

Chapter 5

Oil Shale Processing, Chemistry and Technology

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Glossary

Bitumen	Orga Processing, Chemistry and Technology solvent-soluble portion of oil shale organic matter.
Direct retorting	Retorting in which the process heat requirement is accomplished by combustion of a portion of the oil shale within the retort.
Ex situ retorting	Oil shale retorting performed aboveground (requiring mining of the oil shale).
Indirect retorting	Retorting in which the process heat requirement is provided by heated gaseous or solid heat carriers produced outside the retort, and then brought into contact with the retort contents.
In situ retorting	Heating of oil shale underground in order to release shale oil (also called underground retorting). Confinement of the shale is provided by the surrounding earth, in this case.
Kerogen	Macromolecular and organic solvent-insoluble organic matter of oil shale, but more broadly applied to these sorts of organic components of sedimentary rocks.

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Oil shale	Oil shale has a wide range of definitions. A general definition that encompasses most is that it consists of a sedimentary rock containing various amounts of solid organic material bound dispersedly in a mineral matrix and yielding principally a shale oil upon pyrolysis.
Pyrolysis	A thermochemical decomposition process of organic matter, effected by heating the material in the absence of oxygen.
Retort gas	Noncondensable combustible gas, a mixture of gases from an oil shale retort that remains after particulate matter and condensed liquids have been removed.
Retort water	Water collected during oil shale retorting from offgas stream together with oil.
Retorting	In shale oil recovery technologies, retorting is a pyrolytic process designed to produce oil. Generally, this process is performed by placing oil shale in a sealed vessel heated in order to promote pyrolysis; this reactor is called a retort.
Retorting residue or spent shale	Solid waste material remaining after retorting. This material contains most of the mineral matter of the original shale (possibly partially decomposed) and a carbon-rich (char) residue from the organic fraction (which may sometimes be referred to as a semicoke).
Shale oil	Room temperature liquid phase organic material, oil product, recoverable from the thermal decomposition of kerogen or separated from the offgas stream of an oil shale retort.
Thermobitumen	A bitumen not contained in the original oil shale, but produced by the action of heat on the shale; a thermal degradation (pyrolysis) product of kerogen.

Definition of the Subject

Oil shale is a complex mixture of organic and inorganic phases, in which the organic phase is normally that of the greater economic and practical value. In nature there exists a wide range of materials that include these same components, and not all of these materials are candidates for actual use; in some instances, the organic content is simply too low to make processing of the oil shale of any economic interest. Thus, one of the first things that needs to be answered in asking what oil shales it makes sense to study is the question of what sorts of oil shale should be considered as the subject of practical use. This summary begins with a consideration of this fundamental question, and is guided by what has historically been accepted as definitions of oil shales of practical interest. It is recognized that these definitions come from different locations and time periods, with differing demands for the energy or raw materials that the oil shale could provide. This, in turn, means that these definitions can change with time and place, but here they offer a framework for the discussion that follows.

Because in oil shale the organic and inorganic phases form such an intimate mixture, it is critical to consider how this might influence the practical conversion processes to which the oil shale is ultimately subjected. At the same time, it is essential to recognize how the experimental research used to develop these practical processes can be influenced by decisions on how to prepare the oil shale for testing. Isolation of the kerogen material from the oil shale offers advantages in terms of simplifying or enabling certain types of organic fraction analysis, or the evaluation of proposed processing steps in the laboratory. In many instances, this might make good scientific sense, but in other cases, it is important to note that there might be inadvertent changes induced in the material, and in its potential conversion chemistry, by the separation. This summary will only provide a brief overview of some of the aspects of research performed on the different phases present in the oil shale, and offer only this general warning to be cautious regarding the possibility of artifacts induced by separations of the raw material.

The main focus of this entry is on the chemistry of oil shale conversion. Virtually all oil shale conversion processes begin with a thermal degradation of the organic macromolecular structure. The organic fraction of oil shale is largely unrecoverable in any useful form without such a thermal degradation, since the extractable bitumen content in unheated oil shale is normally but a few percent at most. The thermal degradation is critical whether the oil shale is processed to recover oil or burned directly to generate heat, and from that, electricity. In the case of combustion, the thermal degradation is what releases the small organic molecular fragments that can burn in the vapor phase. The less that remains in a solid semicoke phase after the initial heating in a boiler, the more quickly and smoothly the combustion of the shale can take place, and the more efficiently used will be the organic fraction for its heating value content. Most shale oil combustion processes do operate at very high degrees of burnout of the organic matter.

In the case of oil recovery from the oil shale, there is a much-studied set of conditions used to maximize the recovery of oil. There is a balance between the need to achieve sufficient breakdown of the macromolecular structure of the organic phase, which will permit fragments to escape as oil, and the further pyrolysis of the organic phase to release light gases and leave behind a hydrogen-depleted semicoke that has much lower value than oil (and that is embedded in the remaining mineral matrix, making it difficult to utilize). This entry summarizes several aspects of what is known regarding the chemistry of thermal conversion and its kinetics, and offers an overview of some practical technologies in which the thermal conversion of the material takes place.

Introduction

This entry focuses on the chemical nature of oil shale, and some key aspects of its conversion to oil. One of the first difficulties encountered in this field is deciding what starting materials qualify as “oil shale.” A brief review of various practical

definitions is first offered. Different practical definitions arise from the different applications of the material. Next, the chemical structure of the shale is considered, including both the inorganic and organic phases contained therein. In this section, there is also consideration of how the organic phase can be analyzed, including how it may be separated from the whole shale.

In section “[Definition of the Subject](#)”, the chemical processes that result in the practical conversion processes of oil shale are introduced in general terms. In this section it is noted that not all oil shale is necessarily used to produce an oil product. In some instances, the oil shale may be directly burned in devices similar to those used for combustion of coal. In Sect. 3, attention is turned toward retorting to produce oil products. Except for recent decades in Estonia, where direct firing of oil shale for producing electrical power and heat has been practiced, retorting for oil has been the main driver for worldwide interest in oil shale. This section reviews the parameters that influence the results of retorting, as well as providing an overview of some chemical aspects of the process. This review closes in Sect. 4 with a brief consideration of different classes of technology developed for carrying out the retorting process.

It is important to recognize that there is a much more voluminous literature on oil shale chemistry and conversion than has been discussed here. The authors maintain that the present selection does, however, provide a reasonably comprehensive overview of the topic, while emphasizing some of the newer contributions to the literature.

General Characteristics of Oil Shale

Oil Shale Classification

Oil shale can be defined as a sedimentary rock containing various amounts of solid organic material dispersedly bound in a mineral matrix. Oil shales from different deposits vary in their mineral contents and types, chemical composition of organic matter, geological period of deposition, depositional condition, etc. [22, 31]. Therefore, there are a number of definitions of oil shale based upon application, operational, or scientific point of view [55]. Similarly there are various oil shale classification schemes [32, 54, 55, 76]. Moreover, the term “oil shale” is itself somewhat misleading as the organic matter is not oil-like and the mineral matter is not always classifiable as shale [141].

Following are some selected definitions of oil shale, proposed by several authors in the connection with its energy production or other technological utilization:

1. Gavin [43] defined oil shale as a “compact laminated rock of sedimentary origin, yielding over 33% of ash and containing organic matter that yields oil when distilled, but not appreciably when extracted with ordinary solvents for petroleum.”

2. Ozerov and Polozov have described oil shale as “a hard foliated combustible rock formed by joint accumulation of pelagic plants and animals and mineral mass which had been transformed by the action of geographic conditions and chemical, biochemical and hydro-chemical processes” [90].
3. Schlatter has characterized oil shale as “a heterogeneous mixture of organic and mineral matter. It is a fine-grained, tight rock with essentially no permeability or porosity” [114].

It is important to note that in defining oil shale for energy-technological purposes, the following oil shale characteristics have been emphasized:

- A high mineral matter content, which may be about two to five times higher than the organic matter content (generally significantly higher in comparison to coals, which contain mineral matter, by definition, of less than 40%).
- The major portion of oil shale organic matter is insoluble in organic solvents (this in contrast to tar sands).
- The organic matter has hydrogen/carbon atomic ratios typically in the range 1.2–1.6 (which is significantly enriched in hydrogen compared with coals, but hydrogen deficient relative to crude oil).
- The capacity of oil shales to ignite and burn without separation of the organic matter from the mineral matter.
- They undergo thermal decomposition that results in production of a significant amount of liquid organic product or shale oil (higher grade oil shales can yield 100 L or more per ton of dry oil shale).
- They have a moisture content of less than 10–13%.
- They exhibit a low permeability of the rock to gases, vapors, and oils.

The organic matter (often termed kerogen; see below) content of oil shale varies widely, ranging typically from 10% to 40%. As the organic matter of oil shale is the source of energy and/or synthetic fuels value, there have been several attempts to classify oil shale by minimum and maximum organic matter content. The upper limit of organic matter content has been proposed to be about 50% [2, 76], or even higher [141]. The lower organic matter limit is usually defined in relation to the minimum energy requirement of oil shale as an industrial raw material. For example, a lower limit of 5% of organic matter has been proposed to define “commercial deposits.” This is because the organic matter content of an oil shale should be at least roughly about 2.5 wt% for the latter to provide the calorific requirements necessary to heat the rock to 500°C [38, 82].

Oil shale grade or energy potential is currently classified or characterized for commercial purposes on either a heating value or an average oil yield basis.

1. The heating value is used to evaluate the quality of an oil shale in the context of direct firing of oil shale in a power plant to produce heat, commonly used to raise steam for electricity generation. The heating value of typical oil shale kerogen is about 40 MJ/kg. For example, the heating value of an Estonian kukersite oil shale kerogen has been reported to be 37.3 MJ/kg [2], while for US Green River formation kerogen the value is around 41.1 MJ/kg and for eastern US Devonian kerogen around 37.5 MJ/kg [99]. This is, of course, not the same as the heating

value of the oil shale as would be determined for the whole rock, using a standard calorimeter (in which the dilution effect of the zero, or negative, heating value mineral matter is important). A combustion grade oil shale is defined as that having a minimum upper caloric value (for the whole oil shale rock) of 3.1 MJ/kg (dry basis) [38], though a heating value limit of not less than about 4.2–6.3 MJ/kg has been suggested for practical purposes [50, 141].

2. Average oil yield, or oil production potential, is determined using a “modified” Fischer assay method (the most widely used standardized technique, ASTM D-3904-80) or an equivalent analytical technique in which the shale is subjected to heating in order to liberate oil from the kerogen. The oil yield depends mostly on kerogen per mass of oil shale, but may also depend upon the fraction of kerogen convertible to oil (there are differences between different kerogens). On the basis of this assay, an “oil shale” is a shale that yields at least 42 L/t of dry shale (or 10 US gal/t, the basis used by the US Geological Survey) [99], though a limit as low as 25 L/t has also been suggested. Similarly, a crude dividing line between lower and higher grade shale has been defined at about 100 L of oil/t of shale (with those yielding below 90 L/t considered “low grade,” 90–150 L/t “moderate grade,” and those above 150 L/t “high grade” [2, 38]). Commercial grade oil shales range from about 100–200 L/t of shale. However, the Fischer assay does not actually indicate the maximum oil yield that can be actually produced by a given oil shale. Yields greater than Fischer assay have been obtained by hydrolysis, donor solvents, and rapid heating, especially for lower oil yield, non-softening oil shales [23, 106].

More than 600 oil shale deposits have been discovered around the world [2]. Oil shales are found in many countries around the world, with nearly 100 major deposits in 27 countries [128]. There exist many surveys/reviews on history of oil shale development throughout the world [98, 128, 129].

Oil shale resources are typically expressed in either of two different ways: (1) as tons of oil shale, and (2) as crude-shale-oil equivalents contained in the oil shale. Global deposits have been estimated to be about 411 metric gigatons or to range from 2.8 to 3.3 trillion barrels (4.5×10^{11} to 5.2×10^{11} m³) of recoverable oil equivalent [155].

When talking about known oil shale deposits, there is a need to distinguish between two terms – “resources” and “reserves.” Resources typically refer to estimates of all deposits of oil shales, while reserves refer only to those from which oil extraction can be economically profitable with the use of existing technologies. It should be noted that these technologies are constantly developing, and because of that, estimates of reserves will not necessarily remain constant over time, irrespective of use or discovery of new resources.

Oil Shale Composition

Oil shale is composed of mineral and organic matter whose proportions vary with the grade of oil shale.

