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An Overview of Oil Shale Extraction and Processing

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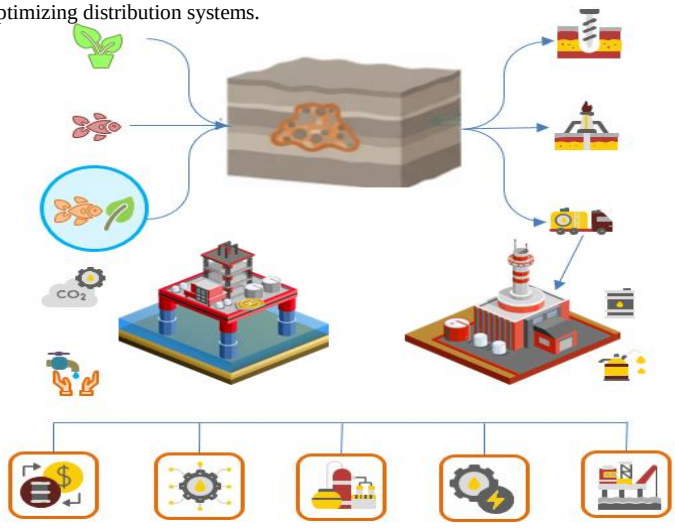
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A B S T R A C T

Oil shale is a dense sedimentary rock containing kerogen, a solid organic material that can be converted by heating into combustible gases, shale oil, and spent shale. It is commonly classified as terrestrial, lacustrine, or marine, depending on its depositional environment. Shale oil can be produced using in situ methods, including True In Situ (TIS) and Modified In Situ (MIS), or by ex-situ Aboveground Retorting (AGR). TIS involves fracturing deposits and retorting underground, while MIS combines partial mining with underground retorting. AGR requires mining the shale and processing it in surface retorts. Mining methods include surface and underground mining, with underground operations often using room-and-pillar systems. Surface mining is selected based on overburden thickness and stripping ratios. Produced shale oil generally requires upgrading through visbreaking, coking, hydrotreating, and additives before transportation or refining. Further refining may involve distillation, hydrocracking, catalytic cracking, or reforming. Underground mining offers greater mechanization potential, higher production rates, easier ventilation, and reduced subsidence, but requires high capital input and may lower recovery due to pillar losses and geological defects. AGR provides high recovery and controllability but involves high operating, safety, and environmental costs. In situ methods are attractive for deep deposits, lower mining costs, reduced solid waste, and broader applicability, but suffer from poor control, high drilling costs, and lower recovery efficiencies. Environmental challenges include dust emissions, waste disposal, air pollution, water demand, water contamination, subsidence, and land reclamation. Shale oil can be used as boiler fuel, refinery feedstock, or petrochemical feedstock, though logistics remain challenging. Future research should focus on reducing costs, improving retorting efficiency, understanding parameter effects, additive use, and optimizing distribution systems.



1. Introduction

1.1. Oil Shale

Oil shale refers to a mixture of a variety of fine-grained sediments which have been formed over a vast geological period, resulting in the formation of a dense, tough rock, with varying colour from light tan to black, containing organic matter called kerogen, from which shale oil and combustible gases can be drawn by thermal deposition with ensuing distillation from the respective reaction zone [1]. Oil shale forms part of a huge, considerably untouched hydrocarbon resource due to its unconventional nature, in that, oil cannot be

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directly produced from the oil shale by sinking a well and pumping oil to the surface. Instead, oil is produced by thermal methods from the kerogen within the shale. Kerogen, contained in the oil shale, refers to a solid material which is intricately lodged within the matrix of the mineral [2-4].

1.2. The Origin and Deposits of Oil Shale

Speight [5] suggests that oil shale contains organic matter sourced from different types of marine and lacustrine algae, together with debris from land plants, however, this composition is dependent on the depositional environment and the source of sediment. The organic matter can also be composed of the carbon-containing remains of spores, plant cuticles, algae, pollen and corky components of woody and herbaceous plants, plant waxes and plant resins [4, 6].

The organic matter constituting the oil shale is unstructured, namely amorphous (bituminite), thus the exact origin of some organic matter is obscure [5]. Some carbon-containing materials such as phosphates and carbonate minerals are assumed to be part of the mineral matrix of the oil shale and are excluded from the definition of the composition of the organic matter in the oil shale [5]. Furthermore, the lack of biological structures which are recognizable implies that the actual precursor organisms which constitute the organic component of the oil shale are still relatively unknown [7]. This is in complete abstract to coal, which contains recognizable biological structures [5]. Thus, it was proposed by Speight [5] that the materials which comprise the organic components be split into four broad groups, namely, bacterial origin, the product of bacterial degradation of algae, other organic matter or all the above. These materials which make up the oil shale are, however, composed mainly of carbon, hydrogen, oxygen, nitrogen and sulphur [5].

Scouten [4] further reported that oil shale does not undergo a similar maturation process when compared to petroleum and coal. Instead, oil shale produces kerogen. However, Speight [8] argued that there are indications which implied that kerogen may be a by-product of some maturation process occurring in the oil shale. It was postulated that the maturation-formed kerogen, which forms the residue which remains in the oil shale, is ejected from the organic matrix due to insolubility and unreactivity under maturation process conditions [8].

Known deposits of oil shale are found in every continent throughout the world. These deposits range in size from tiny deposits posing almost no monetary value to extremely vast deposits with the potential to produce large quantities of shale oil for processing [9-11]. From exploration of deposits using careful drilling and geochemical investigation (Gravimetric, volumetric and heating values), it was shown that oil shale reserves have the potential to supply approximately 4.8 trillion U.S. barrels of shale oil, with the Green River Formation in the western United States having the potential to produce roughly 3 trillion U.S. barrels of shale oil by itself [5].

According to Scouten [4], many authors have published locations of major oil shale reserves. In almost all reporting, the United States is always number one with approximately 60 % of the total reserves, with Asia frequently following at number two.

Table 1 below indicates estimated oil shale reserves and distributions in respective regions.

Table 1. Estimated oil shale reserves per region [12].

Region	Shale Reserves (U.S. Tons × 10^6)
Africa	23 317
Asia	83 836
Australia	4 534
Europe	52 845
Middle-East	5 792
North America	539 123
South America	11 794

Despite the large reserves of oil shale available, petroleum-based crude oil still proves cheaper to produce than shale oil from processed oil shale. This comes down to the additional costs associated with mining and extracting the energy from oil shale. As a result, only few countries, such as China, Estonia and Brazil exploit oil shale resources for shale oil production [9,10]. However, with the declining availability of petroleum, in conjunction with the increasing costs of products made from petroleum sources, oil shale provides an alternative and an opportunity for the supply of energy to cater for energy demands from the world soon [9,11]. Furthermore, considering that nearly 100 major deposits exist worldwide across 27 countries, oil shale can provide a resource for fuel production for more than 400 years [4].

1.3. Oil Shale Types

As per Hutton [14], oil shale was deposited in a large array of environments, including saline to freshwater lakes and ponds, marine basins, subtidal shelves and shallow lakes and ponds related to coal-forming peat in coastal swamp environments suitable for deposition. Hutton [13] further explained that the varying environment types in which the depositions took place resulted in different oil shale types, displaying a variety of organic and mineral compositions [14].

Speight [5] proposed defining different types of oil shale into three main categories based on the mineral content of the shale. These three categories included:

- Carbonate-Rich Oil Shale

This specific type of oil shale contains high proportions of carbonate minerals such as dolomite and calcite. These oil shales usually have the organic-rich layers compressed between the carbonate-rich layers, resulting in hard shales, resistant to weathering and extremely difficult to process concerning mining [5].

- Siliceous Oil Shale

These oil shales are usually dark brown or black in appearance and are deficient in carbonate materials but contain large quantities of siliceous materials such as quartz, clay, opal, chert and feldspar. These shales are more suited towards extraction by mining due to a lower weather resistance and lower degree of hardness as opposed to carbonate-rich oil shale [5].

- Cannel Oil Shale

This type of oil shale is typically black and consists of mineral grains which are completely enclosed by organic matter. This implies a softer oil shale which becomes much easier to process and extract by mining [5].

However, Hutton [13] states that it is much more common to grade and define oil shale based on their respective formation, origin and organic content. As a result, Hutton [13] proposed the following three categories to classify oil shale:

- Terrestrial Oil Shale

This type of shale, as shown below, was formed as a result of deposits of precursors, termed cannel coal, in stagnant and oxygen-deficient waters on land. These areas include coal and peat-forming bogs and swamps.



Figure 1. Terrestrial oil shale (cannel coal) [9].

Cannel coal is composed of resins, spores, waxes and cutinaceous and corky materials which come from terrestrial vascular plants [5]. This shale type is particularly rich in oil-generating organic matter which tends to be thoroughly lipid-rich. Although the deposits are relatively small, the grade of the deposits themselves can be extremely high.

- Lacustrine Oil Shale

These oil shales are usually termed lake-bottom-deposited shales and these deposits include lipid-rich organic matter which was formed from algae residing in freshwater, brackish or saline lakes [5]. The Green River Formation forms part of a lacustrine oil shale deposit which was extensively studied. This deposit, together with various others in Australia and Queensland, is also termed a lamosite deposit [5]. It is a pale, greyish-brown or dark grey to black oil shale which has the main organic constituent lamalginite. Lacustrine planktonic algae result in lamalginite formation. Other minor components, accompanying lamalginite in the shale, include vitrinite, inertinite, telalginite and bitumen [5]. Note that the term bitumen, in this case, is used to refer to a component, soluble in petroleum-based and organic solvents, which is dispersed in the kerogen network in the oil shale. This term is more appropriate when used to describe the organic portions of tar sand (oil sand) deposits or road asphalt in European of African countries. Thus, by using this term to describe a soluble portion of the organic make-up of oil shale, it becomes a term of convenience rather than scientific correctness [5].

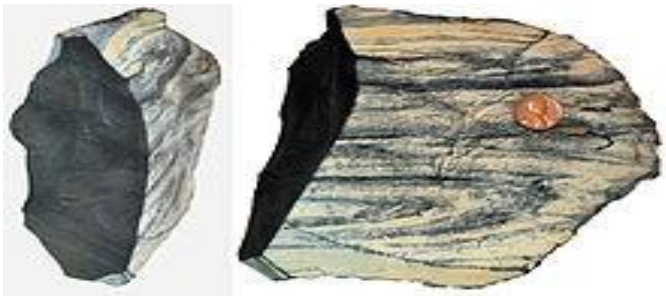


Figure 2. Lamosite oil shale [9].

Torbanite is another form of lacustrine oil shale which is black in colour and composed mainly of telalginite. It is usually found in freshwater to brackish lakes in small deposits of high grade [5].

- Marine Oil Shale

Marine oil shale, commonly known as marine-bottom-deposited shale, consists of organic matter that is rich in lipids. This organic matter was created from marine algae, unicellular organisms such as acritarchs and marine dinoflagellates [5]. The figure below represents the two main settings which can lead to the formation of marine oil shales.

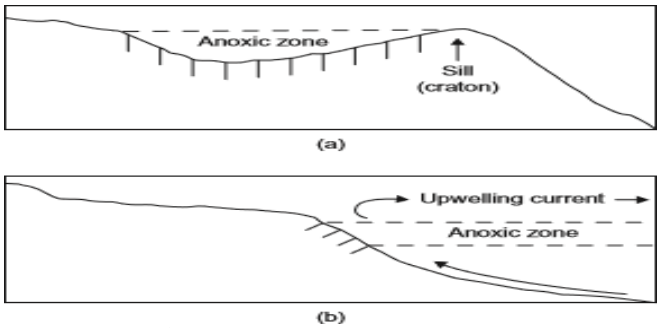


Figure 3. Schematic of an anoxic-silled basin (a) lake shore and (b) sea shore [4].

As per Figure 1 (a), an anoxic-silled basin occurs near shallow waters of continental shelves. High deposition rates occur due to high growth rates of phytoplankton near the surface. The sill, in turn, prevents any oxygen-laden water from entering the water already contained within the sill. Thus, with no oxygen-laden water continuously entering the system, organic matter decomposition rapidly depletes oxygen within the water confined in the basin, providing a highly anoxic environment which promotes preservation [5].

In Figure 1 (b), the circulation of ocean current over an oxygen-depleted, cold bottom layer results in an anoxic zone in an upwelling area. This nutrient-rich current mixes with the carbon-dioxide-rich and light-rich eutrophic zone [5]. As a result, an environment is formed which can sustain extremely high rates of organic production. environments like this occur along the western African coasts and the coast of western America [5].

Marine shales are usually brown to black and occur on broad, flat sea bottoms occurring in thin deposits which are roughly between 10-50 m thick. An example of this can be the Irati Shale in Brazil, extending more than 1000 miles from the north to the south [15]. Marine shales are mainly composed of marinite, tasmanite and kukersite.

Marinite is mainly grey to dark grey to black, comprising lamalginite and bituminite, with small amounts of bitumen, telalginite and vitrinite, derived from marine-based phytoplankton. This type of marine oil shale can be found in seas extending inland from continental margins, usually in areas where there are minimal currents or wave action. An example of marinate deposits is the Devonian- Mississippian oil shale in the eastern United States, covering thousands of square kilometres, with thicknesses of approximately 300 feet [5].

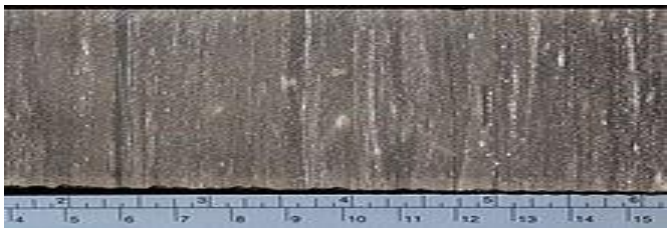


Figure 4. Marinite oil shale [9].

Tasmanite is a brown-to-black marine oil shale type consisting mainly of telalginite. This telalginite originates from unicellular marine algae. This type of marine oil shale contains minimal vitrinite, lamalginite and inertinite. The main deposits are found in Tasmania [5].

Kukersite refers to a marine oil shale which is light brown. It is made up of telalginite, derived from green algae. Main deposits of this type occur in Estonia and western Russia [5].

The following table was drawn up to show the distributions of the different types of oil shale throughout the world.

Table 2. Oil shale distributions by type per major country [5].

