

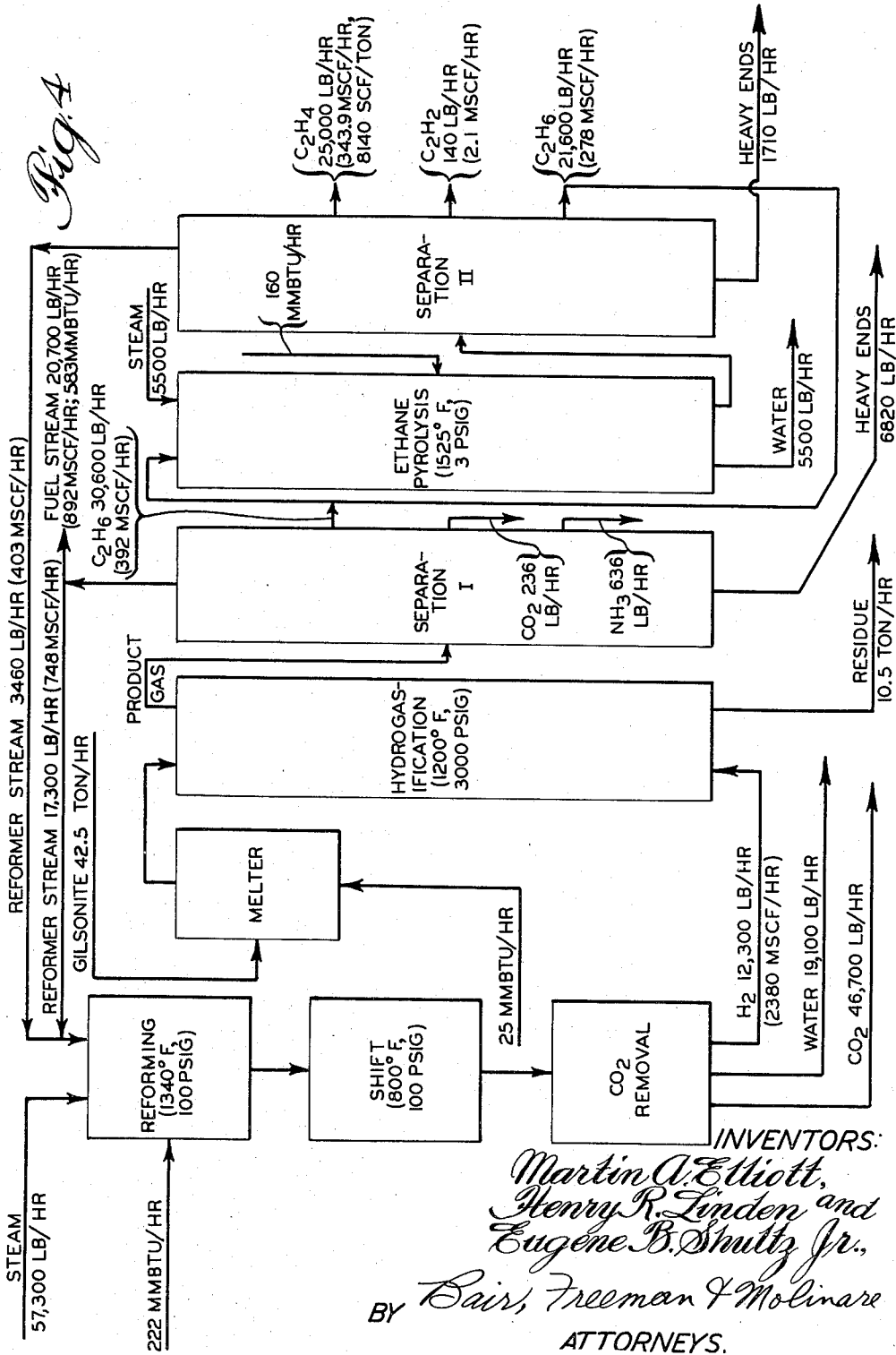
July 4, 1961

M. A. ELLIOTT ET AL  
PRODUCTION OF LOW MOLECULAR WEIGHT HYDROCARBONS  
FROM SOLID FOSSIL FUELS

2,991,164

Filed Jan. 19, 1959

4 Sheets-Sheet 1





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