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UNIVERSITY OF ALBERTA

SUPERCRITICAL WATER EXTRACTION OF OIL SHALES

BY

©

OLUBUNMI M. OGUNSOLA

A THESIS SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

IN

MINERAL ENGINEERING

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FALL 1991

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled SUPERCRITICAL WATER EXTRACTION OF OIL SHALES in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in MINERAL ENGINEERING.

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Dedication

In Blessed Memory of My Father

Benjamin A. Imoru

Whose untimely death gave me inspiration and the perseverance to succeed.

ABSTRACT

The results of a study on supercritical water extraction of two oil shales in a one litre reactor operated in a semi-continuous mode, and of six nitrogen- and sulphur-containing model compounds (quinoline, isoquinoline, benzothiophene, thianthrene, 2(methylthio)benzothiazole and thiochroman-4-ol) in a batch reactor are reported.

The effects of CO and of an iron oxide catalyst under different conditions (temperature 400 °C-450 °C; pressure 14 MPa-21 MPa; extraction time, and particle size) on the quantity and quality (elemental composition, apparent aromaticity, class composition, volatility, and molecular weight) of the extracts were determined and compared with pyrolytically generated material. The response of the six model compounds to pyrolysis were also compared with their interaction with supercritical water (SCW).

The data show that extraction of oil shale with near-critical water generated substantially more toluene-soluble matter than pyrolysis, but pyrolysis "extracts" were relatively more volatile and contained relatively lower molecular weight compounds of higher aromaticity than extracts generated during supercritical water extraction (SCWE). Addition of CO to "supercritical water" was generally found to convert more organic matter in the oil shale to toluene-soluble matter than SCWE itself. The quantity and quality of extract produced during SCWE of oil shale in the presence of

Fe_2O_3 catalyst were found to be generally lower than those in the absence of the catalyst. Catalytic SCWE/CO had no significant effect on the quantity and quality of extract.

Supercritical water extraction at temperatures and pressures above 400 °C and 14 MPa, respectively, did not significantly improve the quantity or quality of extract. In fact, the percentage and quality of toluene-soluble matter generated at 450 °C were found to be lower than material obtained at 400 °C.

As well, more finely subdivided sample furnished a higher yield of better quality extract than a relatively coarser sample.

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CHAPTER 1

INTRODUCTION

The thermodynamic behaviour of a fluid near its critical temperature is well documented(1), and has earned supercritical fluids (SCF) recognition as promising solvents in chemical separation processes. For best performance such solvents have to be at or above their respective critical temperature (T_c), above which they cannot be liquefied, no matter how high the pressure.

Supercritical conditions such as temperature and pressure vary with solvents as shown in Table 1.1, and under such conditions, fluids behave like dense gases with high diffusivities(2), resulting in high mass transfer. For example, many important solvent properties of SCFs (e.g. density, viscosity, and solubility parameter) can be varied widely by changing the pressure, or the dielectric constant may be varied continuously without change in molecular structure through variations in density(3). It has been shown that reaction during supercritical fluid extraction (SCFE) varies from gas-like to liquid-like as the solvent density increases(4), and it would therefore be reasonable to expect two different reaction pathways, depending on density.

Table 1.1 Solvents and Their Critical Properties(19)

Solvent	Critical temp. (T_c), K	Critical press. (P_c), MPa	Critical density (d_c), g/cm3
Carbon dioxide	304	7.4	0.467
Isopropanol	508	4.8	0.272
Methanol	513	8.1	0.272
Ethanol	516	6.4	0.276
n-Heptane	540	2.7	0.232
Isooctane	544	2.6	0.244
Isobutanol	548	4.3	0.272
Cyclohexane	553	4.1	0.273
Benzene	562	4.9	0.302
Toluene	592	4.1	0.292
Pyridine	620	5.6	0.312
Cyclohexanol	623	3.7	0.293
Cyclohexanone	629	3.8	0.273
o-Xylene	630	3.5	0.284
Water	647	22.1	0.315
Decalin	664	2.6	0.254
Aniline	699	5.4	0.340
m-Cresol	706	4.6	0.346
Tetralin	719	3.5	0.309

According to Huppert et al.(5), free radical or pericyclic chemistry may be associated with gas-like conditions and ionic pathways with liquid-like conditions.

The fundamental principles of SCF extraction technology have been reviewed in several papers(1,2,6-10). Gangoli and Thodos(10) outlined the general advantages of supercritical fluid extraction (SCFE), while Penninger(11) examined the advantages of supercritical water. According to Gangoli and Thodos(10), supercritical fluids have following unique characteristics:

1. The solvent power can be varied by varying the pressure, i.e. the physical properties of a fluid are more significant than its chemical properties and, where desirable, a mixture of fluids can therefore be used.

2. Chemical degradation of the extracts is minimal since thermal cracking and consequent regressive reactions leading to generation of gas and coke are reduced.

3. Recovery of an extract is easily achieved by reducing the pressure and/or temperature and thereby causing extracts to fall out.

4. The lower sulphur contents of SCFE coal extracts suggest that high-sulphur hydrocarbons could be utilized for production of environmentally more acceptable fuels.

The particular advantages of water as a solvent for supercritical fluid extraction are

1. Greatly reduced contamination of extracts.

2. Since the critical temperature of water (374.5 °C) is close to the "active" decomposition temperature of coal and similar "heavy" hydrocarbons, the extractability of such hydrocarbons is maximized.

3. Drying costs of feeds are reduced since the presence of water in the solid hydrocarbon could be exploited with advantage.

4. Water is relatively cheap and non-toxic.

Supercritical fluid extraction is considered to combine the best features of solvent extraction and distillation(10). The principal advantage of SCFE over distillation is that separation of extract from the extractant can be accomplished at moderate temperatures, and therefore used to recover heat-labile substances of low volatility. In comparison with liquid solvents, SCF has high diffusivity, low density and viscosity, hence enabling rapid extraction and phase separation. By exploiting the unique solvent properties of SCF, it may also be possible to enhance reaction rates while maintaining or improving selectivity(2). As well, the quality and separation of products from reactants can be manipulated by adjusting the solvent power of the SCF fluid.

Supercritical fluid extraction technology has been widely applied in food processing, where it is now commercially employed(2,8). The initial application centered on decaffeination of coffee by supercritical CO_2 at high pressure(3), but extraction of hops, spices and nicotines from tobacco by supercritical CO_2 has also been employed(8,13).

The need for alternative sources of hydrocarbons and, more specifically, a perceived need for synthetic fuels from oil shales, oil sands and coal has more recently also attracted the interest of energy industries in SCFE.

While reserves(13-14) of hydrocarbons in "unconventional" sources (coal, oil shales and oil sands) are vast, their usefulness will to a large extent depend on successful conversion of macromolecules to smaller and environmentally "clean" molecules in the mid-distillate/naphtha range. But for this, a better understanding of the structures and reactivity of these macromolecules during extraction and processing is essential.

Oil shale is one of the most abundant potential alternative sources of hydrocarbons, but its composition is quite different from conventional petroleum, and shale oil obtained by oil shale retorting has a much higher concentration of heteroatoms than petroleum. Retorting, i.e. pyrolysis, has been an accepted technology for generating organic matter from oil shale. The process involves heating the shales at or above ≈400 °C and thereby "degrading" the oil shale kerogen into non-volatile material called "pyrobitumen"(15). In a higher temperature range (450 - 500 °C), partial volatilization, accompanied by cracking and coking of the pyrobitumen can occur, and up to 35 wt % of the total organic matter will consequently be reduced to gaseous products and solid carbonaceous residues at the expense of liquid products(15).

High-temperature solvent extraction of oil shale has been extensively investigated by Jensen et al.(15). Such processes proved very effective for converting organic matter to soluble components, but suffered from an inability to economically separate the solvent phase from residual shale. As well, crude shale oil tended to polymerize when contacting the inorganic matter at processing temperatures.

The potential of supercritical fluid for hydrocarbon extraction is of current research interest(2,8-10).

The fluids used for supercritical extraction have mostly been organic solvents(19) (see Table 1.1). However, not all conventional solvents are good supercritical extraction fluids: some produce extracts which may undergo polymerization and/or other structural rearrangements that enhance coke formation and reduce oil yields. More recently, water has been used as "solvent" in supercritical fluid extraction by various investigators(21-23), and results from these studies have indicated significant advantages of water over other solvents (e.g., toluene). However, the mechanism of supercritical water extraction has not been fully addressed and is not well understood. While supercritical water can be a source of hydrogen, Berkowitz & Calderon(20), among others, have used CO with SCW to generate "external" hydrogen for stabilization of coal radicals by the water-gas shift reaction:

$$CO + H_2O = H_2 + CO_2 \qquad (R1.1)$$

Supercritical water extraction (SCWE) of some model compounds has been studied(23-25) in order to gain a better understanding of the mechanisms of SCWE and of interaction between SCW and sulphur- and nitrogen-bearing compounds. However, it must be noted that most of these compounds were not representative of structures believed to be present in oil shale.

Despite studies on model compounds and fossil fuels, and heightened industrial interest in SCFE, much remains to be learned about the mechanism of SCWE of oil shale and about the reaction chemistry of related model compounds. In addition, only the effect of SCWE on the yield of liquid products is usually addressed. The effect on product quality (elemental composition, H/C, boiling range and heat content) has not been investigated in any detail.

The work reported here involved a study of oil shale extraction with SCW and also explored interactions between SCW and some sulphur- and nitrogen-bearing model compounds thought to bear some resemblance to structure elements of oil shale kerogens and related "heavy hydrocarbons". The role of water in breaking C-heteroatom bonds and the quality of extracts obtained from pyrolytic and hydrolytic reactions of oil shales, were assessed. Various chemical and structural characteristics of the extracts were related to process conditions.

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CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Supercritical fluid extraction has been used commercially in the food industry for over a decade(1-3). It is basically an extraction process under supercritical solvent conditions, i.e., at or above the critical temperature and pressure of the fluid. In the energy industry, the use of SCFE as a potential technique for converting "heavy hydrocarbon" materials (such as coal) to liquid hydrocarbons is being investigated. Various studies have thus been reported on supercritical fluid extraction of coal(4-22), oil shale(23-34), oil sand(35) and model compounds(37-43). Organic solvents have been typically used for coal SCFE, but water has recently also come to be used for SCFE of coal(11,13,20), oil shale(32-33) oil sand(35) and model compounds(38).

2.2 Principles of Supercritical Fluid Extraction

The extraction capability of compressed gas was demonstrated by Hannay and Hogarth(11) over 100 years ago, and many studies on supercritical fluid extraction have since then been reported(44-48). Paul and Wise(44) used the analogy between extractive distillation and solvent extraction, and regarded upercritical fluid extraction as a process which combines the best features of extractive distillation and solvent extraction processes. In principle, SCFE, of which supercritical water extraction (SCWE) is a special case, enhances the vapour pressure of substances of low volatility. The extraction process also facilitates separation of extracts from residual substrates and allows recovery and recyclying of the solvent.

Unlike solvent extraction, SCFE is directly influenced by the thermodynamic properties(44,47-48) of the solvent. A more quantitative description of the factors controlling solubility in a SCF has been presented by using a binary system in which the solute is a solid(49). The solubility of the solid in the gas can be written as:

$$y = E(P^{s}/P) \qquad (2.1)$$

where

P^{s} is the vapour pressure of the solid (in MPa)

P is the total pressure (MPa)

and E is an enhancement factor derived by Rowlinson and Richardson(50) by using the virial equation of state

$$PV/RT = 1 + B/V + C/V^{2} + ... \qquad (2.2)$$

In this expression, the virial coefficients B and C are functions of temperature and V is the molar volume. Equation (2.2) leads to an approximate relationship

$$\text{In}\ E = (V^{*} - 2B_{12})/V \qquad (2.3)$$

where B_{12} is the cross-virial coefficient which represents interactions between the molecules of the solvent and the solute. The greater the interaction, the more negative the value of B_{12} and the greater E becomes. The value of B_{12} can be estimated by empirical methods such as those used by Prausnitz(49) who defined

$$B_{12}/V_{12} = \Theta(T_r, w_{12}) \qquad (2.4)$$

Here Θ is a generalized function and w is an acentric factor, i.e. a parameter that measures the complexity of a molecule with respect to its non-sphericity and polarity. For typical calculation involving mixtures, the following equations are useful(49).

$$2V_{12} = V_1^{*} + V_2^{*} \qquad (2.5)$$

$$2w_{12} = w_1 + w_2 \qquad (2.6)$$

$$T_r = T/T_{12} \qquad (2.7)$$

$$T_{12} = k(T_1^{*}\ T_2^{*})^{1/2} \qquad (2.8)$$

The asterisked symbols refer to critical points; the subscript 12 indicates that two species are involved; and k is an empirical constant which can in some cases be taken as unity.

From equation (2.3) and a graph of Θ versus T_r obtained from equation (2.4) some general conclusions drawn were(44).

1. For a gas of given T_r, reducing the extraction temperature will decrease V, make B_{12} more negative, and hence increase the value of E; but reducing T will also lower the solute vapour pressure P^*. As a result, the solubility of the solute will have a maximum value at an optimum temperature that represents a compromise between the two effects.

2. Higher values of E will be obtained the closer the extraction temperature is to T_c of the gas, i.e. a gas with high T_c has high negative values of B_{12}.

3. By increasing the pressure, 1/V can be made as large as required and the solvent power of a compressed gas can therefore be continuously adjusted by controlling the pressure.

4. Equation (2.3) suggests that gases of different chemical nature but similar physical properties will have similar solvent effects(44).

Rowlinson and Richardson(50) and Giddings et al.(51) used an alterative approach to correlate the solubility of a solid under supercritical conditions. They regarded the solvent power of a SCF as directly related to its Hildebrand solubility parameter δ, and, proceeding from van der Waals equation, developed

$$\delta(\mathrm{cal}^{1/2}/\mathrm{cm}^{3/2}) = 1.25P_c^{1/2}(\beta_r/\beta_l) \qquad (2.9)$$

where P_c = critical pressure of the solvent in atm.

β_r = reduced density,

β_l = the reduced density of the mixture, usually assumed to be 2.66(10).

Linear correlations were obtained between δ and the extract yields furnished by various solvents(10).

Further understanding of the special properties of a SCF can be gained by considering pressure-density isotherms for a typical SCF. Fig 2.1, which is plotted in terms of reduced variables T_r, P_r and β_r taken from Williams(47), depicts such a graph. At a temperature below T_c (for example, at $0.9T_r$) isothermal compression of the vapour A to B will result in the appearance of a liquid whose density corresponds to C. During further condensation at constant pressure (the saturation vapour pressure) from B to C, condensation proceed

Figure 2.1 has been removed because of copyright restriction

Figure 2.1 Typical Pressure-density Isotherms for SCF(47) until no vapour remains. Compression of the liquid beyond C, e.g. from point C to D, gives the density curve CD, and even a large pressure change produces only a small density change. However, above the critical temperature, for example at $1.06T_r$, small pressure changes in the region of P_r cause large changes in density without any change in phase.

2.3 Oil Shale Extraction

Oil shales were formed in several geological eras and occur in significant amounts in many parts of the world(52). 1World shale oil resources reportedly total over 538 billion tonnes(53), and only coal exceeds these resources. Table 2.1 lists the major known oil shale occurrences(52).

Oil shale is a sedimentary rock that contains organic material in an inorganic matrix(54). The organic matter is made up of two components - the major one, insoluble in common organic solvents at normal temperature and pressure, being "kerogen", and the minor one, soluble in common organic solvents, being a "bitumen". The inorganic material is a mixture of carbonates, silicates and clay minerals(55).

The most common method of extracting organic matter from oil shale is destructive distillation, generally referred to as retorting(56). Retorting can be conducted either above

Table 2.1 Estimate of Known Oil Shale Resources(52)

Country	Site	Age	Estimate (10^6 bbls)
Australia	Rundle Stuart[1] Condor[1]	Tertiary	2,200 2,000 6,250
Brazil	Irati	Permian	800,000
Canada[1]	Albert formation	Ordovician	NA
China	Fushun Maoming	Tertiary NA	1,700 NA
Israel	Zefa-Ef'e Mishor Rotem	Cretaceous	30
Morocco	Timhadit	Cretaceous	15,000
Sweden	Naerke	Cambrian-Silurian	600
United States	Green River Devonian	Tertiary	120,000
Yugoslavia	Aleksinac	Tertiary	210

NA = Not Available

These data were reported in 1983 and may be outdated

[1] Obtained from Symposium papers on synthetic fuels from oil shale II, Nashville, Tennessee, 1981.

ground (surface retorting) or underground (in-situ retorting). For surface retorting, the shale is mined, crushed and sent to a large vessel in which it is heated to about 538 °C (1000 °F) to produce oil vapour which can be condensed and recovered. In-situ processing(57) represented by two types - Modified In-Situ (MIS) and True In-Situ (TIS) retorting, exemplified by the Occidental and Geokinetics processes(57). Both processes rely mainly on strata permeability; and since oil shale is a relatively impermeable rock, it must be fractured underground before a combustion zone is initiated at one end of the "retort".

An alternative technology, at present in its development stage, is SCFE.

2.3.1 Retorting

Oil shale retorting is fundamentally a very simple process, involving the application of heat to break down kerogen, and subsequent removal and quenching of volatile products. The general reaction scheme is(57):

Kerogen ----------> Bitumen ----------> Oil + Gas

Active decomposition of oil shale begins at about 350 -

400 °C, with the peak rate of oil evolution at about 425 °C and devolatization essentially complete in the range of 470 - 500 °C(55). At temperatures above 500 °C, when secondary pyrolysis takes place, the final products (i.e. gases and oil) are evolved. Mineral matter in oil shale consists mainly of calcite and dolomites, and begins to decompose at around 600 °C with evolution of carbon dioxide(55).

Overall decomposition rates of oil shales are higher than those of coal, possibly because more time is required to heat organic material dispersed throughout the mineral matrix. A total heat requirement for raising the feed material to about 500 °C and vaporizing oil at this temperature is about 0.65 - 0.75 MJ/kg shale(58).

Technologies for processing oil shales by retorting have been developed to a commercial stage(55). Table 2.2 shows alternative technologies(55). These have led to the development of various types of retorts for processing a wide range of oil shales.

Oil shale retorts, like coal gasifiers, are classified according to whether they are directly or indirectly heated. In directly heated processes, heat is supplied by burning a fuel, such as recycled retort off-gas, with air or oxygen within the bed of shale. In indirectly heated processes, a

Table 2.2 Oil Shale Technologies for Surface Retorting[55]

Name	**Heating mode**	**Heat transfer**	**Development stage**
Union oil	Direct	Gas-to-solid	Demonstrated
Gas combustion	Direct	Gas-to-solid	Discontinued
Paraho	Direct	Gas-to-solid	Developed
Union oil	Indirect	Gas-to-solid	Developed
Paraho	Indirect	Gas-to-solid	Developed
Petrosix	Indirect	Gas-to-solid	Developed
IGT Hydroretort	Indirect	Gas-to-solid	Developing
TOSCO II	Indirect	Solid-to-solid	Developed
Lurgi-Ruhrgas	Indirect	Solid-to-solid	Commercial

separate furnace is used to raise the temperature of a heat transfer medium that is then injected into the retort to provide heat. Processes using indirect heating can be further subdivided into two categories, depending on whether they use a solid or gaseous heat transfer medium. Paraho, Union and Dravo are among processes that use hot gases, while Lurgi-Ruhrgas, Tosco and Chevron use hot solids.

Processes that use hot solids take advantage of the high specific interfacial areas of solids for heat transfer. Processes using heated recycled pyrolysis gas are thermally inefficient and require large surface areas for heating and cooling recycled gas.

The efficiency of retorting depends both on the type of oil shale (note the variability of type under 2.3) and on operating parameters (e.g. atmosphere, temperature and pressure) at which retorting is carried out. For example, it has been reported that pyrolysis is completed within a narrow range of temperature (400-450 °C), and that evolution of liquids is most rapid at about 425 °C(55). While successful retorting of Colorado oil shale with recycled shale ash has been reported(60), Devonian oil shale (from the Eastern U.S.A) required retorting in a hydrogen atmosphere before comparablle recovery of organic matter could be achieved(60).

Retorting may be conducted at atmospheric or high pressure, but the effect of pressure on the product yield and composition depends also on the atmosphere and oil shale type. Hydro-retorting, i.e. retorting in a hydrogen atmosphere at elevated pressure, has been found appropriate for processing low-hydrogen, high-aromatics oil shales, and has been used for processing Devonian oil shales(55). A bench-scale unit with a nominal 1 ton/d capacity and a process development unit with about 10 times this capacity have been operated by the Institute of Gas Technology (IGT) with hydrogen pressures of 3.5 MPa and greater(55). Green River and Devonian oil shales have been processed, with recovery of organic matter of 95% in the former case and up to 90% in the latter.

Hydro-retorting of oil shales from Eastern Canada has been studied by Furimsky et al.(62) who compared yields from retorting in the presence of hydrogen and nitrogen respectively. The presence of H_2 was found to give higher yields, and furnish lower specific gravity liquids with less sulphur but more nitrogen than retorting in nitrogen. The higher nitrogen contents were attributed to stabilization of precursors to N-compounds that precluded polymerization.

It was reported that extraction of Colorado oil shales in a 60 kg h^{-1} reactor with ash-to-shale ratios of 4 to 5 at about 500 °C gave high oil yields(60). In contrast, oil yields from

Australian Julia Creek oil shale decreased as the ratio of ash-to-shale increased(61). As well, it has been shown that clay minerals, such as illite, kaolinite and montmorillonite, decrease the yield of liquid products(61).

The primary liquid products from oil shale retorting are reportedly comparable in quality to conventional crudes, and the H/C ratios of shale oils are usually higher than those of liquids derived from coal or biomass(63).

2.3.2 SCFE of Oil Shale

Published literature on SCFE of oil shale relates mostly to Green River oil shale(25,28). However, Funazukuri et al.(32), who extracted a Chinese (Maoming) oil shale with supercritical water and toluene, reported that polar components are more easily decomposed by water than by toluene. This is an advantage of water over some organic solvents since it leads to a more stable product.

Kesavan et al.(64) used carbon dioxide to extract Stuart oil shale under supercritical conditions at various pressures, and recorded better yields than from conventional retorting process.

Chong and McKay(28) suggested that the high yields resulting from SCFE are due to solvents acting as free radical scavengers, and thereby reducing polymerization and coking.

Low(31), in his study of shale oil and Arabian Topped crude, found that sulphur and nitrogen contents were considerably reduced by hydrotreating in supercritical media.

The work of Yurum et al.(30) on a Turkish (Goymuk) oil shale showed that removal of mineral matter decreased the yield of liquid products and hence suggests that mineral matter may act as a catalyst.

From their study of two Australian oil shales, which were extracted with supercritical toluene and tetralin, Baldwin and Chen(29) inferred that aliphatic and aromatic shales react differently. While aromatic shales responded well to extraction with toluene, aliphatic shales did not. On the other hand, both shales furnished high yields of liquid products when extracted with tetralin.

Yurum et al.(26) also investigated the effect of time on supercritical fluid extraction of Mishor Rotem (Israel) oil shale with toluene. They observed that under their experimental conditions a steady state at 340 °C was reached within 60 minutes, and a liquid yield of 60 percent was obtained.

Kramer and Levy (65) extracted oil shales from Israel, Kentucky and Wyoming with a number of solvents and solvent mixtures, using both batch and continuous flow systems at 400 °C, and recorded best results with isopropanol/water and water/CO mixtures. Funazukuri et al.(32) also found that polar compounds were more easily decomposed by SCW than with supercritical toluene.

Recent work of Yurum and Karabakan(34) showed the effects of diverse mineral matter on oil recovery from oil shale. Removal of carbonates and silicates from oil shales decreased recovery of organic matter, but pyrite removal did not affect oil yields.

2.4 SCFE of Model Compounds

Little exploratory work has been carried out on SCW interaction with model compounds that exhibit structural features similar to those of hypothesized coal macromolecules.

The early work of Connolly(66) on the solubility of hydrocarbons in water at near-critical solution temperatures and pressures up to 800 atm (80.8 MPa) showed maximum solubilities of benzene, n-heptane, n-pentane, 2-methyl pentane, and toluene near 300 atm (30.3 MPa). However, above these maximum pressures the solubilities of these solvents fell, and a two-phase region was reported to then exist. He also reported that at the same temperature and pressure, solubilities of aromatic compounds were higher than those of aliphatic compounds.

Ramayya et al.(67) examined interaction between SCW and some alcohols in the presence of H_2SO_4 and HCl and found that addition of very dilute mineral acids, capable of acting as homogeneous catalysts, to supercritical water could enhance extraction.

A recent study(42) on SCWE of guaiacol (o-methoxyphenol) at densities between 0 and 0.7 g/cm^3 in the presence of salts showed that hydrolysis to catechol (o-hydroxyphenol) and methanol proceeded through a polar transition state.

Townsend and Klein(41) observed SCWE of dibenzyl ether producing benzyl alcohol which underwent secondary reactions to polymeric materials.

A study of guaiacol(37) under pyrolytic and hydrolytic conditions indicated that yields of the major products from each reaction differed. It was suggested that in SCWE, pyrolysis and hydrolysis proceeded as two competing reactions which also served to reduce char formation.

Pyrolysis of benzylphenylamine, and interaction of this compound with tetralin, methanol and water, showed that the major products from these reactions were aniline, toluene and ammonia(43).

A more recent study by Penninger(40) on extraction of di-n-butylphalate with water at near-critical temperatures and pressures allowed the inference that esters are the reactive entities in some coal macerals (exinite and resinite). It also showed that char formation is reduced when water is the extractor.

Results of all exploratory studies on model compounds indicate that char formation decreases in the presence of supercritical water.

However, of previous SCFE studies on model compounds, only one(39) focussed on nitrogen-containing compounds and none on sulphur- or sulphur- <u>and</u> nitrogen-containing compounds. Since oil shales contain nitrogen and sulphur in heterocyclic combinations, a better understanding of fossil fuel behaviour during extraction requires study of such model compounds.

2.5 SCFE of Coal and Oil Sands

Most work on SCFE of fossil fuels has so far centred on coal(4-22) and was designed as an alternative to coal liquefaction. Various types of coal have been studied under different SCFE conditions.

Studies at the British National Coal Board(6,7) reported extraction of coal with supercritical toluene and p-cresol. The results showed that higher boiling compounds in coal were converted to lower boiling ones, and also suggested that supercritical fluids served to solvate reactive intermediates, thus reducing coke formation.

Towne(1) reported that Stewart and Dyer patented a process for the thermal cracking of coal in the presence of supercritical water. They carried out studies with bituminous coal at 670-770 °K for 1-5 minutes, and obtained 20-25 percent conversion.

Sofianos et al.(20) evaluated the effect of pyrite as a catalyst in SCWE of Waterberg (South Africa) bituminous coal. The results demonstrated that the use of pyrite and/or H_2S as a disposable catalyst improves overall conversion and oil yields.

Another recent study by Canel et al.(21) on supercritical fluid extraction of coal with toluene, tetralin, molecular hydrogen and their mixtures, reported that addition of hydrogen can increase or decrease conversion and extract yields. It was suggested that addition of H_2 can cause phase dilution in the supercritical region.

The work of Modell(68) on SCWE of glucose, cellulose, maple sawdust and a coal-water slurry showed that supercritical water can inhibit the formation of char, which is a significant and generally undesirable major product of coal pyrolysis reactions.

Recently Funazukuri et al.(69) reported liquefaction of lignin sulphonate in subcritical and supercritical water. They reported a higher oil yield in the presence of supercritical water than from pyrolysis.

Ross et al.(13), who extracted low- and high-ash Illinois No. 6 coals with supercritical water (SCW) in the presence of CO, H_2 and/or potassium hydroxide, showed that a SCW-CO combination was more effective in terms of coal conversion than the SCW-H_2, particularly for low-ash coal. Also, conversion was still further increased by a small amount of potassium hydroxide in the SCW-CO system, but the effect of potassium hydroxide on coal conversion was lower in the absence of CO.

Other catalysts were studied by Barton(70) who used stannous chloride and molybdenum trisulphide under hydrogen in a SCW- coal system to achieve up to 54% conversion of coal to pyridine-solubles at 673 °K (400 °C) over 1.6-3.9 hours. Yurum and Tugluhan(22) recorded a similar high yield by deploying ethyl alcohol/NaOH.

Deshpande et al.(11) studied the effect of the critical density of water on coal conversion and found that SCWE of a Bruceton bituminous and a German brown coal at 605 °K over 1-3 hours led to 58 and 75 percent conversion respectively. This implied that SCW must be at or near its critical density to be effective as H-donor or liquefaction solvent, i.e., that an increase in water density enhances extract yield.

Whitehead and Williams(4) employed supercritical toluene to extract coal and reported yields of up to 20%. The extract yield was observed to increase with the volatile matter content of the coal. As discussed by Maddocks et al.(7), the preferred process parameters for SCWE of coal should include a high-density solvent gas at extraction temperature. The extracting gas is therefore chosen to have a critical temperature close to the extraction temperature.

Vasiliakos et al.(8) also concluded that supercritical water is one of the most promising solvents for SCE of coal when they compared the results of coal extraction with water and toluene.

Tomkow et al.(17) found that supercritical fluid extraction increases the porosity of coal, when the residues obtained from carbonization and SCFE of Polish coal were compared.

Kershaw et al.(12) reacted bituminous coal with several hydrocarbon mixtures at 725 °K (479 °C) and were able to correlate extraction rates with the critical temperature and density of the supercritical fluid. They reported low conversion with water at subcritical temperatures and a reduced density of 0.28 (i.e., 87kg/m^3).

In the studies noted above, high conversions were obtained. However, by way of contrast Blessing and Ross(71) reported low conversion (≈10%) when studying SCFE of coal with series of organic solvents, and attributed that to interaction between coal and solvent during heat-up.

Some studies of SCFE of Athabasca oil sands with water and CO at both supercritical and subcritical conditions have been reported by Berkowitz and Calderon(35). A recovery as high as 85 weight percent was recorded, and extraction was accompanied by substantial upgrading of the bitumen to lighter hydrocarbons.

2.6 Nomenclature

y = experimental solubility

E = enhancement factor

P^s = vapour pressure of solid

P = pressure,

V = molar volume

R = universal gas constant

B and C = second and third virial coefficients respectively

B_{12} = cross-virial coefficient

Θ = generalized function for virial coefficient

T = temperature; T_r = reduced temperature, (T/T_c);

T_c = critical temperature

w = accentric factor

V^* = critical molar volume

subscripts and superscripts:

1, 2 = components

12 indicates interaction between components 1 and 2

* indicates critical condition

s indicates solute

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CHAPTER 3

OBJECTIVES OF THIS STUDY

3.1 Statement of the Problem

As already noted earlier, no studies on model compounds with a priori resemblance to organic structures in oil shale have been reported, and exploratory work on SCWE of model compounds has generally been confined to simple configurations, such as dibenzyl ether, quinoline and isoquinoline.

A broad survey of SCWE of oil shale reveals similar lack of information about connections between processing parameters and the chemical composition of the extract. It has been observed from the studies on oil shale retorting that process-dependence of product yield and distribution varies with the type of oil shale(1). While extensive SCFE studies on U. S. oil shale have been conducted, only a few studies have been carried out on Israeli Rotem oil shale(2-4), and only two studies - one centered on solubilization(5) and the other on pyrolysis(6) - of Moroccan oil shale have so far been reported.

In order to develop industrially viable technology for SCWE of fossil fuels, the basic process chemistry, process mechanisms, and optimum process condition must be well understood. The economic viability of such technology requires that the utility of the process for extraction of unconventional fossil fuels be demonstrated more clearly.