Country	Oil Shale Type	Oil Shale Composition	Quantity (U.S. Tons × 10^6)
Australia	Marine, Lacustrine	Marinite, Tasmanite, Lamosite, Torbanite	4 531
Brazil	Marine, Lacustrine	Marinite, Tasmanite, Lamosite, Torbanite	11 734
Canada	Marine	Marinite	2 192
China	Lacustrine	Lamosite	47 600
Estonia	Marine	Kukersite	2 494
Jordan	Marine	Marinite	5 242
Morocco	Marine, Lacustrine, Terrestrial	Cannel Coals, Marinite, Tasmanite, Lamosite, Torbanite	8 167
Russia	Marine	Kukersite	35 470
United States of America	Marine, Lacustrine	Marinite, Lamosite	536 931

It must be noted that apart from the listed countries above, smaller oil shale reserves exist in countries such as Egypt, South Africa, Madagascar, Nigeria, India, Pakistan, Germany, Italy, Spain, Romania, Bulgaria, Hungary, Serbia, Albania, Luxemburg, Poland, New Zealand, Argentina, Chile, Peru, Uruguay and Venezuela. Although smaller in size, these countries can produce vast quantities of shale oil from minor reserves located within their borders [12].

1.4. Properties and Composition of Oil Shale

1.4.1. Organic Component Properties

According to Speight [5], the organic matter, namely kerogen, which occurs within the oil shale allows for significant amounts of shale oil and combustible gases to be drawn by thermal deposition with ensuing distillation from the reaction zone. However, the oil shale itself does not contain any oil and the shale oil must be produced from a process which involves the cracking or thermal decomposition of kerogen to produce the liquid product shale oil.

The required ratio of kerogen-to-shale for commercial grade oil shale is required to be typically within the range of 0.75:5 to 1.5:5 [7]. In comparison to coal, the organic matter-to-mineral ratio found in deposits of coal is usually larger than 4.75:5, indicating that, in some cases of lower hydrogen-containing kerogen, larger quantities of shale have to be processed as opposed to coal to obtain equivalent volumes of synthetic fuel product [7]. This was also indicated by Speight [7], in that, it was reported that oil shale contains approximately 60-90 % inert mineral matter, as opposed to coal, which contains less than 40 % mineral matter. However, the organic matter residing in oil shale does have an advantage in that it contains higher hydrogen and lower oxygen contents as opposed to lignite or bituminous coal [7].

Scouten [4], Koel et al. [16] and, more recently, Speight [8] have reported that the true nature and composition of kerogen are speculative due to the difference in precursors which have led to the formation of the kerogen in the oil shale. The kerogen obtained from different samples indefinitely differs in composition and properties, thus leading to varying qualities of grade, composition and properties of the derived petroleum from these reservoirs [8].

However, considering the largest deposit in the world, namely the Green River Formation, the following composition (by weight) was determined by Baughman [2], who observed that nitrogen and sulphur occurred in much smaller quantities in the organic material as opposed to carbon, hydrogen and oxygen.

Table 3. Composition (% w/w) of the organic matter in the green river formation [8].

Component	Green River Formation Organic Matter Composition (% w/w)
Carbon	80.5
Hydrogen	10.3
Nitrogen	2.4
Sulphur	1.0
Oxygen	5.8
Total	100.0
Hydrogen: Carbon Atomic Ratio	1.54

The following van Krevelen diagram indicates the differing hydrogen-to-carbon ratios which can be used per kerogen type to produce gas or oil. Depending on the type of shale, the kerogen hydrogen-to-carbon ratios can vary greatly. Type I refers to mainly lacustrine oil shale, with Type II and Type III referring to marine and terrestrial oil shale types respectively. Type I kerogen readily produces liquid hydrocarbons with few cyclic or aromatic structures. Type II tends to produce liquid and gas mixtures whilst type III is thick, often resembling coal or wood and this type tends to form coal or gas. Type II has the lowest hydrogen-to-carbon ratio due to the vast ring and aromatic systems in the structure of the kerogen [5].

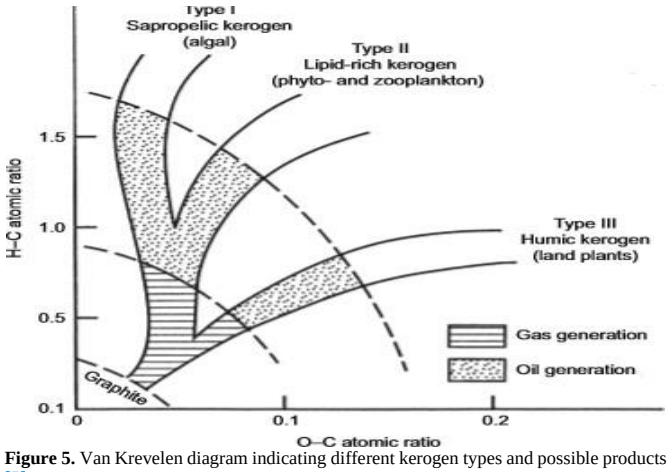


Figure 5. Van Krevelen diagram indicating different kerogen types and possible products [5].

It was also noted by Durand [17], Scouten [4], Speight [8] and Tissot and Welte [15] that due to the high molecular weight of the organic matter, which has been approximated to be in the order of several thousands, and its molecular complexity, oil shale kerogen was almost completely insoluble in petroleum-based and organic solvents such as carbon disulphide. The only

soluble portion, as mentioned earlier, was noted to be bitumen. This implied that, due to the insolubility of the organic matter, temperatures in the order of 500 ºC are required to retort the kerogen and decompose it into shale oil and gas [5]. This process results in a carbon residue or a carbonaceous deposit which remains with the shale residue after retorting. This can be used as an additional source of energy [5].

1.4.2. Mineral Component Properties

The mineral components of oil shale deposits vary greatly based on the relative origin of the shale. However, some carbonate-based oil shale deposits consist of calcite ($CaCO_3$), dolomite ($CaCO_3.MgCO_3$), siderite ($FeCO_3$), nahcolite ($NaHCO_3$), dawsonite ($NaAl(OH)_2CO_3$) and also minute amounts of aluminosilicates such as alum ($KAl(SO_4)_2.12H_2O$) [18]. Beard et al. [18] indicated smaller amounts of sulphur, ammonium sulphate, vanadium, zinc, copper and uranium, which all contain possible by-product value should economically viable recovery processes become developed. Alumina recovery is possible from dawsonite-bearing beds by leaching, precipitation and calcination [5].

Formations such as the Green River deposit contain large carbonate mineral components in the oil shale, including dolomite, nahcolite and dawsonite [5]. This implies that the by-products from oil shale mining and processing have high soda ash and alumina contents, facilitating further use of the remains from processing oil shale. Moreover, Speight [5] proposes that calcium carbonate or calcite provides the potential for low emissions by binding sulphur dioxide and, thus, not requiring limestone for desulphurization. This occurs as follows:

$$CaC0_3 \rightarrow CaO + CO_2 \; 2CaO + SO_2 + O_2 \rightarrow CaSO_4$$

Furthermore, for siliceous-based shale, silicates including quarts (SiO_2), feldspar ($xAl(Al.Si)_3O_8$ (where x can be sodium (Na), calcium (Ca) or potassium (K)) and clay minerals are major components, with carbonates only forming a minor part of the total mineral base [5]. Some oil shale deposits also contain trace amounts of sulphide materials, including pyrite (FeS_2) and marcasite (FeS_2, with distinct physical and crystallographic differences from pyrite).

1.4.3. Thermal Decomposition

Due to studies carried out by Scouten [4], and Speight [7,8], it was found that oil shale kerogen is hydrogen-rich compared to coal. This implies that thermal conversion, mainly by pyrolysis, can lead to higher yields of oil and gas. As a result, per Scouten [4], three carbonaceous products result from thermal decomposition of oil shale, namely:

- Distillable oil
- Non-combustible gases
- High-carbon deposits in the rock pores or on the rock surface as char or a coke-like residue

The relative proportions of oil, gas and char produced varies with the pyrolysis temperature [19]. The proportions are also marginally affected by the organic content composition [4]. It must be noted that each product is contaminated with non-hydrocarbon compounds and these contaminants also vary with pyrolysis temperature [5].

Scouten [4] reported that the yield of oil from kerogen during pyrolysis highly depends on the hydrogen-to-carbon ratio of the organic material. Further investigation showed that South African kerogen containing a 1.35:1 hydrogen-to-carbon ratio showed a lower yield than Brazilian kerogen with a ratio of 1.57. Furthermore, it was shown by Scouten [4] that oil yield and efficiency of conversion are greatly inhibited by higher nitrogen levels in the organic matter.

From Figure 6 shown below, it can be observed that the product yield is largely affected by time in the reaction zone, hence, time is another factor that affects the overall oil or gas yield obtained.

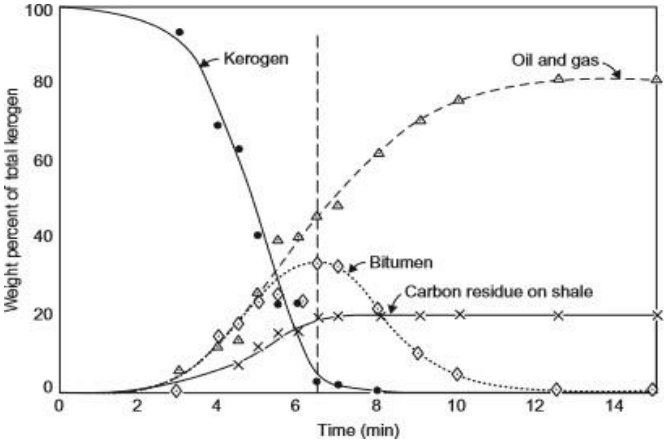


Figure 6. Variation of the product yield from kerogen with time [20].

Temperature plays a crucial role in the decomposition of the organic matter found in oil shale. Scouten [4] reported that low retort temperatures of approximately 300ºC initiate oil shale decomposition, however, the decomposition becomes more rapid at higher temperatures, with the highest rates being reported between temperatures of 480-520ºC. However, Hubbard and Robinson [20] reported that, kinetically, the devolitisation of oil shale begins between 350-400ºC, with the peak rate at 425ºC and devolitisation completing between 470-500ºC. This further emphasises the dependence of processing conditions on relative shale type and origin.

However, with this increase in temperature, oil yield decreases, gas yield becomes higher and the overall aromaticity of the produced shale oil which is dark, odoriferous and waxy, also increases with higher decomposition temperatures [4]. Thus, an upper limit must be imposed on the increase in temperature to prevent the decomposition of the mineral components. In the case of Estonian kukersite shales, calcium carbonate dissociates at high temperatures, namely between 600-750ºC [5], with Scouten [4] reporting that at temperatures approaching 500ºC, calcium, magnesium and calcium carbonates begin decomposing to yield carbon dioxide as the major product. Hence, carbon dioxide must always be presumed as a product in the decomposition process, resulting in vast emission issues related to the processing procedures.

From Figure 6 it can also be seen that the bitumen product peaks and then begins to decrease during longer periods. Scouten [4] associated this with the idea that kerogen decomposes into extractable bitumen at temperatures below 500ºC, however, at temperatures higher than this, occurring over lengthier periods, the extractable bitumen decomposes into oil, gas and carbon-rich residues. However, the lengthier times, higher temperatures and increased resistance to the outward diffusion of the products caused by the mineral matrix severely affect processing costs and quantities produced [4].

The method of retorting or heating the oil shale to produce shale oil are widely documented [21-23]. According to Speight [5], the conversion of kerogen into usable products without the aid of heating has not yet been proven commercially viable, despite schemes being available in demonstration stages. This can be due to the lack of precise molecular understanding of the complex chemical reactions which initially occur to convert kerogen into gas, oil and char [5].

Industrially, kukersite shale poses difficulty in that specific temperature ranges and processing conditions are required to obtain high oil yields. This is due to the higher moisture percentage of the oil shale and the large quantities of calcium carbonate in the mineral structure resulting in higher amounts of specific heat consumption [24]. Furthermore, Yefimov and Purre [24] reported that kukersite forms up to 55-57 wt% of a bitumen-like product during slow-heating within the temperature range of 350-400ºC, also resulting in minimum carbon-rich residue. Moreover, it was also reported that maximum yields occur between 390-39 ºC, whilst heating to 510-520ºC causes the carbon content of the carbon-rich residue to increase rapidly as a result of pyrolysis of unstable, oxygen-containing impurities.

Studies regarding the Green River Formation have also been extensively carried out, especially concerning mineral reactions and the presence of these minerals in the final product [25-27]. Siliceous-rich oil shale has also been found to produce amorphous silica (glass) during high-temperature processing followed by rapid cooling, with other by-products including dawsonite, sulphur, aluminium sulphate, vanadium, zinc, copper and uranium existing in the final products obtained [14].

1.4.4. Oil Shale Grade Determination

Dyni [6] and Scouten [4] have both indicated that the heating value is thoroughly useful in determining the grade of oil shale, especially in the case of shale burnt directly in power plants to produce electricity. However, no information is provided regarding the amounts of shale oil or gas that can be yielded during retorting.

A method to determine the relative quantities of oil, gas and water which will be released during pyrolysis is the Fischer assay test method (ASTM 3904) [5]. Modifications of this method are currently being utilized to evaluate different oil shale types and for different processing methods. The basic method involves heating 100 g of shale sample which has been crushed to 8-mesh (2.38 mm) screen. This heating occurs in an aluminum retort at 500 ºC at a rate of 12 ºC per minute and thereafter held at that temperature for 40 minutes. The vapours containing oil, gas and water are sent through a water-cooled (ice water) condenser and then into a graduated centrifuge tube where the oil and water are separated. Final reported values include weight percentages of shale oil, with specific gravity, water, sale residue and gas, including losses [28].

However, the Fischer assay method does not include measurements of the total energy content of an oil shale sample. This is due to gases, including methane, ethane, propane, butane, hydrogen, hydrogen sulphide and carbon dioxide, which have energy contents, not specified individually [29]. Moreover, retorting in practice using more finely crushed oil shale or by other methods, such as the TOSCO II process, tends to produce more oil, over 100 % more than that reported by the Fischer assay tests, leading to this method only being reliable for providing reference points for different shale types and approximate energy potential [4, 5].