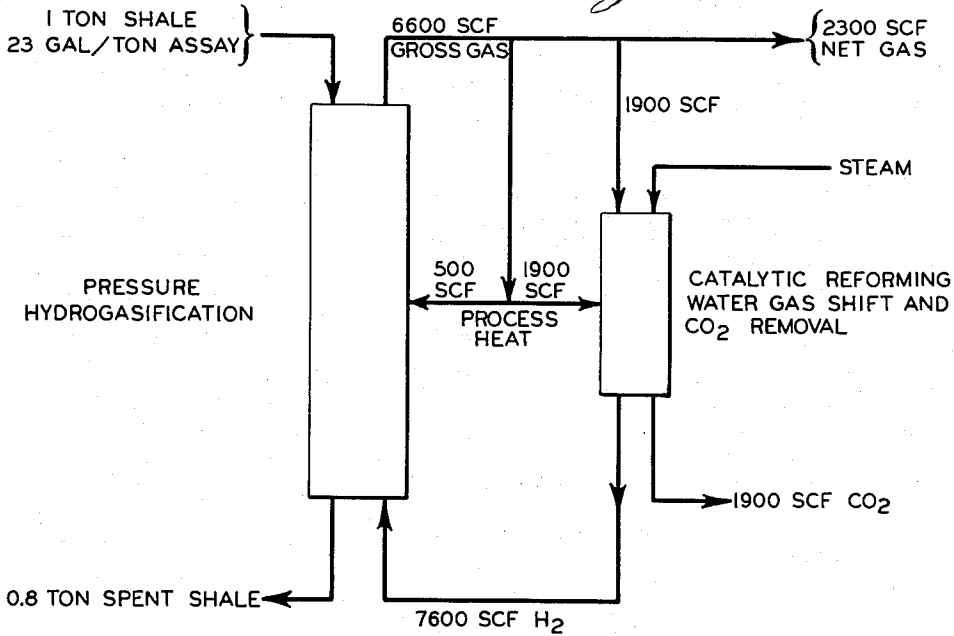
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Fig. 1



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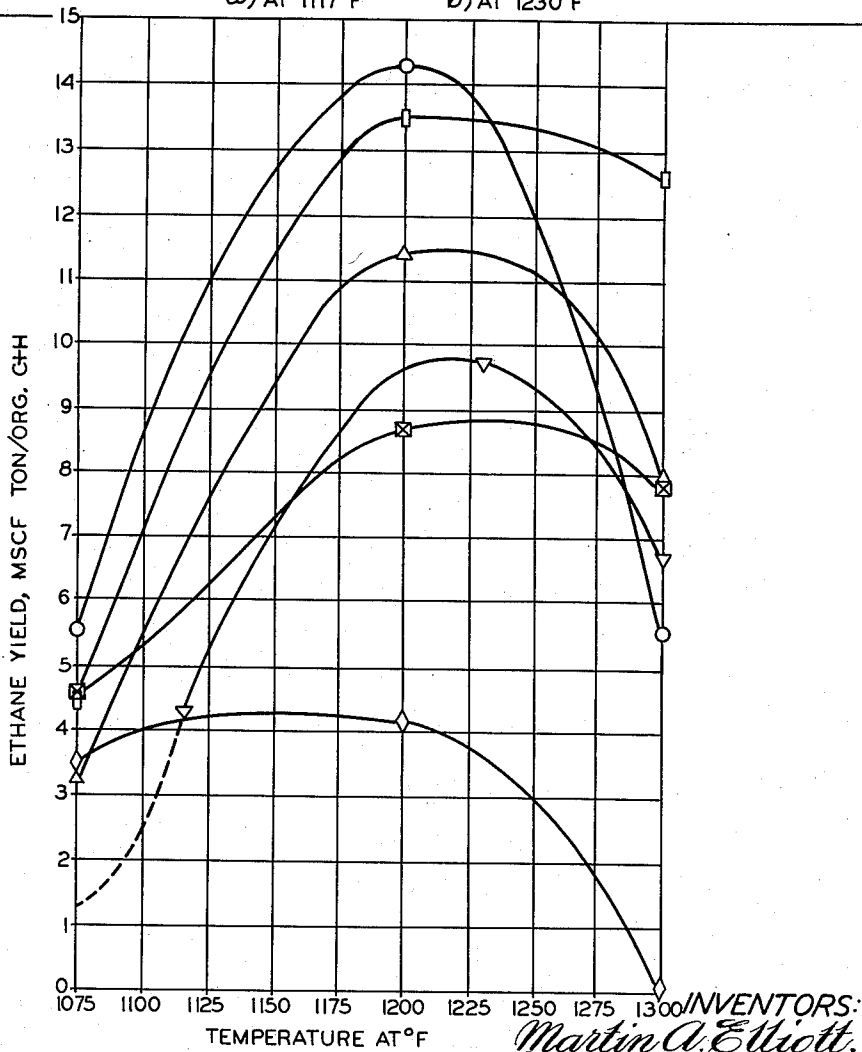
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Fig. 2

