

THERMOCHEMICAL REACTIONS IN SUBCRITICAL AND SUPERCRITICAL INTERACTION BETWEEN MISHOR ROTEM OIL SHALE AND TOLUENE

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ABSTRACT

Thermal chemical reactions which occur during the interaction between Israeli Mishor Rotem oil shale and toluene at subcritical and supercritical conditions were investigated. A high pressure differential scanning calorimetry system was used to simulate our previous experimentation performed in autoclaves. This permitted collection of data related to thermal chemical reactions occurring and sequential experimentation on the same sample provided the yield of interaction and structural characteristics of the organic material recovered. FTIR spectra of products were measured, and the molecular weights of products were determined by GPC high pressure liquid chromatography. DSC thermograms of the oil shale–toluene interaction indicated the presence of two endothermal events at 209 and at 304°C during the heating period. Isothermal experiments at 340°C (at supercritical conditions) were noteworthy for the absence of any heat effects during extended times. The yield of shale–toluene interaction during isothermal experiments at 340°C increased up to 55% in 30 min after which a steady state in the recovery of organic materials was reached. The molecular weights of recovered organic material increased similarly during the first 30 minutes; followed by a reduction in molecular weights after this period. FTIR spectra of the products did not show remarkable changes in the chemical structure of products during extended times of experiments at 340°C. These findings confirmed the absence of pyrolytic reactions during the isothermal supercritical interaction between oil shale and toluene. It appears that material initially soluble as well as products of thermolysis reactions were extracted by toluene at the supercritical temperature of 340°C.

INTRODUCTION

Coals and oil shales contain material readily soluble in the high density solvent vapour formed under supercritical conditions. Some initially insoluble material may be solubilized by chemical changes occurring during the supercritical treatment. Therefore the high efficiency of supercritical extrac-

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tion of fossil fuels superimposed on the high diffusivity of the dense vapour may be due to the formation of additional soluble material by chemical changes. There is controversy concerning the effects of thermal chemical processes occurring during the supercritical extraction of coals and oil shales within the temperature range 300–400°C. The aim of this report is to detail, in part, the thermal chemical reactions that occur and soluble products that are formed during the interaction of an Israeli oil shale and toluene at supercritical conditions, using a high pressure differential scanning calorimetry system which simulated experimentation performed in autoclaves in a recent study [1]. This permitted collection of data related to thermal chemical reactions occurring and sequential experimentation on the same sample provided the yield of interaction and structural characteristics of the organic material recovered.

Preferred solvents for supercritical extraction of coals and oil shales possess critical temperatures in the range 300–400°C (temperatures in which most of the supercritical extractions are conducted) [2]. Homolytic bond cleavage is the rate limiting step in the depolymerization of coals in solvents at subcritical conditions within the range 300–400°C [3]. Blessing and Ross [4], Bartle et al. [5] and Squires et al. [6] indicated the presence of the thermal chemical processes during the supercritical extraction of coals. Chong and McKay [7] attributed the high yield of extract obtained during supercritical extraction of a Green River oil shale to the combined effects of thermal processes and physical extraction.

On the other hand, Ceylan and Olcay [8] relying on their observations in which only small amounts of gases were formed and on the structure of the supercritical toluene extracts from a Turkish bituminous coal reasoned that thermal degradation did not occur. Larsen et al. [9] present evidence for the cleavage of bonds by solvent attack contributing to the coal depolymerization at supercritical conditions with pyridine.

Model thermolysis studies with 1,2-diphenyl ethane in tetralin at 400°C showed a relatively high stability of this pure compound. The half life of 1,2-diphenyl ethane under these specified conditions was measured as 10 h [10,11]. Similar experiments at lower temperatures, i.e., 350°C gave a half life of 32 days [12] which might create the impression that at supercritical conditions at 350°C, the rate of thermolysis reactions of giant kerogen molecule in coal or oil shale was negligible. Thus, conclusions reached from the studies with model compounds may lead to erroneous deductions when carried over to naturally occurring “impure” materials like coal and oil shale. The reaction of coal under even milder conditions is too rapid for convenient measurement [13,14]. Thus, thermal depolymerization occurring at about 350°C would require either the presence of many very labile bonds in the kerogen molecule (of coal or oil shale) or cleavage of the bonds both by solvent attack and thermal reactions with lower activation energies due to solvation. Wisler [15] has suggested that the rates of coal thermolysis may be

