Thermochimica Acta, 134 (1988) 327-331
Elsevier Science Publishers B.V., Amsterdam

COMPARATIVE TGA AND DSC STUDIES OF OIL SHALES

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Abstract. The TGA/DSC equipment offers a simple and accurate method for determination of the amount of the organic matter in oil shales and also for differentiating between volatile and non-volatile fractions. This was done by first carrying out the thermogravimetric analysis in nitrogen, to obtain the volatile fraction, followed by heating the residue in oxygen, to obtain the amount of residual char. The results were quite reproducible and the method was used for comparison of Mishor Rotem shales, from Israel and Kentucky and Green River shales, from the U.S.A. The method was also used as an analytical tool for evaluation of the efficiency of different solvents in supercritical extraction of oil shales and comparison of the extracts with kerogen and retort oil.

Introduction The organic matter present in oil shales, mostly kerogen, is a complex mixture of high MW organic molecules, finely distributed in an inorganic matrix. In order to convert the organic matter into useful liquids or gases it is common practice to use retorting processes under an inert atmosphere. Retorting is usually carried out at 500° to 600° C, a temperature where considerable degradation takes place, resulting in a volatile fraction which is recovered and a char fraction which remains with the inorganic residue. It was widely reported in the literature that extraction of oil shales under supercritical conditions can lead to less degradation and charring. We have studied the supercritical extraction of oil shales from Israel anf from the U.S.A., in a number of solvents and found that some of them are quite efficient.

The determination of the amount of organic matter in oil shales is quite complicated and involves elaborate techniques. One method involves total analysis of C,H,O,S,N and also differentiation between organic and inorganic carbon. Another method involves dissolving all the minerals by different inorganic solvents and reducing mixtures and weighing the residual kerogen. There is also the Fisher assay, which is retorting under controlled heating in an inert atmosphere. The residual char is then determined by combustion. Calorimetry determines the total calorific value of the shales. However, in cases where considerable amount of carbonates are present, the heat measured is lower because the enthalpy of the decomposition of carbonates is also included. The TGA/DSC equipment offers a simple and accurate way of determining the amount of organic matter present in shales and also to differentiate between volatile and non-volatile fractions.

Experimental. Samples of oil shales used in this work were: 1. Israeli shales from Mishor Rotem, 2. Eastern American shales from Kentucky and 3. Western American shales from the Green River oil shale deposit. The TGA was performed in oxygen, in nitrogen and first in nitrogen followed by oxygen, at a heating rate of 50°C.minute. The DSC was done at a heating rate of 5°/minute. A Mettler TA 3000 system used was equipped with a TG 50 thermobalance, a DSC attachment ,a TC10TA processor and a Mettler 03 data interface.

Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21-25 Aug. 1988
0040-6031/88/$03.50

Results and Discussion. TGA of shales in an oxygen atmosphere leads to complete burning of the kerogen and therefore the weight loss can be an accurate measure of the amount of kerogen in the shales. TGA in a nitrogen atmosphere gives only the fraction which degrades thermally and yields volatile products. The residue contains char products which cannot be volatilized but can be burned in oxygen. The results of the TGA experiments with the three shales studied, in an atmosphere of oxygen, nitrogen and nitrogen followed by oxygen, can be seen in Figure 1, and a summary of the respective weight losses is shown in Table 1.

Table 1.

TGA and DSC of initial shales.