MATERIAL	% OF STOICH	INITIAL PRESS.	PRESS. AT 1075°F	PRESS. AT 1200°F	PRESS. AT 1300°F
		PSIG	PSIG	PSIG	PSIG
○ SHALE	100	1710	4705	5125	5540
□ SHALE	200	700	1870	2010	2120
△ SHALE	100	735	2060	2240	2430
▽ GILSONITE	78	1275	3220 <sub>a</sub>	3225 <sub>b</sub>	3190
⊠ SHALE	100	340	1005	1100	1215
◇ SHALE	50	785	2545	3230	4055



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2,991,164

**PRODUCTION OF LOW MOLECULAR WEIGHT HYDROCARBONS FROM SOLID FOSSIL FUELS**

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10 Claims. (Cl. 48-197)

This invention relates to a process for producing from solid fossil fuels such as oil shale, torbanites and asphaltites, a pipeline gas which is interchangeable with natural gas and contains essentially methane and ethane. The present application is a continuation-in-part of our copending application Serial No. 764,804, filed October 2, 1958, now abandoned. The invention is especially useful for producing low molecular weight paraffin hydrocarbons, e.g. ethane, or an ethane-rich gas stream from these fossil fuels. These hydrocarbons are valuable in the production of petrochemicals. The deposits of oil shale in the United States are vast, equivalent to about 3,000 billion barrels of oil. Consequently, this material constitutes an important fuel and hydrocarbon source, providing it can be economically extracted. This is also true of materials related in origin and constitution to oil shale, such as cannel coal and torbanites, and of asphaltites like Gilsonite and glance pitch. In this specification we have chosen to illustrate the invention using oil shale and Gilsonite as feed fuels but it will be understood that the invention is not limited thereto.

It has been proposed heretofore to convert oil shale into liquid fuels by retorting at elevated temperatures. With such a process, considerable success has been achieved in producing fairly good crude shale oil with incidental quantities of fuel gas. The fuel gas produced, however, is not a practical source of ethane or ethylene, and is also seriously lacking in the properties required to make it interchangeable with natural gas. Further, the amount of gas produced in accordance with the prior art process is so low that recovery of its olefin content would not be economical. Moreover, the gas produced in accordance with the prior art contains only unimportant quantities of ethane. In addition to the olefins, the gas contains large quantities of carbon oxides and nitrogen, all of which adversely affect its interchangeability with natural gas. Consequently, the gases having this composition cannot be burned efficiently in appliances which use natural gas, without adjustment of the burners.

Experiments on high-temperature retorting have also been conducted in an effort to increase yields of gaseous products such as ethylene and other unsaturated hydrocarbons. However, in the temperature range where the concentrations of the valuable constituents were high, the total gas yields were low, whereas in the temperature range where the total gas yields were relatively high, dilution of the product gas with hydrogen and carbon oxides resulted. In these experiments, which were conducted at near-atmospheric pressure in the absence of feed hydrogen, even the highest gas yields obtained did not approach those attained in accordance with the present process, and significant amounts of liquid by-products were obtained.

