THE ELECTROCHEMICAL OXIDATION OF OIL SHALE

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ABSTRACT

Huangxian oil shale slurry in alkaline medium was oxidized by electrochemical method to produce some water soluble and water insoluble acids at anode compartment and high purity H_2 as a by-product at cathode compartment. The elemental analysis shows that about 25-50% of the organic carbon in oil shale was oxidized to products. In the gas chromatographic analysis of methyl ester of organic acids obtained from the oxidation shows that the products are composed of normal saturated monocarboxylic acids in range of C_{10}-C_{22}, normal saturated dicarboxylic acids in the range of C_4-C_{24} and other high molecular weight acids. The current efficiency of hydrogen production was approximately 100%. The influences of several experimental parameters of the electrochemical oxidation process, including voltage, pressure, temperature and slurry concentration have been investigated. Some other oil shales were oxidized for comparison with Huangxian oil shale. It has been found that Huangxian oil shale shows better activities. The mechanism of anodic oxidation was investigated preliminarily. It showed that the electrochemical oxidation of oil shale was preferentialy taken place in aromatic rings of kerogen.

INTRODUCTION

Electrochemical oxidation of coal slurries has recently been suggested as a means of gasifying coal at low temperature by Coughlin et.al [1,2]. The process has been studied in acidic medium and at the voltage lower then the potential for conventional water electrolysis. During oxidation of coal slurry in acidic medium the gas produced at the cathode was essentially pure H_2, the gas produced within the anode compartment was CO_2. The volume ratio of the gases collected at the cathode those at anode was greater then 2, a significant portion of surface oxides presumably remained bound to the coal, it prevented the oxidative reaction of coal. Subsequent, the mechanism of the reaction was studied by other investigators[3-5]. This electrochemical methode, however, has the advantages that hydrogen is produced from coal as a pure gas product and high temperature operations are not necessary. But reaction rate of this process was low.

Early investigators used alkaline media for electrolysis of coal slurries[6], probably because chemical oxidations were carried out mostly in basic media. The products of oxidation, humic acids, are soluble in a high pH medium. Later, various improvements were made by other investigators on electrolysis conditions for electrochemical oxidations of peat, bituminous coals and some anthracities.[7-9] They used different electrode, copper, lead, platium, nickel and graphite, results showed that humic acids were generated as products.

In this paper, we report our recent results on electrochemical oxidation of oil shale slurry in alkaline medium to produce chemicals at anode compartment and pure hydrogen as a another product at cathode compartment. It will be of some technological value to this electrochemical process.

EXPEREMENTAL

Materials

The oil shale samples, including Huangxian, Maoming and Fushun oil shales, had been crushed and pulverized to <40 mesh. Table 1 summarizes some characteristics of thsi samples.

Table 1. Characteristics of various oil shale samples (dry basis)

Constituent %	Huangxian oil shale	Maoming oil shale	Fushun oil shale
C	36.40	15.36	10.02
H	3.51	2.13	1.53
O	9.51	6.68	7.63
N	0.73	0.52	0.44
S	1.20	1.37	0.61
Ash	48.66	73.94	74.66
Volatile matter	41.60	23.01	21.38

Apparatus

The electrolysis cell is a concentric circles type, inside is cathode compartment and the outside is anode compartment, they were separated by porous frit. Nickle and iron were used as the electrode. Oil shale slurries in anolyte were held in suspension by agitation with a magnetic stirring bar. All experiments were conducted with stirred slurries of oil shale in aqueous electrolyte (KOH) within the anode compartment of cell. The external emf. was applied by potentiostat. Figure 1 is the flow diagram for separation of products of oxidation.