Another pyrolysis test proposed by the Institut Français du Pétrole called the Rock-Eval test consists of heating a 50-100 mg sample through multiple temperature stages [29]. This results in the determination of the amount of hydrocarbon and carbon dioxide generated. Furthermore, the results can be interpreted for the type of kerogen and the overall potential for oil and gas generation [5]. This method is preferred due to it being faster than the Fischer assay process with less raw material being required [5].

1.4.5. Porosity

Porosity refers to a measurement relating to void spaces in materials such as reservoir rock. It is a fraction of the volume of void space over the total volume of the sample and is expressed as a percentage of the total volume of the sample [5]. Measurements of porosity depend on the pores that are observed and how the void volumes are measured. According to Speight [5], these include:

- Interparticle porosity
- Intra-particle porosity
- Internal porosity
- Porosity by liquid penetration
- Porosity by saturation
- Porosity by liquid absorption
- Superficial porosity
- Total open porosity
- Bed porosity (bed void fraction)
- Packing porosity

Speight [5] reports that the methods used to determine the porosity of petroleum reservoir rocks cannot be used for oil shale since the organic matter within the oil shale occurs as an essentially insoluble solid. The inorganic components contain pore structures of approximately 2.36-2.66 % v/v, however, the porosity measurement is limited to the external surface rather than the internal pore structure [5]. Chilingarian and Yen [30] performed testing for porosity using various oil shale types and it was found that porosity values are almost negligible for commercial-grade, high-yield oil shale with porosity only occurs in rare cases of fractures, faults or structural defects in the shale structure.

1.4.6. Permeability

According to Speight [5], permeability refers to the ability of a rock to transmit fluids, and this value is usually reported in darcies or millidarcies. The permeability concerning oil shale is essentially zero. This is because oil shale is a largely impervious system [5]. This leads to processing techniques that have to incorporate suitable rubbelisation procedures to perform pyrolysis efficiently, especially during in situ processes [5]. However, upon heating to values near 510 ºC, a definite increase in shale permeability and porosity is noticed, with porosities varying from 3-6 % v/v of the initial bulk shale volume. This porosity occurs as a result of the original organic matter placement before the retorting treatment of the oil shale. In carbonate-rich shales, increased porosity can also occur as a result of the decomposition of mineral components in the inorganic portion of the shale. Furthermore, as a result of organic matter decomposition and carbon dioxide formation, internal vapour pressure increases in the impermeable pores. The particle no longer can contain the force caused by the pressure that exceeds the mechanical strength of the particle itself, resulting in cracking [5].

1.4.7. Compressive Strength

Speight [5] reports that raw oil shale possesses high compressive strengths. This compressive strength is high in both the perpendicular and parallel planes concerning the bed. Concerning low-yield shale, high compressive strengths are reported even after retorting, implying inorganic cementation between mineral particles in each layer of the shale [5]. However, with high-yield shale, the compressive strength decreases with retorting due to the strength of the organic-free material decreasing as kerogen is removed from the oil shale [5].

1.4.8. Thermal Conductivity

It was reported by Speight [5] that the thermal conductivity of retorted shale is far lower than that of raw oil shale. This was attributed to the fact that the voids created after retorting conducted heat much more poorly as opposed to the organic matter that resided there before retorting [5]. However, a small portion of the conductivity difference can also be attributed to the formation of amorphous carbon during the retortion process [7].

It must be noted that the thermal conductivity of oil shale is weakly dependent on temperature [5]. However, this effect of temperature must be regarded with extreme caution because the pyrolysis reactions which occur with the oil shale's kerogen are endothermic, hence the temperature gradients within the shale itself become affected by the rate of the heat of reaction together with the rate of heat conduction [5].

1.5. Kerogen Probing Methods

The probing of kerogen occurs to determine detailed information regarding the constituents of the organic matter. The methods utilized are summarized in the table below:

Table 4. Kerogen probing methods.

Method	Description	References
Ultimate (Elemental) Analysis	Used to determine the atomic constituents of kerogen and establish a framework in which other physicochemical means/methods can be more effectively utilized.	[31-33]
Functional Group Analysis	This characterizes the oxygen-based functional groups in the organic matter based on treatments with hydrochloric and hydrofluoric acid.	[34]
Oxidation	Uses alkaline permanganate and chromic acid to perform oxidative degradation to determine kerogen composition.	[35]
Thermal Methods	This includes methods such as micropyrolysis with the aid of gas chromatography-mass spectrometry (GC-MS) to identify structural units in kerogen.	[36]
Acid-Catalysed Hydrogenolysis	Use of hydrogenolysis with stannous chloride ($SnCl_2$) to degrade kerogen followed by chemical analysis of the product.	[37]
Structural Models	Hypothetical models utilized to determine kerogen structure.	[8, 38-41]

This study aims to discuss the methods of processing and technologies that can be used to facilitate the conversion of the organic component of oil shale, namely kerogen, into marketable fuels. Each of these technologies, processing procedures, and oil shale refining procedures have inevitable effects on the physical environment. Furthermore, the technological readiness of each type of technology affects the rate of establishment of a respective oil shale industry. This report entails detailed discussions regarding the general types of processing methods and the major unit operations associated with them; a description of the relevant mining methods that can be utilized to obtain oil shale from the ground and also prepare it for later processing and the different, generic retorting methods which are utilized to convert the oil shale into crude liquid and gaseous fuels. Furthermore, upgrading and refining methods utilized to convert crude shale oil into marketable products are also briefly discussed. Finally, potential markets for shale-derived fuels are briefly discussed with an in-depth analysis of the advantages and disadvantages of each processing step together with possible environmental issues arising from the process.

2. Process Description and Typical Operating Conditions

2.1. Overview of Oil Shale Processing

To facilitate the conversion of oil shale into products usable by consumers, several processing steps are required to ensure that the desired mix of products and by-products is obtained. The approach taken to process the oil shale concerning the mining or retorting procedure also affects the products and by-products obtained from the refinery.

As per Johns et al. [42], three main approaches currently exist to retort the oil shale. These include:

- The True in Situ (TIS) process which involves the oil shale being heated underground by the injection of hot fluids;
- The Modified in Situ (MIS) process which involves only a portion of the oil shale being mined out whilst the rest of the shale is broken down with the aid of explosives to create a zone of high permeability in which hot fluids can be circulated;
- The Aboveground Retorting (AGR) process or ex-situ process whereby shale is mined from the ground and crushed for heating in vessels near the site of the mine.

The figure below represents a process flow diagram that is common to all three of the abovementioned processes.

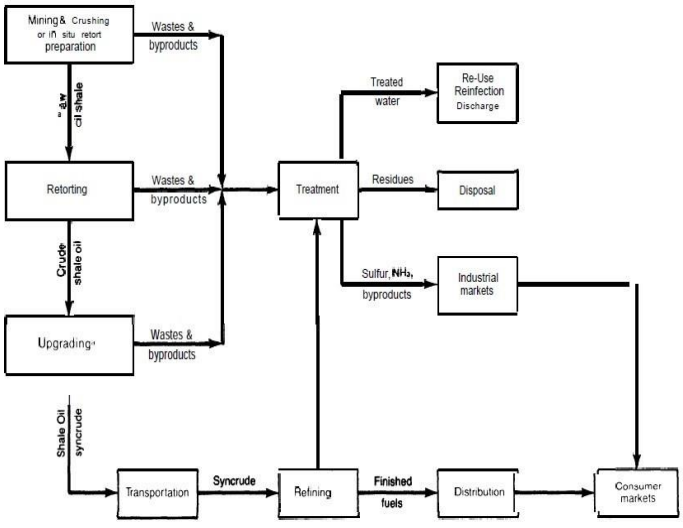


Figure 7. Typical process for oil shale extraction and processing [42].

Figure 8 below represents the integrated approach concerning an AGR facility.

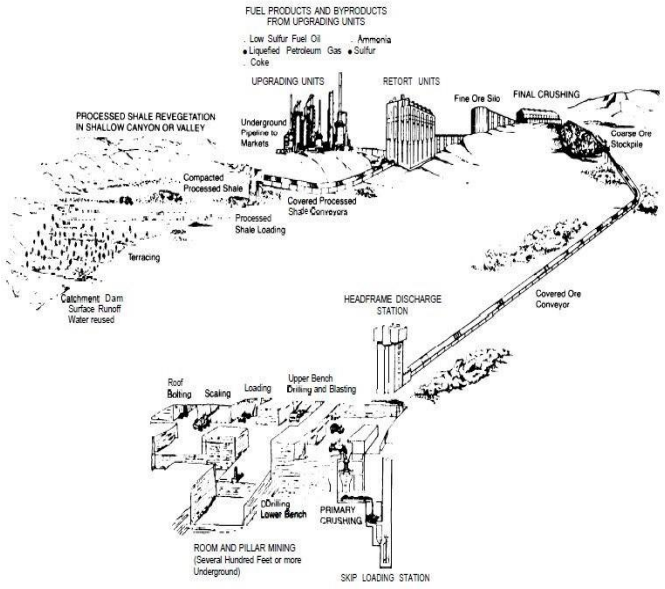


Figure 8. Mining and aboveground retorting in an oil shale complex [42].

During the general process, as per Figure 7, the oil shale is either mined and crushed, to form raw oil shale with appropriate particle sizes to facilitate fast heat transfer (AGR process), or the deposit of oil shale is fractured or rubbled for in situ processing (TIS or MIS processes). TIS or MIS processing is favoured especially in situations when deposits are thick, deep, and not amenable to deep-mining or surface-mining processes [5]. Typical by-products during this initial mining or in-situ treatment phase are nahcolite ore, dawsonite ore, and various carbonates and silicates [42]. Dust and contaminated water are also created during this process, forming part of the waste products generated [42].

Retorting thereafter occurs and this involves heating the oil shale to pyrolysis temperatures of approximately 535 ºC [42]. However, this temperature varies greatly with the type of shale being processed and in certain cases, such as for kukersite-containing shales, lower temperatures may be required [5], whereas in certain cases high temperature processing or coking may be carried out with temperatures between 1000-1200 ºC [7]. Crude shale oil is produced during this process. However, pyrolysis gases, carbon dioxide, contaminated water, and more mineral ore wastes such as dawsonite and nahcolite are produced [42].

The crude shale oil is thereafter sent to an upgrading section. This involves physical and chemical modification of the crude shale oil to aid transportation properties and remove Sulphur, and nitrogen whilst increasing hydrogen content [42]. It must be noted that in some cases, crude shale oils from certain in situ processes may not require physical or chemical upgrading before transportation [42]. During upgrading, contaminated water and air are produced with sulphur and nitrogen-containing gases [42]. Johns et al. [42] report that the extent of treatment can result in the syncrude product becoming a high-quality feedstock for refineries and becoming comparable to the highest grades of conventional crude oil.

The refining of the syncrude shale oil can occur offsite or onsite, depending on the scale of the facility. During this process, hydrogen is added to convert syncrude shale oil into finished fuels including gasoline, jet fuel, and diesel fuel. Johns et al. [42] reported that this syncrude shale oil can be used directly as boiler fuel in industry.

Distribution of the final fuel products to consumer markers thereafter occurs. However, during the process, the waste gases and contaminated condensates have to be treated, either for reuse in the facility, for discharge into surface bodies or water, or reinfection into the aquifer source containing groundwater [42]. This is done for environmental protection and to meet government-specified air and effluent standards, especially when it comes to the discharge of contaminated air and process gases.

The waste gases produced during the process tend to be ammonia-rich, implying use for fertiliser, whilst the sulphur-rich components can be used in the production of sulphuric acid [42]. By ensuring the recovery of these components, these by-products and wastes can be sold to other industries that use these wastes as feedstocks, encouraging industrial symbiosis. Furthermore, nahcolite ore wastes can be used to produce soda ash and can also be utilized for stack gas scrubbing whilst dawsonite is a rich source of aluminum metal [42].

Finally, any spent shale must be moistened to undergo compaction. Thereafter, revegetation must occur to prevent leaching and erosion [42]. Any in situ retorted shale and spent shale that has been backfilled into an underground opening must also be protected from leaching by groundwater to prevent water source contamination [42].

2.2. Oil Shale Mining

Both the MIS process and the AGR process require mining. For the AGR process, the mined shale is transported using a conveyor to the retorting site where oil and gases are recovered via the retorting process, whereas, for the MIS process, the removed shale may be retorted aboveground similarly to the AGR process or it may be discarded as solid waste should the grade of shale not meet requirements for processing [42].

Depending on the type of the deposit, topographical features of the bed, accessibility, overburden thickness, and any groundwater presence in the mining zone, either surface mining or underground mining can be utilised to extract shale for processing in the MIS and AGR processes [42]. Surface mining can be further broken down into strip and open pit mining, whereas underground mining consists of methods such as room and pillar methods. Examples such as the Green River formation represent a thick layer of shale, more than a thousand feet deep, stretching over 1200 mi^2 [42]. Surface mining is only feasible in sections of this formation where thick oil shales occur which is not buried very deeply and also in situations where these areas in the formation bear low yields of oil [42]. In other areas, such as the Uinta Basin and the Wyoming Basin, surface mining possibilities are limited due to the thickness of the overburden [42]. Thus, any shale that cannot be reached by surface mining and any shale occurring in deeply buried beds must be extracted by underground mining.

According to Johns et al. [42], oil shale represents a lean ore as opposed to many ores which contain valuable metals and, as a result, economies of scale tend to encourage vast mining installations to facilitate oil shale extraction. As a comparison, the largest surface mine in the United States, namely Kennecott Copper's Bingham Canyon pit in Utah produces roughly 110 000 tons per day of copper ore whilst the largest underground copper ore mine in America, namely the San Manuel copper mine in Arizona, produces approximately 50 000 tons per day of ore [42]. Now because on average, assuming a 100 % Fischer assay oil recovery from the oil shale (TOSCO II Technology), 560 000 tons per day of oil shale must be mined and AGR processed to provide a production rate of 400 000 U.S. barrels per day of shale oil, a mine which is equivalent to 5 Bingham Canyon Pits or 11 San Manuel mines will be required [42]. However, should MIS be utilized instead, 230 000-460 000 tons per day of oil shale will have to be mined, resulting in a mine size equivalent to 4-7 times the size of the San Manuel mine [42]. Thus, the mining method chosen must be able to achieve the required levels of production with relative ease.

2.2.1. Surface Mining

Surface mining consists of either open pit or strip mining. The figures below represent an open pit mine together with the respective steps for mining.