3.2. Basic Research Objectives

The tasks for the study reported in this thesis were therefore identified as:

(a) generation of useful data for SCWE of some oil shales and, more specifically, definition of optimum conditions which could be related to the quantity and quality of extract produced; and

(b) some definition of the chemistry and mechanisms of sulphur and nitrogen removal by using model compounds chemically similar to structure "elements" believed present in oil shale kerogens.

The experimental work consequently involved an assessment of the effects of pressure, temperature and extraction time, as well as of the presence and absence of a catalyst (Fe_2O_3) and/or carbon monoxide (CO), on the yield and chemical composition of the extract. The quantity and quality of extracts obtained by SCWE were compared with those obtained by pyrolytic retorting.

The oil shales primarily used in this study originated in Israel and Morocco.

3.3 General Approach

The research study was divided into two main phases.

The first phase involved an examination of selected sulphur- and nitrogen-containing model compounds during pyrolysis as well as during interaction with supercritical water. The nature of the products obtained under these conditions was determined.

The second phase involved
(i) processing of oil shales by pyrolysis, and
(ii) extraction of oil shales with supercritical water under various conditions.

Two particle size consist of oil shale were used, and the effect of Fe_2O_3 and CO on product yield and quality were investigated. Various analytical data, including elemental composition, nuclear magnetic resonance (NMR) spectra and class composition by thin layer chromatography (TLC), were obtained for the extracts and evaluated.

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CHAPTER 4

SUPERCRITICAL WATER EXTRACTION OF MODEL COMPOUNDS

4.1 Introduction

Liquid hydrocarbons from oil shale are of interest because of a deemed need for alternative transportation fuels and because the H/C ratio of shale oil is higher than that of coal-derived liquids, (1.63 versus 1.07)(1). However, shale oil contains greater concentrations of heteroatoms such as sulphur, ≈0.6% and nitrogen ≈2% than conventional crude liquid hydrocarbons and the presence of these heteroatoms creates problems during shale oil upgrading in refinery processes. The presence of sulphur will not only adversely affect catalysts used in hydrogenation processes but can also create unacceptable environmental pollution problems(2). Other problems associated with sulphur compounds such as hydrogen sulphide (H_2S), thiols and thiophene include degradation of equipment by corrosion and embrittlement, and consequent high operating and maintenance costs as well as frequent shutdowns. The presence of nitrogen, on the other hand, affects fuel stability as well as causing environmental problems and affecting refinery processes.

If supercritical water extraction (SCWE) is to be fully developed, extraction mechanisms and the accompanying reaction chemistry need to be better understood.

Recently, exploratory studies(3-6) have been reported on interactions of SCW with some model compounds, but these were, as already noted, limited to simple compounds; and since useful information for upgrading of unconventional oils generated by SCWE requires information on more complex model compounds, it was thought particularly useful to examine sulphur- and nitrogen-bearing structures, and heterocycles with both sulphur and nitrogen in the same molecule. Removal of these heteroatoms is a major task of hydrocarbon processing, and an understanding of supercritical fluid extraction of appropriate model compounds could provide helpful background data for supercritical water extraction of oil shale.

This chapter discusses results from reaction of selected sulphur- and nitrogen-bearing model compounds thought to resemble structure elements present in oil shale. Reactions under pyrolytic and SCW interaction conditions at high pressures and temperatures were explored.

4.2 Experimental

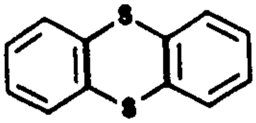
4.2.1 Samples

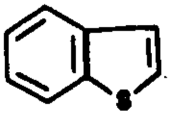
Six reagent-grade model compounds - thianthrene ($C_{12}H_8S_2$), benzothiophene (C_8H_6S), thiochroman-4-ol (C_9H_7OS), 2(methylthio)benzothiazole ($C_8H_7NS_2$), iso-quinoline (C_9H_7N) and quinoline (C_9H_7N) - were obtained from the Aldrich Chemical Company and used as received without further treatment. Their chemical structures are shown in Figure 4.1.

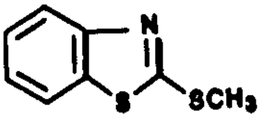
Benzothiophene, quinoline and iso-quinoline have been reported to be present in synthetic fuels such as oil sand bitumen and coal-derived products(7,8), while 2(methylthio)benzothiazole, which contains both S and N, was chosen in order to determine synergistic effects, if any, in the removal of heteroatoms.

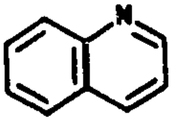
4.2.2 Experimental Procedure

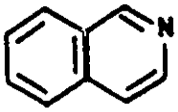
All reactions were carried out in a 10 mL (13cm long, 9mm i.d.) micro-bomb fabricated from 316 stainless steel tubing with 3mm wall thickness. The bomb was sealed at one end with a cap and at the other connected to 0.635 cm o.d tubing that was fitted with (i) a valve for pressurizing the reactor and venting the gas, as well as with (ii) a pressure gauge for

1.

Thianthrene

2.

Benzothiophene
(Thianaphthene)

3.

2(Methylthio)
Benzothiazole

4.

Quinoline

5.

Isoquinoline

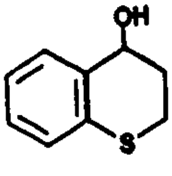
6.

Thiochroman-4-ol

Figure 4.1 Structures of Organic Compounds Used monitoring reaction pressures. The experimental set up is schematically represented in Figure 4.2.

In each run, the micro-reactor was loaded with approximately 1.0 g of solid or 2 mL of liquid sample, and for SCW-interaction reaction approximately 3.2 mL water was added to provide for an initial reactor water density of about 0.31g/cc. After loading and closing, the reactor was purged with nitrogen before pressurizing the system to about 2,000 psig (≈14 MPa) for SCW interaction experiments and approximately 2,050 psig for pyrolysis to provide the required hot system pressure (approximately 3,200 psig ≈22 MPa). The reactor was then immersed in a preheated fluidized sand bath and the time of immersion recorded as the start of the experiment. The reactor was agitated at ≈120 cycles per minute. In all runs the reaction temperature was maintained at about 400 °C. Some experiments were conducted in the presence of 0.06 g of Fe_2O_3 as catalyst.

After a specified time, the reactor was removed from the sand bath and quenched in water. Gaseous products were then collected by salt water displacement, to avoid partial solubility of the gases, in a gas sampling reservoir by opening the exit valve of the reactor. Thereafter the reactor was opened and its contents collected by washing with tetrahydrofuran (THF). The aqueous and organic phases were

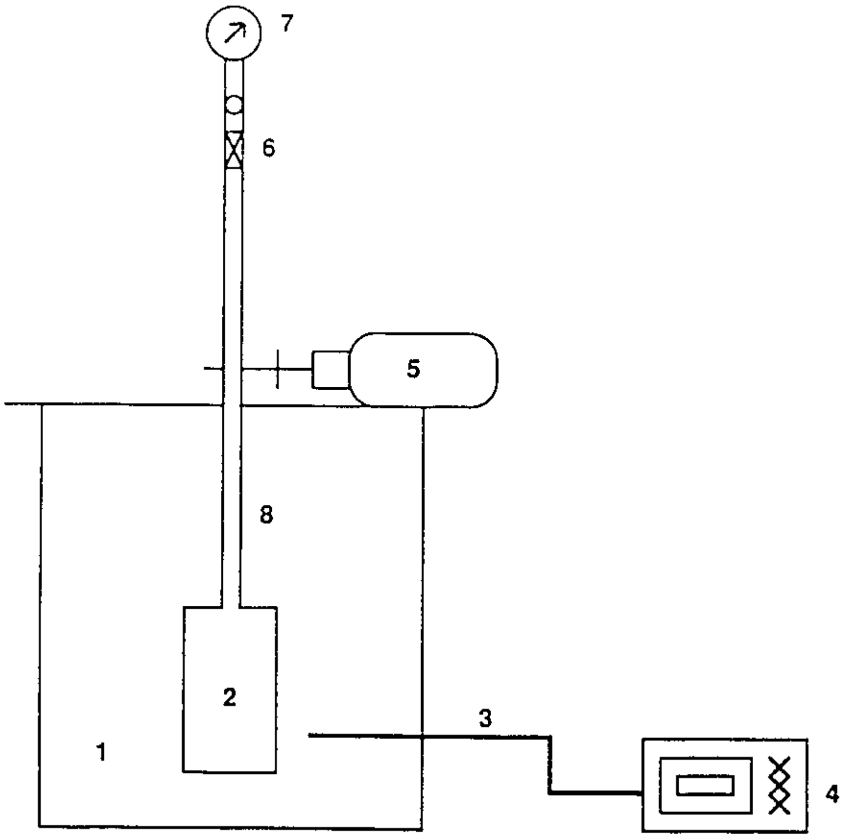


Figure 4.2 Schematic Diagram of Experimental Setup

1. Fluidized sandbath	5. Agitator
2. Microbomb reactor	6. Two-way valve
3. Thermocouple	7. Pressure gauge
4. Temperature controller	8. 1/4" tubing extension

recovered in a separating funnel, and solid residues, if present, were removed by filtration. THF was removed by evaporation.

Gaseous products were analyzed by gas chromatography (g.c.), while liquid products were identified by gas chromatography - mass spectroscopy (g.c.-m.s.). In experiments with quinoline and isoquinoline, which generated ammonia that entered the aqueous phase, concentrations of ammonia were determined by ion specific electrodes.

The gas chromatograph used for analysis of gaseous products was a Fisher Gas Partitioner 1200 that was equipped with two columns and dual thermal conductivity detectors. The first column, which separated carbon dioxide and most hydrocarbon gases, was 6.1m x 0.32cm packed with 27% DC 200/500 on 80/100 mesh Chromasorb P-AW. The second, which consisted of two sections, separated methane and fixed gases such as O_2, N_2, CO, H_2S and H_2 on (1.8m x 0.48cm) 80/100 mesh Chromasorb P-AW followed by (3.35m x 0.48cm) 60/80 mesh Molecular Sieve 13X. The amount of each gas produced was estimated by connecting the gas partitioner to an on-line Spectra Physics model SP4290 integrator and using appropriate internal standards.

Preliminary analysis of liquid products was accomplished with a Varian 3700 Gas Chromatograph equipped with a (30m x 0.53mm) 5µm DB-1 megabore capillary column and a thermal conductivity detector in a temperature programming mode. The temperature program comprised 10 minutes at 50 °C and then raising the temperature at 5 °C per minute to 250 °C. The g.c.-m.s. data were obtained by using a VG 70 E mass spectrometer and a Varian Vista 600 equipped with (30m x 0.25mm) 1.5µm DB-1 megabore capillary column and a flame ionization detector.

Mass spectra were identified by comparison with library records. The extent of reaction was estimated by comparing the peak area for the spectrum of the pure model compound with the peak area of the residual model compound in the spectrum of the reaction product mix.

4.3 Results and Discussion

Tables 4.1 to 4.12 illustrate the distribution of dominant products from (i) supercritical water extraction and (ii) pyrolysis of model compounds, as identified by g.c.-m.s. analysis.

The relative quantities of major products obtained in the reactions were estimated from their peak areas. While these data provide some information about the most predominant product during SCW interaction and pyrolysis, they are only semi-quantitative. From the product distributions some possible reaction sequences during SCW interaction and pyrolysis were proposed, with the intermediate products in the brackets.

4.3.1 SCW Interaction and Pyrolysis of Isoquinoline

Tables 4.1 and 4.2 show the g.c.-m.s. distribution of dominant liquid products from respectively interaction of isoquinoline with supercritical water and its pyrolysis. Isoquinoline is reportedly a structure "element" in coal-derived hydrocarbons(7).

Supercritical water interaction and pyrolysis took place under the following conditions

	SCW Interaction	Pyrolysis
Temperature (°C)	400	400
Pressure (MPa)	22.1	22.1
Water volume (cm^3)	3.15	0.0
Reaction time (h)	48	48

Table 4.1 Major Products from 48 h Isoquinoline-SCW Interaction at 400°C

Product	Formula	MW	Percentage	
			Product	Relative quantity[1]
Toluene	C_7H_8	92	Trace[2]	-
O-xylene	C_8H_{10}	106	0.65	17.9
Ethylbenzene	C_8H_{10}	106	0.68	18.3
Benzene 1,3 dimethyl	C_8H_{10}	106	Trace	Trace
Benzene, 1-ethyl-2-methyl	C_9H_{10}	118	0.77	21.2
Benzene, 1-ethyl-3-methyl	C_9H_{12}	120	0.77	21.2
Isoquinoline	C_9H_7N	129	83.7	-
Benzo F quinoline	$C_{13}H_9N$	179	0.76	20.9
5H-indo 1,2-b-B pyridine	$C_{12}H_9N$	169	Trace	
Unaccounted			12.68	

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[1] Only relative quantities of dominant products other than unreacted isoquinoline are considered.

[2] "Trace" means < 0.1%.

Table 4.2 Major Products from 48 h Pyrolysis of Isoquinoline at 400 °C

Product	Formula	MW	Percentage	
			Product	Relative quantity
Benzene, 1-ethenyl-2-methyl	C_9H_{10}	118	0.45	31
Isoquinoline	C_9H_7N	129	86	-
Naphthalene, 2-methyl	$C_{11}H_{10}$	142	1.0	69
Unaccounted			12.55	

The lower molecular weight compounds generated during SCW interaction suggests that SCW is active as a reactant during its interaction with isoquinoline. Most of the products generated during SCW interaction are alkyl benzenes which are over 70% of the major products. A possible overall reaction sequence is shown in Figure 4.3 and implies that heterocyclic rings are more reactive than homocyclic rings. It appears that the C-N bond ruptures as a result of heterocyclic ring saturation by hydrogen from water and consequent formation of alkyl radicals such as $-CH_3$ and -CN. Similar sequences have been observed by others(5). The formation of ammonia (see Table 4.3) also supports a role of SCW in converting N to NH_3, because water is a proton donor(5) that reacts with nitrogen after ring rupture.

Carbon dioxide (CO_2) is a predominant gaseous product accruing from interaction of quinoline and isoquinoline with SCW. This suggests that either quinoline/isoquinoline and/or their reaction products underwent oxidation reaction. This is expected since it was reported that supercritical water oxidation (SCWO) is an efficient method for organic waste destruction(9).

In contrast to SCWE, pyrolysis of isoquinoline generated fewer products with high molecular weights. A proposed overall reaction scheme is shown in Figure 4.4. The

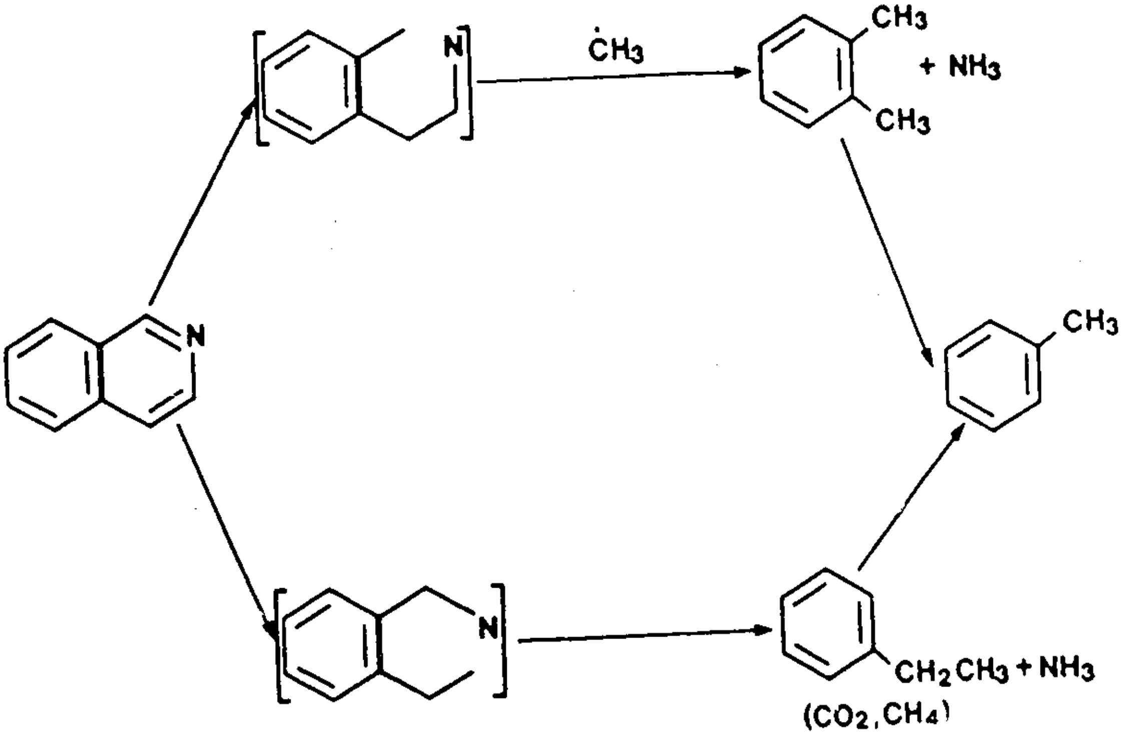

Figure 4.3 Possible Reaction Sequence in Isoquinoline-SCW Interaction

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A similar scheme has been proposed by Houser et al.(5)

Table 4.3 Analysis of Gaseous Products from SCW Interaction of Quinoline and Isoquinoline

Experiment No	Quinoline	Isoquinoline
Temperature (°C)	400	400
Pressure (MPa)	22.1	22.1
Time (min)	48.0	48.0
Fe_2O_3	present	absent
Gaseous Product (%vol)		
NH_3	2.1	2.4
CO_2	36.9	75.6
CH_4	30.5	13.1
C_2H_6	20.7	8.9
C_3H_8	8.2	---
C_4H_{10}	1.5	---

structures of the products from both reactions give an indication that while SCW interaction with isoquinoline proceed through bond rupturing, pyrolysis is mainly due to thermocracking and polymerization.

In summary, the extent of reaction during SCE is greater than in pyrolysis (see Figures 4.3 & 4.4), and SCWE leads to a very different product slate. It is inferred that the dominant reactions during SCWE are

(1) hydrogenation, with H_2 produced from water; and

(2) hydrocracking due to the relatively high reaction temperature.

4.3.2 SCW Interaction and Pyrolysis of Quinoline

Tables 4.4 and 4.5 illustrate the distribution of dominant products from, respectively, SCW interaction and pyrolysis of quinoline in the presence of Fe_2O_3. Experimental conditions were

	SCW Interaction	Pyrolysis
Temperature (°C)	400	400
Pressure (MPa)	22.1	22.1
Water volume (cm^3)	3.15	0.0
Reaction time (h)	48	48

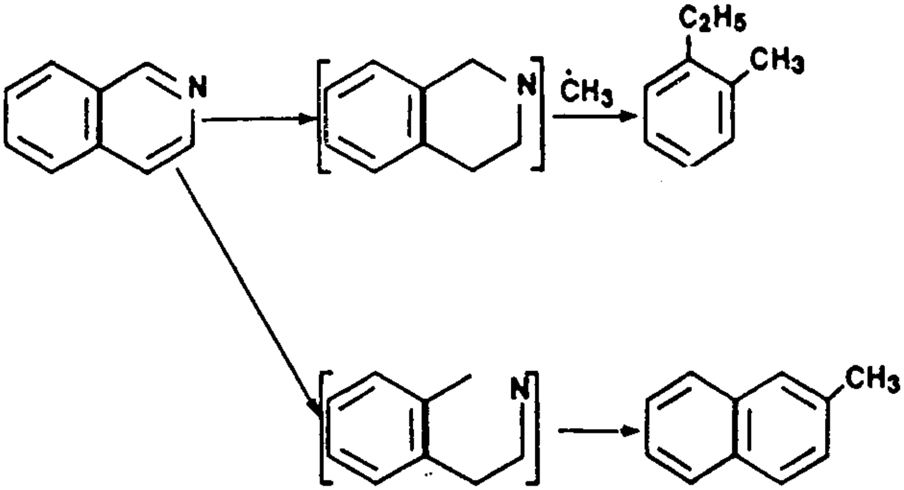

Figure 4.4 Possible Reaction Sequence in Isoquinoline Pyrolysis

Table 4.4 Major Products from 48 h Quinoline-SCW Interaction at 400°C

Product	Formula	MW	Percentage	
			Product	Relative quantity
Aniline	C_6H_7N	93	4.9	9.2
Toluene	C_7H_8	92	1.7	3.2
O-xylene	C_8H_{10}	106	16.7	31.2
Benzene,ethyl methyl	C_9H_{10}	118	0.3	0.6
Benzenamine 2-methyl (Toluidine)	C_7H_9N	107	6.0	11.2
Benzenamine, 4-ethyl	$C_8H_{11}N$	121	10.5	19.6
Quinoline, methyl[1]	$C_{10}H_9N$	143	1.9	3.6
Quinoline dimethyl[1]	$C_{11}H_{11}N$	157	5.0	9.3
Naphthalene dimethyl	$C_{12}H_{12}$	156	1.3	2.4
Quinoline	C_9H_7N	129	31.6	-
8-Quinoline (Hydroxy quinoline)	C_9H_7NO	145	5.2	9.7
Unaccounted			14.9[2]	

[1] isomers

[2] ≈15% unaccounted and probably contained in hydrocarbon gases (see Table 4.3)

Table 4.5 Major Products from 48 h Pyrolysis of Quinoline at 400°C

Product	Formula	MW	Percentage	
			Product	Relative quantity
Benzenamine, 4-methyl	C_7H_9N	107	1.4	10.4
Quinoline,1,2,3,4-tetrahydro	$C_9H_{11}N$	133	0.4	3.0
Quinoline	C_9H_7N	129	77.3	-
Naphthalene, 2-methyl	$C_{11}H_{10}$	142	2.6	19.4
Quinoline,methyl	$C_{10}H_9N$	143	3.5	26.1
Quinoline,ethyl	$C_{11}H_{11}N$	157	1.9	14.2
2,2-Biquinoline	$C_{18}H_{12}N_2$	256	3.6	26.9
Unaccounted			9.3	

In the absence of Fe_2O_3 quinoline did not interact with SCW. The product slate (Table 4.4) suggests that both ionic reaction and free radical capping took place. Quinoline is not as reactive as isoquinoline without a catalyst, and furnishes quite different product slates. Reaction sequence proposed for interaction between quinoline and SCW and Fe_2O_3 is depicted in Figure 4.5. Generation of aniline type products has been regarded by Houser et al.(5) as due to pronounced preference for 1-2 bond rupture - unlike equally possible 1-2 and 2-3 bond rupture in isoquinoline. The presence of naphthalene 2- methyl also suggests that naphthalene is an intermediate product that may arise from methyl-indane interaction(5).

Formation of hydroxyl quinoline must have been initiated by ionic reactions that involve H^+ and OH^- ions. Hydrogenation by H_2 enables the heterocyclic ring to be saturated, and this can be followed by hydrogenolysis of C-N bonds that first open the hetero-ring and then convert the resultant aliphatic and aromatic amine intermediates to hydrocarbons and ammonia(5). Also direct attack of OH^- on quinoline may have led to formation of hydroxyl quinoline. It has been suggested that both ionic reaction and free radical capping are possible under supercritical conditions(6).

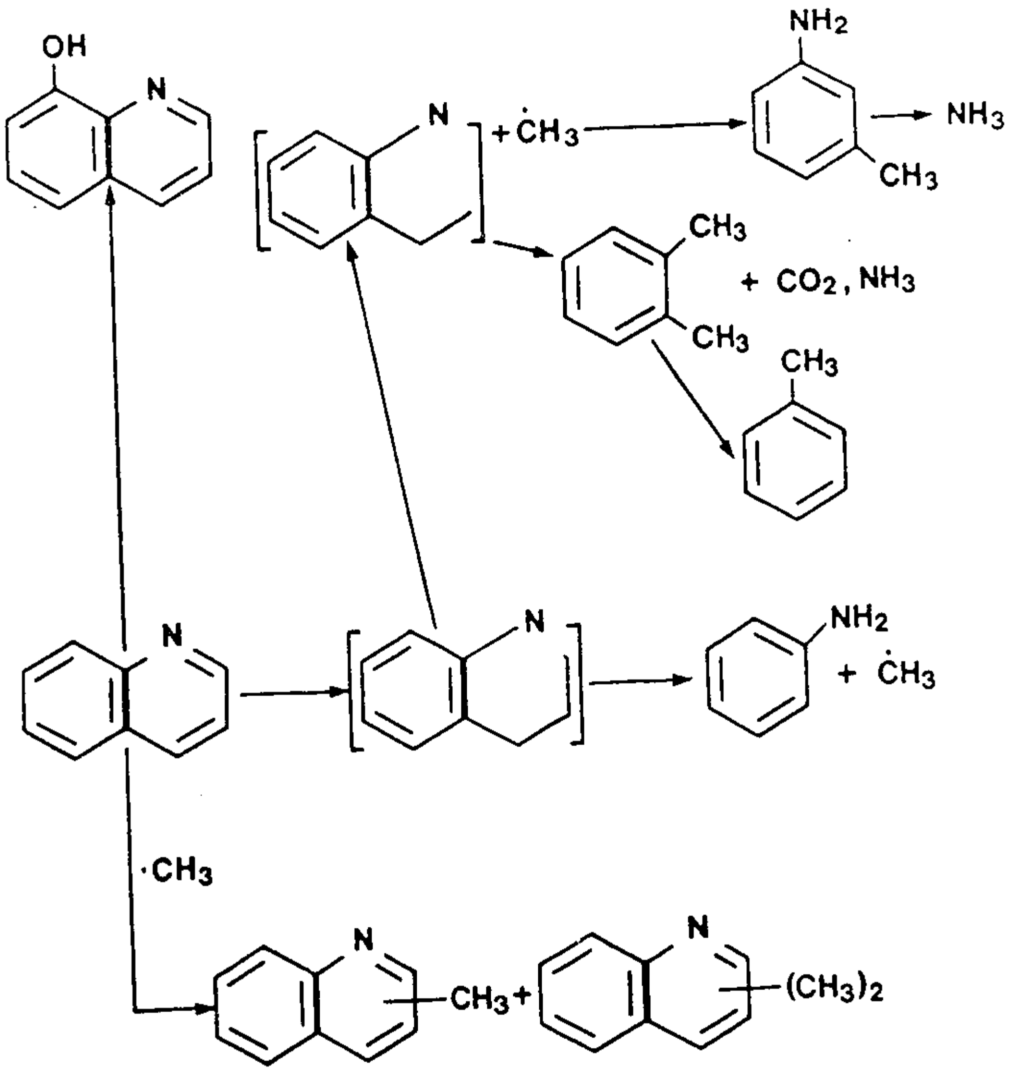

Figure 4.5 Possible Reaction Sequence in Ouinoline-SCW Interaction

The formation of 2,2-biquinoline from pyrolysis of quinoline (Table 4.5) suggest that the main reaction mode is thermal cracking and subsequent random polymerization to heavier molecules. Although it has been reported(5) that both quinoline and isoquinoline were difficult to pyrolyse, Cocchetto and Satterfield(10) have shown that quinoline can be readily reduced to dihydroquinoline by metals and acids; the reaction proceeds via 5,6,7,8-tetrahydroquinoline to 1,2,3,4 tetrahydroquinoline. The reaction sequence for quinoline pyrolysis is depicted in Figure 4.6.

4.3.3 SCW Interaction and Pyrolysis of Benzothiophene

Benzothiophene has been reported as a sulphur-bearing structure element in carbonaceous materials such as coal, oil sand bitumens and oil shale. Interaction with SCW and pyrolysis of benzothiophene were conducted under the following conditions

	SCW Interaction	Pyrolysis
Temperature (°C)	400	400
Pressure (MPa)	22.1	22.1
Water volume (cm^3)	3.2	0.0
Catalyst	Fe_2O_3	Fe_2O_3
Time (h)	3.0	3.0

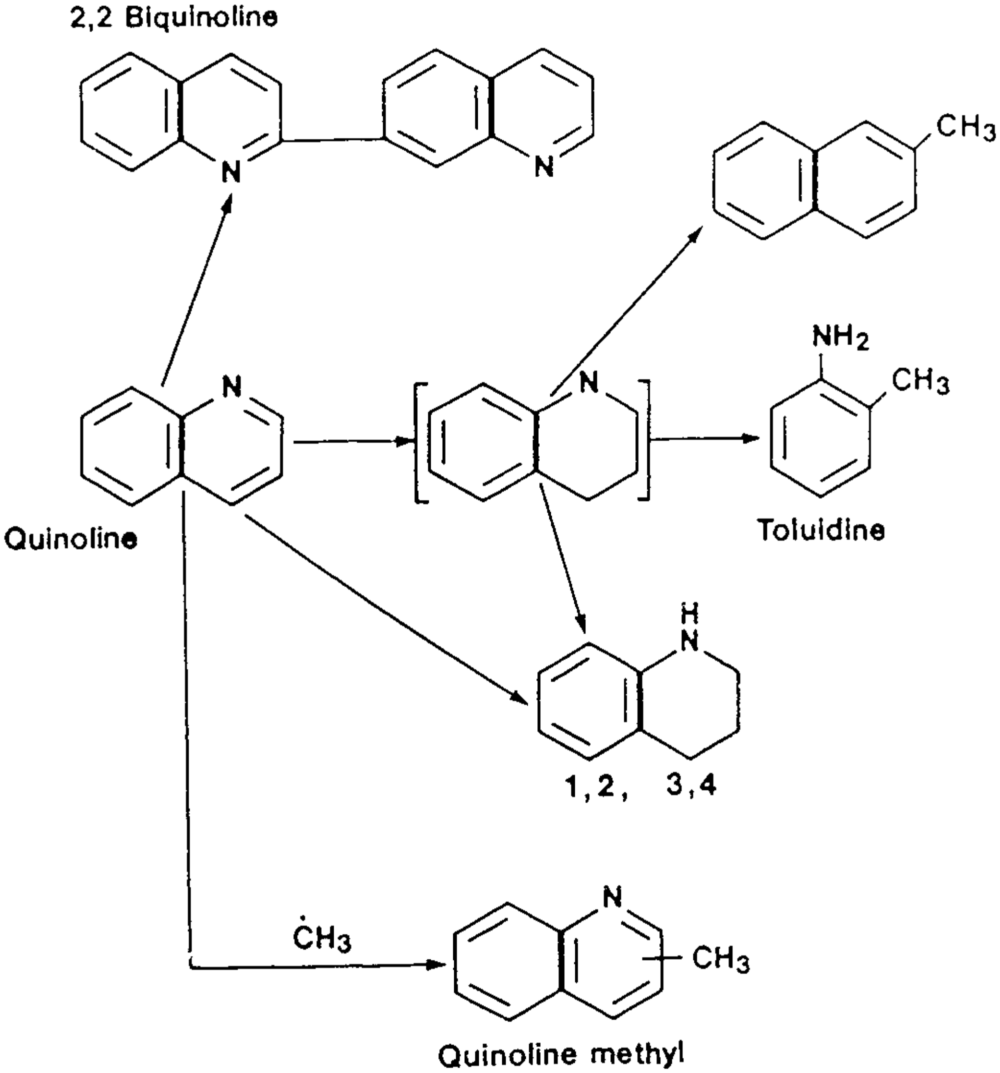

Figure 4.6 Possible Reaction Sequence in Quinoline Pyrolysis

The product slate from interaction of benzothiophene with SCW is presented in Table 4.6, and a reaction sequence is outlined in Figure 4.7. As indicated in that diagram, the reaction leads to saturation of the thiophene ring and to subsequent C-S bond rupture which generates free radicals. The few available methyl radicals then undergo reaction to produce toluene and indene as well as dihydro and dimethyl isomers. The presence of butanediol suggests that hydroxyl participates in the reaction, and formation of naphthalene may be due to the reaction between benzenes.

