

Antiknock Motor Fuels by Cracking Shale Oils¹

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IN THE search for petroleum substitutes as a source of motor fuel, the most important general classes of hydrocarbons found are shale oils and the tars derived from the heat treatment of coal, particularly low-temperature coal tar, lignite, and similar materials. Intermediate classes of substances, such as the solid and semisolid bitumens, which comprise the materials extractable from oil and tar sands, as well as such substances as gilsonite and grahamite, will also furnish large quantities of hydrocarbon materials which can be utilized for this purpose when the economic necessity arises.

Shale oil as a future substitute for petroleum is now generally recognized. Oil shales are widely distributed throughout the world and are of tremendous potential as oil resources for industrial automotive use, particularly as the cracking of shale oil produces a high antiknock motor fuel. It is well recognized that the future of the oil shale industry will depend to a large extent upon the profitable conversion of the crude shale oil into motor fuel, as well as to some extent upon the utilization of the spent residue. Without doubt the cracking of shale oil to produce antiknock motor fuels will be the dominating factor in its commercial exploitation.

Distribution of Oil Shale and Potential World Production of Oil

UNITED STATES—In the United States the richest deposits of oil shale occur in the Rocky Mountain region in the Green River formation. There are also large deposits in Colorado, Utah, Kentucky, Indiana, California, Wyoming, Montana, and Nevada; others are scattered throughout the United States.

The Government is expending large sums of money for the commercialization of oil-shale retorting. Many small units have been constructed in different parts of the United States, but none have reached any magnitude.

The potential oil in our shale deposits is tremendous, and the alertness of some of our large oil companies in plotting out oil-shale deposits indicates their belief that at some time in the near future oil shale will be retorted in a big industrial way. Table I shows the distribution of shale in the United States as given by the American Petroleum Institute.

Table I—Distribution of Available Oil Shale in the United States

State	1000 tons (short)	1000 barrels (42 gal.)
Colorado	113,792,000	40,640,000
Utah	92,159,000	16,588,620
Kentucky	90,604,800	28,993,536
Indiana	69,696,000	13,939,200
California	13,939,200	5,575,680
Wyoming	7,176,000	1,291,680
Montana	6,969,600	1,393,920
Nevada	7,219	2,165
TOTAL	394,343,819	108,424,801

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This enormous amount of potential oil available from retorting American shales would yield by the cracking process over 50 per cent of antiknock gasoline, or over 54 billion barrels of gasoline, which would supply the automotive engines in the United States for more than one hundred and fifty years.

AUSTRALIA—The outstanding commercial company producing shale oil products from Australian shales is John Fell & Company. This company has installed a cracking unit which is the first of commercial proportions to be used for the primary purpose of cracking shale oil, yet flexible so that, without change, crude oil or its products may be cracked into high yields of gasoline.

The crude oil production of Australia is practically zero, and the retorting of oil shale is of great industrial importance. The known oil-shale deposits of New South Wales could produce approximately 300 million barrels of shale oil. The average shale oil of New South Wales will yield approximately 2.5 barrels of shale oil per ton. The crude shale oil can be commercially cracked into over 50 per cent of high antiknock gasoline. This gives a known

potential production of over 150 million barrels of high antiknock gasoline.

Tasmania has known oil-shale deposits covering 300 square miles, which would produce, if all were retorted, approximately 325 million barrels of shale oil. This quantity of shale oil may be converted into over 165 million barrels of gasoline by commercially cracking under heat and pressure.

FRANCE—The crude oil production of France is negligible. France has endeavored to stimulate research by means of prizes for the commercial production of substitutes for gasoline. Much work has been done in exploiting her oil-shale deposits. Although the oil-shale industry in France has not risen to its possibilities, a very keen interest is being shown by the government, which will no doubt insure a successful industrial development.

It is estimated that France has deposits of 50 million tons of oil shales and that under retorting conditions there may be derived approximately 25 million barrels of shale oil. This quantity of shale oil can be converted into over 50 per cent of marketable gasoline by means of heat and pressure.

SCOTLAND—Scotland has the most highly developed oil shale industry in the world. The estimated tonnage of oil shale being retorted per year in Scotland is 3,500,000, producing approximately 2 million barrels of shale oil. From this it is estimated over one million barrels of high antiknock gasoline per year may be produced by heat and pressure treatment.

OTHER COUNTRIES—Oil shale undoubtedly ramifies throughout the world, and in addition to those already discussed the following countries have material deposits: England, Wales, Canada, New Zealand, Africa, Jugoslavia, Spain, Sweden, Bulgaria, Germany, Italy, Switzerland, Estonia, Brazil, Argentina, Chile, Uruguay, and Russia.

Sources of Shale Oil Used in Present Work

The types of shale oil cracked were from American, Australian and French shales. The American shale oil was derived from the retorting of a Green River oil shale. The Australian shale oil charging stock was obtained by the retorting of the New South Wales type of shale. The French shale oil came from the shales of the Autun Basin.

Apparatus

The apparatus used was a heavy 8-inch welded-steel still with appropriate vapor line, condenser, and receiver, all constructed to be operated under pressure. Pressure measurements were determined by gages upon the still and receiver. A calibrated gage glass upon the receiver allowed proper control of the rate of distillation. The vapor temperatures in the still and vapor line, as well as the liquid temperature in the still, were determined by thermometers. Furnace temperature measurements were made with a pyrometer and a Leeds-Northrup potentiometer.

Operating Data and Results

The shale oils were subjected to distillation under operating pressures of 120 and 150 pounds pressure, and liquid temperatures ranging from 398° to 433° C. A charge of 8000 cc. was used for each run.