Shales	% volat. in shales	% char in shales	% total kerogen in shales	%volat. in kerogen	%char in kerogen	ΔH of kerogen KJ/gr shales	ΔH of char KJ/gr shales
Rotem	11.0	3.2	14.2	77.5	22.5	1.9	0.5
Green River	40.4	6.4	46.8	86.3	13.7	10.3	1.4
Kentucky	8.5	6.6	15.1	56.3	43.7	2.9	1.1

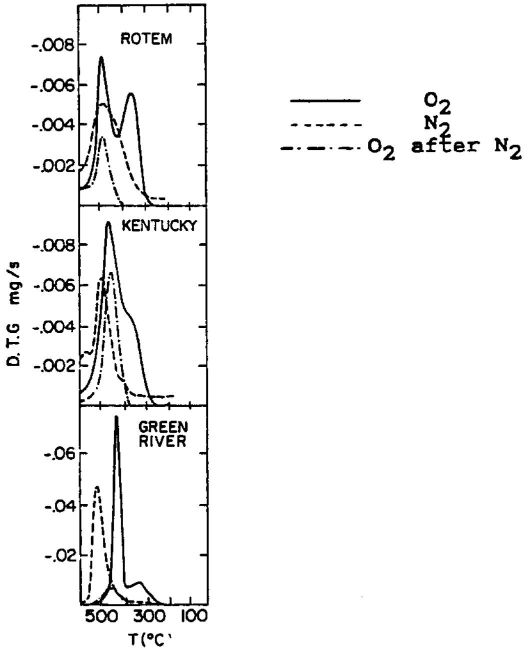


Figure 1. TGA of oil shales.

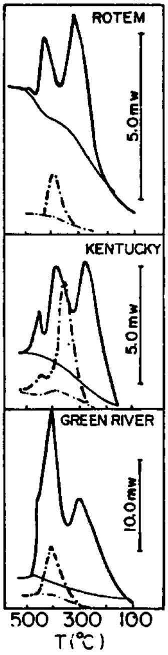


Figure 2. DSC of oil shales

The Rotem shales show two distinct peaks on combustion in oxygen. The first one is probably due mainly to the aliphatic fraction, while the second one is due to the combustion of the aromatic fraction. One can see that the pyrolysis in nitrogen starts at a higher temperature indicating that the combustion in oxygen starts in the condensed phase. The combustion of the char in oxygen also takes place at about the same temperature. The sum of the peak areas for the latter two peaks equals the peak area in oxygen, thus confirming our contention that it is a measure of the total kerogen content of the shales.

The Kentucky shales show a similar behaviour, only one can see that the volatile fraction and the char are almost equal in area.

The Green River shales show a very sharp peak on oxidation and it may be that some solid particles are lost during the intense exothermic reaction. Indeed the kerogen content calculated from the direct oxidation thermogram was 56% which is much higher than the value found by analysis (45.1%). The sum of the weight losses resulting from pyrolysis under nitrogen and combustion of the char, is 46.8% , which is closer to the real value.

The two oxidation reactions, that of the initial kerogen and that of the char can also be seen in the DSC thermograms shown in Figure 2. The respective heats of combustion are given in Table 1. The temperature of the peaks are generally lower than those obtained in the TGA, probably because of the lower heating rates. The shapes are not identical,because in the DSC case, the heat of combustion is a function of the hydrogen content of the molecules. It was also noticed that the calculated heats of combustion for all the three shales were lower than those measured by ordinary calorimetric methods. This may be due to the fact that part of the combustion is carried out in the gas phase after vaporization and the detector cannot register all the heat evolved.

The % char in the kerogens is shown in Table 1. The Green River shales show the lowest char content, 13.7%, while Rotem shales are higher in char content, 22.5%, and Kentucky shales have a very high value of 43.7%. This can be attributed to the high aromaticity of the latter shales. This was also verified by FTIR analysis of the mineral free kerogen and the mineral free char.

We concluded therefore that the TGA method described above can be used as a simple and accurate way of determination of the total kerogen in shales as well as distinguishing between the volatile and the char fractions. We used the same method for the determination of the residual kerogen in the spent shale after supercritical extraction, as will be shown in the next chapter.