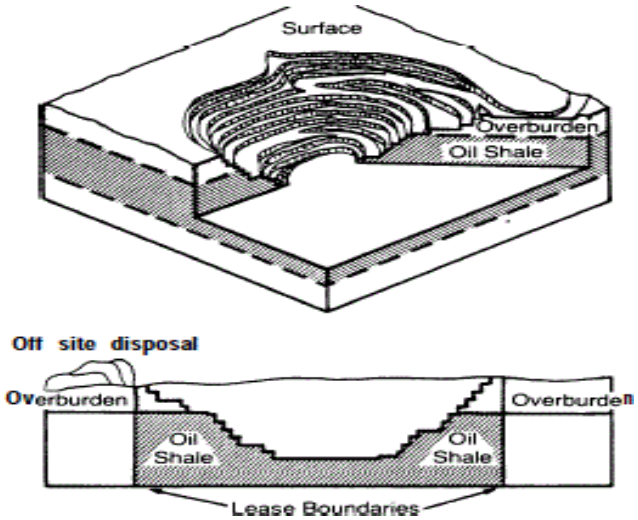


Figure 9. Open pit oil shale mine [42].

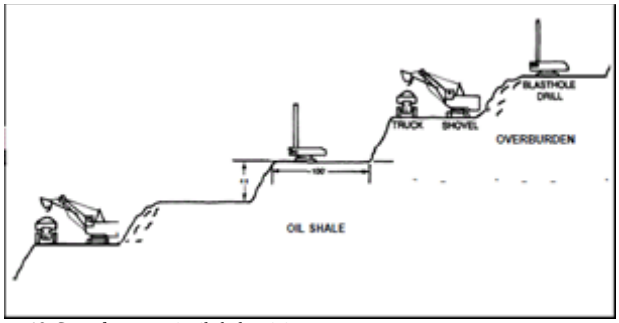


Figure 10. Steps for open pit oil shale mining.

During the initial step of mining, the overburden is drilled using a blasthole drill. The overburden is then blasted loose over vast areas above the oil shale deposits. Thereafter, this blasted solid overburden is transported by trucks or with the aid of conveyors to disposal areas that may be offsite. Over time, more and more burdens become removed until the shale bed becomes exposed. Once exposed, the shale beds become drilled and blasted and the blasted oil shale is transported from the pit to aboveground retorts for further processing [42].

With continuous mining, large holes are formed with extend from the upper portions of the overburden to the deposits of oil shale. The walls of the hole are angled outwards to cope with pressure and prevent the walls from collapsing [42].

During strip mining, the overburden becomes removed by a type of scraper shovel called a dragline. Once the dragline scoop is filled, the overburden is dumped into a mined-out area which is usually adjacent to the current area being mined. Strip mining is usually rarely carried out concerning oil shale mining due to extremely thick overburden covering the oil shale deposits warranting the use of open pit mining instead [42].

It must be noted that stripping ratios usually characterize which method of mining can be carried out. A stripping ratio refers to the ratio of the thickness of overburden to the thickness of the ore body, or in this case, the oil shale [42]. Concerning coal, a stripping ratio of 10:1 is often economically feasible, however, for shale, for ratios between 2:1 and 5:1, open pit mining is favoured, whilst, for ratios lower than 2:1, strip mining becomes a more feasible option. For stripping ratios higher than 5:1, underground mining most probably will have to be performed [42].

2.2.2. Underground Mining

According to Johns et al. [42], only room-and-pillar mining and mining procedures that aid MIS processes have been proven to be economically viable at a significant scale. During room-and-pillar mining, as per Figure 11 below, shale is removed to form large rooms whilst portions of shale are left in place to form pillars, serving as structural support for the mine roof [42]. To determine the size of the rooms and the relative thickness of the pillars, the thickness of the overburden, the physical properties of the shale, and the height of the mine roof have to be precisely determined. A large number of deposits show high compressive strengths and have very few natural faults such as cracking or deformations, hence, compression and vertical stresses are resisted by the shale, allowing for the formation of large rooms with little wastage of unrecovered shale in the form of pillars [42].

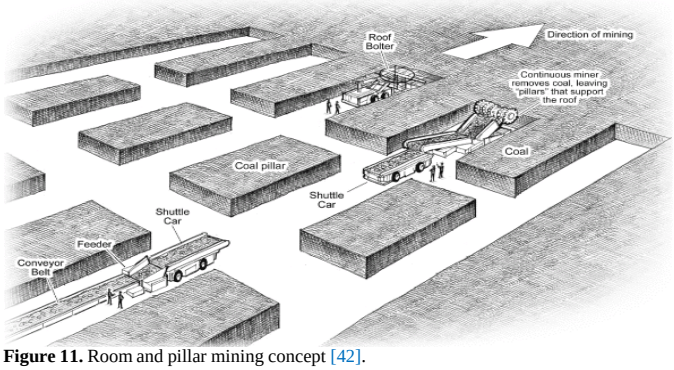


Figure 11. Room and pillar mining concept [42].

Figure 11 also depicts the design followed by many modern mines, patterned after the U.S. Bureau of Mines' (USBM) experimental design. This design involves an upper bench becoming mined first by drilling and blasting into the walls of a room for production and transporting broken, blasted shale to crushers for feed into aboveground retorts. Scaling of the walls and the roof of the newly formed room thereafter occurs to remove any loose shale that remained intact after blasting. Thereafter, roof bolts are inserted into holes drilled into the roof of the room, thus promoting structural integrity and preventing roof falls. These bolts are usually installed in passageways and not in actual areas that are actively being mined [42]. The lower bench is mined thereafter and a similar sequence of drilling, blasting, loading, and scaling is carried out. However, drilling now occurs into the floor of the upper bench, thus ensuring that additional roof bolting is no longer required.

To prepare for the MIS process, underground mining by room-and-pillar methods was not possible due to the relative volume of the deposit which has to become disturbed, and the required configuration of the disturbed area [42]. The mining will also have to occur in confined spaces, to facilitate openings for MIS retorts, shafts for ventilation, drainage, passageways, and means for transportation of combustion and retorting products from the retorting sites. The actual method in which the underground mining is carried out for the MIS process is described hereafter in the section describing the overall MIS process.

2.3. Oil Shale Retorting Methods

2.3.1. True in Situ (TIS) Process

The TIS process consists of four main sequential steps. According to Johns et al. [42], these steps include:

- Dewatering, especially if the oil shale deposit occurs in an area that contains groundwater;
- Fracturing or rubbling, to increase the permeability of the oil shale deposit;
- Injection of a hot fluid to provide heat for pyrolysis or ignition of a portion of the bed to provide heat (underground combustion);
- Retrieving produced oil and gases through wells
- Figure 12 below represents a schematic of the TIS process.

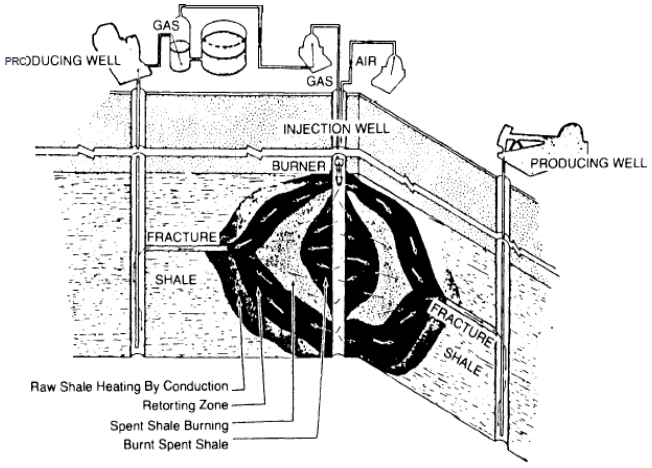


Figure 12. TIS process schematic [42].

Despite differences in each respective TIS process used by facilities concerning the heating medium utilized, all TIS processes use systems of injection and production wells as per Figure 12. The 'five-spot' pattern is commonly encountered, in which four production wells are drilled towards the corners of each square of oil shale deposit to be processed, with an injection well drilled in the middle of the square [42]. Initially, Speight [5] reports that refrigerated fluid is pumped through more wells drilled around the extraction area to create a 'freeze wall' and prevent groundwater from entering the zone in which extraction occurs.

Thereafter, as the heating medium flows through the injection well, heating occurs within the deposit, resulting in the product being recovered from production wells. It must be noted that the TIS process relies strongly on the permeability of the deposit. The Green River Formation possesses relatively good permeability as well as the Piceance basin in which groundwater dissolved deposits of salt in the shale, leading to large rubble-filled zones suitable for TIS processing [42]. However, most commercial-grade oil shale deposits essentially have zero permeability. For deposits near the surface, water injection or explosive slurry injections can be used to increase permeability, however, for deeply buried deposits, mining would be required to increase permeability, ultimately implying that the MIS or AGR processes become more attractive [42].

An example of a facility that uses TIS processing in a portion of its facility is American Shale Oil LLC (AMSO). This facility carries out in situ retorting of the Green River formation oil shale and utilizes a unique recovery and heating method/technology together with proven drilling practices.

This process practiced by AMSO promotes energy efficiency and minimizes environmental impact. It involves the use of superheated steam as the heating medium which is injected into the deposit using a series of pipes below the shale deposit. The produced oil and gas leave through vertically drilled production wells connected to the heating wells, resulting in convection and refluxing improving overall heat transfer to the shale [5].

After start-up, the produced liquid and gas at high temperatures are used to provide heating requirements to superheat steam whilst energy efficiency is improved by heat recovery from the shale rock after retorting is complete [5].

ExxonMobil's Elecrofrac Process uses a general TIS set-up, however, the fracturing proppant is highly conductive concerning electricity, namely calcined petroleum coke. Thus, heating occurs beyond the surface and can be carried into fractures as well. The proppant in this process creates an electrically conductive pathway along the induced fractures in the oil shale, forming essentially, a large electrode. By using a series of vertical fractures created in the oil shale bed using horizontal wells, electricity is conducted across the heating well. These heating wells are parallel to each other with a second horizontal well intersecting these parallel wells at their base. This caters for opposite electrical charges to be applied at each end and allows for shale oil to be extracted by separate production wells originating from each heating well [5].

The Shell in Situ Conversion Process or the ICP method involves the drilling and placement of underground heaters in an oil shale deposit. 15-25 holes are drilled per acre, with distances of 35-42 feet apart from each other with varying configurations depending on shale geometry. These wells reach depths of approximately 2000 feet, with target depths of 1000-2000 feet being required. The fracturing achieved to increase permeability involves existing oil shale

fractures and induced fractures by systematic drilling. The electrical heaters inserted are controlled at temperatures nearing 760ºC, causing the surrounding shale to reach temperatures of 345-370ºC. this low temperature induces chemical and physical changes required for shale oil release. This process takes approximately 2-3 years, however, the final oil and gas retrieved is unique in that it contains no heavy ends. The final mixture obtained contains two-thirds liquid comprising 30% naphtha, 30% diesel, 30% jet fuel, and 10% heavier oils, with the remaining one-third being gas, containing mainly propane and butane. A 'freeze wall' is utilized to prevent groundwater contamination during the process [5].

2.3.2. Modified in Situ (MIS) Process

The general MIS process is accurately depicted in Figure 13.

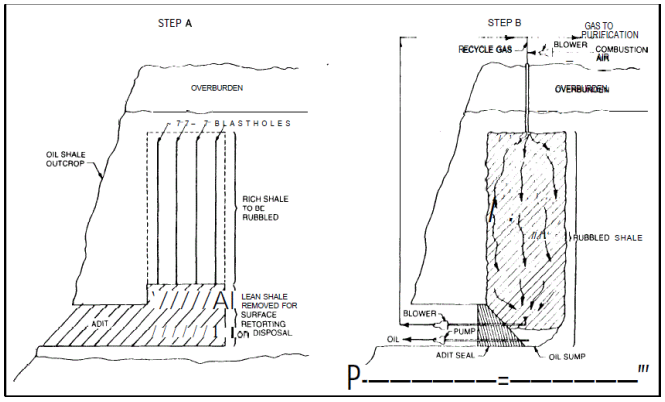


Figure 13. MIS process schematic [42].

As per Johns et al. [42], the general two-step process involves the digging of a tunnel to the bottom of a shale bed. After removing a small portion of shale, the tunnel creates a room that occupies the same cross-sectional area as the future retort. Holes are thereafter drilled into the roof of the room and explosives are placed inside these newly drilled holes. During the second step, the explosives are detonated and a chimney-shaped retort results underground filled with broken shale. The original access tunnel dug in step one is sealed and a new injection hole is created using drilling from the surface to the top of the broken shale. Air and burning fuel gas is injected into the extraction zone through the injection hole and the pile is ignited. The heat generated in the top layers from combustion becomes carried down the broken shale bed in the gas stream resulting in the lower layers becoming pyrolyzed with oil vapours moving down the retort into a sump at the bottom of the pile. The oil within this sump is pumped to the surface thereafter. The burning zone moves down the retort with time and it becomes fuelled by the residual carbon formed during retorting. Once the burning zone reaches the bottom of the bed, the airflow to the retort is stopped, thus ceasing combustion [42].

A vertical burn configuration is preferred to a horizontal burn formation due to extremely low oil recoveries in the case of the latter due to process control difficulty, especially concerning the movement of the burning zone [42]. However, newer technology such as soluble salt dilution in beds that contain large quantities of soluble salts, and long-wall mining may cater for horizontal burn formations to occur, but insufficient testing has been carried out on these processes [42]. Examples of facilities that utilise MIS processing are summarized below:

The Chevron Process includes the use of carbon dioxide as the heating medium for the oil shale. The process involves the drilling of vertical wells into the oil shale formation and horizontal fractures are induced by the injection of carbon dioxide through these wells. The injected carbon dioxide is pressurized, resulting in rubbelisation due to the pressurized gas moving through fractured intervals, this causing more fractures in the bed. Further rubbelisation is caused by propellants and explosives. Finally, used carbon dioxide is routed to a gas generator and is thereafter reheated and recycled. Further combustion of the remaining organic matter in depleted zones generated heated gas, which is pressurized and thereafter fed into newly fractured portions of the bed. This process is repeated with hydrocarbon fluids continuously being brought up for refining through vertical oil wells [5].