The gasoline produced from the crude shale oils showed over 50 per cent Navy end-point gasoline. These high yields can be produced commercially and the product will pass all motor-fuel specifications. The analyses of the charging stocks and the yields of the various products are tabulated in Table II.

Table II—Operating and Distillation Data

	United States		Australia	France
	Charging Stock			Crude
Type of oil	Crude	0.8905	0.8756	0.8956
Specific gravity				
Flash (Cleveland open cup)	113° C.			
Fire (Cleveland open cup)	129° C.			
Viscosity (Saybolt Furol)	13 seconds at 50° C.			
Distillation Analysis				
	° C.	° C.		° C.
Per cent over				
Initial point	221	82		121
10	260	159		196
20	296	201		224
30	324	244		255
40	346	281		290
50	373	318		321
60	393	354		354
70	399	382		382
80	405	396		410
90	405	413		421
End point	407	437		430
Coke, per cent by weight	4.5	1.5		1.7
Operating Data and Summary				
Pressure, pounds	120	150		120
Liquid temperature, ° C. (average)	417	433		426
Vapor temperature, ° C. (average)	399	398		409
Pressure distillate:				
Per cent yield	82.0	55.6		61.0
Specific gravity	0.7985	0.7591		0.7844
Residuum:				
Per cent yield	None	35.4		27.7
Specific gravity		0.9786		1.030
Per cent weight charging stock:				
Water	0.6	Trace		0.5
Coke	17.83	4.53		5.9
Uncondensable gas	6.9	3.2		4.9
Gasoline (Navy end-point):				
Per cent yield	52.8	50.1		51.0
Specific gravity	0.7499	0.7591		0.7762
Gas oil pressure distillate bottoms:				
Per cent yield	24.6	3.4		7.6
Specific gravity	0.8849	0.8740		0.8778

Chemical Analysis of Motor Fuels from Shale Oils

The gasoline produced from the cracking of shale oils is of high antiknock value. This is indicated by the high aromatic hydrocarbon equivalent, which is determined from the chemical analysis of the gasoline. The method of analysis has been previously published.² In valuating the aromatic hydrocarbon equivalent which is related to the antiknock properties in an automotive engine, Ricardo's

² Egloff and Morrell, THIS JOURNAL, 18, 354 (1926).

data for toluene are used.³ Five per cent of unsaturated hydrocarbons is equivalent to 1 per cent of toluene when both are dissolved in paraffin hydrocarbons. Similarly, 4 per cent of naphthenes is equivalent to 1 per cent of toluene. It is to be understood that the accuracy of this relationship is limited, since Ricardo did not work with pure hydrocarbons. The aromatic hydrocarbon value is taken by direct determination.

The unsaturated hydrocarbons are determined by treatment of the oil with 80 per cent sulfuric acid and redistillation of the cut taken for analysis after such treatment, to the temperature at which the original cut was made. The solution losses and distillation residue are, respectively, the unsaturated hydrocarbons removed by the acid and those formed by polymerization on acid treatment. The latter remains in the flask after the second distillation. The sum of the two gives the total unsaturated hydrocarbons present.

The aromatic hydrocarbons are determined by nitration with a special nitrating mixture composed of 58 per cent sulfuric acid, 25 per cent nitric acid, and 17 per cent water by weight. The naphthene hydrocarbons are determined by the lowering of the cloud point of aniline dissolved in the hydrocarbon mixture after the removal of the aromatic hydrocarbons. The paraffin hydrocarbons are determined by difference. The details of these analytical methods are given in the previous paper.²

The analyses herein shown check quite closely with the results obtained by motor test on synthetic mixtures of straight-run gasoline and commercial benzol. For example, a straight-run gasoline from Cushing crude oil having an aromatic hydrocarbon equivalent of 11 per cent in admixture with 22.5 per cent of commercial benzol (total aromatic hydrocarbon equivalent 30.4) is the motor equivalent of the cracked gasoline from the Green River shale oil.

The chemical analyses of the cracked gasolines with the corresponding Ricardo compression ratios are shown in Table III.

Table III—Analyses of Cracked Gasolines and Interpretation in Terms of Antiknock Properties

Source of shale oil	HYDROCARBONS			Aromatic hydrocarbon equivalent %	Ricardo compression ratio %
	Unsaturated %	Aromatic %	Naphthene %		
United States (Green River)	20.1	24.9	6.2	48.8	30.4
Australian (New South Wales)	15.7	26.0	6.0	52.3	30.6
French (Autun)	16.1	28.8	6.1	49.0	33.5

Treatment of Cracked Distillates from Shale Oils

The cracked distillates from shale oils may be treated by several methods. A suitable method which can be readily applied commercially is as follows: The cracked distillate is water-washed and treated with plumbite solution. A short water-wash follows the drawing of the plumbite sludge. The distillate is allowed to settle and then given a preliminary treatment with about one pound of sulfuric acid per barrel of distillate. The main acid treatment (6 to 7 pounds of sulfuric acid per barrel of distillate) is applied after drawing the sludge from the preliminary treatment. After drawing the sludge from the main acid treatment, the cracked distillate is water-washed, the water drawn and the oil then treated with sodium hydroxide or plumbite solution. The oil is finally distilled in the presence of steam. A light sodium hydroxide wash is applied to the gasoline distillate. If the latter is unstable—i. e., has a tendency to go off color—it is treated with a small per cent of fuller's earth. A combination treatment of dilute sulfuric acid followed by treatment with the regular concentration of 1.84 specific gravity sulfuric acid, at the acid stage of treatment, gives good results.

³ Ricardo, Institute of Petroleum Technology, Report of Empire Motor Fuels Committee, pp. 84, 85, 145.