The process of this invention may be employed to convert substantially all of the organic matter in oil shales, torbanites, cannel coals and asphaltites to a high heating value gas which may be employed to produce high-ethane-content streams valuable in the production of petrochemicals. The conversion to ethane is much higher than obtained from petroleum oils and hydrocarbons with similar organic carbon to organic hydrogen weight ratios. This was entirely unexpected, and is an important advantage of this invention.

Although we do not want to be held to any particular

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theory or explanation for our invention, it is believed that these higher ethane yields, under equivalent operating conditions, are caused by distinctive properties of the organic matter of the fossil fuels employed in the practice of the invention. It is well known in the art that the organic matter in oil shales, torbanites and many cannel coals is derived primarily from the remains of algae and plant spores. The fatty and waxy character of these substances is very likely to be preserved through geological time with little change, except that due to polymerization. Since high ethane yields on hydrogasification are associated with aliphatic or cyclic paraffinic materials of both high and low molecular weight, and not with benzenoid materials, it is believed that preferential ethane formation from the feed materials covered in this specification is related to their essentially non-benzenoid structure.

For some time now considerable research work has been going on to develop a process whereby a natural gas consisting primarily of methane can be produced at low cost so as to supplement the available reserves of natural gas in the future, and to overcome local shortages of natural gas. In accordance with the present process such a gas can be produced economically from oil shale and similar solid fossil fuels. Unexpectedly, this substitute gas contains important quantities of ethane, unlike the gases produced by other processes for conversion of coal and lignite to natural gas substitutes. Thus, just as ethane is recovered from natural gas at present to provide the raw material for the production of ethylene, the major aliphatic petrochemical, ethane can be recovered from the substitute gas for the same purpose. The gases produced by the process of this invention have typical properties of 0.5 to 0.75 specific gravity (referred to air=1), 800 to 1000 B.t.u. per standard cubic foot heating value, and up to 25 volume percent ethane content. Unlike gases previously made from oil shale, the product gas of the present invention consists predominantly of methane, ethane and hydrogen, and is low in nitrogen and carbon oxides. Consequently, it has a range of heating values and specific gravities typical of natural gas. The ratio of ethane to methane can be controlled readily by adjustment of process conditions. One embodiment of the process of the invention illustrating the production of a natural gas substitute from Colorado oil shale is shown diagrammatically in the flow sheet of FIGURE 1. Typical quantities of the feed and product are shown.

FIGURE 2 is a graph illustrating the effect of temperature and pressure on ethane yields from Colorado oil shale and Gilsonite.

FIGURES 3 and 4 are flow diagrams illustrating the manufacture of ethylene from oil shale and Gilsonite, respectively, in accordance with modifications of the invention.

The oil shale used in practicing the present invention occurs naturally in many places in the continental United States, particularly rich supplies existing in the State of Colorado. It is estimated that there are about 1200 billion barrels of oil in the Colorado shale deposits alone. These deposits generally yield from 15 to 30 gallons of oil per ton of shale on the basis of the Fischer Assay, a destructive distillation procedure which recovers about 66% of the organic matter as oil and 12% as gas, the remainder being carbonaceous residue. A typical Colorado oil shale analysis is as follows:

Carbon, weight percent:	
Organic -----	10.52
Mineral -----	4.88
Total -----	15.40
Hydrogen, weight percent -----	1.59
Ash, weight percent -----	68.98
Mineral CO <sub>2</sub> , weight percent -----	17.88
Fischer assay, gal. oil/ton -----	22.9

The organic matter, or kerogen, constitutes about 13 weight percent of the above shale. In accordance with the present process, most of this organic matter may be converted to gases rich in methane and ethane.