Table 5.1 Mineral matter composition in some oil shales presented as oxides in ash, wt%

Compound	Green River [USA] [99]	Kukersite [Estonia] [88]	El-lajjun [Jordan] [88]	Dictyonema [Estonia] [88]
SiO ₂	40–60	28.25	28.86	63.72
Al ₂ O ₃	10–15	9.84	7.43	16.43
Fe ₂ O ₃	5–10	5.44	3.70	8.80
CaO	10–25	41.02	52.79	0.85
MgO	5–10	5.05	1.30	0.50
K ₂ O		3.60		8.72
Na ₂ O			0.3	
SO ₃		6.07	1.30	0.70
P ₂ O ₅			5.9	

Mineral Matter

Oil shale mineral matter contains several classes of minerals such as carbonates (calcite and dolomite), silicates, sulfides, and others. The inorganic composition of oil shales varies widely. The oil shale mineral composition can change from mostly calcareous to mostly aluminosilicate. For example, a typical mineral composition (in weight percent of the mineral matter alone) of carbonate-rich Kukersite oil shale from Estonia [100] is dolomite 3%, calcite 65%, quartz 8%, illite 15%, orthoclase 5%, chlorite 1%, and pyrite 3%. For the carbonate-rich Mahogany-zone US Green River formation oil shale [99], the composition is somewhat different: dolomite 32%, calcite 16%, quartz 15%, illite 19%, albite 10%, microcline 6%, pyrite 1%, and analcite 1%. In the case of siliceous Eastern US Devonian oil shale [99], a typical mineral composition is quartz 28%, illite 40%, feldspar 12%, pyrite 14%, and other minerals 6%. Quite often, mineral matter composition is represented by the chemical composition of oil shale ash, in which the mineral components have been converted to their oxides during combustion. This is illustrated in Table 5.1. It is, however, very important to keep in mind that the minerals are fundamentally altered by the combustion process, and the ash composition is only an approximate guide to what minerals existed in the raw oil shale.

In addition to the main minerals, oil shales contain a large number of trace elements (also referred to as minor elements). The content of the trace elements is typically in the parts per million (ppm) range. Trace element data for several deposits are available in the literature [92, 117, 141].

Organic Matter

Oil shale organic matter is composed of solvent-soluble and insoluble organic materials. The organic matter in oil shales is mostly in the form of solvent insoluble cross-linked macromolecular structure or kerogen. However, the term “kerogen” is

often used for whole organic matter of oil shale, including a small solvent-extractable fraction of the oil shale (termed bitumen).

Because organic matter is not easily extractable from the whole oil shale, there is an issue of how to quantify it. One simple way is to assume that it is the fraction that can be burned in air. Of course any loss of mineral components during burning (as by dehydration or decarbonylation reactions) can lead to an overestimate of the organic matter.

The organic matter content is thus often expressed on a dry shale basis as “conditional organic matter,” $\text{Org}_{\text{cond}}^{\text{d}} = 100 - A^{\text{d}} - (\text{CO}_2)_{\text{M}}^{\text{d}}$, in which A^{d} is ash yield upon combustion, $(\text{CO}_2)_{\text{M}}^{\text{d}}$ is carbonate-derived CO_2 released by the mineral matter at high temperatures, and a dry basis is indicated by the superscript d [141]. Basically, this formula embodies the concept that what is not left after combustion as ash, or released by carbonate decomposition, must have been organic matter. Both the ash and decomposable carbonate are available from separate analyses. In reality, the actual organic matter content can be somewhat different than that obtainable from the formula above since, for example, the formation of SO_4^{-2} ion from combustible sulfur can contribute to the mass of ash, even if the sulfur originated in the organic matter. Also, any other volatilization of mineral components, beyond decomposition of the carbonates, would also lead to errors in estimates of organic matter.

Therefore for specific oil shales more detailed equations have been developed. For example, for Kukersite oil shale, which has a true organic matter content somewhat lower than that typically calculated from the “conditional organic matter,” the following formula has been proposed: $\text{Org}^{\text{d}} = 100 - 1.028A^{\text{d}} - 0.964(\text{CO}_2)_{\text{M}}^{\text{d}} + 0.637(\text{SO}_4^{-2} - 0.07)$, where SO_4^{-2} is the sulfate content [104]. For Dictyonema shale, with a true organic matter content somewhat higher than the calculated “conditional organic matter,” the following equation has been recommended: $\text{Org}^{\text{d}} = 100 - A^{\text{d}} + 0.125\text{FeO} - (\text{H}_2\text{O})_{\text{M}} - 0.625\text{S}_{\text{pyr}} - (\text{CO}_2)_{\text{M}}^{\text{d}}$, where FeO is iron oxide content in ash, $(\text{H}_2\text{O})_{\text{M}}$ is the content of mineral water of hydration, and S_{pyr} is the pyritic sulfur content [72]. The difference between true organic matter and “conditional organic matter” is generally not greater than 1–3%.

It is clear that for most technological uses of oil shale, there will be a need to go beyond simple estimates of organic weight fraction in characterizing the material.

Kerogen

Kerogen is the major fraction of oil shale organic matter, and it is insoluble in organic solvents. It has a solid cross-linked macromolecular structure, and in this respect is somewhat similar to coal. Accordingly, kerogen is swellable, but not soluble, in organic solvents. The term “kerogen” was introduced by Professor Crum Brown to describe the insoluble organic matter in oil shales that gives shale oil on heating and decomposition [158]. Nowadays the term kerogen is used to characterize solid organic matter in all sedimentary rocks [56].

Table 5.2 Examples of kerogen [141] (or organic matter,* [99]) elemental compositions

Oil shale	C	H	S	N	O	H/C	O/C
Kukersite (Estonia)	77.3	9.8	1.7	0.4	10.8	1.52	0.105
Green River (USA)	78.3	9.9	1.6	2.1	8.1	1.52	0.078
Dictyonema (Estonia)	70.5	7.4	4.2	2.5	15.4	1.26	0.164
Kasphir (Russia)	67.1	8.0	10.2	1.2	13.5	1.43	0.151
Timahdit (Morocco)	68.9	8.5	7.0	3.0	12.6	1.48	0.137
Eastern USA Devonian*	82.0	7.4	2.3	2.0	6.3	1.08	0.058

There are several excellent publications on kerogens available in the literature [32, 110, 144, 145]. Oil shale kerogens possess relatively high atomic hydrogen to carbon atomic ratios (typically 1.2–1.6), at least in comparison to coals, for which this ratio is typically less than unity. It is the high hydrogen to carbon ratio (combined with low oxygen to carbon ratio) that makes oil shale kerogens of interest as a potential source of liquid fuels. Heating values of kerogens have been shown to be in the range of 24–40 MJ/kg, though as noted above the typical values are around 35–40 MJ/kg [90, 99].

The macromolecular structure of oil shale kerogens is complex – kerogen is not a “homopolymer.” Instead of being built of repeating regular structural units as are synthetic polymers or natural materials such as cellulose, it is composed of highly variable structural units, both in terms of size and chemical character. The exact chemical structure of an oil shale kerogen is difficult to describe, therefore studies of “kerogen structure” can provide data only on average structural parameters. This is the same situation as exists for such natural materials as coals or lignins.

Due to kerogen’s insolubility in organic solvents, it was historically somewhat difficult to characterize with respect to its chemical structure. Attempts to liberate it from the oil shale rock would necessarily involve risk of chemical degradation. Even if the approach involves dissolving away the mineral matter (see below), there are concerns regarding whether the kerogen has been altered, and of course, there remains the problem of reliable characterization of the chemical structure of a solid organic macromolecular substance once it is isolated. This latter point is similar to the situation in the field of coal chemistry, where decades of effort have been expended in establishing structures on which there is now reasonably general, though not yet total, agreement. Aspects of kerogen structure have in recent decades also yielded to more sophisticated characterization methods, though again, one can do little more than characterize average structures or structural elements.

As a result of the intractability of the raw kerogen structure, much has been done using its elemental composition as the simplest indicator of properties or predictor of behavior. The composition of kerogens is typically presented based on carbon (C), hydrogen (H), sulfur (S), nitrogen (N), and oxygen (O) content, since these are by far and away the major elements of interest. For more precise compositional characterization of Kukersite oil shale kerogen, chlorine (Cl) is also included [164]. Table 5.2 presents some sample kerogen (or organic matter) elemental compositions of oil shales from major deposits.

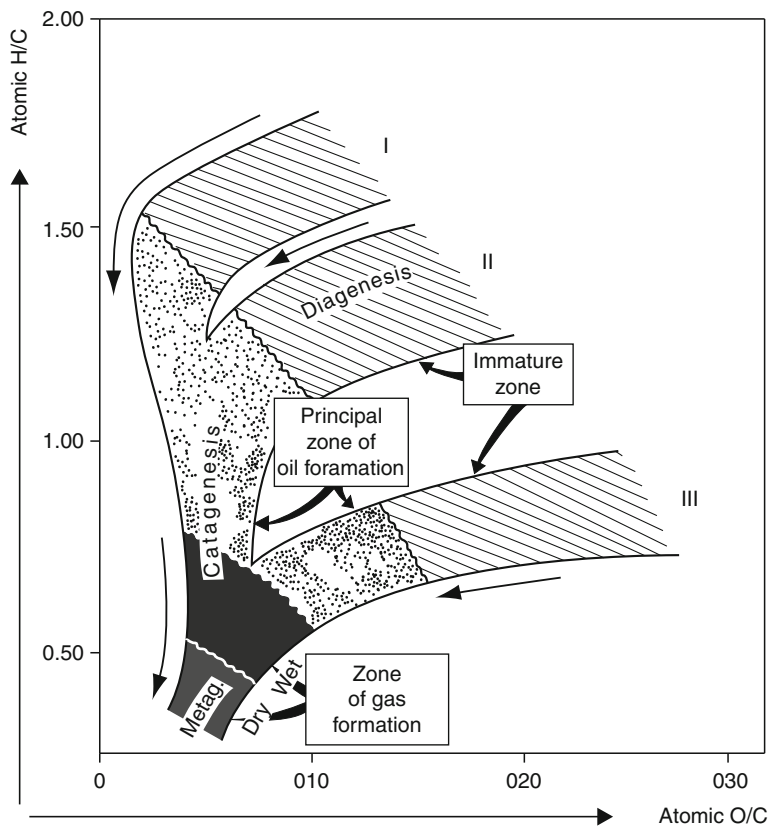


Fig. 5.1 The van Krevelen diagram, showing the approximate locations of different kerogen types, based upon atomic ratios (from [145], with permission)

Kerogens can be classified in different ways on the basis of elemental composition. One of the most common is based on the Van Krevelen diagram originally developed for classifying coals (Fig. 5.1). Kerogens fall into certain groups on the basis of the atomic ratios of hydrogen to carbon and oxygen to carbon. Kerogens can be grouped as Type I, II, III, or IV with further subgrouping according to sulfur content. Oil shale kerogens are predominantly Type I (Green River Oil Shale from Uinta Basin is a typical kerogen of this group) and II (Torcian Oil Shale from the Paris Basin is an example from this group). The less common coaly shales belong to Type III (Upper Cretaceous sedimentary rock from the Doula Basin, as one example) [33, 145]. The following numerical H/C and O/C ratio ranges have been suggested: for Type I $H/C > 1.25$ and $O/C < 0.15$, for Type II $H/C < 1.25$ and $0.03 < O/C < 0.18$, and for Type III $H/C < 1.0$ and $0.03 < O/C < 0.3$ [145]. Somewhat different H/C and O/C, and also O/S, ratios are found for kerogens at the end of diagenesis, but the above are the values for the materials of practical importance.

Table 5.3 Yield of bitumen per conditional organic matter. Atomic H/C ratios of some oil shale kerogens and bitumens are shown for comparison [141]

Oil shale	Yields per conditional organic matter (%) (solvents used)	H/C bitumen	H/C kerogen
Kukersite (Estonia)	0.71 (benzene:methanol (1:1))	1.75	1.52
Kultak-Zevardy (Uzbekistan)	12.01 (benzene:methanol (3:1))	1.42	1.2
Uktha (Russia, Komyi)	21.42 (benzene:methanol (3:1))	1.58	1.21
Green River (USA)	5.4 (chloroform)		
Dictyonema (Estonia)	3.36 (benzene:methanol (3:1))		

Kerogen Isolation

An important tool in the field of kerogen study is that of kerogen isolation (or concentration) from the oil shale matrix. This involves the removal of solvent solubles (bitumen) and mineral matter, leaving behind the kerogen. Several reviews are available on isolation or concentration procedures (for information readers are referred to [6, 34, 108, 128, 145]).

Solvent solubles are removable by ordinary solvent extraction. Since all unextracted organics report as kerogen, the efficacy of extraction is important in establishing actual kerogen content. The amount of extractable obtained, and its properties, may vary considerably depending upon the solvent used for extraction. The amount of the extracted matter also increases with an increase in extraction process temperature and with the polarity and chemical activity of the extractant [159]. Typical extraction yields are low, representing only a few percent of organic matter, but varying significantly from shale to shale see (Table 5.3, for examples).

A number of physical separation methods used to separate kerogen from the mineral part of oil shale are described in the literature [42, 107, 135]. These methods involve primarily such physicochemical processes as flotation and centrifugation. Combination techniques, involving such processes as ultrasonication or electrostatic and magnetic separations are also physical methods used in kerogen enrichment [159]. It is worthwhile to note that for certain oil shales, some physical methods are of value, since particle size reduction is accompanied by an increase in particle organic matter concentration.

The most widely used laboratory techniques for kerogen isolation from inorganic matter are based on chemical methods. In this regard, oil shale minerals can be grouped as carbonates (which are soluble in dilute acids), silicates (soluble in HF), and sulfides (which can be removed by oxidizing and reducing agents). Mineral composition determines the reagents (and the efficiency of reagents) to be used for demineralization [108]. For oil shale demineralization with chemical methods readers are referred to [108].

