

# H-OIL UPGRADING OF SHALE OIL FEEDS

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Reprinted from CHEMICAL ENGINEERING PROGRESS, August, 1966.

## INTRODUCTION

The estimated recoverable reserve<sup>1</sup> of a thousand-billion barrels of oil from the Green River formation shale in Colorado, Utah, and Wyoming periodically rekindles interest, particularly on the part of crude-deficient, domestic oil companies. Recent announcements of a semi-works-scale plant and future plans for a 30,000 to 60,000 barrels per day unit to obtain oil from shale have stirred current interest.

Oil shale is a fine-grained, compact, sedimentary rock (marlstone) which contains an organic substance, kerogen. Kerogen is only slightly soluble in known petroleum solvents but is converted to shale oil when subjected to temperatures above 700°F.

The conventional method to recover oil from shale involves room and pillar underground mining and above-ground retorting. Shale oil thus obtained must be upgraded prior to processing by conventional petroleum refinery operations.

## SHALE OIL CHARACTERISTICS

Conventional crude shale oil resembles petroleum in that it is composed of hydrocarbons plus sulfur, nitrogen, and oxygen derivatives of hydrocarbons. Shale oil differs from petroleum in other characteristics. Shale oil contains larger amounts of non-hydrocarbons, particularly nitrogen- and oxygen-containing organic compounds, which may be the major constituents in the higher boiling fractions. Shale oil hydrocarbons are highly unsaturated, resembling the products of thermal cracking of petroleum.<sup>2</sup> Crude shale oil produced by conventional retorts contains about one weight percent sulfur and two weight percent nitrogen. Inspections of a crude shale oil sample are compared in table 1 with those for oil from the Athabasca Tar Sands and vacuum bottoms from West Texas and Kuwait.

Hydrogenation provides one method to upgrade shale oil and to overcome the major refining difficulties caused by nitrogen and sulfur compounds. The ability of the H-Oil process to upgrade shale oil by hydrogenation has been demonstrated in pilot plant equipment.

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The H-Oil process was developed jointly by Hydrocarbon Research, Inc. (HRI) and Cities Service Research and Development Company. The original application envisioned for the H-Oil process was the upgrading of hydrogen-deficient petroleum residua, but the ability of the process to upgrade other feedstocks was soon realized. Other heavy hydrocarbon feedstocks successfully upgraded by the H-Oil process include coal tar, shale oil, and oil extracted from Athabasca Tar Sands. H-Oil is particularly applicable for upgrading shale oil because the catalyst is not deactivated by nitrogen and sulfur and the process is operable with shale oil feed containing suspended fine solids.

Since the H-Oil process has been described in detail elsewhere<sup>3 4 5 6 7</sup>, only a brief resumé is presented. The H-Oil process features an ebullating catalytic system in which the upward velocity of the gas and liquid maintains the expanded bed of catalyst in continuous random motion. This hydrogenating system can handle any high-boiling liquid that is pumpable. Advantages of the H-Oil system relative to fixed bed systems are:

1. Extraneous inert solids introduced with the liquid feed pass through the reaction space and are discharged with the product. In a 30-barrel-per-day, pilot-plant unit, tar sands oil which contained several percent of fine sand was handled without any process difficulties.

2. Isothermal conditions are maintained throughout the reaction space in

3. Hydrogen distribution problems are eliminated throughout the reactor by the random motion of the catalyst.

4. Catalyst can be either intermittently or continuously added and withdrawn to maintain constant catalytic activity within the reaction bed. This prevents down time and eliminates the necessity for "swing" reactors to permit changing the catalyst.

5. There is no tendency for pressure drop to increase as a result of accumulated foreign materials. Tarry deposits do not accumulate on the catalyst. Removal of inorganic matter by filtration, as required at times in a fixed-bed system, is not necessary.