In accordance with a preferred form of the present invention, when it is desired to produce the aforementioned natural gas substitutes, the fossil fuel is retorted at 1200° to 1300° F., and above 1000 pounds per square inch gauge, with approximately the stoichiometric hydrogen requirement, but not less than 80 percent of this requirement, for complete conversion of the organic carbon to methane. Operation under these conditions results in 85% to 90% conversion of the organic carbon plus hydrogen to an interchangeable fuel gas of the above-mentioned quality. Operation at higher pressures (as high as 5000 to 6000 pounds per square inch gauge) at the same hydrogen to fuel feed ratio results in product gas within the above quality range and in even higher conversions. At these higher pressures, lower operating temperatures can be used to achieve the production of high heating value gases. For example, in a test with the typical Colorado oil shale described above, complete conversion of the organic carbon and hydrogen was approached in the 1100° to 1200° F. temperature range. Operation at pressures as low as 500 pounds per square inch gauge is feasible although the effectiveness of feed hydrogen is reduced. With this shale, operation at lower hydrogen to shale feed ratio (about 50% of stoichiometric) at above 2500 pounds per square inch gauge also resulted in product gas within the above quality range at temperatures as low as 1100° F. Unexpectedly, in spite of the low hydrogen feed ratio, conversions to high heating value gas were in excess of 50%. The temperature limits for the process of the invention when applied to production of natural gas substitutes for fuel uses may range broadly from 1100° to 1400° F. at pressures over 500 pounds per square inch gauge. The preferred minimum quantity of hydrogen in a practical process should be about one-half of the stoichiometric amount to insure conversion of a major portion of the hydrogen and organic carbon in the feed fuel to gaseous paraffin hydrocarbons such as methane and ethane. In the production of a natural gas substitute, the maximum quantity of hydrogen will be limited by dilution of the product gas with unreacted hydrogen to a heating value of less than 800 B.t.u. per cubic foot. Quantities of hydrogen in excess of those required to obtain high conversions could be employed if a separation step is added which permits the removal of enough hydrogen to increase the product gas heating value to 800 B.t.u./s.c.f. or more. Although the excess hydrogen could be recycled, the use of such a separation step in the production of natural gas substitutes may not be economical.

In a batch reactor the reaction to produce interchangeable fuel gases in commercial quantities is carried out in the time required to bring the reactants up to the specified temperature; at the moment of attainment of the specified temperature, the desired product quality is attained. The product gas should never remain in the reactor for over 30 minutes after attaining reaction temperature since decomposition of the paraffin hydrocarbons to carbon and hydrogen may occur. In moving or fluid beds, fossil fuel and gas residence times will depend on the operating pressure, the oil content of the fossil fuel, the bulk density and particle size of the fossil fuel, the geometry of the bed and the nature of gas-solids contacting. Under the optimum operating conditions for pipeline gas production disclosed above, moving or fluid bed reactors would generally give gaseous hydrocarbon production rates of 100 to 1000 standard cubic feet per cubic foot of reactor volume per hour. On that basis, typical Colorado oil shales or their equivalents will require residence times from 5 minutes to one hour, corresponding to gas residence times from 0.5 to 10 minutes

over the normal range of operating conditions. We have found the specified conditions to be critical and they must be observed if the product gas is to be interchangeable with natural gas and if it is to be produced in economical quantities. At temperatures below about 1000° F., the gas produced is merely incidental to the liquid product. Within the preferred range of 1200° to 1300° F. at above 1000 pounds per square inch pressure and a shale feed ratio corresponding to approximately stoichiometric hydrogen supply, over 85% of the organic carbon plus hydrogen is gasified; liquid and residuum are held to an absolute minimum. If the temperature exceeds the upper limit, we have found that the mineral carbonates decompose rapidly yielding carbon oxides, which must be held to a minimum if the gas is to be interchangeable without a carbon oxide removal step, and if fuel economy is to be achieved.

For pipeline gas production, the hydrogen gas required for the hydrogasification reaction preferably is supplied in the theoretical amount sufficient to convert all of the organic carbon and hydrogen in the oil shale to methane; more hydrogen is preferable when high yields of ethane are desired and no lower limit on product gas heating value exists. For example, at 100% of the stoichiometric hydrogen requirements for complete conversion to methane, high yields of ethane have been obtained from Colorado oil shale; at as low as 50% of the stoichiometric hydrogen requirements, ethane yields are only about half as large, although practical net yields of pipeline gas can still be obtained. Further, at 78% of the stoichiometric hydrogen requirements for complete conversion to methane, large yields of ethane have been obtained from Gilsonite, a typical asphaltite having the following properties:

Specific gravity, 60° F./60° F. -----	1.014
Ultimate analysis, weight percent:	
Organic carbon -----	84.99
Hydrogen -----	10.42
Sulfur -----	0.34
Nitrogen -----	0.85
Oxygen -----	13.44
Ash -----	0.23

<sup>1</sup> By difference.