Kerogen Degradative Analysis

Although elemental analysis offers valuable information for classification, other destructive and nondestructive techniques have been used to obtain information on

functional groups and on structural functionalities of different oil shales [46, 110]. Earlier quantitative characterizations of kerogen functionalities were based on destructive techniques [146]. The destructive techniques include thermal degradation (pyrolysis, hydrogenolysis, supercritical extraction) and chemical degradation with different chemical reagents based on the specificity of the reagents (for more information concerning this topic see [128, 146]). Destructive analysis techniques are based on obtaining smaller identifiable compounds that have a structural relationship to the kerogen [146].

To describe the pyrolytic behavior of kerogen, detailed knowledge of kerogen structure is critical since the structural properties and functionalities of kerogen strongly influence its pyrolytic behavior. It has been shown in coal pyrolysis studies that devolatilization rates and product compositions can be correlated with coal organic matter chemical structure [123, 127]. So while certain types of functional groups may be directly related to their pyrolytic products, use of this fairly nonspecific method is of limited value.

The analysis of kerogen thermal degradation product molecular weight distributions has provided some insights into the size of the systems being examined. There was a recent study of kukersite (Type I) and dictyonema (Type II) oil shale samples involving Field Ionization Mass Spectrometry (FIMS) pyrolysis under high vacuum. This investigation indicated number-average molecular weight values of 408 and 383 Da with standard deviation values of 141 and 128 for kukersite and dictyonema oil shale pyrolysis products, respectively (estimated using a three-parameter Gaussian distribution function to describe the results) [111].

Earlier studies have, however, pointed to the possibility of higher molecular weights for the decomposition products. Suuberg and Sherman [131] studied pyrolysis of Green River oil shale under vacuum conditions, and obtained a weight-average molecular weight of around 800 Da, using a gel permeation liquid chromatographic technique. This compared favorably with a weight-average molecular weight of around 850 Da obtained for the same Green River shale, using the FIMS pyrolysis method [125]. The latter studies showed the importance of pressure on molecular weight distributions. Oils obtained using a Fischer assay method showed a much narrower molecular weight distribution, shifted to much lower molecular weights. Hence, it is dangerous to compare the molecular weight distributions from different studies unless the mass transport conditions are known to be identical. In any event, all of the above studies point to the typical characteristics of a macromolecular system being thermally degraded to provide fragments exhibiting a distribution of molecular weights (which are all, of course, lower than the original matrix molecular weight).

Nondestructive Analysis of Kerogen Structure

During the last 3 decades there have been a number of qualitative and quantitative studies aimed at characterizing the structure of oil shale kerogens using nondestructive techniques such as solid-state nuclear magnetic resonance (NMR) techniques

(cross polarization, magic-angle spinning), Electron Spin Resonance (ESR), Fourier Transform Infrared Spectroscopy, and X-ray photoelectron spectroscopy [66, 82, 115, 120].

One recent comprehensive study on the structure of kerogens was carried out using both X-ray photoelectron spectroscopy and solid-state ^{13}C nuclear magnetic resonance techniques [66]. This study determined the average chemical compositions of 18 oil shale kerogens (hydrogen-carbon skeleton, oxygen functionalities, nitrogen functionalities, sulfur functionalities). The data of this study revealed that the average carbon-hydrogen skeletal units of immature Type I and Type II oil shale kerogens (according to H/C and O/C ratios) are generally composed of two to three ring-hydroaromatic/aromatic clusters with a significant number of short attachments and long, roughly linear, alkyl chains. These data also indicated that the number-average molecular weight of the “average repeating structural unit” of oil shale kerogens might be around 400 amu. These values compare favorably with the molecular weight distributions from the actual degradation studies cited above.

Several other studies have been concerned with characterization of kerogen macromolecular structures using solvent swelling in different solvents or solvent mixtures [74, 75, 111, 112]. These studies were performed to evaluate at least semiquantitatively the number-average molecular weight between cross-links (or cross-link density), a fundamental property of a cross-linked macromolecular network. These studies indicate that oil shale kerogen solvent swelling ratios are lower (therefore cross-link density higher and molecular weight between cross-links smaller) than those seen in bituminous coals [76].

Extensive structural data are available for a few oil shale kerogens, especially for oil shales of major deposits. For several kerogens the structural information has been the basis for detailed molecular models of a portion of the structures (e.g., for Rundle Ramsay Crossing [120], Green River [120], and Kukersite [164] (see also [128])). Reviews of the history of development of hypothetical structural models of the Green River Formation kerogen can be found in the literature [128, 158]. For illustrative purposes, a recent two-dimensional model of kukersite oil shale kerogen chemical structure is shown in Fig. 5.2a [164] and another model of Green River Shale in Fig. 5.2b [120]. Again, it needs to be emphasized that what is shown are “averaged” structures that accurately depict elemental ratios and to some extent functional groups, but which cannot be held out as necessarily representing the actual linkages between different groups, and which certainly do not represent the different molecular weight distributions present in the kerogens. It should also be emphasized that kukersite oil shale kerogen is a somewhat unique Type I kerogen due to its high hydroxyl (phenolic) group content [146]. This is apparent in comparing Fig. 5.2a and 5.2b. Hence, care should be exercised in using any published model of kerogen structure in trying to understand the chemical behavior of any other type of kerogen. Due to its high oxygen content, kukersite kerogen is also sometimes categorized as straddling Type I and Type II, since the lines between the different kerogen types is not necessarily as hard and fast as might be inferred from Fig. 5.1.

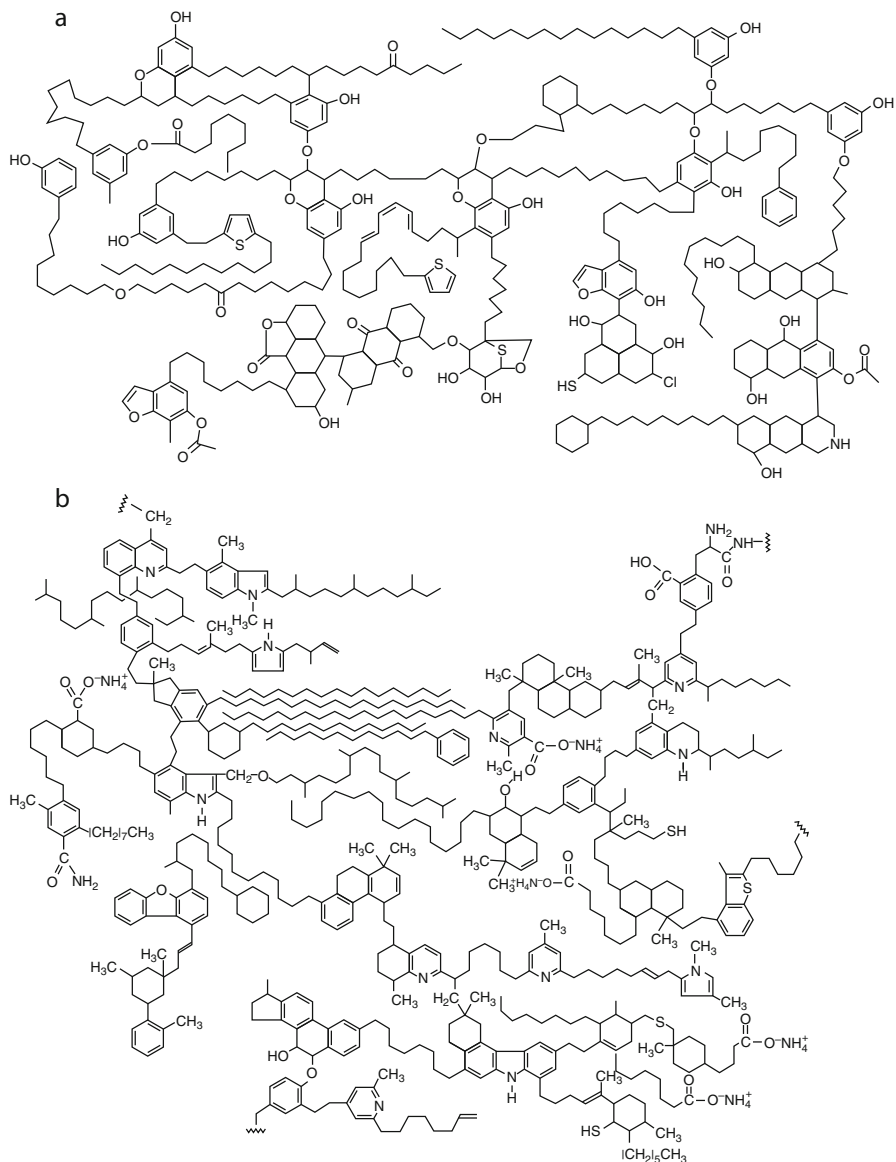


Fig. 5.2 Two-dimensional models of kerogen chemical structure. **(a)** Model of Estonian kukersite kerogen with molecular mass 6,581 Da and empirical formula $C_{421}H_{638}O_{44}S_4NCl$ (from [164], with permission). **(b)** Model of Colorado Green River kerogen (from [120], with permission)

Bitumen or Bitumoid

Bitumen (bitumoid) is a minor fraction of oil shale organic matter that is soluble in common organic solvents (representing up to 20% of organic material [159]) and is therefore recoverable by solvent extraction. Some authors define the bitumen as a benzene-soluble matter, while others define this material as soluble in petroleum-based solvents, yet others define it more broadly as material soluble in any organic solvents, and finally, some define it as material entirely soluble in CS₂. According to [144] there are no standard protocols for extraction procedures, either in terms of the solvent polarity, sample grinding, temperature, duration of extraction, or stirring efficiency. Perhaps the main reason why there has not been greater emphasis on this point is that from a practical point of view, the amounts involved typically represent only a few percent by mass of the organic matter.

These extractables, bitumen, contain biomarkers or organic compounds whose structures are related to the chemical structures of the biological material from which the organic matter was derived [45, 143]. The atomic H/C ratio of bitumen has been shown to be somewhat higher than of corresponding kerogen see (Table 5.3).

Oil Shale Conversion Processes: An Overview

Oil shale resources are abundant and widespread throughout the world and oil shale has been used for energy-technological purposes for hundreds of years (e.g., there is a shale oil extraction patent dating from 1694, granted by the British Crown, [103]). Despite this, currently only few countries (Estonia, China, Brazil, Germany, and Israel) exploit oil shale on a commercial scale. The main reason for this is that oil shale is a low-grade solid fuel. It cannot compete with coal as a solid fuel, since the latter is available in richer (lower ash content) easily accessible deposits. Oil shale is a potential source of liquid fuels, but suffers there from the fact that the world oil market situation has historically been economically unfavorable in terms of fostering development of upgrading technologies. Generally, there has been need of government subsidies in order to consider development of an industry based upon this resource, and the energy market itself (influenced mainly by crude oil price range and electricity cost) has made oil shale upgrading truly economical only in the few countries mentioned. Moreover, the economic feasibility of oil shale development is certain to be strongly affected by further strengthening environmental regulations (air, water, and land use), socioeconomic issues, and market and investment risks. Taken purely on the basis of greenhouse gas emission per unit of energy, oil shale is unattractive in much the same way as is any other solid fossil fuel, such as coal. Therefore oil shale development in recent decades has been quite chaotic and episodic, and there have been many processes/technologies proposed and many have been abandoned due to economic reasons.

Just as is coal, oil shale is also a multiuse organic-mineral raw material whose economic value has sometimes extended beyond its fuel value. From some oil shales, uranium and other minerals and rare elements can be extracted. As an example, in 1946–1952, a marine type of Dictyonema shale [81] was used for uranium production in Sillamäe, Estonia, and in 1950–1989 alum shale was used in Sweden for the same purpose [36].

Integrated retorting techniques (both *ex situ* and *in situ*) have been under consideration to recover shale oil together with nahcolite, alumina, and soda ash from some oil shale deposits [77]. However, the major emphasis in oil shale upgrading has remained on kerogen thermochemical conversion methods (processes using heat to liberate oil). There have also been a few studies (laboratory research) on the use microbial activities to break up kerogen in its mineral matrix [16, 159].

In principle the general thermochemical upgrading processes that have been developed and utilized for coals (combustion, gasification, liquefaction, and pyrolysis) can also be used for oil shale upgrading. The goal is, broadly speaking, to transform the chemical energy locked within oil shale into more concentrated and conveniently useable forms. However, due to oil shale's thermal behavior and character, some types of processes are more favorable than others. It is important to note that the hydrogen/carbon ratio of oil shale organic matter (typically 1.2–1.6) is more favorable to production of liquids than that found in coal (typically 0.7–1), and this reduces the pressure to increase H/C ratio, which has economically been one of the major stumbling blocks of coal to liquid conversion processes. On the other hand, with mineral content of between 70% and 90%, considerably higher than that of commercial coal deposits, oil shale presents the problem of processing a solid with a high mineral rock content, whose handling and heating in any thermal process is economically quite unattractive.