enhanced significantly in the presence of a solvent. Blessing and Ross [4] relying on their findings from supercritical toluene and coal interactions proposed a thermolysis mechanism with the participation of solvent. Yürüm [14], observed that several endothermic reactions were occurring during the interaction between a high volatile bituminous coal and quinoline in the range 325–360°C. Squires et al. [6], indicated the occurrence of two types of thermal processes during the supercritical extraction of a high volatile bituminous coal with methanol. The first process, which occurs at approximately 200°C, apparently alters the coal structure in a way that reduces its pyridine extractability. The second process observed at about 300–350°C was due to thermolysis of bonds and there is evidence for the acceleration of these processes at higher temperatures.

In the present study we utilized a high pressure differential scanning calorimetry system to follow the heat effects occurring during the interaction of toluene and an oil shale at supercritical conditions. We observed two endothermal effects at about 200 and 300°C indicating the presence of pyrolysis reactions during the supercritical interaction.

EXPERIMENTAL

Mishor Rotem oil shale was used in this work. Elemental analysis of the oil shale is presented in Table 1.

Supercritical extraction experiments of shale with toluene were performed in high pressure micro autoclaves of 275 μ l volume, which were the cells of a Mettler TA 3000 system equipped with a differential scanning calorimetry attachment with a TC 10 TA processor via a Mettler 03 data interface. Temperature was measured with a Pt 100 temperature sensor. The measuring cell (microautoclave) was charged with 50 mg toluene and 2.5 mg of powdered oil shale. The calculated vapour density was 0.2 g ml⁻¹. The

TABLE 1
Analysis of Mishor Rotem oil shale

	%	% (dry, mineral matter free basis)
C	9.7	62.2
H	1.1	6.9
N	0.2	1.4
S(total)	1.8	11.5
O(diff.)	2.8	17.9
H ₂ O(crystal)	1.5	
CO ₂	21.0	
Non-volatiles	61.9	

microautoclave was sealed after it was purged with argon. The reference microautoclave was charged with 50 mg toluene, purged with argon and sealed. The microautoclaves were resistant up to 100 atmospheres pressure; the calculated experimental pressure was about 80 atmospheres. Both of the microautoclaves were placed in the furnace of the DSC system and heated from 30 to 340°C at a heating rate of 10°C min⁻¹ and kept at 340°C for varying lengths of time. Time zero was considered as the time when temperature reached 340°C. Experiments run with toluene in both cells provided the blank thermogram. The DSC thermogram of the oil shale without toluene in a sealed microautoclave versus an empty and sealed microautoclave was also measured to determine the heat effects in a medium without solvent. After the DSC experiments the microautoclave was opened, the solution containing the extract was separated by decantation. The spent shale was washed with toluene. The washings separated by decantation were combined with the initial solution. The spent shale was dried under nitrogen and the amount of kerogen remaining, was measured by the thermogravimetric method described previously [1] to determine the yield of extraction. The average molecular weight and the Fourier transform infrared spectra of the extracts were measured as described recently [1].

RESULTS AND DISCUSSION

Differential scanning calorimetry of supercritical interaction between oil shale and toluene

In order to investigate the thermal reactions occurring during the supercritical interaction between toluene and oil shale a DSC system with cells (microautoclaves) resistant to 100 atmospheres pressure was utilized. Figure 1 presents the thermogram obtained while both of the measuring and reference cells were charged with about 50 mg of toluene under an argon atmosphere and heated from 30 to 340°C with a rate of 10°C min⁻¹. Since both of the microautoclaves of the DSC system contained toluene in approximately equal amounts the thermal effects due to toluene itself are eliminated. In each experiment a slight difference in the weight of toluene in both cells was unavoidable. In fact, this minute difference, tenths of a milligram, calls attention to the heat effects due to the transition into the supercritical region. The sharp endothermal peaks at about 320°C ($T_c(\text{toluene}) = 320.8^\circ\text{C}$) was caused by the transition from subcritical to supercritical conditions. The calculated pressure in the microautoclave was 80 atm ($P_c(\text{toluene}) = 41.6 \text{ atm}$). The quantity of heat due to this transition averaged to $91 \pm 24 \text{ J}$ in ten different experiments. In the worst case, assuming the difference in the weight of toluene in both cells was 0.5 mg in all the experiments, we can calculate the heat required for subcritical to

