the demineralization reaction by prolonged acid treatment (HCl/HF) induced itself many parasite oxidation reactions (14, 16-18). We observed in all cases significant spectroscopic changes by FTIR difference spectra and we used the area integration method to quantify these modifications.

#### SAMPLE PREPARATION

The coal was oxidized by spreading about 3g uniformly in a ceramic boat which in turn was placed in a regulated oven. The samples were prepared for infrared analysis by forming standard KBr disks. Spectra were recorded and one hundred co-added interferograms were used to obtain spectra with a resolution of  $2\text{cm}^{-1}$ . Only the  $400 - 3300\text{ cm}^{-1}$  region was examined, so that the OH stretching region of the spectrum was not observed (interferences from water absorbed on the KBr).

#### RESULTS AND DISCUSSION

The infrared spectra (plotted in absorption) of oxidized and fresh coal are compared in fig.1. Major changes in the two spectra appear in the  $1676 - 1900\text{ cm}^{-1}$  range (weak shoulder near  $1695\text{cm}^{-1}$ ) and  $2760 - 3000\text{ cm}^{-1}$  range (aliphatic C-H stretching). These changes were only revealed after subtraction of the fresh coal sample spectrum from the spectra of the oxidized samples (fig.1). A correct degree of subtraction is obtained by using the kaolinite bands ( $1035 - 1010\text{ cm}^{-1}$ ) as a subtraction standard, since this clay should be relatively unaffected by low temperature oxidation (15). After subtraction, the aliphatic C-H stretching mode appears negative, demonstrating a loss in  $\text{CH}_2 - \text{CH}_3$  groups upon oxidation (area  $2760-3000\text{cm}^{-1}$ ) and the carbonyl and carboxylic bands appear positive (area  $1676-1815\text{ cm}^{-1}$ ). The area integration method used to quantify the oxidation reaction is presented in fig.2. The same technique was used for maceral separation characterization (9,10).

The ratio of the integrated peak areas to the total area B+C were calculated ( with C area limits : 1885-1839 to 900-892  $\text{cm}^{-1}$  )

The FTIR study corresponds to a study of the temperature effect ( 20- 110 - 200°C ) for a definite granulometry ( <0.125mm ) followed by a study of the particle size effect ( <0.500 , 0.250 , 0.125 , 0.090 , 0.063 , 0.005mm ) at various temperatures . Coal demineralized with HCl/HF is studied at 20°C for a particle size <0.125mm .

a) Definite granulometry (<0.125mm) .

The results from this analysis \_ disappearance of aliphatic groups ( B/B+C ) and formation of carbonyl or carboxylic compounds ( A/B+C ) as a fonction of temperature and time - are given in figures 3a and 3b .

Upon examination , the curve in fig.3a reveals that the disappearance of aliphatic groups at room temperature occurs mainly during the first few days of oxidation and then seems to level off or at least strongly slow down . At 110°C this disappearance is more important , very significant in the first days and continuing steadily until the end of the experiment . At 200°C , aliphatics disappearance happens very quickly, since the first hours of oxidation - the same remark can be made with regard to the formation of carbonyl or carboxylic compounds ( fig.3b ) .

The "Gardanne coal" studied here presents a relatively low aromaticity level . The corresponding IR spectrum does not clearly show the characteristic adsorptions of aromatic hydrogens (3100 - 3000  $\text{cm}^{-1}$  and ( 900 - 700 $\text{cm}^{-1}$  ) (9-13) . A study using NMR  $^{13}\text{C}$  as well as FTIR reveals that aromaticity is not hardly affected by oxidation (16-19) , whereas a previous study indicated an increase in aromaticity upon oxidation (17) .

After evidencing the formation of carbonyl and carboxylic compounds , we tried to determine the nature of the formed oxidation products , and the best technique seems to be the spectrum subtraction method - (oxidized coal - starting coal) .

We must be careful , particularly when the oxidation products are obtained in very small quantities ( oxidation at 20°C ) . The difference spectra obtained in these cases may be controversial as shown by the comparison of the work of LIOTTA et al. (20) and that of RHOADS et al. (21) ( signal to noise ratio too low , mineral matter nature and content slightly different from one to another sample (22) ) .