Results and Discusstion

(1) Effect of potential on the anode oxidation

A current/potential curve and oxidation efficiency from Huangxian oil shale slurries were shown in Figure 2. The higher the potential, the greater the oxidation current and the coulombs passed through the electrodes. The current efficiency of anode oxidation and the hydrogen production were approximately 100%, at anode compartment no O_2 was detected. But when the potential larger then 2.5V, the current efficiency of anode oxidation drop down. The oxidation efficiency, η_{ox}, is expressed by $\eta_{ox}=(Q_n/Q_t)*100\%$, Q_t is total coulombs passed through the electorde and Q_n is net coulombs consumed for anode oxidation.

(2) Effect of temperature on the anode oxidation

Figure 3 shows that the higher temperature gives the greater oxidation current, the current efficiency of anode oxidation maintain 100% approximately. Effect of temperature on the yield of anode products shows in Figure 4. The yield of WSA and WIA all incresed with the temperture. According to Arrhenius plots the apparent activation energy E_a=21.5*10^3J/mol.

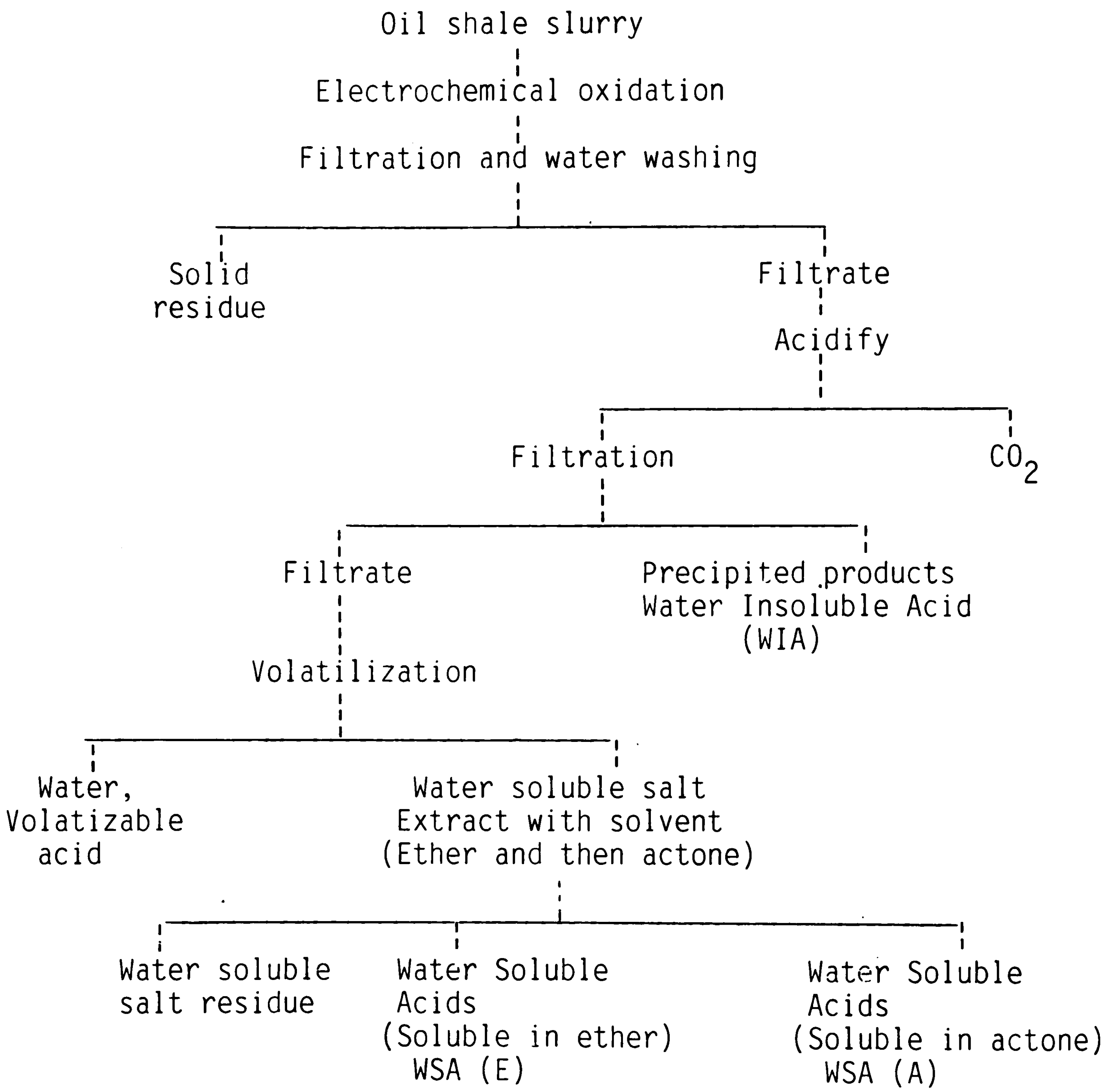

Fig. 1. Flow diagram for separation of products of electrochemical oxidation

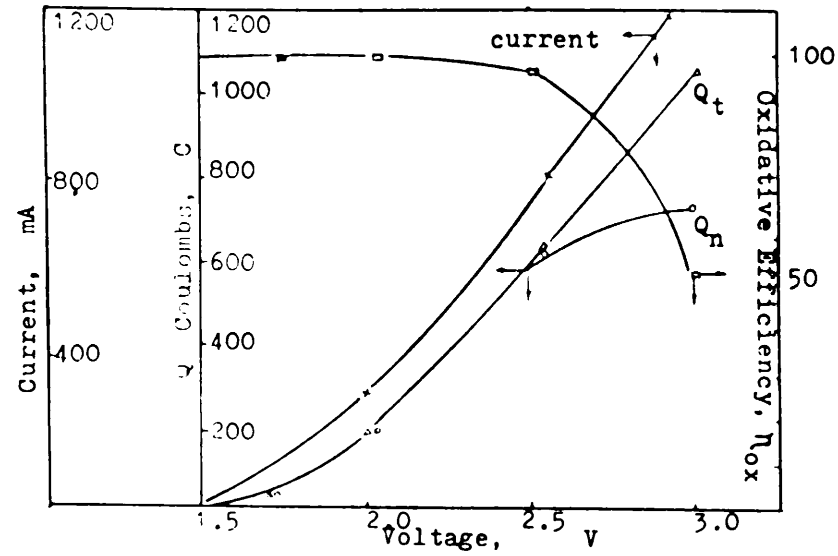

Fig. 2. Current, coulombs and oxidative efficiency vs. voltage (at 70°C, slurry conc. 0.083g/ml, KOH (aq) 10% (wt.))

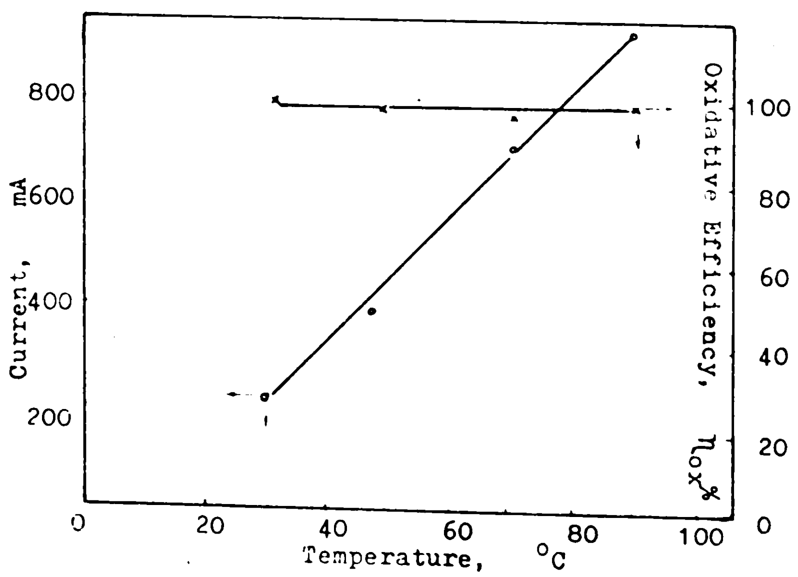

Fig. 3. Influence of temperature on current and oxidation efficiency (at 2.5V, slurry conc. 0.083g/ml)