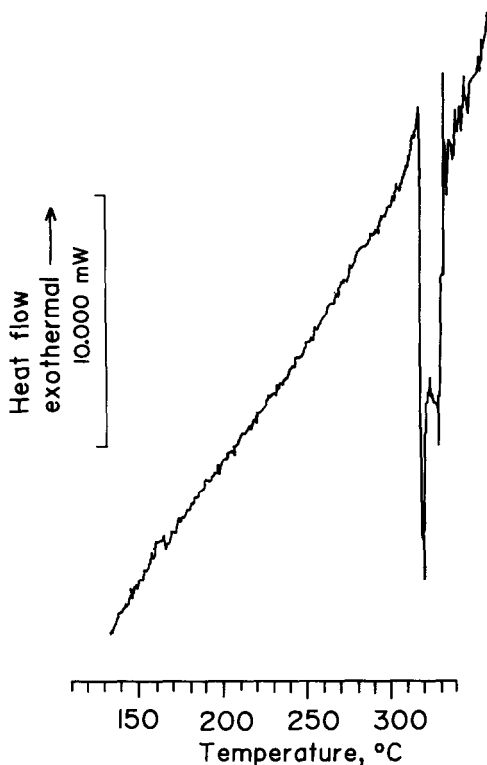


Fig. 1. DSC thermogram of the control experiment in which both measuring and reference cells were charged with toluene. Endothermic peaks at 320°C were due to subcritical to supercritical transition.

supercritical transition. The calculated amount of heat required with this assumption for the transition of 1 mole of toluene was $17 \pm 4 \text{ kJ mol}^{-1}$ ($4 \pm 1 \text{ kcal mol}^{-1}$). This is a rough value indicating order of magnitude. A more accurate value requires more precise experiments which we plan to perform.

Figure 2 shows two sample DSC thermograms obtained during the interaction of toluene and oil shale. Figure 2a presents the thermal events occurring during the heating from 30 to 340°C at a rate of $10^\circ\text{C min}^{-1}$. As discussed earlier since both of the cells contained closely equal amounts of toluene, the peaks obtained are due solely to the oil shale, with the exception of the set of sharp endothermic peaks occurring at 320°C due to the subcritical to supercritical transition of toluene. As in the case of the “blank” experiments with toluene a rising background was also obtained in the experiments with toluene and oil shale. We observed two main endothermic peaks, at 209 ± 5 and $304 \pm 4^\circ\text{C}$. The results presented here were collected from at least 10 experiments. The temperatures of the endothermic peaks observed during the heating up are quite reproducible. The average