Thermolysis of benzothiophene at 400 °C for 3 hours did not reveal any reaction products detectable by g.c.-m.s. even when Fe_2O_3 was present.

Table 4.7 shows the effect of various conditions on sulphur removal from benzothiophene. In the absence of a catalyst, the amount of sulphur removed increased rapidly with time, reached a maximum after 3 hours, and decreased thereafter, due to reincorporation of H_2S into reaction products. As well, sulphur removal in the presence of Fe_2O_3 increased a little after 3 hours before falling, but overall removal was lower than in its absence; and unlike reaction in the absence of Fe_2O_3, when no sulphur removal was recorded after 1 h, up to 2.9% was removed. Parenthetically, it is

Table 4.6 Major Products from 3 h Benzothiophene-SCW Interaction at 400°C

Product	Formula	MW	Percentage	
			Product	Relative quantity
Benzene, methyl	C_7H_8	92	Trace	-
Butanediol	$C_4H_{10}O_2$	90	2.5	75.8
Naphthalene	$C_{10}H_8$	128	0.8	24.2
Benzothiophene	C_8H_6S	134	93.7	-
1 H-indene, dihydro,dimethyl[a]	$C_{11}H_{14}$	148	Trace	-
Benzodioxole,5-(1,1-dimethylethyl)	$C_{11}H_{14}O_2$	178	Trace	-
Unaccounted			3.0	

[a] isomers

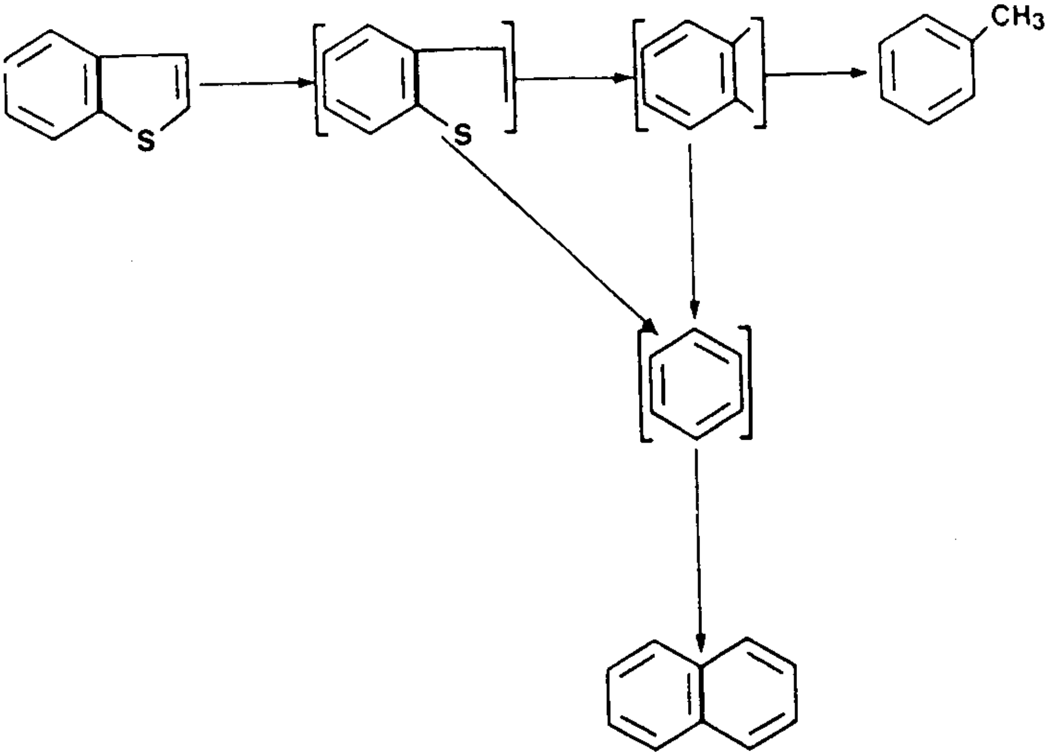

Figure 4.7 Possible Reaction Sequence in Benzothiophene-SCW Interaction

Table 4.7 Effect of Various Conditions on Sulphur Removal From Benzothiophene

Duration (hour)	Percent Sulphur Removed	
	Without Fe_2O_3	With Fe_2O_3
1.0	0.0	2.9
3.0	5.9	3.3
5.0	4.7	2.9
9.0	2.9	2.1

interesting to note that a similar trend was observed by Mobley and Bell(11), who found the presence of $ZnCl_2$ to inhibit thermal decomposition of diphenyl disulphide in benzene.

4.3.4 SCW Interaction and Pyrolysis of Thianthrene

Structure elements resembling thianthrene are other possible sources of H_2S from oil shale extraction. The experimental conditions for reactions with thianthrene were

	SCW Interaction	Pyrolysis
Temperature (°C)	400	400
Pressure (MPa)	22.1	22.1
Water volume (cm^3)	3.16	0.0
Time (hour)	15.0	15.0
Extent of reaction(%)	6.6	40.7

The product slate from interaction with SCW is presented in Table 4.8, and indicates relative stability of thianthrene in SCW. The only product detectable in g.c-m.s spectra is dibenzothiophene (see Figure 4.8), which indicates that only one of the C-S bonds ruptures to generate S and CH_3 radicals. Reactions between these fragments and protons from SCW then yield H_2S and CH_4. As shown in Table 4.9, sulphur removal during interaction of thianthrene with SCW increases with time.

Table 4.8 Major Products from 15 h Thianthrene-SCW Interaction at 400°C

Product	Formula	MW
Dibenzothiophene	$C_{12}H_8S$	184
Thianthrene	$C_{12}H_8S_2$	216

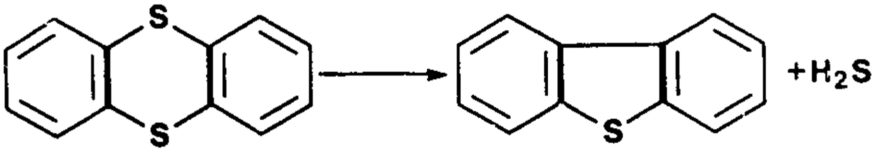

Figure 4.8 Possible Reaction Sequence in Thianthrene-SCW Interaction

Table 4.9 Sulphur Removed from Sulphur-bearing Model Compounds

Compound	T (°C)	P (MPa)	Time (Hr)	H_2O volume cm^3	% S
Thianthrene	400	22.1	15.0	3.16	16.6
Thianthrene	400	22.1	15.0	0.0	0.0
Thianthrene	400	22.1	3.0	3.17	6.0
Thianthrene	400	21.4	0.5	3.17	0.0
Thianthrene	400	19.0	0.5	0.0	0.0
2(methyl)benzo thiazole	400	20.4	0.5	0.0	5.0
2(methyl)benzo thiazole	400	22.1	0.5	3.15	7.2
2(methyl)benzo thiazole	400	22.1	5.0	3.15	33.0
2(methyl)benzo thiazole	400	22.1	5.0	0.0	18.0
2(methyl)benzo thiazole	400	22.1	13.0	3.15	80.0
Thiochroman-4-ol	400	20.0	0.5	0.0	0.0
Thiochroman-4-ol	400	21.4	0.5	3.14	0.0
Thiochroman-4-ol	400	22.1	3.0	0.0	5.2[a]
Thiochroman-4-ol	400	22.1	3.0	3.15	4.5

[a] 0.03 g residue was recovered

Benjamin et al.(12) reported that reaction of thianthrene with tetralin at 400 °C for 18 hours furnished dibenzothiophene and H_2S as major products. The implication of this is that dibenzothiophene is a stable sulphur compound.

Pyrolysis of thianthrene at 400 °C did not produce any degeneration products. The extent of reaction suggests that thianthrene did react when pyrolysed but simultaneously underwent polymerization to high molecular weight compounds not detected by g.c.

4.3.5 SCW Interaction and Pyrolysis of Thiochroman-4-ol

Since oil shales contain oxygen which, like coal-oxygen, is chemically bound(12), it is reasonable to assume that some oil shale structures will behave like phenols, and interaction of thiochroman-4-ol with SCW and its pyrolysis may throw some light on phenolic OH behaviour during oil shale extraction.

The experimental conditions used for SCW interaction and pyrolysis respectively were: temperature 400 °C, pressure 22.1 MPa, reaction time 3 h, and 3.1 cm^3 water for SCW interaction. Tables 4.10 and 4.11 illustrate the dominant products from interaction of thiochroma-4-ol with SCW and pyrolysis respectively. The formation of benzothiophene derivatives (see Table 4.10) suggests that bond rupture occurs preferentially at -OH sites, and this is supported by disappearance of OH bands in IR spectra at 3430 cm^{-1} (Figures 4.9a and 4.9b).

A possible reaction sequence for SCW-thiochroman-4-ol interaction is outlined in Figure 4.10. The C-S bond rupture produces S that reacts with H_2 to furnish H_2S. In pyrolytic reactions (see Figure 4.11) fewer products are formed. Benzothiophene seems to be predominant.

4.3.6 SCW Interaction and Pyrolysis of 2(methylthio)benzothiazole

Tables 4.12 and 4.13 show the product slate for 2(methylthio)benzothiazole-SCW and pyrolysis. The reaction conditions were

	SCW Interaction	Pyrolysis
Temperature (°C)	400	400
Pressure (MPa)	22.1	22.1
Water volume (cm^3)	3.2	0.0
Reaction time (h)	5	5
Extent of reaction (%)	95	84

Table 4.10 Major Products from 3 h of Thiochroman-4-ol-SCW Interaction at 400 °C

Product	Formula	MW	Percentage	
			Product	Relative quantity
Benzene,methylthio	C_7H_8S	124	0.6	1.1
Benzene, 1 ethyl 2-methyl	C_9H_{10}	118	1.4	2.7
Benzene (ethylthio)	$C_8H_{10}S$	138	0.5	1.0
Benzothiophene	C_8H_6S	134	9.2	17.6
Benzothiophene 2,3,dihydro	C_8H_8S	136	4.6	8.7
Phenol,2,3,5,6-tetramethyl	$C_{10}H_{14}O$	150	12.1	22.9
Benzothiophene, methyl[a]	C_9H_8S	148	24.2	46.0
Thiochroman-4-ol	C_8H_7OS	151	29.1	-
Unacccunted			18.3	

[a] isomers

Table 4.11 Major Products from 3 h Pyrolysis of Thiochroman-4-ol at 400 °C

Product	Formula	MW
Benzothiophene	C_8H_6S	134
Benzothiophene, methyl	C_9H_8S	148
Benzene-(1-dimethyl ethyl)-4-methoxy	$C_{11}H_{16}O$	164
2H-1 Benzothiopyran	$C_9H_{10}S$	150
Benzothiophene, -ethyl-methyl	$C_{11}H_{12}S$	176

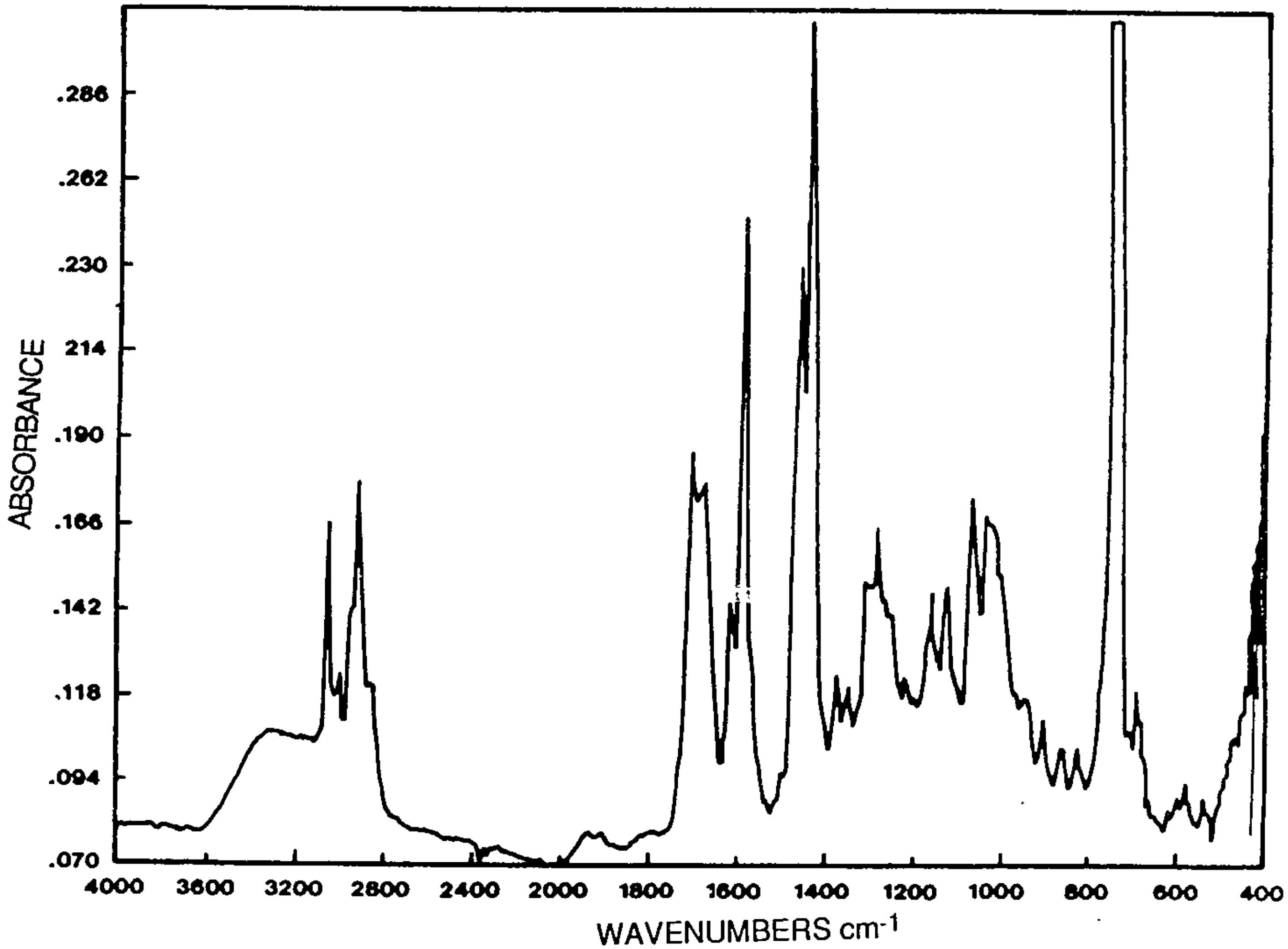

Figure 4.9a IR Spectra of Thiochroman-4-ol-SCW Interaction Products

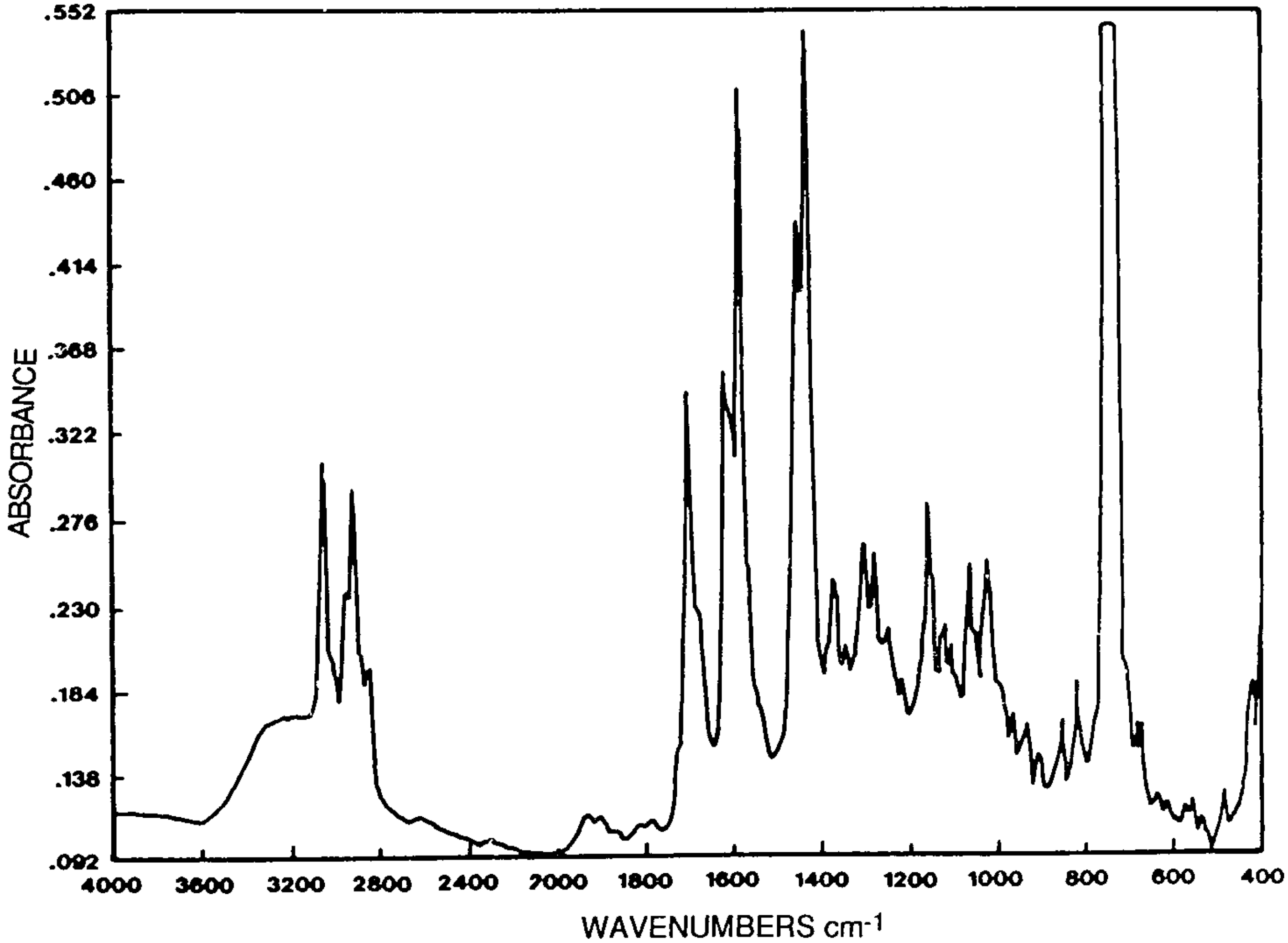

Figure 4.9b IR Spectra of Thiochroman-4-ol Pyrolysis Products

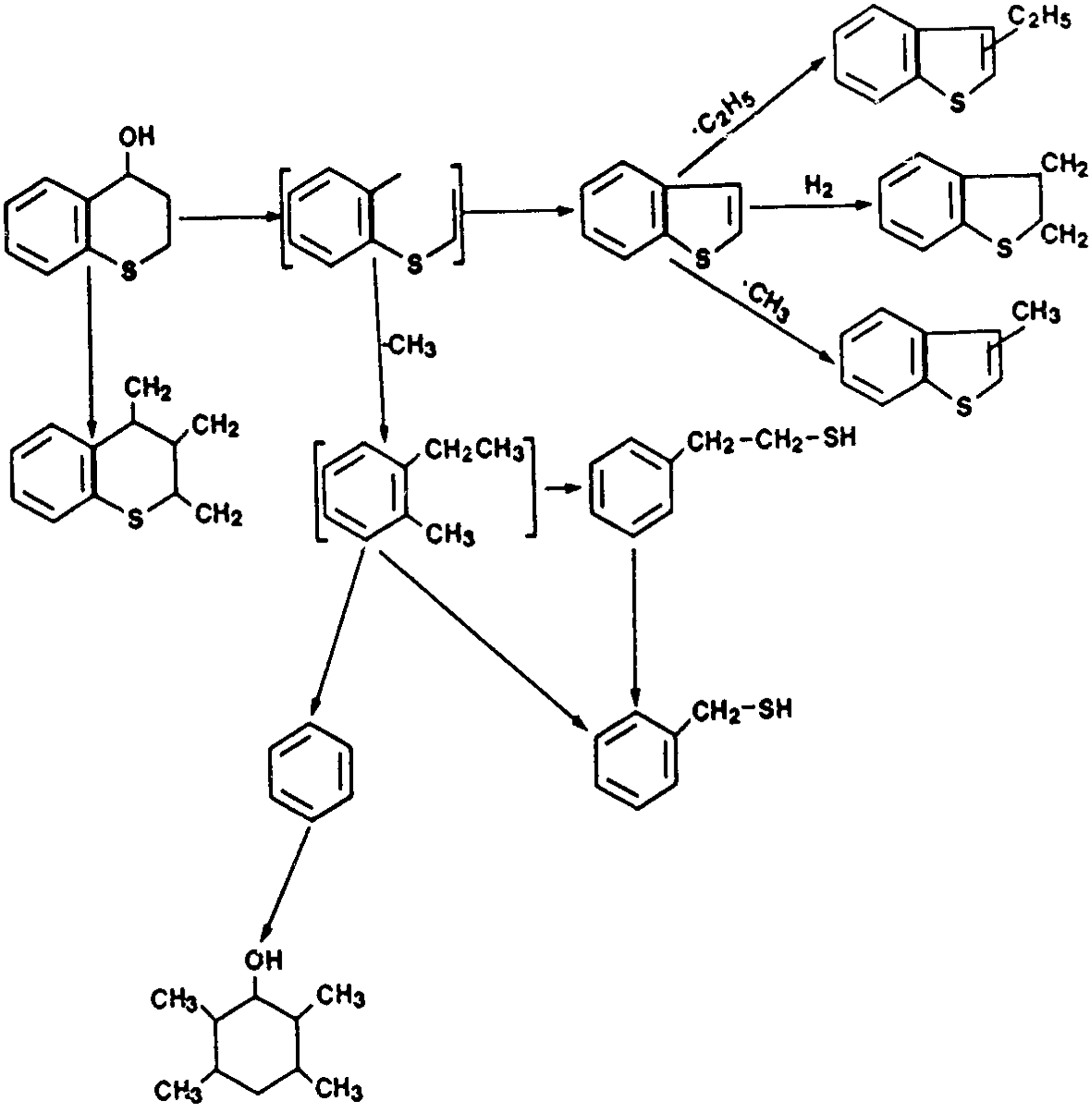

Figure 4.10 Possible Reaction Sequence in Thiochroman-4-ol-SCW Interaction

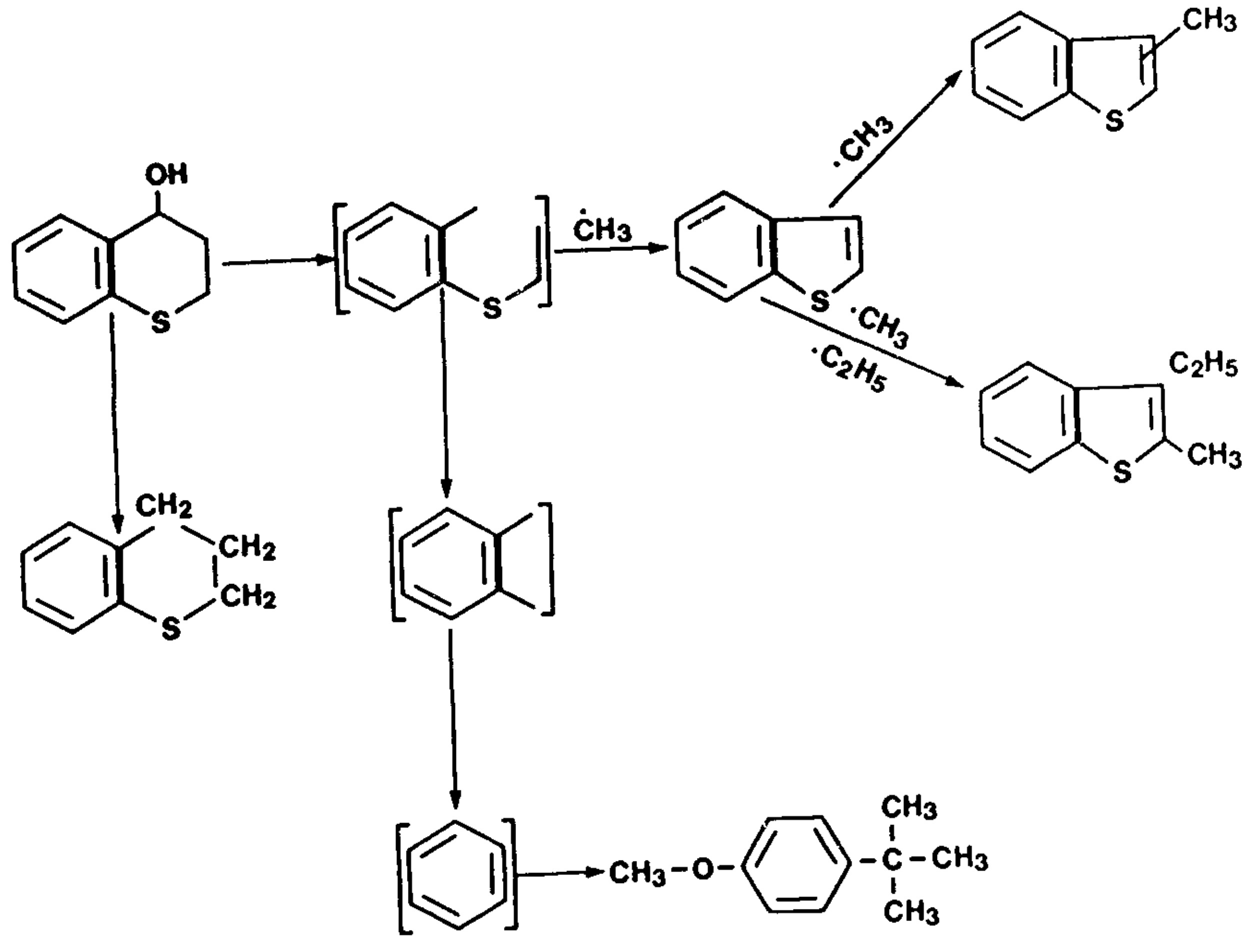

Figure 4.11 Possible Reaction Sequence in Thiochroman-4-ol Pyrolysis

Table 4.12 Major Products from 5 h 2(methylthio)benzothiazole-SCW Interaction at 400 °C

Product	Formula	MW	Percentage	
			Product	Relative quantity
Aniline	C_6H_7N	93	66.9	84.8
Benzenamine,methyl	C_7H_9N	107	0.8	1.0
Benzenemethanol	C_7H_8O	108	3.4	4.3
Benzene methylthio	C_7H_8S	124	0.2	0.3
Naphthalene 1,2,3,4-tetrahydro	$C_{10}H_{12}$	132	0.2	0.3
Benzenamine 2,4-dimethyl	$C_8H_{11}N$	121	0.4	0.5
Benzothiophene	C_8H_6S	134	5.3	6.7
Isoquinoline	C_9H_7N	129	Trace	-
Benzothiazole,2 methyl	C_8H_7NS	149	1.1	1.4
Benzenamine 3-(methylthio)	C_7H_9NS	139	0.6	0.8
Unaccounted			21.1	

Table 4.13 Major Products from 5 h Pyrolysis of 2(methylthio)benzothiazole at 400°C

Product	Formula	MW	Percentage	
			Product	Relative quantity
Benzothiophene	C_8H_6S	134	48.2	55.5
Benzothiazole	C_7H_5NS	135	33.0	38.0
Benzothiazole, 2-methyl	C_8H_7NS	149	4.3	5.0
1,2-Benzothiazole, 3-methyl	C_8H_7NS	149	0.2	0.2
Benzothiazole 2,6-dimethyl	C_9H_9NS	163	0.6	0.7
Benzothiazole, 2-(methylthio)	$C_8H_7NS_2$	181	2.5	-
Benzothiazole, 2-butyl	$C_{11}H_{13}NS$	191	0.5	0.6
Unaccounted			10.7	

Reaction schemes are depicted in Figures 4.12 and 4.13 respectively, and indicate that interaction of 2(methylthio)benzothiazole with SCW readily generates $-SCH_3$ and then leads to heterocyclic ring saturation (i.e., hydrogenation). Hydrogenation of the benzothiazole subsequently opened the hetero-ring, resulting in conversion of aliphatic and aromatic amine and mercaptan intermediates to hydrocarbons and sulphide. The formation of benzene derivatives in the presence of SCW further supports the role of SCW in hydrogenation, i.e. water donates H_2 which helps to saturate the heterocyclic ring and then enhances formation of low molecular weight products.

The dominance of benzothiazole among products from pyrolysis (see Table 4.12) suggests the thermolytic scission of $-SCH_3$, and prompts the view that most of the products are benzothiazole derivatives. The reaction sequence during pyrolysis (Figure 4.12) suggests that free radicals generated from $-SCH_3$ and benzothiazole combine to generate high-molecular-weight compounds, and formation of benzothiophene also suggests significant C-N bond rupture.