The Dow Process practiced by Dow Chemical Company, carries out rubbelizing by explosive fracturing using metalized ammonium nitrate slurry. This process carries out combustion using an electric heater and a propane burner. Furthermore, this company tested the possibility of mechanical underarming to facilitate horizontal burning formations however, extensive rubbelisation did not occur, deeming testing unsuccessful [5].

Occidental Oil Shale Inc. created the Occidental Modifed in Situ Process which follows the general principles relating to MIS processes as explained earlier. This process was considered due to the thick Green River Formation in the area, resulting in MIS processing being required. Ammonium nitrate and fuel oil are used to induce rubbelising, whilst air and fuel gas mixtures are utilized to start the combustion process to initiate the burning zone. The recovery methods utilized include steam leaching, leaching by solvent, high-pressure gas displacement, and water injection [5].

2.3.3. Aboveground Retorting (AGR) Process

AGR process retorts can be split into four main classes as shown by Johns et al. [42]. These classes include:

- Class 1: This class involves heat transfer through the wall of a retort. The Fischer assay retort falls into this category and this type of retort is generally a device used in the laboratory to determine potential oil yields. However, conduction heating is relatively slow, implying no modern retorts falling into the class 1 category.
- Class 2: This type of retort is commonly referred to as the directly heated retort and involves heat transfer by flowing gases created within the retort because of combustion of carbon-rich, previously retorted shale and pyrolysis gases. These retorts produce low-Btu gas and low-carbon spent shale with high energy efficiency due to energy recovery from retorted shale. However, low recovery efficiencies are reported, comprising only 80-90% of Fischer assay.
- Class 3: This type of retort is also referred to as indirectly heated retort and it involves heat transfer by gases that are heated outside the retort vessel. This retort produces carbon-rich spent shale and high-Btu gas with low thermal efficiencies due to heating energy not being recovered from spent shale as with class 2 retorts. However, high oil recovery efficiencies are reported, ranging from 90% to over 100% of Fischer assay.
- Class 4: This type of retort involves heat transfer by combining hot solid particles with the oil shale in the retort vessel. High yields of 100 % of Fischer assay is achieved and a high-Btu gas is produced with spent shale that contains little or no carbon, depending on the shale type and origin. Thermal efficiency depends on whether the spent shale is used for heating of the solid particles. This process lacks internal combustion, as with class 3, with the potential of also being referred to as indirectly heated retorts.

Other methods also include bacterial degradation, microwave heating, circulation of hot solids slurries, and gasification [42]. However, these methods prove to be difficult in commercial application and control [5].

An example of AGR processing using class 2 retorting is the Nevada-Texas-Utah (NTU) Retort. This retort is a modified form of a downdraft gas producer and is a vertical steel cylinder. The outer surface is lined with refractory bricks whilst an air supply pipe is attached at the top of the vessel, with an exhaust pipe located at the bottom of the vessel. The entire top of the vessel can be removed to recharge the retort with a new batch of shale, whilst the bottom can be removed for discharge of spent shale after the retorting process [42]. However, due to batch operation and high labour costs, these units are not favoured in the industry. The figure shown below can be utilized to explain the operation of this vessel [5].

In step A, the vessel is charged with crushed oil shale from the mining process and closed. The gas burner is ignited, and the blower allows for air to enter the system. When the top of the bed begins to burn, the air supply continues but the fuel gas supply is shut off. The air flowing through the burning layer becomes heated to temperatures as high as 815 ºC. In step B, this hot gas begins to heat the shale in the lower regions of the bed, thus inducing pyrolysis of the kerogen. The produced oils and gases are swept down through the bed and exit the vessel through the exhaust. As the kerogen decomposes, the formed residual carbon becomes consumed as the combustion zone moves further down the bed into the areas of newly retorted shale, thus maintaining combustion by providing additional fuel for combustion and additional heat for the retorting process. Finally, when all the carbon from the upper layers becomes burned, four zones as shown in step C are formed, with the first layer containing decarbonized and burned shale. The second layer is burning, releasing more heat for pyrolysis of the third layer, whilst the shale in the fourth layer is being heated but not yet at the suitable pyrolysis temperature [42]. Over time, the first layer moves down the bed and expands, whilst layers 2,3 and 4 move further down the bed. When the combustion zone finally reaches the exhaust port, the air supply is stopped and oil production stops until the vessel is emptied and recharged [42].

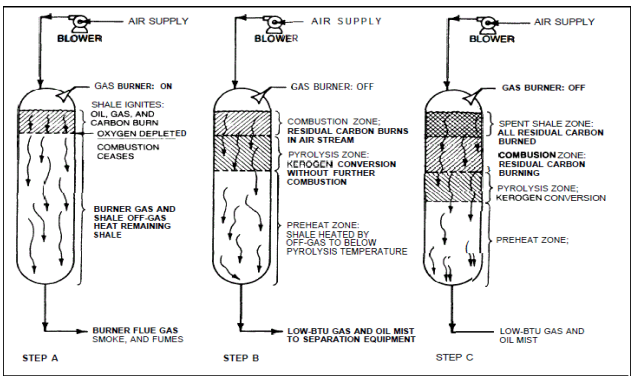


Figure 14. NTU Retort Operation [42].

The Paraho direct and indirect retort also forms part of an example regarding AGR processing. The Pareho direct retort is essentially an inverted, or upside-

down, NTU retort, facilitating a continuous process with some mechanical modification [42]. This specific type of retort works in the manner described by the figure below:

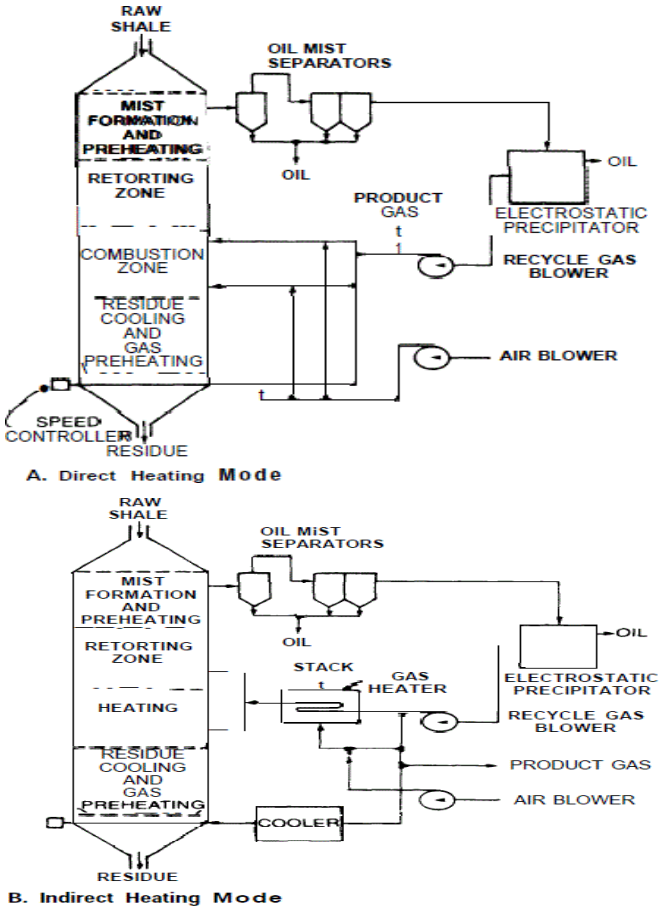


Figure 15. The Pareho retort system [42].

As shown in Figure 15, the direct mode of operation works very similarly to that of the NTU retort. However, a different shale feeding mechanism exists, together with significantly different gas distributors and discharge grates, both of which ensure the maintenance of a continuous process. During operation, the crushed raw shale (10-75 mm) is fed into the system through the rotating distributor at the top of the vessel [42]. This can be seen in Figure 16 to follow. This shale moves through the vessel, essentially as a moving bed, along the vertical axis. During movement, the shale is heated to pyrolysis temperatures over 500 ºC by hot combustion gases which rise through the vessel. The produced oil and gas are swept up through the bed and collected in collecting tubes which then feed the necessary separation equipment required for upgrading. The spent shale still contains residual carbon; hence, this shale is ignited as it reaches the burners near the middle of the vessel, thus providing heat for the pyrolysis of additional shale. Thereafter, the shale is cooled in the following section using a stream of recycled gas. The shale then exits the vessel through the discharge grate and is thereafter moistened and sent for disposal [42].

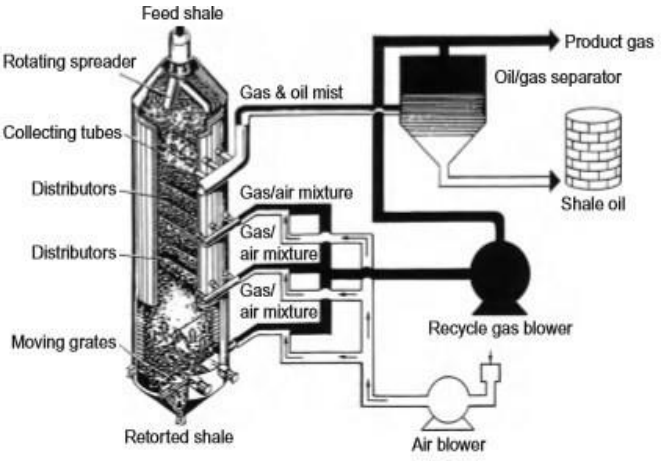


Figure 16. Pareho retort: direct mode operation [4].

The indirect heating mode operates similarly to that of the directly heated operation, however, no air injection into the vessel occurs. Furthermore, the final off-gas stream is split into four components, namely;

- Net product gas
- A portion was sent for reheating in a furnace and thereafter reinjected into the middle of the retort.
- A portion that is not reheated and injected into the bottom of the retort to cool shale before discharge.
- A final portion used as fuel for the reheating furnace.

No combustion occurs within the retort. Heating is provided by the reinjected gases as the process proceeds.

The Lurgi-Ruhrgas Process, which was developed in Germany, is used to retort kerogen and refine the hydrocarbon product into marketable liquid fractions that resemble the products from petroleum [5]. Figure 17 shows a schematic of the operation.

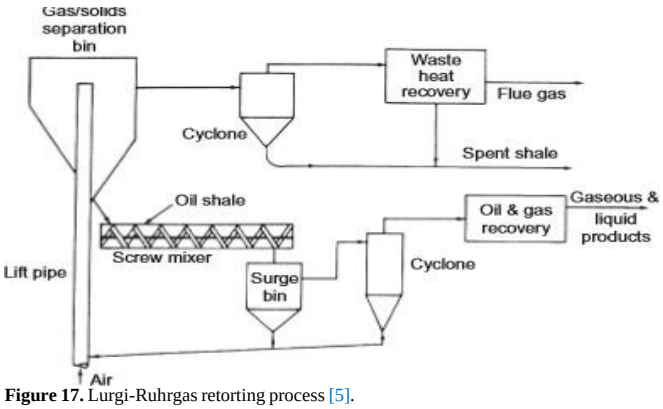


Figure 17. Lurgi-Ruhrgas retorting process [5].

During this process, crushed oil shale of size less than 0.25 inches, is passed through a feed hopper and mixed with 6-8 times the volume of a mixture containing hot spent oil shale and sand. This hot mixture has a temperature of approximately 630ºC. The final mixture, containing raw oil shale, has a temperature of 530ºC and is conveyed up a lift pipe, where the produced gas, shale oil vapour, and water vapour begin to be evolved. The solid mixture then enters a surge hopper where it awaits additional processing causing more residual oil components to be separated by processes such as distillation. Sand acts as a heat carrier and this sand is recovered from the mixture and recycled through the system during the next treatment. The mixture is then allowed to return to the base of the lift pipe where air is introduced at 400ºC, resulting in the burning of the carbon-rich spent shale. This burning mixture is raised pneumatically up the lift pipe to a collection vessel where the spent fines of shale and gases are separated [5].

Hydrocarbon gases and oils released during the process are treated in a series of scrubbers and coolers to eventually recover condensable liquids and gases. Furthermore, the retorted shale from the mixer enters the hopper leading to the bottom of the lift pipe, together with the dust from the fines originating from the cyclone. Air at 550 ºC is introduced at the bottom of the lift pipe and this carries the solids up into the surge bin. The solids are heated as a result of the combustion of residual carbon-rich char in the spent shale. If the residual char is insufficient, the fuel gas is usually added. When in the surge bin, hot solids become separated from combustion gases and, thereafter, the hot solids are returned to the mixer where it is mixed with fresh shale, completing the overall cycle [5].

Another example of an indirectly heated retort is the Petrosix Indirectly Heated Retort developed by Petrobras in Brazil. This system is depicted in Figure 18.

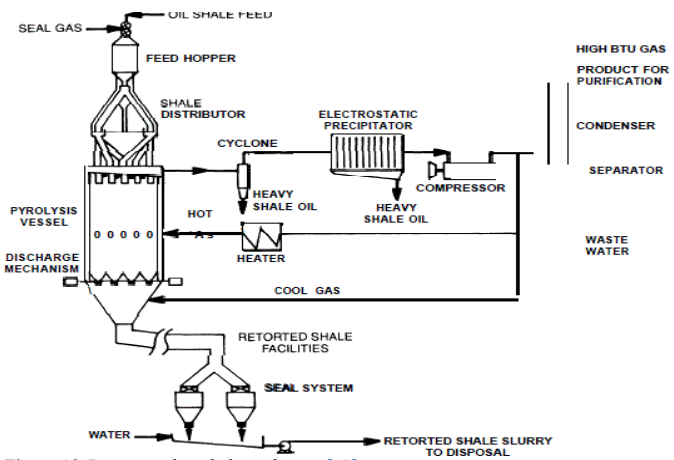


Figure 18. Petrosix indirectly heated retort [42].

This plant has a capacity of 2 200 tonnes of Irati oil shale per day [42]. The operation of the Petrosix retort is extremely similar to that of the Pareho indirectly heated retort mentioned earlier. The production of shale oil occurs at 500 ºC and this is recovered at the top of the retort. The off-gas from the process is cooled with the use of a cyclone, an electric precipitator, and spraying tower for condensation. This gas produced is used in the same four ways as described for the Pareho indirect process [5].

The Union B Indirectly Heated Retort provided great technological advancement concerning continuous operation [42]. A schematic of the process is shown hereafter.