6. Active, rugged catalysts of a relatively small particle size are employed. Catalytic poisoning effects by porphyrin complexes, nitrogen, sulfur, and oxygen in the feed have been mitigated and catalyst life is sufficient to make catalyst regeneration usually uneconomic.

These features make the H-Oil process a versatile system applicable for upgrading shale oil feed.

## EXPERIMENTAL RESULTS

Experimental results discussed below are based on single-stage operation; however, a two-stage system is shown in the simplified schematic flow diagram (fig. 1), since there are inherent advantages in a two-stage process.

Inspections for two shale oil feeds are presented in table 2: charge stock A comprises the entire shale oil feed, charge stock B represents shale oil bottoms with an IBP of 601°F.

In single-stage operation with extinction recycling of 650°F+ oil from charge stock A, the liquid was reduced in pour point from +75 to +10°F while the viscosity was reduced from 153 to 33 SSU at 122°F. Results are presented in table 3 for charge stock A with extinction recycling of 950°F+ (Case 1) and 650°F+ (Case 2) oil, respectively. Inspections are given for the total liquid product and for the individual fractions. H-Oil process yields related to volume percent 650°F material converted for single-stage operation are shown in figure 2. Comparable results for light hydrocarbons are presented in figure 3.

Shale oil bottoms, charge stock B, was processed to yield 97 percent of the distillate products boiling below 950°F. With a consumption of 2000 std cu ft of hydrogen per barrel, the pour point was reduced from 110°F to 70°F and the viscosity was reduced from 96 SF seconds at 210°F to 45 SUS at 122°F. Product inspections are presented in table 3. Single-stage operation resulted in 60 percent nitrogen removal. No operating difficulties were experienced with 0.77 weight percent ash in the feed.

Hydrogen consumption for charge stock A as a function of 650°F conversion is shown in figure 4. Hydrogen production from the propane and lighter hydrocarbons produced during upgrading of whole shale oil is insufficient for consumption in the H-Oil process. However, off gases from shale retorting are expected to be sufficient to balance the hydrogen requirement. Hydrogen balances for an H-Oil unit processing shale oil for Cases 1, 2, and 3 are presented in table 4.

Nitrogen removal in the 650°F+ extinction recycle run (Case 2) was 77.6 percent. The relationship between conversion and nitrogen removal for both single- and two-stage operations is presented in figure 5. Single-stage data are based on laboratory results. Two-stage results are predicted from correlations derived from extensive work on petroleum feedstocks. For a plant processing 50,000 barrels per day of shale oil, the stoichiometric maximum quantity of ammonia produced from the whole shale oil is 192 tons per day. Based on 77.6 percent nitrogen removal, the ammonia production is 149 tons per day. For two-stage operation, the production is predicted to be 168 tons per day.

Economics for upgrading whole shale oil (Case 2) and shale oil bottoms (Case 3) are presented in table 5. Compressors are steam driven by steam produced during cooling of the reactor effluent. Pumps are motor driven. Cooling water requirements are minimized by using air coolers to condense the steam from the turbines driving the compressors. Product streams are fuel gas and "synthetic crude."

Investments are on-site for the H-Oil process and include equipment to deliver ammonia-free fuel gas and synthetic crude. Costs are incremental and include only the H-Oil processing step.

These costs can be readily incorporated into an overall shale oil processing scheme. No credit is taken for co-produced ammonia.

#### ACKNOWLEDGMENTS

The authors express appreciation to the managements of Hydrocarbon Research, Inc., and Cities Service Research and Development Company for permission to publish experimental data on H-Oil treatment of shale oil.