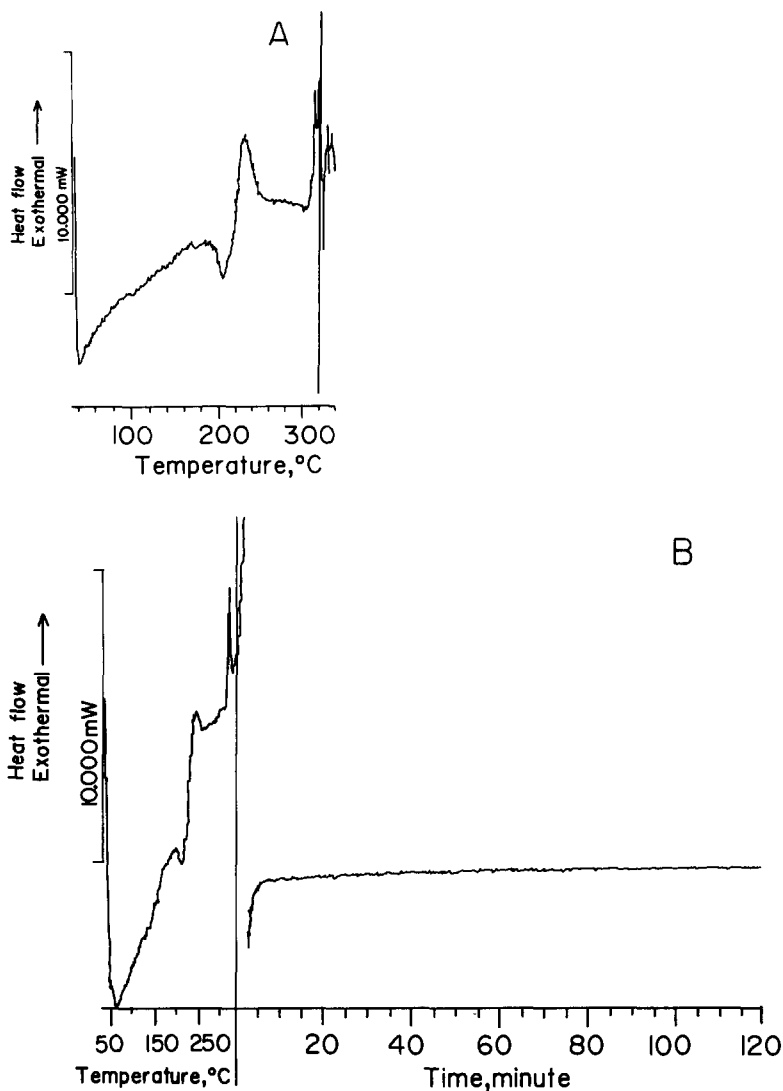


Fig. 2. (A.) DSC thermogram of toluene-oil shale interaction during the heating portion from 30 to 340°C. (B.) DSC thermogram of toluene-oil shale interaction in both heating up from 30 to 340°C and isothermal portion at 340°C for 120 min.

heats of the 209 and 304°C peaks were measured as $216 \pm 61 \text{ J g}^{-1}$ of shale and $1132 \pm 368 \text{ J g}^{-1}$ of shale, respectively. The corresponding values for the production of an extract with an average molecular weight of 630 from the Mishor Rotem shale with an organic matter content of 14.8%, are 221 ± 76 and $1134 \pm 378 \text{ kcal mol}^{-1}$, respectively. These values indicate the occurrence of several bond homolyses during the heating period.

Figure 2b shows the heating interactions up to 340°C and the isothermal regime of a DSC toluene/shale experiment which lasted for 120 minutes.

Some experiments were continued up to 180 minutes; a remarkable endothermal or exothermal event was not observed in any of the isothermal regime of these runs. In the heating portion of Fig. 2b the two characteristic endothermal events occurred at about 200 and 300°C as well as the peaks due to sub- to supercritical transition at about 320°C. The presence of endothermal events during the heating period indicated the occurrence of a degree of thermolysis reactions which we cannot presently define.

The temperatures for these events are lower than those expected for the homolysis reaction of pure compounds. It is probable that, due to solvent participation, as was previously suggested by Wisler [15] and Blessing and Ross [4], the reaction rate may increase. This might occur by the lowering of the necessary heat of activation for the progress of the reaction which is caused mainly by solvation of reactive functional groups of kerogen with liquid solvent molecules. Brower [16] found that the molar activation volume for the reaction of coal and tetralin at 344°C was -27 ± 3 ml. This value suggests a bimolecular ionic transition state in this interaction. Oil shale kerogen contains functional groups [17] which can easily participate in such an ionic interaction of relatively low activation energy that can occur at these low temperatures. Figure 3 gives the DSC thermogram of the pyrolysis of Mishor Rotem shale performed in the microautoclave. The endothermal heat effects observed in this case are at 380 and 485°C which are well above