In this process, shale is fed through the bottom of the vessel. Hot gases retort at the top and the gases pass down through the rising bed, resulting in the pyrolysis of kerogen. The retort gas and shale oil move down through the bed and the oil accumulates in a pool at the bottom. This pool basin seals the retort and also allows for the settling of entrained shale fines. Oil and gas are removed from the top of the pool, with the gases being split into three streams, namely;

- A reheated and reinjected portion to bring about additional pyrolysis.
- A portion used as fuel in the reheating furnace.
- A portion is withdrawn as the net product.

The retorted shale leaves at the top of the retort, from where it enters a water bath and is thereafter conveyed for disposal [42].

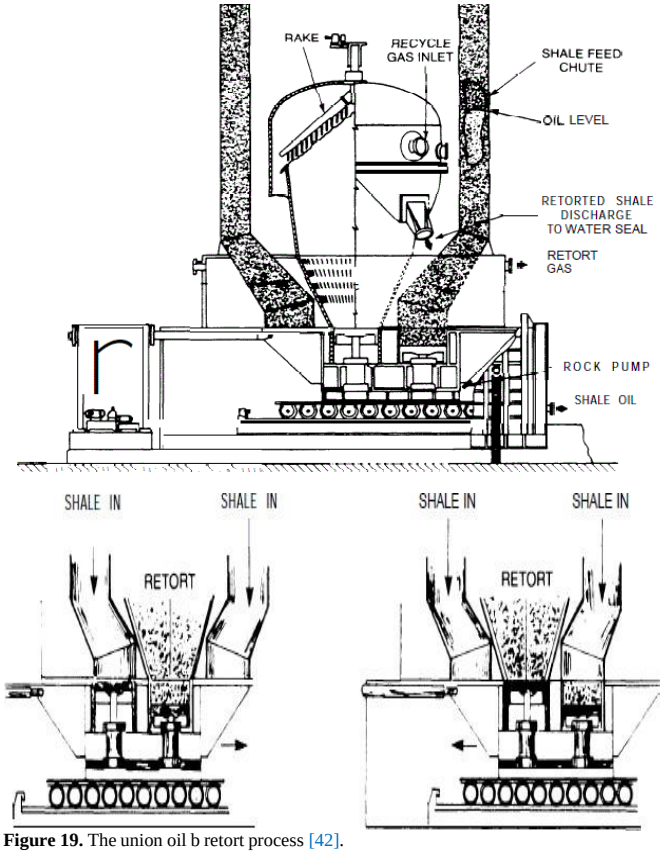


Figure 19. The union oil b retort process [42].

The main difference in this process is the solids pump which moves oil shale through the retort. this pump is on a movable carriage and is also immersed in the shale oil pool. From Figure 19 it can be seen that the pump has two hydraulic assemblies which act in a specific sequence. When one cylinder is filled with oil shale, the other cylinder charges oil shale into the retort base. When this process is completed, the entire carriage moves to ensure that a full cylinder is under the entrance of the retort. Thereafter, a piston moves the shale into the retort, whilst the other cylinder fills up with fresh shale. The carriage then moves back into the former position and the process is repeated with the other cylinder feeding shale into the retort [42].

The Superior Oil Indirectly Heated Retort is another example that shows vast uniqueness in that sodium-bearing minerals are recovered from the process. In shales that contain dawsonite and nahcolite, sodium bicarbonate, soda ash, and aluminum can all be sourced from the respective shale. The block diagram below represents the concept on which the plant is based:

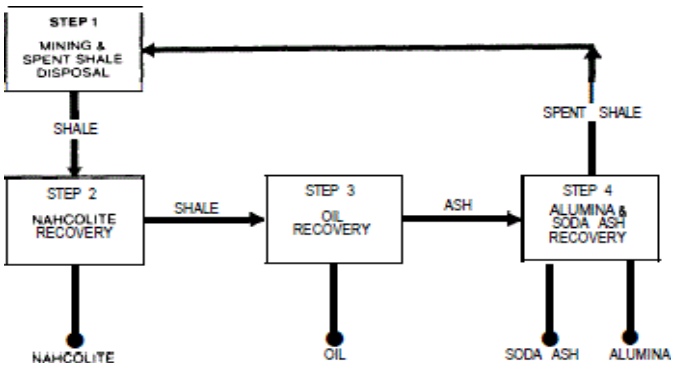


Figure 20. Superior multi mineral concept [42].

During step 1, the oil shale that has been mined is crushed and screened to produce a result of oil shale pieces less than 8 inches in size. Approximately 85-90 % of the nahcolite in the shale becomes a fine powder during the crushing process, and this becomes screened from the larger shale particles during step 2. The remaining separated shale is then crushed into fragments smaller than 3 inches in size. This is then passed into a traveling-grate retort as depicted below;

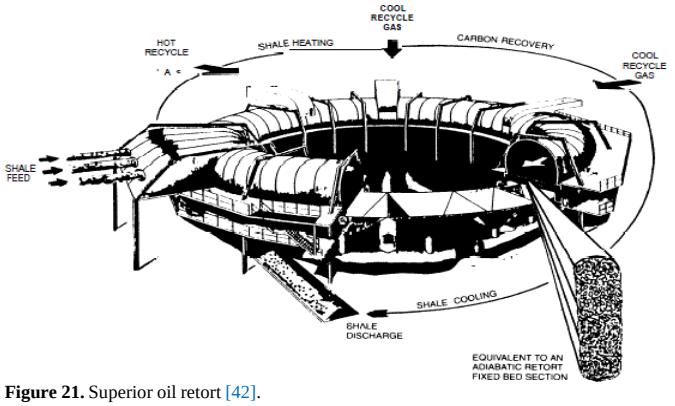


Figure 21. Superior oil retort [42].

This retort enables close temperature control, which is important to maintain the solubility of dawsonite during burning in the retort. The retort has heating, retorting, burning, cooling, and discharge sections. Oil is recovered by passing hot gases through the bed, enabling retorting. Heat recovery occurs by burning spent shale containing carbon residue. In the cooling section, inert gases are utilized and are blown through the bed, also allowing these inert gases to become heated for use in the heating section. During discharge, the outlet is sent to a separation system where alumina and soda ash are recovered from the spent shale, and the spent shale is then recycled into the system for burning. Thus, alumina, soda ash, and nahcolite provide valuable income for the firm [42]. As a result, 20 000 tonnes of shale per day is processed resulting in 10 000-15 000 U.S. barrels of shale oil per day, whilst producing 500-800 tonnes per day of alumina, 3 500-5 000 tonnes per day of nahcolite and 1 200-1 600 tonnes per day of soda ash. However, this is thoroughly dependent on the type and origin of oil shale processed [42].

Finally, the TOSCO II Indirectly Heated Retort is classified as a class 4 retort, using ceramic balls to carry heat and for heat transfer to the crushed oil shale. A process diagram of the plant is shown below;

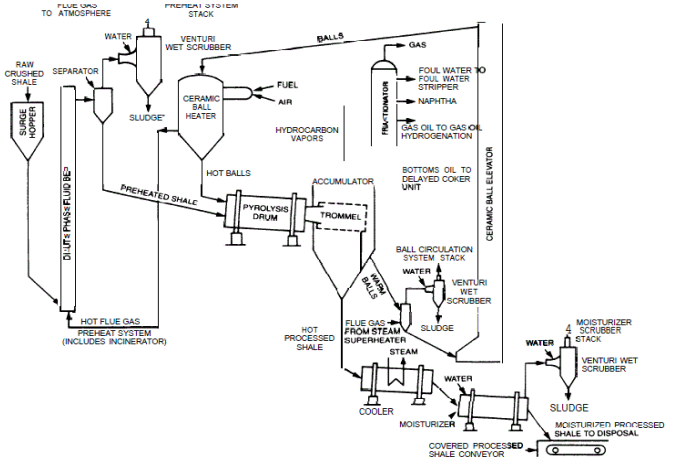


Figure 22. TOSCO II retorting scheme [42].

Oil shale is crushed to fragments smaller than half of an inch and it thereafter enters the system through pneumatic lift pipes. In these pipes, the shale rises with hot gas streams and becomes preheated to 260 ºC. The raw, preheated shale then enters the retort which is essentially a heated ceramic ball mill. Contact between the hot ceramic balls and the raw shale occurs, increasing shale temperature to 510 ºC, resulting in retorting occurring. Shale oil vapours and gases are withdrawn, with the oil vapours condensing in a fractionator. A portion of the gases becomes burned in a heater to reheat the ceramic balls after processing. The final mixture of ceramic balls and retorted shale then leave the retort and passes over a trommel, which is essentially a rotational separation drum with perforations. The finely crushed shale (from retorting) falls through the perforations whilst the ceramic balls remain in the trommel. The retorted shale is cooled and then sent for disposal, whilst the balls are then sent to the ball heater. Oil yields over 100 % of Fischer assay have been reported but lower thermal efficiencies occur due to the spent shale not being utilised for reheating and the majority of product gas being used in the ball heater [42].

2.4. Shale Oil Properties and Refining

The crude or raw shale oil, which has been produced from the off-gas stream of the retorting process, results in synthetic crude oil, known as syncrude, when the crude shale oil undergoes hydrogenation [42]. This crude shale oil is similar to petroleum in that it consists of relatively long-chain hydrocarbon molecules. The boiling points also extend over a similar range which is displayed by typical petroleum crudes [42]. However, three main differences occur concerning crude shale oil and conventional crude oil. These differences are:

- Higher olefin contents possessed by crude shale oils due to the high temperatures during the pyrolysis process.
- Higher nitrogen and oxygen concentrations in crude shale oils due to the chemical makeup of kerogen.
- Higher pour point and viscosity displayed by crude shale oil in most cases.

However, it must be noted that the chemical and physical properties of the crude shale oil produced by any retorting process differ, due to the vast differences in operating conditions and processing prevalent in each respective case [42]. In higher temperature processes, cracking may occur, resulting in crude shale oil with a lower molecular weight, whilst directly heated retorting can lead to lighter components becoming incinerated and destroyed during retorting, resulting in heavier final crude shale oils [42].

As a result, it was determined that the condensing temperature of the retorting system which results in separation of the oil product and the retort gases, is of crucial importance. This temperature inevitably controls the concentration of low molecular weight components in the final crude shale oil produced. The lower the condensing temperature, the higher the concentration of light components in the final oil product [42].

Johns et al. [42] further explains that in situ produced oils are much lighter, thus implying higher yields of material. However, this oil retrieved is rich in low-boiling product such as gasoline and far less concentrated with heavier products such as residual oil. However, the low amounts of residual oils also make shale oils more attractive for use as a refinery feedstock, especially when compared to conventional crudes. Furthermore, even shale oil produced from AGR processes contain roughly less than 30 % of residual oil, which is higher than the content of in situ oils, but still marginally lower than conventional crudes [42]. The following table shows the relative differences between the crude shale oils produced by different facilities practicing the same processing method and also between the AGR and in situ processes.

Table 5. Crude shale oil properties from different facilities and processes [42].

Retort Type	AGR						In Situ
Facility	**NTU**	**Gas Combustion**	**TOSCO**	**nion Oil**	**Paraho Direct**	**Occidental Oil Shale**	**USBM**
Carbon (wt %)	84.61	83.92	85.1	84.80	84.90	84.86	84.60
Hydrogen (wt %)	11.40	11.36	11.6	11.61	11.50	11.80	12.08
Oxygen (wt %)	1.10	1.67	0.8	0.90	1.40	1.13	1.18
Nitrogen (wt %)	2.10	2.14	1.9	1.74	2.19	1.50	1.55
Sulphur (wt %)	0.79	0.70	0.9	0.81	0.61	0.71	0.59
Carbon-to- Hydrogen Ratio	7.42	7.39	7.34	7.30	7.38	7.19	7.00
Gravity (°API)	20.3	9.8	21.2	22.7	19.3	25	28.4
Pour Point (°F)	90	84	80	60	85	40	40

Before refining and upgrading can occur, the major components of the crude oil must be identified. According to Speight [5], these basic components include:

- Saturates: Paraffins and Cycloparaffins
- Olefins and diolefins
- Aromatics: Benzenes. Indans, Tetralins, Naphthalenes, Biphenyls, Phenanthrenes and Chrysenes.
- Heteroatom Systems
- Benzothiophenes, Dibenzothiophenes, Phenols, Carbazoles, Pyridines, Quinolines, Nitriles, Ketones and Pyrroles.
- Nitrogen-containing porphyrins and benzonquinoline in higher boiling point fractions and lower boiling point fractions of shale oil respectively.
- Arsenic and other metals

The typical challenges which plague shale oil processing are summarized in the table shown below:

Table 6. Oil shale processing challenges [5].

Operational Parameters	Limitation on final product components Product Quality Suspended fine rock fragments from entrainment during retorting
Arsenic and metal content	Severe toxicity Catalyst poisoning during hydrogenation
High pour point	Transport and pipeline limitations
Nitrogen content	Catalyst poisoning Instability of the final product Toxicity
Diolefins	Instability of the final product Limitation concerning refining and processing options

Thus, the first step in the refining process includes an upgrading section, which aims to improve the properties of the crude shale oil for transportation, especially if the final refining of the crude shale oil occurs off site.

2.4.1. Upgrading Processes Before Final Refining, Reactions and Catalysts

An insight is given below regarding individual unit operations, with a final discussion showing the combined use of these units in an overall upgrading and refining process.

2.4.1.1. Visbreaking

Visbreaking represents a relatively mild thermal treatment that can be used to reduce the pour point of the crude shale oil and also reduce viscosity, thus enabling more efficient transport by ship, tanker, or pipeline over shorter distances with lower pumping requirements [42]. This process involves heating the raw shale oil to temperatures between 480-525 ºC. The crude shale oil is then held at this temperature for several seconds to several minutes, depending on the initial pour point and viscosity of the crude shale oil and the final requirement for transport or further upgrading [42]. As a result, the final crude shale oil (containing naphtha, gas oil, and furnace oil in most cases) and the evolved gases after heating are removed, with the final pour point of the crude shale oil dropping in certain cases from 85 ºF to about 40 ºF after visbreaking [42]. However, the process is thoroughly energy intensive with little removal of nitrogen, oxygen or sulphur-containing compounds occurring [42]. The main reactions which occur in a visbreaking unit include:

- Splitting of C-C bonds, especially in long hydrocarbon components.
- Oligomerization and cyclisation of olefins and olefinic compounds to naphthenes.
- Formation of polyaromatics by condensation of cyclic molecules.