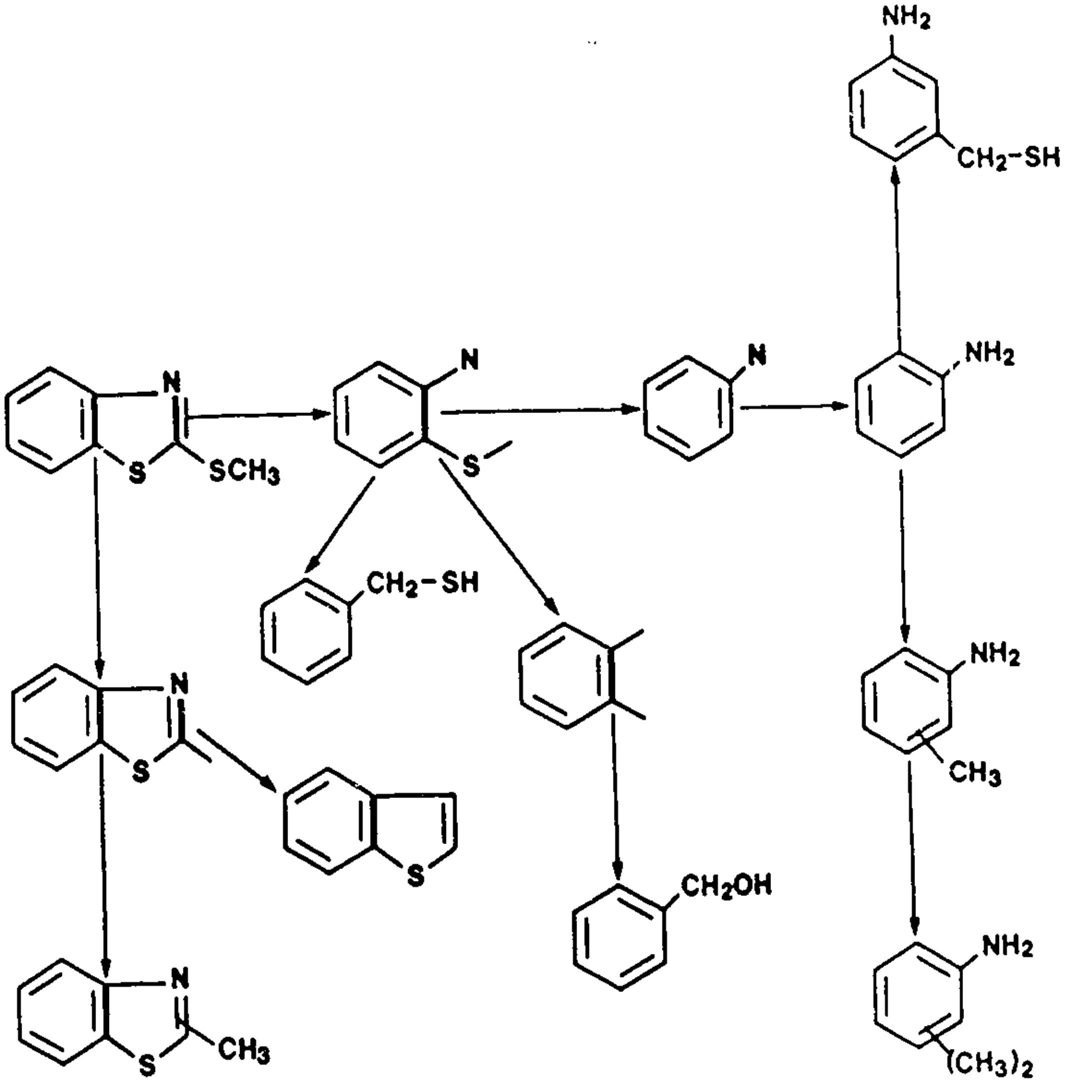

Figure 4.12 Possible Reaction Sequence in 2(methylthio)benzothiazole-SCW Interaction

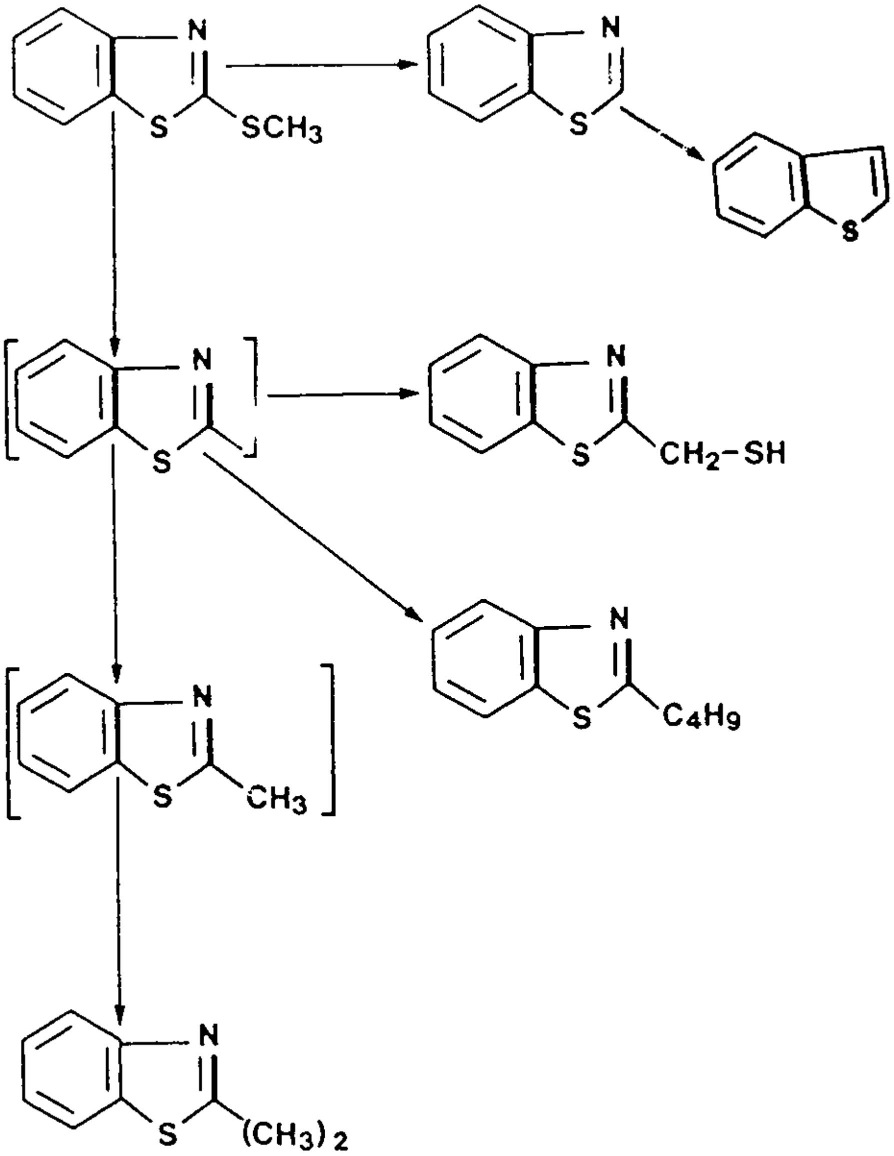

Figure 4.13 Possible Reaction Sequence in 2(methylthio)benzothiazole Pyrolysis

4.4 Conclusions

Sulphur-containing model compounds are generally found to be relatively more chemically altered by SCW than by pyrolysis.

Similarly N-bearing compounds studied, quinoline and isoquinoline, are relatively more reactive in the presence of SCW than during pyrolysis. However, S-bearing compounds are more reactive than N-bearing compounds, since long reaction time and/or catalyst is needed for N-bearing compounds to react. Breaking of C-S and C-N bonds during SCWE was by hydrogenation and hydrocracking while pyrolysis was due to thermocracking mainly.

Compound containing both N and S ($C_8H_7NS_2$, 2(methylthio)benzothiazole) was found to be more reactive than S-bearing and N-bearing compounds, since more products of reaction were generated during SCW-interaction and pyrolysis of $C_8H_7NS_2$. As well, thiochroman-4-ol (C_8H_7OS), an O- and S-containing compound, was found to be more reactive than N- and S-containing compounds.

4.5 References

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CHAPTER 5

SUPERCRITICAL WATER EXTRACTION OF OIL SHALES

5.1 Introduction

Growing interest in oil shales as sources of synthetic fuels is largely due to the fact that such shales are possibly even more abundant and more widely distributed than coal(1) and that shale oils have a higher H/C ratio than coal-derived liquids(2). This latter aspect would reduce hydrogen consumption during subsequent processing (e.g. hydrotreating). But while retorting is a well known means for extracting organic matter from oil shale, a substantial amount of it is lost to gas at the expense of the liquid products.

Supercritical fluid extraction is a new technology that promises higher oil yields as well as better quality oil, and for such extraction, water (T_c, 647°K) is among the solvents of particular interest. The advantages of using water have been discussed earlier (see 2.3), and this chapter therefore focusses on the experimental procedures and on the results of supercritical water extraction of oil shales.

5.2 Oil Shale Compositions

The oil shales used in this study - indexed 'Rotem' and 'MFO' respectively - came from (i) the Rotem Mishor deposit in Israel, and (ii) the Timahdit deposit in Morocco. Both formations are of Cretaceous age and of marine origin.

The raw shales were prepared by crushing to less than 1.16mm and subsequent sieving into various size fractions on a Rotap vibratory sieve shaker. The two size ranges chosen for extraction were -0.833mm +0.6mm and -1.16 +0.833mm. Prepared samples were stored in air-tight containers to reduce oxidation prior to extraction. Detailed analyses of the samples are presented in Tables 5.1 to 5.4.

5.2.1 Chemical Composition

Typical Fisher assays are reported(3) to be 73.7L/tonne and 60.8L/tonne for the Rotem and MFO oil shales respectively. Elemental analyses of the samples were performed by the University of Alberta Microanalytical Laboratory: carbon, hydrogen and nitrogen contents were determined with a Perkin-Elmer CHN Analyzer, model 240, while sulphur was measured by combustion in O_2 followed by $Ba(ClO_4)_2$ titration. Oxygen contents were calculated by difference. Moisture and ash contents were

Table 5.1 Analyses of Rotem Oil Shale

(i) Proximate Analysis(wt %)

Moisture	3.0
Ash	63.7
Volatile matter	28.8
Fixed carbon (by diff.)	4.5

(ii) Elemental Composition (wt %)

	Original shale	**Bitumen**	**Kerogen**
Carbon	15.5	61.4	55.2
Hydrogen	1.4	8.4	6.2
Nitrogen	0.3	0.7	2.1
Sulphur	1.3	4.6	10.3
Atomic H/C	1.06	1.67	1.35
Atomic S/C	0.03	0.03	0.07
Atomic N/C	0.02	0.01	0.03

(iii) Composition (wt %)

Carbonates	65.3
Silicates	22.6
Bitumen	0.9
Kerogen	11.3

Table 5.2 Analyses of MFO Oil Shale

(i) Proximate Analysis (wt %)

Moisture	3.6
Ash	70.0
Volatile matter	23.7
Fixed carbon (by diff.)	2.7

(ii) Elemental Composition (wt %)

	Original shale	**Bitumen**	**Kerogen**
Carbon	12.6	68.1	37.7
Hydrogen	1.6	7.8	4.4
Nitrogen	0.5	1.6	1.8
Sulphur	1.7	6.2	10.0
Atomic H/C	1.55	1.38	1.39
Atomic S/C	0.05	0.03	0.10
Atomic N/C	0.03	0.02	0.04

(iii) Composition (wt %)

Carbonates	47.6
Silicates	32.6
Bitumen	1.5
Kerogen	18.3

Table 5.3 Relative Intensities(1) of Major Functional Groups in FTIR Spectra of Mineral-Free Kerogen Samples

Sample	a 1710cm^{-1}	b 1602cm^{-1}	c 1460cm^{-1}	d 1375cm^{-1}
Rotem	0.77	0.69	0.69	0.61
MFO	0.60	0.96	0.52	0.44

a. C=O stretching
b. aromatic C-C stretching
c. CH_2, CH_3 asymmetric bending (deformation)
d. CH_3 symmetric bending (deformation)

---

[1] Ratio of intensities at reported frequencies to the intensity of the CH_2 stretching at 2925 cm^{-1}

Table 5.4 Mineral Analysis of Oil Shales

Element	Rotem		MFO	
	Weight %	Oxide %	Weight %	Oxide %
Ca	34.6	48.5	5.8	8.2
Al	5.9	11.1	10.3	19.5
Si	13.2	28.2	26.3	56.4
P	1.6	3.7	0.9	2.1
K	0.6	0.7	0.9	1.1
Ti	0.1	0.2	0.4	0.7
Mg	____	____	0.8	1.2
Fe	2.9	3.7	3.6	4.6
S	3.7	3.7	2.5	6.2
O	37.2		48.4	
Total	100.0	100.0	100.0	100.0

determined in the laboratory, using ASTM D3173 and D3174 procedures.

Composition analyses were carried out in the laboratory by following the approach used by Goklen et al(4). Carbonate minerals were determined by leaching the oil shale with HCl, while silicate minerals were determined by leaching with a HF-HCl mixture. Bitumen contents were obtained by Soxhlet extraction with a 3:1 toluene-methanol mixture and the toluene-methanol insoluble fraction was classified as kerogen.

The oil shale kerogens were further characterized by their spectra which were recorded on KBr disks with a Nicolet FTIR model 7199 (see Figures 5.1 & 5.2) and covered the 400 to 4000 cm^{-1} interval. The relative intensities of the major peaks are presented in Table 5.3.

Decomposition characteristics of the shale samples were recorded with a Dupont 900 Differential Thermal Analyzer (DTA) and a 950 Thermogravimetric Analyzer (TGA). Figures 5.3 and 5.4. show typical weight loss curves for Rotem and MFO shale samples respectively. The slight deflection points near 100° C are due to loss of water, which amounted to approximately 2% for the Rotem shale and 3% for the MFO shale. The onset of "primary decomposition" - entailing primary decomposition of kerogen - occurred at ≈400° C for the Rotem and ≈300° C for MFO

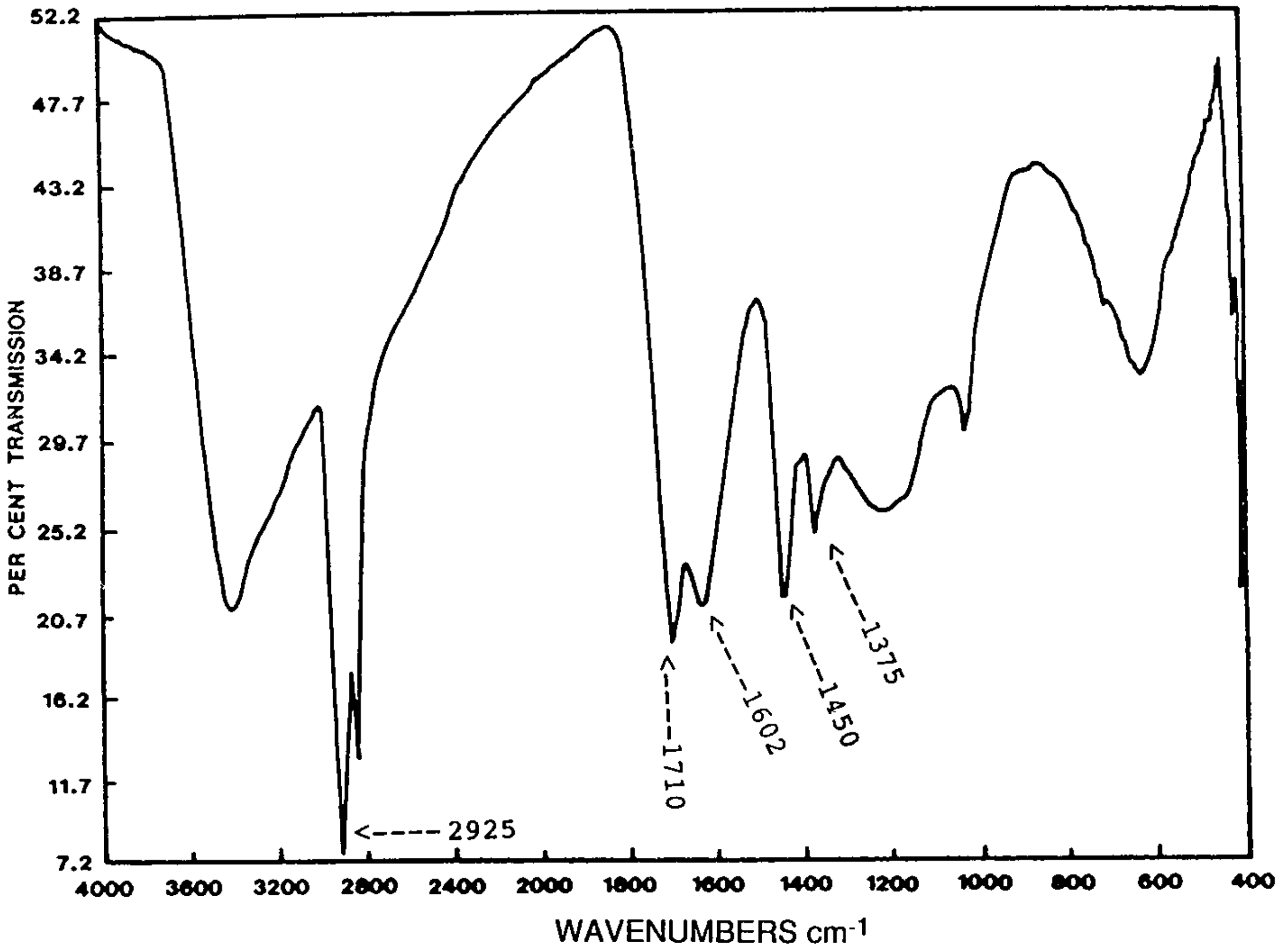

Figure 5.1 FT-ir Spectra of Demineralized Rotem Kerogen

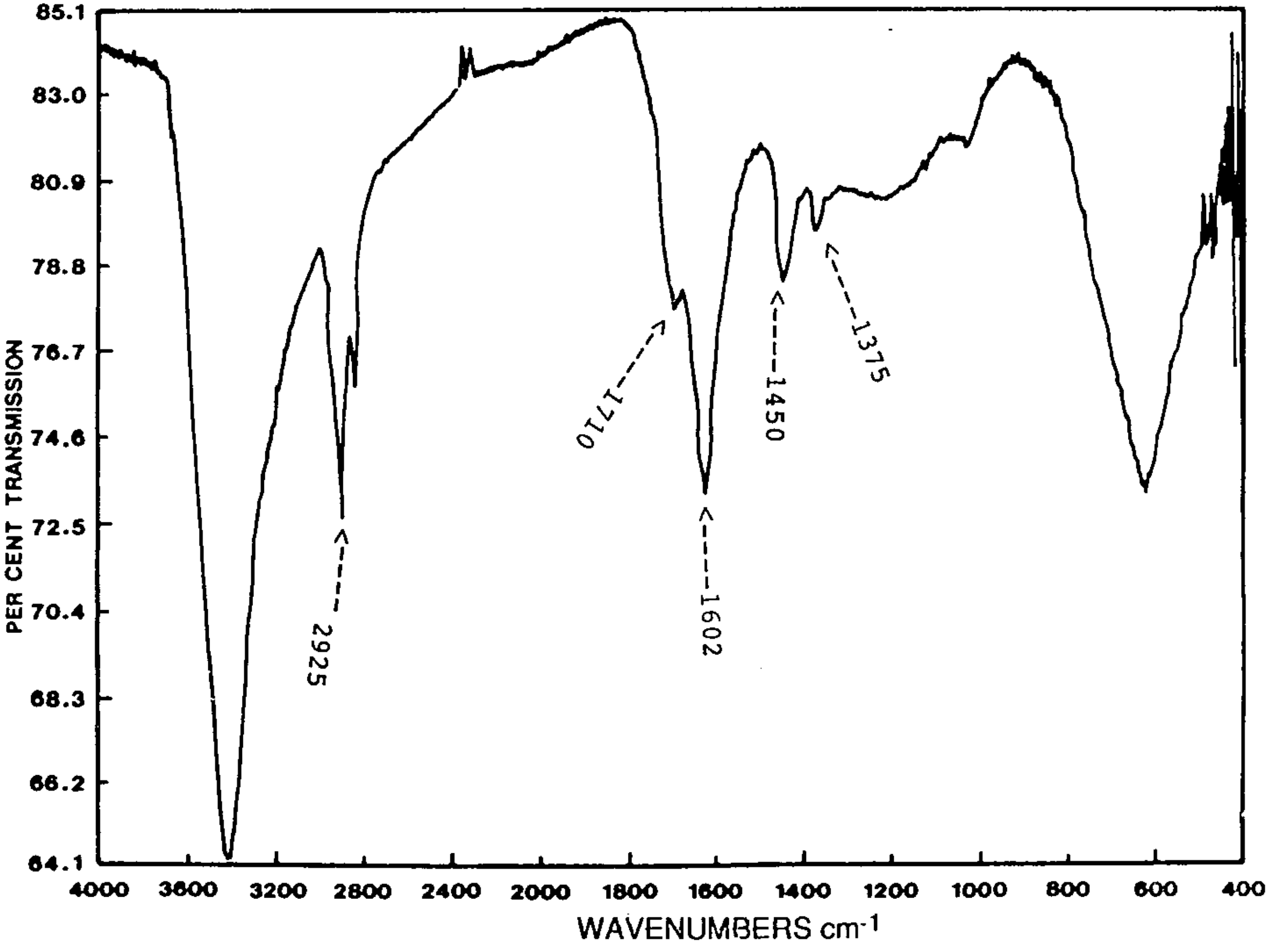

Figure 5.2 FT-ir Spectra of Demineralized MFO Kerogen

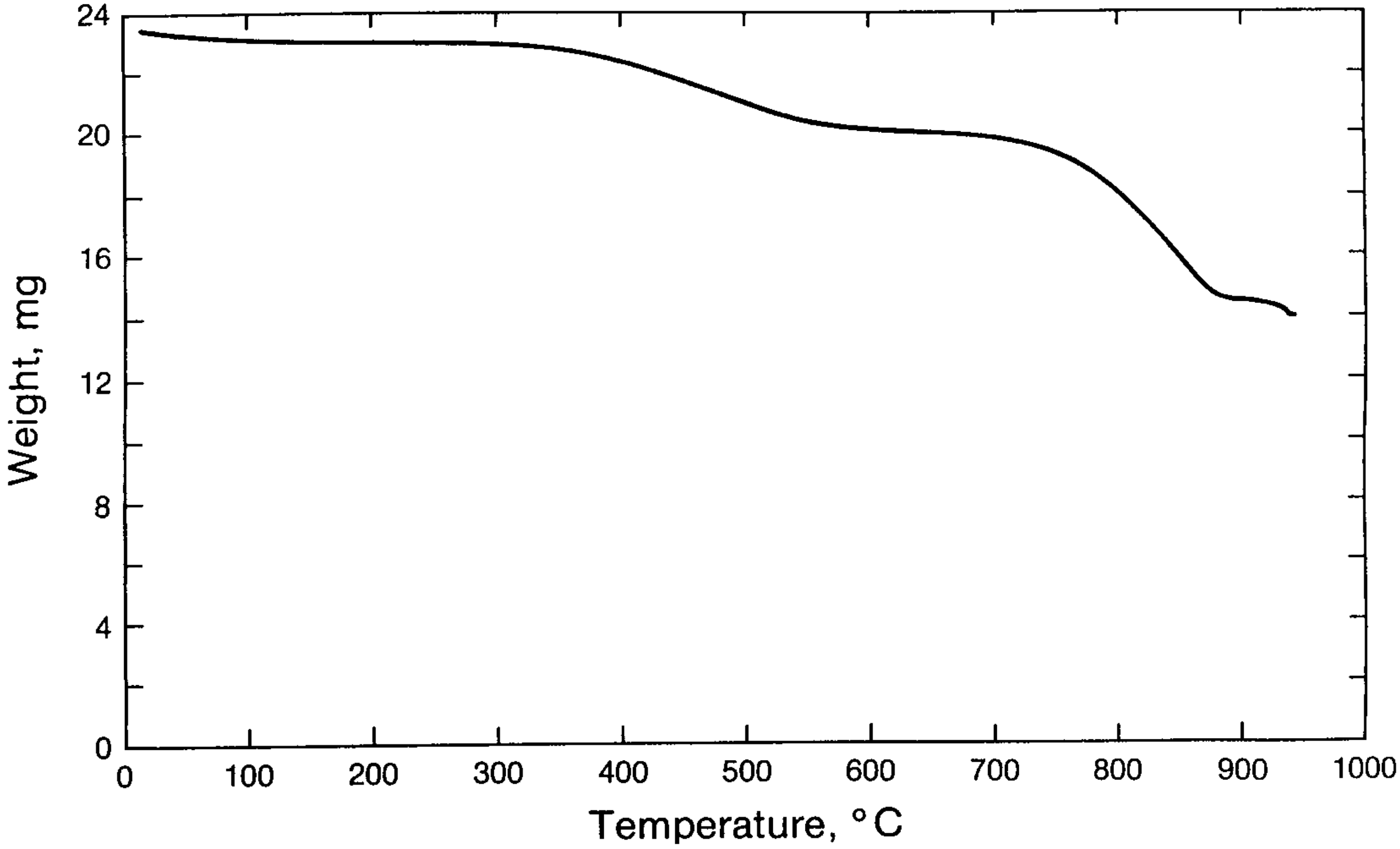

Figure 5.3 TG Plot of Rotem Oil Shale

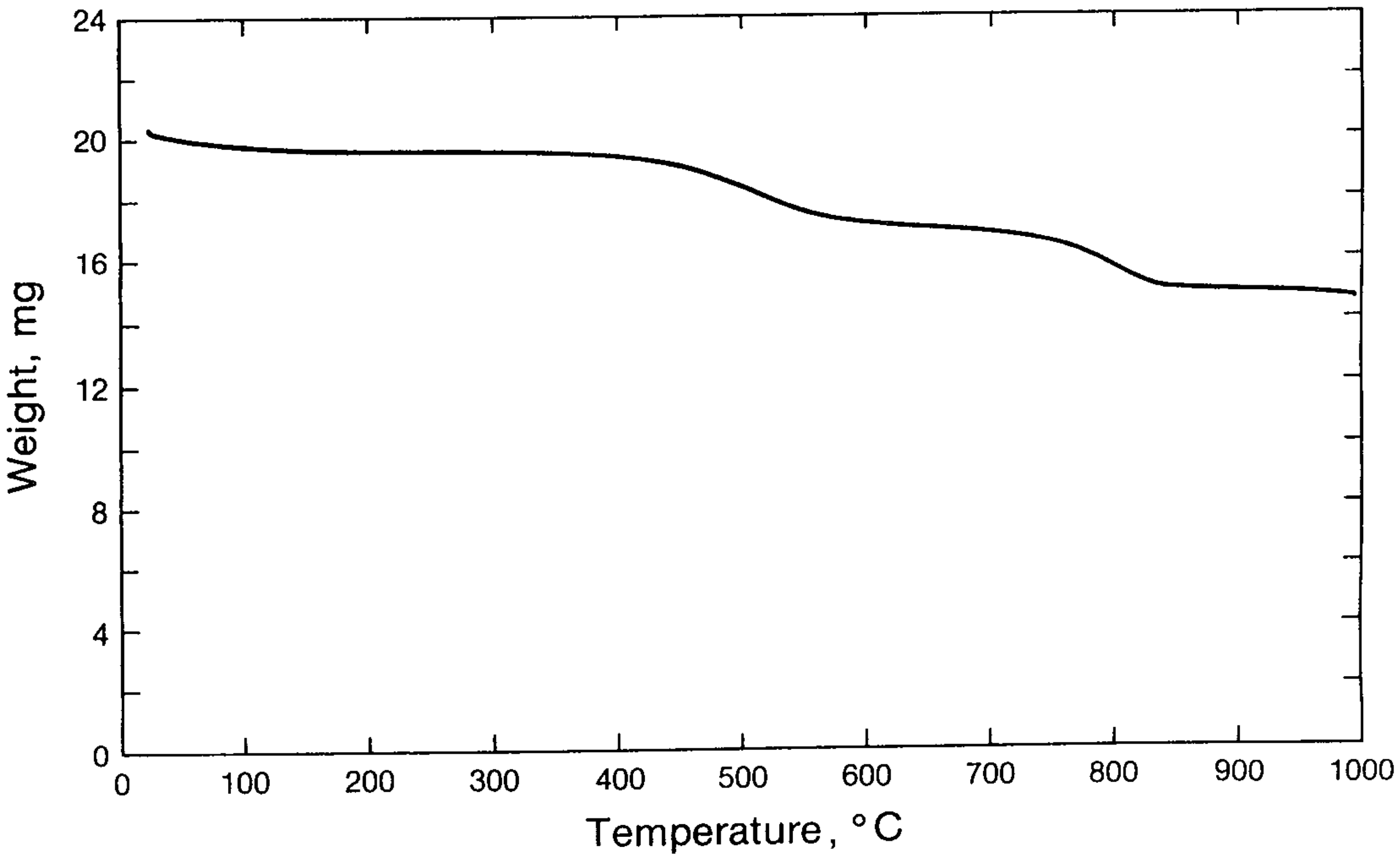

Figure 5.4 TG Plot of MFO Oil Shale

shale. In both cases, primary decomposition ended at about 400° C, as indicated by the slight change in curvature; decomposition of the more resistant hydrocarbons and carbonates then occurred between 400-600° C.

5.2.2 Mineral Composition

Microscopic analyses of the oil shales were carried out with an ISI-60 scanning electron microscope (SEM) fitted with a PGT System 4 Energy Dispersive Analyzer (EDA). This provided some information about the relative proportions of elements in the samples (see Table 5.4). A Philips PW 1009 x-ray diffractometer was used to obtain additional information about the inorganic matter in the samples.

5.3 Experimental

5.3.1 Experimental Procedures

Extraction of the oil shales was conducted in a facility similar to that used by Berkowitz and Calderon(6). Schematically shown in Figure 5.5, this unit comprised a one-litre stainless steel autoclave reactor which was connected to a magnetically stirred stainless-steel pressure let-down vessel in which the extracted materials could be collected. Two solvent reservoirs, for water and toluene respectively,

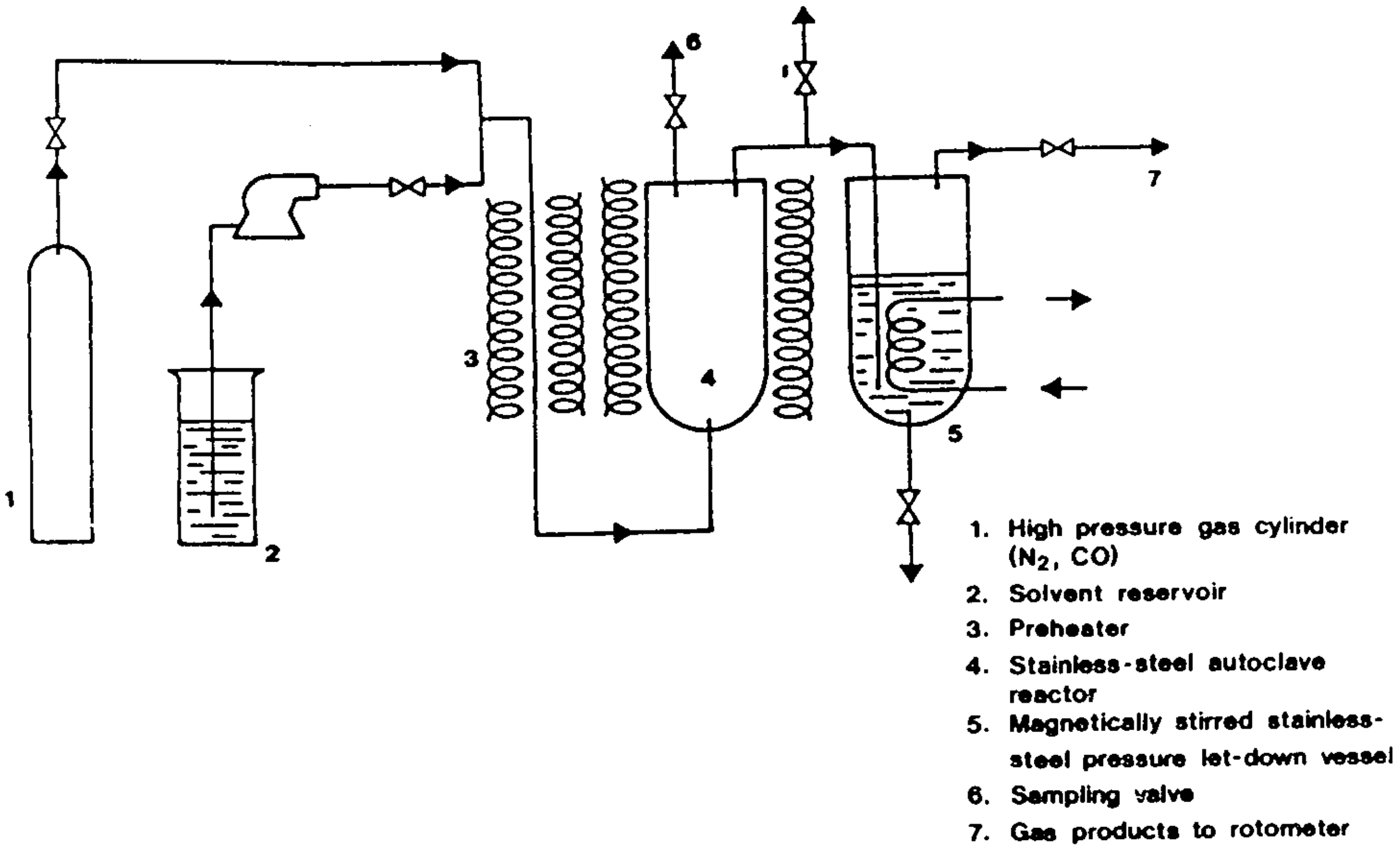

Figure 5.5 Flowsheet of the Extraction Facility

were connected to a highpressure metering pump which supplied solvent to the reactor during runs at required rates.