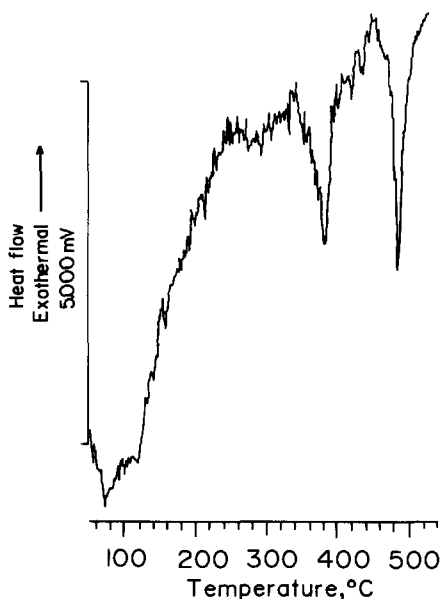


Fig. 3. DSC thermogram of oil shale pyrolysis in a closed cell (microautoclave) versus an empty closed cell.

those observed in the toluene and oil shale interaction. Williams [18] recently reported two endothermal events, at 335 and 445°C, during the atmospheric pressure thermogravimetric pyrolysis of British Kimmeridge Clay oil shale. It is evident that toluene markedly reduces the temperatures of the endothermal events. All of these observations confirm that the bond cleavages during the solvent–kerogen interaction should occur with a lower activation energy than that required in the pyrolysis of bonds in the absence of a solvent. Due to solvent–kerogen interaction of a type which we cannot describe precisely at present, the cleavage of the bonds in kerogen occurs at lower temperatures.

Polarizability, which is a measure of the ease with which the electrons of a molecule are distorted, of toluene may have an effect in this interaction. Toluene possesses a moderate value of polarizability, $7 \times 10^{-24} \text{ cm}^3$ [19]. Although the dispersion forces created by the distortion of the electron system are usually weak they are most important for nonpolar solvents like toluene where other solvation forces are absent. Solvent polarizability may influence rates of certain types of reactions because transition states may be of different polarizability from reactants and so be differently solvated.

The absence of heat events in the supercritical portion of these experiments suggests that the solubilization of kerogen during this part of the experiment was due primarily to physical extraction of the material already present initially and of material produced from thermo-solvolysis reactions in the heating up period. The effect of the heating rate on the occurrence and temperatures of the endothermal events was not investigated in the present study.

Yield of supercritical interaction

Figure 4 represents the change of yield with respect to time of supercritical toluene extraction of the Israeli Mishor Rotem shale in experiments performed in microautoclave cells of the DSC system. 48% of the organic material was extracted during the first 30 min; afterwards, the rate of recovery of organic material was relatively slow. About 55% of the kerogen was recovered in 60 min. In fact, after this period the percentage of recovered organic material averaged 57. After the first 30 min, there was not a great deal of increase in the percentage of the extract obtained. Thus, during the supercritical interaction between oil shale and toluene in the microautoclave a steady state was reached in the first 30 min. Therefore, the products obtained within this first 30 min probably are primary products. After this time no further organic material was recovered. The material recovered thus, remained in contact with spent shale at 340°C which might be converted into secondary products. This confirms our findings concerning the average molecular weights of the product. The change in average molecular weights of the products are presented in Fig. 5. The organic

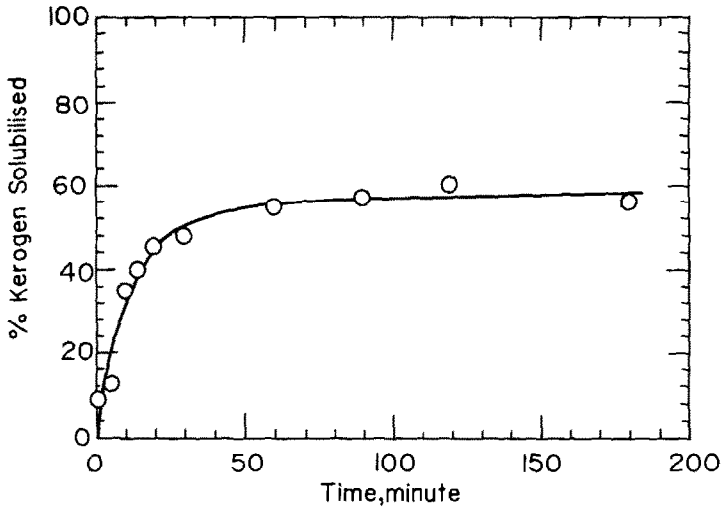


Fig. 4. Kerogen solubilized with time in the interaction of oil shale with supercritical toluene.