TABLE 1.—*Inspection on charge stocks*

<i>Source</i>	<i>Shale oil</i>	<i>West Texas vacuum bottoms</i>	<i>Kuwait vacuum bottoms</i>	<i>Oil from Athabasca Tar Sands</i>
Gravity, °API	18.9	10.5	7.1	6.4
Sulfur, W %	0.8	3.1	5.2	4.6
Ramsbottom carbon, W %	3.6	15.4	17.5	15.8
Vanadium, ppm	4	38	78	120
Nickel, ppm	2	22	26	70
Nitrogen, W %	1.92	0.38	0.38	0.38
Ash, W %	0.04	0.02	0.03	2.6
Hydrogen/carbon atomic ratio	1.6	1.50	1.45	1.47

TABLE 2.—*Inspections on shale oil feed*

<i>Charge stock</i>	<i>A</i>	<i>B</i>
Gravity, °API	18.9	6.0
Sulfur, W %	0.8	0.6
Nitrogen, W %	1.92	2.5
Carbon, W %	84.21	84.98
Hydrogen, W %	11.24	10.19
Oxygen (by diff.) W %	1.79	1.56
Ash, W %	0.04	0.77
Ramsbottom carbon, W %	3.6	13.2
Pour Point, °F (upper)	75	110
Viscosity, SF sec. at 210°F	153*	96
Benzene insolubles, W %		1.0
IBP, °F	432	601
IBP-975°F (IBP-650°F)		
Gravity, °API	(29.2)	12.6
Sulfur, W %	(0.78)	0.6
Aniline Point, °F	(88.)	103
Pour point, °F		80
Volume percent	(32)	57.0
975°F+ (650°+)		
Gravity, °API	(14.0)	-1.3
Sulfur, W %	(0.69)	0.6
Ramsbottom carbon, W %		25.5
Volume percent	(68)	43.0

\*SUS at 122°F

TABLE 3.—*H-Oil processing of shale oil feeds, summary of yields and inspections*

<i>Charge stock</i>	<i>A</i>		<i>B</i>
	<i>Whole shale oil</i>		<i>Shale oil bottoms</i>
<i>Case number</i>	1	2	3
Yields, % on feed			
H <sub>2</sub> S, NH <sub>3</sub> , H <sub>2</sub> O, W %	4.2	4.2	4.0
C <sub>1</sub> -C <sub>3</sub> , W %	2.9	5.8	8.1
C <sub>4</sub> -180°F, V %	6.2	11.6	8.5
180-400°F, V %	15.7	26.4	14.4

TABLE 3. (cont.)

<i>Case number</i>	1	2	3
400-650°F, V %	53.8	70.5	33.4
650°F+ (650-950°F), V %	30.2	....	(40.7)
950°F+, V %			8.6
Total C <sub>4</sub> +liquids, V %	106.0	108.5	105.6
Hydrogen consumption, SCF/Bbl	1320	1930	2000
<b>Inspections</b>			
Collected liquid			
C <sub>4</sub> +gravity, °API	36.3	43.7	28.4
Sulfur, W %	0.02	0.02	<0.07
Nitrogen, W %	0.60	0.43	1.08
Pour point, °F	60	10	70
Viscosity, SUS at 122°F	36	33	45
IBP-400°F			
Gravity, °API	51.6	53.8	52.6
Aniline Point, °F	124	124	120
Nitrogen, W %	0.28	0.16	0.24
Paraffins, V %	45	47	44
Olefins, V %	3	2	4
Aromatics, V %	16	15	16
Naphthenes, V %	36	36	36
400-650°F			
Gravity, °API	34.1	34.6	28.7
Diesel Index	45	47	30
Nitrogen, W %	0.46	0.50	0.67
Sulfur, W %	0.02	0.02	<0.07
650°F+ (650-950°F)			
Gravity, °API	25.1		(18.1)
Diesel Index	40		(25)
Sulfur, W %	0.02		(<0.07)
Nitrogen, W %	0.56		(1.12)
950°F+			
Gravity, °API			5.9
Sulfur, W %			<0.07
Ramsbottom carbon, W %			11.7
Nitrogen, W %			1.7

