DECLARATION

We here declare that this Bachelor's Project is the result of our work, except for some quotations and summaries which have been duly acknowledged.

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APPROVAL

This project named **Hydrocarbon Estimation of Shale Source Rock Formation (Madbi) in Al-Sabatayn Basin, Yemen**, is submitted to the College of Engineering and IT Faculty, Oil and Gas Department in Emirates International University, Sana'a, Yemen. And has been read and approved by **Dr. Yassin Saleh** for meeting part of the requirements and regulations in partial fulfillment for the degree of Bachelor of Science (Petroleum Engineering).

Project Supervisor: **Dr. Yassin Saleh**

Date: …………………………………

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ABSTRACT

Increasing the oil consumption and depletion of conventional oil has caused to focus attention to unconventional oil which represents 80 % of total oil in the world. Our project focus on shale formation (Madbi) which is considered as the source rock for conventional reservoirs in basins of Yemen. Such a study requires complicated technologies and complex calculations. Bituminous shales of the Late Jurassic Madbi Formation from Marib-Shabwah-Al-Jawf depression in the Sab'atayn Basin have been analyzed. The bituminous-analyzed shales contain mainly marine phytoplankton algae and minor land plants and are deposited under reducing environmental conditions. The rich in lipids from phytoplankton algae and land plants suggest high Type II to mixtures of Types II and Type III kerogen as the original organic facies during deposition. The presence of the reducing conditions during deposition consequently enhanced the preservation and subsequently gave rise to the enrichment of organic matter in the analyzed bituminous shale as indicated by the relatively high TOC values between 1 and 14 Wt%. The geochemical maturity indicators show that the analyzed bituminous shales have reached a low maturity stage, and commercial oils have not yet been generated. Therefore, the results presented and discussed in this study suggest that the low maturity bituminous shales can be heated to crack the kerogens and a subsequently significant amount of oil can be generated.

ACKNOWLEDGMENTS

First, we would like to express all gratitude to Allah for helping us and he has given us the needed power to pass this period of our academic life. Then all thanks to our supervisor **Dr. Yassin Saleh** for his great support, motivation, and guidance. He is owed our special thanks for sponsoring this Bachelor's program. We extend our sincere thanks to **Dr. Mohammed Al-Zubiri** for his invaluable time, input, and comments. We also thank our assistants for supporting us in the Bachelor's program and guiding us since the first semester.

Besides, we deeply appreciate contributions from the following people to make this project complete:

- Our Parents and families for their constant support and valuable suggestions throughout our involvement in this project.
- Our Friends for being a constant source of motivation and setting an example of perseverance for us.
- To **Dr. Ibrahim Farea** (The Dean of our College) for graduate program guidance, including scheduling and planning to meet the project timeline.

Finally, Thanks to all faculty, staff, and friends for their great education, support and assistance during our academic program.

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Chapter One

1.1. INTRODUCTION

Oil shale, also known as *kerogen shale*, is an organic-rich fine-grained sedimentary rock containing kerogen (a solid mixture of organic chemical compounds) from which liquid hydrocarbons called shale oil (not to be confused with tight oil crude oil occurring naturally in shales) can be produced. Shale oil is a substitute for conventional crude oil. However, extracting shale oil from oil shale is costlier than the production of conventional crude oil both financially and in terms of its environmental impact Deposits of oil shale occur around the world, including major deposits in the United States. Estimates of global deposits range from 2.8 to 3.3 trillion barrels (450×10^9 to 520×10^9 m^3) of recoverable oil shale in place. Heating oil shale to a sufficiently high temperature causes the chemical process of pyrolysis to yield a vapor. Upon cooling the vapor, the liquid shale oil is separated from combustible oil-shale gas (the term shale gas can also refer to gas occurring naturally in shales). Oil shale can also be burnt directly in furnaces as a low-grade fuel for power generation and district heating or used as a raw material in chemical and construction-materials processing. Oil shale gains attention as a potential abundant source of oil whenever the price of crude oil rises. At the same time, oil-shale mining and processing raise a number of environmental concerns, such as land use, waste disposal, water use, waste-water management, greenhouse-gas emissions and air pollution. Estonia and China have well-established oil shale industries, and Brazil, Germany, Russia also utilize oil shale. Oil shales differ from oil-bearing shales, shale deposits which contain petroleum (tight oil) that is sometimes produced from drilled wells. Examples of oil-bearing shales are the Bakken Formation, Pierre Shale, Niobrara Formation, and Eagle Ford Formation. the most common production technology has been surface mining, followed by processing in above-ground retorts. Process temperatures are about 500°C, which converts kerogen to oil in about an hour. This approach has the virtue of simplicity, but requires expensive surface facilities, and the disposal of vast quantities of spent rock. Both have significant economic and environmental problems.

Raw product quality is poor compared to conventional crude oil. However, upgrading using conventional hydro-processing techniques yields high-quality finished products. The mining + retort method is an old approach that could benefit from new technology. Improved methods for spent shale remediation would clearly make this approach more acceptable. Innovations that allowed oil shale to be processed at lower temperature without an increase in reaction time would result in improved economics and improved product quality. An alternative process still in development, in situ conversion, has captured the industry's attention. Wells are drilled, and the oil shale reservoir is slowly heated to about 350°C, at which point kerogen is converted to oil and gas on a time scale of months. Using an in situ conversion process at pilot scale, Shell has extracted a good quality, middle-distillate refinery feedstock, requiring no further upgrading. In order to contain nascent fluids, and to prevent ingress of ground water into the reaction zone, Shell generates a freeze wall around the production area. Chevron has proposed a simpler technique that takes advantage of the low hydraulic permeability of oil shale formations to isolate heated process volumes from surrounding aquifers. Since in situ conversion technology is just emerging, it is not yet clear which specific technologies can advance the state of the art over the coming decades. However, the efficient use of heat is almost certain to be an important issue. The ability to map the temperature and the saturation of generated oil and gas throughout the reservoir would enable advanced control strategies. It will also be useful to monitor the freeze wall or low permeability barrier, to ensure that there is no fluid mixing between the reaction zone and surrounding formations. As a domestic source of transportation fuel, oil shale could compete with heavy oil and coal derived liquids. Oil shale, heavy oil, and coal are all abundant in North America. Canadian tar sand production is already commercial. Coal can be treated with coal-derived solvents and gaseous hydrogen at high temperature to produce high grade synthetic crude. An advantage of oil shale is that it has the potential to produce a superior liquid-fuel product. However, the direct and indirect costs of fuel production from oil shale have not yet been fully evaluated. [2]

The black shales source rock is widely distributed in Sab'atayn basin in several horizons of different geologic ages. No serious approach had been made to evaluate their geological as well as their economic significance. This may have been due to the lack of interest in developing and using these economically important deposits as a source of fuel, most probably due to the competition of oil. (Mills, 1992; Eills *et al*., 1996; Csato *et al*., 2001; Thomas, 2002; King *et al*., 2003). However, few studies have investigated the geochemical characteristics of the shale source rocks or their thermal and burial histories, and the timing of hydrocarbon generation is therefore poorly constrained (Figure 1.1).

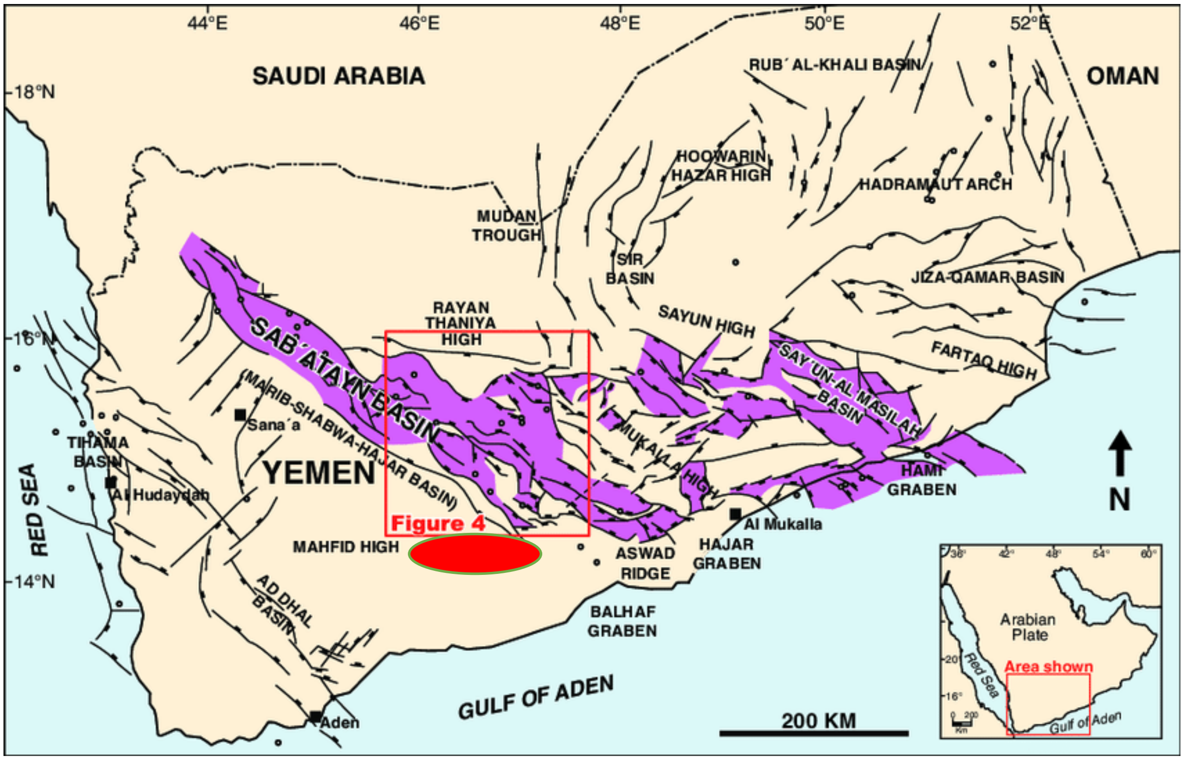


Figure 1. 1. Map of The Study Area

1.2. AIM AND OBJECTIVES

1.2.1. Aim of The Project

The project aims to extend the exploration activities and production contribution for both unconventional and conventional petroleum resources in the whole basin.

1.2.2. Project Objectives

The main objective of our project is targeting shale formation (Madbi) to:

- Improve Oil Recovery
- Increase Basin Reserve

That could be either by

- Oil Shale Methods or
- Shale Oil Techniques

Also,

- Does the Madbi (Lam and Meem) formation get production contribution from shale member? if it does so, then;

1.3. PROJECT ADVANTAGES

- Understanding the recovery mechanism in Madbi formation that considered an important source rock in the Sab’atayn basin.
- The ability to improve recovery.
- Increasing reserve as much as possible.
- Knowing the factors affecting shale contribution.
- Knowing the differences between oil shale and shale oil methodologies to extract hydrocarbons.

1.4. SCOPE OF THE PROJECT

The target of our project is shale formation include Madbi formation that consists of two shale member (Lam and Meem).

1.5. SIGNIFICANCE OF THE PROJECT

The project’s significance is to improve, increase, and maximize the recovery resources in the whole Sab’atayn Basin, basically by proposing suitable methods that are used in fields similar to the characteristics of the basin in the developed world countries.

1.6. SAB’ATAYN BASIN

The earliest exploration for hydrocarbons in Yemen was commenced in 1961 within the Red Sea coastal region. However, the first commercial discovery was made in 1984 in Marib, Shabwah, and Al-Jawf sub-basins, Sab.atayn Basin in the central part of the Republic of Yemen (Figure 1.2). Yemen entered the era of oil in the summer of 1984 when the Yemen Hunt Oil Company announced the first commercial discovery of oil in the Alif field (Figure 1.3). The Alif-1well started with a production rate of 8000 BOPD. Since that time several oil and/or gas fields were discovered in Block 18 (Figure 1.3). Meanwhile, development of Block 18 was carried out through construction of a pipeline to the Red Sea. In September 1986 the production and export of the first oil shipment from Block 18 was executed. In 1987 oil discoveries were announced by Technoexport, a former Russian oil company, in several fields in the Shabwa sub-basin. In September 1996 oil was discovered in the Halewah oilfield, Block 5, in the Sab'atayn Basin (Figure 1.3). It was discovered by a consortium of companies operating in this block.

In 2003 the Vintage Petroleum Company announced another commercial oil discovery within Block S1. There are 36 discoveries in the Sab'atayn Basin with the estimated resource of the Alif reservoir reaching to almost 1.7 billion barrels of oil and condensate as well as 18 trillion cubic feet of gas. The clastics and evaporites of the Sab'atayn Formation are providing the reservoir and regional seal within the Marib and Shabwa sub-basins. The major reservoir was recognized in the Alif Member and in the Yah, Seen and Safer Members as minor reservoir units in blocks 18, 5, 4 and S1 (Figures 1.3,1.4). Further activity spread to the southern and eastern parts of the Republic of Yemen with a series of discoveries made by different petroleum companies from the early 1990.s until now. [1]

1.6.1. Geological Setting

The geological evolution of Yemen was driven by the plate motions that broke southern Gondwana apart in the Mesozoic and formed the Gulf of Aden and Red Sea in the Cenozoic. The stratigraphy and regional geology of Yemen was established by several workers. Hydrocarbon exploration activity increased extensively after 1984 and provided considerable amounts of subsurface data such as the work of which allowed a revised synthesis of the basin evolution in Yemen. Only a few publications have addressed the geology and petroleum geology of the Sab'atayn Basin which is a comparatively poorly studied basin. The interior rift basins of Yemen were formed as a result of the Late Jurassic rifting between East Africa and western India. The Sab'atayn Basin, as a major Mesozoic rift basin of

Yemen, comprises several sub-basins which are from northwest to southeast Al-Jawf, Marib and Shabwa (Figure 1.2). The Sab'atayn Basin is 50.120 km wide and more than 450 km long (Figure 1.2). The stratigraphic column in the Sab'atayn Basin is dominated by a thick Mesozoic succession with an average thickness reaching up to 2500 m (Figure 1.4). The oldest sediments within the northern and north-western parts of the Sab'atayn Basin are of Palaeozoic age (Wajid and Akbarah formations). The Wajid and Akbarah Formations are only recorded as subsurface occurrences in the northern part of the Sab'atayn Basin, particularly within the Al-Jawf sub-basin, and the Akbarah Formation occurs in the north-western part of the Marib sub-basin but with limited extension (Figure 1.4). During the early to middle Jurassic time the Kuhlan Formation was deposited and preserved in small intra-basinal lows surrounded by broad Late Jurassic platforms [8, 10 and 28]. This formation is not recorded in most of the central parts of the Sab'atayn Basin (Figure 1.4). The pre-rift phase sequences in the basin are represented by the Wajid, Akbarah, and Kuhlan Formations (Figure 1.4). The Kuhlan Formation is conformably grading upwards into the platform carbonates of the Shuqra Formation. The Marib and Shabwa sub-basins were dominated by filling of the Amran Group sequences as a result of the first major NW-SE oriented rifting phase which included Shuqra, Madbi, Sab'atayn and Nayfa Formations (Figure 1.4). The Shuqra Formation was deposited during Bathonian/Callovian-Oxfordian time as a result of the early-rift phase events. The syn-rifting phase created horst and graben structures which provide the organic rich sediments of the Madbi Formation (Figure 1.4). The syn-rift phase strata within the Sab'atayn Basin are of Kimmeridgian age with maximum subsidence and sedimentation rates occurring in this time. The late syn-rift phase events during Tithonian time caused the formation of the thick sequence of clastic and evaporate sediments of the Sab'atayn Formation (Figure 1.4). The Marib and Shabwa sub-basins were isolated and filled with fluvial-deltaic to shallow-nearshore clastics and evaporites of this formation during late-rift phase events. Madbi and Sab'atayn Formations constitute the source, reservoirs and seal rocks of the Marib and Shabwa sub-basins. The Nayfa Formation is formed by the postrift phase events during the Late Tithonian to Early Berriasian time (Figure 1.4). The Tawilah group sediments were predominantly deposited by the second major NW-SE oriented rifting phase of the Sab.atayn Basin during Cretaceous time (Figure 1.4). This study is mainly focused on the main source rocks of the Madbi Formation, which consists of argillaceous strata with porous lime-grainstone to argillaceous lime-mudstone. The lithofacies represents deposition within an open marine to shallow marine environments. Increased organic content indicates restricted basin conditions with anoxic bottom waters. This succession is classified into two lithostratigraphic units. The lower unit, Meem Member, is commonly made up of argillaceous limestone whereas the upper one, Lam Member, is composed of laminated organic-rich shale, mudstone, and calcareous sandstone and is a prolific source rock in the Sab'atayn Basin (Figure 1.4). Both of these have organic-rich black shale deposited in the deeper portions of the Marib sub-basin. Therefore, they are considered to represent the main source rocks among all the productive sedimentary basins of Yemen. [1]

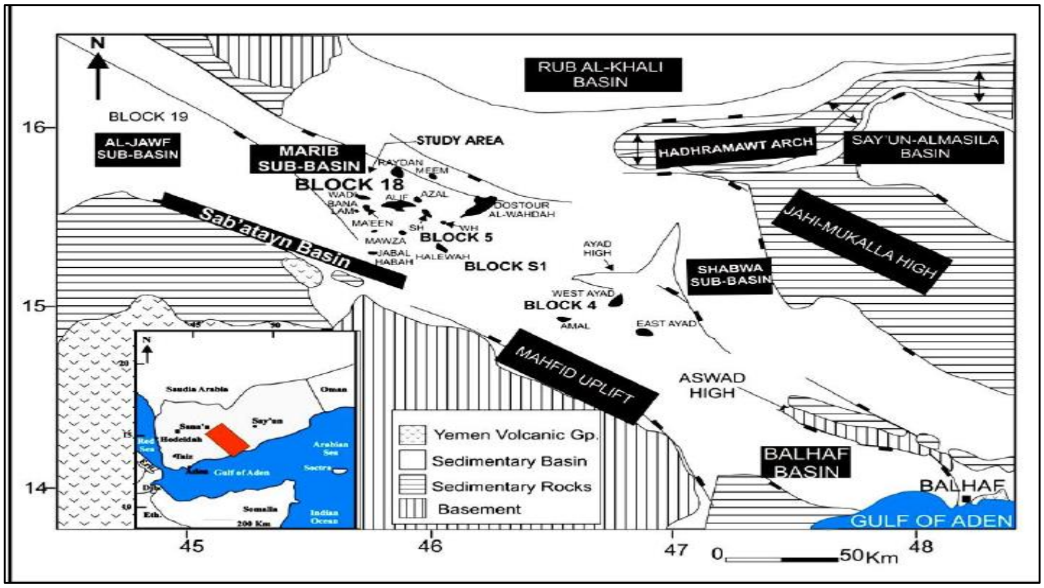


Figure 1. 2. Simplified map of the Sab'atayn Basin

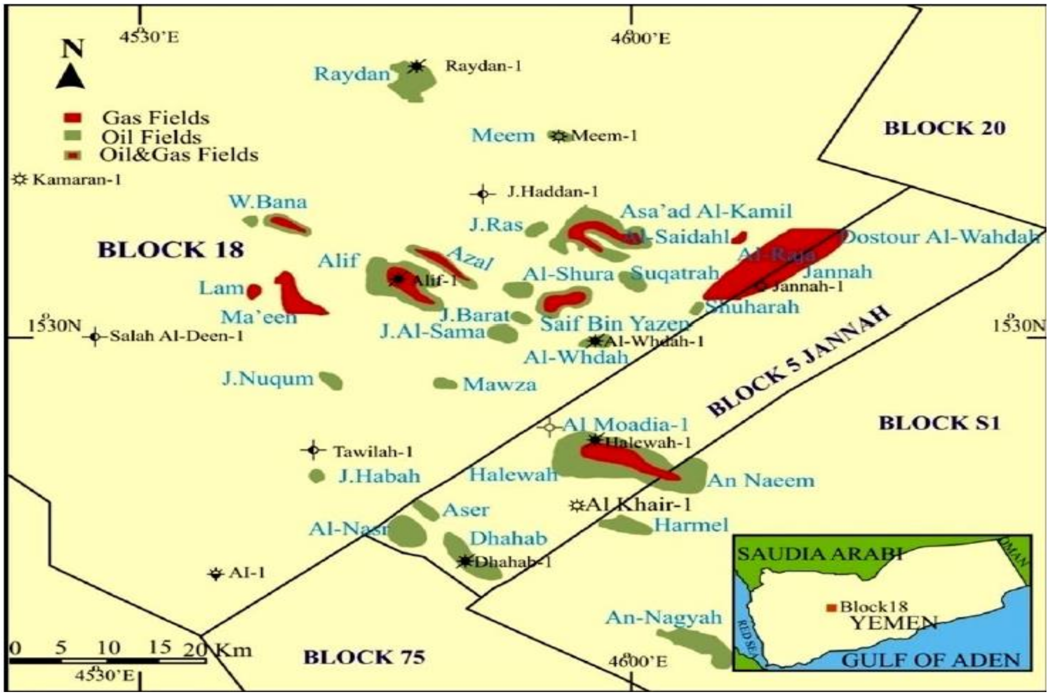


Figure 1. 3. Simplified location map of the studied wells

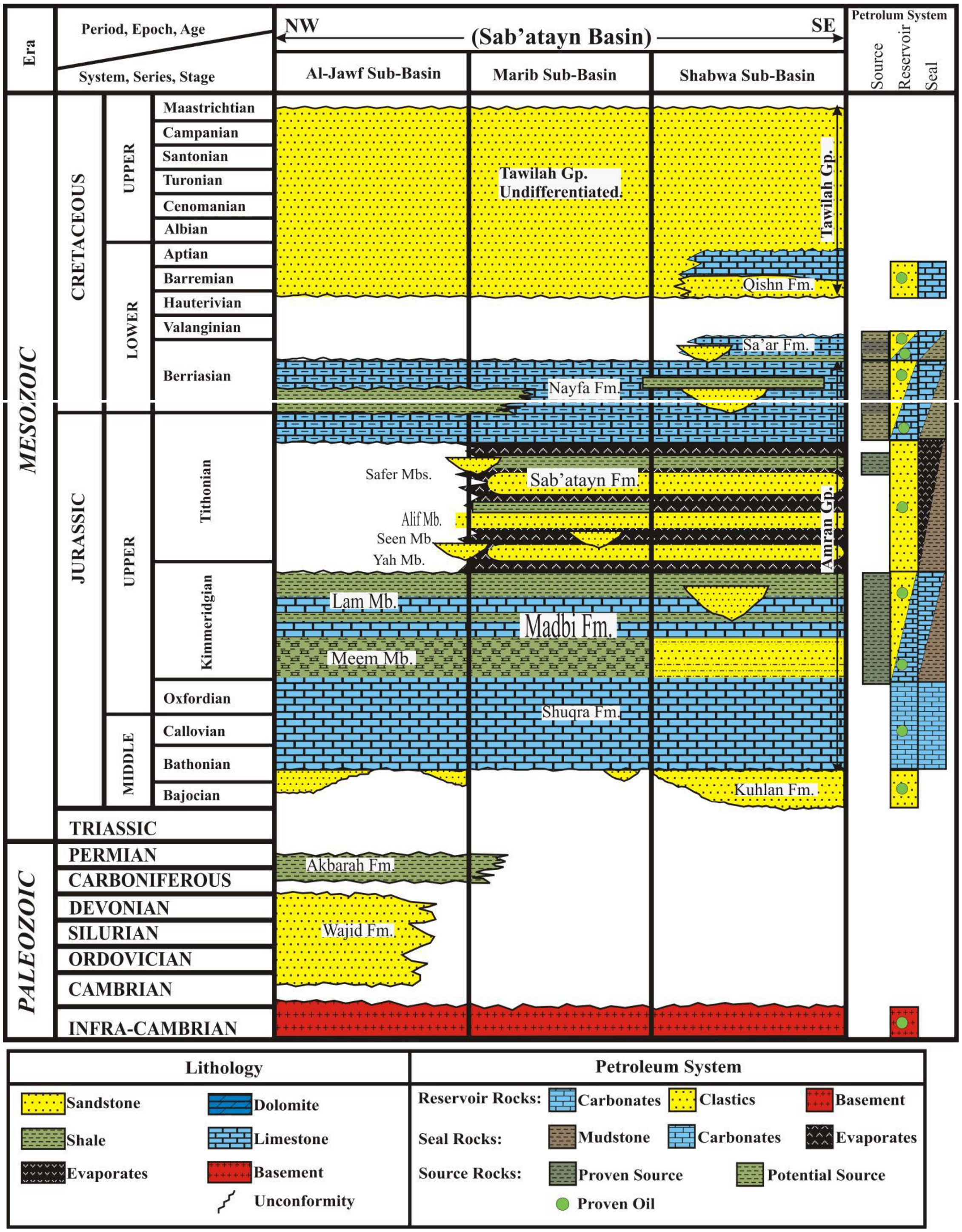
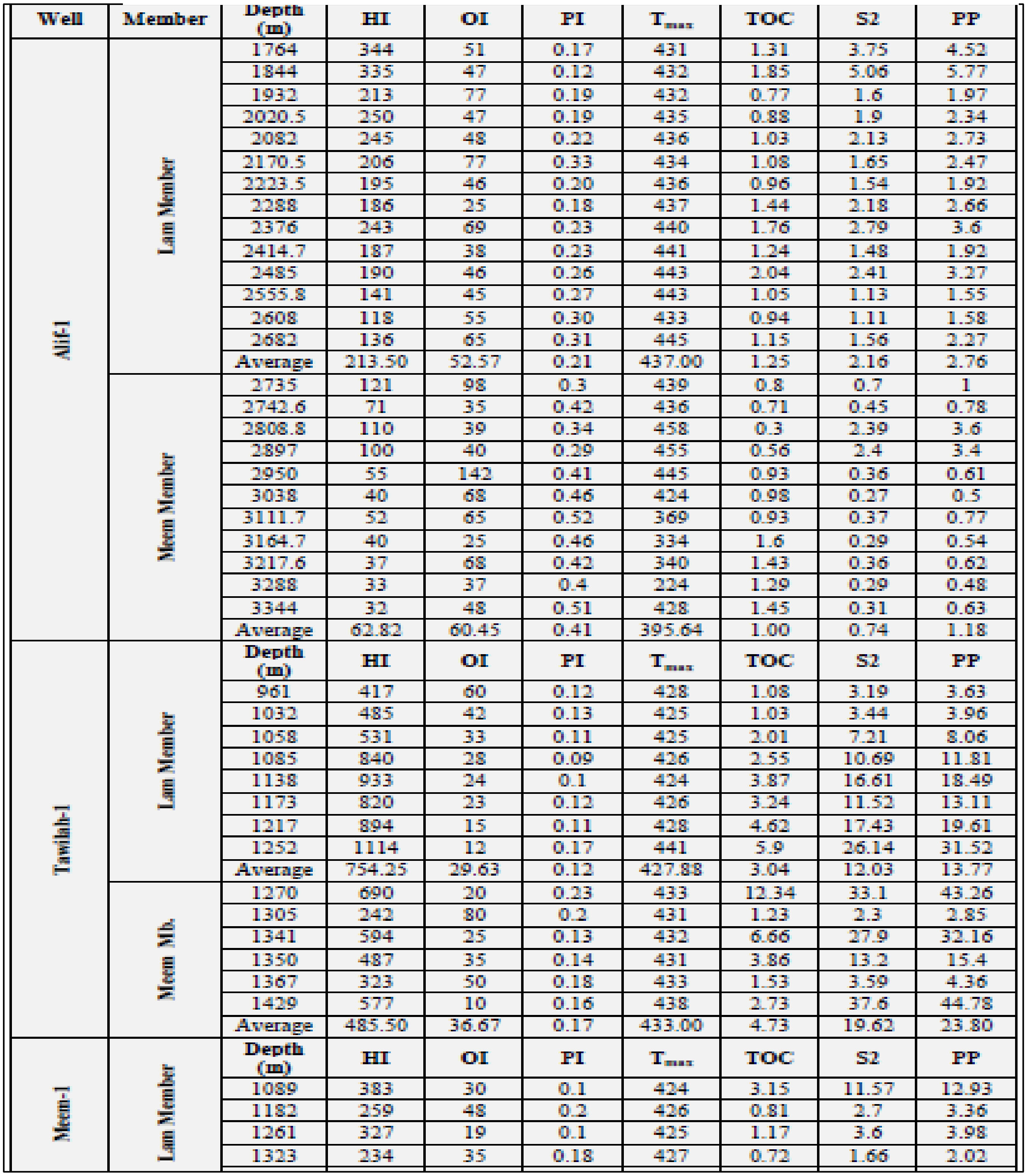


Figure 1. 4. Lithostratigraphic chart of the Sab'atayn Basin with a summary of the petroleum system elements