material obtained when the temperature reached 340°C , defined as time zero, has an average molecular weight of 580. The average molecular weight of the extracts increased to 630 as the interaction at 340°C continued up to 30 min. This is in accordance with the yield graph in Fig. 4. After 30 min there is a decrease in the average molecular weight to about 520 after 180 min of interaction. The decrease in molecular weight indicates formation of secondary products, i.e., the products obtained during the first 30 min retained their molecular weights as they were recovered from the oil shale.

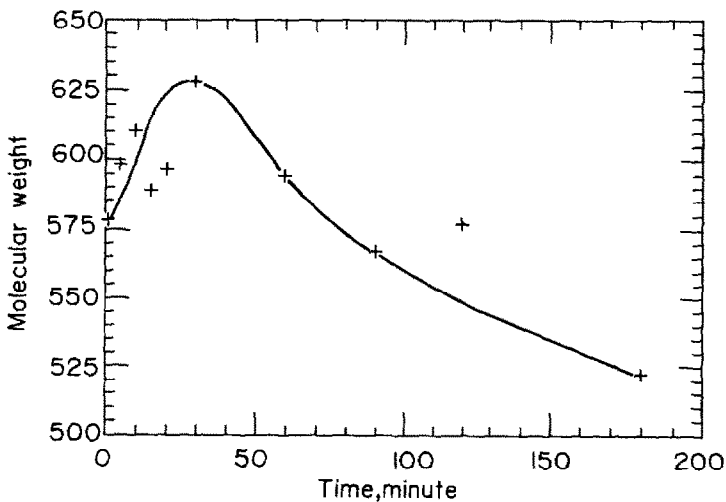


Fig. 5. Molecular weights of supercritical toluene extracts of oil shale during extraction.

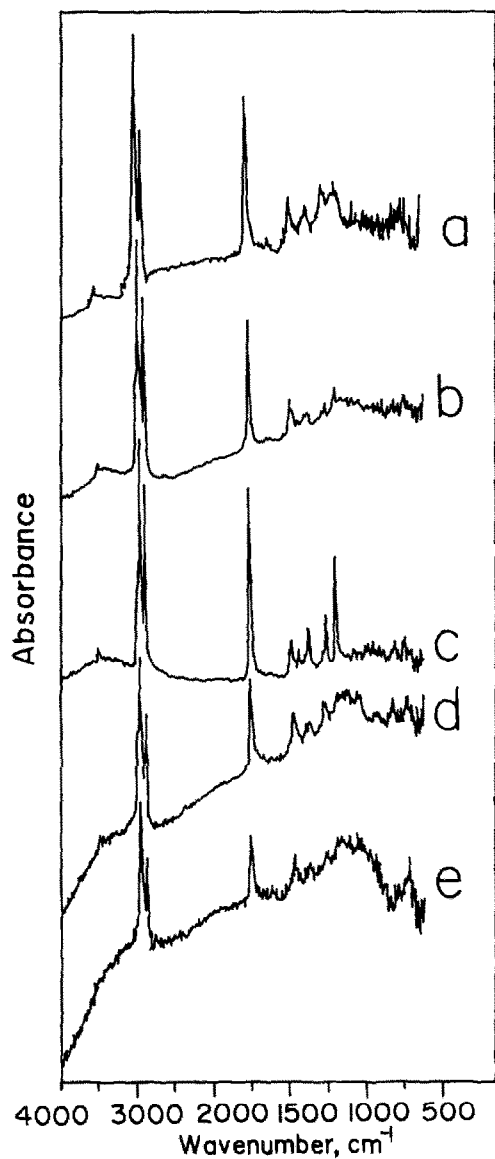


Fig. 6. FTIR spectra of supercritical toluene extracts of oil shale obtained sequentially during interaction. (a) 1 min, (b) 30 min, (c) 60 min, (d) 120 min, (e) 180 min of the interaction.