(3) Effect of pressure on anode oxidation

Effect of pressure on the yield of oxidation products is shown in the Figure 5. The yield of oxidation product (WSA, WIA) increased with the pressure at the same coulombs passed. Why the pressure causes increasing in oxidation product. Research to discover the mechanism is now going on. Meanwhile the higher pressure, the higher temperature may be used for oxidation reaction, and obtained more products. At 140°C the yield of oxidation product is about 12% and about 50% of the organic carbon in oil shale was oxidized to product.

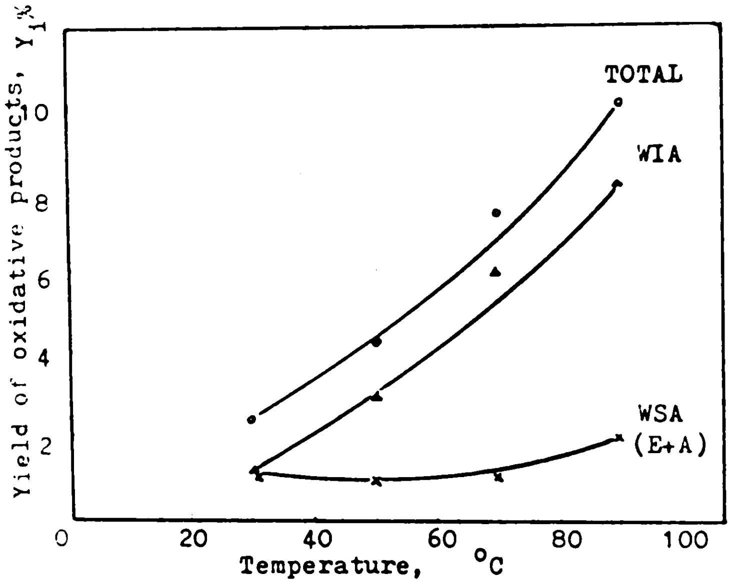

Fig. 4. Influence of temperature on yield of products
(at 2.5V slurry conc. 0.083g/ml 7 hr.)

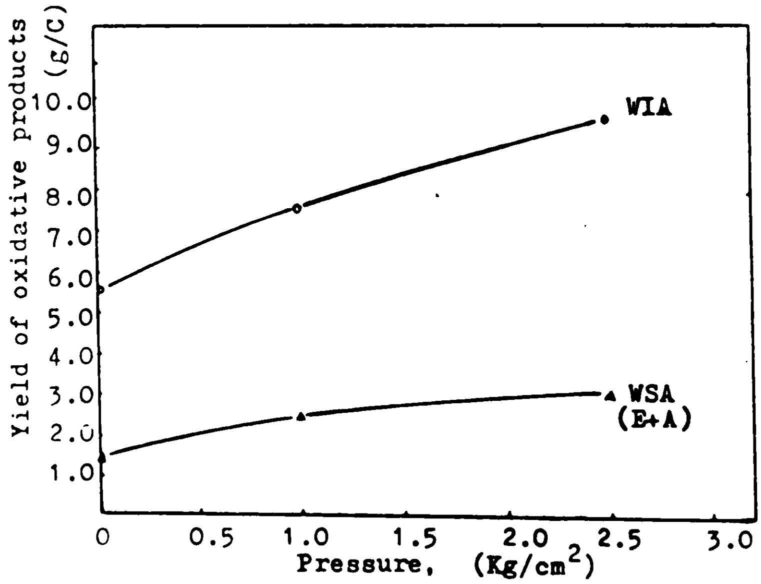

Fig. 5. Influence of pressure on yield of product
(2.5V slurry conc. 0.083g/ml 80°C)

(4) Effect of slurry concentration on the anode oxidation

Figure 6 gives the effect of concentration on the current and oxidative efficiency of anode oxidation. The current is not incresed with the slurry concentration, but the oxidative efficiency of anode oxidation increased linearly with the slurry concentration when concentration less then 0.095g/ml. and when large then 0.095g/ml. the current efficiency of anode oxidation approximately equals 100%.