At 110 and 200°C difference spectra evidence without ambiguity the formation of the various oxidation compounds (figures 4a and 4b) . The broad band between 1900 and 1500 $\text{cm}^{-1}$  shows mainly four different absorptions located at 1569\_1596 , 1725\_1710 , 1778\_1770 and 1850\_1840 $\text{cm}^{-1}$  . Furthermore , a prominent new band near 1575\_1600  $\text{cm}^{-1}$  is now revealed in the difference spectrum. This band is not detectable in the original spectrum and can be assigned to an ionized carboxyl group  $\text{COO}^-$  - the major product of oxidation (23,24) . On the broad band 1500 \_ 1900 $\text{cm}^{-1}$  , we used the second derivative spectroscopic technique which revealed all the absorptions (figures 5a and 5b) . Attributions are given in table 2 . Some of them are corroborated by NaOH and  $\text{NaHCO}_3$  selective chemical reactivity (25) .

TABLE 2  
Coal oxidation  
Absorptions in 1900 - 1500  $\text{cm}^{-1}$  range .

Wavelength $\text{cm}^{-1}$	Attributions
1850	. Anhydrides
1837	
1818	
1779	
1760	. Esters type O=C-O-Aryl
1739	. Esters type O=C-O-Alkyl
1725	. Carboxylic acids Aryl-( $\text{CH}_2$ ) <sub>n</sub> -COOH
1709	. Carboxylic acids Aryl-COOH
1675	. Quinones
1600 -1540	. $\text{COO}^-$ carboxylates

Upon examination, figures 5a and 5b at 20°C and 200°C reveal that the nature and repartition of oxidized species is not the same. This poses the problem of comparison of natural ageing ( weathering ) of coals and laboratory oxidation at high temperatures.

Weak broad residual absorption between 1200 - 1300cm<sup>-1</sup> in the difference spectrum could possibly be due to C-O bands, as in phenols or ethers, but these bands would be difficult to identify.

This phenomenon is more significant at 20°C and 60°C than 110°C and 200°C. From a purely mechanistic point of view, this observation calls for confirmations, since it allows to suggest different mechanisms.

A number of studies have concluded that the formation of ether cross-links is critical to loss of coking ability (2,4).

b) Particle size effect.

We can see (figures 6a and 6b) the appearance of oxygenated groups (A/B+C) and disappearance of aliphatics (B/B+C) as a function of time for different grindings. The study presented here corresponds to an utmost oxidation at 200°C. Upon examination, the curves reveal that the appearance of oxygenated groups is proportional to the inverse of particle size, as well as the disappearance of aliphatics, since the two phenomena are linked chemically. This is a logical result, as the specific surface likely to react is larger for a coal of lower granulometry. In order to estimate the role played by the initial grinding, the areas a and b were integrated immediately after grinding and the "zero points" were thus obtained (table 3).

TABLE 3

"Zero points", area integrations  
Grinding effect, initial state

Granulometry < à	0,063	0,090	0,125	0,250	0,500
Ratio A.10 <sup>3</sup> /B+C	4,8	4,7	3,9	2,8	2,5

In this manner, we verified that when the particle size decreases ( longer grinding times), the oxidation increases - Even coals ground under demineralized and cooled water give "zero points" characteristic of an oxidation (12,16). It is then problematic to present comparison studies when the initial products are not strictly identical. It must be noted that grinding effect affects minerals and macerals specifically with a proper reactivity. Therefore grinding results in organic-mineral mixtures with a reactivity to oxidation different from that of the initial heterogeneous mixture. This observation let us to leave the selective sieving in favor of the notion of grinding time.

c) Demineralized coal.

The acid demineralization technique, as well as the grinding technique, results in chemical disturbances in the coal, mainly by oxidation (12,16). If we observe the natural evolution of a demineralized coal (figure 7), we can see that the appearance of oxygenated species corresponds to two curves, which are considerably different in the early stage of oxidation and become later identical. The shifting of the curves in figure 7 corresponds to a shifting of the "zero point" due to the initial effect of demineralization technique by oxidation (12,14,16) and the fact that for fresh coal the ratio A peak area / total area B+C is calculated with remaining traces of mineral matter ( evolution by oxidation and non homogenous sampling ). Whereas for the demineralized sample the ratio A / B+C is calculated without interference. It seems that mineral matter affects oxidation particularly in its early stages

## UV FLUORESCENCE STUDIES

UV fluorescence by synchronous excitation - emission technique allows the approach of the polyaromatic structure of coal before and after treatment (1,14). This treatment may correspond to a natural or induced oxidation (12) or a demineralization treatment before a maceral separation study (9,10) or a reactivity study.