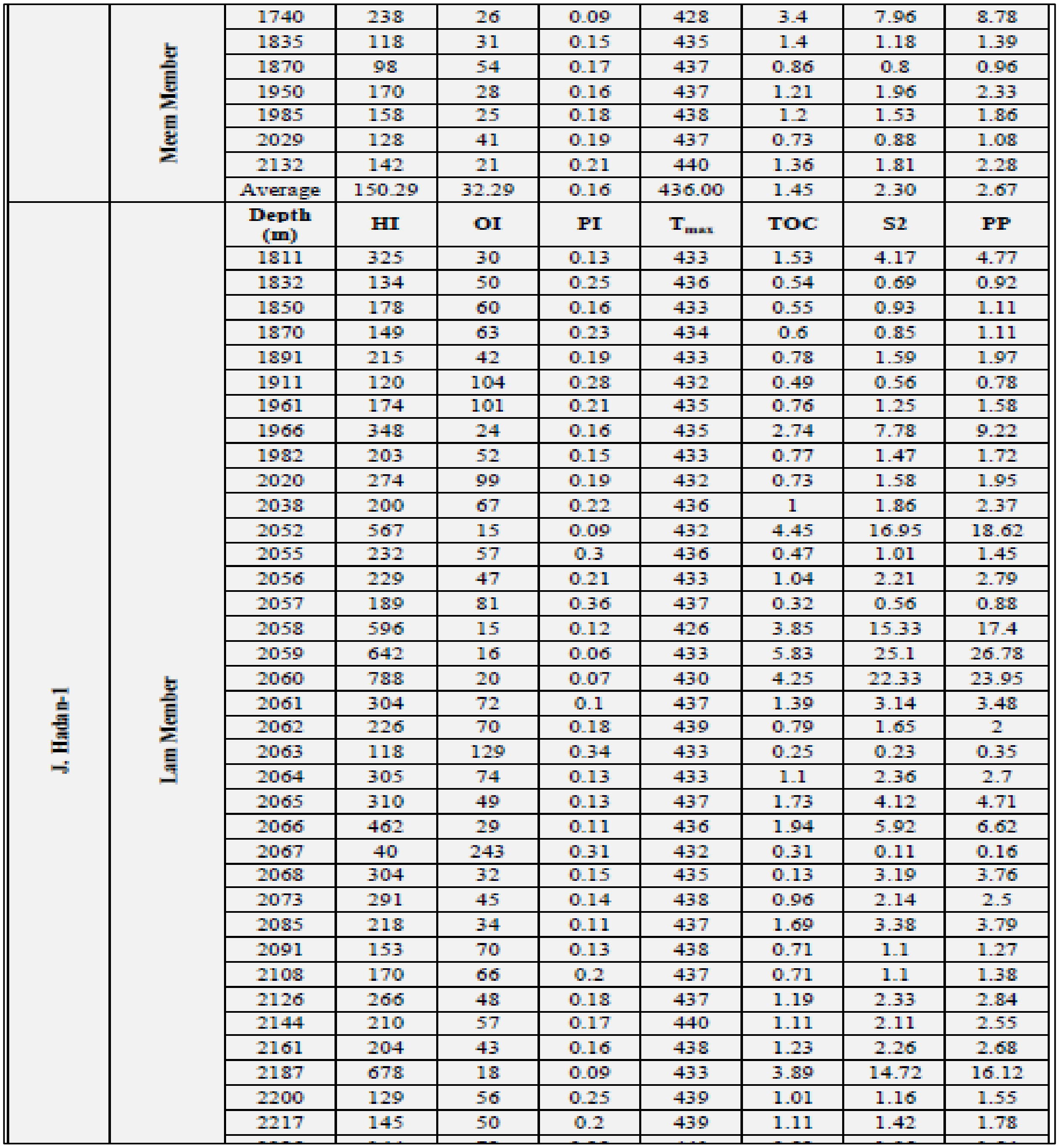
1.7. MADBI SHALE RESOURCE PALY

The Py/TOC measurements were done on organic rich samples using a Rock-Eval 6 instrument. This technique provides four fundamental parameters in which S1 represents free and adsorbed hydrocarbons, S2 shows pyrolysis generated hydrocarbons, S3 provides CO2 released during the pyrolysis phase of the analysis, and T_{max} gives the temperature of maximum pyrolytic hydrocarbon yield in °C. These fundamental parameters are used to deduce the values of TOC wt%; Hydrogen Index (HI=S2/TOC×100, in mg HC/g TOC); Oxygen Index (OI= S3/TOC×100, in mg CO2/g TOC); Petroleum Potential (PP=S1+S2, in mg HC/g of rock or kg HC/ton of rock) and Production Index (PI=S1/S1+S2, in mg HC/g of rock or kg HC/ton of rock). The precision of these parameters are ± 0.1% for TOC; ± 1 °C for T_{max}; ± 10 mg HC/g TOC for HI; ± 5mg CO2/g TOC for OI; ± 1 mg HC/g of rock or kg HC/ton of rock for PP and ± 0.1 mg HC/g of rock or kg HC/ton of rock for PI. The vitrinite reflectance (R_0), T_{max} and surface temperature measurements of Alif-1 well and raw well log data were used in PetroMod 1D and Surfer 7 to generate burial history-maturity models and isopach maps of the Alif Sandstone reservoir. [1]

Table 1. 1 Rock-Eval pyrolysis/TOC results of the studied wells of Al-Sabatayn Basin



Well	Member	Depth (m)	HI	OI	PI	T_{max}	TOC	S2	PP
Alif-1	Lam Member	1764	344	51	0.17	431	1.31	3.75	4.52
		1844	335	47	0.12	432	1.85	5.06	5.77
		1932	213	77	0.19	432	0.77	1.6	1.97
		2020.5	250	47	0.19	435	0.88	1.9	2.34
		2082	245	48	0.22	436	1.03	2.13	2.73
		2170.5	206	77	0.33	434	1.08	1.65	2.47
		2223.5	195	46	0.20	436	0.96	1.54	1.92
		2288	186	25	0.18	437	1.44	2.18	2.66
		2376	243	69	0.23	440	1.76	2.79	3.6
		2414.7	187	38	0.23	441	1.24	1.48	1.92
		2485	190	46	0.26	443	2.04	2.41	3.27
		2555.8	141	45	0.27	443	1.05	1.13	1.55
		2608	118	55	0.30	433	0.94	1.11	1.58
		2682	136	65	0.31	445	1.15	1.56	2.27
		Average	213.50	52.57	0.21	437.00	1.25	2.16	2.76
	Meem Member	2735	121	98	0.3	439	0.8	0.7	1
		2742.6	71	35	0.42	436	0.71	0.45	0.78
		2808.8	110	39	0.34	458	0.3	2.39	3.6
		2897	100	40	0.29	455	0.56	2.4	3.4
		2950	55	142	0.41	445	0.93	0.36	0.61
		3038	40	68	0.46	424	0.98	0.27	0.5
		3111.7	52	65	0.52	369	0.93	0.37	0.77
		3164.7	40	25	0.46	334	1.6	0.29	0.54
		3217.6	37	68	0.42	340	1.43	0.36	0.62
		3288	33	37	0.4	224	1.29	0.29	0.48
		3344	32	48	0.51	428	1.45	0.31	0.63
		Average	62.82	60.45	0.41	395.64	1.00	0.74	1.18
Tawilah-1	Lam Member	Depth (m)	HI	OI	PI	T_{max}	TOC	S2	PP
		961	417	60	0.12	428	1.08	3.19	3.63
		1032	485	42	0.13	425	1.03	3.44	3.96
		1058	531	33	0.11	425	2.01	7.21	8.06
		1085	840	28	0.09	426	2.55	10.69	11.81
		1138	933	24	0.1	424	3.87	16.61	18.49
		1173	820	23	0.12	426	3.24	11.52	13.11
		1217	894	15	0.11	428	4.62	17.43	19.61
		1252	1114	12	0.17	441	5.9	26.14	31.52
		Average	754.25	29.63	0.12	427.88	3.04	12.03	13.77
	Meem Mb.	1270	690	20	0.23	433	12.34	33.1	43.26
		1305	242	80	0.2	431	1.23	2.3	2.85
		1341	594	25	0.13	432	6.66	27.9	32.16
		1350	487	35	0.14	431	3.86	13.2	15.4
		1367	323	50	0.18	433	1.53	3.59	4.36
		1429	577	10	0.16	438	2.73	37.6	44.78
		Average	485.50	36.67	0.17	433.00	4.73	19.62	23.80
Meem-1	Lam Member	Depth (m)	HI	OI	PI	T_{max}	TOC	S2	PP
		1089	383	30	0.1	424	3.15	11.57	12.93
		1182	259	48	0.2	426	0.81	2.7	3.36
		1261	327	19	0.1	425	1.17	3.6	3.98
		1323	234	35	0.18	427	0.72	1.66	2.02



	Meem Member	1740	238	26	0.09	428	3.4	7.96	8.78
		1835	118	31	0.15	435	1.4	1.18	1.39
		1870	98	54	0.17	437	0.86	0.8	0.96
		1950	170	28	0.16	437	1.21	1.96	2.33
		1985	158	25	0.18	438	1.2	1.53	1.86
		2029	128	41	0.19	437	0.73	0.88	1.08
		2132	142	21	0.21	440	1.36	1.81	2.28
		Average	150.29	32.29	0.16	436.00	1.45	2.30	2.67
J. Hadan-1	Lam Member	**Depth (m)**	**HI**	**OI**	**PI**	**T_{max}**	**TOC**	**S2**	**PP**
		1811	325	30	0.13	433	1.53	4.17	4.77
		1832	134	50	0.25	436	0.54	0.69	0.92
		1850	178	60	0.16	433	0.55	0.93	1.11
		1870	149	63	0.23	434	0.6	0.85	1.11
		1891	215	42	0.19	433	0.78	1.59	1.97
		1911	120	104	0.28	432	0.49	0.56	0.78
		1961	174	101	0.21	435	0.76	1.25	1.58
		1966	348	24	0.16	435	2.74	7.78	9.22
		1982	203	52	0.15	433	0.77	1.47	1.72
		2020	274	99	0.19	432	0.73	1.58	1.95
		2038	200	67	0.22	436	1	1.86	2.37
		2052	567	15	0.09	432	4.45	16.95	18.62
		2055	232	57	0.3	436	0.47	1.01	1.45
		2056	229	47	0.21	433	1.04	2.21	2.79
		2057	189	81	0.36	437	0.32	0.56	0.88
		2058	596	15	0.12	426	3.85	15.33	17.4
		2059	642	16	0.06	433	5.83	25.1	26.78
		2060	788	20	0.07	430	4.25	22.33	23.95
		2061	304	72	0.1	437	1.39	3.14	3.48
		2062	226	70	0.18	439	0.79	1.65	2
		2063	118	129	0.34	433	0.25	0.23	0.35
		2064	305	74	0.13	433	1.1	2.36	2.7
		2065	310	49	0.13	437	1.73	4.12	4.71
		2066	462	29	0.11	436	1.94	5.92	6.62
		2067	40	243	0.31	432	0.31	0.11	0.16
		2068	304	32	0.15	435	0.13	3.19	3.76
		2073	291	45	0.14	438	0.96	2.14	2.5
		2085	218	34	0.11	437	1.69	3.38	3.79
		2091	153	70	0.13	438	0.71	1.1	1.27
		2108	170	66	0.2	437	0.71	1.1	1.38
		2126	266	48	0.18	437	1.19	2.33	2.84
		2144	210	57	0.17	440	1.11	2.11	2.55
		2161	204	43	0.16	438	1.23	2.26	2.68
		2187	678	18	0.09	433	3.89	14.72	16.12
		2200	129	56	0.25	439	1.01	1.16	1.55
		2217	145	50	0.2	439	1.11	1.42	1.78

		2447	152	36	0.19	446	1.07	1.29	1.6
		2482	180	80	0.28	446	0.86	1.2	1.66
		2500	168	80	0.27	441	0.56	0.72	0.98
		2517	203	70	0.31	443	0.81	1.24	1.81
		2523	220	23	0.24	449	2.86	4.72	6.24
		2535	198	53	0.28	446	0.98	1.43	1.98
		2553	237	36	0.25	448	1.34	2.33	3.1
		2570	353	70	0.26	443	1.02	1.62	2.19
		2588	150	57	0.29	440	1	1.07	1.51
		2605	604	33	0.2	448	0.12	4.62	5.76
		2623	183	43	0.22	447	1.2	1.52	1.95
		2641	184	53	0.22	446	0.58	0.73	0.93
		2658	194	36	0.27	450	0.76	0.99	1.35
		2676	172	30	0.23	450	0.82	0.93	1.2
		2694	167	32	0.25	449	1.07	1.16	1.55
		2711	151	37	0.26	449	0.79	0.76	1.03
		2729	225	36	0.26	450	1.06	0.84	1.13
		2747	557	35	0.2	442	2.03	1.61	2.02
		2764	269	34	0.28	452	1.06	0.94	1.3
		2782	156	34	0.31	451	0.89	0.82	1.18
		2800	563	27	0.28	453	2.11	1.42	1.97
		2817	619	27	0.23	443	1.59	1.11	1.44
		2835	262	32	0.31	450	0.74	0.56	0.81
		Average	270.4	53.4	0.2	440.2	1.4	3.4	3.9
	Meem Member	2853	270	33	0.3	447	0.87	0.66	0.94
		2870	173	24	0.27	442	0.71	0.64	0.88
		2888	132	20	0.33	442	0.66	0.45	0.67
		2902	194	55	0.27	432	0.87	0.43	0.59
		2905	257	27	0.24	440	0.98	0.67	0.88
		2906	188	84	0.29	427	0.74	0.35	0.49
		2922	152	76	0.33	458	1.24	0.46	0.69
		2923	239	37.5	0.09	456	1.07	0.62	0.68
		2941	618	22	0.27	458	2.27	1.02	1.4
		2955	263	22	0.6	453	1.28	0.76	1.9
		2958	202	25	0.32	459	2.25	1.1	1.49
		2962	265	29	0.04	455	1.09	6.63	6.93
		Average	246.08	37.88	0.28	447.42	1.17	1.15	1.46
Kamran-1	Lam Member	**Depth (m)**	**HI**	**OI**	**PI**	**T_{max}**	**TOC**	**S2**	**PP**
		888	131	188	0.14	433	1.3	1.69	1.96
		1170	119	214	0.25	429	0.64	0.76	1.01
		1269	132	71	0.18	432	0.77	1.03	1.25
		1329	106	131	0.24	431	0.68	0.72	0.95
		1464	113	82	0.22	436	0.68	0.77	0.99
		1561	84	155	0.26	437	0.74	0.62	0.84

		1667	154	56	0.21	440	0.7	1.08	1.37
		1800	92	27	0.27	439	0.78	0.72	0.99
		1932	149	29	0.27	444	0.87	1.3	1.77
		2073	127	33	0.27	447	0.83	1.05	1.44
		Average	120.7	98.6	0.231	436.8	0.799	0.974	1.257
	Meem Member	2241	108	65	0.36	436	0.81	0.68	1.06
		2479	29	36	0.5	474	1.03	0.21	0.42
		2585	28	57	0.48	444	0.77	0.15	0.29
		2647	26	57	0.48	435	0.79	0.14	0.27
		2744	27	62	0.54	432	0.88	0.16	0.35
		2841	34	79	0.51	359	1.03	0.24	0.49
		3000	15	51	0.69	422	1.01	0.1	0.32
		3150	22	63	0.51	354	1.13	0.7	1.42
		3300	16	47	0.63	401	1.06	0.11	0.3
		3435	24	64	0.56	367	1.14	0.18	0.41
		3560	19	56	0.64	377	1.11	0.14	0.98
		Average	39.06	61.30	0.51	411.48	0.96	0.32	0.63
Salah Al-Deen-1	Lam Member	**Depth (m)**	**HI**	**OI**	**PI**	**T_{max}**	**TOC**	**S2**	**PP**
		1650	201	20	0.22	405	1.2	2.4	3.1
		1710	190	21	0.29	400	1	1.9	2.7
		1790	210	18	0.25	410	1.1	2.3	3.1
		1870	199	25	0.25	406	0.7	1.45	1.95
		Average	200	21	0.25	405	1	2.0	2.7
	Meem Member	1950	227	22	0.24	410	0.8	1.82	2.4
		2064	207	25	0.2	421	0.9	1.99	2.49
		2130	156	34	0.12	442	0.66	1.38	1.58
		2180	197	33	0.1	435	1.03	2.03	2.28
		2204	204	18	0.07	394	1.01	2.1	2.27
		Average	198.2	26.4	0.15	420.4	0.88	1.86	2.20
AI-1	Lam Member	**Depth (m)**	**HI**	**OI**	**PI**	**T_{max}**	**TOC**	**S2**	**PP**
		1100	442	130	0.37	421	0.7	3.1	4.9
		1150	233	140	0.42	422	0.9	2.1	3.6
		1190	409	80	0.34	427	1.1	4.5	6.8
		1220	411	95	0.40	430	0.9	3.7	6.2
		1300	448	110	0.27	432	1.85	8.3	11.4
		1350	371	112	0.34	437	1.75	6.5	9.9
		1400	387	90	0.26	430	1.83	7.1	9.6
		1500	432	95	0.28	435	1.92	8.3	11.5
		1600	333	120	0.40	438	1.86	6.2	10.3
		1700	490	114	0.39	441	1.1	5.4	8.9
		Average	395.6	108.6	0.34	431.3	1.391	5.52	8.31
	Meem Member	1750	175	110	0.60	440	1.2	2.1	5.3
		1800	545	113	0.44	442	1.1	6	10.7
		1850	538	95	0.39	445	1.3	7	11.4
		Average	419.3	106.0	0.45	442.3	1.2	5.0	9.1

1.8. OIL SHALE ORIGIN

Oil shale represents a large and mostly untapped hydrocarbon resource. Like tar sand (oil sand in Canada) and coal, oil shale is considered unconventional because oil cannot be produced directly from the resource by sinking a well and pumping.

Oil has to be produced thermally from the shale. The organic material contained in the shale is called kerogen, a solid material intimately bound within the mineral matrix (Allred, 1982; Baughman, 1978; Lee, 1996; Scouten, 1990; US DOE, 2004a, b, c; Speight, 2007, 2008, 2013).

Oil shale is distributed widely throughout the world with known deposits in every continent. Oil shale ranging from Cambrian to Tertiary in age occurs in many parts of the world (Table 1.1). Deposits range from small occurrences of little or no economic value to those of enormous size that occupy thousands of square miles and contain many billions of barrels of potentially extractable shale oil. However, petroleum-based crude oil is cheaper to produce today than shale oil because of the additional costs of mining and extracting the energy from oil shale. Because of these higher costs, only a few deposits of oil shale are currently being exploited; in China, Brazil, and Estonia. However, with the continuing decline of petroleum supplies, accompanied by increasing costs of petroleum-based products, oil shale presents an opportunity for supplying some of the fossil energy needs of the world in the future (Andrews, 2006; Bartis et al., 2005; Culbertson and Pitman, 1973).

Oil shale is not generally regarded as true shale by geologists nor does it contain appreciable quantities of free oil (Scouten, 1990; Speight, 2008). The fracture resistance of all oil shales varies with the organic content of the individual lamina, and fractures preferentially initiate and propagate along the leaner horizontal laminas of the depositional bed.

Oil shale was deposited in a wide variety of environments, including freshwater to saline ponds and lakes, epicontinental marine basins, and related subtidal shelves as well as shallow ponds or lakes associated with coal-forming peat in limnic and coastal swamp depositional environments.

These give rise to different oil shale types (Table 1.3) (Hutton, 1987, 1991), and therefore, it is not surprising that oil shales exhibit a wide range of organic and mineral compositions (Mason, 2006; Ots, 2007; Scouten, 1990; Wang et al., 2009). Most oil shale contains organic matter derived from varied types of marine and lacustrine algae, with some debris from land plants, depending on the depositional environment and sediment sources. Organic matter in the oil shale is a complex mixture and is derived from the carbon-containing remains of algae, spores, pollen, plant cuticle, corky fragments of herbaceous and woody plants, plant resins, and plant waxes, and other cellular remains of lacustrine, marine, and land plants (Dyni, 2003, 2006; Scouten, 1990).

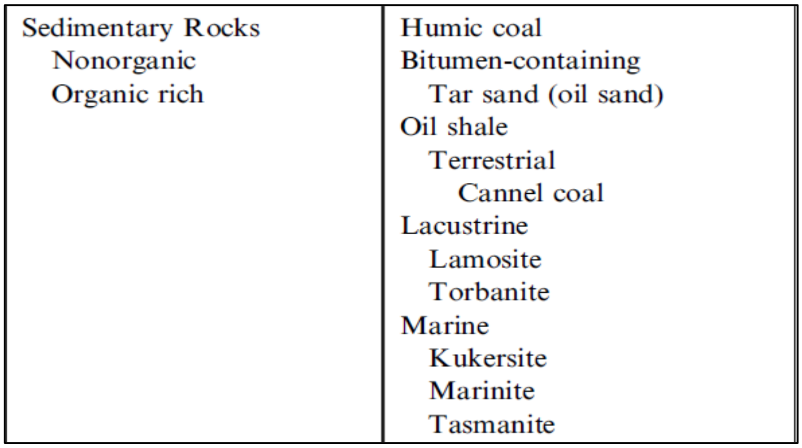
These materials are composed chiefly of carbon, hydrogen, oxygen, nitrogen, and sulfur. Generally, the organic matter is unstructured and is best described as amorphous (bituminite) the origin of which has not been conclusively identified but is theorized to be a mixture of degraded algal or bacterial remains. Other carbon containing materials such as phosphate and carbonate minerals may also be present, which, although of organic origin, are excluded from the definition of organic matter in oil shale and are considered to be part of the mineral matrix of the oil shale. [9]

Oil shale has often been called high-mineral coal, but nothing can be further from reality. Maturation pathways for coal and kerogen are different, and, in fact, the precursors of the organic matter in oil shale and coal also differ (Durand, 1980; Hunt, 1996; Scouten, 1990; Speight, 2013; Tissot and Welte, 1978). Furthermore, the origin of some of the organic matter in oil shale is obscure because of the lack of recognizable biological structures that would help identify the precursor organisms, unlike the recognizable biological structures in coal (Speight, 2013). Such materials may be of (1) bacterial origin, (2) the product of bacterial degradation of algae, (3) other organic matter, or (4) all of the above.

Table 1. 2.Estimate of Oil Shale Rserves (Tons × 10^6)

Region	**Shale Reserves**	**Kerogen Reserves**	Kerogen in Place
Africa	12 373	500	5900
Asia	20 570	1100	-
Australia	32 400	1700	37 000
Europe	54 180	600	12 000
Middle East	35 360	4600	24 000
North America	3 340 000	80 000	140 000
South America	-	400	10 000

Table 1. 3. General Classification of Oil Shale



Sedimentary Rocks	Humic coal
Nonorganic	Bitumen-containing
Organic rich	Tar sand (oil sand)
	Oil shale
	Terrestrial
	Cannel coal
	Lacustrine
	Lamosite
	Torbanite
	Marine
	Kukersite
	Marinite
	Tasmanite

Furthermore, oil shale does not undergo the maturation process that occurs for petroleum and/or coal but produces the material known as kerogen (Scouten, 1990). However, there are indications that kerogen may be a by-product of the maturation process. The kerogen residue that remains in the oil shale is formed during maturation and is then ejected from the organic matrix because of its insolubility and relative unreactivity under the maturation conditions. Furthermore, the fact that kerogen, under the high-temperature pyrolysis conditions imposed upon it in the laboratory, forms hydrocarbon distillates (albeit with relatively high amounts of nitrogen) does not guarantee that the kerogen of oil shale is a precursor to petroleum.

The thermal maturity of oil shale refers to the degree to which the organic matter has been altered by geothermal heating. If oil shale is heated to the maximum highest temperature the actual historical temperature to which the shale has been heated is not known with any degree of accuracy and is typically speculative—as may be the case if the oil shale were deeply buried, the organic matter may thermally decompose to form liquids and gas. Under such circumstances, there is highly unfounded speculation (other than high-temperature laboratory experiments) that oil shale sediments can act as the source rocks for petroleum and natural gas.

Moreover, as stated above, the fact that the high-temperature thermal decomposition of kerogen (in the laboratory) gives petroleum-like material is no guarantee that kerogen is or ever was a precursor to petroleum. The implied role of kerogen in petroleum formation is essentially that implied, but having no conclusive experimental foundation. However, caution is advised in choosing the correct definition of kerogen since there is the distinct possibility that it is one of the by-products of the petroleum generation and maturation processes, and may not be a direct precursor to petroleum. Petroleum precursors and petroleum are indeed subject to elevated temperatures in the subterranean formations due to the geothermal gradient. Although the geothermal gradient varies from place to place, it is generally in the order of 25°C/km to 30°C/km (15°F/1000 feet or 8°C/1000 feet, i.e., 0.015°F per foot of depth or 0.008°C per foot of depth). This leaves a serious question about whether or not the material has been subjected to temperatures greater than 250°C (>480°F). Such experimental work is interesting insofar as it shows similar molecular moieties in kerogen and petroleum (thereby confirming similar origins for kerogen and petroleum). However, the absence of geological time in the laboratory is not a reason to increase the temperature and it must be remembered that application of high temperatures (>250°C, <480°F) to a reaction not only increases the rate of reaction (thereby making up for the lack of geological time) but can also change the nature and the chemistry of a reaction. In such a case, the geochemistry is altered. Furthermore, introduction of a pseudo-activation energy in which the activation energy of the kerogen conversion reactions is reduced leaves much to be desired because of the assumption required to develop this pseudo-activation energy equation(s).

It is claimed that the degree of thermal maturity of an oil shale can be determined in the laboratory by any one of several methods. One method is to observe the changes in the color of the organic matter in samples collected from varied depths—assuming that the organic matter is subjected to geothermal heating (the temperature being a function of depth), the color of the organic matter might be expected to change from a lighter color (at relatively shallow depths) to a darker color (at relatively deep depths). Then, another unknown issue of shifting of the sedimentary strata comes into play. Suffice it to state that the role played by kerogen in the petroleum maturation process is not fully understood (Durand, 1980; Hunt, 1996; Scouten, 1990; Speight, 2007; Tissot and Welte, 1978). What obviously needs to be addressed more fully in terms of kerogen participation in petroleum generation is the potential to produce petroleum constituents from kerogen by low-temperature processes rather than by processes that involve the use of temperatures greater than 250°C (>480°F) (Burnham and McConaghy, 2006; Speight, 2007).

If such geochemical studies are to be pursued, a thorough investigation is needed to determine the potential for such high temperatures being present during the main phase, or even various phases, of petroleum generation in order to determine whether kerogen is a precursor to petroleum (Speight, 2007).

Finally, much of the work performed on oil shale has referenced the oil shale from the Green River Formation in the western United States. [9]

1.9. OIL SHALE TYPES

Mixed with a variety of sediments over a lengthy geological time period, shale forms a tough, dense rock ranging in color from light tan to black. Based on its apparent colors, shale may be referred to as black shale or brown shale. Oil shale has also been given various names in different regions. For example, the Ute Indians, on observing outcroppings burst into flames after being hit by lightning, referred to it as the rock that burns.

Thus, it is not surprising that definitions of the types of oil shale can be varied and confusing. It is necessary to qualify the source of the definition and the type of shale that fits within it.

For example, one definition is based on the mineral content of the shale, in which three categories can recognized namely, (1) carbonate-rich oil shale, which contain a high proportion of carbonate minerals (such as calcite and dolomite) and which usually have the organic-rich layers sandwiched between carbonate-rich layers—these shales are hard formations that are resistant to weathering and are difficult to process using mining (ex situ); (2) siliceous oil shales, which are usually dark brown or black. They are deficient in carbonate minerals but plentiful in siliceous minerals (such as quartz, feldspar, clay, chert, and opal) these shales are not as hard and weather-resistant as the carbonate shales and may be better suited for extraction through mining (ex situ) methods; and (3) cannel oil shales, which are typically dark brown or black and consist of organic matter that completely encloses other mineral grains—these shales are suitable for extraction through mining (ex situ).

However, mineral content aside, it is more common to define oil shale on the basis of their origin and formation as well as the character of their organic content. More specifically, the nomenclature is related to whether or not the shale is of (1) terrestrial origin, (2) marine origin, or (3) lacustrine origin (Hutton, 1987, 1991).

This classification reflects differences in the composition of the organic matter and of the distillable products that can be produced from the shale. This classification also reflects the relationship between the organic matter found in the sediment and the environment in which the organic precursors were deposited. [9]

1.9.1. Terrestrial Oil Shale

The precursors to terrestrial oil shale (sometimes referred to as cannel coal) were deposited in stagnant, oxygen-depleted waters on land (such as coal-forming swamps and bogs).

Cannel coal is brown to black oil shale composed of resins, spores, waxes, and cutinaceous and corky materials derived from terrestrial vascular plants, together with varied amounts of vitrinite and inertinite. Cannel coals originate in oxygen-deficient ponds or shallow lakes in peat-forming swamps and bogs. This type of shale is usually rich in oil-generating lipid-rich organic matter derived from plant resins, pollen, spores, plant waxes, and the corky tissues of vascular plants. The individual deposits usually are small in size, but they can be of a very high grade.

The latter also holds for lacustrine oil shales. This group of oil shales was deposited in freshwater, brackish, or saline lakes. The size of the organic-rich deposits can be small, or they can occur over tens of thousands of square miles as is the case for the Green River Formation in Colorado, Utah, and Wyoming. The main oil-generating organic compounds found in these deposits are derived from algae or bacteria. In addition, variable amounts of higher plant remains can be present. [9]

1.9.2. Lacustrine Oil Shale

Lacustrine oil shales (lake-bottom-deposited shales) include lipid-rich organic matter derived from algae that lived in freshwater, brackish, or saline lakes. The lacustrine oil shales of the Green River Formation, which were discussed above, are among the most extensively studied sediments.

However, their strongly basic depositional environment is certainly unusual, if not unique. Therefore, it is useful to discuss the characteristics of the organic material in other lacustrine shales. Lacustrine sequences from the Permian oil shales of Autun (France) and the Devonian bituminous flagstones of Caithness (Scotland) exhibited several series of biomarkers that were prominent in extracts from these shales—hopanes, steranes, and carotenoids. Algal remains were abundant in both shales. Blue-green algae, similar to those that contributed largely to the Green River oil shale kerogen, were found in the Devonian shale, for which a stratified lake environment similar to Green River has been proposed (Donovan and Scott, 1980).

In contrast, Botryococcus remains were found in the Permian Autun shale and are presumed to be the major source of organic matter, except for one sample. No Botryococcus remains were found in this sample and the oil produced by its retorting was nearly devoid of the straight-chain alkanes and 1-alkenes which are prominent in oils from Botryococcusderived shales.

Evidently, some as yet unidentified algae contributed to the organic matter in this stratum. Biodegradation cannot be ruled out but seems unlikely due to the lack of prominent iso- and ante-iso-alkanes. Straight-chain alkanes and 1-alkenes were also prominent in gas chromatograms of the retorted oils from the Devonian shale. However, in this case, a pronounced hump, which usually indicates polycyclic derivatives, was also prominent. Both extracts and oil from the Devonian shale were found to be rich in steranes and tricyclic compounds. Diterpenoids and triterpenoids have been suggested as precursors for the bicyclic and the tricyclic compounds found in many oil shales. Rock-Eval pyrolysis results indicate that these shales have high hydrogen indices; the kerogens are all type I or type II, with one of the Devonian samples being clearly type I. Lamosite is pale, grayish-brown, and dark gray to black oil shale in which the chief organic constituent is lamalginite derived from lacustrine planktonic algae. Other minor components include vitrinite, inertinite, telalginite, and bitumen. The Green River oil shale deposits in western United States and a number of the tertiary lacustrine deposits in eastern Queensland, Australia, are lamosites. Other major lacustrine oil shale deposits include the Triassic shales of the Stanleyville Basin in Zaire and the Albert shales of New Brunswick, Canada (Mississippian). Torbanite, named after Torbane Hill in Scotland, is a black oil shale whose organic matter is composed mainly of telalginite found in freshwater to brackish water lakes. The deposits are commonly small, but can be extremely high grade. [9]

1.9.3. Marine Oil Shale

Marine oil shales (marine-bottom-deposited shales) are composed of lipid-rich organic matter derived from marine algae, acritarchs (unicellular organisms of questionable origin), and marine dinoflagellates. Marine oil shales are usually associated with one of two settings (Figure 1.5). The anoxic silled basin shown (Figure 1.5) can occur in the shallow water of a continental shelf. High phytoplankton growth rates near the surface will give a high deposition rate. The sill shields the trough from the circulation of oxygen-laden water. Under these conditions, the decomposition of organic sedimentary matter will rapidly deplete oxygen within the confines of the basin, thereby providing the strongly anoxic (reducing, low-Eh) environment that is needed for efficient preservation.