Direct Combustion

Oil shale can be utilized as a fuel for thermal power plants, where it is burned directly as is coal. Currently there are several countries that utilize oil shale as fuel for power plant fuel: Estonia, Israel, Germany, and China [14, 102]. Some countries have closed their oil shale-fueled power plants (Romania) or turned to other fuels (Russia). Other countries are planning to build such plants (Jordan and Egypt), or burn oil shale together with coal (Canada and Turkey) [14, 51].

There are three commercial technologies in use for oil shale combustion [3]: (1) pulverized combustion or pulverized firing (PF), as is used in the older units in Estonia; (2) fluidized bed combustion (FBC), used by Rohrbach Zement in Dotternhausen, Germany; and (3) circulating fluidized bed combustion (CFBC), used in two new units at the Narva Power Plant in Estonia, Huadian Power Plant in China, and PAMA power plant at Mishor Rotem in Israel. Generally speaking, PF technology is no longer in favor, because it operates at such a high temperature that

there can be no sulfur capture by the carbonates present in the mineral matter, and therefore it is environmentally much more problematic. The thermal efficiency of the new Estonian CFBC units has been reported to be in the neighborhood of about 36%, which is typical of this sort of fluidized bed combustion system. The older PF units operated at only about 30% thermal efficiency to electricity [52].

An exceptionally extensive study of the correlation between the heating value and various compositional parameters of Estonian kukersite has been presented by [7]. While the quantitative results of that study are applicable only to this particular oil shale, the methodology may well be generalizable. That study suggested that a good working formula for estimation of the higher heating value of the organic part of oil shale is

$$Q_H = 0.3566C + 1.0623H - 0.1339O + 0.0658S \\ + 0.0106N - 0.0280Cl$$

in which the heating value is in MJ/kg and the element symbols represent the mass percentages of the respective elements in the organic fraction of the oil shale. As part of the same original study by Saar, the lower heating value of the typical dried whole Estonian shale is (see [89])

$$Q_L = 34.45 - 0.302A - 0.4369(CO_2)_c$$

in which A is the dry oil shale ash content and $(CO_2)_c$ represents the content of carbonate mineral CO_2 in the dry oil shale.

Since direct combustion of oil shale is not the main focus of this review, the reader is referred to the comprehensive volume recently published by Ots on this topic [89].

Low-Temperature Pyrolysis

Low-temperature pyrolysis up to at about 500°C (also referred as retorting or semicoking or low-temperature carbonization) has been historically the most favored thermochemical conversion process for high-grade oil shales. In this pyrolysis or retorting process, the organic matter is converted to oil (termed retort oil, shale oil, shale crude oil), gas (typically called retort gas), and solid residue (typically termed semicoke in the oil shale industry). The processes can be carried out either by mining the oil shale and then producing oil by heating it in above-ground retorting facilities (termed *ex situ* processing), or by heating the oil shale underground without mining it and bringing it to the surface (termed *in situ* processing). Limiting the processing temperature to below 500°C is desirable, in terms of maximizing oil yield.

Oil shales are commonly retorted in commercial *ex situ* retorts without beneficiation (organic matter is not concentrated). Commercial *ex situ* shale oil production facilities are in operation in Estonia, Brazil, and China. Commercially produced shale oils are presently used as heating fuels or as feedstocks for producing chemicals [85]. Due to their broad boiling point distributions, high pour points, high viscosities, and high heteroatom contents (nitrogen, sulfur, and oxygen), raw shale oils need to be upgraded to be considered for higher value uses. Retorts could be included within a petroleum refinery. There have been a number of investigations on the use the shale oils as refinery feedstocks for manufacture of motor fuels [87].

High-Temperature Pyrolysis and Gasification

High-temperature pyrolysis (or gasification) under self-generated atmospheres was historically used to produce town gas (e.g., commercial-scale chamber ovens used in Estonia, [30]). Just as in the case of town gas produced from coal feedstocks, gas production from oil shale was abandoned due to economic reasons, largely having to do with the low cost of production of natural gas.

Modern gasification technologies, applied to conversion of coals or biomass, use partial oxidation (steam, oxygen) or hydrogen environments. In these gasification processes, the solid feed material is converted to synthetic gases (composed mainly of hydrogen and carbon monoxide) that can be further used as combustion fuel in, for example, Integrated Gasification Combined Cycle (IGCC) plants designed to produce electrical power, or further catalytically converted (via Fischer–Tropsch reactions) to produce chemicals, including liquid fuels. However, existing commercial gasification technologies that would lend themselves to integration with upgrading plants are not economically/technically suitable for oil shale feed materials, unless the mineral matter is reduced before gasification. There have been no demonstrations of large-scale oil shale beneficiation technologies for concentrating oil shale organic matter (to reduce mineral matter) to levels suitable for proven gasification technologies. Although in principle, oil shale gasification could be more attractive than shale oil extraction via retorting, especially for low oil yield oil shales, this thermochemical conversion process has not been a subject of commercial interest. Over the course of time a number of laboratory-scale to pilot-scale studies have been carried out on this topic [8, 10, 37, 57, 113].

Other Thermochemical-Based Conversion Technologies

Thermal dissolution or heating in presence of solvent has been considered as an alternative to “dry” thermochemical conversion such as classical retorting. These attempts have included those in subcritical and supercritical fluids, reactive and

nonreactive fluids, and of special interest have been hydrogen-donor solvents that can provide hydrogen in the conversion process. In the latter case, gaseous molecular H_2 can also be introduced. Again, there is strong analogy to methods that have been suggested for direct liquefaction or solvent refining of coals. Examples include processes such as Solvent-Refined Coal processes (SRC-I and the improved version, SRC-II), the Exxon Donor Solvent (EDS) process, and the H-Coal process [8, 94, 99]. A brief review on recent advances in direct coal liquefaction and a list of major direct coal liquefaction processes is given by Shui et al. [118].

The thermal dissolution processes generally involve heating the oil shale to temperatures below those characterized by active devolatilization, as there is a desire to maximize oil yields and minimize gas production. The temperature range of active devolatilization depends somewhat upon gas pressure applied to the system.

The thermal dissolution of oil shales has been mainly of academic or research interest as the H/C ratio of oil shale organic matter is already much more favorable than of coal. For more information on oil shale thermal dissolution, there are recent brief reviews covering the topic [48, 136] and, separately, supercritical extraction [67, 139]. One step toward commercial development is the proposed 1 ton/h so-called Rendall process demonstration plant under construction in Australia by Blue Ensign Technologies Limited. This process is designed to use oil shale from the Julia Creek deposit in Queensland and to hydrotreat it in a two-stage process using a petroleum-based solvent. Again, this proposal is only at a laboratory stage.

A considerable amount of work (up to process-development unit scale) has been published on hydrolysis or pyrolysis under high hydrogen pressures, including catalytic hydrolysis and hydrogasification [8, 109]. Indeed, this technology was already explored in Estonia in the 1930s [68].

Shale Oil Production

General Considerations Regarding Process Temperatures

Technologies to recover oil from oil shale are based on thermal breakup of kerogen, the cross-linked macromolecular organic matter of oil shale. All present technological approaches require heat to take kerogen to temperatures at which thermochemical conversion processes are sufficiently fast to be of interest from a practical point of view. As noted above, depending on process conditions the thermochemical conversion results in three general classes of products with different quantities and varying qualities. These products are the oil (more generally non-polymeric organic compounds with a wide molecular weight distribution), a carbon-rich solid residue, and gas (including water vapor).

Kerogen decomposition rates increase with temperature, subject to the Arrhenius rate law. The rates will be quantitatively explored in a later section. Kerogen decomposition is slow at low temperatures and occurs on a time scale of days to years below 350°C, which is why practical processes are generally carried out at higher temperatures. The decomposition becomes fast enough for practical purposes at temperatures of 400°C and above. Cummins and coworkers [25] studied Green River oil shale low-temperature isothermal pyrolysis from 150°C to 350°C. They showed that 2% of kerogen was converted to benzene solubles in 90 days at 150°C and in 360 days 7.7% of kerogen was converted. At 200°C in 90 days 3% was converted, and in 360 days 8.9%. When the temperature was raised to 300°C in 0.5 days 3.3% was converted and in 4 days 12.8% yield was obtained. Finally, at 350°C in 0.5 days 27.6% and in 4 days 65.1% of kerogen was converted into benzene solubles.

The above demonstrates that there is actually no lower temperature limit for kerogen decomposition, consistent with what would be concluded from Arrhenius kinetics; rather, the question lies in establishing the time scale needed at any particular temperature. It is the fact that practical *ex situ* (i.e., in retort) conversion processes must be carried out on the timescale of minutes or hours, at most, that sets the commonly cited “lower temperature limit” for decomposition. These limits may be extended for *in situ* techniques, where confinement volume in an aboveground retort is no longer a consideration, but there is still a lower limit at which the process would simply take too long to be practical.

Real processes can be run under conditions varying from slow heating rate and long residence time to fast heating rate and short residence time. For example, in aboveground (*ex situ*) retorting equipment, heating rates, and residence times can vary from the order of 1°C/min and hours to of order of 1,000°C/min and seconds, respectively. The former is encountered, for example, in moving bed coal gasifier type retorting equipment, which utilizes particles with size on order of 100 mm (e.g., 10–125 mm for the Kiviter process, [101]). The latter high heating rate conditions are encountered in fluidized bed reactors, which use small particles with sizes below a few millimeters. In all these retorting processes (which take place in an inert gas environment or under self-generated gas environment with very low oxygen content, or in a reactive, non-oxygen environment), the oil shale is heated up to the active pyrolytic reaction region from 450°C to 550°C, where oils and gases evaporate and hydrogen-deficient organic matter or semicoke is left in the solid phase.

In situ processes generally involve heating rates below 1°C/min, because of the impracticality of rapid heating in an *in situ* environment. The relatively low-temperature range of 340–370°C, with time scales of years, is utilized by Shell in its *in situ* (underground) conversion process (Shell Oil Shale Test project) [77]. The above-cited timescales for kerogen conversion show that it is not the kinetics of conversion alone that determine these long times; rather, they are also influenced by the time needed to heat the large volumes of rock and to allow the released oil to flow out of the shale.

Other Processes Taking Place During Retorting

Destruction of kerogen by heating is accompanied by processes in other oil shale constituents, that is, in bitumen and mineral matter. These processes include:

- Solvent-extractable organic matter or bitumen (non-covalently linked non-polymeric compounds) can vaporize or decompose, depending on their thermal stability. Depending on the oil shale, the bitumen content can constitute up to 20% of organic matter [159], though as noted above it is generally much less than this. If able to quickly escape the hot oil shale and be cooled, these compounds should be captured in a relatively minimally altered form.
- Mineral matter present in oil shale can have catalytic effect on thermochemical conversion processes of kerogen [41, 116]. Also, the minerals themselves can decompose at temperatures of thermochemical conversion of kerogen. Some minerals can partly or fully decompose even under typical retorting conditions (e.g., nahcolite, dawsonite, analcite, smectite, kaolinite, siderite, and pyrite) [76, 89, 92]. These decomposition reactions are generally endothermic. At temperatures around 450°C magnesium carbonate starts to decompose [76]. The interaction of a mineral with organic matter or other minerals present in the oil shale can cause altered thermal behavior, relative to the pure mineral [103]. Rajeshwar and coworkers have summarized thermal characteristics/behavior of minerals (17 minerals) commonly found in oil shale deposits [103]. Thermochemical properties and mineral reactions of oil shale minerals have been reviewed by many authors (e.g., [76, 77, 88, 92, 103]).
- Trace elements of oil shale can distribute between retorting gas, oil, solid residue, and retort water [93]. For example, there may be the presence of trace elements of environmental concern (arsenic, selenium, mercury) in retort oil, gas, or water [8, 92], or trace elements in oil (vanadium, iron, nickel, arsenic) can poison refinery catalysts [92, 93]. Actual concentration values depend on the retorting process and, of course, the trace element composition of specific oil shale. Most of the trace elements are retained in the solid spent shale itself [8].

Thermal Effects During Retorting

Large quantities of heat are required to manufacture a usable fuel (liquid or gaseous) from oil shale. Heat requirements include (1) heating the mineral and organic matter to reaction temperature; (2) providing the heat of reaction related to organic matter decomposition and heat effects covering chemical changes in mineral matter; (3) providing the heat of vaporization of volatiles (oil and water). The thermal management of processes must also include provision for cooling the products of the process back to ambient temperatures. The major amount of process heat is consumed with heating mineral matter. The total heat requirement for heating oil shale to 500°C, including allowing for vaporizing volatiles, is observed

to be about 650–750 kJ/kg of oil shale [99]. The heat of the pyrolysis reactions is by itself relatively small [8, 99]. A review of some recent applications of differential scanning calorimetry (DSC), mainly aimed at providing kinetic information, also provides reference to some recent work on thermal effects of pyrolysis [70].

Assay Methods: Determining Potential Oil Yield and Its Relationship to Other Properties

Procedures for determining oil production potentials are known as assay methods. Assay methods generally involve laboratory scale slow heating rate (order of 10°C/min) batch pyrolysis systems or so-called carbonization tests. The procedures were developed to provide a simple and reproducible basis for fossil fuel (coal, lignite, oil shale) characterization and comparison, as opposed to providing scientific insights into the material.