TABLE 4.—*Hydrogen balance*

<i>Case number</i>	1	2	3
<b>Items</b>			
H-Oil capacity, barrels/day	50,000	50,000	16,000
Chemical hydrogen consumption, SCFB	1320	1930	2000
Chemical hydrogen consumption, MMSCFD	66	97	32
20% allowance for losses, MMSCFD	13	19	7
Total hydrogen consumption, MMSCFD	79	116	39
Hydrogen production from H-Oil C <sub>3</sub> -MMSCFD	43	86	42
Percent hydrogen deficiency	46	26	0

TABLE 5.—*Economics for H-Oil upgrading of shale oil*

<i>Feedstock Case number</i>	Unit cost	<i>Whole shale oil 2</i>		<i>Shale oil bottoms 3</i>	
		Req't	\$/yr.	Req't	\$/yr.
Feed rate, Bbl/SD		50,000		16,000	
Investment, \$		12,800,000		5,800,000	
Costs		Req't	\$/yr.	Req't	\$/yr.
Hydrogen, SCF/Bbl	30¢/MSCF	1,930	9,554,000	2,000	3,168,000
Catalyst			1,120,000		448,000
Power, KW	0.9¢/KWH	11,000	784,000	3,700	264,000
Fuel, MM Btu/hr	31¢/MM Btu	100	246,000	34	83,000
Cooling water, gpm	1.0¢/M gal.	5,500	26,000	1,800	9,000
Labor, men/shift	3.35\$/hr.	4	119,000	3	89,000
Supervision & overhead			190,000		143,000
Maintenance & supplies	4.3% inv.		552,000		250,000
Insurance & local taxes	2% inv.		256,000		116,000
Depreciation	18-yr. st. line		713,000		322,000
Incremental total cost			13,560,000		4,892,000
Incremental cost, \$/Bbl feed*			0.82		0.93
Ammonia Production, tons/day			149		49