Furthermore, side reactions may occur in the process. These side-reactions may include the formation of H_2S, depending on the sulphur content of the crude shale oil, together with the formation of thiophenes, phenol, and mercaptans in certain cases depending on the raw kerogen content and make-up [42]. The final visbreaking product contains crude naphtha (including olefins, aromatics, paraffins and naphtenes), light gas oil, heavy gas oil, and residuum. All components contain minor volumes of tar acids and tar bases, with sulphur and nitrogen [43,44].

2.4.1.2. Coking

Coking represents a severe heating treatment and caters to lowering the pour point and viscosity of the crude shale oil whilst also reducing the sulphur content. Furthermore, nitrogen-containing compounds tend to concentrate on the heavier products, thus improving the overall properties of the lighter products from the process [42]. This process involves the heating of crude shale oil to approximately 480-525ºC, or the relevant coking temperature required for the specific type of crude shale oil. If the heated oil is pumped into a coke drum, the process becomes a delayed coking process [42]. The coking drums normally function in pairs and the coke formed is usually deposited at the bottom of the drum [42].

The following main reactions occur during this process, facilitating the cracking of heavy oils into valuable light liquid products with gas and solid coke as by-products:

- Splitting of C-C bonds, especially in long hydrocarbon components.
- Partial vaporization of the crude shale oil feed
- Partial cracking and successive cracking resulting in the polymerization of the liquid phase and formation of coke in the vessel.

The coke is allowed to fill roughly two-thirds of the drum before the feed is switched to the second drum in parallel with the first drum, allowing for the first drum to be cleaned. The final product contains crude naphtha (including olefins, aromatics, paraffins and naphtenes), light gas oil, heavy gas oil, and residuum. All components contain minor volumes of tar acids and tar bases, with sulphur and nitrogen [43].

Fluid coking can also be utilized to achieve a similar desired result; however, a fluidized bed of coke particles is utilized instead. The hot oil coats these particles, decomposing to form lighter gases and another layer of coke. During this process, coke must be withdrawn continuously at a rate that ensures an active stock of coke is continuously maintained within the bed [42].

2.4.1.3. Hydrotreating

During the hydrotreating process, the raw shale oil is treated with hydrogen in the presence of a catalyst. However, due to crude shale oil containing

emulsified water and suspended solids, dewatering and desalting processes usually precede the hydrotreating process [5]. These inorganic salts and solids must be removed to prevent:

- Decomposition in heat exchangers and heaters in the refiner itself, leading to products such as hydrochloric acid which can corrode equipment.
- Plugging of heat exchangers, tower trays, and heater tubes.
- Abrasion and erosion in pumps.
- Corrosion by salts.

The desalting process occurs by passing the raw shale oil through a cold preheat train, and thereafter, into a desalter unit. Before entering the desalter unit, recycled dilution water (containing sediments and produced salt water) from the desalter is injected and dispersed into the raw shale oil before the mixture is passed into an emulsifying device where the mixture is homogeneously emulsified. The injection of the recycled wash water occurs near the emulsifying device to avoid the separation of crude oil in the pipeline before reaching the emulsifying device. The mixture from the emulsifying device then enters the desalter where the mixture is split into a phase rich in oil and another phase rich in water, sediments, and other contaminants. This is carried out by electrostatic coalescence using an external electric source. By polarizing the water droplets, it is removed from the oil, together with any salts dissolved in the water. The final crude shale oil product is then sent for further upgrading [5].

The hydrotreating process for crude oil shale upgrading occurs thereafter, which caters to the removal of nitrogen and sulphur-containing heteroaromatics as well as organometallic compounds present.

Nitrogen and sulphur-containing compounds, including organometallic compounds containing arsenic and iron, can pose serious disadvantages when introduced into conventional refineries, hence, these compounds must be removed during the upgrading process. These disadvantages include:

- Arsenic and iron poisoning and fouling hydrotreating catalysts in refineries.
- Nitrogen being poisonous to most refinery catalysts, together with sulphur.
- Olefins and diolefins can lead to gum formation in later refining processes.

As a result, an initial guard bed may be utilized before the hydrotreating reactor, usually consisting of alumina, to remove organometallic compounds. However, a main disadvantage of this includes having to specially dispose of the alumina material fouled with heavy metals and organometallic compounds, posing severe environmental problems [5]. Furthermore, actual processes available to remove these organometallic compounds separately, efficiently, and without producing detrimental products prove to be extremely rare [5].

Thereafter, in a reactor bed utilizing special clay-based metallic catalysts, the main reactions as follows occur:

- Sulphur reacts with hydrogen to form hydrogen sulphide.
- Nitrogen reacts with hydrogen to form ammonia.
- Oxygen reacts with hydrogen to form water.
- Olefins and diolefins react with hydrogen to form lighter, low-molecular-weight paraffin equivalents such as methane, ethane, propane, and butane.
- Cracking of long-chain hydrocarbons to form shorter, lower-boiling hydrocarbons.

Further processing may be utilized to convert the by-products, namely ammonia and hydrogen sulphide, into usable, saleable products.

The hydrotreating process can occur in a variety of reactors. These reactors include fixed-bed reactors, fluidized bed reactors, and ebulliating-bed reactors. The latter consists of injecting the feed into the bottom of the reactor with a high velocity to cause a boiling motion to be exhibited by the catalyst bed, termed catalyst ebullition. This ensures that the bed does not become plugged with coke or liquid tars which are produced during the hydrotreating process during side reactions. It also ensures that spent catalysts and coke can be removed effectively during operation to ensure that the bed is continuously stocked with active catalyst [5].

However, in industry, fixed-bed reactors are usually used for initial treatment, whilst fluidized bed or ebulliating-bed reactors are used for fractionator products or complete treatment of the whole shale oil during upgrading [5].

2.4.1.4. Additives

In practice, two main additives are added to shale oil to upgrade it concerning transport properties. Firstly, the shale oil can be mixed with a pour point depressant which lowers the pour point considerably with no chemical change. However, this is disadvantageous especially when transport costs are low, and the shale oil compositions change per retorting treatment [42].

Another option includes the use of light petroleum crudes, usually produced on the same site as shale oil due to petroleum reserves almost always being present near shale reserves. the light petroleum crude ca be mixed with shale oil to produce a transportable blend [42]. However, the selling price of the light petroleum product by itself must be compared to the selling price of the blended product to determine whether this process is profitable [42].

2.4.2. Shale Oil Refining Processes

The refinery design for a shale oil refinery process must be carried out by first considering the characteristics of the raw shale oil feedstock supplied, the desired finished products, and also constraints caused by equipment and operating procedures [42].

The main characteristics of the raw feedstock, namely either upgraded or raw shale oil, include nitrogen and arsenic contents. The type of product required also needs to be considered, especially concerning gasoline production. Finally, the overall modifications that must be carried out, especially concerning conventional crude oil refineries, must be considered. For a typical crude oil refinery to handle shale oil, the economics of the process have to be accurately determined to check whether the production rate possible for shale oil can cancel out the funding spent on modifications to the original plant [42].

According to Johns et al. [42], six main basic operations occur in a refinery that handles conventional crude oil. These include:

- Coking
- Hydrotreating
- Distillation
- Hydrocracking
- Catalytic Cracking
- Reforming

Crude oil shale refineries may require all of the above units or only certain units due to the large variations that occur concerning their compositions. As a result, Johns et al. [42] elaborate that two main approaches exist when it comes to shale oil refining. These include:

- The distillation of the crude shale oil in its entirety, followed by catalytic or thermal treatment.
- Catalytic or thermal treatment of the whole crude shale oil followed by distillation.

The latter of the two processes is commonly practiced in industry due to minimal upgrading processes occurring on the mine site. Hence, upgrading has to occur in the refinery before products can be supplied [42]. Furthermore, the second process promotes the yield of high-value hydrocarbons and reduces the strain of successive processing units [42].

An example of refining processes can be drawn from Chevron U.S.A and USBM as per the figures shown below.

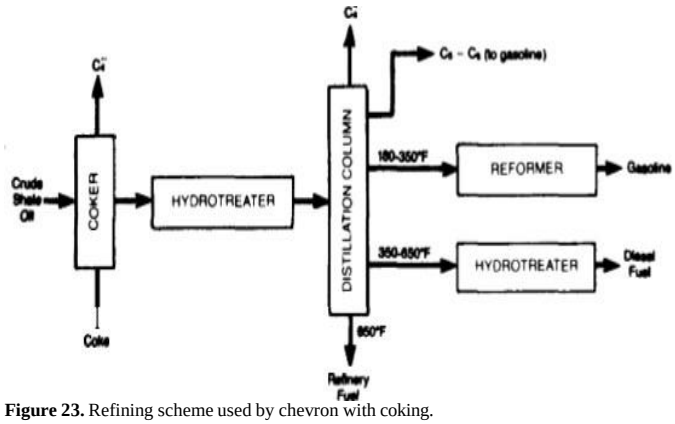


Figure 23. Refining scheme used by chevron with coking.

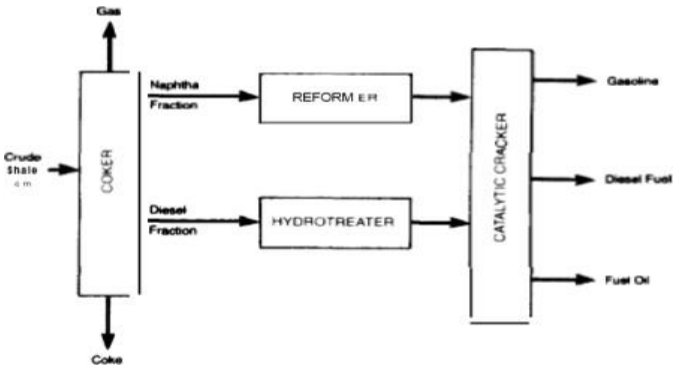


Figure 24. Refining scheme used by usbm for maximum gasoline production from crude shale oil.

Both of the above processes use coking to upgrade the crude shale oil and to produce streams that are easier to refined by units downstream from the upgrading unit. Furthermore, both of these processes produce coke, which has a suitable demand by the market.

In the case of the Chevron and USBM processes, a hydrotreater is utilized after the coker, with only diesel fractions being sent to this unit in the case of the USBM process. In both cases, the operation of the hydrotreater is the same as that which was mentioned earlier in the upgrading section, using a catalytic fixed-bed reactor, however, in both of the above processes, coke formation in the reactor is minimal due to the presence of a coker before the hydrogenation unit. Furthermore, most of the heavy components are converted into lighter components during the hydrotreating upgrading process, resulting in minimal coke formation [42].

It can be seen from above that three more processes are present for refinery upgrading over those mentioned earlier, namely reforming, catalytic cracking, and hydrocracking (which can be used to treat the refinery fuel from the distillation column in the Chevron process to produce more gasoline and refinery fuel).

Reforming using naphthas as feedstock, usually from the coking or distillation phase. The catalyst used for the process is usually made up of noble metals including platinum or rhenium and is at high risk of poisoning by nitrogen and sulphur compounds, hence, it is pivotal for these components to be removed beforehand using either hydrodesulphurization or preliminary hydrotreating on the mine site. The unit operates at roughly 495-525 ºC and higher pressures of between 5-45 atm depending on the feedstock type and quality [5]. The main reactions include:

- Naphtene dehydrogenation to form aromatic compounds and hydrogen. An example includes methylcyclohexane which yields toluene and hydrogen.
- Isomerization of conventional paraffins to isoparaffins, such as octane into 2,5-dimethylhexane.
- Paraffin dehydrogenation and aromatization, such as heptane to toluene and hydrogen.
- Hydrocracking of long-chained hydrocarbons into short-chained ones, such as n-heptane hydrogenation to form isopentane and ethane.

Catalytic cracking and hydrocracking both involve the breakdown of long-chain hydrocarbons into light, simpler hydrocarbons which are more valuable. However, hydrocracking differs from catalytic cracking in the following ways:

Table 7. Differences between catalytic cracking and hydrocracking.

Catalytic Cracking	Hydrocracking
Carbon rejection	Hydrogen addition
Zeolite/Alumina catalysts	Noble metal catalysts (Pd, Pt) or Non-noble metal sulphide catalysts (Mo, Wo, Co or Ni)
Reactor is of the riser-regenerator type	Reactor is of the packed-bed type
Produces mainly LPG/gasoline	Produces mainly kerosene and diesel
Products are rich in unsaturated hydrocarbons	Very few unsaturated products and few aromatics

Catalytic cracking usually leads to the formation of paraffins as well as olefins, LPG olefins, naphtenes, coke, cyclo-olefins, aromatics, alkyl aromatics, and unsubstituted aromatics. During hydrocracking, cracking reactions occur together with hydrotreating reactions, thus resulting in fewer unsaturated products [5].

Apart from using shale oil as feedstock for petrochemical and refinery feedstocks, the residues left from mining can also be used in cement preparation. Raw fuels such as marine fuel, jet engine fuel, and carbon black can be produced from shale oil residue which is a waste usually discarded after shale oil refining. Furthermore, gases such as hydrogen, carbon monoxide, and carbon dioxide can also be produced from shale oil raw material. Shale oil can also be utilized as boiler fuel due to the small capital investments required and short lead times [42].

3. Advantages and Disadvantages of the Equipment and Methods Used for Processing and Refining Shale Oil

3.1. Mining Procedures

When comparing underground mining to surface mining, underground mining poses the following significant advantages as opposed to surface mining:

- High flexibility with ease of modification to compensate for new equipment, conditions, or newer advancements in the process.
- This type of mining can pose a very high degree of mechanization, implying much higher production rates due to the possibility of mining various areas of the deposit at once.
- In the case of room and pillar mining, ventilation is relatively easy to compensate for.
- In the development of access paths and ventilation paths, production is indirectly being achieved due to oil shale removal in the process of creating these paths.
- Some underground mining processes, especially those practicing the room and pillar method can be designed to keep surface subsidence to a minimum.
- The thickness of the overburden surrounding the deposit does not significantly hamper the underground mining process.
- Underground mining can become more feasible than surface mining, especially in cases where deposits are 1000-2000 feet deep below overburden, hence, the overall stripping costs are greater than the starting cost of an underground mine.