The modified Fischer assay method has been widely used (since 1946) to evaluate the approximate oil potential of oil shale deposits and compare different oil shales. The term “modified” denotes that the original Franz Fischer method [161], used in Germany to characterize coals was taken over to characterize oil shales and has gone through improvement in this process. The technique has been standardized as the American Society for Testing and Materials Method (ASTM method) D-3904-80, D3904-85, and D3904-90 or as the International Organization of Standardization (ISO) standard ISO 647-74 or as the GOST 3168-93 (the GOST is the former Soviet Union Standard).

The standardized modified Fischer assay method (ISO 647-74; GOST 3168-93) consists of heating a 50-g dried and crushed oil shale (90% particles passing through a 1-mm mesh, with not more than 50% particles passing through a 0.2-mm mesh) in a specially designed cast aluminum retort (made of 99.5% aluminum) to 520°C in 70 min with decreasing heating rate, followed by holding the sample at that temperature for 10 min. The process is performed in a self-generated atmosphere. The distilled vapors of oil, gas, and water are passed through a condenser cooled with ice water, and collected into a graduated centrifuge tube. The oil and water are then separated by centrifuging. The quantities reported are the weight percentages of shale oil (and its specific gravity), water, shale residue, and “gas plus loss” by difference.

The above procedures were developed to provide a reproducible basis for oil shale characterization/comparison. Estimated errors are not expected to be greater than 5% (relative) under the standardized conditions used [55]. However, the Fischer assay is a static assay under self-generated “inert” atmosphere and factors such as cracking of volatiles due to long residence time in a hot zone, and char forming reactions [38] can limit the oil yield. Therefore, for example, use of an inert gas sweep [38] provides greater oil yields than from Fischer assay under a self-generated atmosphere. It is not uncommon to encounter laboratory retorting results in which oil yields exceed Fischer Assay results.

Table 5.4 Fischer assay yields, dry organic matter basis, of some selected Type I and II oil shales. Parent organic matter H/C and O/C ratios are also shown

	Green River (Utah, USA) [141]	El-lajjun [88]	Kukersite [141]	Eastern USA Devonian (Antrim) [141]	Dictyonema [141]
H/C ratio of organic matter	1.52	1.42	1.51		1.14
O/C ratio of organic matter	0.08	0.05	0.11		0.23
Kerogen type	I	I	I/II	II	II
Oil yield, wt%	59.3	61.9	60.0	22.2	19.8
Gas yield, wt%	22.7	20.9	21.5	25.1	16.5
Semicoke yield, wt %	11.8	10.8	9.1	42.5	45.4
Retorting water	6.2	6.4	9.4	10.2	18.3

Other assays, developed for carbonization tests of fossil fuels, have also been applied to characterizing oil shales, and include the Heinze retort [24], the Gray and King method (developed in England) [152, 161], the original Franz Fischer method [161], the Bureau of Mines oil shale method [161], the Tosco material balance assay (with collection of gaseous products) [8], and the “material balance” Fischer assay method (modification for collection of gaseous products) [47]. Also, results based upon various TGA analyses have been used by many investigators, and are not necessarily directly comparable to the results from Fischer assay methods.

One widely applied oil shale rapid characterization and screening method is Rock-Eval analysis [9, 73]. Rock-Eval pyrolysis has been used to evaluate the maturity of the rock, as well as its richness (organic carbon content) and quality (oil and gas potential) [95]. The technique is based on temperature-programmed heating of a small sample (under 100 mg) in an inert atmosphere (helium or nitrogen) up to 600°C (to 800°C using version Rock-Eval 6). Evolution of hydrocarbon volatiles is monitored by a flame ionization detector, and carbon dioxide (CO₂) by other means, such as an infrared analyzer or a thermal conductivity detector, for example. The basic method was designed to measure the amount of free hydrocarbons in the sample (S₁), the evolution peak temperature (T_{max}) and the amount of hydrocarbons generated through thermal cracking of nonvolatile organic matter (S₂), and the amount of CO₂ produced during pyrolysis of kerogen (S₃). Based on these, the Hydrogen Index (HI) as mg S₂ per gram of total organic carbon, Oxygen Index (OI) as mg S₃ per gram of total organic carbon, and Productivity Index (PI) as S₁/(S₁ + S₂) can be calculated. Rock-Eval pyrolysis temperature T_{max} and HI are used to evaluate maturity of oil shales. HI and OI have been used to construct a modified van Krevelen diagram.

Thus the approximate grade of oil shale (average oil yield) has been determined historically in laboratory batch retorts such as the “modified” Fischer assay method or the Rock-Eval technique. There are high and low oil yield kerogens based on modified Fischer assay results. Tables 5.4–5.6 are compiled to show how the

Table 5.5 Fischer assay gas compositions of the selected Type I and II oil shales shown in Table 5.4

Gas composition, vol%	Green River	El-lajjun [88]	Kukersite [141]	Eastern USA	
	(Utah, USA) [141]			Devonian (Antrim) [141]	Dictyonema [141]
CO ₂	30.3	14.5	25.0	9.7	13.6
H ₂ S	3.3	25.2	8.8	29.1	20.3
C _m H _n	2.0	9.3	16.1	2.6	7.5
CO	16.8	1.0	7.9	14.3	5.7
H ₂	24.2	21.6	8.2	22.4	27.1
C _n H _{2n+2}	21.2	28.4	34.0	19.2	25.8

Table 5.6 Fischer assay oil elemental compositions of the some selected Type I and II oil shales shown in Table 5.4 [141]

	Green River	Kukersite	Eastern USA	
	(Utah, USA)		Devonian (Antrim)	Dictyonema
C	84.7	83.0	83.8	83.3
H	12.0	9.9	10.6	9.3
S	0.6	1.1	1.8	2.6
N	2.1	0.1	0.7	1.0
O (by difference)	0.6	5.9	3.1	3.8
H/C	1.7	1.43	1.52	1.34
O/C	0.005	0.05	0.03	0.03

composition of kerogen affects the product yield and product composition. Table 5.4 also confirms a general observation that the amount volatiles generated during thermochemical conversion under an inert environment up to about 500°C decreases from kerogen Type I to Type II, and gas to oil ratio and semicoke to oil ratio increase from Type I to Type II [128]. It should be noted that a Van Krevelen diagram-based classification of oil shale behavior (based upon H/C and O/C ratios) provides only a rough prediction of behavior, and better correlations between pyrolysis yields and organic matter types might need additional indicators or different classification approaches [166].

As the modified Fischer assay has been a standardized method for evaluating oil yields of different oil shales, the chemical and physical properties of different oil shale deposits have been correlated with Fischer assay results. Properties that are successfully correlated include, for example, density, thermal conductivity, organic carbon, total hydrogen, aliphatic/aromatic carbon, and unpaired electron concentration [82]. In general, each specific deposit exhibits its own correlations and these correlations need to be derived for the specific deposit, as the relationships are mostly empirical.

Thermochemical conversion of oil shale kerogen to oil produces changes in oil chemical composition relative to the original oil shale organic matter. Analysis of data on hundreds of oil shales (compiled by Urov and Sumberg [141]) indicates that the Fischer assay oil H/C ratio can be either lower or higher than that of the parent

organic matter. This is consistent with an observation that shale oil aromaticity can be greater or lower than that of the parent kerogen [82].

There are a number of papers [90, 141] concerned with characterization of Fischer assay oils, examining, for example, elemental composition, molecular weight (varying from 190 to 310 Da), density (or specific gravity varying from 0.8 to 1.04, with only a few exceptions <1), heating value (39–44 MJ/kg), viscosity, boiling range (30–70% boiling over up to 350°C), and chemical groups (nonaromatic hydrocarbons, aromatic hydrocarbons, heteroatomic compounds, etc.).

It was already noted that the Fischer assay is a standard method and it does not provide either the maximum or minimum oil yield that can be produced from a given oil shale. Changes in parameters such as reactor configuration, particle size, heating rate, pressure, or pyrolysis environment also can affect product yields and compositions [8, 23, 157]. In real processes these factors are not always independent, as, for example, high heating rates require fine particles or hydrogen environment is used with high pressure.

Heating Rate Effects on Retorting Oil Yields

Fluidized bed retorting, where heating rates reach 1,000°C/min and particle sizes below a few millimeters are used, produce higher oil yields than obtainable from Fischer assay. For example, yields about 110% relative to Fischer assay have been reported in the case of Green River oil shale and about 150% of Fischer assay for eastern US Devonian shale [23]. Fluidized bed pyrolysis shows, in addition to increased oil yield and decreased gas yield, different oil properties such as higher aromaticity, molecular weight, density, and viscosity [23], as compared to Fischer Assay oils. It should also be noted that laboratory-scale fluidized bed retorting experiments usually resulted in higher oil yield than commercial-scale design retorts [23].

In large-scale retorting systems, high heating rates require high heat-transfer rates, and thus, a finely ground feed. Therefore differences in products from low and high heating rate thermochemical conversion processes are influenced also by the effect of particle size. The larger the particle, the slower the mass transfer rate of volatiles to the outer surface of particle, and thus, the more opportunity for the products to undergo secondary reactions that would alter their nature. Hence, it is difficult in most cases to separate the effects of heating rate and particle size.

Pressure Effects on Retorting Yields

The mass transfer of oil out of pyrolyzing particles is affected by the pressure difference between the particle interior, where the products are produced, and the surrounding atmosphere. Delayed escape of the volatiles can result in secondary

cracking reactions of higher molecular weight products, resulting in lower oil yields and increase gas and char yields.

With an increase in pressure under an inert environment (or self-generated environment) the oil yield decreases, the gas yield increases, the char yield increases, and oil specific gravity and viscosity decrease. Also, the amount of lighter distillate oil fraction increases [8]. All of these phenomena are consistent with a process of cracking of higher molecular weight oils to lighter oils (with deposition of coke). Different results can be seen when reactive pyrolysis atmospheres (such as hydrogen or steam) are used. On the other hand, these conclusions are not necessarily general, as in high heating rate (1,000 K/s), small particle pyrolysis, oil yields were observed to be quite similar, decreasing only a small amount with increasing pressure above a temperature range of 800–900 K [131]. The oil loss at higher pressures was associated with the occurrence of cracking reactions. The molecular weight distributions of the shale oil were relatively insensitive to pressure, though at higher temperatures, higher pressures tended to slightly favor lower molecular weights. The results of this work also showed clearly that there was an evaporative equilibrium responsible for determining the molecular weight distribution in the oil, as the average molecular weights in the oil were significantly below those of the extractable thermobitumen left in the shale. Hence the effects of pressure are associated with evaporative processes, though these effects are not as significant as they are in determining the yields of tars from coal pyrolysis [127, 132].

Effect of Gas Atmosphere on Retorting

An inert gas sweep of a retort provides greater oil yields than obtained from the Fischer assay procedure under self-generated atmospheres [38]. Pyrolysis in a steam atmosphere has been shown to have favorable effect on products by improving yield and quality of shale oil [38] relative to Fischer assay. In fluidized bed experiments, steam has been studied as one possible fluidization medium [23, 38]. However, the beneficial effect of steam relative to nitrogen is the subject of dispute among different researchers [38].

Pyrolysis under high hydrogen pressure (hydroretorting, hydrolysis) is shown to be a potential way to upgrade low-oil grade oil shales to oil. Hydroretorting results in increased oil yield and more aromatic oil with lower heteroatom content and lower molecular weight distribution [106]. Hydrogen pressures of ca 5–10 MPa were sufficient to have an effect [106]. In some studies, higher pressures, 15 MPa, have been used [24]. A hydroretorting assay unit has been developed along with a standardized procedure for its use [106]. In this unit (538°C and hydrogen pressure 6.9 MPa) for low oil yield oil shales (Type II kerogens), oil yields can be increased several times relative to Fischer assay, even 400% over Fischer assay yield [106].

Chemical Aspects of Oil Recovery by Retorting

Shale Pyrolysis in Comparison to Coal Pyrolysis

The process of recovering shale oil is concerned with decomposition of kerogen, the major portion of oil shale organic matter. Kerogen is a cross-linked macromolecular structure whose thermal behavior depends upon the severity of heating, yielding either mostly hydrogen-rich solvent soluble material or light volatiles (oil, gas) and a carbon-rich solid residue. The overall pyrolysis process is extremely complex with a variety of physical-chemical mechanisms. The composition and yields of pyrolysis products depend on the type and characteristics of oil shale (primarily of kerogen), and as noted above, the particle size, final temperature, heating rate, residence time of vaporizing products in hot zone, pressure, and pyrolysis atmosphere. The possibly important role of secondary reactions has been noted in several places above.

In the period from 1970 to 1990, there were extensive theoretical and experimental studies on coal pyrolysis, and relatively fewer such studies on oil shale. The aim of both research communities was to improve the fundamental understanding of pyrolysis chemistry with an ultimate objective of developing realistic simulation models. The examination of coal pyrolysis tended to place great emphasis on the importance of the interplay between chemical and physical processes encountered in pyrolysis, something that received less attention in the shale pyrolysis work.