Most often in order to be analyzed by UV fluorescence, coal must be treated - either by chemical treatment transforming for example a solid in to liquid (hydroliquefaction and pyrolysis); in this case the reaction products are characterized (26) and the initial coal structure may be estimate by the Knowledge of the reaction mechanisms - or a treatment with a solvent, in which case a coal fraction is characterized more or less important depending on the coal, solvent and technique used (27).

### a) Analytical technique.

Different types of spectra may be obtained by UV fluorescence - Emission spectra are obtained by exciting the compound with a fixed wavelength and determining the definite fluorescence intensity proper to that particular wavelength. In the case of complex mixtures, this method does not prove satisfactory, as the definite excitation wavelength chosen cannot correspond to the maximum extinction coefficient of each of the mixture components, and this induce for certain compounds a decrease in fluorescence intensity.

Synchronous excitation - emission spectra are the result of the technique which consists in recording the emission spectrum of a mixture and varying the excitation wavelength, while maintaining  $\Delta\lambda$  optimum at 23nm. This technique clarifies the emission of each of the mixture components and results in a better resolved spectrum (28,29).

### b) Solvent coal extract study.

Several methods of solvent extraction may be used in the case of "Gardanne coal", dissolution at refluxing, Kumagawa, Soxhlet, sonication... They all give extraction yields close to 15% but extraction by sonication is more rapid (45min). It is carried out at a low temperature ( $\leq 50^{\circ}\text{C}$ ), which prevents from a too long contact period and also significant parallel oxidation reactions. Fluorescence spectra of extracts obtained by the various extraction techniques reveal the presence of the same aromatic compounds (emission peaks at 371 and 393nm characteristic of aromatic derivatives with 3 and 4 condensed rings (fig.3)). Further differentiation can be made by examining hexane, THF and pyridine fractions obtained from the initial extract. However this differentiation is fastidious as there is a "levelling" of the extracts directly linked to the solvent selective extraction power towards the polyaromatic species in the coal (14).

In order to try to better evidence the spectrum differences between fresh, demineralized and oxidized coal, multiple steps fractioning has been adjusted. Four successive extractions are carried out with hexane, toluene, THF, and then the last residue is dissolved in pyridine. Each fraction thus obtained is analyzed for the three types of coal. The obtained spectra show that it is possible to compare coals (fig 9, table 4) by emphasizing the characteristic signs. For "Gardanne coal" we notice that the oxidation ( $200^{\circ}\text{C}$ , 34days) as well as demineralization affects the repartition of polyaromatics with 3 or 4 condensed rings by causing a bathochrome shift, characteristic of a loss of substituents (28, 30).

### c) Study of solid state coal.

The analysis of the extracts allows the characterization of only a fraction of the coal. In order to obtain a more complete characterization we studied uv fluorescence on sample in powder (particle size  $< 0,125\text{mm}$ ).

The obtained fluorescence profile are clearly different (14,30) from those of the extracts. The maxima characteristics of aromatic compounds with 2, 3, 4 condensed rings are no longer present and maxima between 440 and 550nm are observed which correspond to more condensed aromatic structures (5 or more rings): the basic structural units (BSU) or basic skeleton.

In reference to the structural pattern of DRYDEN coal (31), the solvent swells the miceral mesh and the small units are transported by diffusion through the matrix pores. In the case of the "Gardanne coal", we observe that the small units have a significant extraction facility, since this coal has a very open porosity. Therefore oxidation and demineralisation affect mainly these small units and UV fluorescence is particularly adapted for evidencing this phenomenon. In contrast, in the coal matrix itself, the general structure of the basic structural units (BSU) common to all the coal samples is found (polyaromatics with 5 to 8 piled condensed rings).

TABLE 4  
 UV Fluorescence characteristics  
 Comparison between — coal extract  
                           — demineralized coal extract  
                           — oxidized coal extract

Emission wavelength (nm) of the main bands.

Fractions	Fresh coal		Demineralized coal			Oxidized coal				
	$\lambda$ (nm)		$\lambda$ (nm)			$\lambda$ (nm)				
Hexane .....	315	318	310	318					318	
Toluene.....	322	339	401	325	349	401	325	349	381	401
THF.....		354	404	327	345	404	327	345	383	404

### CONCLUSION

FTIR, UV fluorescence and NMR lead to the same conclusion with regard to oxidation and demineralization of "Gardanne coal" - loss of aliphatic groups attached to polyaromatics with 3 or 4 rings - appearance of oxygenated species, mainly carbonyls and carboxylic acids - no change in the BSU pattern.