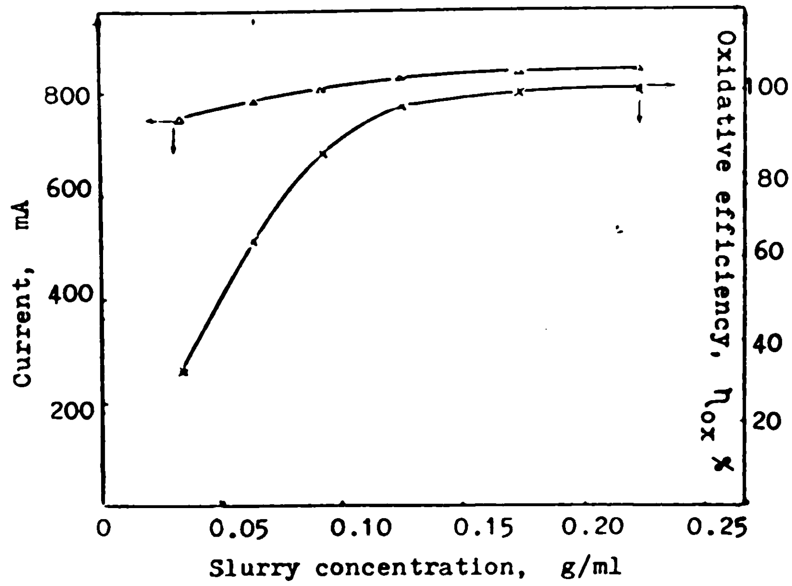

Fig. 6. Current and oxidative efficiency vs. slurry concenration (2.5V. 70°C)

(5) Comparison of electrochemical oxidation character of different oil shale samples

Three oil shales were studied at the same condition. Table 2 shows the typical results.

Table 2. Comparison of oxidation character of oil shales

Oil Shale	Y_{WIA}%	Y_{WSA}%	Y_P%	η_{ox}%	Y_P/Q_n(g/C)	Y_P/Q_t(g/C)
Huangxian	6.19	1.15	7.34	94.3	$1.25*10^{-4}$	$1.18*10^{-4}$
Maoming	1.25	0.52	1.77	43.9	$0.60*10^{-4}$	$0.26*10^{-4}$
Fushun	0.12	0.41	0.53	25.7	$0.27*10^{-4}$	$0.07*10^{-4}$

(at 2.5V. 70°C slurry concentration 0.083g/ml 7 hr.)

This Table indicates that the Huangxian oil shale shows the better activities. Previous workers [10] have reported that the aromaticity of kerogen of Huangxian oil shale is higher then the others. The combustion performence of Huangxian oil shale before and after electrochemical oxidation using DSC method is shown in Figure 7. In the figure the first peak of DSC curve in the range 200-390°C arise from combustion of the aliphatic portion of the sample and the second peak in the range 400-550°C from the aromatic.[11] The DSC curves of Huangxian oil shale indicates that after oxidation the change of first peak at 340°C was no significance and the second peak at 437°C decreased repidly. The aromaticitys of Huangxian oil shale before and after oxidation are 0.36 and 0.22 respectively. It means that aromatic ring systems were destroyed and the aliphatic structures of oil shale were preserved.