Coal pyrolysis is an important phenomenon inasmuch as it is an initial step in all major coal thermochemical conversion processes such as combustion, gasification, carbonization, and liquefaction. The past 4 decades resulted remarkable advances in the modeling of coal pyrolysis. There was a shift away from simple, empirical kinetic models to use of more complex “network” devolatilization models. Those models provide detailed predictions of pyrolytic behavior for a wide variety of coals under variable temperature, pressure, and heating rate conditions. There are many extensive reviews and books published on coal pyrolysis [76, 127], covering the chemistry of pyrolysis, mass transfer effects, comparison of experimental data and models, etc.

In some ways oil shale is similar to coal as the organic matter is mostly a macromolecular three-dimensional structure, however, with different organic compositions and hydrogen-carbon skeletons. Therefore, oil shale pyrolysis is characterized by different product characteristics and by different rates and extents of pyrolytic process events (cross-linking, swelling, softening, resolidification, and devolatilization). The pyrolytic devolatilization processes of oil shales occur at somewhat lower temperatures than do the same sorts of processes in coals. The active devolatilization starts at about 350–400°C with a maximum in the range of 400–500°C and completes at about 500–550°C. The oily pyrolysis products are more volatile (with higher hydrogen/carbon ratio and lower molecular weight distribution) than the coal tarry products. Oja has demonstrated that the kukersite oil shale primary tar (oil) produced during moderate rate pyrolysis ($\sim 5^\circ\text{C}/\text{s}$) under

a nitrogen sweep in a tubular furnace is easily volatile below the temperatures of active devolatilization [86]. This is not generally the case for coal liquid (tar) pyrolysis products.

It can be assumed that the general principles used to model the mechanisms of coal pyrolysis could also be used to describe oil shale kerogen pyrolysis. For coal, the following pyrolysis event sequence was proposed [127]: disruption of hydrogen bonds; vaporization and transport of non-covalently bonded “guest” molecules; low-temperature cross-linking (in low rank coals) that is accompanied with CO₂ and H₂O evolution; bridge breaking and fragmentation of the macromolecular network (depolymerization); hydrogen utilization to stabilize free radicals; vaporization and gas phase transport of light fragments; moderate temperature cross-linking reactions to resolidify the macromolecular network; decomposition of functional groups to produce light species or gases; and high-temperature condensation of the macromolecular network involving hydrogen elimination. In most respects, the same processes must take place in oil shale pyrolysis.

The importance of the extent and timing of cross-linking in the pyrolytic processes of coals has been emphasized in coal pyrolysis models. A number of studies have been performed on swelling of thermally pretreated coals indicating loosening and/or tightening of coal structures in the temperature region prior to tar evolution or active pyrolysis. This phenomenon was found to depend on coal rank: changes in lower rank coals indicate low-temperature cross-linking whereas trends in higher rank coals vary from no observable changes to structural relaxation. It was observed that the extent of low-temperature cross-linking was associated with decomposition of carboxyl groups and possibly hydroxyl groups as formation of new cross-links before devolatilization happened together with CO₂ and water release. It has been concluded that low-temperature cross-linking results in low tar yield and can be a reason for the non-softening pyrolytic behavior seen in low rank coals. The importance of such processes in oil shale pyrolysis will be considered below.

General Observations of Oil Shale Pyrolysis Phenomena

A large number of studies (including reviews) on pyrolysis of oil shales have been conducted and reported over the course of history. The pyrolytic behavior of oil shales have been investigated generally based on individual oil shales or in some cases generalized to oil shale kerogen types (Type I, II, or III in accordance of Van Krevelen diagram) [35, 46, 121]. Although kerogen types (similar to coal ranks) have been shown to be useful for generalizing oil shale kerogen (organic matter) behavior, it should be kept in mind that differences between kerogens make a large difference in behavior, and the trends with kerogen type have not been firmly established.

There have been a number of studies of the changes in kerogen structure (in the solid organic residue) during pyrolysis/heating. These changes involve elemental composition, functional group losses and other structural modifications, as well as

changes in the number of free radicals. Techniques employed for tracking the changes include, for example, elemental analysis, Fourier transform infrared spectroscopy, solid-state nuclear magnetic resonance (NMR) spectroscopy, electron microscope or electron spin resonance [28, 119]. There are of course also a great number of studies on volatile product evolution during pyrolysis. This includes evolution of volatile products correlated with kerogen functional group decomposition. Techniques used have included Fourier transform infrared spectroscopy, mass spectrometry, or gas chromatography [105].

For properties of crude shale oils readers are referred to [8, 85, 99, 142].

Observations Regarding Changes in the Macromolecular Structure of Oil Shale Kerogens During Pyrolysis

In relation to the different oil yields observed in the case of pyrolysis of Type I and Type II kerogens (see Tables 5.4–5.6), solvent swelling experiments on thermally pretreated oil shales have indicated that high oil yield kukersite kerogen (Type I), which exhibits softening pyrolysis behavior during pyrolysis, shows a tendency toward structural relaxation in the low-temperature pre-pyrolysis region [111]. This observation is qualitatively comparable to that seen in high tar-yield softening coals. On the other hand, low oil yield Dictyonema kerogen (Type II), which exhibits non-softening pyrolysis behavior, shows a tendency for pre-pyrolysis cross-linking or structural tightening [163], similar to what happens in low rank non-softening coals [126].

Mechanisms and Kinetics of Kerogen Decomposition

Mechanisms of kerogen decomposition have been the subject of numerous studies, including many different experimental techniques, and have involved both isothermal and non-isothermal procedures. Techniques used have included thermogravimetry, differential scanning calorimetry, differential thermal analysis, Rock-Eval, and various other types of reactors. These studies tracked changes in at least one pyrolyzing kerogen-related component (parent material or product) as a function of time and temperature. In many such studies, complex materials, such as pyrolysis oil, are considered as single pseudo-components. There are many papers that consider the mechanisms and kinetics of kerogen decomposition, and only a sampling of these is offered here [4, 5, 13, 18, 26, 27, 29, 39, 53, 58, 61, 63, 69, 76, 103, 121, 130, 134, 136, 138, 148, 150, 153, 154, 156]. Despite the existence of a relatively extensive literature on oil shale pyrolytic behavior, very few analyses and reviews are available that offer comparison between the available information or comparison to coal and biomass research results.

Different mechanisms, with various degrees of complexity, have been proposed to describe oil shale pyrolytic behavior. Generally, these are based on tracking intermediate, primary, and secondary pyrolysis products, often without a clear

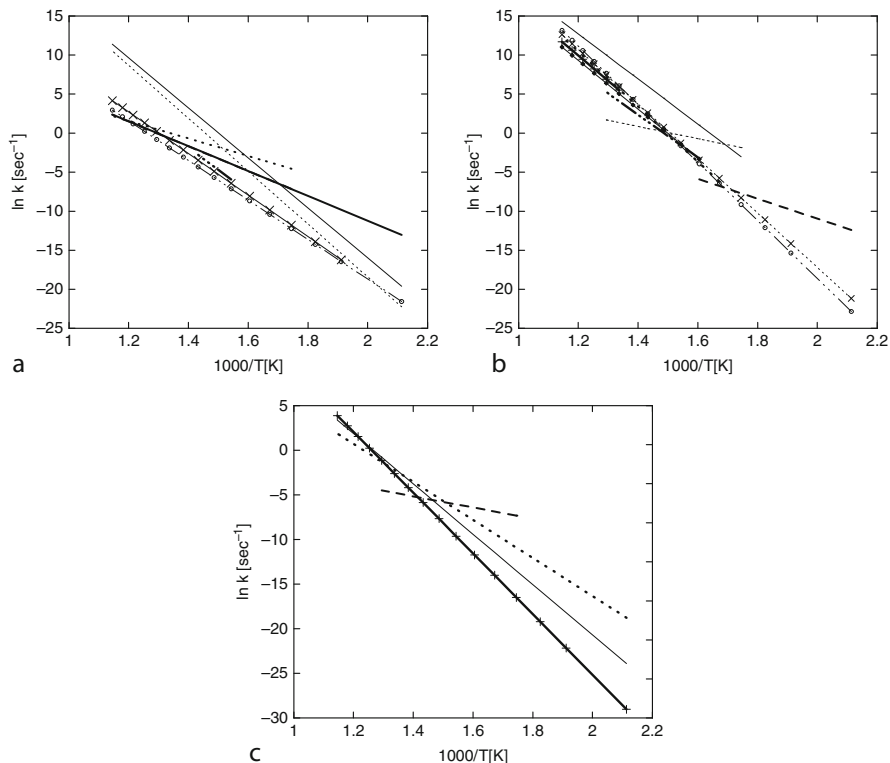


Fig. 5.3 Comparisons of kinetics of kerogen pyrolysis. (a) A comparison of rates on Estonian kukersite kerogens. Thick lines [59, 60, 62]; thin lines from Oja (unpublished results); lines with crosses [96]; line with small circles, [160]. (b) A comparison of rates obtained on Colorado Green River Oil Shale. Dark line with crosses [12]; thin solid line [78]; heavy dashed line [25]; heavy dotted line [21]; heavy dashed-dotted line [149]; thin line with small black points [124]; thin dotted line with crosses [96]; thin dashed-dotted line with circles [19]; thin dashed line [84]. (c) A comparison of rates obtained on kerogens from Rundle Australian Oil Shale. Heavy line with crosses, [147]; thin line [96]; heavy dashed line [84]; dotted line [91]

identification of all of the products in any of the classes being tracked. Kinetic parameters have been calculated by fitting experimental data to an assumed semi-empirical model of the pyrolysis process. There is, thus, not surprisingly a large variation in reported kinetic parameters (activation energies and frequency factors). Consequently, the results are often of limited generality, applicable to the particular experimental conditions studied, often potentially influenced by heat and mass transfer limitations on observed kinetics.

A sampling of kinetic results is shown in Fig. 5.3. These results have been taken from studies in which both activation energies and pre-exponential factors have been reported. Except as noted, they are based upon a model of pyrolysis that is first order in kerogen, and normally the rate data are those either for total mass loss or the production of oil. Hence, the “model” can be simply represented as:

$$dX/dt = -A \exp(-E/RT)X$$

in which X is a conversion parameter, expressed in terms of remaining unconverted fraction. In many of these studies, a variety of different fitting techniques were employed (e.g., Friedman, Coates-Redfern, and simple Arrhenius). The point here is not to evaluate the different methods or studies one against the other, but to provide a rough sense of how much agreement there is in the literature on pyrolysis kinetics.

It is immediately apparent that despite the clustering of results on the graphs, the actual rates in the temperature regions of most interest can diverge from one another by significant amounts. In the case of the kukersite samples of Fig. 5.3a, the difference near 400°C ($1,000/T[\text{K}] = 1.49$) is about two orders of magnitude. The spread in reported values for Green River oil shale is not as great near 400°C see (Fig. 5.3b, which shows an order of magnitude spread), but there are still significant differences in reported activation energies that lead to differences of even greater magnitude near temperatures of interest. Likewise, there is a significant disparity in the results reported for Rundle Australian oil shale kerogen in Fig. 5.3c. Also, these results point out that there can be significant differences between the kerogens from different samples. The kerogen from kukersite shows typically higher reactivity than is shown by the Green River or Rundle samples. Hence, there is not surprisingly a dependence of kinetics on the origin of the shale.

This comparison of kinetics is not offered to evaluate the relative merits of any one study over another. It is to point out that there remain significant unresolved differences in reported kinetics, and that this is an issue that will seemingly require further work to resolve.

The Nature and Role of Thermobitumen

At many pyrolysis conditions, thermobitumen (also referred as pyrolytic bitumen or “metaplast” in coal chemistry) is an important intermediate of oil shale pyrolysis. The formation of the thermobitumen has historically caused technological problems in retort design and development due its sticky and plugging character. The thermobitumen can be defined as an intermediate organic substance, which is organic solvent-soluble but nonvolatile at its formation temperatures. Several researchers define the bitumen more specifically as a benzene soluble pyrolysis intermediate [165]. The nonvolatile thermobitumen is used in models as a single pseudo-component that precedes oil generation. In contrast to the thermobitumen, the oil is defined as a volatile organic product of the pyrolysis process. The kinetics of thermobitumen formation have been described in several papers, for Green River oil shale in [18, 165] and for Kukersite oil shale [62, 64, 136].