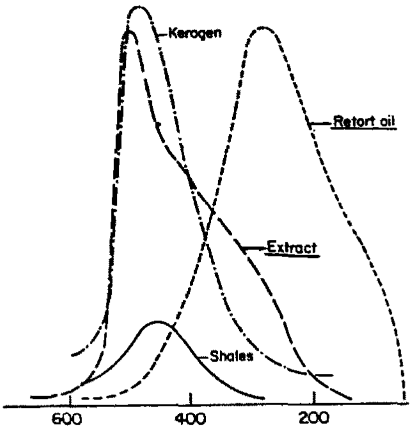
The results of the supercritical extraction of the shales studied are given in Table 2. One can see that Rotem and Green River shales can be extracted quite efficiently by isopropanol or water/CO mixtures. However, Kentucky shales are less amenable to extraction. This is probably due to the high aromaticity of it's kerogen.

Table 2
SCE of shales in an autoclave.

Shale	Solvent	P at	%SCE +volat.	% SCE	% Volat.	% Char	MW
R	Isop.	70	94.6	85.4	9.2	5.4	-
GR	"	"	98.7	97.2	1.5	1.3	370
K	"	"	63.1	49.5	13.6	36.9	270
R	Toluene	120	91.9	79.1	12.8	8.1	420
GR	"	"	97.9	95.5	1.6	2.9	510
K	"	"	75.9	58.6	17.3	24.1	430
R	Water pH 12.3	180	87.8	83.0	4.8	12.3	280
GR	"	"	91.6	89.8	1.8	8.4	290
K	"	"	63.3	51.6	11.7	36.7	240
R	Water/CO pH 12.3	210	96.6	90.0	6.6	3.4	360
GR	"	"	98.7	96.2	2.5	1.3	380
K	"	"	66.4	53.3	13.1	33.6	310

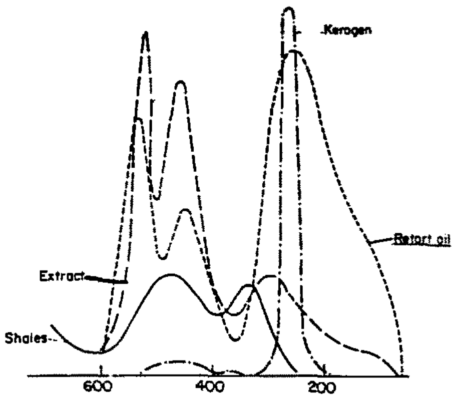
Some extaction experiments were also run in the DSC equipment itself, using a 275 microliter autoclave. The results were similar to those obtained in a regular large autoclave.

TGA can also give us an insight into the changes in the structure of the kerogen taking place during the extraction process in comparison to the retorting process. Figures 3 and 4 show the results of TGA in nitrogen and in oxygen, respectively, of four samples: initial Rotem shales, kerogen obtained by demineralization, retort oil and supercritical extract in toluene.



T° C

Figure 3. TGA in nitrogen



T° C

Figure 4. TGA in oxygen

Figure 3 shows that the volatility of the kerogen in the initial shales, in the demineralized form and in the extract, are quite similar. However, the retort oil is much more volatile, indicating that the retorting process involves considerable degradation.

Figure 4 shows the burning characteristics of the four samples in oxygen. The initial shales show too distinct peaks, probably due to the alipahatic and the aromatic fractions. The kerogen obtained from demineralization burns at a very low temperature, 250° C. This is probably due to the fact that demineralization results in a highly open structure that burns very efficiently when heated at a high rate of 50°/minute. However, when the rate is reduced to 10°/minute, only a small fraction burns at 250° and the main fraction burns at 500° C. The retort oil burns mainly at a low temperature showing that it is highly degraded. The extract burns mainly at a high temperature more or less paralel to the initial shales.

Comparative DSC thermograms of the same four samples show some interesting features. However, further work is needed in order to get a full interpretation of the results.

Acknoledgement.

We would like to thank Prof. Yuda Yürum from the Chemistry Department, Hacettepe University, Ankara, Turkey, who initiated this work during his tenure as Visiting Scientist at the Weizmann Instiute of Science.

This work was supported by a grant from the U.S. Department of Energy, in the framework of the cooperation agreement with the Israeli Ministry of Energy and Infrastructure.