For the typical Colorado oil shale previously described, the feed ratio corresponding to 100% of stoichiometric for conversion of organic carbon and hydrogen to methane amounts to 30.6 standard cubic feet per pound of organic carbon and hydrogen. It will be understood that the specification for hydrogen feed does not imply that methane is always sought as a product, but that it is a simple and generally applicable method of concisely describing this process requirement.

In a preferred form of the invention, process hydrogen requirements are supplied by diverting a portion of the product gas and converting it in the conventional manner into a hydrogen-rich gas by catalytic steam reforming or partial combustion with oxygen under pressure. Preferably the oxides of carbon found in the hydrogen product gas produced by reforming or partial combustion would be removed by conventional methods. This will minimize product gas dilution with low heating value and high specific gravity components, which is undesirable if a natural gas substitute is the desired product. In both fuel gas and ethane production by the process of this invention, the presence of diluents will reduce the hydrogen partial pressure and therefore adversely affect the conversion of organic matter to the desired products. It will be understood, of course, that the hydrogen may be supplied from an external source, thereby increasing the net yield of product gas substantially. A typical example of an operation for production of pipeline gas where hydrogen is produced by catalytic reforming, and

all of the fuel requirements of the process are satisfied with product gas, is given in the flow diagram of FIGURE 1.

To specifically illustrate the invention and its modifications, Table I, following, sets forth data from actual runs made on the batch basis in converting the Colorado oil shale described above to product gases rich in ethane and methane. It can be seen that at temperatures of

about 1200° F., ethane production is favored over methane production, whereas at a temperature of about 1300° F. methane production is favored over ethane production. Furthermore, as the reaction time is increased at a constant temperature of about 1300° F., increased conversion of ethane and unreacted hydrogen to methane takes place, thereby producing a high-methane content gas which can be substituted directly for natural gas.

TABLE I

RUN 11.—0.100 LB. ORGANIC C+H, 50% OF STOICHIOMETRIC

Feed shale:							
Charge weight, lb.	0.8257						
Organic C+H, lb.	0.1000						
Feed hydrogen:							
Initial pressure, p.s.i.g.	785						
Feed ratio:							
Percent of stoichiometric <sup>1</sup>	51.5						
SCF/lb. of organic C+H	15.78						
SCF/ton of shale	3,822						
Operating results:							
Reactor temperature, ° F.	950	1,025	1,075	1,200	1,300	1,330	1,290
Reactor pressure, p.s.i.g.	2,100	2,450	2,545	3,230	4,055	4,145	4,075
Time above room temp., min.	93	103	107	127	147	157	177
Time at nominal run temp. (1,300° F.), min.					0	10	30
Product gas yield: <sup>2</sup>							
SCF/lb. organic C+H	15.76	17.44	17.52	20.54	24.30	24.42	24.56
SCF/ton of shale	3,817	4,224	4,244	4,974	5,886	5,915	5,949
Net B.t.u. recovery, M B.t.u./ton of shale <sup>3</sup>	490	1,511	2,332	3,582	3,696	3,423	3,330
Gasification of organic C+H in shale, percent of total <sup>2</sup>	11.2	31.7	49.5	72.3	76.7	70.8	68.8
Gasification of organic C in shale, percent of total <sup>4</sup>							69.2
Gaseous hydrocarbon space-time yield, SCF/cu. ft. reactor-hr.			294.9	120.6	73.0	57.2	40.6
Thermal space-time yield, M B.t.u./cu. ft. reactor-hr.			618.8	139.4	77.9	59.9	42.8
Spent shale, weight percent of shale charged							81.8
Material balance, percent							97.5
Product gas properties, composition, mole percent:							
N <sub>2</sub> +CO	2.4	3.6	4.4	3.3	4.1	5.4	6.1
CO <sub>2</sub>	3.5	5.1	6.1	10.0	13.8	14.9	16.1
H <sub>2</sub>	85.1	87.2	49.6	3.2	3.8	4.7	5.3
CH <sub>4</sub>	3.5	10.4	18.3	71.4	75.4	74.0	71.6
C <sub>2</sub> H <sub>6</sub>	1.9	5.9	10.4	10.1	2.0	0.6	0.4
C <sub>3</sub> H <sub>8</sub>	1.6	4.4	7.2	0.5	0.1		0.1
Higher paraffins	1.0	2.1	2.8	0.2			
C <sub>2</sub> H <sub>4</sub>			0.1	0.1			
Higher olefins	1.0	1.3	1.1	0.3			
Benzene				0.7	0.7	0.4	0.4
Toluene				0.2	0.1		
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Heating value, B.t.u./SCF	448.2	646.8	837.1	955.6	835.4	785.2	765.1
Specific gravity (air=1)	0.238	0.411	0.565	0.728	0.712	0.708	0.719