The observed particle size effect seems to show that there is a surface reticulation effect (destroyed on re-grinding and determined by measuring of the Gieseler index). This reticulation might be favored by the increase in the number of hydrogen bridges available resulting from the loss of cumbersome alkyl substituents and the appearance of many oxygenated sites. The nature and evolution of the species formed at low temperatures as well as higher temperatures may allow to suggest different mechanisms revealing an influence of the mineral matter in the first stage of oxidation.

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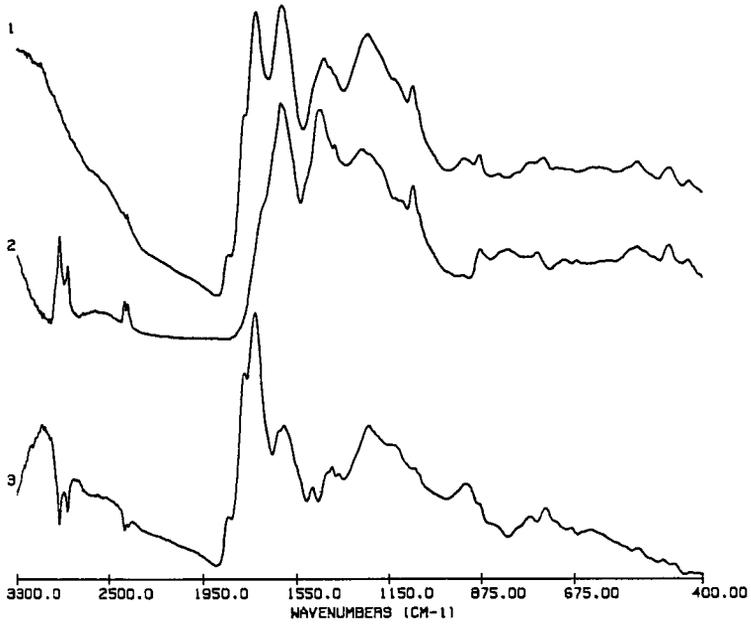


FIGURE 1

1. Infrared spectrum of fresh coal
2. Infrared spectrum of oxidized coal
3. 2 - 1 difference spectrum

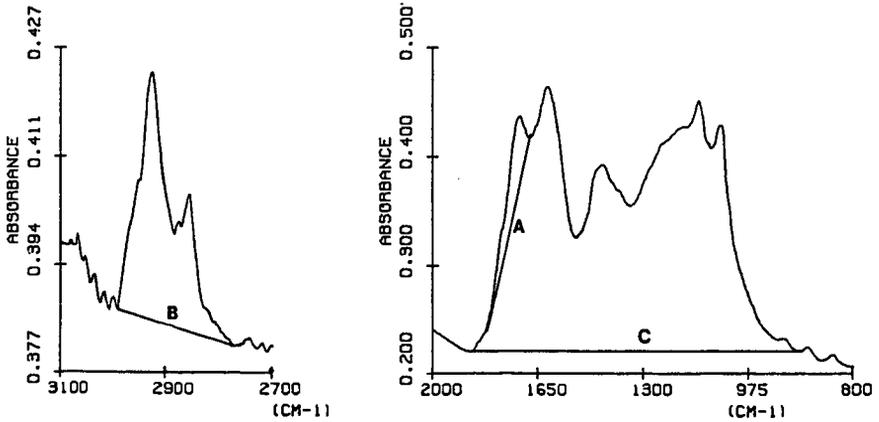


FIGURE 2

Areas integration method used

1. 2700 - 3100  $\text{cm}^{-1}$
2. 800 - 2000  $\text{cm}^{-1}$

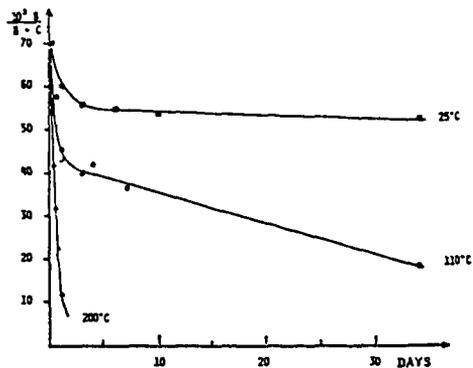
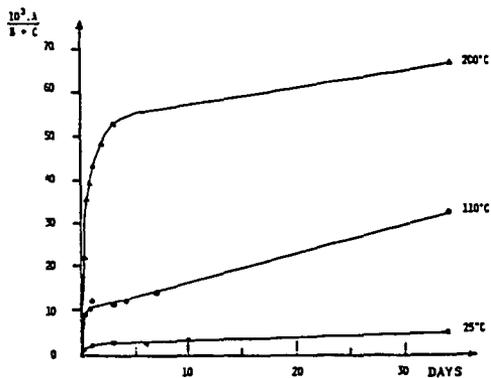