The anoxic zone in an upwelling area (Figure 1.5) arises from circulation of an open-ocean current over a cold, oxygen-depleted bottom layer. Mixing of a nutrient-rich current, such as the Gulf Stream, into the carbon dioxide-rich and light-rich eutrophic zone gives an environment capable of sustaining very high rates of organic production. Such environments occur today along the west coasts of Africa and the Americas, where good fishing is found along with the potential for organic-rich sediments (Debyser and Deroo, 1969).

Information about the nature of organic matter in marine environments has resulted from studies of recent deposits and the contemporary oceans (Bader et al., 1960; Bordovskiy, 1965). Only a small part of primary production in the oceans reaches the bottom. Of an estimated annual production of 9 × 10^{19} tons of dry matter, it has been estimated that about 2% reaches the floor in the shallows and only about 0.02% in the open sea. The major part of marine primary production is consumed by predators, and most of the remainder by microbes. The principal marine microbial scavengers are bacteria that live free in the water or are attached to organic particles. In ocean water, organics occur in solution, in colloidal suspension, and as particulate matter comprising bodies and body fragments of living and dead organisms. Except in regions of a seaweed or plankton "bloom," the dissolved organics usually predominate. As a result, marine bacteria are most abundant only in the upper part of the water column and the organic detritus at the bottom. Even in the oceans, the adsorption of organics onto inorganic detritus, such as the silica parts of diatoms, plays an important part in sedimentation. After the organic sediment reaches the bottom, reworking begins.

Bottom-dwelling (benthic) organisms feed on both the sediment and the dissolved organics and, in turn, are fed on by predators (e.g., crustaceans). In this sphere, the benthic bacteria are largely responsible for the decomposition of organics and the synthesis of new organics through enzymatic transformations. Approximately 60–70% of the sedimentary organic carbon is typically liberated as carbon dioxide during this reworking, while most of the remainder is converted into new compounds, resulting in an extremely complex mixture.

The various organic compound classes in oil shales include carbohydrates, lignins, humates and humic acids, lipid-derived waxes and the saturated and polyene acids in algal lipids, which can serve as precursors of these waxes, and biological pigments and their derivatives (e.g., carotenoids and porphyrins). Only the latter three were judged to have sufficient inertness to be major contributors to oil shale kerogen (Cane, 1976) that about 2% reaches the floor in the shallows and only about 0.02% in the open sea. The major part of marine primary production is consumed by predators, and most of the remainder by microbes. The principal marine microbial scavengers are bacteria that live free in the water or are attached to organic particles. In ocean water, organics occur in solution, in colloidal suspension, and as particulate matter comprising bodies and body fragments of living and dead organisms. Except in regions of a seaweed or plankton “bloom,” the dissolved organics usually predominate. As a result, marine bacteria are most abundant only in the upper part of the water column and the organic detritus at the bottom. Even in the oceans, the adsorption of organics onto inorganic detritus, such as the silica parts of diatoms, plays an important part in sedimentation. After the organic sediment reaches the bottom, reworking begins.

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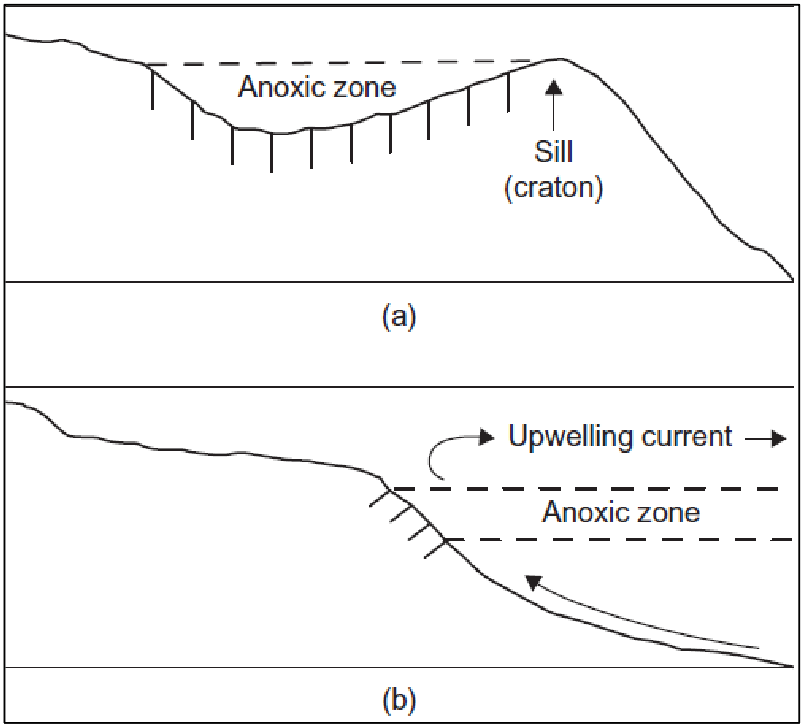


Figure 1. 5. The anoxic zone in an upwelling area

Chapter Two

2.1. INTRODUCTION

Oil shale represents a large and mostly untapped source of hydrocarbon fuels. Like tar sands (oil sands in Canada), it is an unconventional and/or alternate fuel source and it does not contain oil. Oil is produced by thermal decomposition of kerogen, which is intimately bound within the mineral matrix of the shale and, as such, is not readily extractable.

Many estimates have been published for oil shale reserves (in fact resources), but the rank of countries vary with time and authors, except that US is always on number one over 60 %. Brazil is the most frequent number two. The United States has vast known oil shale resources that could translate into as much as 2.2 trillion barrels (2.2×10^{12} bbls) of oil-in-place.

In fact, the largest known oil shale deposits in the world are in the Green River Formation, which covers portions of Colorado, Utah, and Wyoming. Estimates of the oil resource within the Green River formation vary from 1.5 to 1.8 trillion barrels (1.5 to 1.8×10^{12} bbls) (Scouten, 1990; Dyni, 2005, 2006). However, not all resources in place are recoverable but, for policy planning purposes, it is enough to know that any amount in this range is very high. For example, the half-way point in the estimate (800e900 billion barrels, (800 to 900×10^{9} bbls) is more than triple the proven oil reserves of Saudi Arabia. With present demand for crude oil products in the United States at approximately 17 to 20 million barrels per day, oil shale (by only meeting a quarter of that demand) would last for more than 400 years. Oil shale occurs in nearly 100 major deposits in 27 countries worldwide (Duncan and Swanson, 1965; Culbertson and Pitman, 1973; Culbertson et al., 1980; Bauert, 1994). It is generally shallower (<3000 feet) than the deeper and warmer geologic zones required to form oil. On a worldwide basis, the oil shale resource base is believed to contain approximately 2.6 trillion barrels (2.6×10^{12} bbls) of which the vast majority (eastern plus western shale) approximately 2.2 trillion barrels (2.2×10^{12} bbls) e is located within the United States. [4]

2.2. WORLD OIL SHALE RESOURCES

There are vast quantities of oil shale around the world in deposits located in 27 countries. The quality, quantity, and origins of these shale deposits vary greatly. The United States has the largest known resource of oil shale in the world – an estimated 6 trillion barrels. Other significant deposits of oil shale can be found in Russia, Brazil, Estonia, and China. The world's oil shale resources are largely untapped and may represent considerable oil reserves with suitable economic conditions and advances in extraction technology.

It is estimated that there are at least 8 trillion barrels of oil shale resource around the world. Countries are ranked according to the respective volumes of oil shale resource in place. The United States' oil shale resources surpass all other countries with an estimated 6 trillion barrels of resource in place. Russia, the Democratic Republic of Congo, and Brazil are the next highest ranked countries with volumes ranging from 80 billion barrels to almost 250 billion barrels of resource. (Figure 2.1) displays the world oil shale resources estimated in each country and also provides the country's rank of the twenty-seven countries around the world with known deposits of oil shale, (Table 2.1) presents the top ten with the most abundant resource.

Following the chart, there are descriptions of eight of the top ten countries and some additional deposits around the world. Based on available data, the origin characteristics (Figure 2.2), and other details about deposits (Table 2.2,2.3). [6]

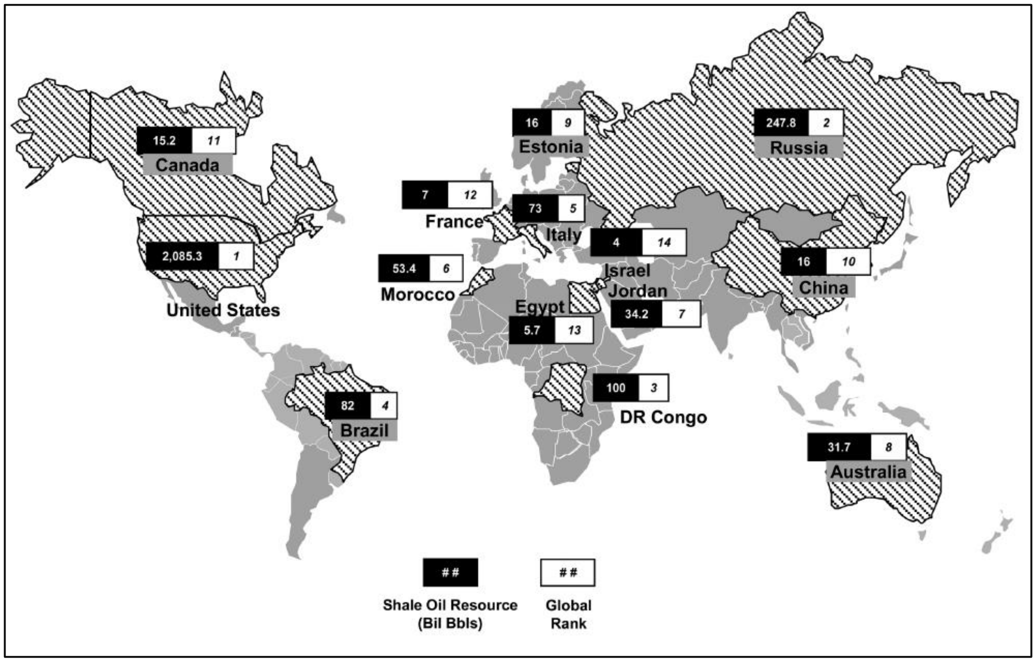
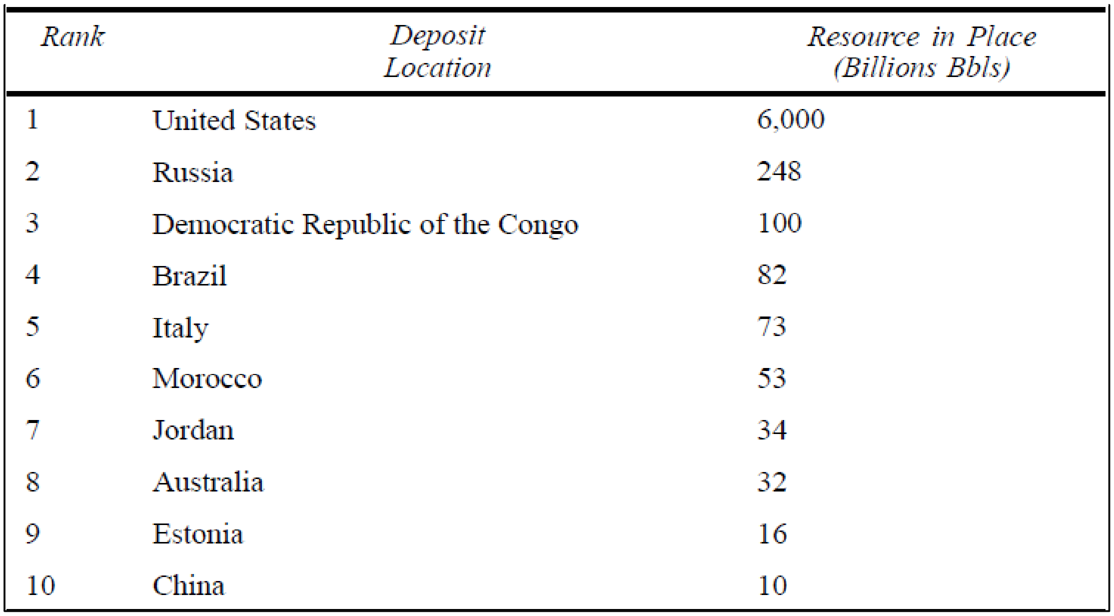
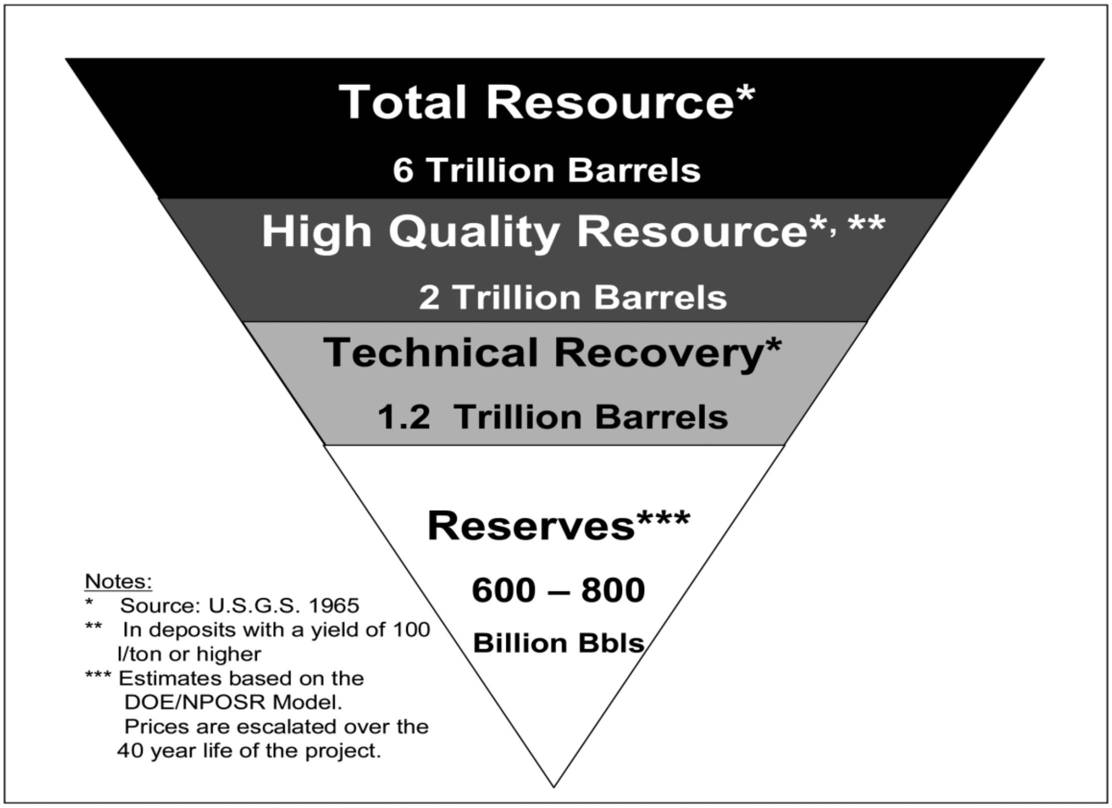


Figure 2. 1 Map of World Resources

Table 2. 1.Top Ten Ranked Countries by Oil



Rank	*Deposit Location*	*Resource in Place (Billions Bbls)*
1	United States	6,000
2	Russia	248
3	Democratic Republic of the Congo	100
4	Brazil	82
5	Italy	73
6	Morocco	53
7	Jordan	34
8	Australia	32
9	Estonia	16
10	China	10



Notes:
* Source: U.S.G.S. 1965
** In deposits with a yield of 100 l/ton or higher
*** Estimates based on the DOE/NPOSR Model. Prices are escalated over the 40 year life of the project.

Figure 2. 2. Oil Shale Resource Characterization

Table 2. 2.Oil Shale Quality by Region (Billions of Barrels)

	Quality		
Deposit Location	*20–40 (l/t)*	*40-100 (l/t)*	*100-400 (l/t)*
Western (Green River)	4,000	2,800	1,200
Eastern (& Central)	2,000	1,000	N/A
Alaska	Large	200	250
Total	6,000+	4,000	2,000+

Table 2. 3. U.S. Oil Shale Characteristics by Region

Deposit Location	*Origin*	*Area (km²)*	*Geologic Period*
Western	Lacustrine	65,000	Eocene
Eastern	Marine	725,000	Devonian/Mississippian

The commercial development of an oil-shale deposit depends upon many factors. The geologic setting and the physical and chemical characteristics of the resource are of primary importance. Roads, railroads, power lines, water, and available labor are among the factors to be considered in determining the viability of an oil-shale operation. Oil-shale lands that could be mined may be preempted by present land usage such as population centers, parks, and wildlife refuges. Development of new in-situ mining and processing technologies may allow an oil-shale operation in previously restricted areas without causing damage to the surface or posing problems of air and water pollution. The availability and price of petroleum ultimately effect the viability of a large-scale oil-shale industry. Today, few, if any deposits can be economically mined and processed for shale oil in competition with petroleum. Nevertheless, some countries with oil-shale resources, but lack petroleum reserves, find it expedient to operate an oil-shale industry. As supplies of petroleum diminish in future years and costs for petroleum increase, greater use of oil shale for the production of electric power, transportation fuels, petrochemicals, and other industrial products seems likely. [8]

2.4. OIL SHALE ESTIMATION IN ARAB COUNTRIES

Significant oil shale deposits are located in Palestine (equal to about 250 billion barrels (4.0×10^{10} m^3) of shale oil and in Jordan (equal to about 10^2 billion barrels (1.62×10^{10} m^3) of shale oil. In 2008, these resources were estimated 4 billion barrels (640,000,000 m^3) of shale oil and 34.172 billion barrels (5.4329×10^9 m^3) of shale oil correspondingly.

Jordan oil shales are high quality, comparable to western US oil shale, although their sulfur content is high. The best-explored deposits are El Lajjun, Sultani, and the Juref ed Darawish are located in west-central Jordan, while the Yarmouk deposit, close to its northern border, extends into Syria. Most of Palestine's deposits are located in the Rotem Basin region of the northern Negev desert near the Dead Sea. Palestine oil shale is relatively low in heating value and oil yield. [17]

2.5. OIL SHALE DEFINITION

The term ‘‘oil shale’’ does not have a definite geological definition nor a specific chemical formula, but is a general term used for usually fine-grained sedimentary rocks that yield significant amounts of shale oil upon pyrolysis.

Gavin described oil shale as any compact laminated sedimentary rock with more than 33% ash which is capable of yielding a certain amount of organic matter under a suitable process. Lithologically, oil shale covers a broad range of rocks from shales to marl and carbonates, which forms a mixture of tightly bound organic and inorganic materials. The general composition of oil shales is given in (Figure 2.3) The nature and extent of inorganic materials depend mainly on depositional conditions and the characteristics of the host rock. For instance, true shales contain primarily clay minerals while the well-known Green River shale is mainly carbonates in association with quartz, feldspars, and illite. The organic matter in oil shales is predominantly kerogen, which is an insoluble material. Bitumen and/or prebitumen may also exist in addition to kerogen, but in relatively low amounts. [14]

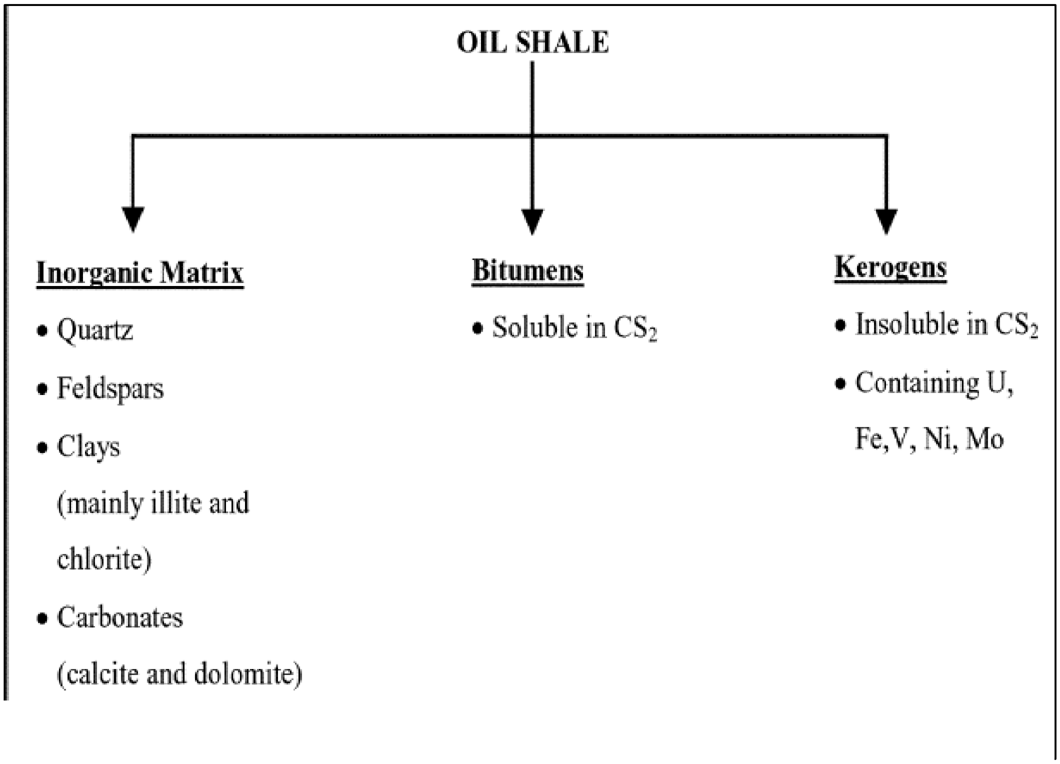


Figure 2. 3. General composition of oil shale

2.6. PETROLEUM, BITUMENS, KEROGENS

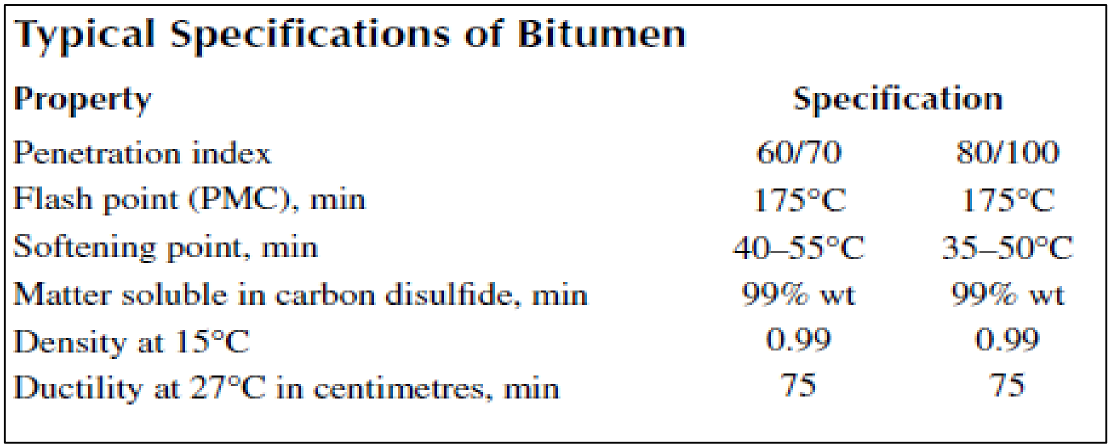
2.6.1. Petroleum

Petroleum is a fossilized mass that has accumulated below the earth’s surface from time immemorial. Raw petroleum is known as crude (petroleum) oil or mineral oil. It is a mixture of various organic substances and is the source of hydrocarbons, such as methane, ethane, propane, butane, pentane, and various other paraffinic, naphthenic, and aromatic hydrocarbons, the building blocks of today’s organic industry. Various petroleum products, such as gaseous and liquid fuels, lubricating oil, solvents, asphalts, waxes, and coke, are derived from refining crude oil. Many lighter hydrocarbons and other organic chemicals are synthesized by thermal and catalytic treatments of these hydrocarbons. The hydrocarbon processing industry is basically divided into three distinct activities—petroleum production, petroleum refining, and petrochemical manufacture. Refineries produce cooking gas (liquefied petroleum gas or LPG), motor spirit (also known as petrol or gasoline), naphtha, kerosene, aviation turbine fuel (ATF), high speed diesel (HSD), lubricating base oils, wax, coke, bitumen (or asphalt), etc., which are mostly a mixture of various hydrocarbons (the organic compounds made of carbon and hydrogen as the major constituent elements). In a petrochemical plant (where one or more petrochemicals are produced) or in a petrochemical complex (where many petrochemical products are produced), pure hydrocarbons or other organic chemicals with a definite number and type of constituent element or compound are produced from the products in refineries. Thus, petrochemicals are derived from petroleum products obtained from refineries. Products from a petrochemical complex are plastics, rubbers, synthetic fibers, raw materials for soap and detergents, alcohols, paints, pharmaceuticals, etc. Since petroleum is the mixture of hundreds of thousands of hydrocarbon compounds, there is a possibility of synthesizing many new compounds. In fact, due to the advancement of new technology, new petrochemicals are being invented and will continue to be added to this industry in the near future. Hence, the petrochemical industry is still a growing industry. The manufacture of valuable petrochemicals from low-valued petroleum products has been the main attractive option for the refining industry investing in the petrochemical industry. Thus, modern refineries are, in fact, refinery cum petrochemical complexes. [14]

2.6.2. Bitumen

Asphalt or bitumen is obtained from short residue (residual mass from the bottom of the vacuum distillation unit) after extraction of valuable oil (known as bright stock) by propane. Asphalt is a very sticky, semi-solid, viscous petroleum, containing various hetero-atomic compounds of hydrocarbons enriched with metallic, sulfurous, nitrogenous, and oxygenated compounds. At a temperature above 90°C, it flows like liquid and solidifies at room temperature. It is mainly used as paving material, paint, water-proofing agent, etc. As a paving grade material, it should have a desirable penetration index, which is defined as the depth of submergence or penetration of a standard weight through a needle penetrator. The greater the penetration, the greater the softness of the asphalt. Typical paving grade bitumen has a penetration of 60/70 or 80/100 using a 100-g cone (1/100 cm) at 25°C for 5 secs during the test. The other property is the flash point. As this has to be applied on the open space surface, the flash point should be above 175°C and the softening point should be above the ambient temperature depending on requirements. In addition to these, mechanical properties like ductility must also be measured. A list of the important properties of a typical paving grade bitumen is given in (Table 2.4). [14]

Table 2. 4.Typical specification of Bitumen



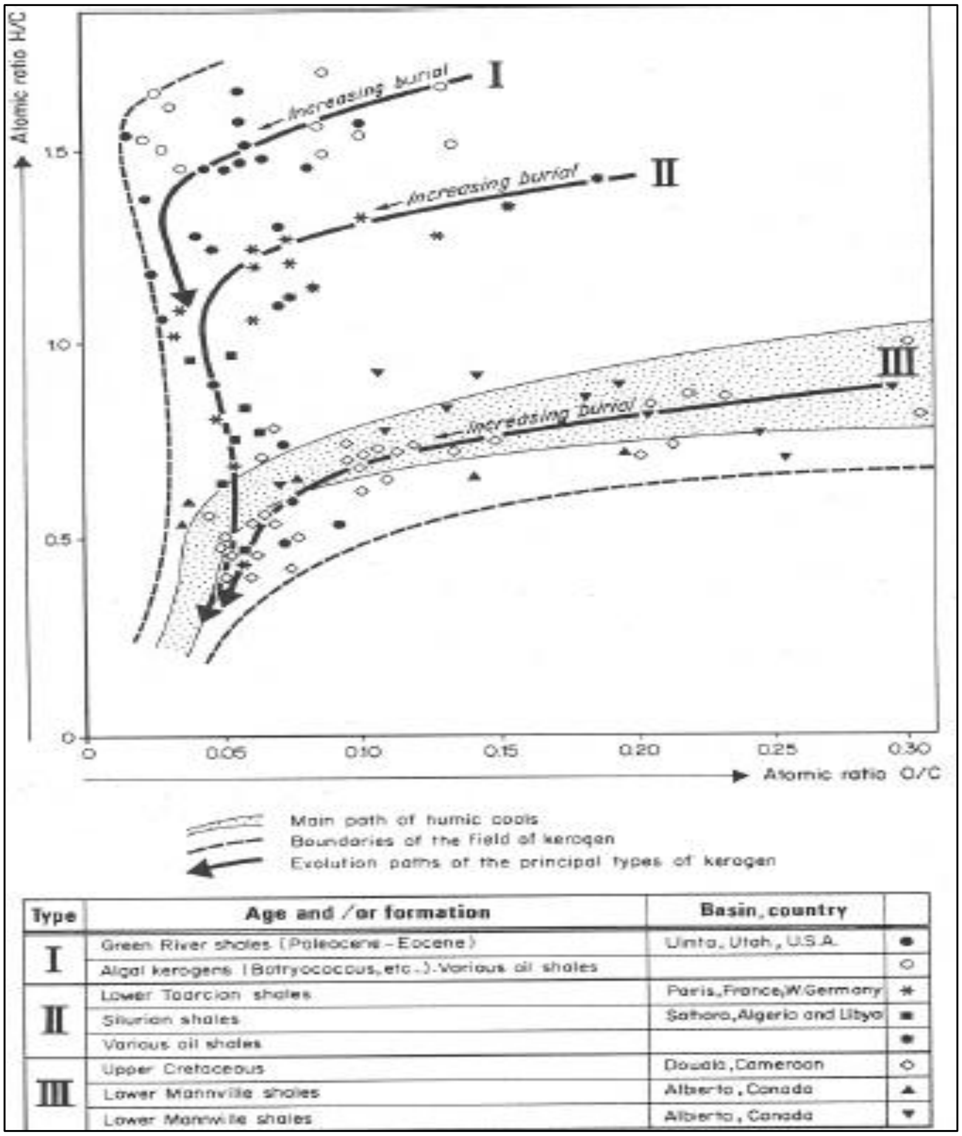
Typical Specifications of Bitumen

Property	**Specification**	
Penetration index	60/70	80/100
Flash point (PMC), min	175°C	175°C
Softening point, min	40–55°C	35–50°C
Matter soluble in carbon disulfide, min	99% wt	99% wt
Density at 15°C	0.99	0.99
Ductility at 27°C in centimetres, min	75	75

2.6.3. Kerogen

Kerogen which is an insoluble material. Bitumen and/or prebitumen may also exist in addition to kerogen, but in relatively low amounts. Although it has been shown that kerogen predominates in the makeup of the organic matter, the chemical form or composition of the kerogen may vary extensively from deposit to deposit. This is due to variations in the amounts of organic carbon, hydrogen and oxygen. Classification of oil shales according to their kerogen type using the van Krevelen diagram is useful. The van Krevelen diagram interprets the kerogen type within a solid fossil fuel through thermal evolution paths as a function of burial depths on plots of atomic H/C versus O/C ratios of the kerogen. Thus, classification of the kerogen type is made as a function of hydrogen, carbon and oxygen content of the fossil fuels (Figure 2.4).