The observation of thermobitumen formation has been incorporated into a number of mechanisms [8, 76, 83]. Generally pseudo-first-order formation reactions are assumed. For example, a qualitative thermal degradation mechanism

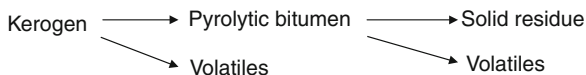


Fig 5.4 A generally accepted mechanistic scheme for pyrolysis of kerogen

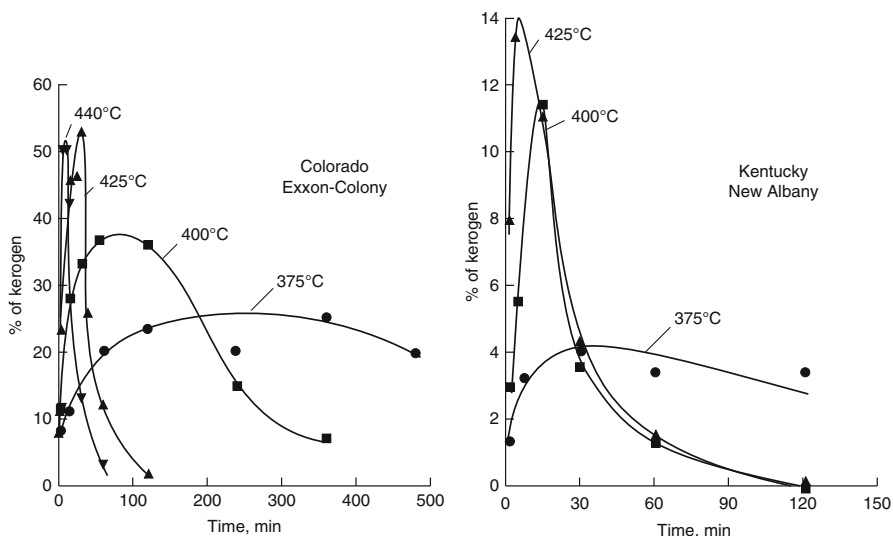


Fig. 5.5 Time and temperature dependence of pyrolytic bitumen for Colorado and Kentucky oil shales ([165], with permission)

proposed by [1], and now fairly widely accepted in general form by many other researchers, is shown in Fig. 5.4. It embodies the well-established feature that there is a breakdown of kerogen to extractable bitumen that precedes a significant amount of oil release. The thermobitumen formation, its composition, and yield, are related to the time–temperature history of the process and to the oil shale kerogen structure. It is now more generally believed that it is the second stage of volatiles formation (from the thermobitumen) that gives rise to most of the oil product. Light gases may be released in both volatiles’ release periods.

Figure 5.5 shows the time and temperature dependence of thermobitumen yields for western US high oil yield Colorado oil shales (Type I kerogens) and eastern US low oil yield Kentucky New Albany oil shale (Type II kerogens). Figure 5.5 indicates that low oil yield non-softening oil shales cannot form considerable amounts of intermediate pyrolytic bitumen. This has been explained by cross-linking behavior of these oil shale kerogens and direct kerogen conversion to residue, but also by autocatalytic reactions between bitumen and kerogen [165].

There are few studies on thermobitumen characterization, but generally its chemical, physical, and thermodynamic properties have been little studied. The properties and composition (elemental composition, molecular weight distribution)

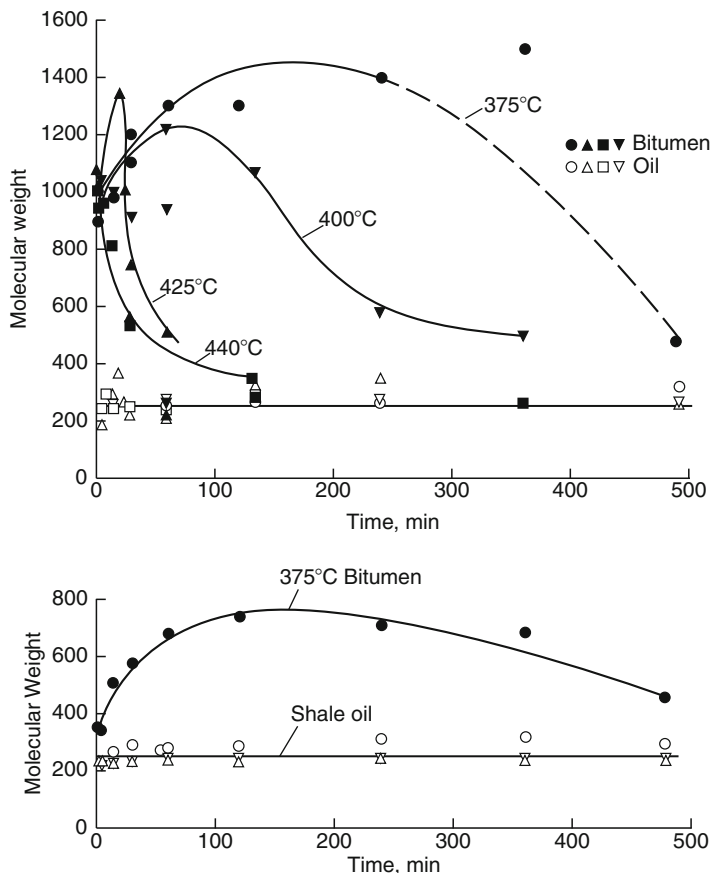


Fig. 5.6 Molecular weights of oil and bitumen versus time and temperature for (a) Colorado (Exxon-Colony) and (b) Kentucky (New Albany) oil shale ([165], with permission)

of thermobitumen is temperature and time dependent. Figure 5.6 shows the average molecular weights of oil and bitumen as a function of time and temperature for western US Colorado (Exxon-Colony) and eastern US Kentucky (New Albany) oil shales, and Table 5.7 presents thermobitumen characteristics of Estonian kukersite oil shale. The results of Table 5.7 show the expected decrease in bitumen molecular weight as conversion progresses to greater extents at higher temperatures.

These and other available studies [136, 137] indicate that the thermobitumen relative to oil produced at same temperature has lower H/C atomic ratio (and higher aromaticity) and higher number-average molecular weight (depending on oil shale and temperature-time history, the thermobitumen can exceed a value of 1,500 Da). It was noted by Miknis and Turner [165] that atomic H/C and number-average molecular weights of the thermobitumen produced were strongly time and temperature dependent, while oil showed remarkably constant values at all times and

Table 5.7 Thermobitumen characteristics of Kukersite oil shale (elemental composition of organic matter C 82.1%, H 10.63%, S 0.75%, O + N 6.5% and atomic H/C 1.55) from thermochemical conversion in a Fischer retort [65, 162]

Process conditions (temperature, time)	Yield, % thermobitumen per organic matter	Elemental composition, %					
		C	H	S	O + N	H/C	Mol. weight
275°C, 456 h	17.9	83.0	10.1	0.50	6.7	1.46	710
300°C, 387 h	69.8	85.1	8.77	0.32	5.8	1.24	1,300
340°C, 12 h	59.8	83.8	9.78	0.52	5.9	1.40	1,240
360°C, 4 h	63.8	83.6	9.56	0.50	6.3	1.37	790
380°C, 4 h	35.6	85.3	8.85	0.53	5.3	1.25	651

temperatures. These results on bitumen are in general agreement with the results of [131] on Colorado oil shale, which showed that this fraction had a very high molecular weight (a significant fraction >1,000 Da). In this latter study, the oil itself had a higher number-average molecular weight than observed by Miknis and Turner [165], presumably due to the difference in pyrolysis conditions, which favored evaporation of higher molecular weight fractions.

In addition to direct pyrolysis (retorting) other technological solutions, such as supercritical gas extraction, hydrolysis, or thermal dissolution with solvents, take advantage of the chemical processes that occur at thermobitumen formation stage.

Competitive Reaction Processes and Hydrogen

An important concept in coal thermochemical decomposition is formation of volatile and nonvolatile reactive radical components as a result of bond breaking in the macromolecular structure. Reactions between radical components can lead to char formation, if the radical species involved are located on large fragments of the network structure. Stabilization of radicals by hydrogen can result in volatiles (or potential volatiles), if the hydrogen capping of the structures prevents their incorporation into a new network structure.

On the other hand, the formed volatiles can undergo secondary reactions prior to escaping the reacting particles. This may happen in contact with solid material or in the vapor phase. Such secondary reactions are promoted by long residence times in high-temperature zones within a particle or a reactor. Thermochemical conversion in the presence of hydrogen can result in an increase in non-polymeric volatile hydrocarbons, if a radical secondary reaction pathway can be intercepted by hydrogen capping of a radical. In addition to helping reduce the macromolecular structure to smaller species by the above routes, hydrogen is also consumed in reducing sulfur, nitrogen, and oxygen that exist in the kerogen structure [99]. Hydrogen can be introduced into these roles either directly from the gas phase or from a hydrogen-donor solvent [99]. There are effects of temperature, pressure, and catalysts on these hydrogen reaction pathways [99, 107].

Technological Aspects of Shale Oil Recovery

The fundamental chemical and heat and mass transfer processes in oil shale retorting have been described to a limited degree in comparison to similar coal and biomass processes. By comparison, there is a rich literature on practical oil shale retorting technologies (including flow sheets, process descriptions, and product characterizations) [8, 30, 99]. There are also reviews/reports covering processes from laboratory scale through process-development unit scale to commercial scale: [15, 20, 85, 97, 101, 122, 140, 142]. The above books and reviews also cover a number of other important topics associated with oil shale processing, such as availability of oil shale reserves [77, 85, 142], oil shale mining [8, 85], research and development needs [77, 85], socioeconomic problems [85], environmental impact [77, 85, 142], oil shale upgrading economics and shale oil cost components [38], shale oil refining [85, 129] and future perspectives [129, 142].

Over hundreds of years of oil shale development, hundreds of retorts (retorting processes) have been invented [85]. Through the long history of oil shale utilization, *ex situ* (above the ground or surface) retorting technologies have been practically the only commercial technology for oil production from oil shale. In *ex situ* processing, the oil shale must be mined (using surface mining or underground mining), crushed, and transported to the processing plant for retorting. By comparison, *in situ* processes cause less land surface disturbance associated with mining. This may involve limited excavation to access oil shale sources or to create permeability by fracturing or drilling heater holes or production wells. Because the oil shale is retorted in the ground, *in situ* processing requires that the produced oil be extracted through an oil well in the same way as is conventional crude oil [20]. Therefore, commonly cited advantages of *in situ* process are limited mining and solids' (oil shale and spent shale) handling, and no expense associated with aboveground retorting equipment. The disadvantage of *in situ* processing involves the complexity in controlling process parameters. There are also concerns raised regarding the ability to capture all of the oil produced underground.

In addition to the issues of technical viability (including process controllability) and capital cost, the choice to use *ex situ* as opposed to *in situ* processes depends on factors such as richness of the oil shale, the depth or thickness of the shale bed, the accessibility to deposits, and environmental considerations (associated with escape of oil into groundwater or extraction of materials from spent shale, e.g.). Again, *ex situ* processes are often also regarded as environmentally problematic beyond their mining impacts, due to problems of solid residue disposal and potential for groundwater pollution from that source.

Besides the simple *ex situ* and *in situ* classifications, there are many other retorting classification schemes used in the literature as technologies can differ in various aspects such as process principle. These include process modes such as batch, semi-batch, or continuous, as well as process flows including cocurrent, counter-current, or crosscurrent. An important classification is based upon heat-transfer mechanism to the

shale (direct or indirect, and what the carrier is in direct) as well as heat generation method. In addition, retort style, complexity of technology or by-product processing can be bases of classification.

A vitally important design consideration is always thermal management, both in terms of heat generation and heat transfer to the shale to be retorted. Heat can be transferred to oil shale by different means:

1. *By conduction through a retort wall.* To this group belonged ex situ technologies such as the vertical Pumpherson retort (Bryson retort) [79] or Davidson horizontal rotary retort [80]. In these types of ex situ technologies, heat is transferred through the retort wall. Due to the slow conduction that characterizes such retorts, many such processes are mainly of historical interest as their throughputs per unit of vessel volume are low. Development phase processes of this genre are the Oil-Tech electrically heated vertical retort process (Ambre Energy Limited) [140] and the A.F.S.K. Hom Tov co-pyrolysis process (Mishor Rotem). The principle of wall conduction can also be applied to in situ technologies. In that case, it involves placing heating elements or heating pipes into the oil shale deposit. Representative of this approach is the Shell In Situ Conversion Process (ICP) technology (Shell Mahogany Project) [140], which uses electric-resistance heaters combined with a surrounding “freeze wall” to confine the retorting products. Another example is the EGL Oil Shale process [140] in which heat is transferred by superheated steam (in a closed system) through a series of pipes serving as heat exchangers below the oil shale bed. The Geothermic Fuel Cell™ approach (GFL™) developed by Independent Energy Partners, Inc. (IEP) uses a high-temperature fuel cell stack [140].
2. *By gases from shale combustion in the retort* (referred to as the directly heated retorts approach). These technologies utilize heat that originates from burning materials (char and oil shale gas) inside the retort and is therefore also called internal combustion retorting. The heat is transferred through the retort by gases generated in the combustion process. In combustion retorts the retorting gas is diluted and has low calorific value (for syngas classification depending on the heating values, see [77]). A currently used commercial ex situ retorting technology of this type is the Fushun process [101] in China. Other examples of thoroughly investigated ex situ technologies based upon this approach are the Kiviter process (early versions), Nevada-Texas-Utah (NTU), Paraho Direct, Union “A” and Superior Multimineral processes [8, 77]. In situ retorting also utilized this principle in technologies that burned oil shale underground. An example of this was the Occidental Petroleum Corporation Oxy process [85] (modified in situ combustion retorting process).
3. *By gaseous heat carrier heated outside retort* (referred as indirectly heated retorts). In this case, heat is transferred by hot gases heated in an outside furnace and then injected into the retort (or retorting bed). Again, in these systems the retorting gas is diluted and has low calorific value. Currently used commercial ex situ technologies of this group are the current Kiviter process in Estonia and Petrosix process in Brazil [8]. Other main ex situ technology examples are Union

“B,” Paraho Indirect, Superior Indirect processes [8], and fluidized bed-based processes. Similarly, in situ technologies can utilize gases that are heated aboveground (such as by combustion), which are then injected into the oil shale formation as heat carriers. Examples of such hot-gas injecting methods are the Chevron CRUSH process and the Petro Probe process and the in situ gas extraction technology (IGE) of Mountain West Energy [140].