FIGURE 3a and 3b

3a. Aliphatic groups decrease : B/B+C ratio versus oxidation time at 25 , 110 and 200°C

3b. Carboxylic and carbonyl groups increase : A/B+C ratio versus oxidation time at 25 , 110 and 200°C

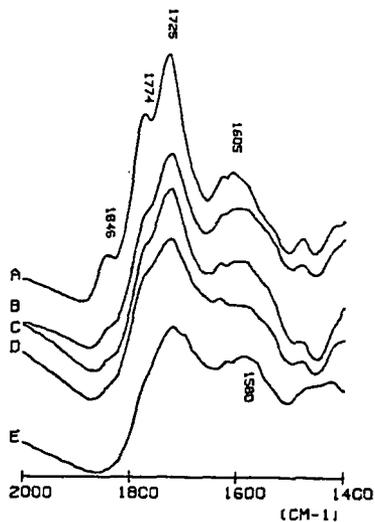
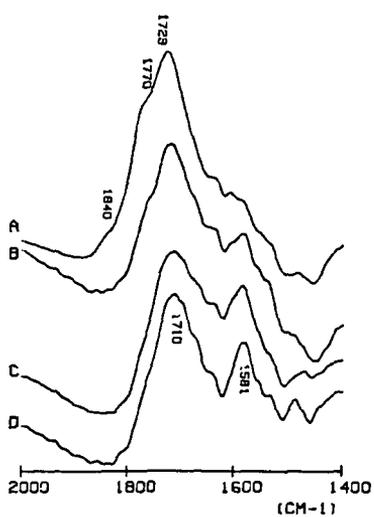


FIGURE 4a and 4b

4a. Difference spectra between 2000 and 1400  $\text{cm}^{-1}$  of oxidized coals at 200°C, (a , 34 days ; b , 4 days ; c , 18hrs ; d , 6hrs .)

4b. Difference spectra between 2000 and 1400 $\text{cm}^{-1}$  of oxidized coals at 110°C, ( a , 34 days ; b , 4 days ; c , 18hrs ; d , 6hrs.)

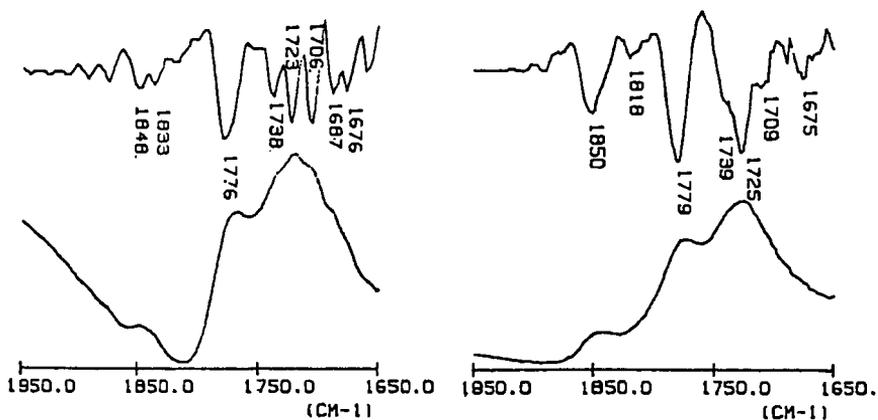


FIGURE 5a and 5b

5a . Infrared spectrum of oxidized coal at 20°C after 78 days and the corresponding derivative spectrum

5b . Infrared spectrum of oxidized coal at 200°C after 34 days and the corresponding derivative spectrum