Type I refers to kerogen content with a high initial H/C, but a lower O/C ratio. Type I kerogen oil shales are derived from algal lipids or from organic matter enriched in lipids by microbial activity, which are mostly aliphatic chains. They yield a larger amount of volatile or extractable compounds than other types upon pyrolysis. Hence, from the theoretical view, type I kerogen oil shales provide the highest yield of oil and are the most promising deposits in terms of conventional oil retorting. Type II kerogen is common in many oil shale deposits. This type is also characterized with relatively high H/C and low O/C ratios. Type II kerogen is based on marine organic materials which are formed in reducing environments. In type II kerogen, the polyaromatic nuclei, the heteroatomic ketone and carboxylic groups are more significant than in type I, but still less than type III. The naphthenic rings in the chemical structure are also abundant and aliphatic chains occur with moderate lengths. Sulphur is found in substantial amounts in the associated bitumen and generally higher than the Sulphur content of type I or III kerogen. Although pyrolysis of type II kerogen yields less oil than type I, the amount acquired is still sufficient to consider type II bearing rocks as potential oil sources. Type III kerogen refers to a low H/C ratio, but a high O/C atomic ratio that is derived from terrestrial higher plants. Another distinct characteristic is their relatively higher proportion of polyaromatic nuclei, heteroatomic ketone and carboxylic acid groups. Aliphatic groups contain only a few long carbon chains, the rest being composed of medium and dominantly short ones. Type III kerogen involving rocks are found to be the least productive on pyrolysis and probably the least favorable deposits for oil generation. Geothermal maturation of oil shale could lower the H/C ratio to suggest a type III kerogen when, in fact, it may be a type I or II kerogen. In addition to classification of kerogen types, oil shale deposits can be characterized by their depositional history including the organisms from which they were derived. The age and depositional history are major factors that determine the extent and nature of the organic and mineral content, and relative quality, of any deposit. [14]



Type	Age and /or formation	Basin, country	
I	Green River shales (Paleocene – Eocene)	Uinta, Utah, U.S.A.	●
	Algal kerogens (Botryococcus, etc.). Various oil shales		○
II	Lower Toarcian shales	Paris, France, W. Germany	✱
	Silurian shales	Sahara, Algeria and Libya	■
	Various oil shales		●
III	Upper Cretaceous	Douala, Cameroon	◇
	Lower Mannville shales	Alberta, Canada	▲
	Lower Mannville shales	Alberta, Canada	▼

Figure 2. 4. Classification of kerogen types from various oil shale samples according

2.7. WHY WE NEED OIL SHALE?

2.7.1. Global Issue:

China, India, Pakistan and many other countries continue to modernize and develop; the demand for oil will continue to grow at a record pace. The U.S Energy Information Administration projects that the oil demand of Asian countries will increase by 88% from 2007 to 2035. [3]

2.7.2. World Oil Scenario:

The current world oil production and consumption rates are almost equal. World oil consumption grew 2.9%. Oil demand is projected to rise to 121 million barrels per day by 2025. [3]

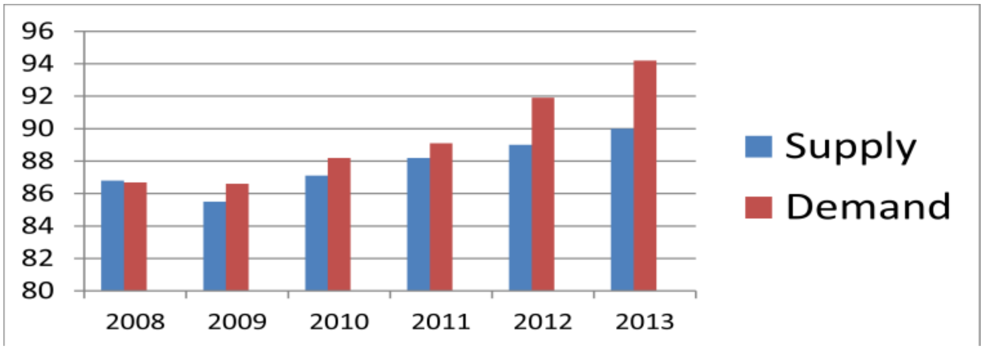
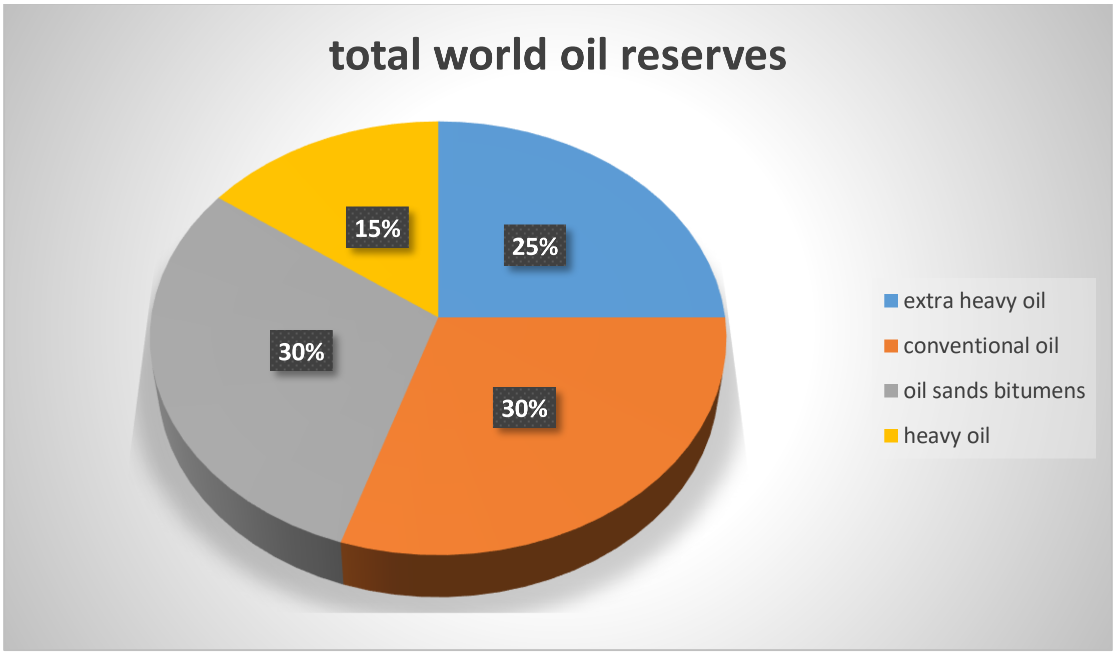


Figure 2. 5. Graph of world oil supply and demand

The above graph clearly shows that the oil demand has surpassed the oil supply in the recent years and the main reason being the depletion of conventional oil reserves. As the world is heading towards energy intensive era it is imperative to explore and produce fossil fuels from sources like tar sands, oil shale and heavy oil. These oil reserves have slightly different physical characteristics and cannot be recovered from conventional techniques.



2.7.3. Oil Prices:

Demand for oil is constantly increasing while production has remained the same and will ultimately decline. The effect of this supply and demand relationship has been the significant price volatility and dramatic overall increase in oil prices. Higher oil prices translate into record prices at the petrol pump. Rising energy costs are passed on to every family and the entire world economy is, in effect, at the mercy of a few oil-rich countries and their leaders. [3]

2.8. ORIGIN AND TYPE OF OIL SHALE

It is possible to present only a very generalized concept of the genesis of oil shales, because of the wide range of their properties observed in different areas. Certain factors, however, appear to be necessary for deposition and accumulation of the inorganic and organic material, which become oil shale upon burial and diagenesis. Oil shales result from the contemporaneous deposition of fine-grained mineral debris and organic degradation products derived from the breakdown of biota. Conditions required for the formation of oil shales, therefore, include abundant organic productivity, early development of anaerobic conditions, and a lack of destructive organisms.

Oil shales were probably deposited in bodies of tranquil, either marine or fresh-water, depositional environment, such **as** isolated marine basins, lakes, or deltaic swamps. The prevailing climate during deposition was similar to that favorable for coal formation. Continued sedimentation, perhaps coupled with subsidence, provided overburden pressure necessary for the compaction and diagenesis of organically-rich strata. Chemical activity at low temperature (≈150°C) results in the loss of volatile fractions, which ultimately produces a sedimentary rock having a high content of refractory organic residues.

Most investigators agree that kerogen and bitumen are of biological origin and are largely derived from the lipid fraction of algae. During taphonomy and biostratinomy further conversion is possible for the fossilized material. [16]

CLASSIFICATION OF OIL SHALE

Oil shale has received many different names over the years, such as cannel coal, boghead coal, alum shale, stellarite, albertite, kerosene shale, bituminite, gas coal, algal coal, wollongite, schistes bitumineux, torbanite, and kukersite. Some of these names are still used for certain types of oil shale. Recently, however, attempts have been made to systematically classify the many different types of oil shale on the basis of the depositional environment of the deposit, the petrographic character of the organic matter, and the precursor organisms from which the organic matter was derived.

A useful classification of oil shales was developed by A.C. Hutton (1987, 1988, 1991), who pioneered the use of blue/ultraviolet fluorescent microscopy in the study of oilshale deposits of Australia. Adapting petrographic terms from coal terminology, Hutton developed a classification of oil shale based primarily on the origin of the organic matter. His classification has proved to be useful for correlating different kinds of organic matter in oil shale with the chemistry of the hydrocarbons derived from oil shale. Hutton (1991) visualized oil shale as one of three broad groups of organic-rich sedimentary rocks:

(1) humic coal and carbonaceous shale,
(2) bitumen-impregnated rock, and
(3) oil shale.

He then divided oil shale into three groups based upon their environments of deposition—terrestrial, lacustrine, and marine (Figure 2.6). [11]

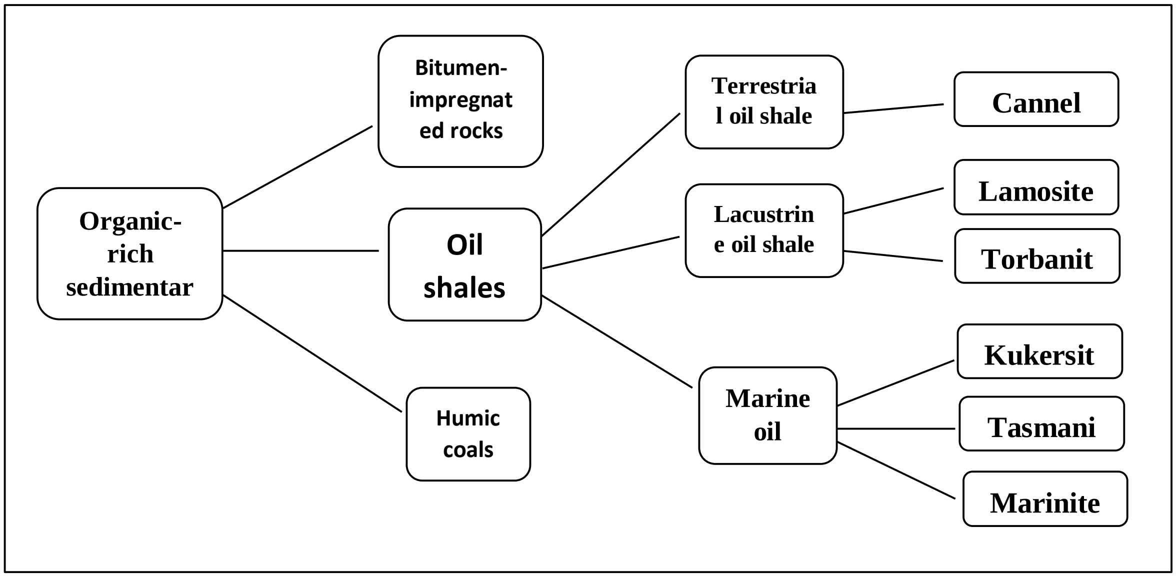


Figure 2. 6. Classification of oil shales. Adapted from Hutton (1987).

- Terrestrial oil shales include those composed of:

- lipid-rich organic matter such as:

1- resin spores, 2- waxy cuticles, 3- and corky tissue of roots

- stems of vascular terrestrial plants commonly found in coal-forming swamps and bogs.

- Lacustrine oil shales include lipid-rich organic matter derived from algae that lived in freshwater, brackish, or saline lakes.
- Marine oil shales are composed of lipid-rich organic matter derived from marine algae, acritarchs (unicellular organisms of questionable origin), and marine dinoflagellates.

Several quantitatively important petrographic components of the organic matter in oil shale telalginite, lamalginite, and bituminite are adapted from coal petrography. Telalginite is organic matter derived from large colonial or thick-walled unicellular algae, typified by genera such as Botryococcus. Lamalginite includes thin-walled colonial or unicellular algae that occurs as laminae with little or no recognizable biologic structures. Telalginite and lamalginite fluoresce brightly in shades of yellow under blue/ultraviolet light. Bituminite, on the other hand, is largely amorphous, lacks recognizable biologic structures, and weakly fluoresces under blue light. It commonly occurs as an organic groundmass with fine-grained mineral matter. The material has not been fully characterized with respect to its composition or origin, but it is commonly an important component of marine oil shales. Coaly materials including vitrinite and inertinite are rare to abundant components of oil shale; both are derived from humic matter of land plants and have moderate and high reflectance, respectively, under the microscope. Within his three-fold grouping of oil shales (terrestrial, lacustrine, and marine), Hutton (1991) recognized six specific oil-shale types: cannel coal, lamosite, marinite, torbanite, tasmanite, and kukersite. The most abundant and largest deposits are marinites and lamosites.

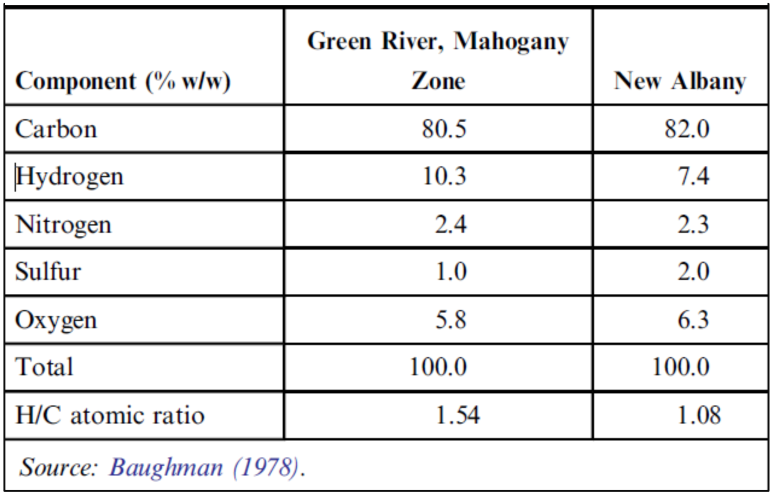
Cannel coal is brown to black oil shale composed of resins, spores, waxes, and cutinaceous and corky materials derived from terrestrial vascular plants together with varied amounts of vitrinite and inertinite. Cannel coals originate in oxygen-deficient ponds or shallow lakes in peat-forming swamps and bogs (Stach and others, 1975, p. 236–237). Lamosite is pale- and grayish-brown and dark gray to black oil shale in which the chief organic constituent is lamalginite derived from lacustrine planktonic algae. Other minor components in lamosite include vitrinite, inertinite, telalginite, and bitumen. The Green River oil-shale deposits in western United States and a number of the Tertiary lacustrine deposits in eastern Queensland, Australia, are lamosites. Marinite is a gray to dark gray to black oil shale of marine origin in which the chief organic components are lamalginite and bituminite derived chiefly from marine phytoplankton. Marinite may also contain small amounts of bitumen, telalginite, and vitrinite. Marinites are deposited typically in epeiric seas such as on broad shallow marine shelves or inland seas where wave action is restricted and currents are minimal. The Devonian–Mississippian oil shales of eastern United States are typical marinites. Such deposits are generally widespread covering hundreds to thousands of square kilometers, but they are relatively thin, often less than about 100 m. [11]

2.9. OIL SHALE PROPERTIES

Oil shale is typically a fine-grained sedimentary rock containing relatively large amounts of organic matter (kerogen) from which significant amounts of shale oil and combustible gas can be extracted by thermal deposition with ensuing distillation from the reaction zone. However, oil shale does not contain any oil— this must be produced by a process in which the kerogen is thermally decomposed (cracked) to produce the liquid product (shale oil). Thus, any estimate of shale oil reserves can only be speculative, based on estimates from applying the Fischer assay test method to (often) non representative samples taken from an oil shale deposit. The assay data (in terms of oil yield in gallons per ton) must not to be taken as proven reserves. Kerogen that has not thermally matured beyond the diagenesis (low-temperature) stage occurs typically due to the relatively shallow depth of burial. The Green River oil shale of Colorado has matured to the stage that heterocyclic constituents have formed and predominate, with up to 10% normal paraffins and isoparaffins that boil in the range that includes natural naphtha and gasoline constituents. The relatively high hydrogen/carbon ratio (1.6) is a significant factor in terms of yielding high-quality fuels. However, the relatively high nitrogen content (1–3%w/w) is a major issue in terms of producing stable fuels (petroleum typically contains less than 0.5% nitrogen), as well as producing environmentally detrimental nitrogen oxides during combustion.

In the United States, there are two principal oil shale types: the shale from the Green River Formation in Colorado, Utah, and Wyoming, and the Devonian-Mississippian black shale of the East and Midwest (Table 2.5) (Baughman, 1978). The Green River shale is considerably richer, occurs in thicker seams, and has received the most attention for synthetic fuel production. The mineral matter (shale) consists of fine-grained silicate and carbonate minerals. The ratio of kerogen-to-shale for commercial grades of oil shale is typically in the range 0.75:5 to 1.5:5—as a comparison, for coal, the organic matter-to-mineral matter ratio in coal is usually greater than 4.75:5 (Speight, 2013). The common property of these two types of oil shale is the presence of the ill-defined kerogen. The chemical composition of the kerogen has been the subject of many studies (Scouten, 1990) but whether or not the data are indicative of the true nature of the kerogen is extremely speculative. Based on solubility/insolubility in various solvents (Koel et al., 2001), it is, however, a reasonable premise (remembering that regional and local variations in the flora

Table 2. 5. Composition (% w/w) of the organic matter in the Mahogany zone and new Albany.



Component (% w/w)	Green River, Mahogany Zone	New Albany
Carbon	80.5	82.0
Hydrogen	10.3	7.4
Nitrogen	2.4	2.3
Sulfur	1.0	2.0
Oxygen	5.8	6.3
Total	100.0	100.0
H/C atomic ratio	1.54	1.08

Source: Baughman (1978).

that were the precursors to kerogen) led to differences in kerogen composition and properties. Kerogen from different shale samples will differ in composition and properties—similar to the varying in quality, composition, and properties of petroleum from different reservoirs (Speight, 2007). The organic matter is derived from the varied types of marine and lacustrine algae, with some debris of land plants, and its composition is largely dependent on the depositional environment and sediment sources. Bacterial processes were probably important during the deposition and early diagenesis of most oil shale deposits these processes could produce significant quantities of biogenic methane, carbon dioxide, hydrogen sulfide, and ammonia. These gases in turn could react with dissolved ions in the sediment waters to form authigenic minerals (minerals generated where they were found or observed) such as calcite ($CaCO3$), dolomite ($CaCO3 \cdot MgCO3$), pyrite ($FeS2$), and even rare authigenic minerals such as buddingtonite (ammonium feldspar—$NH4 \cdot Al \cdot Si3O8 \cdot 0.5H2O$). The organic matter in oil shale is composed chiefly of carbon, hydrogen, and oxygen with lesser amounts of sulfur and nitrogen. Because of its high molecular weight (best estimates are in the order of several thousands) and molecular complexity, oil shale kerogen is almost totally insoluble in petroleum-based and conventional organic solvents (such as carbon disulfide) (Durand, 1980; Hunt, 1996; Scouten, 1990; Speight, 2007; Tissot and Welte, 1978). A portion of the organic matter in oil shale is soluble and is (incorrectly and confusingly) termed bitumen. The bitumen, which is soluble, is dispersed throughout the kerogen network, although even in finely crushed shale much of it may be inaccessible to the solvent. As a result, only a small fraction of the hydrocarbonaceous material in oil shale can be removed by conventional solvent-extraction techniques.

Briefly, the term bitumen is more appropriate when applied to the organic content of tar sand (oil sand) deposits, although the name also applies to road asphalt in European countries and other countries (Speight, 2007, 2008). Using this name in reference to the soluble portion of the organic constituents of oil shale is more for convenience than scientific correctness. Small amounts of bitumen that are soluble in organic solvents are present in some oil shales. Because of its insolubility, the organic matter must be retorted at temperatures in the order of 500°C (930°F) to decompose it into shale oil and gas. After thermal decomposition of the organic matter, some carbon (in the form of a carbonaceous deposit) remains with the shale residue after retorting but can be burned to obtain additional energy. The organic matter of kukersite is considered to be entirely of marine origin and consists almost entirely of accumulations of discrete bodies, telalginite derived from a colonial microorganism termed G. prisca. Compared to other rocks containing telalginite, kukersite has a low atomic hydrogen-to-carbon ratio (H/C = (1.48) and high atomic oxygen-to-carbon ratio (O/C = 0.14) and generally falls into the type II kerogen on the van Krevelen diagram (Figure 2.7) (Cook and Sherwood, 1991). Major components of this kerogen are phenolic moieties with linear alkyl side chains. In spite of the predominance of phenolicmoieties, kukersite appears as a highly aliphatic kerogen due to the presence of associated long, linear alkyl chains (Derenne et al., 1989). The formation of kukersite kerogen is believed to have occurred through the selective preservation pathway, and the phenolic moieties correspond to important basic structures of the resistant macromolecular material (Derenne et al., 1994).

Different extraction methods yield bitumen from kukersite on the order of 1 to 3% w/w.

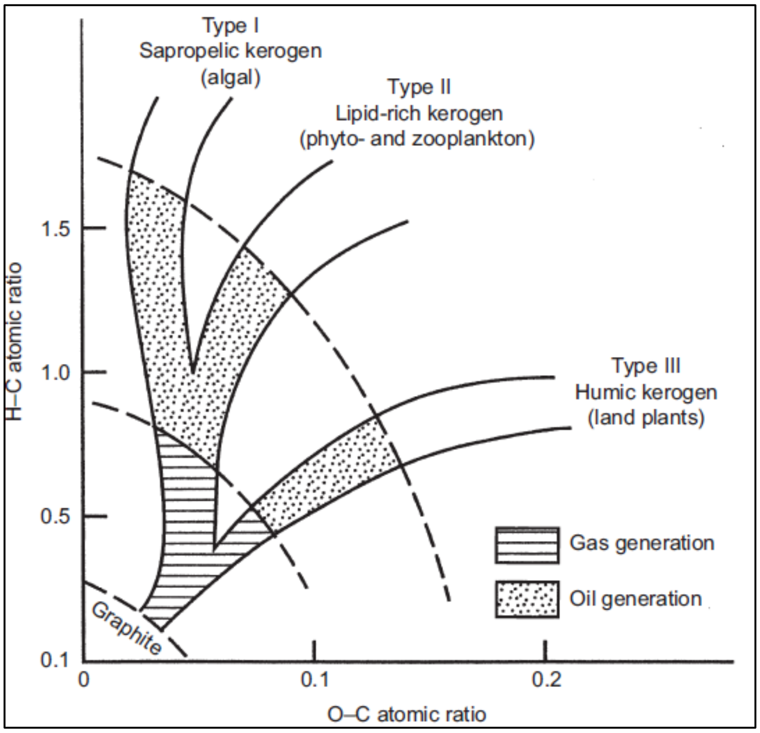


Figure 2. 7. The Van Krevelen diagram showing the different types of kerogen.

The yield of oil and gas under slow retorting conditions is not the same as under Fischer assay. Gas compositions reported for slow, modest pressure retorting indicate that the energy content of the gas could be as much as 70% greater than achieved by Fischer assay (Burnham and Singleton, 1983). This increase has at least three sources of uncertainty:

(1) possible leaks in the gas collection system at the slowest heating rate at elevated pressure,

(2) difficulty in recovering light hydrocarbons dissolved in the oil at elevated pressure, and

(3) the likelihood that oil cracking at higher geological pressures in the liquid phase is less than in the self-purging reactor, which requires volatilization for expulsion. Nevertheless, it is likely that the gas yields will be higher for methane due to oil coking reactions, which was the main reason for the 70% increase, so it

is likely that slow retorting would generate gases with good heat content (Burnham, 2003).

Finally, the gross heating value of oil shales on a dry-weight basis ranges from about 500 to 4000 kcal/kg of rock. The high-grade kukersite oil shale of Estonia, which fuels several electric power plants, has a heating value of approximately 2000 to 2200 kcal/kg. By comparison, the heating value of lignite ranges from 3500 to 4600 kcal/kg on a dry-mineral-free basis (Speight, 2013). [9]

2.9.1. Mineral Components

Oil shale has often been termed as (incorrectly and for various illogical reasons) high-mineral coal. Nothing could be further from the truth than this misleading terminology. Coal and oil shale are fraught with considerable differences (Speight, 2008, 2013) and such terminology should be frowned upon.

Furthermore, the precursors of the organic matter in oil shale and coal also differ. Much of the organic matter in oil shale is of algal origin, but may also include remains of the vascular land plants that more commonly compose much of the organic matter in coal (Dyni, 2003, 2006; Scouten, 1990; Speight, 2013). In addition, the lack of recognizable biological structures in oil shale that would help identify the precursor organisms makes it difficult to identify the origin of the organic matter. In terms of mineral and elemental content, oil shale differs from coal in several distinct ways. Oil shale typically contains much larger amounts of inert mineral matter (60–90%) than coal, which has been defined as containing less than 40% mineral matter (Speight, 2013). The organic matter of oil shale, which is the source of liquid and gaseous hydrocarbons, typically has a higher hydrogen and lower oxygen content than that of lignite or bituminous coal. The mineral component of some oil shale deposits is composed of carbonates including calcite (CaCO3), dolomite (CaCO3 · MgCO3), siderite (FeCO3), nahcolite (NaHCO3), dawsonite [NaAl(OH)2CO3], with lesser amounts of aluminosilicates—such as alum [KAl(SO4)2 · 12H2O] and sulfur, ammonium sulfate, vanadium, zinc, copper, and uranium, which add by-product value (Beard et al., 1974). For other deposits, the reverse is true—silicates including quartz (SiO2), feldspar [xAl(Al · Si)3O8, where x can be sodium (Na) or calcium (Ca) or potassium (K)], and clay minerals are dominant and carbonates are a minor component. Many oil shale deposits contain small, but ubiquitous, amounts of sulfides including pyrite (FeS2) andmarcasite (FeS2, but physically and crystallographically distinct from pyrite), indicating that the sediments probably accumulated in dysaerobic (a depositional environment with 0.1–1.0ml of dissolved oxygen per liter of water) to anoxic waters that prevented the destruction of the organic matter by burrowing organisms and oxidation.

Green River oil shale contains abundant carbonate minerals including dolomite, nahcolite, and dawsonite. The latter two minerals have potential by-product value for their soda ash and alumina content respectively. The oil shale deposits of the eastern United States are low in carbonate content but contain notable quantities of metals, including uranium, vanadium, molybdenum, and others, which could add significant byproduct value to these deposits. There is a potential for low emissions due to the inherent presence of carbonate minerals. Calcium carbonate present in oil shale ash binds sulfur dioxide, and it is not necessary to add limestone for desulfurization:

$$CaCO_3 \rightarrow CaO + CO_2$$

$$2CaO + SO_2 + O_2 \rightarrow CaSO_4$$

Illite (a layered aluminosilicate [K H_2O) $(Al,Mg,Fe)_2(Si,Al)4O10(OH)_2$, (H_2O)] is ever-present in Green River oil shale—it is generally associated with other clay minerals but also frequently occurs as the only clay mineral found in the oil shale (Tank, 1972). Smectite (a group of clay minerals that includes montmorillonite, which tends to swell when exposed to water) is present in all three members of the Green River Formation, but its presence frequently shows an inverse relationship to both analcime (a white, gray, or colorless tectosilicate mineral, which consists of hydrated sodium aluminum silicate, NaAlSi2O6 · H2O) and loughlinite [a silicate of magnesium, Na2Mg3Si6O16 · 8(H2O)]. Chlorite (a group of mostly monoclinic but also triclinic or orthorhombic micaceous phyllosilicate minerals) occurs only in the silty and sandy beds of the Tipton Shale Member. The distribution of random mixed-layer structures and amorphous material is irregular. Several independent Lines of evidence favor an in situ origin for many of the clay minerals. Apparently, the geochemical conditions favoring the accumulation of the oil shale also favored the in situ generation of illite.

Finally, precious metals and uranium are contained in good amounts in oil shale of the eastern United States. It may not be viable to recover these mineral resources in the near future, since a commercially favorable recovery process has not yet been developed. However, there are many patents on recovery of alumina from dawsonite-bearing beds [NaAl (CO3) (OH)2] by leaching, precipitation, and calcination. [9]

2.9.2. Thermal Decomposition

Compared to coal, oil shale kerogen is relatively hydrogen-rich and can, therefore, be subjected to thermal conversion leading to higher yields of distillable oil and gas. This is in keeping with volatile products from fossil fuels being related to the hydrogen content of the fossil fuel (Scouten, 1990; Speight, 2007, 2008, 2013).

High-yield oil shale sustains combustion, hence the older Native American name, the rock that burns, but in the absence of air (oxygen), three carbonaceous end products result when oil shale is thermally decomposed. Distillable oil is produced as are noncombustible gases, and a carbonaceous (high-carbon) deposit remains on the rock (on the surface or in the pores) as char, a coke-like residue. The relative proportions of oil, gas, and char vary with the pyrolysis temperature and to some extent with the organic content of the raw shale. All three products are contaminated with nonhydrocarbon compounds, and the amounts of the contaminants also vary with the pyrolysis temperature (Bozak and Garcia, 1976; Scouten, 1990).

At temperatures in the order of 500–520°C (930–970°F), oil shale produces shale oil, while the mineral matter of the oil shale is not decomposed. The yield and quality of the products depend on a number of factors, whose impact has been identified and quantified for some of the deposits, notably the US Green River deposits and the Estonian Deposits (Brendow, 2003, 2009; Miknis, 1990). A major factor is that oil shale ranges widely in organic content and oil yield. Commercial grades of oil shale, as determined by the yield of shale oil, range from about 25 to 50 g/t of rock (typically using the Fischer assay method). The correlation of the shale oil yield with the chemical and physical properties of the oil shale or kerogen has been based on different kinds of measurements, ranging from simple, qualitative tests that can be performed in the field to more complicated measurements in the laboratory. One simple aspect of the thermal decomposition of oil shale kerogen is the relationships of the organic hydrogen and nitrogen contents and the Fischer assay oil yields. Stoichiometry suggests that kerogen with a higher organic hydrogen-to-carbon atomic ratio can yield more oil per weight of carbon than can kerogen that is relatively hydrogen-poor (Scouten, 1990). However, the hydrogen-to-carbon atomic ratio is not the only important factor. South African kerogen with an atomic hydrogen-to-carbon ratio of 1.35 has a lower oil yield than Brazilian kerogen with an atomic hydrogen-to-carbon ratio of 1.57. In general, the oil shale containing kerogen that can be converted efficiently to oil contains relatively low levels of nitrogen (Scouten, 1990). During retorting, kerogen decomposes into three organic fractions:

(1) shale oil, (2) gas, and (3) carbonaceous residue.