However, underground mining does pose significant disadvantages compared to surface mining. These include:

- High costs of roof supports and the systems to put them into place, which are not required during surface mining procedures.
- In the case of underground procedures such as the room and pillar method, recoveries become hampered by the use of oil shale as pillars during the mining process for structural integrity, resulting in portions of shale not being recovered, ultimately affecting the overall yield.
- If severe fractures or natural defects occur on the surface of the shale or internally, this can severely hamper the progress of underground mining, resulting in excess costs to build new supports for the area to be mined.

3.2. Retorting Procedures

TIS processing offers the main advantage of mining not being required during the process, with shale that has been spent not being produced on the surface. As a result, the environmental, technical, and economic issues that have become associated with AGR waste disposal are avoided. MIS processing does require mining and waste disposal as well, however, the extent to which this is performed is far less than that of AGR processing. MIS processing also produces overburden or raw oil shale wastes to improve the shale permeability. As a result, these materials are exposed on the surface, causing possible leaching of soluble organic materials from the disposal piles.

Spent shale underground in both the MIS and TIS processes also has severe environmental concerns associated with it. Soluble salts in the spent shale can become leached by groundwater, thus requiring expensive environmental controls.

The TIS processing type also has some major advantages over the MIS and AGR types concerning the required surface facilities for processing. Wells, gas cleaning, pumps, and mainly product recovery systems, together with other peripheral systems, are only required for processing, implying minimal requirements as opposed to the AGR and MIS processes. MIS requires facilities to enable the mine support and waste disposal procedures. Furthermore, AGR processing has the vastest number of facility requirements, also resulting in the largest degree of surface disruption.

Furthermore, ex-situ processing by AGR processes provides the following advantages:

- Effectively high organic matter recovery in terms of yield, often between 70-90% w/w of the total organic matter content within the shale.
- The operating variable for the processes shows a high degree of controllability, thus also facilitating the minimization of undesirable conditions for processing.
- The recovery of the product is relatively simple as opposed to in-situ processes.
- The units utilized within the process can be used for a large number of operations concerning retorting.

However, the following disadvantages plague ex-situ processing options:

- The need for mining, crushing, transporting, and heating the shale results in high operating and safety costs.
- The high operating costs limit the overall process to deposits that are rich in organic material to ensure the economic viability of the process.
- Environmental risks associated with improper waste disposal.
- Revegetation costs for the site after completion of the withdrawal of shale deposits.
- Large-scale units are associated with extremely high capital investment requirements.

Concerning in-situ processing options such as the TIS and MIS processes, the following advantages are proposed:

- This processing option facilitates the recovery of oil from extremely deep deposits of oil shale.
- Mining costs can be minimized in the case of MIS and eliminated in the case of TIS.
- Solid waste disposal issues are eliminated.
- Leaner shales can be used for processing.
- Greater economic viability due to minimal mining, transportation, and crushing costs associated with the in-situ process.

However, the following disadvantages were also determined for the process type;

- Difficult control of combustion in the subsurface due to inadequate permeability within the shale deposit.
- Large costs associated with drilling.
- Poor recovery efficiencies in these processes are common, especially in inadequately permeable shale deposits.
- The achievement of the desired permeability and porosities in the shale formation can prove to be difficult.

3.3. Environmental Aspects During Mining, Processing, Upgrading and Refining

As with any mining procedure, processing procedure, and refining procedure, contribution to environmental pollution becomes inevitable at certain points. However, technologies are put into place to minimize the effect of oil shale processing and refining on the environment. The following table summarizes the main environmental issues associated with oil shale processing and refining and the relevant safeguards put into place to limit the effects on the environment.

Table 8. Environmental issues and control measures associated with oil shale refining and processing.

Environmental Issue	Contaminant/Pollutant	Hazard	Source	Safeguards
Dust Emissions and Particulate Matter	Dust, particulates (containing silica)	Explosion hazard, respiratory tract penetration leading to pneumoconiosis, silicosis, and bronchitis	Blasting, earthmoving operations, crushing, sizing, transfer conveying, transportation, wind erosion.	Water spraying, proper site selection, dilution and dispersion by ventilation, dust collection by filtration, cyclones, baghouses, centrifugal devices, disintegration and electrostatic precipitation.
Mine Waste Disposal	Spent shale, extracted shale, dust, soluble organic components, soluble salts, toxic pollutants.	Groundwater contamination, diminished ecological habitats, oxidation of pyrites to produce acidic compounds that can be leached, spontaneous combustion in waste tips, and destruction of indigenous vegetation.	Waste from processing operations, deep mine shaft sinking, roadway creating, and ventilation tunnel creation.	Reduced and controlled waste tipping, proper site selection, waste compaction, mine land reclamation, land revegetation, chemical treatment of contaminated water sources, and 'freeze all' creation.
Hazardous Air Pollutants	Hydrogen sulphide, ammonia, carbon monoxide, sulphur dioxide, carbon dioxide, nitrogen oxides, unburned hydrocarbons, metal carbonyls, heavy metals, and trace metals.	Acid rain formation, and air pollution lead to respiratory tract diseases.	Oil shale retorting, refining, and upgrading processes.	Modified combustion designs, flame temperature regulation, electrostatic precipitation, gas scrubbers.
Water Quality	Suspended solid matter and material, fine shale dust, biological matter, dissolved inorganic and organic material.	Waterway poisoning, depletion of local wildlife using the water sources, destruction of species.	Mine drainage water, retort condensate streams, cooling water dust pick-ups, leaching from waste piles, organic compounds in raw shale, wash water, overburden removal.	Systematic mining plans for waste treatment, usage and minimization, aesthetic rehabilitation of mined lands, water testing procedures, and utilisation of 'freeze walls'.
Water Requirements	-	Water depletion from surrounding water bodies.	Oil shale retorting requires 1-3 barrels of water per barrel of oil production [5]	Implementing water recycling procedures, and minimising excess water disposal.
Subsidence	-	Displacement of the surface, resulting in structural damage to buildings, railroads, roadways, and pipeline ruptures.	Improper mining processes and poor site selection.	Mine planning and design, proper reclamation procedures, and proper overburden removal procedures.
Reclamation	-	Disruption of the environment, ecosystem, and vegetation.	Surface and underground mining practices.	Periodic land reclamation, proper overburden and waste handling, and proper site selection.

4. Shale Oil Markets

Crude shale oil has the potential for use in three main areas of industry. These uses include:

- Boiler fuel
- Refinery feedstock
- Petrochemical feedstock

4.1. Boiler Fuel

Shale oil is used as boiler fuel in most applications due to small investments of capital being required and short leadtimes. The use of shale oil as boiler fuel frees up the use of coal, natural gas, and other oil products for domestic and industrial use. However, transportation and logistical issues associated with transporting the oil to areas further away from mines do pose an issue [42].

4.2. Refinery Feedstock

Johns et al. [42] stated that little research was carried out by refineries regarding the use of shale oil as feedstock due to uncertainty around the idea of using shale oil as a feedstock. However, to use the oil as a feedstock, modification of equipment together with pilot plant creation can take over three years to create.

Furthermore, shale oil is a source of heavier distillates, not gasoline fractions, thus previous use of shale oil for gasoline production was undesirable. However, with current crude oil fractions containing more and heavier distillates as opposed to gasoline, shale oil is becoming more attractive as a feedstock for refineries [42].

4.3. Petrochemical Feedstock

The use of shale oil as petrochemical feedstock must be subject to three considerations, namely;

- The overall yield of petrochemicals using the shale oil feedstock;
- The ability of plants to use shale oil as a feedstock;
- The logistical concerns surrounding shale oil supply to the facilities in question.

Shale oils have an approximate olefin content of 12 % which is higher than conventional crude oil [42]. Furthermore, it also has a high hydrogen content, implying that it is appropriate for use as feedstock [42]. However, these are shadowed by the main disadvantage of distances between oil shale regions and petrochemical plants in most countries, with oil-fired boilers and general oil refineries situated much closer than petrochemical firms. As a result, shale oil becomes very difficult to use as feedstock for petrochemical industries due to economical transportation solutions being rare [42].

5. Research and Development Needs for Oil Shale Processing and Refining

The major areas requiring development and insight in each processing case and refining case are summarized below per section of the processing or refining of oil shale as per Johns et al. [42].

5.1. TIS Retorting

- Inexpensive drilling methods;
- Cost-efficient rubbelisation methods;
- Development of ignition procedures which form uniform burn fronts;
- Effect of infiltration of groundwater on retorting procedures;
- Evaluation of the effects of creep on retorting;
- Evaluation of possible uses for surface subsidence.

5.2. MIS Retorting

- Improvement of rubbelising procedures;
- Newer, more improved sensing methods for permeability, temperature, and flow of fluid;
- Development of ignition procedures which form uniform burn fronts;
- Evaluation of the effects of creep on retorting;
- Determination of the effects of infiltration of groundwater on retorting;
- Effects of retort geometry and particle size distribution on yield or organic material.

5.3. AGR Retorting

- Evaluation of scale-up on flow patterns in the retort vessels;
- Improvement of pollution control, product separation, and reliability of retorts;
- Evaluation of heat carrier effects on product recovery;
- Improvement of mechanical component reliability in the plant.

5.4. Upgrading, Distribution and Refining

- Effects of heavy metals in crude shale oil on refining catalysts and retorting;
- Feasibility of using chemical additives to alter pour point;
- Improvement of distribution patterns and logistical ease concerning transport systems.

6. Conclusions

- Oil shale is a mixture of many fine-grained sediments formed over a large geological period, containing a solid organic-based, hydrocarbon material called kerogen, which when heated or retorted, results in combustible gases, raw shale oil and spent or retorted shale.
- Oil shale roughly consists of 60-90% inert mineral matter, with the remainder comprising processable organic matter.
- The composition of the oil shale itself varies with location and the source which makes up the organic matter.
- Oil shale deposits are found throughout the world, with the largest deposits found in North America, containing approximately 539 123 000 000 tonnes of oil shale.
- Oil shale can be classified into three main types, namely, terrestrial oil shale, lacustrine oil shale, and marine oil shale.
- Terrestrial oil shale was formed from cannel coal deposits in stagnant, oxygen-deficient waters on land.
- Lacustrine oil shale formation occurred from algae residing in freshwater, brackish, or saline lakes, resulting in these deposits forming near lake bottoms.
- Marine oil shale was formed from marine algae and can be found in aquatic, marine environments.
- Lacustrine oil shale mainly occurs as lamalginite-rich lamosite deposits or telalginite-rich torbonite deposits.

- Marine oil shales either occur as marinite, tasmanite, or kukersite deposits.
- The required kerogen-to-shale ratio for commercially viable production is between 0.75:5 to 1.5:5.
- The kerogen contains high levels of carbon and hydrogen; however, considerable amounts of nitrogen, sulphur, and oxygen are also found in its composition, posing considerable processing difficulties.
- The inert mineral components that make up the oil shale consist of calcite, dolomite, siderite, nahcolite, dawsonite, silicates, sulphur-based compounds, and small portions of vanadium, zinc, copper, and uranium.
- The yield of oil from the thermal decomposition of kerogen is a function of the hydrogen-to-carbon ratio of the organic matter, the time in the reaction zone, and the temperature at which the decomposition occurs.
- Low retort temperatures of nearly 300ºC initiate kerogen decomposition, with the highest decomposition rates occurring near temperatures of 480-520ºC. However, this value varies with the type of oil shale and composition, with some authors reporting values of 425ºC for the temperature at which the maximum rate of decomposition occurs.
- Increases in retorting temperatures decrease oil yields and increase gas yields.
- At higher temperatures approaching 500ºC, inert mineral matter in the oil shale also begins to decompose.
- The Fischer assay test method (ASTM 3904) is commonly used to determine the quantities of gas, oil, and water that will be released during retorting from a particular oil shale sample.
- The TOSCO II process test and the Rock-Eval test pose alternate methods to test for oil shale grade and possible product formations.
- Voidage, permeability, compressive strength, and thermal conductivity of the oil shale are all important factors that must be determined before processing operations.
- Kerogen probing methods such as ultimate analysis and functional group analysis are also utilized to determine the detailed constituents of the organic matter.
- Shale processing can occur via three main methods, namely, the TIS process, the MIS process, and the AGR process.
- The TIS process involves underground retorting, whilst the MIS process requires rubbelisation and then underground retorting.
- The AGR process involves mining and then heating in retorting vessels.
- The TIS process offers the main advantage in that mining is not required during operations, with less environmental, technical, and economic issues associated with it, thus making it more attractive as opposed to the AGR process.
- MIS processing has significant leaching risks associated with spent overburden on the surface.
- MIS and TIS processing also leave spent shale underground, thus posing leaching risks.
- The TIS process requires fewer facilities, whilst the AGR process requires the most facilities and economic input.
- However, AGR provides high organic matter recovery, high process controllability, simple recovery, and multi-functional units.
- The AGR process uses four main types of retorts, namely class 1, class 2, class 3, and class 4 retorts, which all differ in their manner of heat transfer to the oil shale.
- Both the MIS process and the AGR process require mining of either the surface mining type or the underground mining type.
- Surface mining can occur either by open pit or strip mining, with strip mining being rarely used due to thick overburden covering shale deposits.
- Underground mining mainly occurs by the room and pillar method, except in the case of MIS processing, where special extraction techniques must be carried out to ensure space for openings, ventilation, drainage, passageways, and transportation systems for products.
- Underground mining shows high flexibility, ease of modification, high production rates, and decreased surface subsidence with minimal influence by overburden, however, it also poses high economic investment, hampered recoveries, and severe hampering by deformations in the shale.
- Typical upgrading processes for produced shale oil include visbreaking, coking, hydrotreating, and additive additions.
- Typical refining processes for shale oil include coking, hydrotreating, distillation, hydrocracking, catalytic cracking, and reforming.
- Typical environmental constraints posed by the processing of oil shale include dust emissions, particulate matter emissions, mine waste disposal issues, hazardous air pollutants, water quality issues, water requirements subsidence, and reclamation.
- Shale oil can be used as boiler fuel and feedstock for refineries and petrochemical firms.
- Logistical issues plague these ideas of the uses for shale oil, together with heavier distillates being resent in shale oil.
- Various opportunities exist for research and development of shale oil processing procedures, refining upgrading, and transportation methods.

Credit authorship Contribution Statement

Sameer Jayram: Conceptualization, Investigation, Resources, Writing - Original Draft. Amir Hossein Mohammadi: Conceptualization, Supervision, Project administration, and Writing - Review & Editing.

Conflicts of Interest

The authors declare that they do not have any personal or financial conflicts of interest.

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