4. *By solid heat carrier heated outside the retort* (referred indirectly as heated retort). In this instance, heat is transferred by mixing hot solid particles (heated outside the retort) with the oil shale. Reactive heat carriers, such as oil shale ash, or nonreactive, such as sand or ceramic balls, have been used. In these processes retort gases with high calorific value are produced. These are ex situ processes that typically take place in rotating kiln-type retorts. Currently used commercial ex situ technology of this type includes the Galoter process [44] in Estonia, which utilizes hot shale ash as the heat-carrying medium. Other main technologies of this type include the Alberta Taciuk Process (ATP), TOSCO II (developed by The Oil Shale Corporation, utilizing externally heated ceramic balls 15 mm in diameter as heat carrier) Lurgi-Ruhrgas (retorting is accomplished by mixing with spent shale/sand) [77], the Shell SPHER Process (Shell Pellet Heat Exchange Retorting) [49], and the LLNR HRS (Lawrence Livermore National Laboratory Hot Recycled Solid) process [20].
5. *By other means* such as radio frequency [15], microwave [11], solar [17] or nuclear explosion (e.g., Project Bronco) [8], etc. A number of recent shale oil in situ recovery schemes (e.g., Raytheon/Schumberger; PyroPhase) have been proposed based on volumetric heating by means such as radio frequency or microwave heating [140]. These have thus far been mostly of interest on the research and development level [15].
6. *By combinations of the above*. For example, a combination of solid and gaseous heat carriers is utilized in hot recycle solids fluidized bed retorting systems (e.g., KENTORT II, [23, 133]). Since gas density is about 1,000 times lower than that of oil shale, assuming that roughly same mass heat carrier must be contact the shale, then a large volume of gas is needed to heat the oil shale [18]. The KENTORT II [23, 133] uses recirculating hot spent shale from a gasification section.

The above-mentioned Shell SPHER process and LLNR HRS process could arguably also be included in this class of processes.

An example of an in situ combined heat-transfer mode process could be Electrofrac™ (Exxon Mobil Corporation) [140], which combines wall conduction and volumetric heating through electrically conductive material (used to fill fractures).

There are a large number of different retorting solutions. Generally, the performance of retorts (in situ or ex situ reactors) are typically evaluated or compared based on the percentage of Fischer assay yield achieved and an overall thermal efficiency (as energy efficiency). Typical commercial-scale retorts, with the exception of fluidized bed retorts, have lower oil yields than obtainable from Fischer

Table 5.8 Some selected ex situ retorting technologies

Process/retort	References
Fushun retort	[101]
Brazilian Petrosix	[77, 85]
The Nevada-Texas-Utah retort or NTU (also known as the Dundas-Howes retort)	[8, 85]
The Paraho direct/indirect process	[85, 99]
The Union Oil retort “A” (Union Oil Company)	[8, 76, 77, 159]
The Union Oil retort “B” indirectly heated retort (Union Oil Company)	[8, 76, 77, 85, 159]
The Union Oil Steam Gas Recirculation (RSG) retorting process (Union Oil Company)	[8]
The Superior Oil process	[8, 85]
TOSCO II (Tosco corporation)	[77, 85, 99]
The Lurgi-Ruhr gas process	[8, 76, 77, 85, 142]
Kiviter process	[8, 101, 159]
Galoter process	[8, 44, 101, 159]
Aostrat Taciuk Process (ATP)	[8, 101, 142]
Chamber oven (similar to coke batteries)	[159]
HYTORT (Institute of Gas Technology, IGT)	[38, 106]
Chattanooga process (pressurized fluid bed reactor)	[140]
Gas combustion retort, US Bureau of Mines	[8, 76, 77, 142, 159]
Oil-Tech vertical surface retort technology (Millenium Synfuels, LLC)	[140]
KENTOR II	[133]
Shell SPHER processes (Shell Pellet Heat Exchange Retorting)	[49]

assay. For example, for modified in situ internal combustion retorting, it is around 60% [99] of Fischer assay. For a Fushun generator type of retort, this value is 65% [101] and for the Kiviter type of retort 70% [101]. Higher values are obtained with Petrosix retorting 85–90% [101], Galoter retorting 85–90% [101], and for Taciuk retorting 82% [101].

The thermal efficiency is defined as heat of desired product divided by the total heat of the process [99]. For example, some comparisons may involve using the equation

$$\text{Thermal efficiency} = \frac{\text{Gross calorific value of (oil + gas)}}{\text{Gross calorific value of shale + heat of retorting}}$$

which can be found in Probstein and Hicks [99].

More detailed evaluation of processes comes down to desired product yields (oil and gas) and energy consumption per unit of desired product produced, including additional energy requirement such as for gas purification, spent shale disposal, or water treatment.

References offering insights regarding the construction details and operational principles of the retorting equipment referred to above, including product characteristics, are found in Tables 5.8 and 5.9. As there are hundreds of retorting

Table 5.9 Some selected in situ retorting processes and technologies

Process/retort	References
Occidental Petroleum “Oxy”	[8, 77, 85]
Sinclair oil and gas company process	[76, 77]
Equity Oil company process	[76, 77]
Shell Oil’s thermally conductive in situ conversion process	[77, 140, 142]
Osborne’s in situ process	[77]
Dow Chemical Co.’s process	[8, 77]
Equity Oil company process	[8]
Chevron’s Technology for the Recovery and Upgrading of Oil from Shale (CRUSH) process	[140]
EGL oil shale process	[140]
Electrically enhanced oil production (EEOP) (Electro-Petroleum, Inc.)	[140]
PetroProbe process (Petro Probe, Inc.)	[140]
Electrofrac™ (Exxon Mobil Incorporation)	[140]
Geothermic Fuel Cell™ technology (GFL™)	[140]
In situ gas extraction technology (IGE), Mountain West Energy	[140]
Radio frequency/critical fluid oil extraction technology (Ryethon and CF technology)	[140]
EchoShale in-capsule process (Red Leaf Resources, Inc.)	[140]
PyroPhase	[140]
American Shale Oil Company (AMSO) process: Conduction, Convection, Reflux (CCR) process (former EGL Resources process)	[140]

options that have been considered, this is far from being a complete list of possibilities. Nonetheless, it offers some insight into some significant processes. The next sections offer a few more details on selected ex situ and in situ processes.

Ex Situ Technologies: An Example and Some Further Considerations

There are many ex situ retorting technologies that differ by reactor types (fluidized bed, moving packed bed, solid mixers), by operating conditions (temperature, residence time), technical details such as drying of feed, feed distributor, discharge of spent shale, oil and gas separation (oil and gas separation from offgas), heat recovery or by-product utilization. Therefore in addition to the pyrolysis reactor, the heart of retorting process, a particular retorting technology includes various other components (unit operations) in the plant.

Figure 5.7 shows a principal schematic diagram of the Galoter process [44]. The principle of the Galoter process is heating fine-grained oil shale (particles with size below 25 mm) in a horizontal rotary kiln-type retort, with contact of hot oil shale ash obtained from solid retorting residue combustion outside of the retort. The process operates in continuous mode with oil shale and ash in cocurrent flows. The

properties of the shale oil produced (specific gravity, H/C ratio, viscosity, boiling range, and hydrocarbon types) depend upon retorting temperature and residence time, of course, but can also depend on other factors such as condenser construction and temperature of recovery and separation of shale oil and the reactive properties of the hot shale residue heat carrier.

A heat-transfer medium (the heat carrier) can generally be reactive or nonreactive. Examples of reactive heat carriers include the gaseous heat carriers such as hydrogen or solid heat carriers such as oil shale ash. Oil shale ash from carbonate oil shales has chemisorptive properties, due to its alkaline nature, and can reduce the concentration of H_2S in the product gas as well as phenolic compounds in the oil [88]. Also the iron oxide in ash shows potential to reduce H_2S in the gas, but has little effect on phenolic compounds [88]. It should, however, be emphasized that heat carrier ash used in solid heat carrier retorts does not affect significantly the sulfur concentration in oils (i.e., organic sulfur) [40, 88].

It needs to be emphasized again that an important parameter in ex situ retorting design is the heat up time of the retorted shale. This determines overall process time and therefore reactor volume and thus retorting process cost [18], but also impacts retort oil quality. The time to transfer heat to shale depends on the feed oil shale particle size. Often, operational details require specific particle size ranges [8]. It has been indicated that [18] the heat up time of the oil shale particles larger than 1 cm scales roughly as diameter squared and thus a heat up time of 2.5 min can be estimated for 10-mm particles and 4 h for 100-mm particles. Accordingly, the ex situ technologies have been divided in three groups, based upon particle size:

1. Processes with large feed particle sizes (so-called lump oil shale). These processes take place over the longest time scale; the shale residence time in retorts is measured in hours. For example, the industrial Kiviter process [8] uses a feed size of 10–125 mm and the Fushun process of 10–75 mm [2].
2. Processes that use coarsely ground particles. The shale residence time scale is of minutes. For example, the industrial Galoter process [8] uses a feed size of 0–25 mm [2].
3. Processes fed with pulverized oil shale with size below 5 mm. The residence time is shortest, with the time scale of seconds. This is used in fluidized bed retorting units [151]. The fluidized bed retorting systems are less developed than the two former types and no commercial units are yet in use.

In Situ Technologies: Further Considerations

The common principle of in situ processes is heating the oil shale deposit underground. Different versions use different methods of heat transfer, as already described. With in situ technologies there is an opportunity to utilize poorer and deeper oil shale deposits than can be used for conventional aboveground processing [71]. Although a number of field-scale experiments have been conducted over the

last decades in several countries [15, 77, 85, 97] no in situ technology-based commercial plant has been placed in operation to date. However, several of the latest innovative technological approaches involve in situ processes [140].

There are different possible ways of classifying in situ technologies (see [77]). The most common is classification into true in situ processes and modified in situ processes. Some define the true in situ processes as involving minimal disturbance of the oil shale ore bed, and the modified in situ as processes as any that use rubblizing either through blasting or partial mining. Therefore the distinction between true and modified in situ processes is a matter of degree of the bed disturbance.

True in situ processes thus do not generally require significant mining. This category of in situ processes uses natural rock permeability or permeability created by artificial fracturing (by explosives or hydrostatic pressure) in place. The true in situ processes follow a general sequence involving dewatering and establishing measures to minimize contact between groundwater and the reaction zone; fracturing or rubblizing to create permeability (if natural permeability is not sufficient); heating the oil shale by ignition, hot fluids, or other means; recovering oil and gas through wells [85].

The modified in situ processes involve partial mining under the oil shale deposit to create void space followed by rubblizing the rest into the created void. To create voids about 10–25% of overall space is mined out [77].

Final Considerations and Future Directions

This review was intended to capture many aspects of the current state of knowledge and basic research directions in the field of oil shale research. It did so in the context provided by currently and historically explored technologies for oil shale conversion. Generally speaking, there is more new development interest in oil production processes, but the direct combustion processes will remain in use in particular instances (such as in Estonia). While the pyrolytic phenomena that shale undergoes are common to both oil production and combustion processes, there has not been as much emphasis on fundamental exploration of these phenomena from the combustion side, and in that case there are other technologically important issues that have captured more basic research interest (e.g., the behavior of ash in the boilers, the high-temperature corrosion of boilers, the problems of ash handling and disposal, the problems of sulfur capture). For the combustion community, the behavior of the organic portion of the ash has been somewhat secondary, and even the final phases of organic materials' burnout, which has captured the attention of many researchers in the coal combustion community, has been of less interest, because of the inherently higher reactivity of oil shale chars as compared to coal chars.

From the perspective of those who seek to produce oil, the major problems have been those of thermal management and the handling of large amounts of solids, as well as dealing with a range of environmental problems associated with the

processing (whether aboveground or in situ). What can be economically done with oil shale in light of the above has dictated the nature of the processes more than consideration of the chemical aspects. Nonetheless, it has been observed that there can be factors whose importance may be sometimes overlooked. Issues of mass transport can materially impact both yields and quality of the product oils, and may be sensitive to factors such as pressure, particle size, heating rate, temperature, and residence time in a hot environment and gaseous environment. All of these factors have been studied, but the general impression is that more work is needed to better establish general trends. Likewise, there have been an enormous number of studies performed on elucidating the kinetics of pyrolysis, but rarely has there been a critical examination of results obtained on the same material examined by different means in different laboratories. As a result, there is a crude understanding of rate processes, but one that for predictive purposes cannot be claimed to be better than an order of magnitude. Despite large numbers of carefully performed studies, there has not yet been closure on the overall nature and rates of the many processes that determine behavior in practical processes.

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