Oil shale decomposition begins at relatively low retort temperatures (300°C, 572°F) but proceeds more rapidly and more completely at higher temperatures (Scouten, 1990). The highest rate of kerogen decomposition occurs at retort temperatures of 480–520°C (895–970°F). In general, the shale oil yield decreases, the gas yield increases, and the aromaticity of the oil increases with increasing decomposition temperature (Dinneen, 1976; Scouten, 1990). Furthermore, variation of product distribution with time in the reaction zone can cause a change in product distribution (Figure 2.8) (Hubbard and Robinson, 1950).

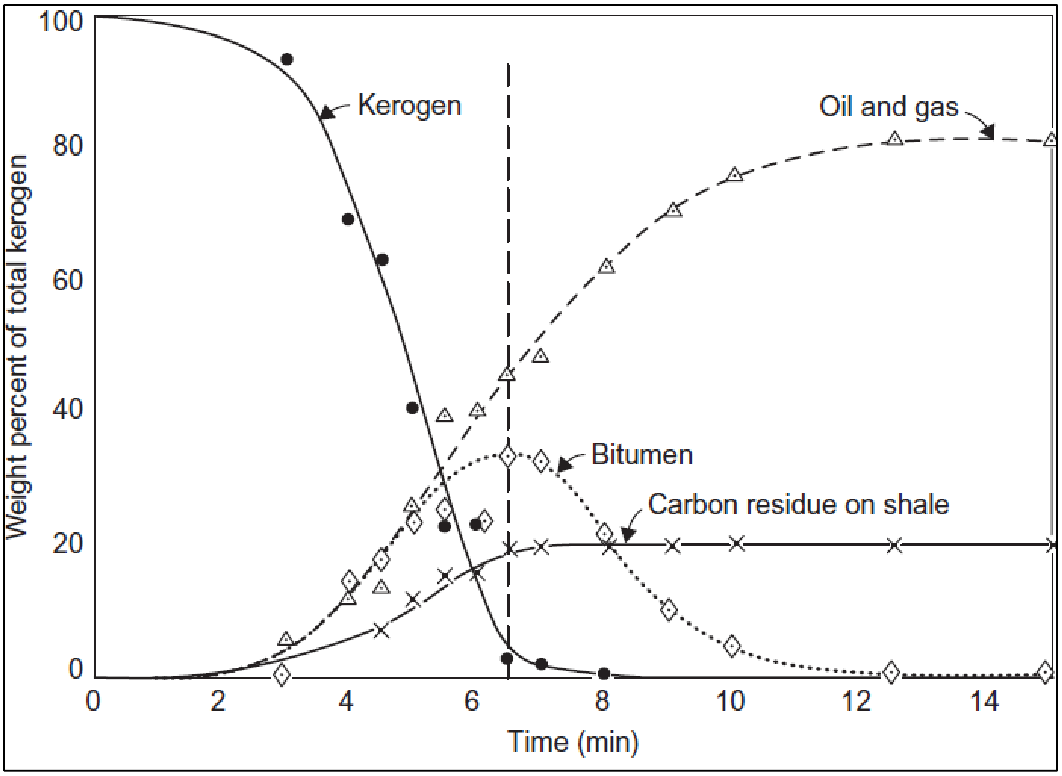


Figure 2. 8. Variation of product yield with time (Hubbard and Robinson, 1950)

However, there is an upper limit on optimal retorting temperature, as the mineral content of the shale may decompose if the temperature is too high. For example, the predominant mineral component of Estonian kukersite shales is calcium carbonate, a compound that dissociates at high temperatures (600–750°C and 1112–1382°F for dolomite; 600–900°C and 1112–1652°F for calcite). Thus, carbon dioxide must be anticipated as a product of oil shale decomposition process, which will dilute the off-gases (adding to emission issues) produced from the retorting process. The gases and vapors leaving the retort are cooled to condense the reaction products, including oils and water. Kinetically, the active devolatilization of oil shale begins at about 350–400°C (660–750°F), with the peak rate of oil evolution at about 425°C (800°F) and with devolatilization being essentially complete in the range of 470–500°C (890–930°F) (Hubbard and Robinson, 1950; Shih and Sohn, 1980). At temperatures close to 500°C (930°F), the mineral matter, consisting mainly of calcium/magnesium and calcium carbonates, begins to decompose yielding carbon dioxide as the principal product. The properties of crude shale oil are dependent on the retorting temperature, but more importantly on the temperature–time history because of the secondary reactions accompanying the evolution of the liquid and gaseous products. The produced shale oil is dark brown, odoriferous, and tending to waxy oil. Kinetic studies (Scouten, 1990) indicate that at temperatures below 500°C (930°F), the kerogen (organic matter) decomposes into an extractable product (bitumen) with subsequent decomposition into oil, gas, and carbon residue. The actual kinetic picture is influenced by the longer time required to heat the organic material that is dispersed throughout the mineral matrix and the increased resistance to the outward diffusion of the products by the matrix that does not decompose. From the practical standpoint of oil shale retorting, the rate of oil production is the important aspect of kerogen decomposition. The processes for producing oil from oil shale involve heating (retorting) the shale to convert the organic kerogen to a raw shale oil (Burnham and McConaghy, 2006; Janka and Dennison, 1979; Rattien and Eaton, 1976). Conversion of kerogen to oil without heat has not yet been proven commercially. Although there are schemes for accomplishing such a task, in spite of the claims made about them, they have not moved into the viable commercial or even demonstration stage.

However, since there are issues to consider when using the Fischer assay to determine the potential yields of oil from shale, there are other issues to consider relating to the rate of heating (Allix et al., 2011; Dyni et al., 1989). The reactions that convert kerogen to oil and gas are understood generally, but not in precise molecular detail and can only be represented by simple equations. The amount and composition of generated hydrocarbons depend on the heating conditions, the rate of temperature increase, the duration of exposure to heat, and the composition of gases present as the kerogen breaks down. Generally, surface-based retorts heat the shale rapidly. The time scale for retorting is directly related to the particle size of the shale, which is why the rock is crushed before being heated in surface retorts. Pyrolysis of particles on the millimeter scale can be accomplished in minutes at 500°C (930°F), while pyrolysis of particles of sizes in tens of centimeters takes much longer. In situ processes heat the shale more slowly. However, slow heating has advantages—the quality of the oil increases substantially. Coking and cracking reactions in the subsurface tend to leave the higher molecular weight (higher boiling), less desirable components in the ground. As a result, compared with surface processing, an in situ process can produce lighter lower boiling products with fewer contaminants. From the standpoint of shale oil as a substitute for petroleum products, its composition is of great importance. Oils of paraffin types are similar to paraffin petroleum. However, the composition of the kukersite shale oil of Estonia is more complicated and very specific—it contains abundant oxygen compounds, particularly phenols, which can be extracted fromoil. The oil cannot serve directly as raw oil for high-quality engine fuel, but it is easily used as a heating fuel. It has some specific properties, such as lower viscosity, lower pour point, and relatively low sulfur content, which make it suitable for other uses such as marine fuel. Contrary to other oil shales, obtaining high oil yields of distillable oil from kukersite needs specific conditions of processing. This can be explained by the fact that on thermal processing of kukersite, its elevated moisture percentage and the predominance of calcium carbonate in its mineral part result in high values of specific heat consumption (Yefimov and Purre, 1993). Also, shale is rich in organic matter and must be able to withstand the higher temperatures of thermobitumen formation and coking at a relatively high speed to avoid caking and secondary pyrolysis of oil. One of the characteristics of kukersite that causes considerable difficulties in its commercial scale processing is its conversion to a bitumenlike product on slow heating—the transition to the plastic state takes place within the temperature range 350–400°C (660–750°F). The maximum yield of thermobitumen is produced at 390–395°C (735–745°F) and it constitutes up to 55–57% w/w of the organic products. At these temperatures, carbon content of solid residue (remaining after extraction with mixture of ethanol–benzene) at a minimum. However, as the heating continues up to 510–520°C (950–970°F), the carbon content of the residue increases two to threefold. As a result, most of the carbonaceous residue in semicoke is of secondary origin, formed by the pyrolysis of unstable components like oxygen-containing compounds (Yefimov and Purre, 1993).

The thermal characterization of Australian oil shale was undertaken by the separation of the unique components of oil shale, the kerogen (organic component) and the clay minerals (inorganic components), using chemical and physical techniques (Berkovich et al., 2000). The heat capacity and the enthalpy changes for kerogen and clay minerals were measured using nonisothermal modulated differential scanning calorimetry from 25°C to 500°C (77–930°F). Heat capacity data was obtained over a temperature range spanning several hundred degrees in a single experiment. Heat capacity was also estimated by incorporating thermogravimetric data during regions where thermal reactions involving mass loss occurred. Enthalpy data for dehydration and pyrolysis of kerogen were also determined (Berkovich et al., 2000; Scouten, 1990). The mineralogy of Green River Formation is radically changed when the raw oil shale is subjected to extreme processing temperatures (Essington et al., 1987; Milton, 1977; Smith et al., 1978). Mineral reactions from high temperature oil shale retorting can be summarized by two general steps: (1) decomposition of raw minerals and (2) crystallization from the melt. Complete decomposition of carbonate minerals and silicate minerals forms a pyro-metamorphic melt containing the principal ions such as Ca^{2+}, Na^{+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, K^{+}, Si^{4+}, Al^{3+}, and O2+ (Mason, 2006; Park et al., 1979). Trace elements are abundant in the Green River Formation and are undoubtedly present in the melt, but their low abundance is believed to make their contribution to the crystallization of new minerals negligible, although some partitioning has been recorded (Shendrikar and Faudel, 1978). Silicate mineral products of high temperature oil shale processing fall into several general types: olivine group, melilite group, ortho- and clinopyroxenes, amphibole, feldspar group, quartz, and clay minerals. Amorphous silica (glass) is also a common product in oil shale that is processed at high temperatures and then cooled rapidly. Although variation within the mineral groups can be in part due to minor differences in the composition of the raw oil shale, the final mineral suite appears to vary very little when examining material from different processes and localities (Mason, 2006). However, some oil shale deposits contain minerals and metals that add by-products such as dawsonite [NaAl (OH)2CO3], sulfur, ammonium sulfate, vanadium, zinc, copper, and uranium. [9]

2.9.3. Oil Shale Grade

The grade of oil shale has been determined by different methods with the results being expressed in various units (Dyni 2003, 2006; Scouten, 1990).

For example, the heating value is useful for determining the quality of an oil shale that is burned directly in a power plant to produce electricity. Although the heating value of a given oil shale is a useful and fundamental property of the rock, it does not provide information on the amounts of shale oil or combustible gas that would be yielded by retorting (destructive distillation). Alternatively, the grade of oil shale can be determined by measuring the yield of distillable oil produced from a shale sample in a laboratory retort (Scouten, 1990). This is perhaps the most common type of analysis that has been, and still is, used to evaluate an oil shale resource. However, the end result of the evaluation depends on the source of the sample and whether or not it is representative of the deposit. The method commonly used in the United States is the modified Fischer assay test method (ASTM D3904). Some laboratories have further modified the Fischer assay method to better evaluate different types of oil shale and different methods of oil shale processing. The standard Fischer assay test method (ASTM D3904, now withdrawn but still used in many laboratories) consists of heating a 100-g sample crushed to 8-mesh (2.38-mm) screen in a small aluminum retort at 500°C (930°F) at a rate of 12°C (21.6°F) per minute and held at that temperature for 40 min. The distilled vapors of oil, gas, and water are passed through a condenser cooled with ice water and then into a graduated centrifuge tube. The oil and water are separated by centrifuging. The quantities reported are the weight percentages of shale oil (and its specific gravity), water, shale residue, and (by difference) gas plus losses. The Fischer assay method does not measure the total energy content of an oil shale sample because the gases, which include methane, ethane, propane, butane, hydrogen, hydrogen sulfide, and carbon dioxide, can have significant energy content, but are not individually specified (Allix et al., 2011). Also, some retort methods, especially those that heat at a different rate or for different times, or that crush the rock more finely, may produce more oil than that produced by the Fischer assay method. Therefore, the method can only be used as a reference point and, at best, the data from the Fischer assay test method can only be employed to approximate the energy potential of an oil shale deposit. Other retorting methods, such as the Tosco II process, are known to yield in excess of 100% of that reported by Fischer assay. In fact, some methods of retorting can increase oil yields of some oil shales by as much as three to four times that obtained by the Fischer assay method (Dyni, 2003, 2006; Scouten, 1990).

Another method for characterizing the organic richness of oil shale is a pyrolysis test developed by the Institut Français du Pétrole for analyzing source rocks (Allix et al., 2011). The Rock-Eval test heats a 50–100-mg sample through several temperature stages to determine the amounts of hydrocarbon and carbon dioxide generated. The results can be interpreted for kerogen type and potential for oil and gas generation. The method is faster than the Fischer assay and requires less sample material (Kalkreuth and Macauley, 1987). [9]

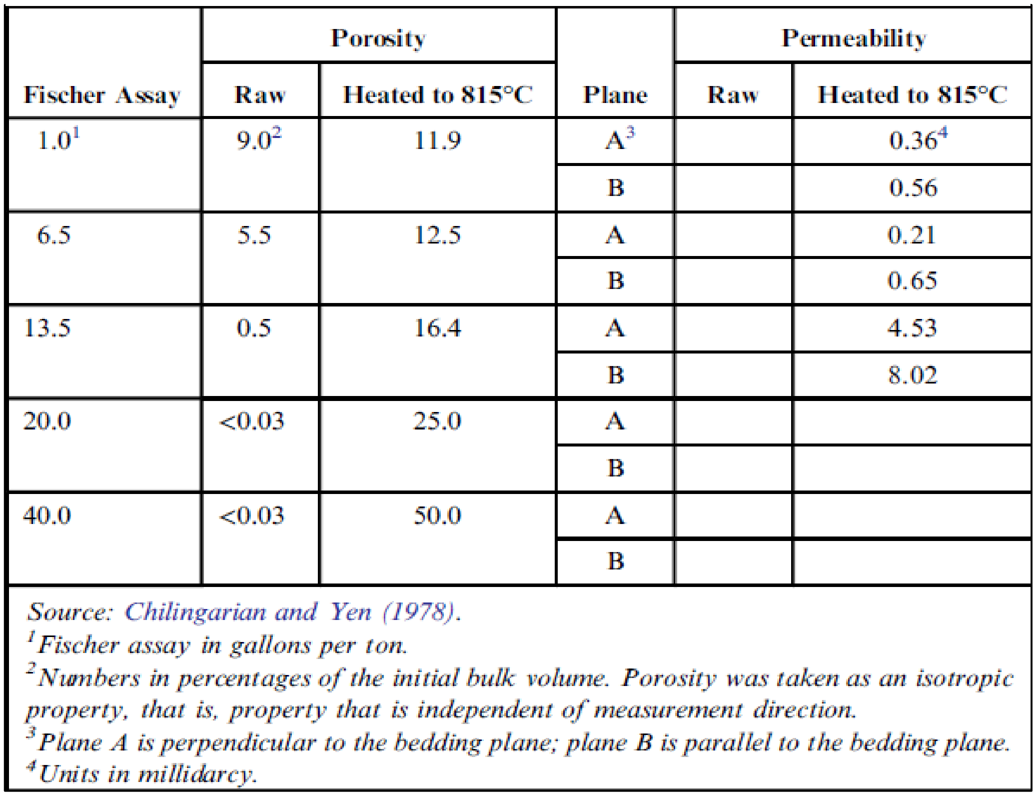
2.9.4. Porosity

Porosity (void fraction) is a measure of the void spaces in a material such as a reservoir rock and is a fraction of the volume of void space over the total volume, and is expressed as a fractional number between 0 and 1 or as a percentage between 0 and 100. The porosity of a porous material can be measured in a number of different ways, depending on what specific pores are looked at and how the void volumes are measured. They include (1) interparticle porosity, (2) intraparticle porosity, (3) internal porosity, (4) porosity by liquid penetration, (5) porosity by saturation, (6) porosity by liquid absorption, (7) superficial porosity, (8) total open porosity, (9) bed porosity—the bed void fraction, and (10) packing porosity.

The porosity of the mineral matrix of oil shale cannot be determined by the methods used to determine the porosity of petroleum reservoir rocks because the organic matter in the shale exists as a solid and is essentially insoluble. However, inorganic particles contain a micropore structure, about 2.36–2.66% v/v, and although the mineral particles have an appreciable surface area, 4.24–4.73m2/g for oil shale capable of producing 29–75 g/t in the Fischer assay, the measurement of porosity may be limited to the characteristics of the external surface rather than to the actual pore structure. Except for the two low-yield oil shale samples, naturally occurring porosities in the raw oil shales are almost negligible and they do not afford access to gases (Table 2.6). Porosity may exist to some degree in the oil shale formation where fractures, faults, or other structural defects have occurred. It is also believed that a good proportion of pores are either blind or inaccessible. Cracking and fractures or other structural defects often create new pores and also break up some of the blind pores—closed or blind pores are normally not accessible by mercury porosimetry even at high pressures. Due to the severity of mercury poisoning, the instrument based on pressurized mercury penetration through pores is no longer used.

In the process of the production of shale oil from oil shale, both the chemical and physical properties of oil shale play important roles. The low porosity, low permeability, and high mechanical strength of the oil shale rock matrix make the extraction process less efficient by making the mass transport of reactants and products much harder as well as reducing the process efficiency (Eseme et al., 2007; Scouten, 1990).

Table 2. 6. Porosity and Permeability of Raw And Treated Oil Shale



Fischer Assay	Porosity		Plane	Permeability	
	Raw	**Heated to 815°C**		**Raw**	**Heated to 815°C**
1.0[1]	9.0[2]	11.9	A[3]		0.36[4]
			B		0.56
6.5	5.5	12.5	A		0.21
			B		0.65
13.5	0.5	16.4	A		4.53
			B		8.02
20.0	<0.03	25.0	A		
			B		
40.0	<0.03	50.0	A		
			B		

Source: Chilingarian and Yen (1978).
[1] *Fischer assay in gallons per ton.*
[2] *Numbers in percentages of the initial bulk volume. Porosity was taken as an isotropic property, that is, property that is independent of measurement direction.*
[3] *Plane A is perpendicular to the bedding plane; plane B is parallel to the bedding plane.*
[4] *Units in millidarcy.*

Furthermore, the changes in properties as a function of temperature and pressure present implications of the evolution of these properties for in situ exploitation and basin modeling. While the mechanical properties at room temperature are well known, the existing data suggest a positive correlation between oil shale grade (organic matter content) and Poisson ratio, whereas tensile and compressive strength and modulus of elasticity show negative correlations. These properties are strongly affected by temperature—an increase in temperature results in loss of strength and decrease in Young's modulus (Scouten, 1990). Strength follows a logarithmic decrease with increasing temperature, depending on grade. Creep is much enhanced by elevated temperature. Extrapolation of laboratory data to nature suggests that tensile fracturing may occur more easily during petroleum generation, and creep is more prominent in oil shales than in other rocks at this depth in the crust (Eseme et al., 2007). [9]

2.9.5. Permeability

Permeability is the ability, or measurement of a rock's ability, to transmit fluids, typically measured in darcies or millidarcies. Permeability is part of the proportionality constant in Darcy's law, which relates the flow rate of the fluid and the fluid viscosity to a pressure gradient applied to the porous media. The permeability of raw oil shale is essentially zero because the pores are filled with a non-displaceable organic material. In general, oil shale constitutes a highly impervious system. Thus, one of the major challenges for any in situ retorting project is in the creation of a suitable degree of permeability in the formation. This is why an appropriate rubbelization technique is essential to the success of an in situ pyrolysis Project of practical interest is the dependency of porosity or permeability on temperature and organic content. Upon heating to 510°C (950°F), an obvious increase in oil shale porosity is noticed. These porosities, which vary from 3 to 6% v/v of the initial bulk oil shale volume, represent essentially the volumes occupied by the organic matter before the retorting treatment. Therefore, the oil shale porosity increases as the pyrolysis reaction proceeds. In an oil shale that produces a low yield of oil by the Fischer assay method (lean oil shale), structural breakdown of the cores is insignificant and the porosities are those of intact porous structures. However, in the high-yield Fischer assay oil shale, that is, rich oil shale, this is not the case because structural breakdown and mechanical disintegration due to retorting treatment become extensive and the mineral matrices no longer remain intact. Thermal decomposition of the mineral carbonates, such as magnesium carbonate (MgCO3) and calcium carbonate (CaCO3), actively occurring around 380–900°C (715–1650°F) also results in an increase in porosity. The increase in porosity from low-yield to high-yield Fischer assay oil shale varies from 2.82 to 50% (Table 2.6). These increased porosities constitute essentially the combined spaces represented by the loss of the organic matter and the decomposition of the mineral carbonates. Cracking of particles also occurs, due to the devolatilization of organic matter that increases the internal vapor pressure of large nonpermeable pores to an extent that the mechanical strength of the particle can no longer contain. Liberation of carbon dioxide from mineral carbonate decomposition also contributes to the pressure buildup in the oil shale pores. [9]

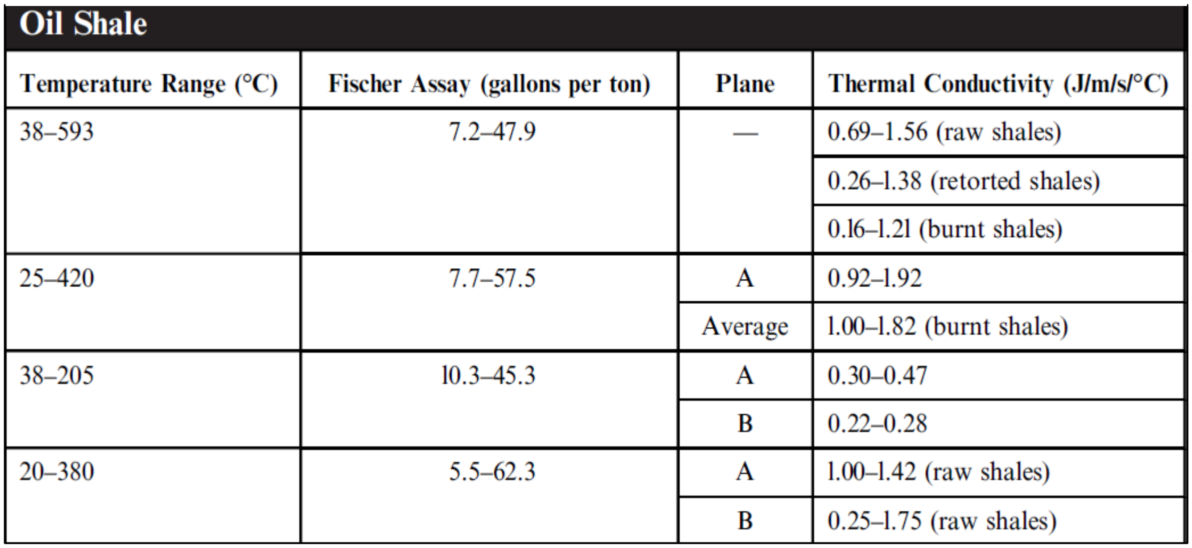
2.9.6. Compressive Strength

Raw oil shale has high compressive strengths both perpendicular and parallel to the bedding plane. After heating, the inorganic matrices of low-yield Fischer assay oil shale retain high compressive strength in both perpendicular and parallel planes. This indicates that a high degree of inorganic cementation exists between the mineral particles comprising each lamina and between adjacent laminae. With an increase in organic matter of oil shale, the compressive strength of the respective organic-free mineral matrices decreases, and it becomes very low in those rich oil shale. [9]

2.9.7. Thermal Conductivity

Measurements of thermal conductivity of oil shale show that blocks of oil shale are anisotropic about the bedding plane and thermal conductivity as a function of temperature, oil shale assay and direction of heat flow, parallel to the bedding plane (parallel to the earth’s surface for a flat oil shale bed), was slightly higher than the thermal conductivity perpendicular to the bedding plane. As layers of sedimentary material were deposited to form the oil shale bed over geological time, the resulting strata have a higher resistance to heat flow perpendicular to the strata than parallel to the strata (Table 2.7). The thermal conductivity of retorted and burnt shale is lower than those of the raw shales from which they are obtained (Table 2.7). This is attributable to the fact that the mineral matter is a better conductor of heat than the organic matter, and, on the other hand, the organic matter is still a far better conductor than the voids created by its removal. While the first of the above hypotheses is well justified when one takes into account the contribution of the lattice conductivity to the overall value, the effect of the amorphous carbon formed from the decomposition of the organic matter could also be of importance in explaining the difference in thermal conductivity values for retorted shales and the corresponding burnt samples. The role of voids in determining the magnitude of the effective thermal conductivity is likely to be significant only for samples with high organic contents. The thermal conductivity of oil shale is, in general, only weakly dependent on the temperature. However, extreme caution needs to be exercised in the interpretation of results at temperatures close to the decomposition temperature of the shale organic matter. This is due to the fact that the kerogen decomposition reaction (or pyrolysis reaction) is endothermic in nature, and as such the temperature transients can be confounded between the true rate of heat conduction and the rate of heat of reaction. [9]

Table 2. 7. Comparison between Thermal Conductivity Values for Green River



Oil Shale

Temperature Range (°C)	Fischer Assay (gallons per ton)	Plane	Thermal Conductivity (J/m/s/°C)
38–593	7.2–47.9	—	0.69–1.56 (raw shales)
			0.26–1.38 (retorted shales)
			0.16–1.21 (burnt shales)
25–420	7.7–57.5	A	0.92–1.92
		Average	1.00–1.82 (burnt shales)
38–205	10.3–45.3	A	0.30–0.47
		B	0.22–0.28
20–380	5.5–62.3	A	1.00–1.42 (raw shales)
		B	0.25–1.75 (raw shales)

2.10. OIL SHALE EXTRACTION METHODS

Extraction of ***oil*** *from* ***oil*** *shales.* The organic matter in oil shale contains both bitumen and kerogen. Inasmuch **as** the bitumen fraction is soluble in most organic solvents, it is not difficult to extract it from oil shale. Unfortunately, bitumen content in oil shale constitutes only a minor portion. The bulk of the organic matter is composed of kerogen, which is insoluble and inert. Several approaches are used for the separation of oil (organics) from the mineral matrix (inorganics):

(1) to drastically break the bonds of the organics,

(2) to mildly degrade the organics, and

(3) to erode the inorganics and keep the organics intact.

The first approach is used widely in the industry at the present time. It involves a "retorting" process, which had been developed **as** early **as** 1850 by James Young of Ireland (see Chapter 9). The latter two approaches are being investigated at the University of Southern California since 1972, using a biochemical technique (Figure 2.9). [16]

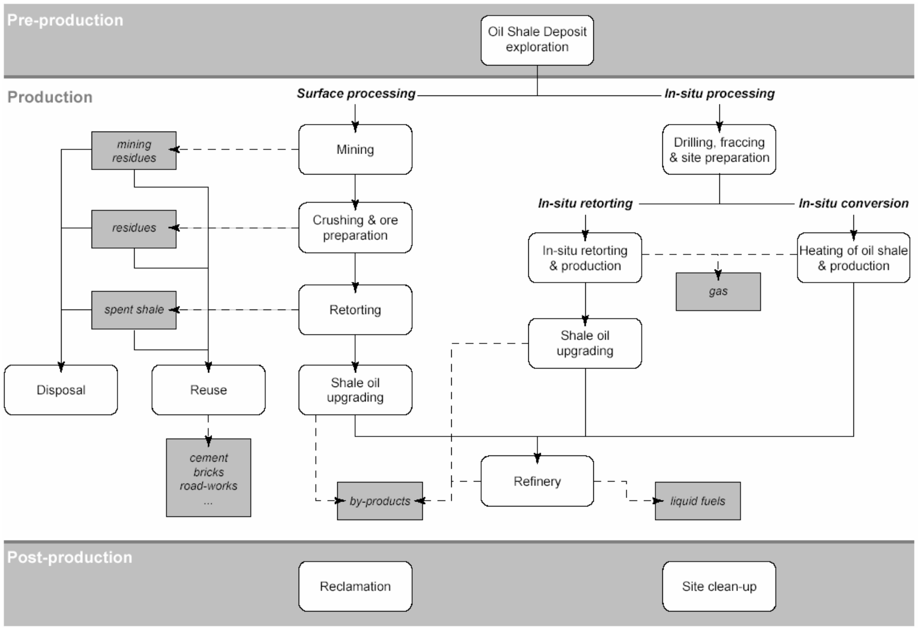


Figure 2. 9. Oil Shale Recovery Methods

2.10.1. Surface retorting (ex-situ)

In the case of surface retorting processes, oil shale is mined (surface or underground), crushed, and then conveyed to a retorter, where it is subjected to temperatures ranging from 500 to 550°C. **As** a result, the chemical bonds linking the organic compounds to the remainder of the rock matrix are broken. The liberated compounds, in the gaseous state, are collected, condensed, and upgraded into a liquid product that is the rough equivalent of a crude oil. This oil is shipped by pipeline to a refinery, where it is refined into the final product.

The first major experimental retort, which was built and operated by the Bureau of Mines in Rifle, Colorado, 25 years ago, was capable of processing 6 tons of oil shale daily. Since that time, many private firms have become interested in the oil-shale extraction and have developed alternate retorting methods. Among these are the Union Oil, Cameron and Jones, TOSCON, TU and Lurgi-Ruhrgas processes. These systems have several limiting factors in common:

(1) Each system requires the use of energy to produce energy.

(2) Current retorting methods are very inefficient with respect to liberating the organic material found in oil shale and, at best, can remove only 70% of the organic material contained in oil shale. The remaining **30%** is closely tied to the inorganic matrix and, therefore, cannot be extracted.

(3) The retorting processes give rise to a large volume of expended shale that must be disposed. A 100,000 bbl/day plant would require the daily disposal of 4,000 tons of spent shale. Not only must this amount of material be moved and stored, but means must be found to insure that the minerals contained in the spent shale are not introduced into the ground water and/or the local streams flowing in the area. Thus, ecologists fear a “nightmare”. In the opinion of the writers, although these factors represent drawbacks in the current processes, the enormous gain resulting from the energy made available by their use more than outweighs the disadvantages. [16]

2.10.2. In-situ processing

In-situ processes do not require removal of shale from underground. The three steps inherent in this process, i.e., fracturing, injection to achieve communication, and fluid migration, take place at the underground location of the shale bed. Several processes, which have been developed to accomplish each step, are discussed here. In-situ processing does not require removal of shale, which is, perhaps, the single most important factor from both the environmental and economic standpoint. Consequently, there is a sharp rise in interest in developing the in-situ processes.