For extraction, about 30 g of samples were placed into two porous ceramic thimbles which were supported on a stainless steel stand inside the autoclave. The tightly closed reactor was then pressurized to the cold pressure that would furnish the extraction pressure at the selected temperature, and electrically heated to the final temperature at approximately 4°C/min.

Extractions were carried out at 400° C and 450° C under hot system pressures of 14, 17.5 and 21 MPa. Carbon monoxide (CO) was used instead of N_2 as pressurizing gas when its effect on SCWE was to be studied, and in a few runs Fe_2O_3 was used as catalyst. For comparison, retorting was also carried out.

After the desired operating temperature and pressure were reached, water was continuously pumped from the reservoir at approximately 14ml/min through a preheater into the reactor. The steam so produced was near its critical condition, solubilized and extracted hydrocarbon material, and then moved with its extract load into the pressure let-down vessel at a rate that maintained the extraction pressure in the autoclave. At the end of each run, which varied from 20 - 80 minutes, hot toluene was swept through the reactor. After allowing the system to cool, most of the extract material and condensed steam was recovered through a bottom drain in the pressure let-down vessel. The residual shale was then removed from the reactor and further successively Soxhlet-extracted with toluene and THF. Toluene-soluble extract from the pressure let-down vessel and the Soxhlet extraction were combined, and toluene was removed at atmospheric pressure in a rotary evaporator heated in an oil bath.

Extraction efficiences were expressed as percentages organic matter removed from the oil shale and recovered as toluene-soluble material. Conversions determined in this manner were reproducible to within +/-3%. The toluene-insoluble but THF-soluble fractions represented preasphaltenic matter.

Gas chromatographic analyses of gaseous products reported mostly CO_2, N_2 and CO when nitrogen and/or carbon monoxide was used in a run, but also showed traces of H_2S and C_1-C_3 hydrocarbons.

5.3.2 Compositions

Toluene-soluble matter was analyzed in the same way as the bitumen of the raw shale - i.e., carbon, hydrogen and nitrogen contents were determined with a Perkin-Elmer 240 CHN Analyzer, sulphur was measured by combustion in O_2 followed by $Ba(ClO_4)_2$ titration, and oxygen contents were calculated by difference.

Further, more specific compositional information was sought from ^1H nmr spectra which were recorded with a 80-MHz Bruker WP-80 Spectrophotometer, and broad-band from ^{13}C nmr spectra which were obtained with a 200-MHz Bruker WH-200 Spectrophotometer. The samples used for both spectral analyses were prepared by dissolving the toluene-soluble extract in deuterated chloroform and adding tetramethylsilane (TMS) as a reference for chemical shifts. Chromium acetonyl acetate was added as relaxation reagent to samples for ^{13}C nmr measurements. Data were collected on a sweep setting of 15 kHz, pulse width of 28s, and acquisition time of 0.5s. Chemical assignments of ^1H nmr spectral features were based on the work of Bartle et al.(7). Tables 5.5a and 5.5b show these assignments and their corresponding structures as in Khorasheh et al(8).

Class compositions of selected samples of toluene-soluble matter were obtained by thin-layer chromatography in an Iatroscan model TH-10 equipped with a flame ionization detector. Separation of the extracts into aliphatic oils, aromatic oils, polar compounds and asphaltenes was recorded by an on-line Spectra Physics integrator connected to the

Table 5.5a Assignments for ^{1}H and ^{13}C nmr Chemical Shifts

Chemical shifts (ppm)	**Assignments**	
^{1}H nmr		
9.0-6.0	H_{ar}	Aromatic hydrogen
6.0-4.0	H_{ol}	Olefinic hydrogen
4.0-2.3	H_{α}	α-CH2 attached to aromatic ring
2.3-1.9	H_{α}	α-CH3 attached to aromatic ring
1.9-1.6	H_{n}	Naphthenic H attached to ring
1.6-1.0	H_{β}	-CH2 & -CH3 attached to a saturated β-carbon
1.0-0.5	H_{g}	gamma-methyl
^{13}C nmr		
170-105	C_{ar}	Aromatic carbon
75-10	C_{al}	Aliphatic carbon

Table 5.5b Structures of Hydrogen Type

Hydrogen Type	Structure
Aromatic hydrogen	
Olefinic hydrogen	$CH_2 = CH_2$
α-methylene	●—CH_2—○
α-methyl	●—CH_3
Naphthenic methylene	⌀—CH_2—⌀
Naphthenic methyl	⌀—CH_3
β-methyl	⊠—CH_3
gamma-methyl	○—CH_3

Notation: ●—bound to aromatic carbon
⊠—bound to α carbon in ethyl groups on aromatic ring
○—bound to carbon in linear alkyl structures β or further from aromatic rings
⌀—bound to naphthenic or hydro-aromatic carbon

Iatroscan, and the proportion of each class was calculated from the areas under the respective absorption peaks.

Decomposition characteristics of some of the extracts were studied by thermogravimetric and derivative thermogravimetric analyses (TGA/DTGA). Rates of weight change were recorded with a DuPont 1090 Thermogravimetric Analyzer, using nitrogen at flow rates of 100 ml min^{-1}. Heating rates were 10 °C min^{-1}.

Apparent activation energies of decomposition were determined from the Arrhenius equation on the assumption that decomposition was a first-order process that followed the relationship

$$-dW/dt = KW \qquad (5.1)$$

where dW/dt = instantaneous rate of weight loss;
W = weight of unburned combustible matter; and K= the specific reaction rate.
The reaction rate is then related to the Arrhenius equation by

$$\log K = \log A - E_a/2.303RT \qquad (5.2)$$

where A= the frequency factor, E_a = activation energy, R = the universal gas constant, and T= absolute temperature.

5.4 EXPERIMENTAL RESULTS AND DISCUSSION

5.4.1 Extraction with Supercritical Water

The results in Tables 5.6 to 5.12 show the effects of various operating modes (pyrolysis, SCWE with and without CO, SCWE/CO with and without Fe_2O_3) and operating conditions (pressure, temperature, particle size and extraction time) on conversion of organic matter in the Rotem shale to toluene-solubles. The effects of pressure and CO during SCWE of MFO shale on conversion are presented in Table 5.13.

Previous work on supercritical fluid extraction of various oil shales were carried out under different conditions from this study, it is therefore not appropriate to compare the results.

5.4.1.1 Effects of Pressure and Temperature

The quality and quantity of extract produced during extraction (retorting) depend on pressure and temperature. High pressures favour gas production, and extraction at temperatures below the active decomposition temperature T_d furnish small extract yields that can be increased by raising the extraction temperature to T_d. Extractions at temperatures above T_d may lead to thermocracking of the primary extract.

Table 5.6 Effect of Temperature and Pressure on SCWE of Rotem Shale; size = -1.16+0.833mm, t= 60 min

Run No	**R-32**	**R-02**	**R-35**	**R-31**
Temp, °C	400	450	400	400
Pressure MPa	14	14	17.5	21
% Conversion	**34.9**	**22.2**	**29.7**	**32.4**
Elemental composition, %				
C	76.8	77.0	79.2	80.4
H	8.6	8.4	9.1	9.0
N	1.1	1.3	1.3	1.5
S	9.97	12.4	8.3	6.4
O(diff)	3.5	0.9	2.2	2.7
H/C	1.34	1.31	1.38	1.35
From ^{1}H nmr, %				
H_{ar}	12.5	18.9	13.8	14.8
H_{ol}	0.0	0.0	0.0	0.0
H_n	7.6	6.6	5.1	7.8
Paraffinic				
$-H_\alpha$	23.4	36.5	25.3	30.9
$-H_\beta$	39.1	28.0	39.6	31.3
$-H_g$	17.4	9.9	16.1	15.2
H_{ar}/H_α	0.53	0.52	0.53	0.48
Aromaticity (f_a)	**0.50**	**0.57**	**0.47**	**0.53**

Table 5.7 Effect of Pressure on Class Composition of Toluene-soluble Matters (Rotem Shale)

Run No	**R-32**	**R-35**	**R-31**
Temp, °C	400	400	400
Press, MPa	14	17.5	21
Extraction time, Min	60	60	60
Extractor fluid	H_2O	H_2O	H_2O
Oils (al)	22.8	10.6	19.0
Oils (ar)	28.1	45.1	27.7
Polar compounds	46.9	40.7	49.7
Asphaltenes	2.2	3.6	3.6

Oil is n-pentane and n-hexane soluble

Polar compounds, also referred to as "resins", are hydrocarbons containing S, N, and O

Asphaltene is n-pentane/n-hexane-insoluble, but soluble in toluene

Table 5.8 Effect of Time on SCWE of Rotem Oil Shale; s = -0.833+0.6mm, T= 450°C, P= 17.5 MPa

Run No	**R-16**	**R-15**	**R-19**	**R-14**
Extraction time, Min	20	40	60	80
% Conversion	**15.6**	**26.0**	**30.4**	**33.0**
Elemental composition, %				
C	80.10	77.8	64.6	57.6
H	7.70	7.2	6.3	6.3
N	1.20	0.9	0.9	0.6
S	8.15	11.55	21.7	25.0
O(diff)	2.80	2.5	6.5	10.5
H/C	1.16	1.10	1.17	1.32
From ^{1}H nmr, %				
H_{ar}	34.9	41.0	28.9	23.1
H_{ol}	0.0	0.0	0.4	4.3
H_{n}	5.1	3.3	7.8	3.9
paraffinic				
$-H_{\alpha}$	38.4	38.4	34.0	24.1
$-H_{\beta}$	17.1	13.1	21.1	27.7
$-H_{g}$	4.5	4.3	7.8	17.0
H_{ar}/H_{α}	0.91	1.07	0.85	0.96
Aromaticity (f_a)	**0.68**	**0.73**	**0.66**	**0.58**

Table 5.9a Effect of Extraction Time on Class Composition

Run No	R-15	R-19	R-14
Temp, °C	450	450	450
Press, MPa	17.5	17.5	17.5
Extraction time, Min	40	60	80
Extractor fluid	H_2O	H_2O	H_2O
Oils (al)	33.8	33.3	39.6
Oils (ar)	33.0	24.3	27.8
Polar compounds	31.2	40.0	30.8
Asphaltenes	2.0	2.4	1.8

Table 5.9b Effect of Extraction Time on Class Composition of SCWE/CO Extractts

Run No	R-23	R-22	R-18
Temperature, °C	400	400	400
Pressure, MPa	14	14	14
Extraction time, Min	20	40	60
Extractor fluid	H_2O/CO	H_2O/CO	H_2O/CO
Oils(al)	29.5	22.3	21.8
Oils(ar)	30.8	25.1	26.3
Polar compounds	37.4	42.4	46.2
Asphaltenes	2.3	10.2	5.7

Table 5.10 Effect of Fe_2O_3 on SCWE of Rotem Shale; size= -1.16+0.833mm, T= 400 °C, t= 60 min

Run No	**R-32**	**R-43**	**R-35**	**R-37**
Pressure, MPa	14	14	17.5	17.5
Catalyst	none	Fe_2O_3	none	Fe_2O_3
% Conversion	**34.9**	**22.8**	**29.7**	**24.7**
Elemental composition, %				
C	76.8	74.6	79.2	77.6
H	8.6	7.9	9.1	9.2
N	1.1	0.8	1.3	1.2
S	10.0	9.9	8.3	8.9
O(diff)	3.5	6.8	2.1	3.1
H/C	1.34	1.28	1.38	1.31
From ^1H nmr, %				
H_{ar}	12.5	17.0	13.8	13.7
H_{ol}	0.0	0.0	0.0	0.0
H_n	7.6	5.0	5.1	9.4
paraffinic				
$-H_\alpha$	23.4	23.5	25.4	30.1
$-H_\beta$	39.1	35.0	39.6	31.8
$-H_g$	17.4	19.5	16.1	15.0
H_{ar}/H_α	0.53	0.72	0.53	0.55
Aromaticity (f_a)	**0.50**	**0.49**	**0.47**	**nd**

nd = not determined

Table 5.11 Effect of Pressure on SCW/CO Extraction of Rotem Oil Shale; size = -0.833+0.6mm, T= 400°C, t= 60min

Run No	**R - 18**	**R - 09**	**R - 27**
Press, Mpa	14	17.50	21
% Conversion	**55.5**	**67.5**	**48.6**
Elemental composition, %			
C	80.3	83.6	82.0
H	10.1	9.6	10.2
N	1.7	1.0	1.7
S	5.7	3.3	4.2
O(diff)	2.2	2.5	1.9
H/C	1.50	1.38	1.49
From ^{1}H nmr, %			
H_{ar}	10.5	9.6	9.4
H_{ol}	0.0	0.0	0.0
H_n	6.8	8.1	9.0
Paraffinic			
$-H_\alpha$	23.4	27.8	27.0
$-H_\beta$	41.9	35.9	38.3
$-H_g$	15.4	18.7	16.3
H_{ar}/H_α	0.45	0.35	0.35
Aromaticity (f_a)	**0.35**	**0.42**	**nd**

Table 5.12 Effect of Pressure on SCW/CO Extraction of Rotem Oil Shale; size = -1.16+0.833mm, T = 400°C, t= 60 min

Run No	**R-32**	**R-40**	**R-35**	**R-38**	**R-31**	**R-28**
Press, MPa	14	14	17.5	17.5	21	21
Extractor fluid	H_2O	H_2O/CO	H_2O	H_2O/CO	H_2O	H_2O/CO
% Conversion	**34.9**	**45.9**	**29.7**	**45.9**	**32.4**	**69.5**
Elemental composition %						
C	76.8	82.1	79.2	82.1	80.4	76.9
H	8.6	9.3	9.0	9.7	9.0	10.1
N	1.2	1.5	1.3	1.6	1.5	1.7
S	9.9	3.9	8.3	3.7	6.4	5.1
O(diff)	3.5	3.2	2.2	2.8	2.7	6.2
H/C	1.34	1.36	1.38	1.42	1.35	1.57
From ^{1}H nmr, %						
H_{ar}	12.5	8.7	13.8	7.5	14.8	9.4
H_{ol}	0.0	0.0	0.0	0.0	0.0	0.0
H_n	7.6	7.4	5.1	7.5	7.8	9.0
Paraffinic						
$-H_\alpha$	23.4	22.9	25.4	24.1	30.9	30.5
$-H_\beta$	39.1	46.3	39.6	43.9	31.3	33.6
$-H_g$	17.4	14.9	16.1	17.1	15.2	17.5
H_{ar}/H_α	0.53	0.38	0.53	0.31	0.48	0.31
Aromaticity (f_a)	**0.50**	**0.42**	**0.47**	**nd**	**0.53**	**0.44**

Table 5.13 Effect of Pressure on SCW/CO Extraction of MFO Oil Shale; size = -1.16+0.833mm, T= 400°C, t= 60 min

Run No	M-01	M-02	M-03	M-04
Press, MPa	14	14	17.5	21
Extractor fluid	H_2O	H_2O/CO	H_2O/CO	H_2O/CO
% Conversion	12.43	30.33	31.87	29.60
Elemental composition, %				
C	75.2	79.2	82.7	81.8
H	7.7	8.5	9.0	9.1
N	1.2	1.9	2.0	1.8
S	14.6	5.1	4.1	5.1
O(diff)	1.3	3.1	2.2	2.2
H/C	1.24	1.29	1.30	1.33
From ^{1}H nmr, %				
H_{ar}	16.8	13.8	13.7	12.1
H_{ol}	0.0	2.6	0.0	0.0
H_n	5.1	6.1	5.69	6.57
paraffinic				
$-H_\alpha$	21.8	22.1	22.8	23.7
$-H_\beta$	35.0	32.8	37.9	39.4
$-H_g$	21.3	22.6	19.9	18.2
H_{ar}/H_α	0.77	0.63	0.61	0.51
Aromaticity (f_a)	nd	0.48	0.48	0.36

Since these temperature and pressure effects depend on the type of oil shale(2), it is important to explore the appropriate conditions for SCWE of Rotem and MFO oil shales.

Values of K were obtained at various temperatures by using data from TG and DTG curves, and the apparent activation energies for the extracts were determined from plots of logK versus 1/T. A typical plot is shown in Figure 5.6 in which three regions delinated themselves, the first being due to water loss, the second to devolatization, and the third region probably associated with secondary reactions such as bond breaking.

Other useful data obtained by TGA/DTGA were the maximum decomposition rate, indicated by the peaks in the DTG curves (see Figures 5.7-5.14), and the temperatures at which it occurs. These parameters have been related to thermal reactivity of coal(9). From a kinetic view point the peak rate is related to the reactivity R by

$$R = 1/W_i(dw/dt)_{max} \qquad (5.3)$$

where W_i = initial weight of coal (mg)

and

$(dw/dt)_{max}$ = maximum loss (mg min^{-1}).

Molecular weights of some samples of toluene-soluble

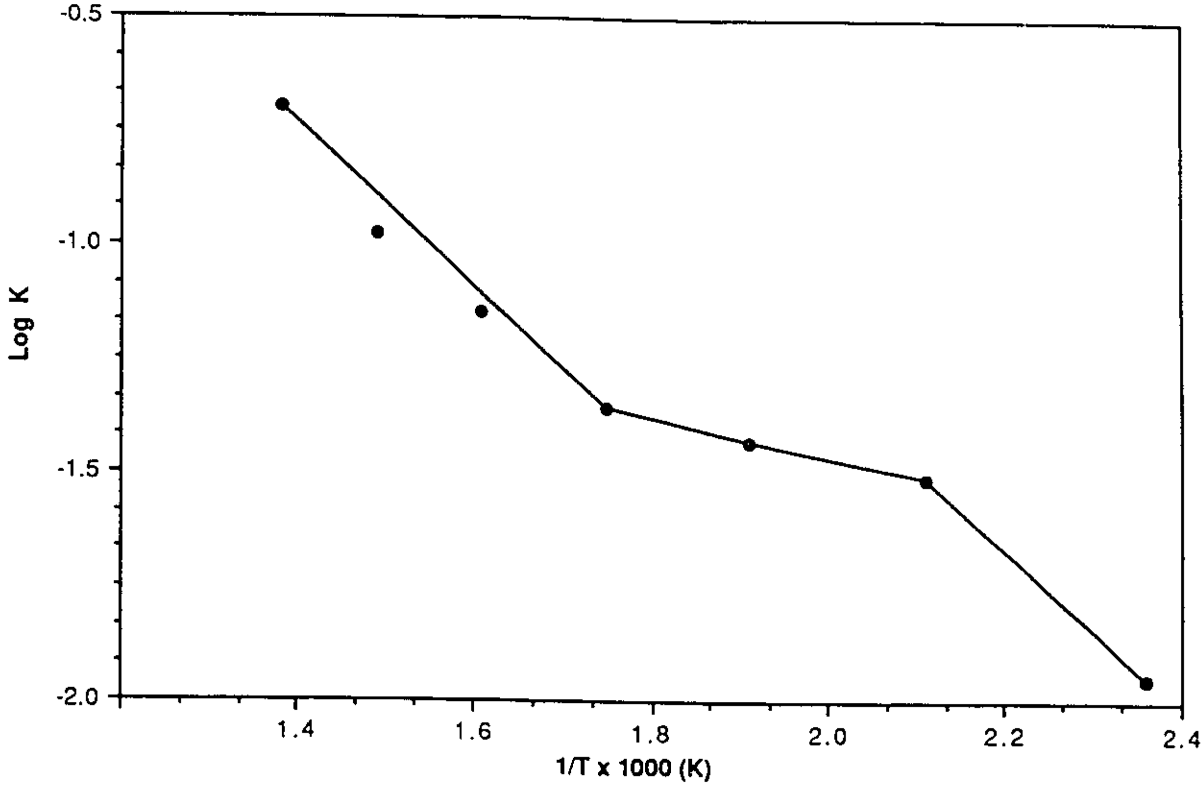

Figure 5.6 Arrhenius Plot of Extract from SCWE of Rotem Oil Shale (R-27)