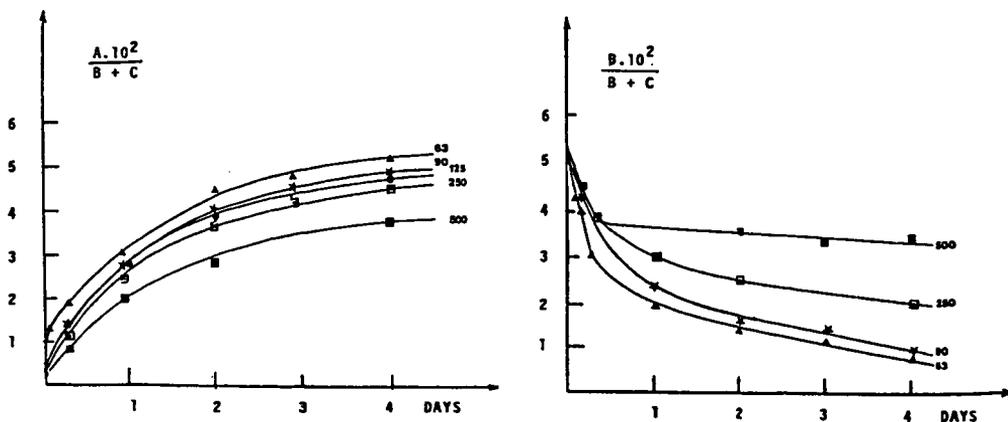


FIGURE 6a and 6b

6a . Aliphatic groups decrease : B/B+C ratio versus oxidation time at 200°C and particle size effect .

6b . Carboxylic and carbonyl groups increase : A/B+C ratio versus oxidation time at 200°C and particle size effect .

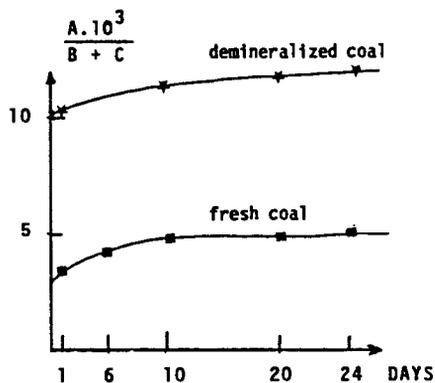
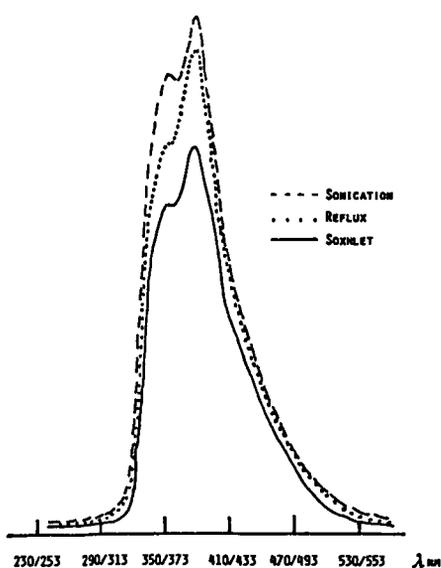


FIGURE 7

Comparison of aerial oxidized raw coal at 20°C and demineralized coal  
 Carboxylic and carbonyl groups increase: A/B+C ratio versus oxidation time.

PYRIDINE EXTRACTS (GARDANNE COAL)



MULTIPLE STEP EXTRACTION

THF FRACTION

GARDANNE COAL

- fresh coal
- - - demineralized coal
- ..... oxidized coal

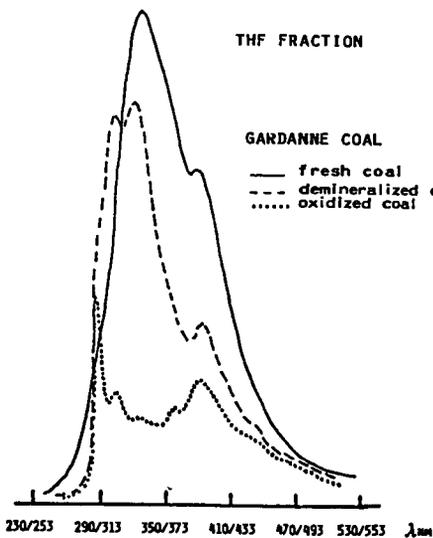


FIGURE 8 and FIGURE 9

UV fluorescence spectra of coal extracts (pyridine) obtained by different extractive methods: sonication, dissolution and Soxhlet

UV fluorescence spectra of coal extracts (THF) obtained from a fresh coal, demineralized coal and oxidized coal.