Fracturing. Fracturing can be achieved through the use of explosives, both conventional and nuclear.

In conventional fracturing, a series of wells are drilled and explosives are placed at the bottom of each well. The degree of fracturing resulting from detonation of these explosives is a function of the explosive power, rock strength, and depth of the well. It has been suggested that nuclear explosives can be used in a similar manner. The resulting explosion will form a “nuclear chimney” which is a mass of fractured rock**.** The extensive fracturing and the great amount of shale oil available for extraction would seem to make this an ideal method. The associated environmental hazards, however, are great. There is a possibility of

(1) radioactive gases being released to the atmosphere, and

(2) incorporation of radioactive materials into the ground water.

In addition, the radioactive materials would have to be removed from the shale oil. The Test Ban Treaty has presently eliminated any possibility of carrying out experiments in this area.

A second method to achieve fracturing is to drill a series of wells and use electrical arcing to fracture the rock. A limited amount of success on using this method has been reported in the literature.

Injection of fluids to achieve intercommunication. Hot gases, water, and other fluids can be injected into the wells and forced through the fractures. These fluids are able to expand the width of the fractures and push the fractures deeper into the shale bed, i.e., extend the fractures. The possible use of direct electric current to achieve flow should be investigated**.** If the wells are very close to each other, then it is feasible to have continuous fractures to extend from one well to another; this has been reported in the literature.

Fluid migration. If hot gases are passed through the rock bed, liberation of organic compounds may occur. The latter may, then, flow along with the gases to a producing well where they can be brought to the surface. As a result of the sharp increases in oil prices, the commercial exploitation of oil shale by in-situ methods may become a reality. Occidental Petroleum Company has announced recently the formation of a chimney with the use of conventional explosives. [16]

2.10.3. Disadvantages of retorting processes

The. limitations and disadvantages of retorting processes can be summarized as follows:

(1) Shale for surface retorting must be mined and transported to the processing plant, which may cause environmental damage in addition to transport expense.

(2) Present retorting methods all require an expenditure of thermal energy, which may be supplied by electrical arc, gas combustion, or other energy sources. Even in-place retorting methods still require expenditure of a considerable fraction of the energy contained in the fuels released from oil shales. This diminishes the net energy production.

(3) Retorting is not an efficient method for the liberation of organic material locked in oil shales. For example, shales that produce 25 gallons of oil per ton of rock by retorting, may produce 40 gals/ton if all available kerogen is removed.

(4) Present retorting techniques require high temperatures (about 550" C), which, in the presence of minerals in the rock, cause the formation of organic chemicals that are difficult to refine into fuel. In addition, these high temperatures burn off a great deal of otherwise useful organic material.

(5) Retorting produces large volumes of waste rock, which undergoes a volume increase (about 10%) during processing. These large volumes of spent shale present an important disposal problem.

(6) Preliminary findings by the Denver Research Institute have shown that retorting results in the formation of large amounts of the carcinogenic compounds found in the smoked meat by the Food and Drug Administration, i.e, 3,4-benzopyrene.

(7) At high temperatures, dehydrogenation of hydrocarbons precedes aromatization. As a consequence, large amounts of hydrogen have to be used during subsequent refining processes.

In conclusion, one can state that retorting is not an efficient recovery method. Consequently, there is a need for research and development of economically and environmentally more favorable alternative methods to recover oil from oil shales.[16]

2.11. Case study: JORDAN'S EXPERIENCE IN OIL SHALE STUDIES EMPLOYING DIFFERENT TECHNOLOGIES

The GOJ has recently invited many interested and qualified developers to submit their proposals to develop this source commercially. Of oil shale deposits with low overburden concentrated in six main sites, deposits in central Jordan were selected for detailed study based on the following aspects (Table 2.8):

- Favorable conditions for surface mining and presence of phosphate raw materials.
- Adequate reserves with oil shale of good quality and sufficient quantity.
- Availability of good infrastructure including adequate ground water for future commercial utilization.

Table 2. 8. Main Characteristics of the Studied Oil Shale Deposits

Indices	El-Lajjun	Sultani	Juref Ed-Darawish	Attaraat Um-Ghudran	Wadi Maghar	El-Thamad	Khan Ezzabib
Geologic reserves, billion tons	1.3	0.99	8.6	11.3	32	11.4	n.a
Surface area, sq. km	20	24	150	226	29	150	n.a
Overburden thickness, m	31	69	47	47	40	142-400	66
Oil shale thickness, m	29	32	68	36	40	72-200	39-45
Number of drilled wells	135	57	50	41	21	12	-
Organic matter, %	28	25	18	29	20	25	n.a
Average oil content, %	10.5	9.7	5.7	11.0	6.8	10.5	6.9
Moisture content, %	2.1	5.5	4.5	3.25	2.9	2.5	n.a
Ash content, %	54.7	55.5	58.4	53.2	57.5	54.7	n.a
Sulfur content, %	3.1	2.4	2.4	2.6	2.6	3.2	n.a
Density, g/cm3	1.81	1.96	2.1	1.8	2.03	1.8	n.a
Calorific value: Kcal/kg KJ/kg	1650 6906	1526 6380	1100 4603	1730 7235	1090 4773	1800 6903	n.a n.a

Studies and test programs on oil shale retorting to produce syn-crude (50,000 b/d) and on circulating-fluidized-bed (CFB) combustion for power generation were carried out. It was concluded that:

- Geological conditions of El-Lajjun oil shale are reliably proven for a 50,000-b/d oil shale retorting plant operation during 30 years.
- Open-cast mining method is viable both technically and economically.
- El-Lajjun oil shale is rich in sulfur (3.5 %). Hydrogen sulphide produced can be converted to 99-% elemental sulfur.
- The pilot test has demonstrated smooth operation.
- Combustion tests on spent shale proved an almost burn-out of residual carbon at 800 ºC, the residual oil shale being a suitable material for building and road construction.
- Economic assessments indicated that oil production cost is in the range of 20–25 USD/b and electricity production cost is 19 fils/kWh (1988 prices).

Combustion Tests Results

Test in Finland

Based on the results of combustion of 75 tons of Jordan Sultani oil shale by *Pyropower* (Finland) the following can be concluded:

1. Jordan oil shale is acceptable to be fuelled in an *Ahlstrom Pyroflow* CFB
where it burns cleanly and efficiently.
2. Combustion efficiency in excess of 98.5 % was demonstrated.
3. Both SO2 and NO*x* emissions, as well as CO emissions were acceptably low. The tests demonstrated that over 90 % of sulfur was absorbed by the inherent calcium present in shale. Typical emissions measured during these tests were:

(SO_2 below 20 ppm)
(NO_x in the range between 60–120 ppm)
(CO below 50 ppm)

These values will generally meet the stringent environmental requirements.

Test in Germany

Based on the results of combustion of 75 tons of Jordan Sultani oil shale by *Lurgi* (Germany) the following can be concluded:

1. There were no upsets in the fluidizing behavior of the circulating material
and/or in plant operation.
2. Combustion of oil shale was self-sustained.
3. Combustion of oil shale 3-5-mm particles has not posed any problems.
4. Carbon burn-out reached 98 %.
5. $CaCO_3$ present in oil shale ash binds SO_2 and it is not necessary to add limestone for dersulfurization:

$$CaCO_3 \rightarrow CaO + CO_2$$

$$CaO + SO_2 + \tfrac{1}{2}O_2 \rightarrow CaSO_4 \text{ (calcium sulfate like plaster)}$$

6. As combustion temperature is low, the amounts of SO_2, NO_x and CO emissions did not exceed the international standards.

Solvent Extraction

Solvent extraction of organic matter is one of the well-known techniques for dissolving organic matter within rock composite. R&D activities were carried out in Jordan. El-Lajjun oil shale has been investigated using 75 % benzene and 25 % cyclohexane (by volume) solvent mixture. It was found to be the best one among various organic solvents, such as toluene, benzene, cyclohexane, pentane, ethylether and ethylbenzene, to produce as high as 73 % yields of extracted oil in a continuous sterling tank reactor (CSTR). It was found that extraction yield from fine particles exceeded that from the course particles. Extract amount decreased with the increase in residence time. The higher the temperature to which the oil shale is preheated (less than the boiling point of the solvent) the higher the extraction yield for the same residence time. The impact of extraction time on the yield was much stronger for larger particles (>2 mm) than for smaller ones. The optimum mass of solvent used per 1 kg of oil shale was 0.5 kg. A joint study by

NRA and NERC using Soxhlet extractor was aimed at extracting oil from El-Lajjun oil shale. Different solvents were examined to find out the best solvent and the best technique based on the quality and quantity of the yield and solvent obtained. Maximum oil recovery reaching 23.37% was achieved using carbon disulfide.

Conclusions

- Due to the importance of oil shale to Jordan as the only major proven indigenous energy source, extensive studies were carried out with an objective to assess the quality, quantity and suitability of using oil shale as a reliable energy source.
- The studies have indicated that Jordan possesses a large quantity of good quality oil shale. All tests have proven the environmental, technical and economical feasibility, and the studies have suggested constructing pilot demonstration plants prior to embarking upon any commercial-scale project.
- The Government of Jordan believes that oil shale utilization for power generation and retorting should be pursued because it will result in significant energy supply security and savings in foreign exchange, and create new jobs.
- The oil shales in Jordan are considered by international standard highest grade oil shales, which are available at shallow overburden near the existing infrastructure needed for an oil shale industry. [12]

Chapter Three

3.1. INTRODUCTION

This project aims to focus light on the shale formation, which is a source of oil in the reservoirs in the field, to study its properties, composition, structure, and type of hydrocarbons in it, as well as to study its production capacity and contribution for oil, and suggested a development method to increase the general reserve of the basin from unconventional oil.

3.2. TYPES OF THE NEEDED DATA

The data required for our project is shown in (Table 3.1)

Table 3. 1.Needed Data

Our study needs the following data	
No.	Data Required
1	**Core Analysis Results** such as absolute permeability, porosity, rock saturation, and some other properties.
2	**PVT Analysis.**
3	**Final Logs Results** for instance (ΔLogRSonic, ΔLogRDensity, and ΔLogRNeutron).
4	**Final Results for some Tests** for example Rock-Eval Pyrolysis, geochemical test, …etc.

3.3. ANALYSIS APPROACH

The analysis approach for the available data is a Qualitative, Quantitative Descriptive, and Analytical approach. **TOC** Calculation will be used to determine the quantity of the remaining hydrocarbons. **Rock-Eval pyrolysis** for the calculation of formation saturation, maturity, kerogen type, and the extractable hydrocarbon. And some other tests will be discussed in chapter 4.

3.3.1. TOC Calculation

The limited well distribution in the large area of the **Sab'atayn** basin makes a basin-wide study not warranted at this stage. A focused look into the Madbi formation was carried out instead. General TOC estimation methods, such as Schmoker and ∆Log were employed for TOC calculation. TOC relationships of single and multivariate regressions were also derived from wireline data and TOC rock sample measurements.

3.3.1.1. Single Method

$$\text{TOC} = -3.68 \times \text{RHOP} + 10.08$$

$$\text{TOC wt\%} = (154.497/\rho b) - 57.261$$

3.3.1.2. Multivariate Methods

$$\text{TOC} = 0.000435 \times \text{GR} - 2.469 \times \text{RHOP} + 6.48$$

$$\text{TOC} = 0.0060 \times \text{GR} - 3.219 \times \text{RHOP} - 1.333 \times \text{NPHI} + 8.45$$

$$\text{TOC} = 0.0026 \times \text{GR} - 8.22 \times \text{RHOP} - 0.0226 \times \text{DT} + 23.57$$

- Multiple (Resistivity and the Sonic logs)

$$\Delta\text{LogRSonic} = \text{Log10 (R/Rbaseline)} + 0.02 \times (\Delta t - \Delta t \text{ baseline})$$

- Multiple (Resistivity and Density logs)

$$\Delta\text{LogRDensity} = \text{Log10 (R/Rbaseline)} - 2.5 \times (\rho\text{Pb} - \rho\text{b baseline})$$

- Multiple (Resistivity and the Neutron logs)

$$\Delta\text{LogRNeutron} = \text{Log10 (R/Rbaseline)} + 4.00 \times (\text{ɵN} - \text{ɵNbaseline})$$

3.3.2. Rock-Eval pyrolysis

Pyrolysis is the decomposition of organic matter by heating in the absence of oxygen. Organic geochemists use pyrolysis to measure richness and maturity of potential source rocks. In a pyrolysis analysis, the organic content is pyrolyzed in the absence of oxygen, then combusted. The amount of hydrocarbons and carbon dioxide released is measured. The most widely used pyrolysis technique is Rock-Eval.

In Rock-Eval pyrolysis, a sample is placed in a vessel and is progressively heated to 550°C under an inert atmosphere. During the analysis, the hydrocarbons already present in the sample are volatized at a moderate temperature. The amount of hydrocarbons is measured and recorded as a peak known as S1. Next pyrolyzed is the kerogen present in the sample, which generates hydrocarbons and hydrocarbon-like compounds (recorded as the S2 peak), CO_2, and water. The

CO_2 generated is recorded as the S3 peak. Residual carbon is also measured and is recorded as S4. [5]

(Figure 3.1) shows the cycle of analysis and the corresponding recording.

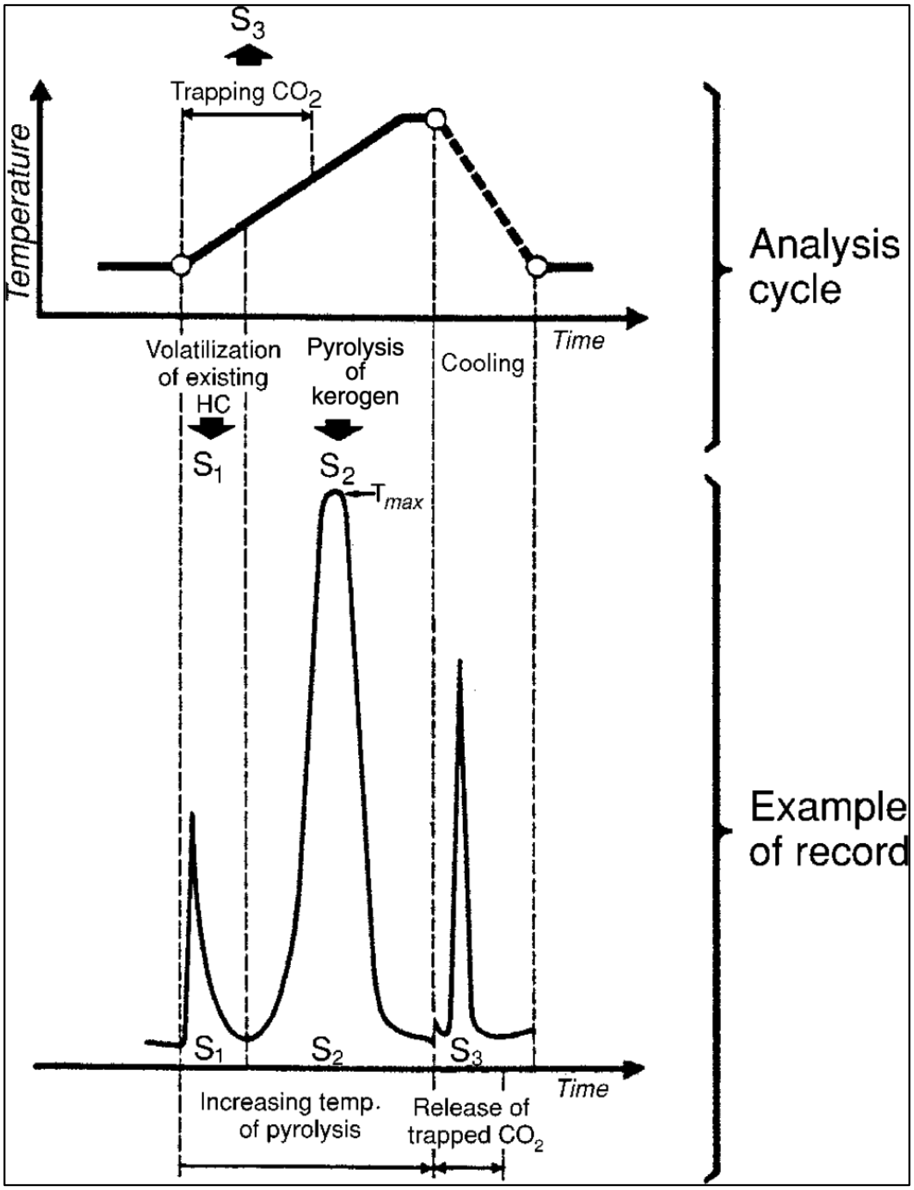


Figure 3. 1.Cycle of analysis and the corresponding recording.

Pyrolysis indices

Table 3. 2.The table below lists the Rock-Eval pyrolysis peaks and explains what they represent.

Peak	**Is a measurement of…**	**Comment**
S1 mg Hc/g rock.	The free hydrocarbons present in the sample before the analysis	Can be thought of as a residual hydrocarbon phase. When S1 is large relative to S2, an alternative source such as migrated hydrocarbons or contamination should be suspected
S2 mg Hc/g rock.	The volume of hydrocarbons that formed during thermal pyrolysis of the sample	Used to estimate the remaining hydrocarbon generating potential of the sample
S3 mg Co2/g rock	The CO_2 yield during thermal breakdown of kerogen	Most prevalent in calcareous source rocks.
S4 mg carbon/g rock	The residual carbon content of the sample	Residual carbon content of sample has little or no potential to generate hydrocarbons due to a lack of hydrogen and the chemical structure of the molecule

3.3.3. Estimating Total Organic Carbon (TOC) with Pyrolysis

The percent total organic carbon (TOC) is actually a value that is calculated, not measured directly, using the following formula:

$$\%\mathrm{TOC} = [0.082(\mathrm{S1} + \mathrm{S2}) + \mathrm{S4}]/10$$

Units are usually given as wt % organic carbon per weight of dry rock (milligrams hydrocarbon per gram of rock). [5]

3.4. EXPECTED RESULTS

The expected results after complete our project can be as following:

- Estimates of hydrocarbon in place in Madbi formation.
- Select the optimum development method for extracting oil shale in the Basin.
- Optimizing daily production in the whole Basin.
- Supporting the economics of the country.

Chapter Four

4.1. INTRODUCTION

In this chapter, we will explain some common methods of extracting oil from the shale formation, knowing which of these methods have more advantages, benefits, and fewer disadvantages. And give an example of one method used in the Green River Formation. Also make a comparison between the Green River Formation and Madbi formation in terms of structure, properties, and reserves. And selecting one of these suitable methods to be used for extracting oil from Madbi formation in the Sab’atayn basin (in Chapter 5). Further explaining some related details. Then explain the importance of this economically.

4.2. IN SITU OIL SHALE RETORTING PROCESSES

Oil shale retorting can also be achieved underground, i.e., without mining the shale. Such a process is called an *in situ oil shale retorting process* or *subsurface retorting*. In a typical *in situ* process, the shale is fractured by either explosives or hydrostatic pressure. A portion of the oil shale organic matter is then burned to obtain heat necessary for retorting. The retorted shale oil is pumped out of the production zone in a manner similar to the extraction of crude petroleum. [15]

The advantages of *in situ* processing include:

1. Oil can be recovered from deep deposits of oil shale formation.
2. Mining costs can be eliminated, or minimized.
3. There is no solid waste disposal problem, as all operations are conducted through well bores. Therefore, the process may be environmentally more desirable, as long as mineral leaching or harmful side effects of the processed shales are absent or controlled.

4. Shale oil can be extracted from leaner shale, e.g., deposits containing <15 gal/ton of oil.

5. The process is ultimately more economical owing to elimination or reduction of mining, transportation, and crushing costs. [15]

<u>However, the disadvantages of *in situ* processing are:</u>

1. It is difficult to control subsurface combustion because of insufficient permeability within the shale formation.
2. Drilling cost is still high.
3. Recovery efficiencies are generally low.
4. It is difficult to establish the required permeability and porosity in the shale formation.
5. There is a concern for possible contamination of aquifers. If not controlled or treated, effects may linger for an extended period of time even after the project completion. Tests and control may require extensive efforts.

In situ retorting processes can be roughly classified into two types, i.e., ***modified in situ*** **(MIS)** and ***true in situ*** **(TIS)**. MIS retorting, the brainchild of Occidental Petroleum, involves partial mining of the oil shale deposit to create a void space and rubblizing the rest into this space so as to increase the overall permeability of the shale. The underground rubblized shale is then ignited using an external or internal fuel source. TIS retorting is similar to MIS, but no mining is done in this process. The shale deposits are rubblized to increase the permeability, and then the underground burning is begun.

A review of the oil shale literature indicates that all *in situ* oil shale processes can be classified into the following categories:

1. Subsurface chimney
    - A. Hot gases
    - B. Hot fluids
    - C. Chemical extraction

2. Natural fractures
    A. Unmodified
    B. Enlargements by leaching
3. Physical induction
    A. No subsurface voids

Other ways of classifying the *in situ* oil shale retorting processes are:

1. Formation of retort cavities
    A. Horizontal sill pillar
    B. Columnar voids
    C. Slot-shaped columnar voids
    D. Multiple zone design
    E. Multiple horizontal units
    F. Multiple adjacent production zones
    G. Multiple gallery-type retort zones
    H. Spaced-apart upright retort chambers
    I. Permeability control of rubble pile
    J. Formation of rich and lean zones
    K. Successive rubblization and combustion
    L. Thermomechanical fracturing
    M. Water leaching and explosive fracturing
    N. Inlet gas means
    O. Fluid communication
    P. Cementation to minimize plastic flow
    Q. Near-surface cavity preparation
    R. Dielectric heating

2. Retorting techniques
    A. Ignition techniques
    B. Multistage operation

C. Steam leaching and combustion
D. Pressure swing recovery
E. Multistratum reservoir
F. Production well throttling
G. Combined combustion techniques
H. Laser retorting
I. Low-heat fans for frontal advance units
J. Gas introduction and blockage
K. Water injection
L. Oil collection system
M. Handling system for feed and products
N. Uniform gas flow
O. Postretorting flow
P. Sound monitoring
Q. Underground weir separator
R. Emulsion breaking technique
S. Offgas recycling
T. Prevention of offgas leakage

3. Others
    A. Molecular sulfur and benzene recovery
    B. Hydrogen sulfide and carbon dioxide treatment
    C. Hot-fluid injection into solvent-leached shale
    D. Steam treatment and extended soak period
    E. Steam-driven excavating unit
    F. Anaerobic microorganisms
    G. Hot aqueous alkaline liquids and fluid circulation
    H. Plasma arc

In the second half of the 20th century, extensive research and development efforts were devoted to the commercialization of the *in situ* pyrolysis of oil shale. However, most of these efforts were either shelved, halted, or scaled down in the late 20th century because of the unfavorable process economics in the short term. As mentioned earlier in the chapter, the comparative economics of shale oil has become substantially more favorable in the 21st century. Several noteworthy processes are described in the following sections. [15]

4.2.1. Sinclair Oil and Gas Company Process

In 1953, Sinclair Oil and Gas Co. performed one of the earliest experiments on *in situ* oil shale retorting. Their process concept was similar to that shown in (Figure 4.1). Their study found that: (1) communication between wells could be established through induced or natural fracture systems, (2) wells could be ignited successfully, and (3) combustion could be established and maintained in the oil shale bed. They also realized that high pressures were required to maintain injection rates during the heating period. These tests were conducted near the outcrop in the southern part of the Piceance Creek Basin. Additional tests were done several years later at a depth of about 365 m in the north-central part of the Piceance Creek Basin with some limited success, which was believed to be due to the inability to obtain the required surface area for the heat transfer. However, their experiments established the basic technology required for *in situ* retorting of oil shale and suggested further study areas. [15]

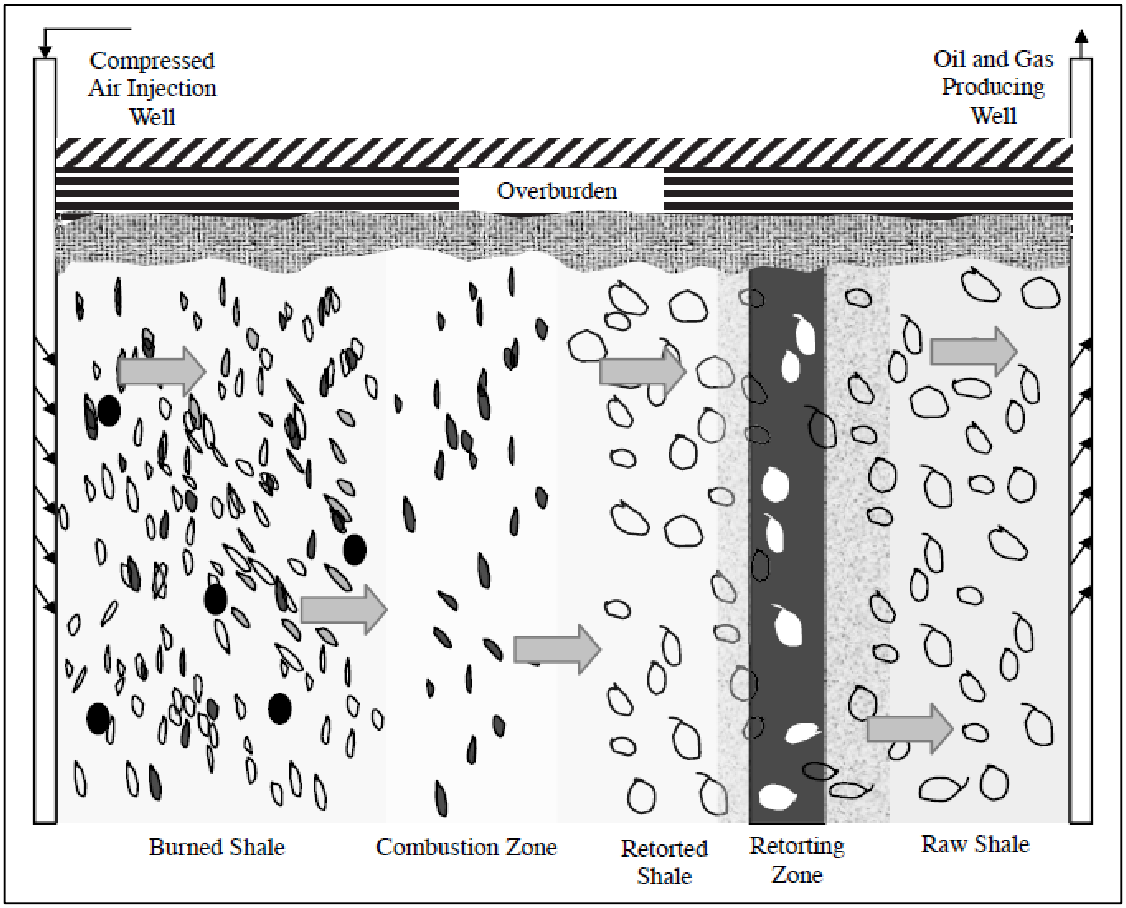


Figure 4. 1. An in situ oil shale retorting process.

4.2.2. Chevron Process

The Chevron technology for the recovery and upgrading of oil from shale (CRUSH) process is an in situ conversion process, which involves the application of a series of fracturing technologies that rubbelize the formation, thereby increasing the surface area of the exposed kerogen. The exposed kerogen in the fractured formation is then converted through a chemical process, resulting in the kerogen changing from a solid material to a liquid and gas. The hydrocarbon fluids are then recovered and improved to refinery feedstock specifications (US

DOE, 2007). In the process, heated carbon dioxide is used to heat the oil shale. Vertical wells are drilled into the oil shale formation and horizontal fractures are induced by injecting carbon dioxide through drilled wells. This is then forced under pressure through the formation for circulation through the fractured intervals to rubbelize the production zone. For further rubbelization, propellants and explosives may be used. The used carbon dioxide can then be routed to the gas generator to be reheated and recycled. The remaining organic matter in previously heated and depleted zones is combusted in situ to generate the heated gases required to process successive intervals (Figure 4.2). These gases would then be pressured from the depleted zone into the newly fractured portion of the formation and the process would be repeated. The hydrocarbon fluids are brought up in conventional vertical oil wells (US DOE, 2007, 2010). [8]

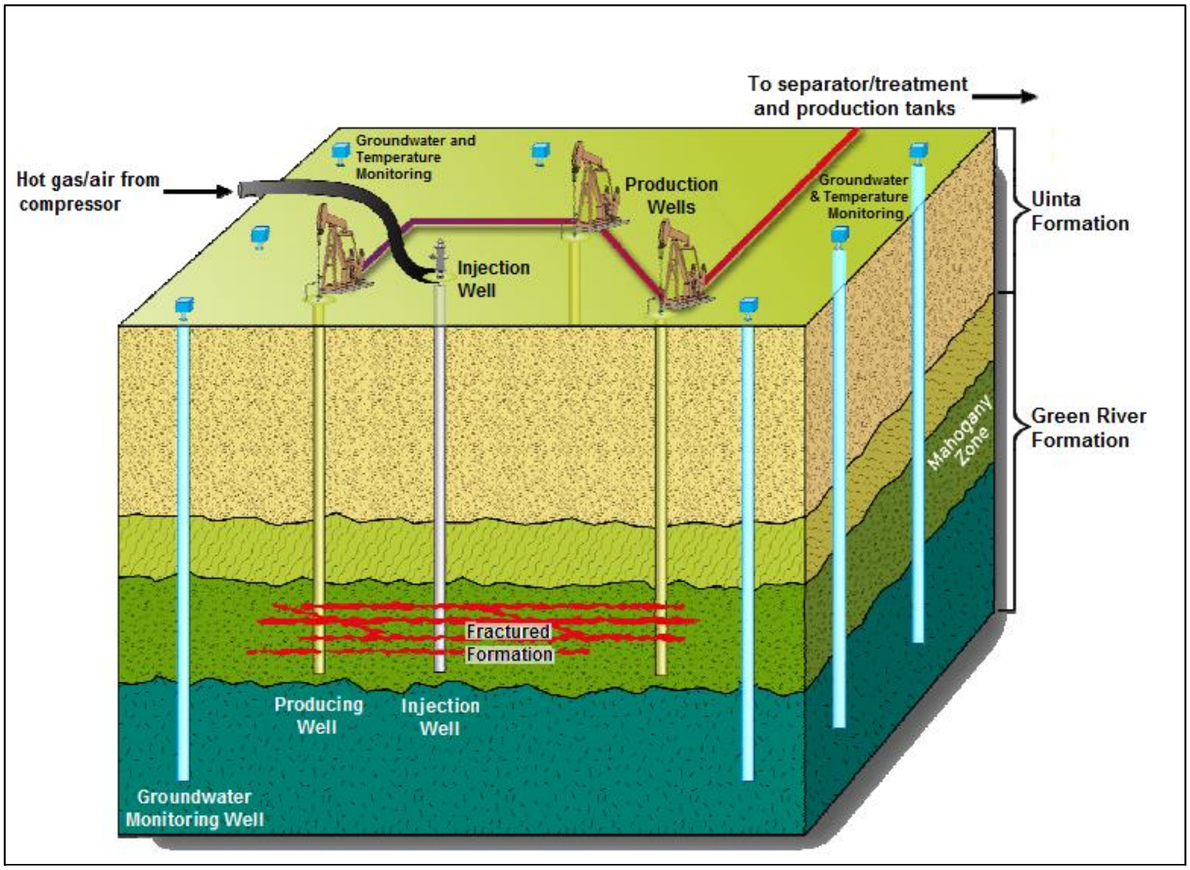


Figure 4. 2. Chevron's Technology

4.2.3. Occidental Petroleum Process

Starting in 1972, Occidental Oil Shale, Inc., a subsidiary of Occidental Petroleum, began research on a shale oil extraction process, ending research in 1991. The company conducted the first modified in situ (MIS) oil shale experiment in 1972 at Logan Wash, Colorado. Modified in situ processes attempt to improve performance by exposing more of the target deposit to the heat source, by improving the flow of gases and liquid fluids through the rock formation, and by increasing the volumes and quality of the oil produced. Modified in situ (MIS) processes involve mining beneath the target oil shale deposit before heating. It also requires drilling and fracturing of the target deposit above the mined area to create void space of 20–25% (Figure 4.3). This void space is needed to allow heated air, produced gases, and pyrolyzed shale oil to flow toward production wells. The shale is heated by igniting the top of the target deposit. Condensed shale oil that is pyrolyzed ahead of the flame is recovered from beneath the heated zone and pumped to the surface. The Occidental vertical modified in situ process was developed specifically for the deep, thick shale beds of the Green River Formation. About 20% of the shale in the retort area is mined; the balance is then carefully blasted using the mined out volume to permit expansion and uniform distribution of void space throughout the retort. A combustion zone is started at the top of the retort and moved down through the shale rubble by management of combustion air and recycled gases. Full-scale retorts would contain 350 000 cubic meters of shale rubble (Petzrick, 1995). In a modified in situ retorting method, a portion of the underground shale was mined and then the remaining portion was crushed through a series of explosions. This method overcame many of the difficulties of burning shale underground by allowing the necessary combustion air to permeate the crushed shale. The underground shale was then retorted in place and the mined shale was sent to surface retorts for processing. There were several companies interested in this technology in the early 1980s, but that interest faltered when oil prices collapsed (Bartis et al., 2005; US OTA, 1980). The process used explosives to create underground chambers (retorts) of fractured oil shale. About 20% was mined out, after which blasting was used to fracture oil shale. The commercial-sized retort covered 333 by 166 feet area and had a height of 400 feet. Oil shale was then ignited on the top by external fuel, and air or steam was injected to control the process. As a result, combustion moved from the top to the bottom of the retort (US DOE 2004a, b, c, 2007).