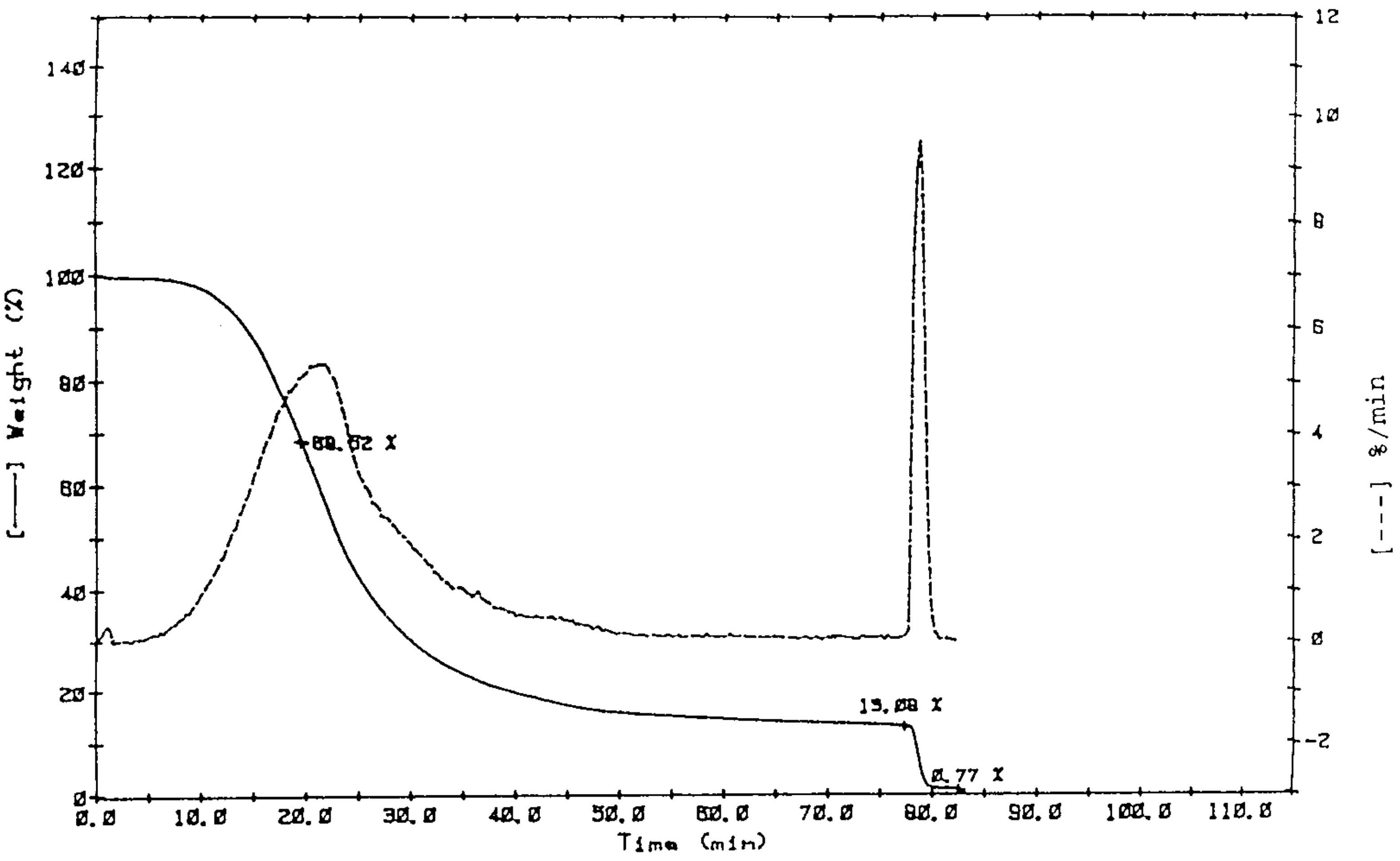

Figure 5.7 TG/DTG Curves of R-20 Extract

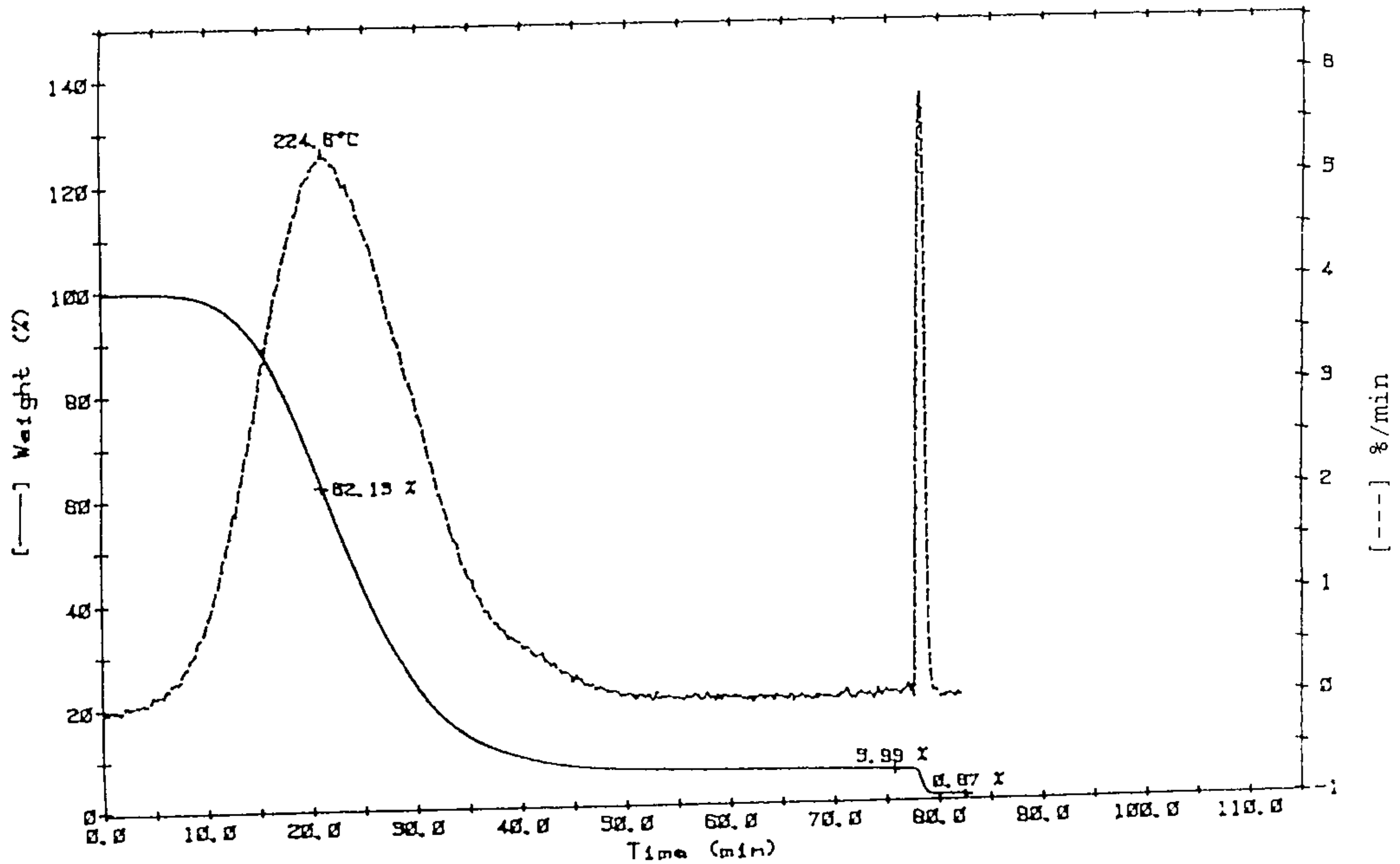

Figure 5.8 TG/DTG Curves of R-33 Extract

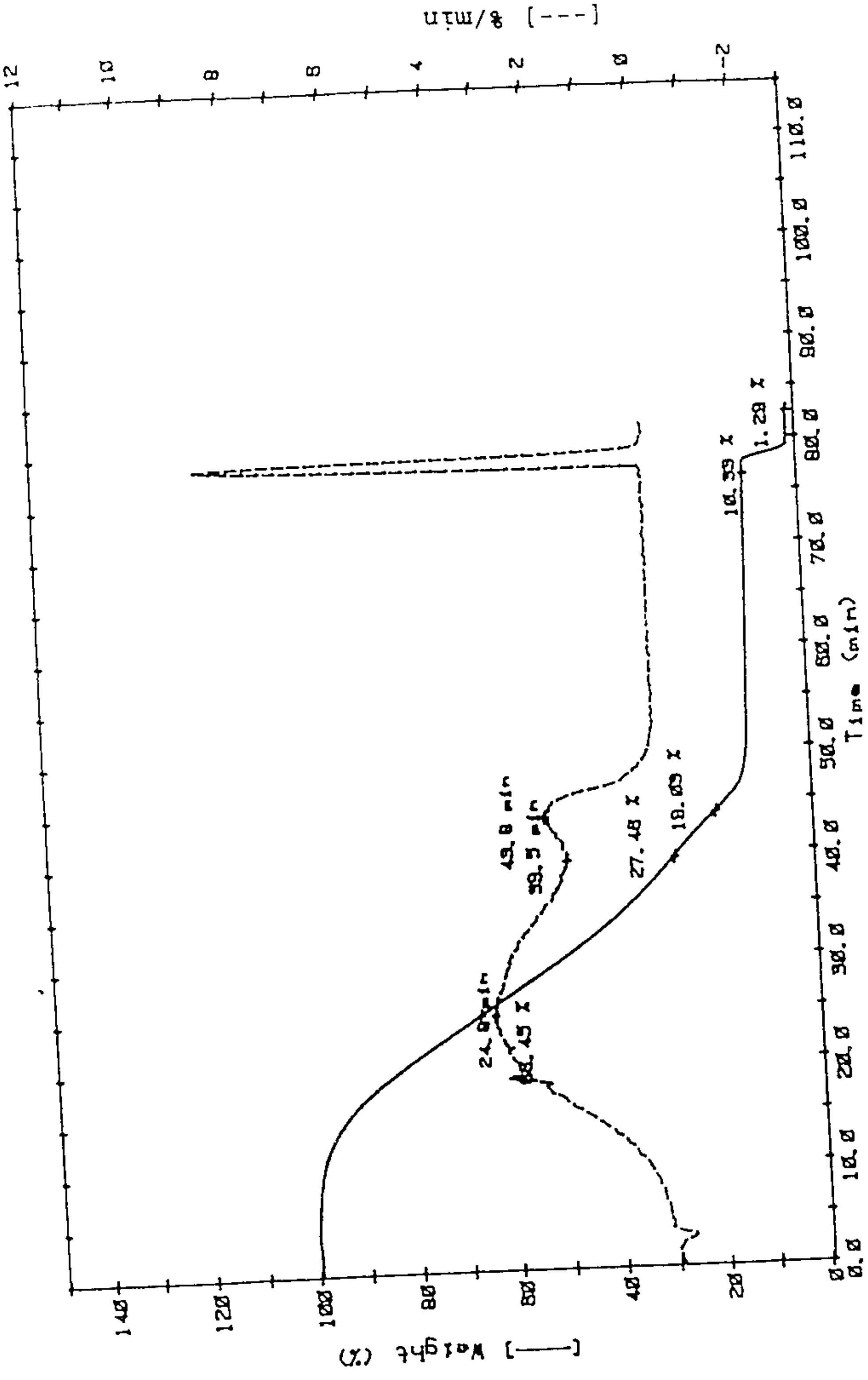

Figure 5.9 TG/DTG Curves of R-22 Extract

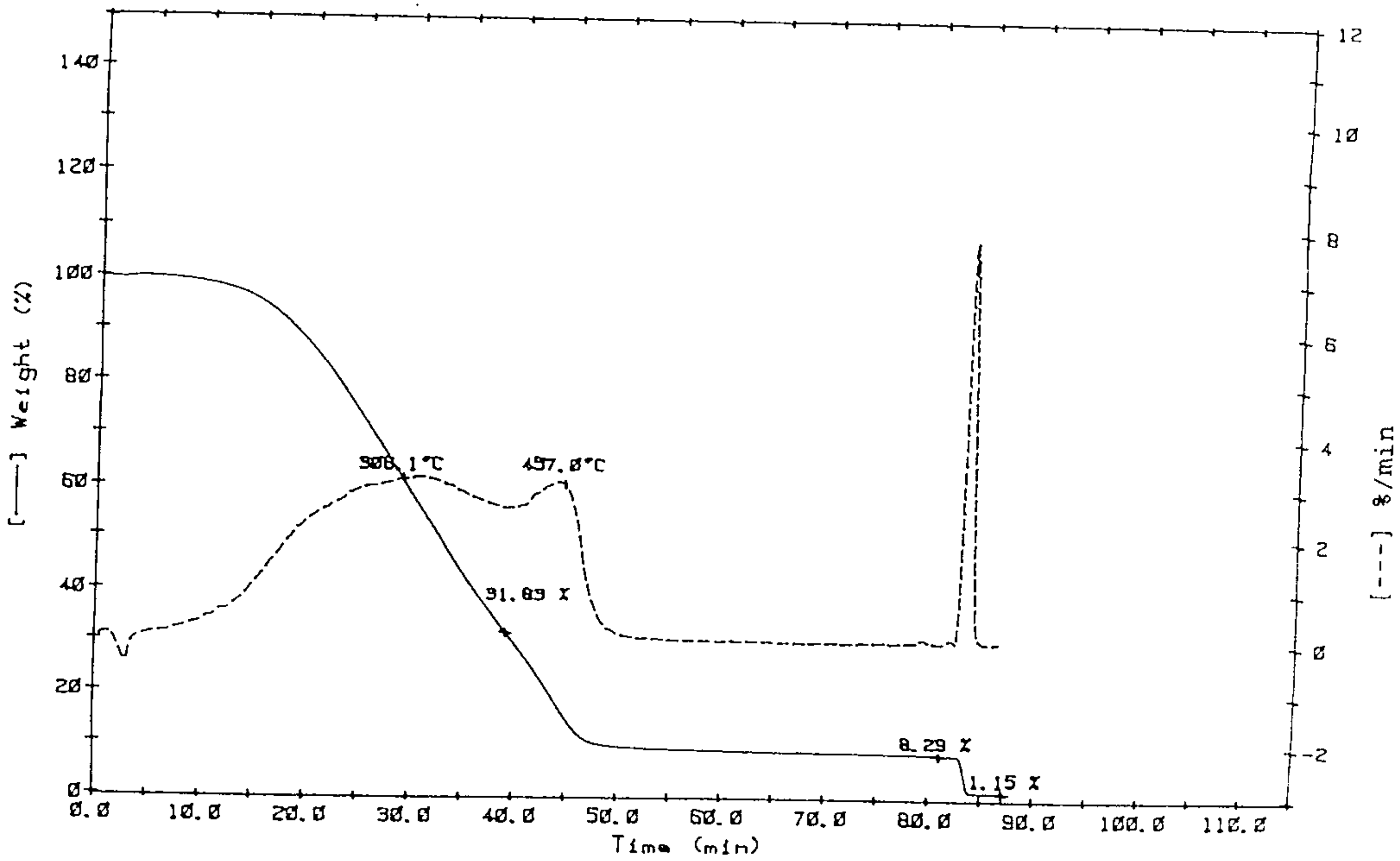

Figure 5.10 TG/DTG Curves of R-27 Extract

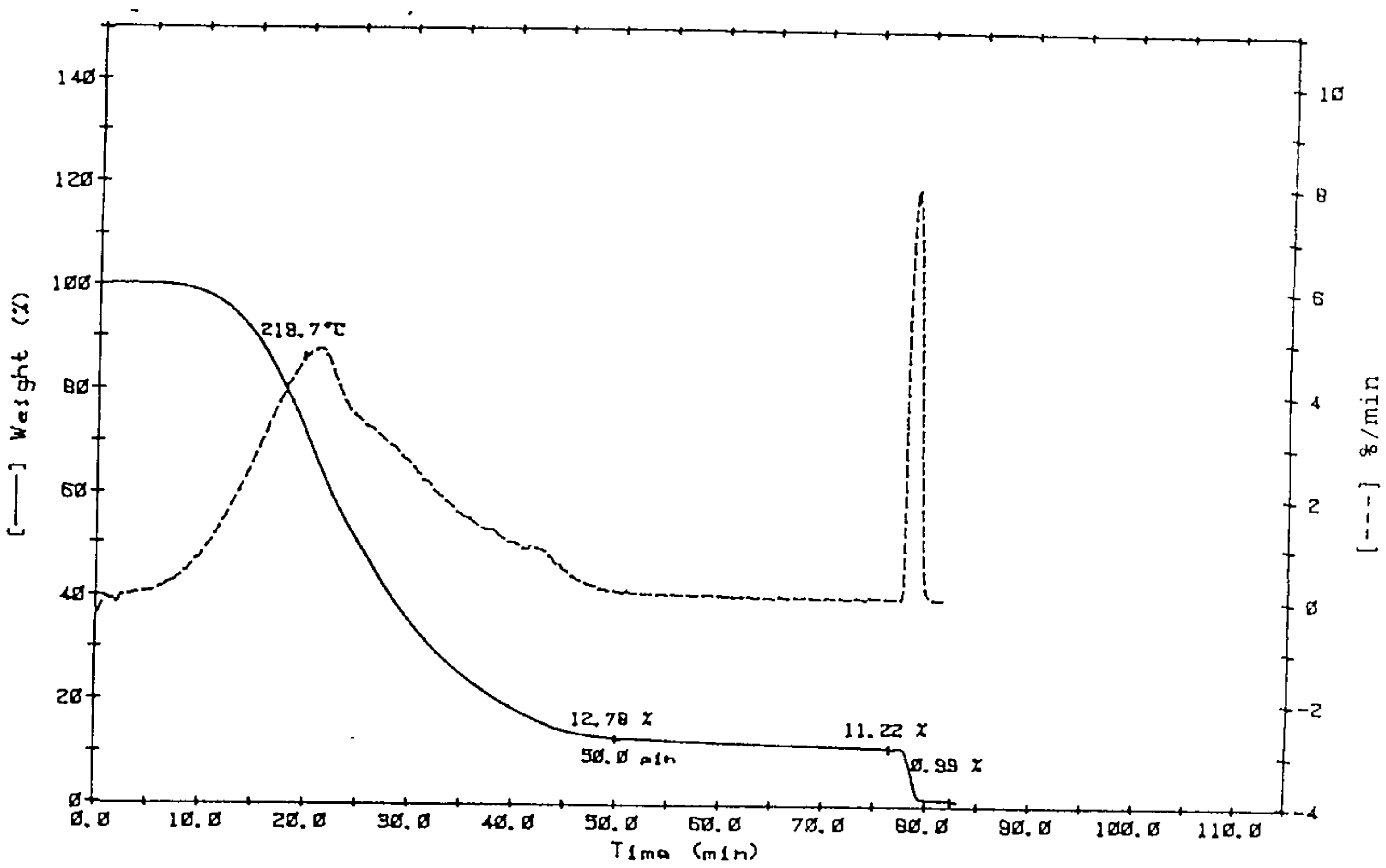

Figure 5.11 TG/DTG Curves of R-32 Extract

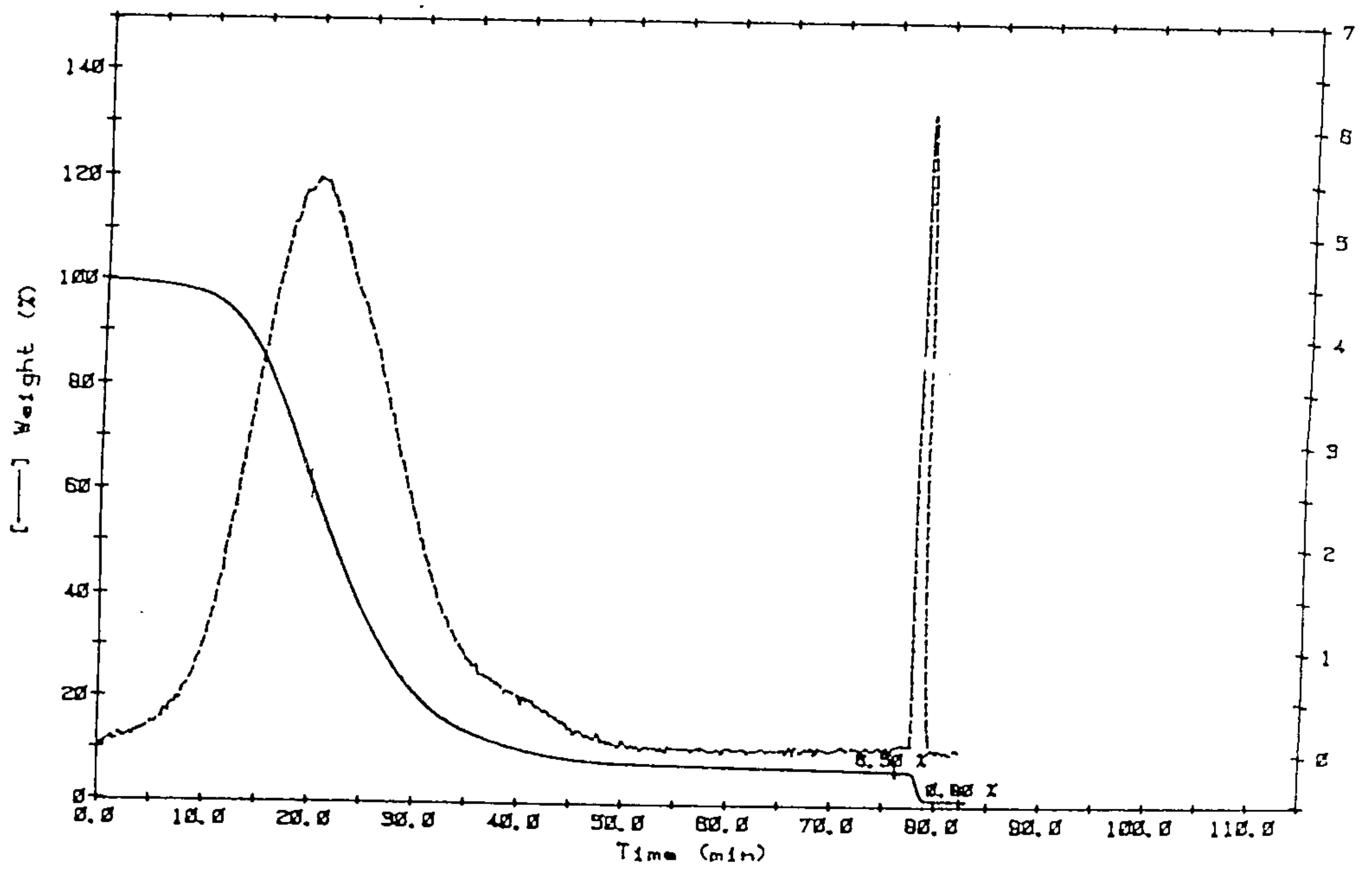

Figure 5.12 TG/DTG Curves of R-36 Extract

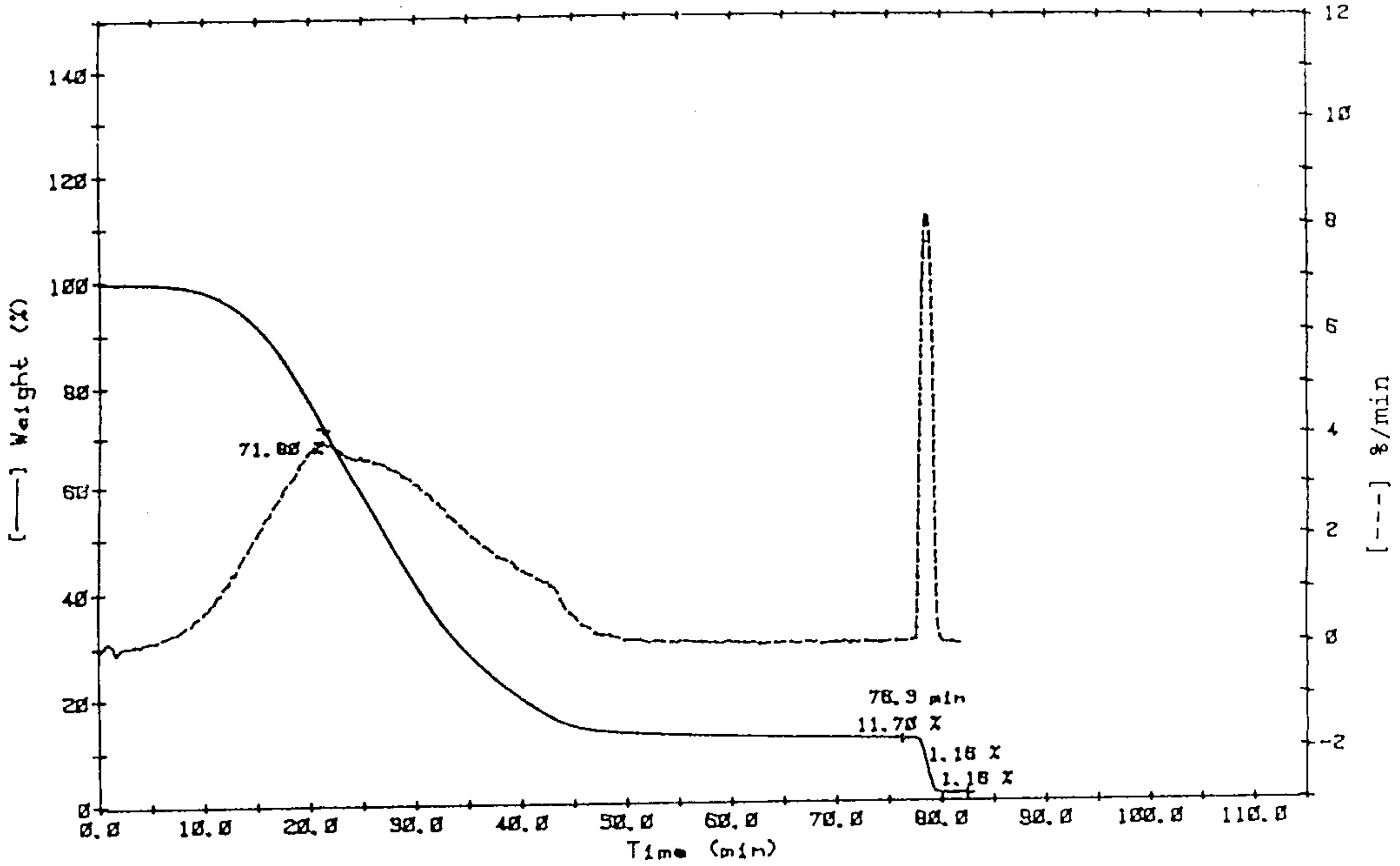

Figure 5.13 TG/DTG Curves of R-35 Extract

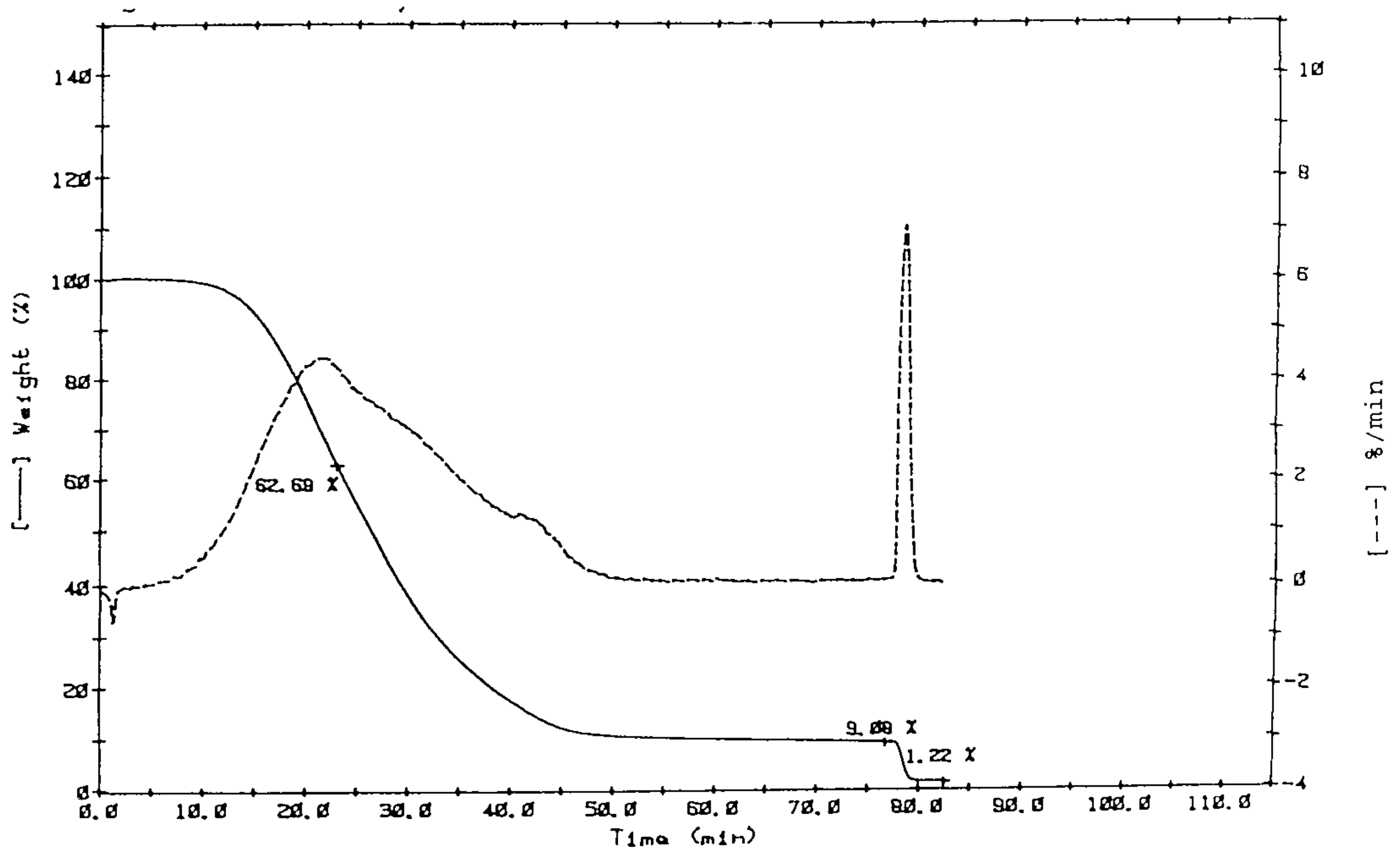

Figure 5.14 TG/DTG Curves of R-37 Extract

matter were obtained with a Luescan 232A vapour pressure osmometer, using benzene as solvent.

Table 5.6 shows the effects of pressure and temperature on the quantity and some properties of SCWE extracts from Rotem oil shale.

Yields of toluene-solubles tend to vary between 30 and 35%, with the highest conversion at 14 MPa and 400 °C. Decreasing conversion with increasing pressure in the absence of CO has also been reported for Green River oil shales(2). At high pressures both cracking and coking take place, but the net effect of increasing pressure depends on the type of shale and the pyrolysis atmosphere. As reported for Green River oil shales, yields of liquid product fall with increasing pressure under inert gases such as N_2 or He, but rise in H_2.

Although operating pressures were lower than the critical pressure of water (22.1 MPa), the results of this study suggest that extraction at high pressures does not necessarily offer a particular advantage and may indeed, in certain instances, be counterproductive. Extraction under near- or sub-critical pressure may be adequate and, on occasion, be preferable. The actual optimum extraction condition may depend on the desired product slate and on the nature of the shale.

Similarly, conversion fell with increasing temperature, with greater conversion of organic matter to toluene-soluble matter observed at 400 °C than at 450 °C. Extract yields fell from about 35% at 400 °C to 22% at 450 °C, presumably because kerogens decompose primarily between 210 °C and 400 °C (Figure 5.3) and temperatures above 400 °C will promote secondary changes that produce char and gas at the expense of liquids. As well, high temperatures promote oxidation that destroys organic waste matter. This phenomenon was observed in the works of Thomason et al (10) and Swallow et al.(11) where supercritical water oxidation was used to break down organic waste materials to carbon dioxide, water and other compounds.

A similar drop in yield with increase in temperature is to be expected during H_2O/CO extraction since, according to Helling and Tester(12), H_2 will be consumed at higher temperature where oxidation reactions, if chemically allowed, are favoured. This can be illustrated:

$$CO + H_2O ===== H_2 + CO_2 \quad (5.4)$$

$$H_2 + 1/2O_2 ==== H_2O \quad (5.5)$$

On the other hand, a high temperature (450 °C) and relatively high pressure (17.5 MPa) appear to favour low nitrogen contents in the extract (Table 5.8). Organic nitrogen has been converted to molecular nitrogen at temperatures above 400 °C(10-11, 13-14). Presumably organic nitrogen that would otherwise accumulate in the extract was converted to N_2 at 450 °C. Increasing pressure has no significant effect on elemental composition ([C], [H], and the H/C ratio) of extracts generated.

The effect of temperature on [C], [H] and H/C ratios depends on pressure, as illustrated by Table 5.6. At 14 MPa there was relatively little change when temperatures were raised from 400 °C to 450 °C. Nitrogen content is slightly increased at higher temperature and pressure.

Sulphur contents of extracts tend to increase when temperatures are raised. The trend in [S] and [N] can be explained by high thermal stability of nitrogen-bearing entities which are difficult to remove during oil shale processing, and by the generally high reactivity of S-bearing moieties. However, [S] in extract decreased with increase in pressure.

Toluene-soluble matter becomes more aromatic as temperatures increased from 400 °C to 450 °C (see Table 5.6, f_a, 0.50 versus 0.57). As well (Table 5.8), all extracts are characterized by high aromaticities ($f_a > 0.50$). For comparison, it is noted here that extracts generated at 400 °C under 14, 17.5 and 21 MPa showed f_a at ≈0.50, 0.47 and 0.53 respectively. The increase in f_a can be caused by the cleavage of alkyl side groups on aromatic rings to give gases or by dehydration of naphthenes and hydroaromatics(15). Regressive reactions such as coking, which cause more carbon to be incorporated in aromatic rings is another factor for increase in f_a values.

Of interest in this connection is that H_β in extracts generated at 14 and 17.5 MPa are virtually identical - an observation which implies that extraction was accompanied by mild decomposition and by removal of relatively stable paraffins. If the objective is to produce high fraction of oily materials, 14 MPa appears to be a good pressure to work at; however, higher pressure will favour generation of more toluene-solubles.

The effect of pressure on the class composition of some extracts is shown in Table 5.7 where class compositions are expressed in terms of the relative concentrations of oils, polar compounds and asphaltenes in the extract. An increase in pressure from 14 MPa to 17.5 MPa raised the oil fraction from ≈51% to 56%, but a further increase in pressure to 21 MPa, caused it to fall to 47%. This implies that the oil fractions are generated and preferentially removed at lower pressures.

It appears that the extraction temperature (400 °C or 450 °C) has relatively little or no quantitative effect on the oil fraction, as shown by R-35 in Table 5.7 and R-19 in Table 5.9a. For example: under 17.5 MPa, 60 minutes extraction at 400 and 450 °C yielded total oil fractions amounting to 56% and 58% respectively (R-35 and R-19), but the higher temperature tends to favour generation of aliphatic oil.

5.4.1.2 Effect of Extraction Time

Table 5.8 shows the effect of time on conversion and on properties of extracts generated from -0.833+0.6mm oil shale at 450 °C and 17.5 MPa. Increased conversion to toluene-solubles with lengthened extraction period is seen in Table 5.8, with the highest conversion (33%) occurring after 80 minutes.

Carbon and hydrogen contents decreased while H/C ratios increased as extraction was prolonged, with relatively more drastic changes occurring after 40 minutes. In contrast to nitrogen contents, which decreased when the extraction period was increased, sulphur contents increased dramatically. H_{ar} and f_a attained maximum values at 40 minutes.

Class compositions show that oil fractions of extracts generated at 450° C and 17.5 MPa tended to decrease initially, from about 69% to ≈58% with increase in time, but then increased to ≈68% at 80 minutes. It appears therefore that there is no consistent trend.

5.4.1.3 Effects of a Potential Catalyst (Fe_2O_3)

Iron compounds have been commonly used to catalyze coal liquefaction(16); such compounds, including $FeCl_2$, can enhance liquefaction without simultaneously promoting hydrocracking to light oils. In Bergius hydrogenation, iron oxides have been used, and a similar effect was expected during SCWE of oil shale. Hence, Fe_2O_3 was chosen as a cheap, once-through catalyst in the hope of enhancing hydrogenation of oil shale.

However, Table 5.10 shows that extraction of Rotem oil shale in the presence of Fe_2O_3 generated <u>less</u> toluene-soluble matter than in its absence. This trend was observed both at 14 and 17.5 MPa. For example, at 14 MPa conversion decreased from 34.9% in the absence of Fe_2O_3 to 22.8% in presence of this compound, and at 17.5 MPa conversion dropped from 29.7% to 24.7%. The detrimental effect of Fe_2O_3 on conversion can be explained by the consumption of hydrogen generated from SCW through the following reaction(17):

$$Fe_2O_3 + 2H_2S + H_2 \text{ -----> } 2FeS + 3H_2O \qquad (5.6)$$

The H_2S is a known product of oil shale extraction.

The carbon and hydrogen contents of the extracts generated by SCWE, as well as their H/C ratios, were slightly reduced when Fe_2O_3 was added, and extracts with relatively low nitrogen contents were produced at 400° C and 14 MPa. A similar trend was observed during interaction of quinoline with SCW (see 4.3), when Fe_2O_3 enhanced decomposition of quinoline.

5.4.2 SCWE in Presence of CO

In SCWE, as in liquefaction, there is need to stabilize free radicals generated during extraction. In liquefaction, donor solvents are commonly used for this purpose, and in SCWE, a CO atmosphere can be used to promote H formation by the water-gas shift (WGS) reaction. With this in mind, the oil shale samples were extracted with SCW/CO under various conditions. Although the exact function the shift reaction in thermal decomposition of carbonaceous materials is not clear, the impact of CO on kerogen decomposition during SCWE has been explained by various mechanisms. As explained by Cummins and Robinson(18), mineral carbonates in oil shale may react with CO and H_2O to form intermediate compounds, possibly alkaline formates which can transfer hydrogen as a hydride ion to the free radicals formed from kerogen during thermal degradation.

As well, Helling and Tester[12] suggested that reaction of CO with SCW proceeded with a lower activation reaction and that the shift reaction may occur in the gas-phase by a free radical or activated complex reaction. However, an ionic pathway is also possible according to the following reactions:

$$H_2O == H^+ + OH^- \qquad (5.7)$$

$$CO + OH^- == HCO_2^- \qquad (5.8)$$

$$HCO_2^- + H_2O == H_2CO_2 + OH^- \qquad (5.9)$$

$$H_2CO_2 == H_2 + CO_2 \qquad (5.10)$$

Hydroxyl ions from (5.7) could react with CO to yield H_2 with formic acid as intermediate product.

The results of extraction of Rotem shale with supercritical water in the presence of CO are summarized in Tables 5.11 and 5.12, and Table 5.13 shows corresponding results for MFO oil shale. In both instances the presence of CO enhanced conversion of organic matter to toluene-solubles.

5.4.2.1 Pressure Effects in SCW/CO Extraction

A pressure increase from 14 MPa to 17.5 MPa did not affect conversion of -1.16+0.833mm Rotem oil shale, but a further increase to 21 MPa raised conversion from 45.9% to 69.5%. The reverse was observed with MFO oil shale, which responded with increased conversion when pressure was raised to 17.5 MPa, but then yielded less extract when the pressure was further increased (see Table 5.13). As well, when Rotem shale was extracted with SCW at 14 MPa and 400 °C in the absence of CO, conversions as high as 34% were obtained and only ≈12% conversion was observed with MFO shale.

The relatively low extract yield observed with MFO oil shale was probably due to the fact that its kerogen contains more aromatic hydrocarbons than Rotem oil shale (see Table 5.3). Further explanation for the low conversion with MFO shale is evident from FT-i.r analyses of the mineral-free kerogens (see Figures 5.1 and 5.2). Spectra of Rotem sample (Figure 5.1) show the presence of additional bands at 1200 and 1040 cm^{-1} which, following Rouxhet et al.(19), can be attributed to relatively volatile alcoholic OH-functions. The peak shoulder near 1030 cm^{-1} is due to C-O vibration in aryl-alkyl ethers.

It has also been reported(2) that the presence of sulphur affects extraction of Devonian oil shale due to the consumption of hydrogen in formation of H_2S, i.e. H_2 that would otherwise be available for oil production, and MFO shale contained more sulphur than Rotem shale.

Yurum and Karabakan(20) reported that yield of extracts was enhanced by carbonates in oil shale, and it is likely that carbonates in Rotem oil shale also enhanced its generation of more liquid products. The pathway involving carbonates could not be ruled out as a route of extracting oil shale with SCW/CO. The higher liquid products generated from Rotem shale serve as a convincing indication.

As in extraction of the Rotem shale, the presence of CO during SCWE of the MFO shale generated extracts with higher [C], [H] and H/C ratios (see Table 5.12), and a similar effect of pressure was observed, i.e. H/C ratios increased with pressure, but there was no clear trend in carbon contents. The relatively high H/C ratios of extracts generated in the presence of CO suggest that the amount of carbon in aromatic rings is comparatively low.

In all cases, [S] of extracts generated in the presence of CO are lower than [S] of those obtained in its absence. This observation can be supported by the ability of formic acid to act as a desulphurization agent. Buren et al(21) were able to desulphurize various sulphur-containing model compounds, such as diphenyl sulphide and benzothiophene in H_2O/CO systems at 450 °C with conversion as high as 83%. For example, diphenyl sulphide was converted to benzene, toluene, benzoic acid and thiophenol while the corresponding pyrolysis showed no significant conversion.

5.4.2.2 Effect of Extraction Time on SCW/CO Extraction

The effect of extraction time on SCW extraction in the presence of CO was explored at 400° C and 14 MPa for 20, 40 and 60 minutes, and results (see Table 5.14) show that conversion did not change much with time. Conversions of over 50% were recorded in all three runs (see Figure 5.15). But it is worth noting that a time-effect on conversion in the presence of CO is the reverse of a time-effect in its absence in which case conversions were low (≈33%) even after 80 minutes (see Table 5.8). Tables 5.8 and 5.14 show that the impact of time on conversion was influenced by other parameters, notably temperature and reaction atmosphere.