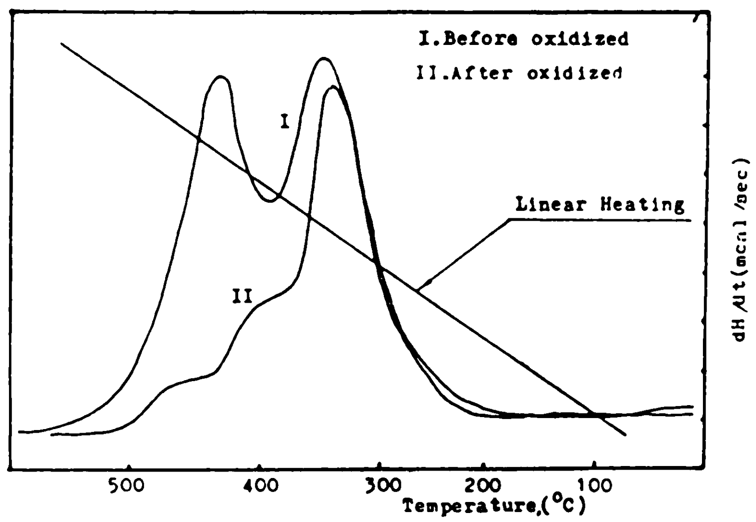

Fig. 7. DSC curves of Huangxian oil shale before and after electrochemical oxidation

(6) Products of electrochemical oxidation

A gas chromatogram of methyl ester of organic acids obtained from the oxidation of Huangxian oil shale showed the products to be composed of saturated monocarboxylic acids in the range of C_{10}-C_{22}, normal dicarboxylic acids in the range of C_4-C_{24}. Identification of peak was accomplished by co-injection of known standards and by comparison of the chromatographlic retention time of each compound with those of standard kits. Figure 8 (a, b, c) shows the gas chromatogram of methyl esters of the organic acids obtained from the oxidation. After extracted with actone the residue of WIA was subjected to infrared spectroscopic analysis. The results indicated that this portion of the WIA is composed of aromatic acids as a predominate compound.