Thus, these might comprise the original physical structure of the kerogen molecule, these then disintegrated as the reaction was allowed to continue.

We also measured the FTIR spectra of the organic material recovered to identify the main functional groups in the products in order to get an insight to the structure of the giant kerogen molecule. Figure 6 contains the FTIR spectra of the recovered organic material from the oil shale.

The FTIR spectra of the supercritical toluene extracts of Israeli Mishor Rotem shale possess the general characteristics observed in extracts from Green River oil shale [20]. The most intense bands in the infrared spectra are near 2990 cm^{-1} and 2850 cm^{-1} which are due to asymmetric and symmetric CH stretching of methylene groups, respectively [21]. The second strongest absorption bands which occur near 1700 cm^{-1} are due to carbonyl functional groups. Aromatic ring stretching vibrations observed near 1600 cm^{-1} are relatively weak. There are sets of bands at 1450 and 1375 cm^{-1} which are due to asymmetric and symmetric CH_3 bending vibration. The out-of-plane vibrations in the range of $900\text{--}700\text{ cm}^{-1}$ are not well resolved. The intensities of the major bands relative to the intensity of asymmetric CH_2 stretching band at 2925 cm^{-1} in the FTIR spectra are presented in Table 2. The intensities of the OH groups and C=O groups slightly decrease gradually during extraction at 340°C from 1 to 180 min. The intensity of the aromatic stretching modes stayed constant in all the extracts obtained throughout the experiment. The same trend was also observed in the intensities of the CH_3 groups near 1457 and 1376 cm^{-1} .

The findings in Table 2 indicate that as extraction continues, the average molecular structure of the extract stayed unchanged though a slight decrease in OH and C=O functionalities was observed. This confirms that there are no major cracking reactions throughout the isothermal supercritical period as stated previously. The decrease in the molecular weight, therefore, was probably due to the loosening of entangled groups of molecules produced by bond cleavage during heating period and/or naturally existing in the kerogen molecule.

Our findings point to the occurrence of two main endothermal events of the toluene and oil shale interaction during the heating period up to 340°C . Although the temperatures of these two events, 209 and 304°C , seem to be

TABLE 2

Change of the intensities of major functional group frequencies relative to the intensity of asymmetric CH_2 stretching band at 2925 cm^{-1} in the FTIR spectra of organic material recovered with time

Time (min)	Relative intensity				
	OH 3450 cm^{-1}	C=O 1711 cm^{-1}	Ar. C-C 1602 cm^{-1}	CH_2, CH_3 Asym. bending 1457 cm^{-1}	CH_3 Symm. bending 1376 cm^{-1}
1	0.08	0.63	0.05	0.19	0.12
30	0.10	0.65	0.05	0.18	0.11
60	0.10	0.65	0.05	0.15	0.19
120	0.08	0.50	0.04	0.18	0.11
180	0.05	0.47	0.05	0.19	0.11

low for thermolysis to occur, there is evidence that bond cleavage may occur by solvolytic [9] and bimolecular ionic mechanisms [16] at temperatures below 350°C. The polarizability of toluene which might be significant at higher temperatures may influence rates of thermolysis reactions by lowering their activation energy which naturally would occur at higher temperatures in the absence of solvent.

Thermal events were absent during the supercritical interaction. Therefore, it appears that the chemical changes during the whole process occurred only in the heating period at subcritical conditions. At supercritical conditions the material originally susceptible to solubilization and new material produced from the thermolysis reactions were extracted from the kerogen. FTIR spectra of the extracts revealed that there were no significant structural changes in the extracts obtained at longer periods of the reaction. The decrease of the molecular weights after the 30th minute of reaction at supercritical conditions may be due to the loosening of aggregates of molecules by the effect of the dense supercritical toluene vapour. One can speculate on the type of endothermal reactions occurring during the interaction between toluene and kerogen molecule. Hopefully, our further work will produce hard evidence to resolve speculations. Our present findings provide the initial data pointing to future research.

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