\*Profits are not included

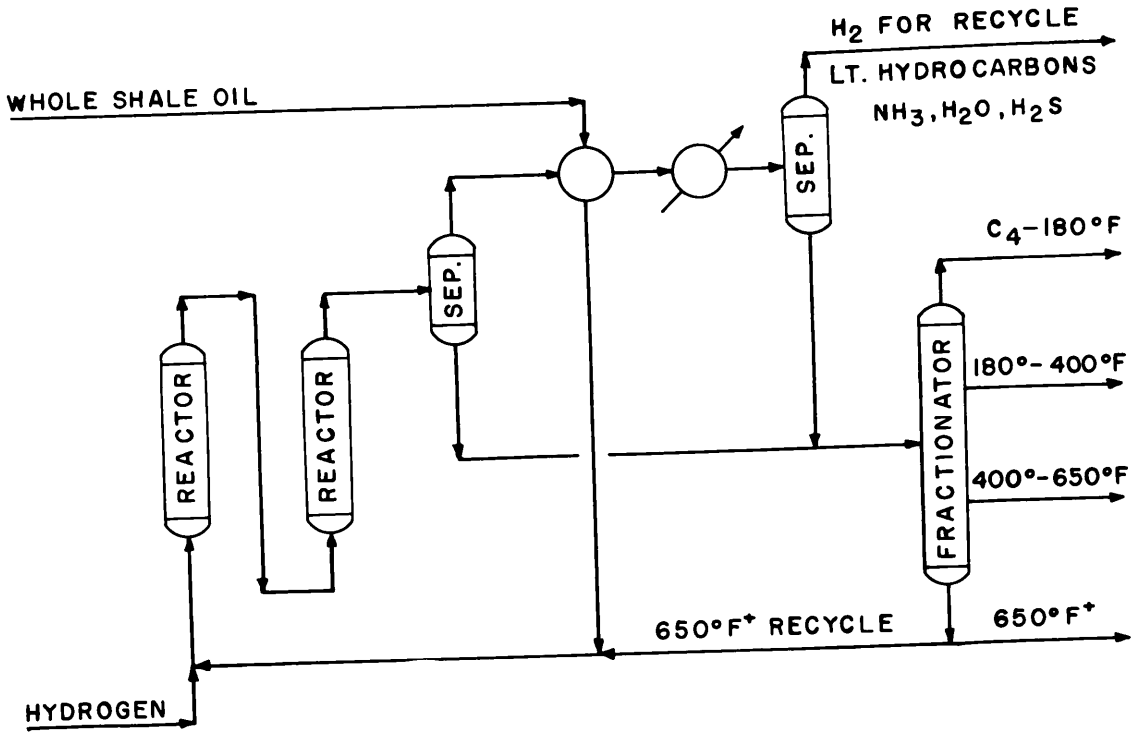


FIGURE 1.—H-Oil upgrading of shale oil. Schematic flow diagram.

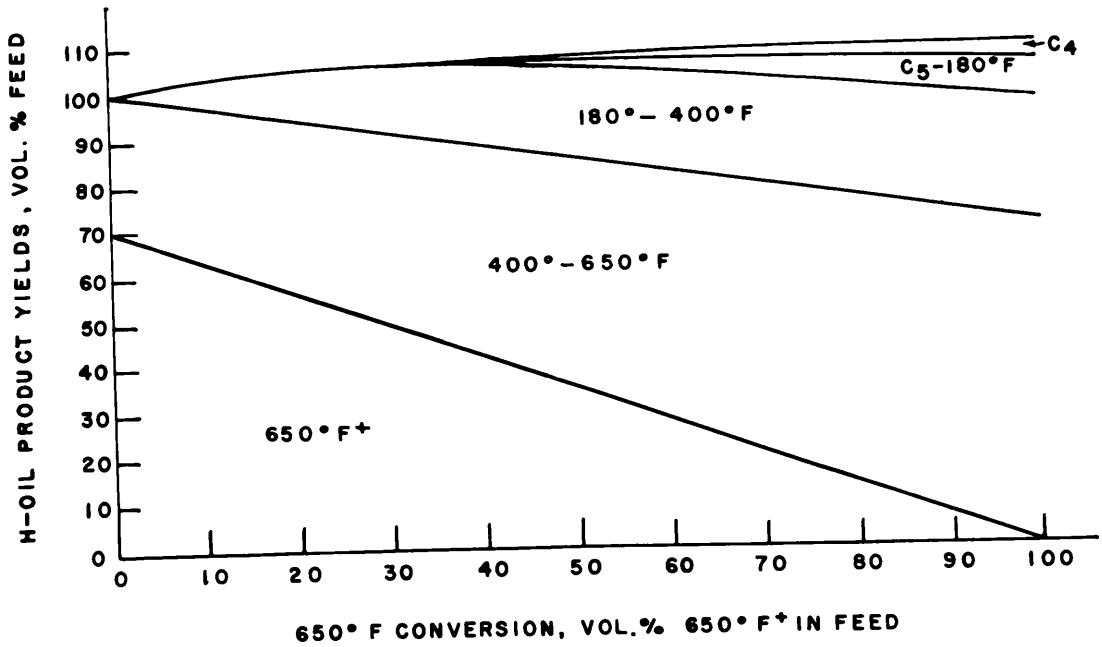


FIGURE 2.—H-Oil upgrading of whole shale oil. Yield distribution vs. conversion. Single stage data.



