Value Added Products from Oil Shale

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Abstract

Oil shale is more than an energy source. It is also a source for various valuable materials. These materials include pyridine, carbonate minerals, alumina, ammonium sulfate, phosphate, sulfur, uranium, vanadium, and zinc, to name a few, from which numerous value-added products can be manufactured. For example, catalysts are made from vanadium and zinc, while alumina is a widely used material for catalyst support. Spent shale from oil shale retorting has also been used in the cement industry. Other potential by-products from oil shale include carbon fibers, adsorbent carbons, construction and building blocks. This paper reviews the viable materials that are found in oil shale and their beneficial use.

Introduction

Oil shale is one of the most abundant potential alternative sources of hydrocarbons, but the product composition is quite different from conventional petroleum. The world's known deposits of oil shale are vast. They are greater than the proven resources of crude oil and natural gas (Russell, 1990). Oil shale has potential for economic recovery of energy such as shale oil, combustible gas, heat and various byproducts.

Oil shale has been viewed as an alternative source of energy but the full chemical and economic potential of oil shale is yet to be explored. Besides its hydrocarbon potential, some oil shale deposits contain minerals and metals that can add value. The mineral contents of some oil shale consists mainly of carbonates such as calcite, dolomite, and siderite, with some aluminosilicate minerals. The major minerals in other oil shales are quartz, feldspar and clay with minor carbonate minerals. Many oil shale deposits contain small amounts of sulfide minerals such as pyrite, and marcasite (Dyni, 2003).

Though producing oil from oil shale may not yet be competitive with conventional petroleum, oil shale is used in some countries (*e.g.* Estonia) as an energy source. Some oil shale deposits contain minerals that may add value. Products like alum, nahcolite, dawsonite, ammonium sulfate, vanadium, copper, uranium, pyridine, carbonate minerals, alumina, ammonium sulfate, phosphate, sulfur, and zinc may add considerable value to some oil shale deposits. Other potential by-products from oil shale include carbon fibers, adsorbent carbons, construction and building blocks. Also, Koel and Bunger reviewed development of new products from oil shale (Koel and Bunger, 2005). Recovery of uranium from the Sillamae, Estonia oil shale processing plant has been discussed by Lippmaa, et al, 2006. The economic viability of value-added products from oil shale as cement feedstock and refinery and chemical feedstock can not be over-emphasized. Table 1 shows the summary of some products from oil shale and their uses.

Objective

The objective of this paper is to review and discuss the various value-added products that have been produced from oil shale, and oil shale ash processing.

Value-Added Products from Oil Shale

Uranium at Sillamae Oil Shale Processing Plant

Up to 180 tons per annum of uranium was produced at the Sillamae Oil Shale Processing Plant (Lippmaa et. al, 2006). A total of 1,360,654 kilograms of enriched uranium dioxide were produced from 1983 to 1990. Production ceased due to the break-up of the Soviet Union. Table 2 shows the summary of production of ^{235}U-enriched UO_2 in 1983-1989 at the Sillamae Oil Shale Processing Plant.

Adsorbent from Oil shale Ash

Adsorbents can be produced from oil shale fly ash. Oil shale by-product was converted into zeolite by alkali hydrothermal activation using sodium hydroxide. Activation was performed at different temperatures using 1, 3 and 8 M sodium hydroxide. The produced zeolite was used as ion exchanger for cleaning metal ions from wastewater.

Other Products from Oil Shale Ash

There are other ways to use oil shale ash (OSA). Spent oil shale is used as a construction material, soil stabilizer and fertilizer for liming acid soil, foundry cores, supplement to animal food, and so on. The most effective use of OSA is as feedstock for cement production. This application was common in Estonia, Germany, and China.

Table 1: Value-Added Products from Oil Shale

Product	**Uses**
Vanadium	For making steel alloys (ferrovanadium) used in armor plate, car engine parts
Uranium	Nuclear fuel
Pyridine	Chemicals
Carbonates	For chemicals, cements
Phenols	Chemicals
Copper	Electrical conductors Coins, Plumbing
Nickel	Stainless steel alloy, Coins
Zinc	Dry batteries, Paints, Cosmetics Construction materials
Phosphate	Fertilizer
Spent shale	Road construction -mineral filler, fine aggregates in asphalt paving -cement feedstock

Cement

Oil shale can be used in manufacturing

Table 2: Production of ^{235}U-enriched UO_2 in 1983-1989 at Sillamae Oil Shale Processing Plant (Lippmaa et. al, 2006)

Nominal ^{235}U-Enriched (%)	**Content of Uranium in ^{235}U-Enriched UO_2 (kg)**						
	1983	***1984***	***1985***	***1986***	***1987***	***1988***	***1989***
2.0	34,523	79,109	98,606	53,489	103,547	119,173	40,119
2.4					78,036	58,679	150,569
3.0	13,190	25,504			40,347	73,816	66,082
3.3	68,025	52,056	71,492	88,342	22,571	4,252	
3.6				19,027			
TOTAL	*115,838*	*156,669*	*170,098*	*160,858*	*244,501*	*255,920*	*256,770*

Portland cement. It was discovered that utilization of spent oil shale for cement production can reduce the required temperature for clinkering reactions. Jordanian oil shale was been used in the cement industry. Table 3 compares the properties of conventional cement and oil shale ash (OSA) from Jordanian and Estonian oil shales. Kikas and coworkers studying the influence of OSA on the properties of OSA cement and concluded that the concrete made with burnt shale possesses high strength, high frost resistance, and low permeability. It was also showed that the addition of about 30% OSA into Portland cement clinker can enhance compressive strength of the ordinary Portland cement.