However, it seems reasonable that conversion of oil shale during SCW/CO extraction did not change much with time. Since H_2O/CO systems are stable up to about 250 °C(22), above which formic acid will form and decompose to H_2 and CO_2 at a significant rate(21), most of the extraction will take place within a short period if extraction proceeds through formic acid formation according to these reactions:

$$CO + H_2O ====== HCO_2H_{(aq)} ===== H^+_{(aq)} + HCO_2^-{}_{(aq)} ===== H_{2(g)} + CO_{2(g)}$$

Table 5.14 Effect of Time on SCW/CO Extraction of Rotem Oil Shale; size= -0.833+0.6mm T= 400°C, P= 14 MPa

Run No	R-23	R-22	R-18
Extraction time, Min	20	40	60
% Conversion	52.6	51.4	55.5
Elemental composition, %			
C	81.1	82.5	80.3
H	10.0	10.1	10.1
N	3.1	1.8	1.7
S	5.1	4.2	5.7
O(diff)	0.7	1.5	2.2
H/C	1.48	1.46	1.50
From ^{1}H nmr %			
H_{ar}	11.2	11.3	11.6
H_{ol}	0.0	0.0	0.0
H_n	6.6	9.8	6.8
paraffinic			
$-H_\alpha$	26.0	25.4	23.9
$-H_\beta$	39.9	39.4	41.9
$-H_g$	16.3	14.1	15.8
H_{ar}/H_α	0.43	0.44	0.45
Aromaticity (f_a)	0.41	0.39	0.35

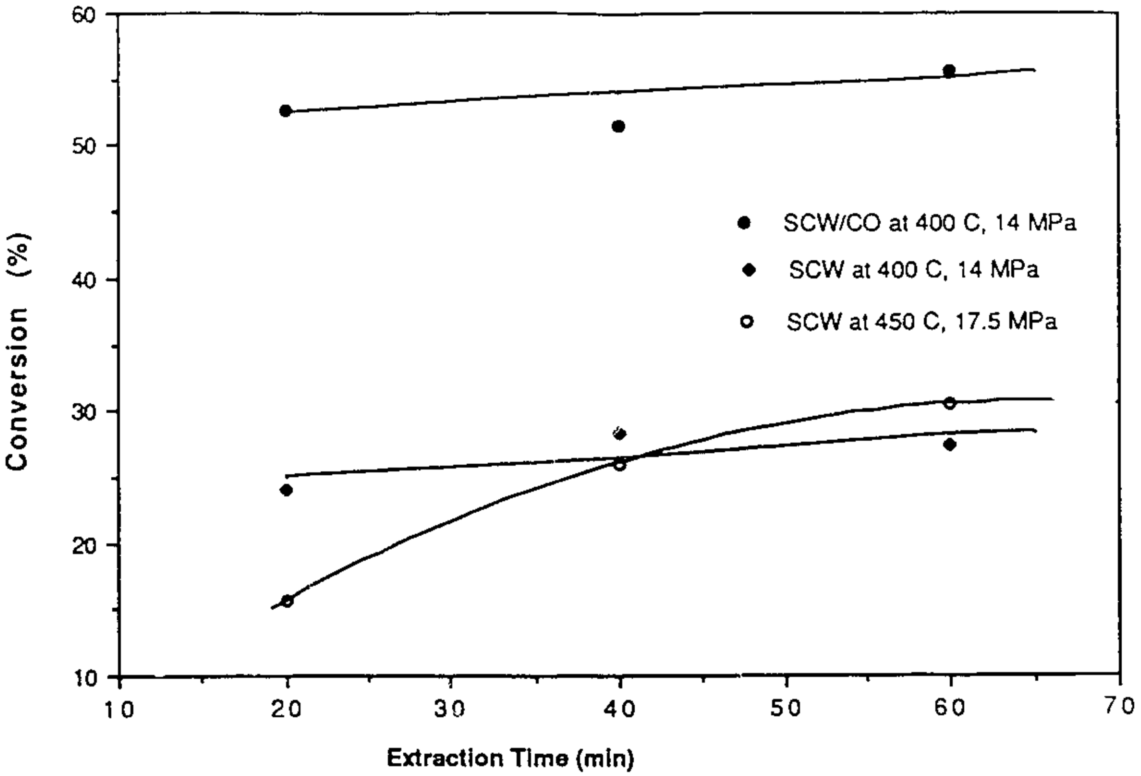

Figure 5.15 Effect of Extraction Period on Conversion of -0.833+0.6mm Rotem Oil Shale

The carbon contents of extracts generated with SCW/CO (Table 5.14) in the three runs are +/-1% of 81%, and hydrogen contents and H/C ratios remained likewise virtually constant over the three reaction periods. Nitrogen contents in the extracts decreased with increase time while S contents showed no clear trend.

With extracts furnished during SCW/CO extraction, a decrease in f_a with increasing time was observed.

At 14 MPa and 400 °C, the effect of CO on the magnitude of the oil in the extract depends on time. Little or no effect on class composition could be observed at 60 minutes despite increasing overall conversion (35% versus 55%). A similar trend was observed at 17.5 MPa and 400 °C. However, at much shorter extraction times, the oil fraction increased while resin production was inhibited by the presence of CO. It seems therefore that the advantage of CO in enhancing production of oily matter is more pronounced in a short-duration extractions. For example, at 20 minutes about 60% of the extract was hydrocarbon oil while only 48% was obtained after 60 minutes.

5.4.2.3 Effect of Fe_2O_3 on SCW/CO Extraction

Like its detrimental effect in SCWE, Fe_2O_3 inhibited conversion of organic matter during SCW/CO extraction of Rotem oil shale at 14 MPa. However, at 17.5 MPa conversions in the presence and absence of Fe_2O_3 were substantially the same (≈49% and ≈46% respectively; see Table 5.15). Presence of Fe_2O_3 in the SCW/CO system had little or no effect on [C], [H] and the H/C ratios of the extracts.

Fe_2O_3 increased the H_{ar}/H_α ratio at 14 MPa, but had no effect on the structure of the extracts generated at 17.5 MPa.

5.4.2.4 Effect of Particle Size

Generally, extract yields are higher when more finely subdivided shale samples are extracted, probably because there is less opportunity for secondary reactions than in coarser material(23). As well, rates of mass transfer may be lower in coarser material than in finer material. Two different particle size fractions (-1.16+0.833mm and -0.833+0.6mm) were extracted with SCW/CO at 400° C under 14 and 17.5 MPa and the results are presented in Table 5.16.

As expected, the smaller particle size (-0.833+0.6mm) allowed more toluene-solubles to be generated than the larger

Table 5.15 Effect of Catalyst on SCW/CO Extraction of Rotem Oil Shale size= -1.16+0.833mm, T= 400°C, t= 60 min

Run No	**R-40**	**R-41**	**R-38**	**R-39**
Pressure, MPa	14	14	17.5	17.5
Catalyst	none	Fe_2O_3	none	Fe_2O_3
% Conversion	**45.9**	**37.4**	**45.9**	**48.8**
Elemental composition, %				
C	82.1	82.3	82.1	81.3
H	9.3	9.4	9.8	9.6
N	1.5	1.6	1.6	1.7
S	3.9	4.3	3.7	4.4
O(diff)	3.2	2.4	2.8	3.0
H/C	1.36	1.37	1.42	1.41
From ^1H nmr, %				
H_{ar}	8.7	10.7	7.5	7.4
H_{ol}	0.0	0.0	0.0	1.0
H_n	7.4	4.6	7.5	6.4
paraffinic				
$-H_\alpha$	22.9	19.3	24.1	24.3
$-H_\beta$	46.3	43.1	43.9	44.1
$-H_g$	14.7	22.3	17.0	16.8
H_{ar}/H_α	0.38	0.65	0.31	0.31
Aromaticity (f_a)	**0.42**	**0.51**	**nd**	**0.47**

Table 5.16 Effect of Particle Size on SCW/CO Extraction of Rotem Oil Shale

Run No	**R-18**	**R-40**	**R-09**	**R-38**
Pressure, MPa	14	14	17.5	17.5
Particle size	a	b	a	b
% Conversion	**55.5**	**45.9**	**67.5**	**45.9**
Elemental composition, %				
C	80.3	82.1	83.6	82.1
H	10.1	9.3	9.6	9.8
N	1.7	1.5	1.0	1.6
S	5.7	3.9	3.3	3.7
O(diff)	2.2	3.2	2.5	2.8
H/C	1.50	1.36	1.38	1.42
From ^{1}H nmr, %				
H_{ar}	11.6	8.7	9.6	7.5
H_{ol}	0.0	0.0	0.0	0.0
H_n	6.8	7.4	8.1	7.5
paraffinic				
$-H_\alpha$	23.9	22.9	27.8	24.1
$-H_\beta$	41.9	46.3	35.9	43.9
$-H_\gamma$	15.8	14.7	18.7	17.1
H_{ar}/H_α	0.45	0.38	0.35	0.31
Aromaticity (f_a)	**0.35**	**0.42**	**0.42**	**nd**

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a = -0.833+0.6mm

b = -1.166+0.833mm

size. As well, while extraction of the -1.16+0.833mm fraction at 14 and 17.5 MPa showed no differences in extract yield and quality, the extract yield from the -0.833+0.6mm increased from 55.5% at 14 MPa to 67.5% at 17.5 MPa.

5.4.3 Comparison of Retorting (Pyrolysis) and SCWE

Since retorting is a well established process for extracting hydrocarbons from oil shale, it is useful to compare extracts generated by pyrolysis and SCWE. Table 5.17 shows the results of pyrolysis and hydrolysis (by SCW) of Rotem oil shale at 400 °C under 14 and 17.5 MPa. As expected, oil yields from SCWE were higher than from pyrolysis, and at both pressures (14 MPa and 17.5 MPa) pyrolysis yielded virtually the same conversion (20.9% and 20.6% respectively).

Carbon and hydrogen contents, and the H/C ratios of extracts generated by pyrolysis and hydrolysis under 14 MPa and at 400 °C appear to be comparable, but the H/C ratio of extract generated from SCWE at 17.5 MPa is higher than that obtained by pyrolysis.

As well, extracts generated at 14 MPa and 17.5 MPa by pyrolysis and SCWE showed relatively constant sulphur and

Table 5.17 Comparison of Pyrolysis and SCWE of Rotem Shale; size = -1.16+0.833mm, T = 400°C

Run No	**R-42**	**R-32**	**R-36**	**R-35**
Pressure, MPa	14	14	17.5	17.5
Process	Pyrolysis	SCWE	Pyrolysis	SCWE
% Conversion	**20.9**	**34.9**	**20.6**	**29.7**
Elemental composition, %				
C	78.7	76.8	80.3	79.2
H	8.7	8.6	8.8	9.0
N	1.1	1.1	1.3	1.3
S	9.4	10.0	6.5	8.3
O(diff)	2.1	3.5	3.1	2.2
H/C	1.32	1.34	1.30	1.38
From ^{1}H nmr, %				
H_{ar}	19.6	12.5	17.0	13.8
H_{ol}	0.0	0.0	0.0	0.0
H_n	5.7	7.6	8.3	5.1
paraffinic				
$-H_\alpha$	27.3	23.4	33.2	25.4
$-H_\beta$	30.9	39.1	28.6	39.6
$-H_g$	16.5	17.4	12.9	16.1
H_{ar}/H_α	0.72	0.53	0.51	0.53
Aromaticity (f_a)	**0.68**	**0.50**	**0.45**	**0.47**

nitrogen contents. Nitrogen contents of pyrolysis extracts are lower than SCWE extracts, and this is analogous to results obtained with quinoline and isoquinoline (see 4.3), whose decomposition is enhanced by SCW. Higher sulphur and nitrogen contents were reported in the extracts generated by SCW because C-N bond rupture was enhanced.

5.4.4 Comparison of Retorting (Pyrolysis), SCWE, and SCWE/CO

The structural characteristics of toluene-soluble matter obtained by extraction under various process conditions were determined from ^1H and ^{13}C nmr spectra (see Tables 5.6-5.17).

Table 5.18 identifies average structural parameters expressed as numbers of protons or carbon atoms per molecule in extracts generated by pyrolysis, SCWE and SCW/CO extraction, and Table 5.19 shows the average structural parameters calculated from ^1H and ^{13}C nmr spectra. Their notation follows Suzuki et al.(24)

Calculation of the parameters identified in Table 5.19 used the following relationships

$$C^n_{ar} = C^n \times f^c_{ar} \quad (5.11)$$

$$H^n_{ar} = H^n \times H_{ar} \quad (5.12)$$

$$C^n_{al} = C^n - C^n_{ar} \quad (5.13)$$

$$H^n_{al} = H^n - H^n_{ar} \quad (5.14)$$

Table 5.18 Average Structural Parameters Calculated from ^1H and ^{13}C nmr Spectra

Notation	Meaning
C_{ar}^n	Number of aromatic carbon atoms in an average single molecule
H_{ar}^n	Number of aromatic hydrogen atoms in an average single molecule
C_{al}^n	Number of aliphatic carbon atoms in an average single molecule
H_{al}^n	Number of aliphatic hydrogen atoms in an average single molecule
C_c^n	Number of carbon atoms in condensed points in aromatic ring systems in an average single molecule
C_c/C_{ar}	Degree of condensation of aromatic ring systems (= C_c^n/C_{ar}^n)
r_{al}	Ratio of aliphatic hydrogen to carbon
$C_{29.7}/C_{14.1}$	Ratio of intensities of peaks at 29.7 ppm and 14.1 ppm
C_α^n	Number of alkyl substituents on aromatic ring systems in an average single molecule

Table 5.19 Average Structural Parameters of Toluene-soluble Matter from -1.16+0.833mm Rotem Oil Shale under Various Conditions(a)

Run No	R-42	R-32	R-40
C^n_{ar}	11.1	10.2	10.7
C^n_{al}	5.3	10.0	15.1
H^n_{ar}	4.3	3.4	3.1
H^n_{al}	17.5	23.7	32.1
r_{al}	3.3	2.4	2.1
C^n_{α}	1.8	2.7	3.8
C^n_c	4.7	3.4	3.1
C^n_c/C^n_{ar}	0.42	0.29	0.31
$C_{14.1}/C_{29.7}$	0.3	0.3	0.1
$C_{22.7}/C_{29.7}$	0.32	0.3	0.2
f^H_a	0.6	0.5	0.5
δ	0.4	0.5	0.35
H_{aru}/C_{ar}	0.7	0.6	0.54
$H_{1.25}/H_{0.9}$	0.3	0.3	0.22

---

[a] Experimental conditions are defined in previous tables

[b] f^H_a, δ and H_{aru}/C_{ar} were obtained by Brown-Ladner equations

$$r_{al} = H^n{}_{al}/C^n{}_{al} \quad (5.15)$$

$$C_\alpha{}^n = H^n \times H_\alpha/ar_{al} \quad (5.16)$$

$$C_c{}^n = C_{ar}{}^n - H_{ar}{}^n - C_\alpha{}^n - O^n \quad (5.17)$$

5.4.4.1 ^{13}C nmr Spectroscopy

Typical ^{13}C nmr spectra for toluene-soluble matter generated at 400 °C and 14 MPa by, respectively, pyrolysis, SCWE and SCW/CO extraction of -1.16+0.833mm Rotem oil shale are shown in Figures 5.16-5.18. A number of sharp peaks in the aliphatic regions and broad envelopes of spectra in the aromatic regions (≈110-170 ppm) are observed. The relative intensities of peaks at 14.1 and 22.7 ppm (terminal methyl and β-methylene) versus a peak at 29.7 ppm (methylene in longer paraffinic chains) decreased as the extraction process changed from pyrolysis to SCWE and to SCW/CO extraction (Table 5.19). $H_{1.2}/H_{0.9}$ from ^{1}H nmr is close to the values of $C_{29.7}/C_{22.7}$. Pyrolytically generated extracts have the highest degree of aromatic ring condensation (C_c/C_{ar} ≈0.42), while extracts from SCW had the lowest (0.29).

Apparent aromaticities (f_a) derived directly from the integral of the peak area of ^{13}C nmr spectra showed extracts generated by pyrolysis to be significantly more aromatic than those from SCWE (f_a≈ 0.50) or SCW/CO (f_a≈ 0.41). Higher f_a

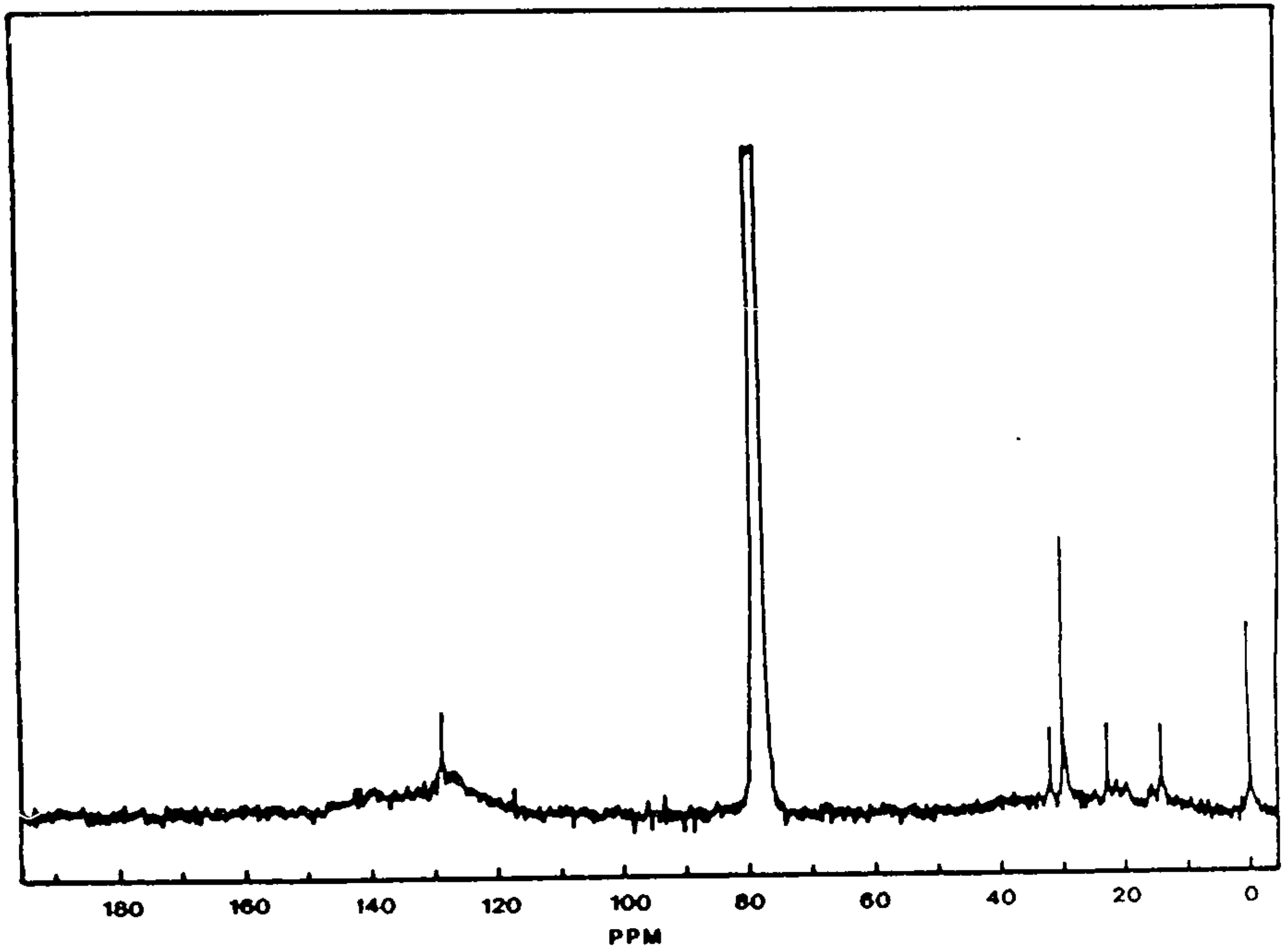


Figure 5.16 ^{13}C nmr Spectrum of Pyrolysis Extract of -1.16+0.833mm Rotem Oil Shale (R-42)

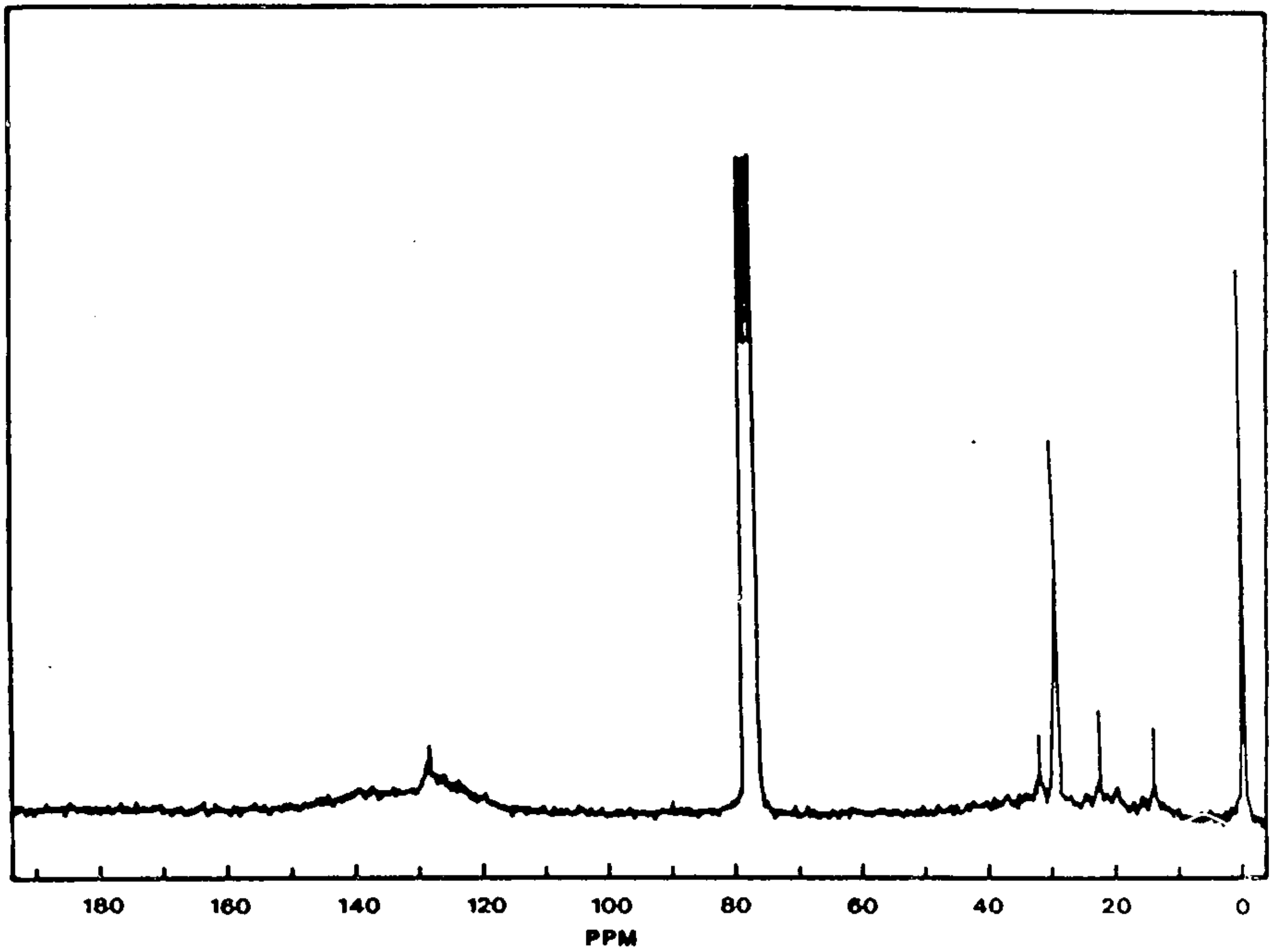


Figure 5.17 ^{13}C nmr Spectrum of SCW Extract of
-1.16+).833mm Rotem Oil Shale (R-32)

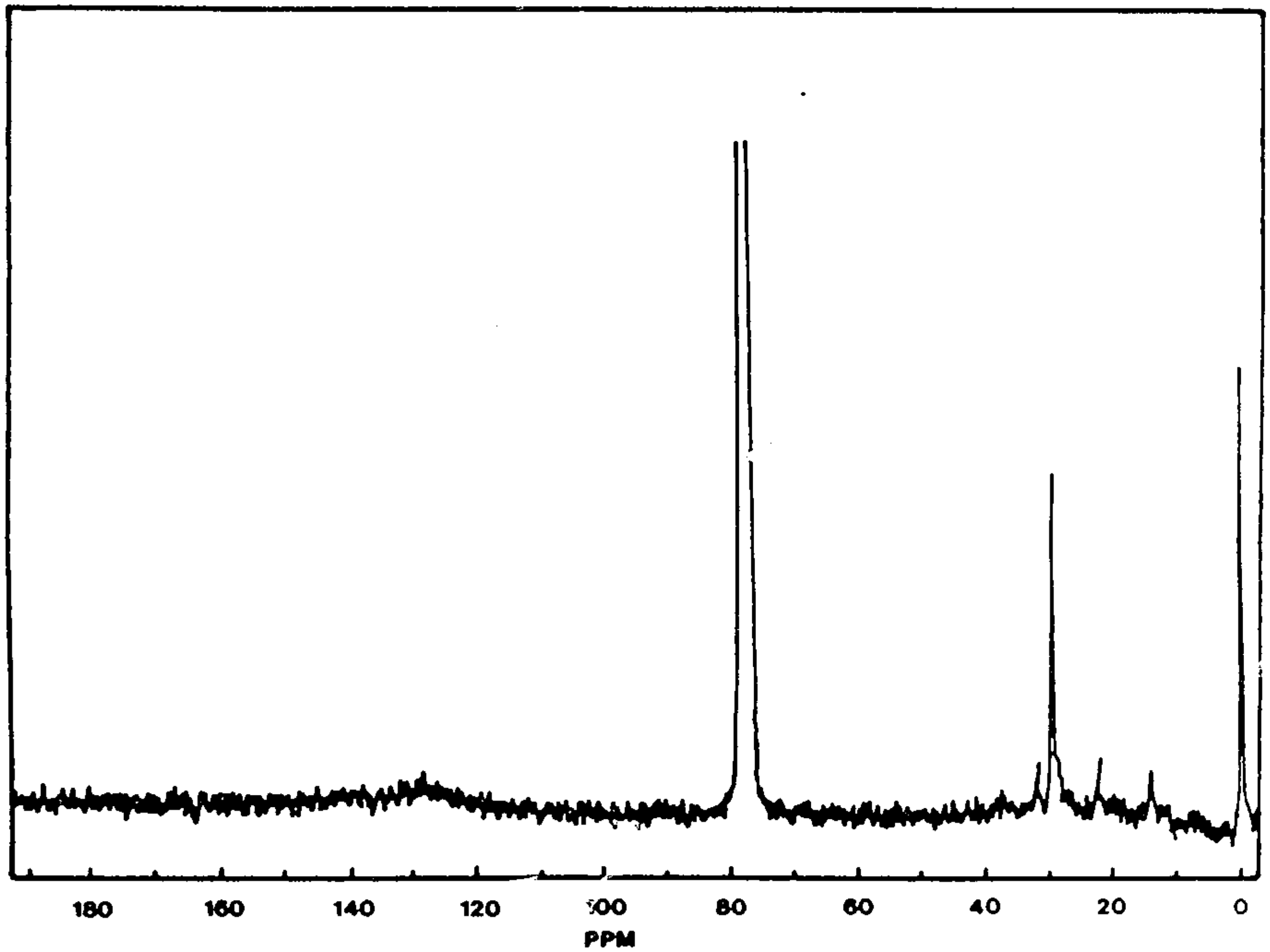


Figure 5.18 ^{13}C nmr Spectrum of SCW/CO Extract of -1.16+0.833mm Rotem Oil Shale (R-40)

value for pyrolysis extract is due to the cleavage of aliphatic groups during pyrolysis and the loss of light hydrocarbon was more severe during pyrolysis than SCW and SCW/CO extraction. The relatively low f_a values of extracts generated SCW/CO are in agreement with their H/C ratios discussed above: the inverse relationship between H/C and f_a supports the view that extracts generated with SCW/CO have relatively low concentrations of carbon in aromatic rings.

Also significant is that such extracts show f_a decreasing with increasing extraction time.

5.4.4.2 ^{1}H nmr Spectra

The ^{1}H nmr spectra provide some information about the molecular environment of hydrogen atoms in toluene-soluble matter generated under various experimental conditions. This is illustrated in Figures 5.19-5.21 which show ^{1}H nmr spectra of toluene-soluble extracts generated by pyrolysis, SCW and SCW/CO extraction of -1.16+0.833mm Rotem oil shale at 400 °C and 14 MPa.

Each spectrum was divided into assigned bands (see Table 5.5a), with the intensity of each band being proportional to the relative amount of hydrogen in that bonding environment.

Additional structural parameters were estimated by means of the Brown-Ladner equations$^{(25)}$. The hydrogen aromaticity (f^H_a), the degree of aromatic substitution (δ, i.e. the fraction of available aromatic edge sites occupied by substituents), and the atomic hydrogen to carbon ratio of the hypothetical unsubstituted aromatic material (H_{aru}/C_{ar}) were estimated from:

$$f^H_a = (C/H - H^*_\alpha/x - H^*_o/y)/(C/H) \qquad (5.18)$$

$$\delta = (H_\alpha^*/x + O/H)/(H_\alpha^*/x + O/H + H_{ar}^*) \qquad (5.19)$$

$$H_{aru}/C_{ar} = (H_\alpha^*/x + H_{ar} + O/H)/(C/H - H_\alpha^*/x - H_o^*/y) \qquad (5.20)$$

where C/H and O/H are atomic ratios obtained from elemental analyses,

H_α^* = fraction of total hydrogen on α-carbon (H_α/H);

H_o^* = fraction of total hydrogen on non-aromatic carbon (H_o/H);

H_{ar}^* = the fraction of total hydrogen on aromatic carbon (H_{ar}/H);

and

$y = x = 2.5$.