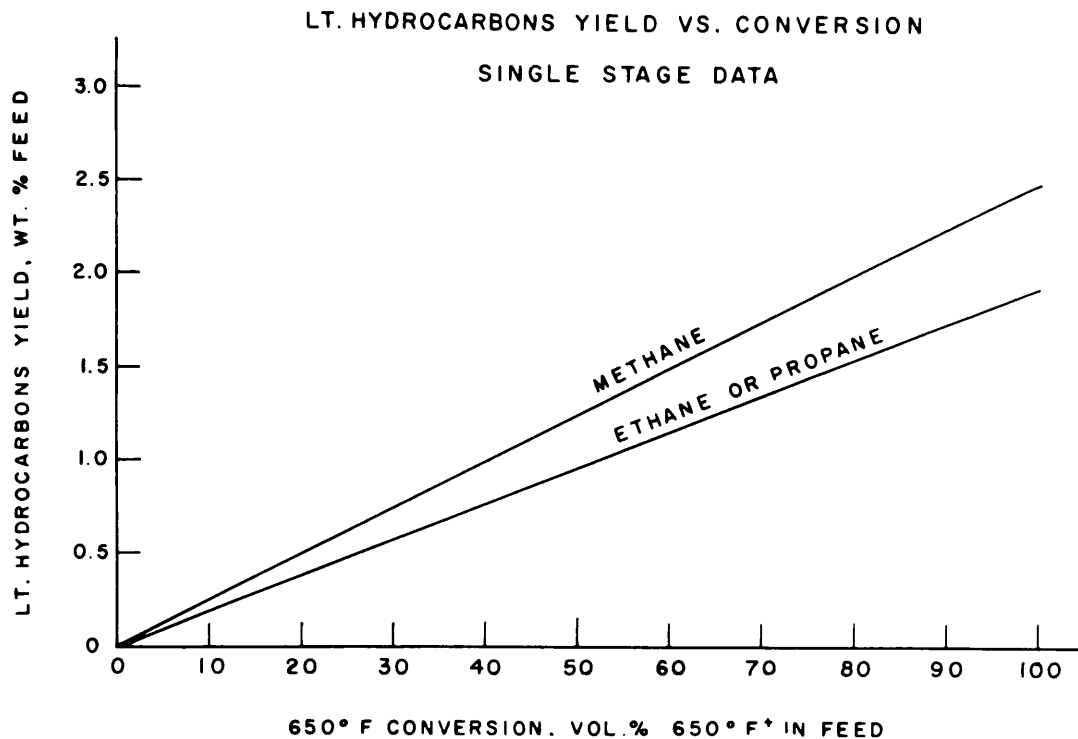


FIGURE 3—H-Oil upgrading of whole shale oil. Lt. hydrocarbons yield vs. conversion. Single stage data.