The retorting technology involved creating a void in the oil shale formation using conventional underground mining techniques. Explosives (ammonium nitrate) and fuel oil were then introduced to cause the rubbelizing of some of the shale on the walls of the void and to expand existing fractures in the formation, improving its permeability. Access to the void was sealed and a controlled mixture of air and fuel gas (or alternatively, commercial fuel such as propane or natural gas) was introduced to initiate controlled ignition of the rubbelized shale. Combustion using this external fuel continued until the rubbelized shale itself was ignited, after which external fuel additions were discontinued and combustion air continued to be provided to the void to sustain and control combustion of the shale. The resulting heat expanded downward into the surrounding formation, heating and retorting the kerogen. Retort products collected at the bottom of the retort void and were then recovered from conventional oil and gas wells installed adjacent to the void. Careful control of combustion air or fuel mixtures was the primary control over the rate of combustion occurring in the heavily instrumented and monitored void. Once recovery of retorted oil shale products equilibrated, a portion of the hydrocarbon gases was recycled back into the void to be used as fuel to sustain in situ combustion. Two separate retorts were constructed and operated during Phase II of the project, with the last two retorts shutting down in February 1983. Ultimately, oil recovery was equivalent to 70% of the yield predicted through Fisher assay. Design of the experiment was directed toward potential future commercial applications so that numerous such in situ retorts were operated simultaneously to demonstrate the practicability of an approach that would likely have been desirable in commercial development ventures. Differences in approaches among modified in situ technologies center on the manner in which formation voids are formed, the shape and orientation of such voids (horizontal vs. vertical), and the actual retorting and product recovery techniques used. Retorting techniques can include controlled combustion of rubbelized shale or formation heating by alternative means such as the introduction of electromagnetic energy. Product recovery techniques have included steam leaching, chemically assisted or solvent leaching, and displacement by high-pressure gas or water injection. Some of these formation sweeping techniques can also be seen as aiding or promoting additional refining of the initial retorting products. [15]

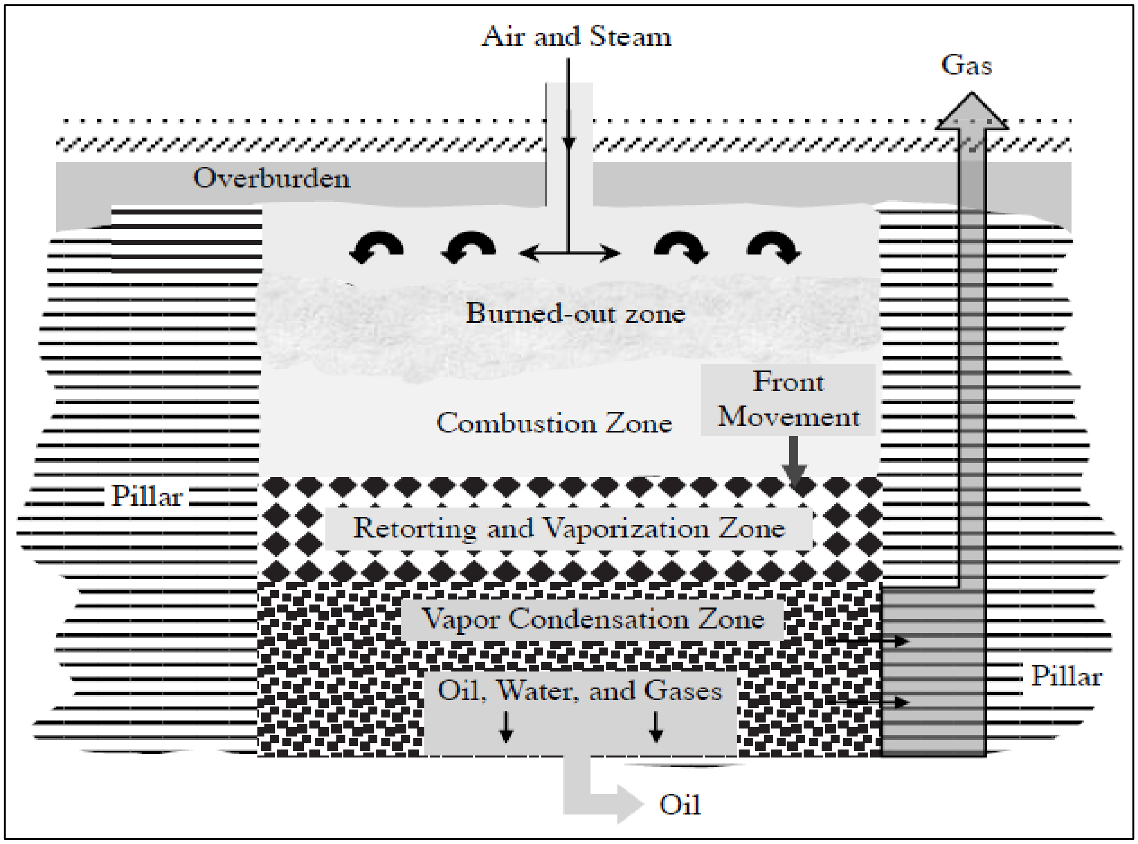


Figure 4. 3. A modified in situ retort of Occidental Petroleum.

4.2.4. LETC Process (LERC Process)

Laramie Energy Technology Center (LETC), currently Western Research Institute, has been sponsoring several field projects to demonstrate the technical and economic feasibility of shale oil recovery by *in situ* technology. LETC initiated their study on *in situ* retorting in the early 1960s with laboratory tests, simulated pilot plant tests on 10-ton and 150-ton retorts, and field tests at Rock Spring, WY. The test results demonstrated that it was possible to move a self-sustaining combustion zone through an oil shale formation and to produce shale oil. The underground shale bed is prepared for the LETC process by first boring injection and production wells into the shale, and then increasing the permeability of formation by conventional fracturing techniques. Based on the LETC tests, the sequential use of hydraulic fracturing and explosives worked best. Once the formation is fractured, hot gases are forced into it to heat the area surrounding the injection point. As the desired temperature is reached and air is substituted for the hot gas, combustion begins and becomes self-sustaining across a front that gradually moves through the bed. As retorting progresses, oil and gas products are pumped out through the predrilled production wells. A schematic for the LETC process is shown in (Figure 4.4). [15]

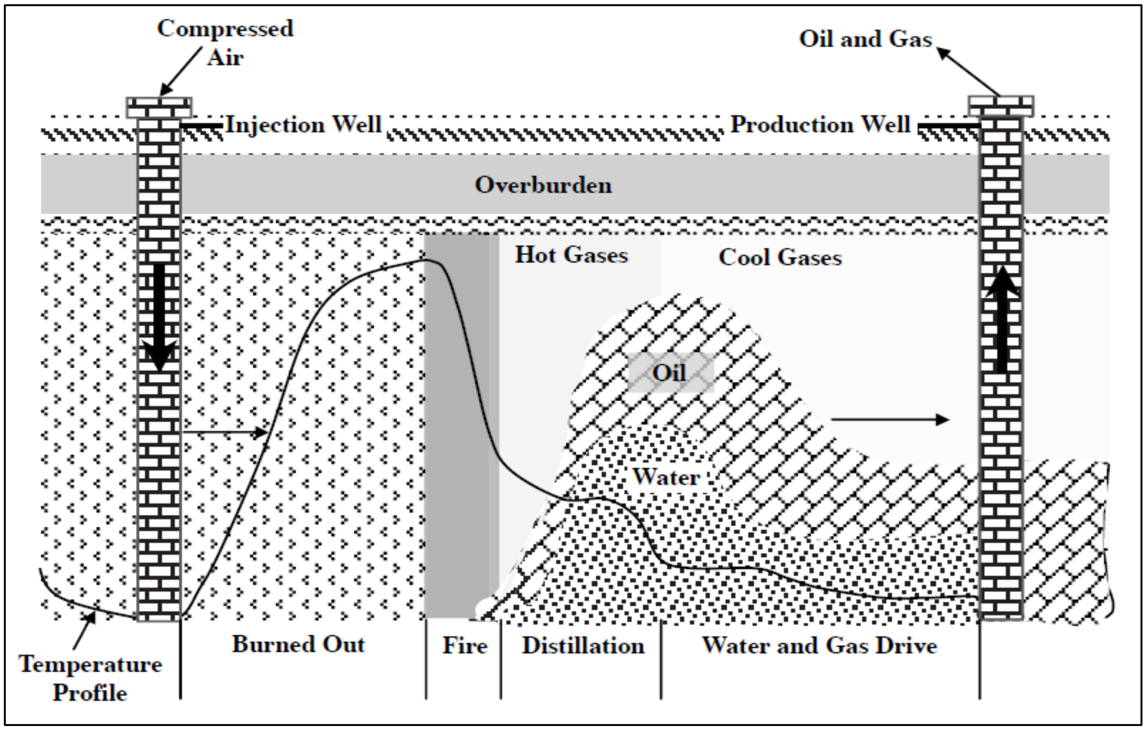


Figure 4. 4. The Laramie Energy Technology Center (LETC) in situ retorting process).

4.2.5. Dow Chemical Co.'s Process

The Dow Chemical Co., under contract with the U.S. DOE, conducted a 4-year research program to test the feasibility of deep *in situ* recovery of low-heat content gas from Michigan Antrim Shale. The Antrim shale is part of the eastern and Midwestern oil shale deposits, formed some 260 million years ago during the Devonian and Mississippian ages. These oil shales underlie an area of 400,000 mi^2 ($l.07 \times 10^{12}$). In Michigan, the oil shale is approximately 61 m thick and is in a basin at depths ranging from about 0.8 km to outcroppings in three northern counties. The Michigan Antrim shale is believed to contain an equivalent hydrocarbon volume of 2,500 bbl barrels. Even applying a 10% recovery factor, this resource is about 9 times the amount of the U.S. proven oil reserves. Extensive fracturing (rubblizing) of the oil shale is considered essential for adequate *in situ* retorting and recovery of energy from the Antrim shale. Two wells were explosively fractured using 19,000 kg of metalized ammonium nitrate slurry. Their test facility was located 75 mi north east of Detroit, MI, over 1 acre of field. The process used was TIS retorting. Combustion of the shale was started using a 440-V electric heater (52 kW) and a propane burner (250,000 Btu/h). The special features of this process include shale gasification and tolerance to severe operating conditions. Their tests also showed that explosive fracturing in mechanically under reamed wells did not produce extensive rubblization. They also tested hydro fracturing, chemical under reaming, and explosive under reaming. [15]

4.2.6. Osborne's *in Situ* Process

This process was developed by Osborne in 1983; a U.S. patent describing the process has been assigned to Synfuel (an Indiana limited partnership). The process is unique, and enhanced oil recovery is achieved by forming generally horizontal electrodes from the injection of molten metal into preheated or unheated fractures of formation. A nonconductive spacing material is positioned in the casing of the borehole between the electrodes. A fracture horizontally intermediate between the metallic electrodes is propped up with a nonconductive granular material. Unterminated standing waves from a radio frequency (RF) generator are passed between the electrodes to heat the oil shale formation. The hydrocarbons in the formation are vaporized and recovered at the surface by their transport through the intermediate fracture and tubing. By this method, radial metallic electrodes can be formed at various depths throughout a subterranean oil shale formation to devolatilize the hydrocarbons contained within the oil shale formation. One advantage of this process is in the uniform heating of the rock formation that can be achieved by using RF electrical energy that corresponds to the dielectric absorption characteristics of the rock formation. An example of such techniques is described in U.S. Patent numbers 4,140,180 and 4,144,935, in which many verticals conductors are inserted into the rock formation and bound to a particular volume of the formation. A frequency of electrical excitation is selected to attain a relatively uniform heating of the rock formation. The energy efficiency of the process is very good; however, the economics of the process strongly depends on the cost of the electrodes and RF generation. The other merits of the process include the relative ease of controlling the retort size. The difficulty, however, with this process is in the necessity of implanting an electrode within the subterranean rock formation at a precise distance. A schematic of this process is shown in (Figure 4.5). [15]

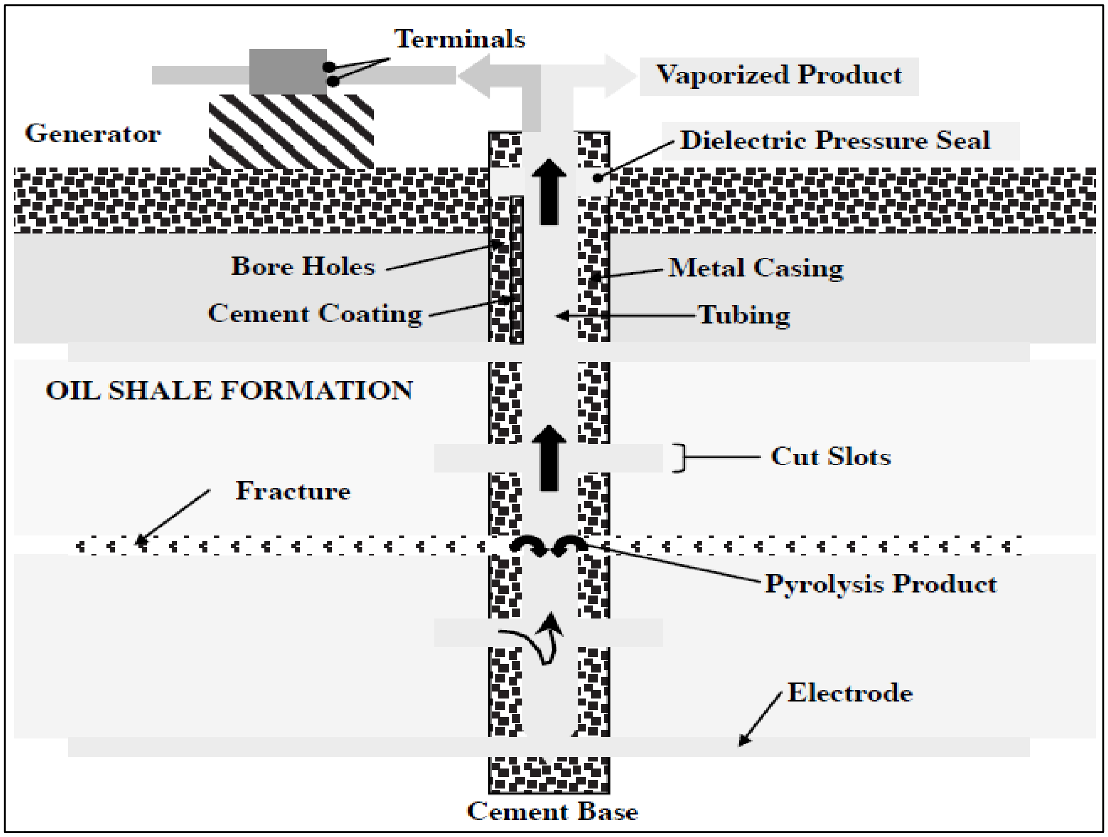


Figure 4. 5. A vertical sectional view of a borehole penetrating a subterranean oil shale formation in completed condition for the recovery of hydrocarbons from oil shale

4.2.7. Shell Oil's Thermally Conductive *In Situ* Conversion Process

Shell Oil is currently developing an *in situ* retorting process known as *thermally conductive in situ conversion.* This process involves *in situ* heating of underground oil shale using electric heaters placed in deep vertical holes drilled through a section of oil shale. The entire volume of oil shale is heated over a period of 2 to 3 years until it reaches 650 to 700°F, at which point oil is released from the shale. The released product is gathered in collection wells positioned within the heated zone. Shell's current plan also involves use of ground-freezing technology to establish an underground barrier called a *freeze wall* around the perimeter of the extraction zone. The freeze wall is created by pumping refrigerated fluid through a series of wells drilled around the extraction zone. The freeze wall prevents groundwater from entering the extraction zone, and keeps hydrocarbons and other products generated by the *in situ* retorting from leaving the project perimeter and contaminating the surrounding soil. In 1997, Shell Oil successfully conducted small-scale field tests of this novel *in situ* process based on slow underground heating via thermal conduction, on Mahogany property. After deferring further tests because of economic reasons, Shell returned to Mahogany for further tests in 2000, and the R & D program is currently in operation. Larger-scale operations need to be conducted to establish technical viability, especially with regard to eliminating or alleviating any adverse impacts on groundwater quality. The process has a number of merits that can contribute to lowering the processing cost of oil shale, as well as toward environmentally benign processing of this vast energy resource. The Shell Oil process is technologically classified as one of the TIS retorting processes, as there is no mining of shale involved. [15]

4.2.8. ExxonMobil Electrofrac Process

ExxonMobil's Electrofrac Process uses a method of heating oil shale in situ based on established principles of oil and gas well horizontal drilling and hydraulic fracturing. The proppant used in fracturing is highly electrically conductive and is a means of extending heat beyond the borehole and into the fractures. The proppant creates an electrically conductive pathway along the length of the fracture system, turning it into a large, plate-like electrode. ExxonMobil has conducted a 100-feet scale test (which it calls “The Giant Toaster”) at its Colony Mine near Parachute, Colorado. The process uses a series of hydraulic fractures created in the oil shale formation. The fractures should be preferably longitudinal vertical fractures created from horizontal wells and should conduct electricity from the heel to the toe of each heating well. For conductibility, an electrically conductive material such as calcined petroleum coke is injected into the wells through fractures, forming a heating element. Heating wells are placed in a parallel row with a second horizontal well intersecting them at their toe. This allows opposing electrical charges to be applied at either end. Planar heaters require fewer wells than wellbore heaters and offer a reduced surface footprint. The shale oil is extracted by separate dedicated production wells (Plunkett, 2008; Symington et al., 2006, 2008; US DOE, 2007) (Figure 4.6). [8]

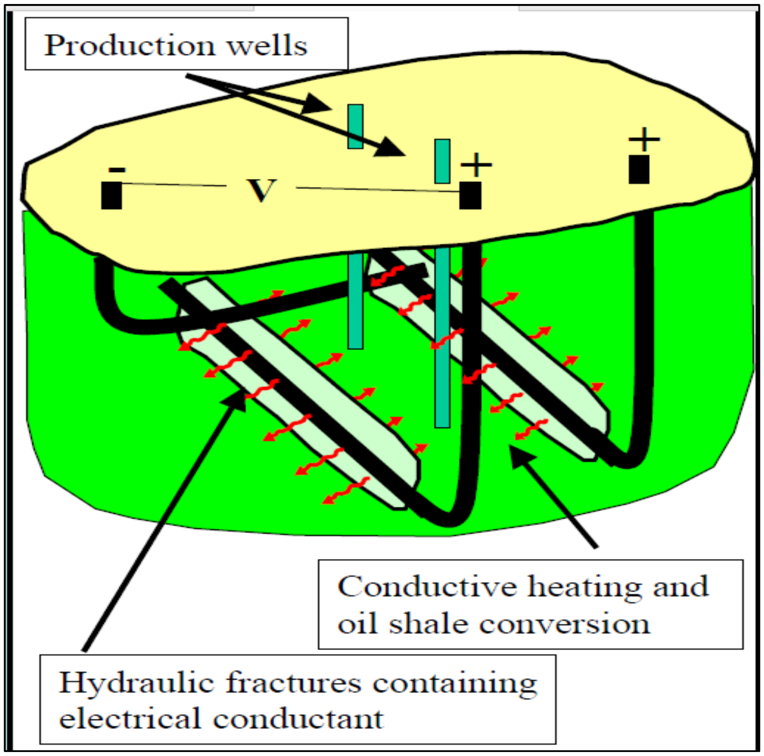


Figure 4. 6. ExxonMobil Electrofrac technology

4.3. ESTIMATING OF OIL IN PLACE IN THE SHALE FORMATION(MADBI)

Table 4. 1.Geological Data

Parameters	Madbi Formation
K	***0.0003 – 3.4 md***
Area	***5.573 × 10^6 acres***
Avg. Thickness	***200 m***
Φ	***5%***
S_w	***40%***
Depth	***480-2800 m***
API Gravity	***42-50 API***
P_r	***7435 psia***

First Methodology of Estimating (OIP) For The Madbi Formation

The specifics of shale formations saturated with liquid hydrocarbons make it possible to undertake the task of oil-in-place assessment taking advantage of direct geochemical measurements of hydrocarbons contained in rock samples collected from liquid-rich shale interval. An advantage of the oil resource assessment method based on geochemical data results from the fact that it does not require the availability of porosity and fluid saturation data which are not always available. It applies mainly to fluid (oil) saturation information, usually resulting from well log data interpretation, which could be ambiguous in the case of shale formations.

Available laboratory methods to assess the amount of liquid hydrocarbons present in rock samples include:

(i) the extraction of hydrocarbons contained in the sample (EOM extractable organic matter) by leaching them using organic solvents and determination of extract amount after solvent evaporation at the temperature of 60°C; the EOM measures C_{12+} components, including nonvolatile hydrocarbons.
(ii) pyrolytic analysis (Rock Eval) of shale rock samples an assessment of liquid hydrocarbons is based on S_1 parameter expressing the weight of free hydrocarbons contained in rock sample (mg HC/g rock) which are released in a pyrolytic oven at temperatures of up to 300°C; S_1 parameter measures volatile hydrocarbons in the C_5-C_{25} carbon number range.

The Rock Eval pyrolysis and S_1 parameter determination is much more convenient than solvent extraction, since it is a fast and straightforward method which can be introduced early in the exploration process. It can easily be scaled up to reflect oil-in-place potential for a given shale formation thickness. In this study, we considered Rock Eval S_1 data as the primary measurement type for oil-in-place estimation methodology being adopted, and solvent extraction procedures were used for the elaboration of one of the correction coefficients. The calculation procedure of oil resources based on Rock Eval S_1 data for shale formation of a specified volume originates from the following formula:

$$\text{Oil content} = \frac{Vo}{Vr} = \frac{S1 * \rho r}{\rho o}$$

where Oil content is expressed in ($m^3$of oil/$m^3$of rock); Vo is the volume of oil (m^3); Vr is the volume of rock (m^3); S_1 is the oil content (mg HC/g of rock) present in rock volume determined with Rock Eval measurement; ρr is rock density (kg/m^3); and ρo is oil density (kg/m^3).

To employ this formula for oil-in-place estimation, it is necessary to address those amounts of liquid hydrocarbons which are not recorded in S_1 values. As mentioned above, the underestimation of hydrocarbons presents in rock sample with S_1 parameter (compared to in situ conditions) results from,

(i) the evaporation of the lightest compounds of crude oil published data refers to the loss of up to C_{15} compounds: however, partial evaporation of C_{12}-C_{15} compounds is observed (Figure 4.7). The loss of lighter hydrocarbons is a consequence of rock samples handling in the RE laboratory procedure, which requires, among others, its grinding.

(ii) temperature conditions while S_1 peak is recorded, which is up to 300°C; hydrocarbons released in a pyrolytic oven in a higher temperatures are not included in S_1; however, they represent a fraction of S_2 peak of Rock Eval pyrogram.

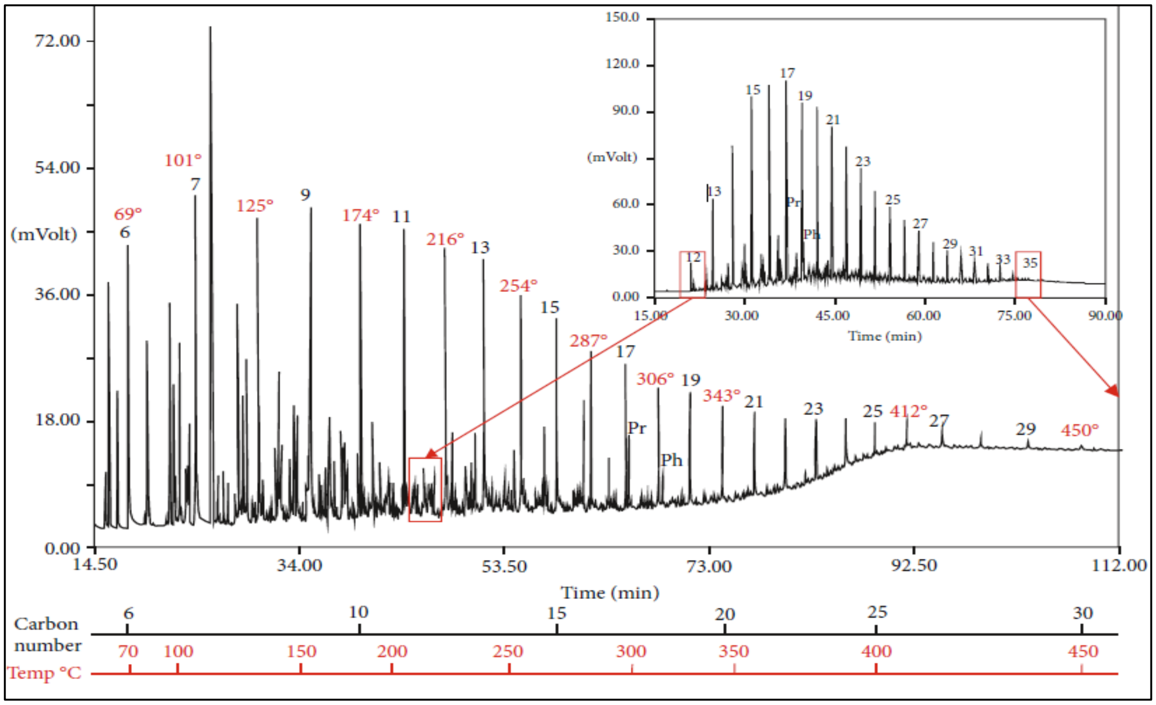


Figure 4. 7. Exemplary chromatogram of Sabatayn Basin crude oil sample; blue shadow indicates hydrocarbons lost during saturated fraction separation; right upper corner chromatogram of saturated fraction. It was assumed that the amount of hydrocarbons lost.

In the methodology we used, those sources of inaccuracies in oil-in-place estimation (if carried out only on the basis of S_1 values directly) are facilitated by the introduction of appropriate correction coefficients: c_1 correction coefficient for loss of C_{15} compounds which is dependent on oil API gravity and shale rock maturity level, c_2 correction coefficient for underestimation of heavier compounds which are included in S_2 peak (fraction of S_2), but through the introduction of c_2 coefficient they are expressed as a fraction of S_1 values. The scale of correction needed which would compensate for the lightest compound loss due to evaporation process (c_1 value) was approximated on the basis of published data, which relates liquid hydrocarbon loss due to evaporation as a function of crude oil API gravity and time of its exposure (Figure 4.8 below). The estimation of oil-in-place reserves taking into account evaporation loss can be expressed by the introduction of the c_1 coefficient, according to the formula:

$$\mathrm{OIIP}_{\mathrm{Free}} = \frac{V_r * \rho_r * S1 * c1}{\rho_o} * 10^{-3}$$

where $\mathrm{OIIP}_{\mathrm{Free}}$ is oil resources (m^3) calculated for given shale rock volume, which approximate “free”/“mobile” oil, S_1 is the oil content (mg HC/g of rock) present in rock samples determined with Rock Eval pyrolysis method, Vr is the volume of rock (m^3), ρr is the rock density (kg/m^3), ρo is the oil density (kg/m^3), and c_1 is the correction coefficient for loss of C_{15} dependent on oil API gravity and maturity level. Oil-in-place resources calculated in that way include hydrocarbons measured in Rock Eval analysis and expressed in S_1 values, together with lighter oil compounds lost due to the evaporation process. Generally, this amount would presumably represent “free” or “mobile” oil.