As presented in Table 5.19, f_a^H for extracts obtained by pyrolysis was higher than in extracts obtained by SCW and SCW/CO, and extracts generated by SCW/CO extraction consistently gave the lowest f_a^H, δ and H_{aru}/C_{ar} values. The

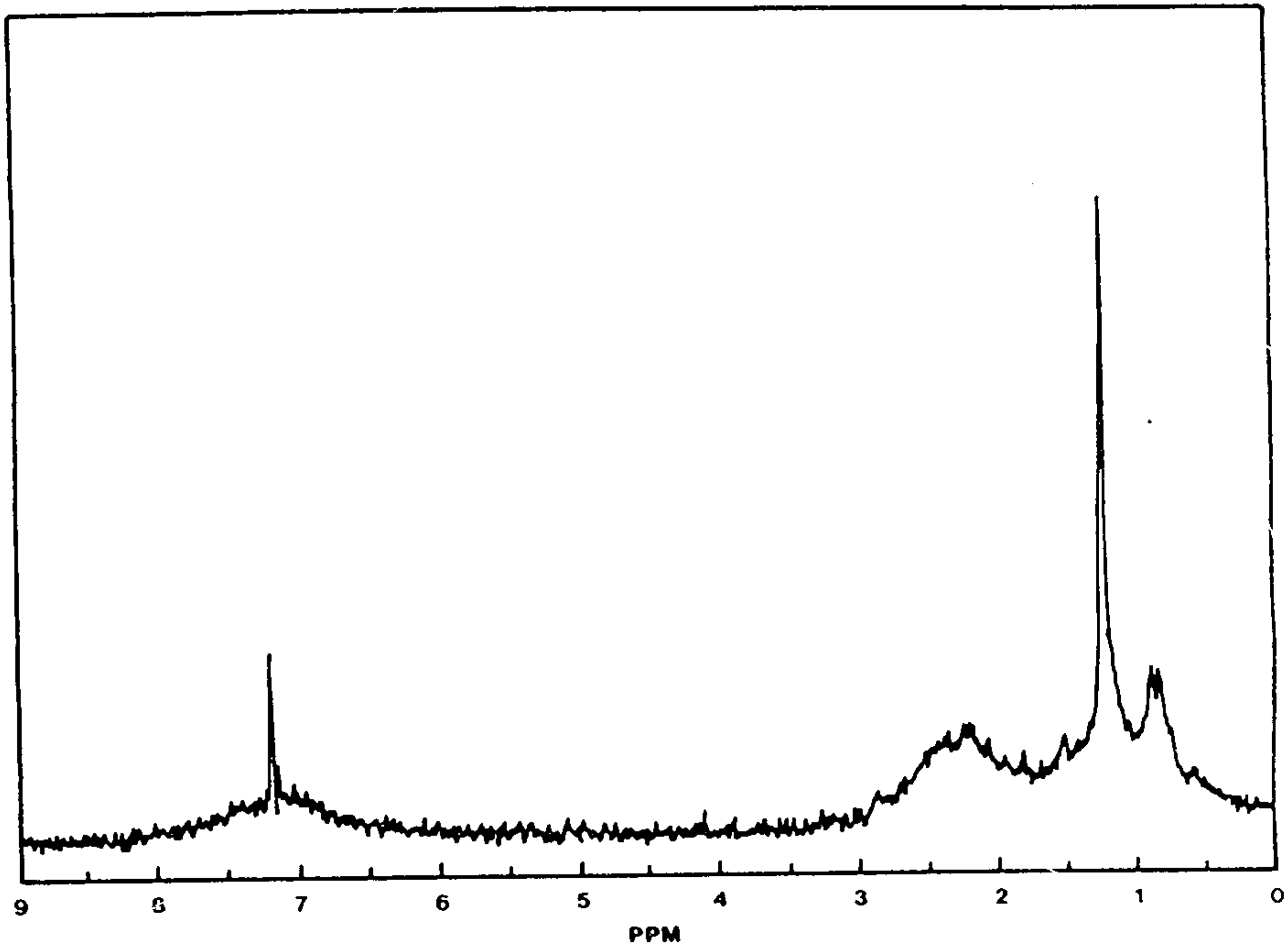


Figure 5.19 ^{1}H nmr Spectrum of Pyrolysis Extract of Rotem Oil Shale

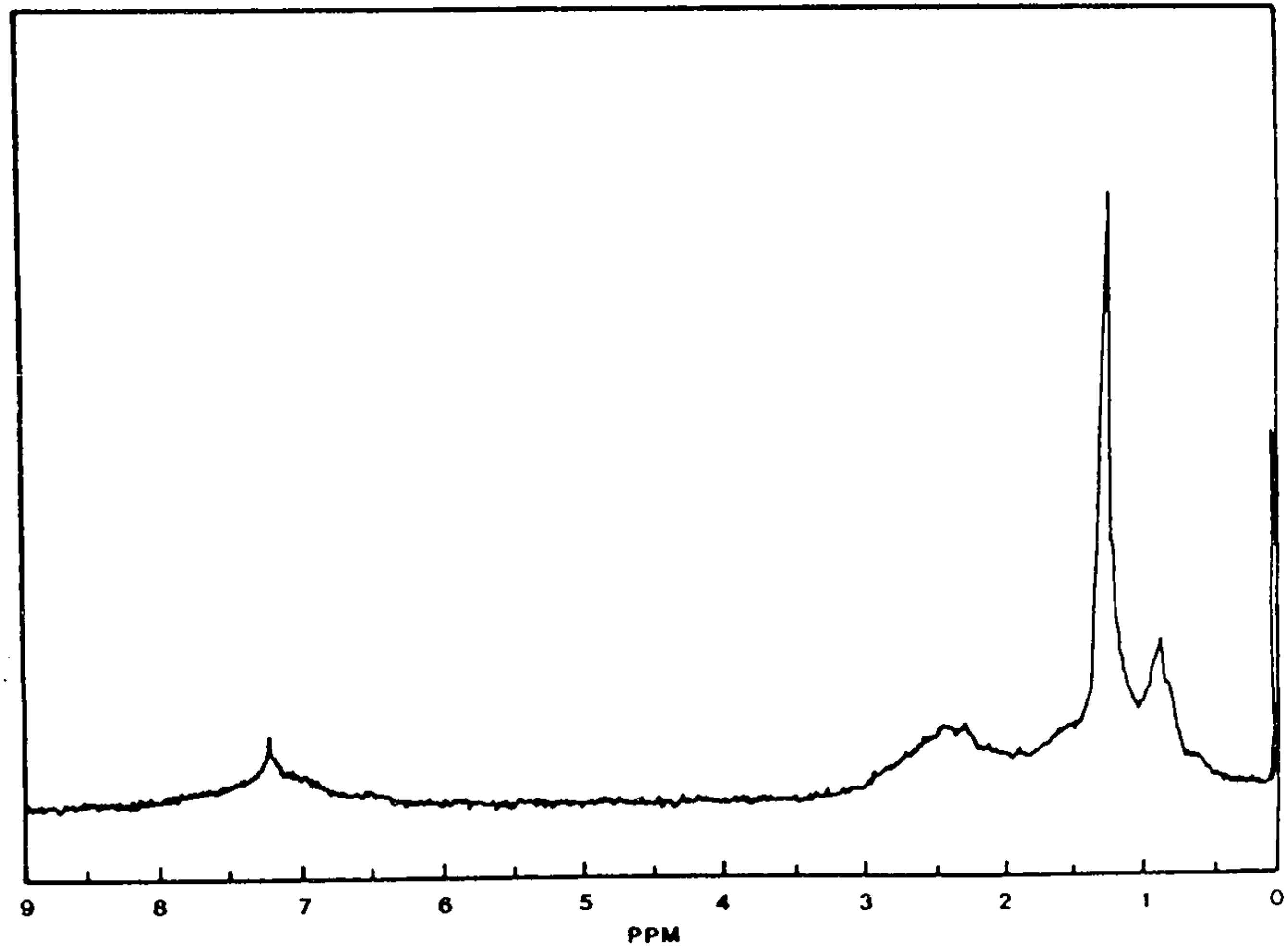


Figure 5.20 ^{1}H nmr Spectrum of SCW Extract of Rotem Oil Shale

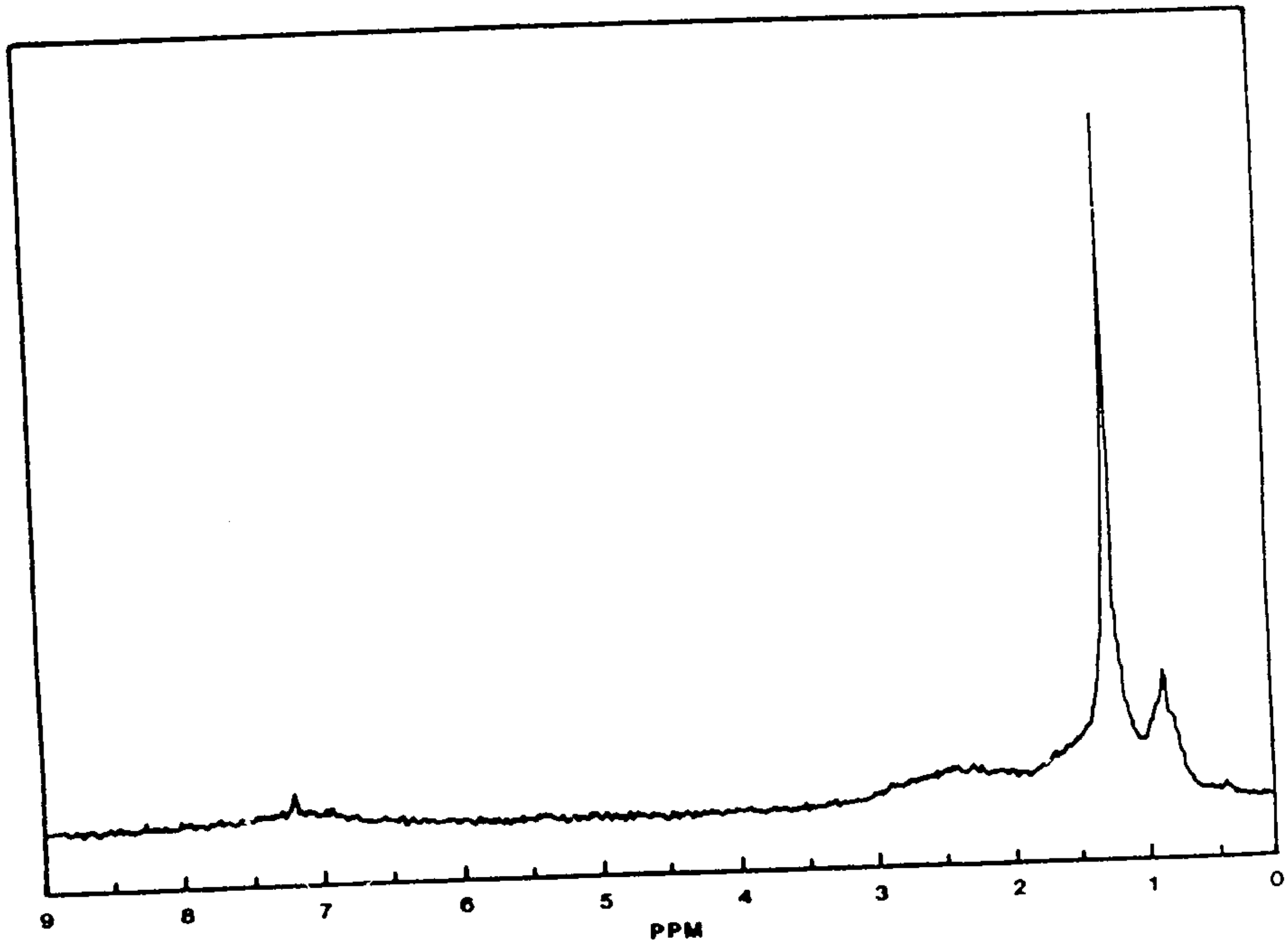
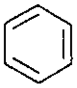
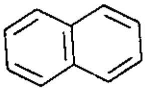
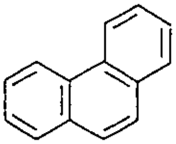
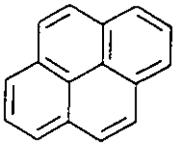
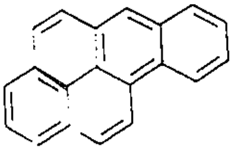


Figure 5.21 ^{1}H nmr Spectrum of SCW/CO Extract of Rotem Oil Shale

value of H_{aru}/C_{ar}, indicates the extent of condensation of aromatic rings, Table 5.19a shows the ratio for different aromatic hydrocarbons$^{(15)}$. The SCW/CO extract has an average of 5 condensed rings, i.e. benzopyrene type structure, while SCW and pyrolysis extracts have average of 4 and 3 condensed rings respectively. These average structures do not exclude compounds or groups which differ from the average, but are indication of the major structural features. H_{ar}/H_{α} of extracts obtained by pyrolysis were also higher than for SCW extracts. The relatively high H_{ar}/H_{α} of extracts generated by pyrolysis suggests a lower degree of aromatic substitution, in agreement with δ for pyrolytically generated toluene-soluble matter. The relative intensities of $C_{29.7}$ and $C_{14.1}$ can be used to estimate the length of alkyl chains. From the data shown in Table 5.19, extract generated by SCW/CO shows the longest alkyl chains, that is $C_{29.7}/C_{14.1}$ of ≈6, while the extracts generated by pyrolysis and SCWE have chain lengths of ≈3. The chain length of SCW/CO extract indicates that on average it is less aromatic, this has been shown by the other aromaticity determining parameters.

Since a high H/C ratio is advantageous for subsequent upgrading (i.e. hydrogenation) of shale oil, SCW extracts generated in the presence of CO are clearly of better quality than extracts from pyrolysis and simple SCW extraction.

Table 5.19a Expression of Size and Ring Condensation for Some Aromatic Rings

H_{aru}/C_{ar}	Compound	Structure
1	Benzene	
0.8	Naphthalene	
0.71	Phenanthrene/ Anthracene	
0.63	Pyrene	
0.55	Benzopyrene	

5.4.5 Thermogravimetric Analysis of Extracts

From Figures 5.6-5.13 semi-quantitative evaluations have been made for selected extracts (see Tables 5.20 and 5.21). The results show that these extracts have low ash contents (0.8 - 1.3%) and that devolatilization generally occurs between 225 and 258 °C. An exception was R-27 which showed a much higher devolatilization peak temperature (325 °C). Above 400 °C, some extracts showed a second peak, associated with additional weight loss; this suggests secondary reactions, such as thermocracking of heavy fractions produced during extraction. Both extracts obtained with CO showed such second peaks (Table 5.20) and thereby allow the inference that the additional H_2 provided in H_2O/CO systems solubilized more high molecular weight kerogen but did not suffice to enhance its subsequent hydrogenation to lower molecular weight fractions.

Extracts obtained by short-duration (20 min) extraction appear to have lower peak temperature than those generated over longer periods - an observation that implies that little high molecular weight material is initially extracted. Pyrolytic extract in the absence of Fe_2O_3 possess a low apparent activation energy (8.9kJ mol^{-1}) and relatively low peak temperature, but pyrolytic extract generated in the presence of Fe_2O_3 have much higher activation energy ($\approx$22kJ mol^{-1}). The extracts generated by SCWE in the absence of CO

Table 5.20 TGA of Toluene-soluble Matters from Extraction of Rotem Oil Shale size = -0.833+0.6mm, T= 400°C

Run No	R-20	R-33	R-22	R-27
Press, MPa	14	14	14	21
Extraction time, Min	60	20	40	60
Extractor fluid	H_2O	H_2O	H_2O/CO	H_2O/CO
Peak temp. °C	230	224.6	257.5 447.5	325 450
% V.M.	83.9	91.0	87.7	89.2
% F.C	12.3	5.3	9.0	7.1
% Ash	0.8	0.7	1.3	1.2
% H_2O	3.0	3.0	2.0	2.5
E_a, $KJmol^{-1}$	nd	nd	17.1	21.4

Table 5.21 TGA of Toluene-soluble Matters from Extraction of Rotem Oil Shale; size = -1.16+0.833mm, T= 400°C, t= 60 min

Run No	**R-32**	**R-36**	**R-35**	**R-37**
Press, MPa	14	17.5	17.5	17.5
Process	SCWE	Pyrolysis	SCWE	Pyrolysis
Catalyst	none	none	none	Fe_2O_3
Peak temp. °C	232.5 435	217.8	239.3 446.5	230
% V.M.	86.8	89.5	86.2	89.9
% F.C.	10.2	5.7	10.5	7.9
% Ash	1.0	0.8	1.2	1.2
% H_2O	2.0	4.0	2.1	1.0
E_a, $KJmol^{-1}$	nd	8.9	13.8	22.1

nd = not determined

have relatively lower activation energy than that in the presence of CO (13 and 17.1-21.4kJ mol^{-1}). The high E_a values shown by SCW/CO extracts might be due to cracking of the asphaltenes (see Table 5.9b). Generally, E_a higher than 21kJ mol^{-1} (5kcal mol^{-1}) indicates reaction limiting while low E_a is diffusion control(17,26). This observation implies that under the experimental conditions used in this study the processes are diffusion controlled. This is not unexpected since agitation was not employed during the extractions.

5.4.6 Effect of Process Conditions on Yield and Volatility of Distillable Fractions

The quality of crude oil (synthetic or natural) is usually determined by the quantity and volatility (boiling range) of the distillable fraction of the crude. The higher the quantity of distillables and the lower their boiling range the better the quality of the crude. Conventional ASTM distillation methods are generally used to characterize quality of crude.

However, in view of the limited quantity of extract generated in each case during this study, TGA data for selected extracts were used to assess quality. The quantity of distillables was taken as the area under the symmetrical part of the TGA curves (Fig. 5.7-5.14). The initial and final temperatures of the distillables correspond respectively, to the temperatures at the onset and end of the symmetrical part of the curves. In a few cases more than one symmetry occurred, and here the quantities of distillables were determined for each symmetrical area and then added to obtain the total estimated distillables. It is worth noting that the second peak may contain gases as a result of thermocracking, thereby introducing error in estimating its distillables.

Table 5.22 shows the quantity and the boiling range of extracts generated during various extraction conditions.

There was no significant difference in the quantity of total distillables of extracts generated under the various extraction processes (pyrolysis, SCWE, SCWE/CO and SCWE with Fe_2O_3), except for the catalyzed SCWE (R-37) which generated slightly less total distillables (see Table 5.22). However, this is compensated by a lower and narrower boiling range.

Another important observation allowed by the data of Table 5.22 and Figures 5.6-5.13 is that in some cases distillates were evolved in more than one temperature interval. This suggests a relatively less homogeneous product, possibly due to secondary reaction of the primary extract material. Examination of data in Table 5.22 shows that extracts with more than one region of distillables

Table 5.22 Boiling Range and Quantity of Distillables

Run No	T_1	T_2	T_3	Q_1	Q_2	Q_T
R-20	70	400	---	81	___	81
R-33	50	425	___	86	---	86
R-22	80	400	500	70	14	84
R-27	75	400	500	64.5	23	87.5
R-32	60	260	450	48	36	84
R-36	70	430	___	85	___	85
R-35	70	250	450	35	49	84
R-37	30	250	400	45	36	81

T_1, T_2 and T_3 are the initial and final temperatures (°C)

Q_1, Q_2 and Q_T are the distillables under the symmetrical areas (1 & 2) and total (%)

The experimental conditions defined in the previous Tables evolution (R-22, R-27, R-32, R-35 and R-37) generally produced distillables with relatively higher final temperature and a wider boiling range than extracts with only one region (R-20, R-33 and R-36).

The view that the presence of more than one region indicates secondary reactions in the extract is supported by a comparison of the results of R-20 and R-32 (see Tables 5.20-5.22), which refer to extracts generated from -0.833+0.6mm and -1.16+0.833mm oil shale samples respectively. It was mentioned earlier that extracts generated from the larger particle size have a greater tendency to undergo secondary reactions than those from smaller size fractions. As well, evolution of distillables from extracts generated by smaller particle size occurred only over one region, with distillable product of lower and narrower boiling range than the distillables produced by extracts from the larger particle size.

5.4.7 Molecular Weights

Table 5.23 shows the average molecular weights of Rotem oil shale extracts obtained by pyrolysis and by SCWE with and without CO. The results indicate that soluble matter furnished by pyrolysis has the lowest molecular weight, while those generated by SCW/CO have the highest. This trend agrees

Table 5.23 Average Molecular Composition of Extracts from Pyrolysis, SCW and SCW/CO Extractions

Run No[1]	R-42	R-32	R-40
C	78.8	76.8	82.1
H	8.7	8.6	9.3
N	1.1	1.1	1.5
S	9.4	9.9	3.9
O[2]	2.1	3.5	3.2
MW	251	315	377
Avg. mol. comp.	$C_{16.5}H_{21.8}N_{0.20}S_{0.7}O_{0.4}$	$C_{20.2}H_{27.1}N_{0.2}S_{0.9}O_{0.7}$	$C_{25.8}H_{35.2}N_{0.4}S_{0.5}O_{0.8}$

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[1] extraction conditions defined in the previous Tables
[2] by difference

with results from class composition and TG analyses. In general, pyrolysis generated more light fractions but low conversion. On the other hand, extracts generated with SCW/CO gave high yields of extract with heavier hydrocarbons.

5.5 Conclusions

The quantity and quality of extract obtained during SCWE of oil shale depend on oil shale type and extraction process and process conditions. SCWE of the relatively more aliphatic Rotem shale produced more extracts than SCWE of MFO shale.

More toluene-soluble materials were obtained in the presence of CO than SCWE alone, which, in turn, generated more extract than pyrolysis. However, the yield of extract obtained by SCW/CO extraction was at the expense of the volatility of the extract as pyrolytic extract is generally of lower molecular weight as a result of thermal devolatilization.

Extraction by pyrolysis involves extensive thermocracking, while hydrogenation through ionic reaction predominate during SCW and SCW/CO extractions.

The presence of mineral matter enhances extraction of hydrocarbons from oil shale.

Extract yields increase with increase in pressure from 14 to 17.5 MPa, but extraction at pressures above 14 MPa and 400°C may not generate high yields of oily material.

5.6 References

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CHAPTER 6

GENERAL DISCUSSION AND CONCLUSIONS

6.1 General Discussion

The development of any process for extracting (potentially liquid) hydrocarbon material from oil shales depends on its economic, engineering, and environmental merits and demerits. While process conditions (pressure, temperature and extraction time) determine engineering requirements, the environmental advantages and/or disadvantages of the process can be measured by the aromaticity and the concentrations of nitrogen and sulphur in the extract.

As mentioned earlier, the presence of sulphur and nitrogen in the extract can create environmental and process problems (emission of SO_x and NO_x, catalyst poisoning, corrosion and embrittlement of equipment). Aromatic fuels are relatively more hazardous during handling and utilization than relatively less aromatic ones.

The quantity of relatively high quality extract generated in unit extraction time is a useful economic index. The higher the quantity of stable extract produced within a relatively short time and under relatively moderate conditions of temperature and pressure, the better the process. However, it is difficult to obtain a set of operating conditions that will provide advantages in all three aspects, i.e. economic, environmental and engineering. Hence, an acceptable compromise between process conditions and extract quantity and quality has to be reached.

While the specific effects of individual process conditions on the quantity and quality of extracts generated during pyrolysis (retorting), and "supercritical" water extraction (SCWE) of oil shale have been discussed in chapter 5, the appropriate optimum conditions which provide a suitable compromise between the severity of process conditions and extract yield and quality is addressed in this chapter.

6.1.1 Comparison of Pyrolysis with SCWE and SCW/CO Extraction

The effect of various conditions (pressure, temperature and extraction time) on both the quantity and quality of extract generated from oil shale depends on the type of process involved. Table 6.1 summarizes the general trends that accompany increasingly severe process parameters in each process.

Table 6.1 Influence of Process on Measured Parameters

Measured Parameters	EXTRACTION PROCESSES		
	Pyrolysis	SCWE	SCWE/CO
Extract yield	L	M	H
H/C ratio	L	M	H
S concentration	M	H	L
N concentration	L	M	H
Distillables		Approximately equal	
Boiling range of distillables	L	M	H
Oils	H	M	L
Polar compounds	L	M	H
Asphaltenes	L	M	H
Aromaticity (f_a)	H	M	L
H_{ar}/H_{α}	H	M	L
C_c/C_{ar}	H	M	L
MW	L	M	H

Trends in each process are designated as
H high; M medium; L low

That the quantity and quality of extracts appear to depend on the extraction process is almost certainly due to differences in extraction mechanisms.

Pyrolysis is mainly a thermal cracking reaction which can involve C-C bond scission, dehydrogenation, isomerization and polymerization. SCWE, on the other hand, is a form of liquefaction, with water acting as the "solvent". The mechanisms believed to be involved in coal liquefaction(1) can equally well be used to explain SCWE of oil shale and would mainly characterize a two-step process - dissolution and hydrogenation. However, mechanism by which SCW extracts oil shale can be better explained by considering the properties of water as a function of temperature and pressure. At about 400 °C and between 20 and 30 MPa both the density and dielectric constant of water will decrease(2). Variation of dielectric constant with temperature is presented in Table 6.2. Under the experimental conditions used in this study (400-450 °C and 14-21MPa), dielectric constant of water will lie between 1 and 10 which is similar to those of organic solvents. It is therefore reasonable to explain that SCWE of oil shale proceeded through ionic reaction thereby generating H_2 that enhances extract yield. A similar reaction has been suggested by Penninger(3) according to the following reaction:

Table 6.2 Variation of Dielectric Constant with Temperature[2]

Temperature °C	Dielectric Constant	Density(g/cm^{-3})
25	80	--
130	50	0.9
260	25	0.8
374	5	0.315

$$H_2O \text{ ------> } H^+ + OH^- \qquad (6.1)$$

$$H^+ + H^+ + 2e^- \text{ -----> } H_2 \qquad (6.2)$$

By Equation (6.2), SCWE is resembles solvent extraction.

Similarly, SWC/CO extraction of oil shale can be explained by ionic reaction with the formation of formic acid as intermediate according to the following reactions at 25°C and 400°C(4) :

Reaction	$LogK_{25}$	$LogK_{400}$
H_2CO_2 ===== $H_2O + CO$	0.34	5.30
H_2CO_2 ===== $H^+ + HCO_2^-$	-3.72	-
H_2CO_2 ===== $H_2 + CO_2$	3.83	6.30

Since the reaction between CO and H_2O is favourable at 400 °C, production of H_2 and CO_2 by the water gas shift reaction (R1.1) would be expected. It is reasonable that under the temperature condition in this study, extraction with SCW/CO provides an external source of H_2 which further increases extract yields. Since the shift reaction is reversible, consumption of H_2 will drive the reaction forward; however, if there is no continuous supply of CO, as in this study, most of the available H_2 will be used up within a short extraction time. This provide further explanation as to why conversion of oil shale by SCW/CO with time did not change much (see Fig. 5.15).

The results of this study (see 5.3) harmonize with the implications of this scheme by showing pyrolysis yield < SCWE yield < SCW/CO yield. However, while pyrolysis produced the lowest yield, it generates material with the lowest boiling range and molecular weight, and with the lowest concentration of asphaltenes and polar compounds (Table 6.1). The relatively high molecular weight and E_a shown by SCW/CO extracts are reflected in high asphaltene fractions which are known to be of high molecular weight(5).

The study also shows (see Table 5.18) 15% more extract being produced by SCWE than by pyrolysis under the same conditions of pressure, temperature and time (14 MPa, 400 °C, and 60 minutes respectively). Extracts generated by SCWE were less aromatic than those produced by pyrolysis. As mentioned earlier the relatively high aromaticity of pyrolytic extract is due to cleavage of alkyl as a result of thermocracking.

There was no apparent effect of increasing pressure on the yield of toluene-soluble (conversion) generated during pyrolysis, but conversion during SCWE was pressure-dependent and increased pressure were raised from 14 MPa to 17.5 MPa (see Tables 5.6 and 5.17). However, the aromaticity of extracts generated by pyrolysis and SCWE were reduced by increases in pressure.

Supercritical water extraction achieved more break-out of nitrogen and sulphur from extract precursor materials than pyrolysis (Table 5.17), and this accords well with the results obtained with model compounds detailed (see chapter 4). For example, no nitrogen could be detected during pyrolysis of quinoline and isoquinoline, but both compounds produced NH_3 during SCWE. Similarly, SCWE of thianthrene generated dibenzothiophene but its pyrolysis did not result in any detectable decomposition. Even in the presence of a catalyst, pyrolysis of benzothiophene failed to show any g.c.-m.s. detectable sulphur-containing products.

The S and N contents of toluene-solubles suggest that an increase in pressure enhances the breaking of C-N and C-S bonds in the organic matter with consequent formation of NH_3 and H_2S.

In general, SCW/CO extraction appears to be the best choice, although the additional cost of CO needs to be borne in mind.

6.1.2 Influence of SCWE Process Conditions

The specific effects of varying process conditions (P, T and t) on the yield and quality of extracts generated by the different processes (pyrolysis and SCWE with and without CO) have been discussed in detail in chapter 5. This section therefore addresses only general trends.

Table 6.3 summarizes the trends of measured functions when operating parameters are increased. In general, a pressure increase lowers extract yields as well as the S and N contents of extracts; and after an initial increase the H/C ratio also falls. The degree of substitution (H_{ar}/H_{α}) appears to decrease slightly, but f_a tends to increase.

Increasing extraction temperatures beyond ≈400 °C cause the yield, H/C ratio, H_{ar}/H_{α} and N content to decrease, but increase f_a and S contents. At 400 °C, both pyrolysis and hydrolysis by SCW are taking place, but increases above 400 °C, (e.g., 400 °C - 450 °C) enable the already extracted hydrocarbons to undergo further pyrolysis and coking with consequent yield reduction.

This study also allows the conclusion that extraction need not be extended beyond 20 minutes, since conversion of organic matter in the oil shale proceeds quite quickly.

Table 6.3 Influence of Increasingly Severe Operating Parameters on Measured Parameters (+ increasing; - decreasing; +/- increasing before decreasing; -/+ decreasing before increasing)

Operating Parameters	Measured Parameters					
	Yield	H/C	[S]	[N]	H_{ar}/H_{α}	f_a
Pressure	-	+/-	-	-	-	-/+
Temperature	-	-	+	-	+/-	+
Extraction time	+	+	+	-	+/-	+

Incremental conversion after 40 and 60 minutes may not justify the additional energy required to generate this amount.

In summary, SCWE at >400 °C and >14 MPa, and over extraction periods longer than 20 minutes may offer only little advantage.

6.2 Summary and Conclusions

"Supercritical" water extraction of two oil shale samples under varying conditions of pressure, temperature and extraction time has been studied. Useful data on the effects of various process conditions, and hence the ability of SCWE to convert kerogen to toluene-solubles, were obtained and compared with corresponding data for pyrolysis and SCWE in the presence of CO. The influence of process variations and process conditions on the chemical properties of extracts was also evaluated.

In addition, some nitrogen- and sulphur-containing model compounds were subjected to pyrolysis and hydrolysis (in SCW) conditions similar to those used for oil shale SCWE in order to gain some understanding of the mechanisms by which desulphurization and denitrogenation occur during extraction of N- and S-bearing heavy hydrocarbon material or oil shales.

From the experimental results of this research, the following conclusions are reached:

SCWE in the presence of CO will convert more organic matter in the oil shale to toluene-solubles than SCWE alone; and the latter, in turn will generate more extract than pyrolysis. However, pyrolysis extracts had the lowest boiling range and molecular weight, presumably due to thermal cracking of the precursor organic matter.

Relatively more nitrogen and sulphur was 'liberated' from the precursor organic matter during SCW and SCW/CO extractions. This was due to the ability of SCW to desulphurize and denitrogenate organic matters.

In general, extraction at pressures above 14 MPa offered no appreciable advantage. The specific effect of increasing extraction pressure was found to depend on the process and the measured parameter. While the quantity of extract generated during pyrolysis was not pressure-dependent, conversion of organic matter in the shale to toluene-solubles during SCWE increased when the pressure was raised from 14 MPa to 17.5 MPa. Extracts generated by both pyrolysis and SCWE at the higher pressures were less aromatic than when produced at the lower pressure.

The concentrations of N and S in toluene-soluble matter suggest that pressure increases enhanced rupture of C-N and C-S bonds in the precursor organic matter and in the extract.

Supercritical water extraction at temperatures above 400 °C proved to be disadvantageous, as both quantity and quality of toluene-soluble matter decreased above this temperature.

There is no economic and process advantage in extending the extraction beyond 20 minutes, as neither conversion nor the quality of extract generated improved beyond that period. Additional benefits of short extraction periods arise from the possibility of burning the residual shale to generate energy for subsequent shale oil processing.

Higher yields of better quality extract were obtained with smaller feed particle sizes than with coarser samples.

Supercritical water extraction depends on oil shale type. Despite the higher organic matter content and H/C ratio of MFO, its conversion to toluene-solubles is lower than that of Rotem oil shale which contained higher concentrations of aliphatic moieties. This is due to the fact that aliphatic hydrocarbons are relatively more volatile and more easily removed. A similar trend has been reported(6,7) for two U.S.A.

oil shales - Green River shale, which contained more aliphatics, generated higher liquid yields than its counterpart, Devonian oil shale.

^{1}H nmr data also indicated that extracts generated from MFO extraction are mainly aliphatic, and this may further support the view that aromatic moieties of the kerogen are difficult to extract.

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