Chemicals from oil shale

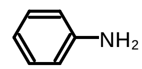
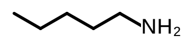
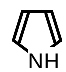
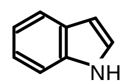
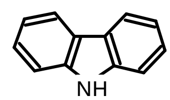
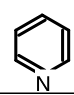
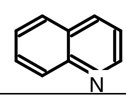
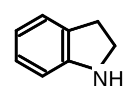
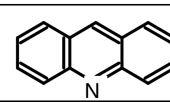
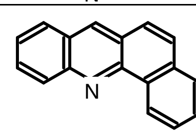
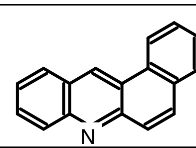
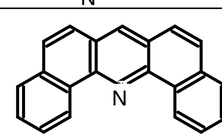
It was proposed by Akar and Ekinci (1995) to use the abundant alkane and alkene content of shale oils as a source for the production of related value-added chemicals. Table 4 shows representative nitrogen-containing compounds in petroleum, shale oil, and coal derived liquids, while Figure 1 shows the model structure of oil shale with nitrogen widely distributed. The C[6]-C[10] fraction can be used for the production of plastifiers via the synthesis of alcohols by the oxo-reaction. The production of biodegradable linear dodecylbenzene from the C[10]-C[13] fraction as a detergent raw material is considered. The C[14]-

Table 3: Chemical Compositions of OSA and Conventional Cement

Oxide	Jordanian OSA (%)[1]	Estonian OSA (%)[2]	Cement (%)
CaO	49.72	46-58	60-69
SiO_2	30.97	20-28	18-24
Al_2O_3	4.71	6-8	4-8
Fe_2O_3	1.71	4-6	1-8
MgO	0.01	3-4	<5
K_2O	0.65	1-2	<2
Na_2O	0.43	0.1	-
TiO_2	0.17	0.4-0.5	-
MnO	0.01	-	-
P_2O_5	5.71	-	0-1

[1] Al-Hasan
[2] Hanni

Table 4: Representative Nitrogen-Containing Compounds in Petroleum, Shale Oil, and Coal Derived Liquids.

Compound	Formula	Structure
Nonheterocyclic compounds:		
Aniline	$C_6H_5NH_2$	
Pentylamine	$C_5H_{11}NH_2$	
Nonbasic heterocyclic compounds		
Pyrrole	C_4H_5N	
Indole	C_8H_7N	
Carbazole	$C_{12}H_9N$	
Basic heterocyclic compounds		
Pyridine	C_5H_5N	
Quinoline	C_9H_7N	
Indoline	C_8H_9N	
Acridine	$C_{13}H_9N$	
Benz(a) acridine	$C_{17}H_{11}N$	
Benz(c) acridine	$C_{17}H_{11}N$	
Dibenz(c, h)acridine	$C_{21}H_{13}N$	