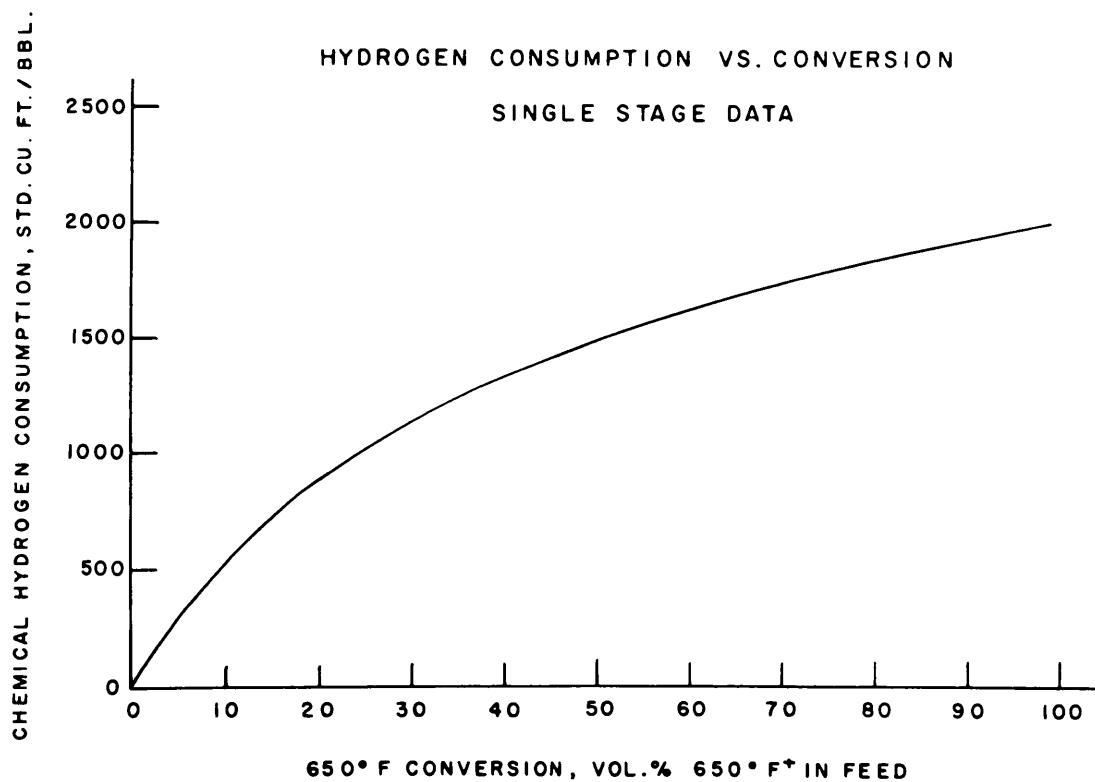


FIGURE 4.—H-Oil upgrading of whole shale oil. Hydrogen consumption vs. conversion. Single stage data.

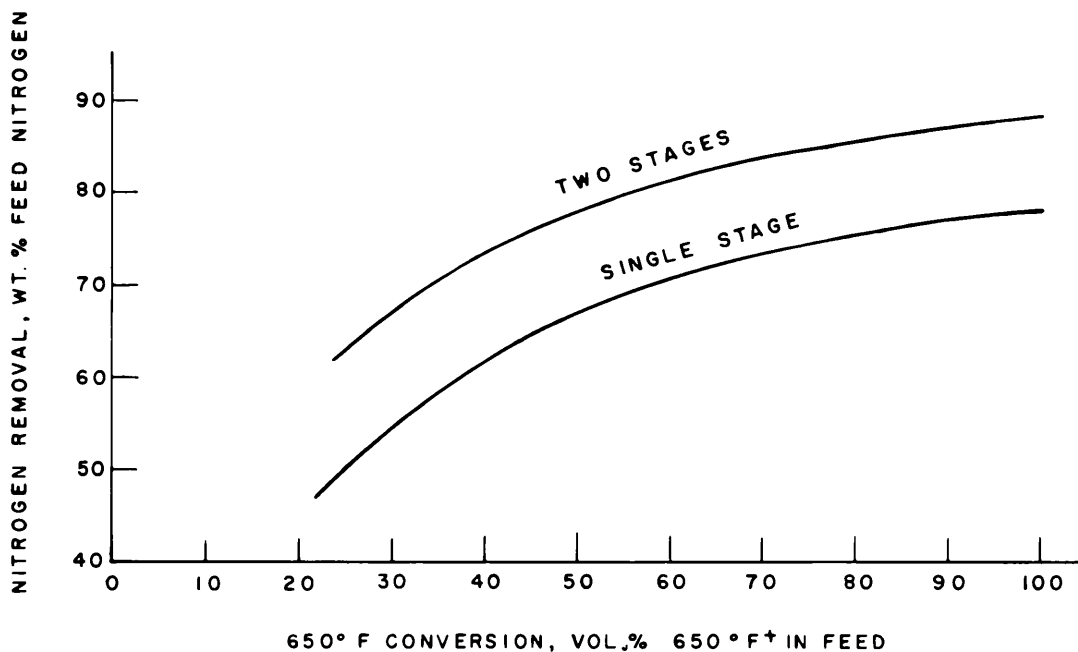


FIGURE 5.—H-Oil upgrading of whole shale oil. Nitrogen removal vs. conversion.

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