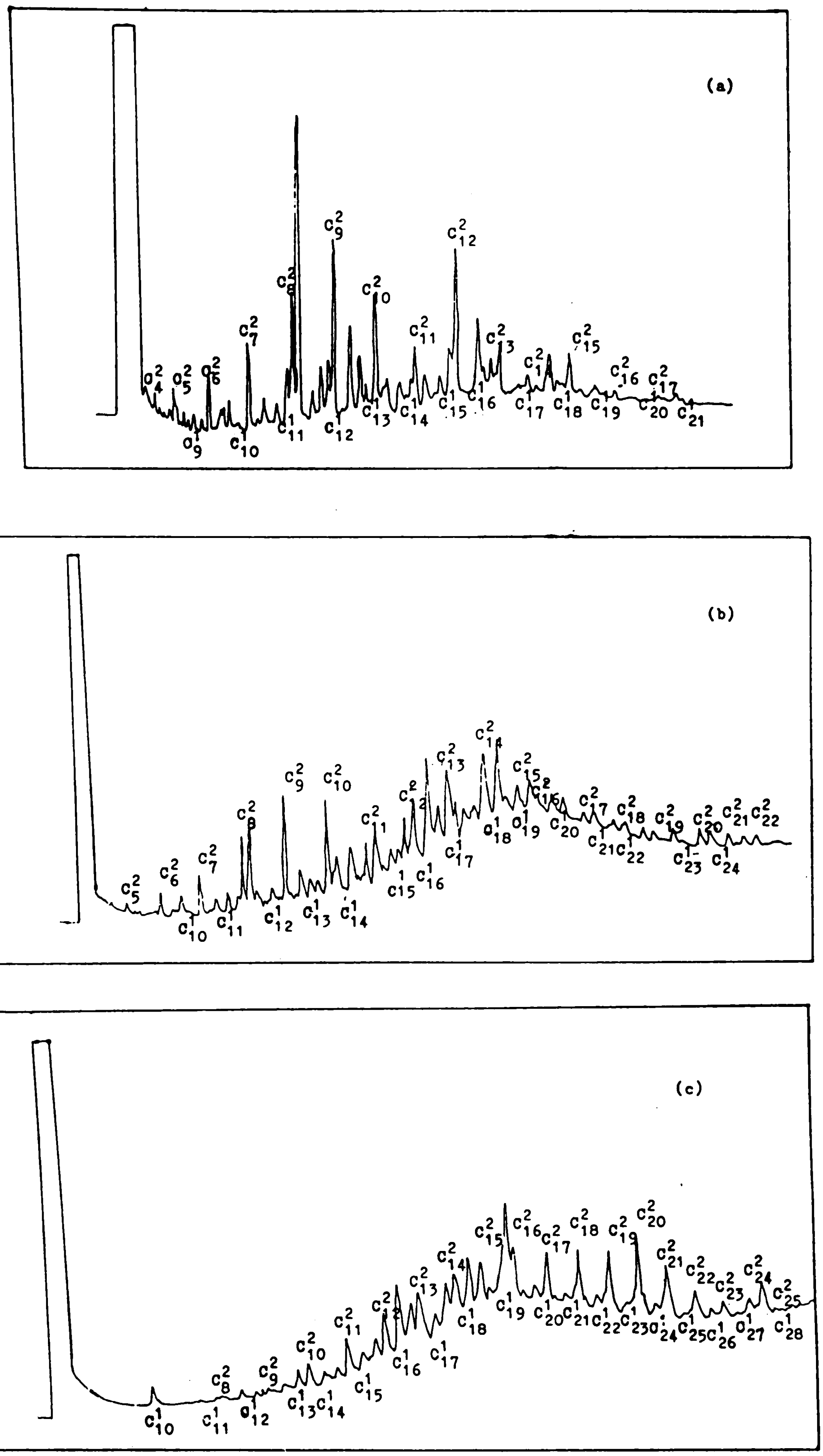

Fig. 8. (a) Gas chromatogram of methyl esters of the WSA (E)
(b) WSA (A)
(c) WIA (A)

CONCLUSIONS

1. Oil shale slurries were oxidized directly by electrochemical method in alkaline media to produce carboxylic acid and H_2 as a by-product. Huangxian oil shale was chosen as the most suitable material for the oxidation than the Fushun and Maoming oil shales.

2. The influences of several experimental parameters of electrochemical oxidation process have been investigated. Among them the effect of pressure on electrochemical oxidation is a important problem.

3. Prelimenary study was shown that, the electrochemical oxidation of oil shale was preferentially take place in aromatic rings of kerogen.

REFERENCES

(1) R.W.Coughlin and M.Farooque, Nature (London) 279, 301 (1979).

(2) R.W.Coughlin and M.Farooque, Ind. Eng. Chem. Process Des. Dev. 19, 211 (1980).

(3) R.P.Baldwin, K.F.Jones, T.T.Joseph and J.L.Wong, Fuel, 60, 739 (1981).

(4) P.M.Dhooge, D.E.Stilwell, and S-W Park, Journal of the Electro-Chemical Society 129, 1719 (1982).

(5) P.M.Dhooge and S-W Park, ibid, 130, 1029 (1983).

(6) C.S.Lynch and A.R.Collett, Fuel, 11, 408 (1932).

(7) R.Eddinger and D.Demorest, ibid, 26, 157, (1947).

(8) R.Belcher, J.Soc. Chem. Ind. 67, 213, 265 (1948).

(9) M.H.Khundkar and M.M.Kawal, Fuel, 45, 9 (1966).

(10) Lao Yongxin and Qin Kuangzong, 82, Collected Paper on Oil Shale Research (1983), (in Chinese).

(11) V.Marinov, Journal of Thermol Analysis, 7, 333, (1975).