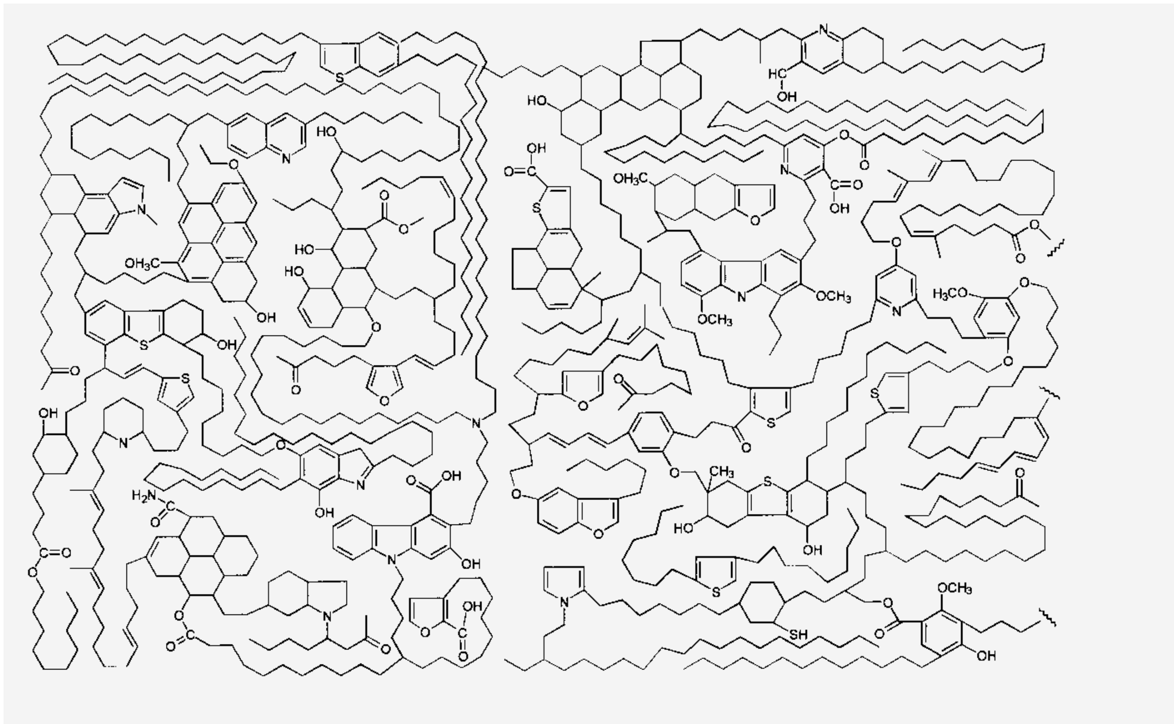


Figure 1: Structural Model of Oil Shale (Freud, 1992)

C[18] fraction is proposed as a raw material for fatty alcohols and alkyl sulfonate production. The heavy-end alkane fraction may be cracked for the production of various lower-molecular-weight alkenes. The high nitrogen content of the shale oil may also be advantageous in the production of new materials. Asphalt and carbon fibers are obtainable from the heavy shale oil fraction. The processes available in the chemical and petroleum industry can be utilized.

Pyridine

Pyridine is a basic, organic, and aromatic nitrogen compound with many uses and markets. Pyridines are valuable for manufacturing chemicals. They may be used among other purposes as an asphalt additive. The pyridine makes up approximately 2% of the shale oil. Value enhancement processes in DOE Report II, 2004, and Bunger, 2001, outlined the approach where heteroatom-containing compounds are extracted and refined to marketable chemicals. The schematic of the approach is presented in Figure 2. These valuable compounds are selectively extracted from the kerogen oil. The chemicals may also be used for manufacturing agrochemicals, detergents/surfactants and so on.

Natural Gas

Shale oil development could contribute to domestic natural gas supply in following two ways (US DOE, 2004):

1) shale oil can be used as a substitute for natural gas feedstock in chemical processes, and free up natural gas for other uses, and

2) in-situ technologies for shale oil production can produce as much as one third of the heating value of its total production in the form of natural gas.

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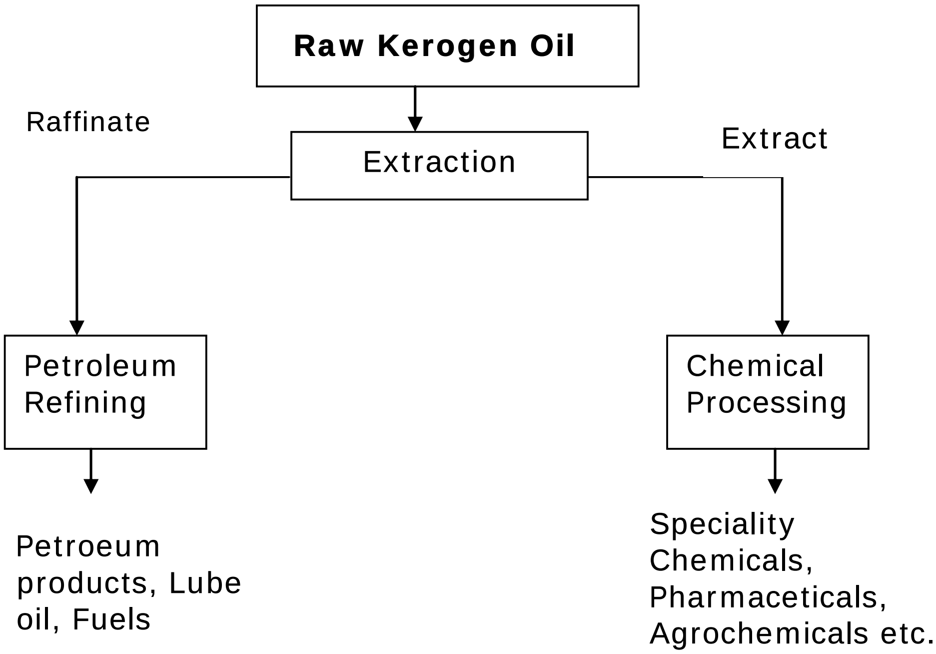

Figure 2: Value Enhancement Processing for Oil Shale (DOE Report, 2004)

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