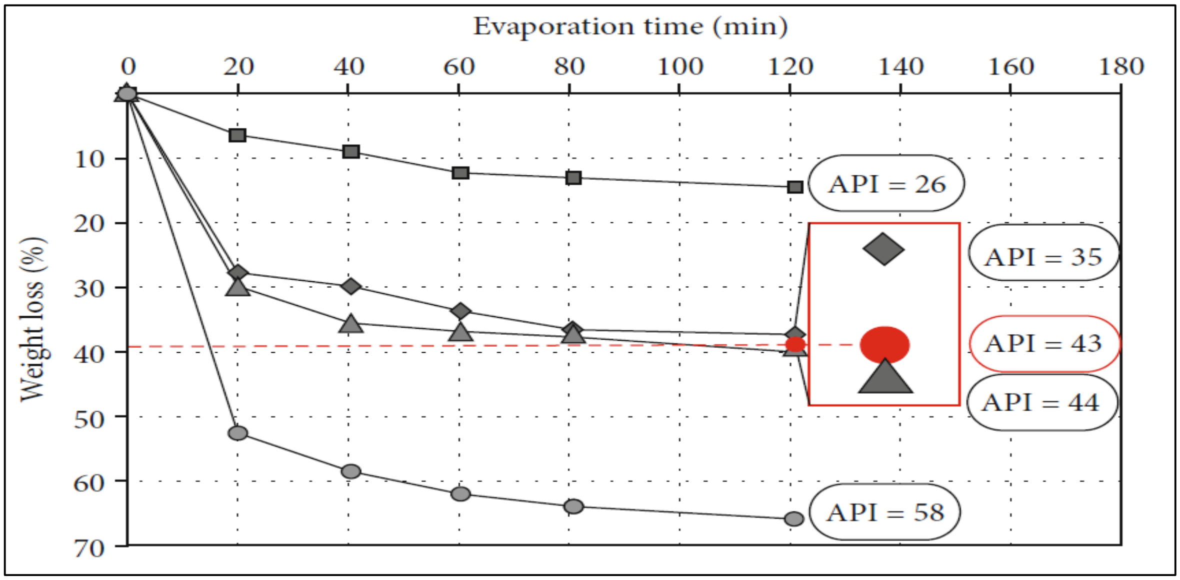


Figure 4. 8. Loss of lighter hydrocarbons of crude oil due to evaporation process vs. oil API gravity and time after Noble et al. 1997. in a red rectangle crude oils collected in the study area and its vicinity are presented with the average API = 43.

The implementation of the abovementioned correction leads to the formula for heavier liquid hydrocarbons resources calculation:

$$\mathrm{OIIP}_{\mathrm{Immobile}} = \frac{Vr * \rho r * S2}{\rho o}$$

where $\mathrm{OIIP}_{\mathrm{Immobile}}$ is the oil resources (m3) of heavier fraction of liquid hydrocarbons compounds calculated for given shale rock volume. The calculation formulas presented above produces an assessment of heavier fractions of liquid hydrocarbons in place (nC_{25}). Thus, the calculation formula could be rewritten into the following form, in which only $S1$ and $c2$ values are sufficient:

$$\text{OIIP}_{\text{Immobile}} = \frac{V_r * \rho_r * S1 * c2}{\rho_o}$$

where $\text{OIIP}_{\text{Immobile}}$ is the oil resources represented by heavier fractions (m^3) calculated for given shale rock volume; V_r is the volume of rock (m^3); ρ_r is the rock density (g/cm^3), $S1$ is the oil content (mg HC/g of rock) present in rock samples determined with the Rock Eval pyrolysis method; ρ_o is the oil density (g/cm^3); and $c2$ is the correction coefficient for C_{25+} oil compounds (part of $S2$ parameter). Consequently, total oil-in-place calculation, including lighter (C_5-C_{25}) and heavier (C_{25}-C_{35}) compounds of oil can be received as a sum of “free” and “immobile” liquid hydrocarbons: [7]

$$\text{OIIP}_{\text{Total}} = \text{OIIP}_{\text{Free}} + \text{OIIP}_{\text{Immobile}}$$

$$\text{OIIP}_{\text{Total}} = \frac{Vr * \rho r * S1 * c1}{\rho o} + \frac{Vr * \rho r * S1 * c2}{\rho o}$$

$$= \frac{Vr * \rho r * S1 * (c1 + c2)}{\rho o}$$

Second Methodology of Estimating (OIP) For The Madbi Formation

The second methodology focuses on the application of hydrocarbon distillation from Rock-Eval that requires rock samples, preferably whole core, properly collected. It determines volumes of distillable hydrocarbons in the rock in mg of hydrocarbon/g of dry rock by taking the average values of S1 for “free” oil and average values of S2 for “immobile” oil. Then up-scale oil-in-place to acre-feet or section-feet (i.e. one square mile of surface area × one thick foot × hydrocarbon richness), the resulting volume from core measurements is a minimum value for the oil-in-place volume. These calculations can be estimated by using the following equations:

Step 1: *grams of oil per section*

$$M_{S1HC} = \frac{Ah(\rho AV)(S1AV)(0.001)}{8.11\times10^{-10}}\ acre\text{-}ft/cm^{3}$$

Where M_{S1HC} mass of S1 hydrocarbons per section (g); A area of interest in acres (sectional area –640 acres); h reservoir height *(ft);* ρAv average bulk density *(g/cm³); S1Av* average S1 *(mg/g).*

Step 2: volume of oil per section (cm³)

$$V_{S1HC} = M_{S1HC} \times \rho_{oil}$$

Where V_{S1HC} Volume of S1 hydrocarbons per section *(cm³);* M_{S1HC} Mass of S1 hydrocarbons per section *(g);* ρ_{oil} Density of oil *(g/cm³).*

Step 3: *Barrels of oil per section*

$$Oil\ in\ Place\ per\ section\ (bbl) = V_{S1HC} \times 6.29 \times 10^{-6}\ \ bbl/cm^{3}$$

<u>Simplifies equation</u>

$$Oil\ in\ Place\ per\ 640\ acre/ft = 4965.36 \times (\rho_{Av})\ (S1_{Av})\ (\rho_{oil})$$

With assuming $\rho_{Av} = 2.5$ *(g/cm³),* $\rho_{oil} = 7.788$ *(g/cm³), and API Gravity = 50 API. The equation would be as follows:*

Simplifies equation

$$Oil\ in\ Place\ per\ 640\ acre/ft = 9677.48 \times (S1_{Av})$$

Where $S1_{av}$ is the average value in (mg/g) that established from Rock-Eval Pyrolysis, with assuming 2.5 g/cm^3 bulk density and 50^o API gravity.

These two methods are used to calculate the Oil-in-Place of the shale formations, and in our study, we used the second method because for several reasons, including the lack of sufficient data, also there are no similar studies such ours in our country and therefore we did not find some data for some necessary tests to determine some variables to use other methods. [13]

Table 4. 2.Calculation of oil in place for Madbi formation in Sabatayn basin for a random wells in block (18,3,S2,7). [18]

Name	Depths (m)	TOC Wt%	S1 (mg/g)	S2 (mg/g)	M_{S1HC} (g)	V_{S1HC} (cm^3)	OIL Per Section (bbl/cm^3)	Oil in place (bbl)	Free OIP in the sections(bbl)	S2/S1
GHAMDAN-1 Well	457.2	6.11	2.3	30.31						
block 18	472.4	12.9	6.12	69.5						
	518.2	20.2	19.6	143.4						
	640.1	11.6	14.26	62.98						
	701	15.2	21.91	85.71						
	762	12.8	14.24	61.66						
	868.7	11.4	10.56	70.85						
	883.9	11.2	7.09	63.03						
	1127.8	15.7	14.24	78.78						
	1153.4	8.2	7.2	36.01						
	1188.7	8.32	12.31	45.45						
	1209.4	3.02	3.04	12.66						
	1260	1.59	0.78	5.1						
	1310.6	2.57	1.72	12.13						
	1356.4	2.97	3.29	16.71						
	1371.6	1.93	1.32	7.05						
	1463	2083	1.96	12.29						
	1478.3	3.01	1.18	11.4						
	1493.5	2.85	2.81	13.5						
	1539.2	6.43	2.42	20.6						
	1569.7	4.42	4.24	23.9						
	1615.4	3.35	3.31	21.2						
	1630.7	5.96	6.21	36.39						
	1645.9	5.28	3.08	22.8						

	1661.2	7.06	5.68	30.81						
	1663	5.76	5.56	36.5						
	1676.4	7.56	5.33	31.43						
	1767.9	8.12	9.95	61.77						
	1767.8	10.6	11.12	65.33						
	1783.1	9.17	3.4	35.38						
	1798.3	8.48	5.94	42.81						
	1836.7	8.91	9.53	58.72						
AVERAGE VALUES		72.6772	6.928125	41.4425	3.57973×10^{-7}	4.43585×10^{-6}	2.79015×10^{-11}	67046.79	219493762	5.981777
IMMOBILE OIP IN THE SECTIONS(BBL)	1312962776 bbl									
Well Name	Depth	TOC Wt%	S1	S2						
MAEEN-1 Well	894.6	45.1	33.88	387.4						
	897.3	26	19.36	206.8						
	1214.6	22.5	15.68	215						
	1240.5	27.2	18.09	143.1						
	1315.2	5.74	3.61	38.02						
	1583.4	4.17	0.86	24.18						
	1588	1.35	0.35	4.36						
	1594.1	1.98	0.48	7.09						
	1641.3	5.24	1.76	25.74						
AVERAGE VALUES		15.4756	10.45222	116.8544	4.72553×10^{-7}	5.85568×10^{-5}	3.68322×10^{-10}	101151.2	331067784.4	11.17987
IMMOBILE OIP IN THE SECTIONS(BBL)	1312962776									

Name	Depth	TOC Wt%	S1 (mg/g)	S2 (mg/g)	M_{S1HC}	V_{S1HC}	OIL Per Section (bbl/cm^3)	OIL (bbl)	Free OIP in the sections(bbl)	S2/S1
Block 3 (GARDAN)	2506	1	0.3	2.26						
Misah-1	2534	1.2	0.5	2.62						
	2546	2	0.89	4.21						
	2554	2.1	0.9	4.92						
	2566	1.7	0.62	4.12						
	2574	2.4	0.72	6						
	2586	2	0.69	5						
	2594	2.1	0.59	5.92						
	2606	2.75	0.89	8.4						
	2613	2.7	0.75	8.89						
	2621	3.6	0.8	12.72						
	2628	2.4	0.65	8.67						
	2640	3.2	1.1	12.8						
	2651	2.9	1.5	12.31						
	2659	2.1	0.8	8.58						
	2670	2.7	0.7	11.25						
	2677	3.3	1.6	13.49						
	2689	4.5	2.1	17.68						
	2696	4.9	2.3	18.47						
	2708	3.2	1	11.84						
AVERAGE VALUES		2.6375	0.97	9.0075	4.40296×10^{-6}	5.65352×10^{-7}	3.55606×10^{-12}	9387.156	10691876.36	9.286082
IMMOBILE OIP IN THE SECTIONS(BBL)	99285645.65									
Bin Haydar-1	2571	1.3	2.7	4.58						
	2587	3.1	1.8	12.3						
	2597	1.2	0.8	3.69						
	2680	1.6	1.1	7.57						
	2618	2.8	1.7	10.58						
	2623	3.9	2.4	14.46						
	2633	7.4	4.7	28.42						
	2644	2.3	1.4	7.37						
	2659	5	3.8	23.2						
	2664	8.1	5	35.75						
	2674	3.4	1.9	13.92						
	2680	6.8	4.5	23.96						
	2685	5.5	5	23.57						
	2695	3.9	5	17.21						
	2710	3.4	2.5	13.49						
	2721	2.6	3.6	10.8						
	2726	5.2	2.4	20.97						
	2731	4.3	2.3	14.88						
	2751	3.7	1.9	13.98						
	2756	3.3	1.3	9.95						
	2772	2.4	0.9	5.61						
	2787	2.3	0.8	4.79						
	2838	1.3	0.6	3.47						

	2848	1.9	0.7	4.14						
	2858	2.4	1.3	5.46						
	2868	6.5	3.7	8.61						
	2883	1.3	1.8	3.6						
	2893	2.4	2.2	4.51						
	2903	1.9	1.5	4.26						
AVERAGE VALUES		3.489655	2.389655	12.24483	1.72907 × 10^{-5}	2.22017 × 10^{-6}	1.396 × 10^{-11}	23125.84	26317206.08	5.124098
IMMOBILE OIP IN THE SECTIONS(BBL)	134851946.3									
Block S2(AL-Uqla)										
West Riyam-1	1844	11.3	9.25	43.52						
	1853	7.46	3.39	25.06						
	1868	9.36	2.81	35.55						
	1878	9.95	2.97	46.29						
	1905	1.24	0.45	2.79						
	1914	6.83	3.04	30.73						
	1923	4.02	1.68	14.36						
	1932	2.04	0.64	5.05						
	1942	3.44	0.91	11.63						
	1951	4.38	1.57	13.15						
	1960	10.5	4.59	40.12						
	1969	1.45	9.81	44.61						
	1981	7.32	4.36	30.2						
	1990	5.38	2.88	15.19						
	1999	5.11	2.07	15.42						
	2009	6.32	3.25	23.83						
	2018	7.09	4.5	29						
	2027	4.06	1.74	13.45						
	2039	9.3	6.02	40.54						
	2045	5.97	3.4	27.02						
	2054	3.68	2.13	13.26						
	2063	3.56	2.3	11.33						
	2073	4.28	2.13	13.02						
	2082	2.66	1.45	7.78						
	2091	2.49	1.49	5.74						
	2100	2.3	1.37	5.25						
	2131	3.08	1.39	7.71						
AVERAGE VALUES		5.354444	3.021852	21.17037	5.97205 × 10^{-6}	7.66827 ×10^{-7}	4.82334 × 10^{-12}	29243.91	10206124.89	7.005761
IMMOBILE OIP IN THE SECTIONS(BBL)	71501666.71									
Al-Uqla-7	2534	3.87	2.13	9.7						
	2556	3.76	2.1	9.13						
	2570	3.3	1.56	7.43						
AVERAGE VALUES		3.643333	1.93	8.753333	4.27938 × 10^{-6}	5.49484 ×10^{-7}	3.45626 × 10^{-12}	18677.54	6518460.204	4.535406
IMMOBILE OIP IN THE SECTIONS(BBL)	29563862.69									

Block 7 (SHABWAH)										
Shabwah-02	2443	6.46	3.24	21.83						
	2529	10.44	6.96	70.89						
	2658	4.43	4.61	14.53						
AVERAGE VALUES		7.11	4.936667	35.75	5.33033×10^{-5}	6.84429×10^{-6}	4.30506×10^{-11}	47774.49	91058183.53	7.241729
IMMOBILE OIP IN THE SECTIONS(BBL)	659418648.5									
Total OIP in these mentioned blocks (bbl)		2.48×10^9								

4.4. THE GREEN RIVER FORMATION

The largest known oil shale deposits in the world are in the Green River Formation, which covers portions of Colorado, Utah, and Wyoming. These deposits were formed over millions of years during which two large lakes covered the area. (Figure 4.9) shows the location of the formation and its major oil shale–bearing basins: The Piceance, Uinta, Green River, and Washakie. The oil shale in these basins is a sedimentary rock known as marlstone and consists primarily of carbonate and silicate minerals. Estimates of the oil resource in place within the Green River Formation range from 1.5 trillion (Smith, 1980; Dyni, 2003) to 1.8 trillion barrels (Culburtson and Pitman, 1973; Federal Energy Administration, 1974).2 About 1 trillion barrels (Smith, 1980; Pitman, Pierce, and Grundy, 1989) are located within the Piceance Basin, meaning that this 1,200 square mile area in western Colorado holds as much oil as the entire world's proven oil reserves (*BP Statistical Review*, 2005). Within the Piceance Basin, about a half trillion barrels of oil are contained in deposits yielding more than 25 gallons per ton (Dyni, 2003). Most of the oil shale is contained in deposits more than 500 feet in thickness and located beneath 500 or more feet of sedimentary rock, although in some cases the deposits are more than 2,000 feet in thickness and covered by more than 1,000 feet of overburden (Donnell, 1987). The potential yield per surface acre is enormous, with portions of the basin yielding more than 2.5 million barrels per acre (Smith, 1980; Donnell, 1987). This is well beyond the areal concentration of any known oil reserves. Worldwide, the closest we get to this energy yield are the hundred-foot thick coal seams in Campbell County, Wyoming, which yield the oil equivalent of less than 0.5 million barrels per acre.

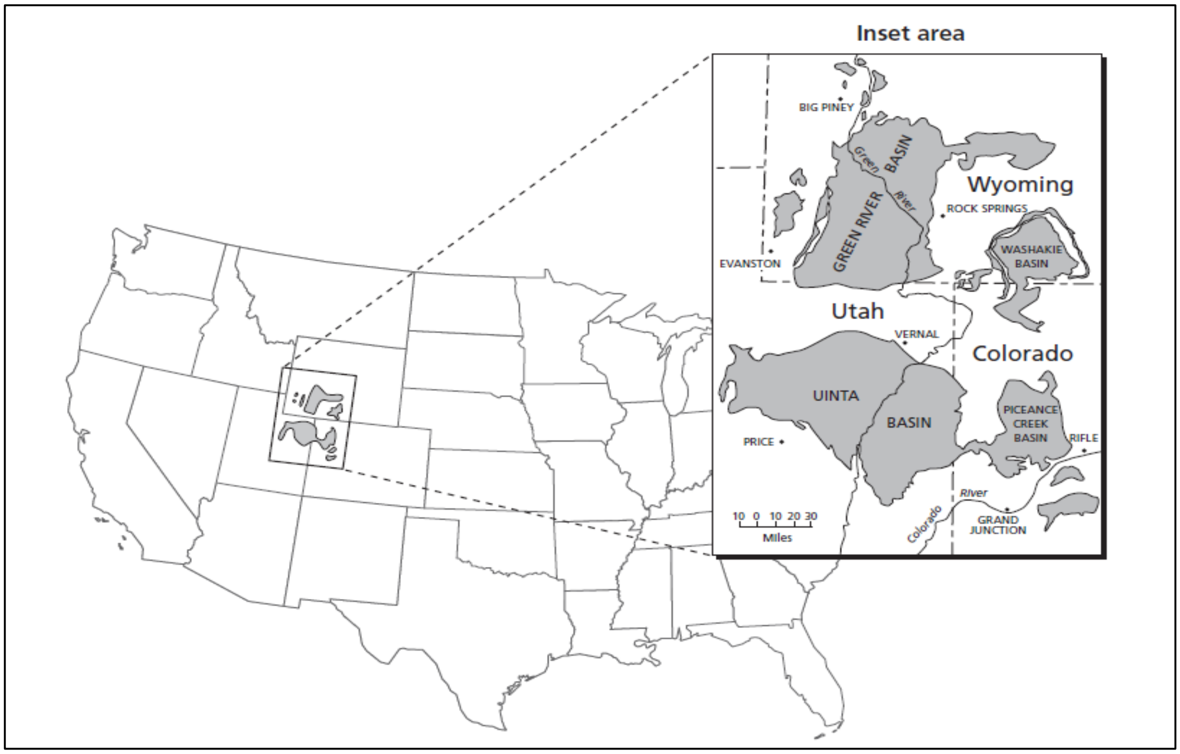


Figure 4. 9. Location of the Green River Formation Oil Shale and Its Main Basins

Less is known about shale resources in place in Utah and Wyoming. Several widely varying estimates for the Uinta Basin in Utah have been published, including 56 billion barrels (Dyni, 2003), 165 billion barrels (Smith, 1980), 214 billion barrels (Trudell et al., 1983), and 321 billion barrels (Cashion, 1964). While smaller than the Colorado resource base, much of the high-grade oil shale in Utah is close to the surface and in seams of appreciable thickness. When commercial oil shale operations begin, operations are likely in both Utah and

Colorado. The deposits in Wyoming are appreciable. The Green River Basin is estimated to contain 250 billion barrels (Culbertson, Smith, and Trudell, 1980) and the Washakie Basin 50 billion barrels (Trudell, Roehler, and Smith, 1973), giving a total of 300 billion barrels. About 14 billion barrels of this are in oil shale deposits holding more than 30 gallons per ton (Dyni, 2003). In general, the rich Wyoming deposits are situated in thinner, less continuous layers and represent a less favorable development target, compared with the Colorado and Utah deposits (Smith, 1980). [10]

4.4.1. Recoverable Resources in the Green River Formation

Not all resources in place are recoverable. Some fraction of the in-place oil shale will not be accessed because it lies under land that is off-limits to mining or other extraction methods. Off-limit lands would include those under towns, but since the area is sparsely populated, the primary reasons for setting land aside will be ecological and environmental considerations. Assuming that low environmental impact extraction methods can be developed over the next hundred or so years, a rough upper bound for the accessible portion of the resource base is 80 percent. At best, about 75 percent of the accessible resource can be extracted and converted to useful fuels, yielding an upper bound of 60 percent (0.8 × 0.75) for the net recovery factor. Applying this net recovery factor to estimated resources in place of 1.5 to 1.8 trillion barrels yields an upper bound of between 900 billion and 1.1 trillion barrels of oil. The same method can be used to develop a rough estimate of the lower bound of recoverable resources. Assuming that at least 60 percent of the resource base can be accessed and at least 50 percent of the accessible resources can be extracted and converted to useful fuels, we obtain a lower bound of roughly 500 billion barrels. Whether the actual amount is 1.1 trillion barrels or 500 billion does not matter for policy deliberations over the foreseeable future. Any number in this range is very large. For example, the midpoint of this range is 800 billion barrels of recoverable oil. To better grasp the magnitude of this midpoint estimate, consider that current U.S. demand for petroleum products is 20 million barrels per day. If U.S. oil shale resources could be used to meet a quarter of that demand, 5 million barrels per day, the recoverable resource would last over 400 years. In the face of such a long recovery period, it is appropriate to recognize the futility of trying to develop accurate estimates of recoverable resources. How and how much oil shale is eventually developed depends less on today's technologies than on the performance of technologies available a hundred or more years hence. [10]

4.4.2. Thermally Conductive In-Situ Conversion

Technical Viability and Commercial Readiness

Shell has tested its in-situ process on the Green River formation. Shell's private holdings in the Piceance Basin. The energy yield of the extracted liquid and gas is equal to that predicted by the standardized assay test. The heating energy required for this process equals about one-sixth of the energy value of the extracted product. These tests have indicated that the process may be technically and economically viable. This approach requires no subsurface mining and thus may be capable of achieving high resource recovery in the deepest and thickest portions of the U.S. oil shale resource. Most important, the Shell in-situ process can be implemented without the massive disturbance to land that would be caused by the only other method capable of high energy/resource recovery namely, deep surface mining combined with surface retorting. The footprint of this approach is exceptionally small. When applied to the thickest oil shale deposits of the Piceance Basin, drilling in about 150 acres per year could support sustained production of a half-million barrels of oil per day and 500 billion cubic feet per year of natural gas. Shell reports that it has spent tens of millions of dollars in developing its in-situ conversion technology. Its current plan is to gain access to a small tract of federal land for a precommercial demonstration operation that would produce about 1,000 barrels per day. Shell's estimate of the costs for this demonstration is between $150 million and $200 million. Other petroleum companies appear to be evaluating thermally conductive in-situ retorting concepts, although none has publicly announced ongoing efforts, if any.

Scientists from the DOE have reviewed the Shell in-situ process and report that the technology is very promising. Confirmation of the technical feasibility of the concept hinges on the resolution of two major technical issues: controlling groundwater during production and preventing subsurface environmental problems. Shell plans to use ground-freezing technology to control groundwater during production. Ground-freezing technology is a well-established method for controlling groundwater during construction and mining operations. Multi-kilometer barriers have been constructed and sustained for years. Nonetheless, applying ground-freezing to in-situ conversion of oil shale requires resolving significant technical uncertainties to ensure that the frozen barrier is structurally sound. [10]

Cost

Shell anticipates that the petroleum products produced by its in-situ method are competitive, given crude oil prices in the mid-$20s per barrel (Fletcher, 2005). The company is still developing the process, however, and cost estimates are likely to increase as more information is obtained and more detailed designs become available. No independent cost estimates are available. This cost estimate is substantially lower than the cost estimate for mining and surface retorting. One reason for this is that the Shell approach is, in some ways, more akin to a conventional petroleum drilling process than to either mining and surface retorting or modified in-situ processes. As such, it benefits from the technical advances and accompanying cost reductions achieved by the petroleum extraction industry over the past 25 years. Other comparative benefits include lower up-front costs, reduced need for product upgrading, and lower reclamation costs. Up-front costs are lower because most capital expenditures would be made incrementally as the areal extent of drilling increases. Product upgrading costs are lower because all produced liquids are distillable (i.e., they contain no residual oil) and stable. Reclamation costs, while not insignificant, should be lower because Shell's process involves much less land disturbance than mining and does not require disposal of spent shale. How down-hole heating is supplied affects costs. As currently configured, the Shell in-situ retorting process uses electric power as the source for down-hole heating. About 250 to 300 kilowatt-hours are required for down-hole heating per barrel of extracted product. Assuming electricity at $0.05 per kilowatt-hour, power costs for heating amount to between $12 and $15 per barrel (crude oil equivalent). An operation producing 100,000 barrels per day requires approximately 1.2 gigawatts of dedicated electric generating capacity. Sources for electric power include coal, natural gas (produced from the oil shale), nuclear power, and wind energy (listed in presumed order of increasing costs in the general area of the Green River Formation). With abundant supplies nearby, coal can be used for power generation. While coal is the least expensive choice, its use will result in a significant increase in greenhouse gas emissions compared with conventional petroleum production or surface retorting. If natural gas were to be selected, roughly all the natural gas coproduced with the shale oil would be consumed in power generation. In the future, however, the value of natural gas may preclude its use in stationary power generation, leaving coal or nuclear as nearer-term choices and wind as a longer-term option. Requirements to sequester carbon dioxide produced by power plants could result in power cost increases of 30 percent (Buchanan, Schoff, and White, 2002), but the net impact on shale-derived oil costs would likely be less than 15 percent.20 An alternative to electrical heating is to heat the shale by down-hole natural gas burning. Compared with using electric power produced by natural gas, this approach halves natural gas use. Implementing down-hole gas burning requires the development of appropriate combustion technology. Presently, the net impact on shale oil production costs is uncertain. [10]

4.5. COMPARISON BETWEEN MADBI AND GREEN RIVER FORMATIONS

Table 4. 3. COMPARISON BETWEEN MADBI AND GREEN RIVER FORMATIONS

Green River Formation	Madbi Formation
1) Lithology • Organic rich component(shale). • Storage component (adjacent siltstone/ sandstone or micro fractures within shale).	1) Lithology • Shale is a Jurassic source rock. • Organic rich shale below laminated siltstone, carbonate component.
2) Within the hydrocarbon generation window: • Hydrocarbon generation results in overpressuring which produces pervasive micro-fractures throughout the shales.	2) Within the hydrocarbon generation window: • Madbi shales may lies at acritical depth where active HC generation is occurring.
3) Structure and fracturing: • Interconnectivity between regional and tectonic fractures with micro-fractures increase the flow capacity of the reservoir.	3) Structure and fracturing: • Extensional setting with normal faulting and tensile fracturing-potential to enhance fluid pathway in an overpressured shale has existing micro-fractures.

Table 4. 4. main key points for both formations

Parameters	Green River Formation	Madbi Formation
OOIP	$1.5 – 1.8 \times 10^{12}$ (bbl)	$> 2.4 \times 10^{9}$ (bbl)
K	> 1 md	0.003-3.4 md
Area	10.5599×10^{6} acres [16]	5.573×10^{6} acres
Avg. thickness	>500 ft	>500 ft
Porosity	4%	5%
Depth	≈ 1600 m	480-2800 m
API Gravity	42 API	42-50 API

4.6. ECONOMICS PROFITS

A competitive oil shale industry producing 3 million barrels per day will generate about 1 billion barrels of oil per year. The value of this production will depend on where world oil prices lie 30 years hence. If by 2035 world crude oil prices are at \$50 per barrel, the annual value of 3 million barrels per day of domestic shale oil production would be \$50 billion, and larger or smaller depending on future world crude oil prices. So long as a domestic oil shale industry can produce shale-derived oil at costs, including return on capital, below the prevailing market price for oil, the industry will be generating economic profits. The \$50 billion in total revenue, which includes these economic profits, would be broadly distributed among investors, workers in oil shale production facilities as well as in the industrial and service base supporting those production facilities, and the government through taxes and royalties. If production costs, including a normal rate of return on capital, drop to $30 per barrel by the time production reaches 3 million barrels per day, the oil shale industry would annually generate $20 billion in economic profits, above and beyond revenues required to cover operating expenses and returns on capital investments. Through lease bonus payments, royalties, and taxes on profits, roughly half of these profits will likely go to local governments, landowners, and thereby, broadly benefit the public. In particular, lease bonus payments and royalty income provide a direct means for the nation to be compensated for resource depletion, temporary diversion of land use, unavoidable environmental damages, and possibly permanent decrease in surface land value. Just as private landowners would not allow resource extraction unless they each thought that they were being adequately compensated, so too does the government, as part of its stewardship, “manage or influence resource use to enhance public benefit, promote responsible use, and ensure optimal value”.

Chapter Five

5. CONCLUSION, LIMITATIONS, RECOMMENDATIONS

In this chapter, we will conclude our project with several points. In the beginning, we will discuss the selecting of an appropriate method from the methods that we have discussed previously in (Chapter 4) to use in Al-Sabatayn Basin to extract hydrocarbons from the Shale formation. Then we will explain some disadvantages and limitations of the selected method. Finally, we will give Some recommendations associated with our project.

5.1. CONCLUSION

5.1.1. Selecting The Proper Process (our point of view)

We have selected process no. 3 which have been disused in chapter 4 that called Occidental Petroleum Process because of several reasons will be as following:

- Its attempt to improve performance by exposing more of the target deposit to the heat source.
- It is improving the flow of gases and liquid fluids through the rock formation.
- It is increasing the volumes and quality of the oil produced.
- The Occidental vertical modified in situ process was developed specifically for the deep, thick shale beds.
- Full-scale retorts would contain 350 000 cubic meters of shale rubble.
- This method overcame many of the difficulties of burning shale underground by allowing the necessary combustion air to permeate the crushed shale.
- The commercial-sized retort covered 333 by 166 feet area and had a height of 400 feet.

- Rubbelizing some of the shale walls of the void to expand existing fractures in the formation, improving its permeability.
- Can access the void to seal and control a mixture of air and fuel gas (or commercial fuel such as propane or natural gas) to introduce and initiate ignition for rubbelizing the shale.

5.2. RECOMMENDATIONS

1) Presenting such a study can open the horizons for expanded studies of this kind of unconventional oil to increase the country's reserves locally and nationally.
2) This also will lead to a huge alternative potential of unconventional resources and provide a sense of extending the exploration activities for both unconventional and conventional petroleum resources in the whole Basin.

5.3. LIMITATIONS

1. Today’s Crude Price Decreasing.
2. Lack of Necessary Data Required to Estimate Madbi Formation Recoverable Resources and Complete this Project Professionally.
3. None of These Technologies Applied in Yemen Basins Which Led to the Reduction in Objectives of the Nominal Project to what it is.
4. Extraction Difficulties.
5. Environmental Impacts.
6. Processing of Oil Shale and Retorting Requires a Long Time.
7. Unavailability of Appropriate Technology That Reduces Extraction cost and Minimizing the Timeline.

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