RUN 10.—0.050 LB. ORGANIC C+H, 735 P.S.I.G. INITIAL PRESSURE

Feed shale:							
Charge weight, lb.	0.4129						
Organic C+H, lb.	0.0500						
Feed hydrogen:							
Initial pressure, p.s.i.g.	735						
Feed ratio:							
Percent of stoichiometric <sup>1</sup>	102.9						
SCF/lb. of organic C+H	31.52						
SCF/ton of shale	7,633						
Operating results:							
Reactor temperature, ° F.	950	1,025	1,075	1,200	1,300	1,300	1,300
Reactor pressure, p.s.i.g.	1,850	2,030	2,060	2,240	2,430	2,480	2,520
Time above room temp., min.	90	103	109	126	142	152	172
Time at nominal run temp. (1,300° F.), min.					0	10	30
Product gas yield: <sup>2</sup>							
SCF/lb. organic C+H	29.09	31.12	30.56	30.70	31.40	32.04	32.56
SCF/ton of shale	7,241	7,538	7,401	7,435	7,605	7,760	7,886
Net B.t.u. recovery, M B.t.u./ton of shale <sup>3</sup>	158	995	1,895	4,033	4,187	4,117	3,915
Gasification of organic C+H in shale, percent of total <sup>2</sup>	0.5	18.1	37.7	84.7	89.9	88.8	86.8
Gasification of organic C in shale, percent of total <sup>4</sup>							91.9
Gaseous hydrocarbon space-time yield, SCF/cu. ft. reactor-hr.			86.4	60.8	47.9	40.3	30.8
Thermal space-time yield, M B.t.u./cu. ft. reactor-hr.			251.6	98.0	59.1	46.6	32.1
Spent shale, weight percent of shale charged							78.0
Material balance, percent							98.3
Product gas properties, composition, mole percent:							
N <sub>2</sub> +CO	1.1	2.2	3.1	5.5	6.5	6.0	5.3
CO <sub>2</sub>	1.6	2.4	3.1	4.5	9.4	11.4	15.2
H <sub>2</sub>	94.6	84.8	73.7	36.0	13.6	9.6	2.2
CH <sub>4</sub>	1.0	4.6	8.6	31.5	56.8	63.5	74.8
C <sub>2</sub> H <sub>6</sub>	0.5	2.7	5.4	18.8	12.8	8.9	2.4
C <sub>3</sub> H <sub>8</sub>	0.4	1.8	3.3	2.5	0.6		
Higher paraffins	0.4	0.9	1.5	0.7			
C <sub>2</sub> H <sub>4</sub>			0.2				
Higher olefins	0.4	0.5	0.6	0.4	0.1		
Benzene				0.1	0.2	0.2	0.1
Toluene							
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Heating value, B.t.u./SCF	358.4	455.2	585.4	870.2	871.0	844.5	805.5
Specific gravity (air=1)	0.133	0.225	0.331	0.578	0.678	0.692	0.724

TABLE I—Continued

RUN 4.—0.100 LB. ORGANIC C+H, 1,710 P.S.I.G. INITIAL PRESSURE

Feed shale:							
Charge weight, lb.....							0.8257
Organic C+H, lb.....							0.1000
Feed hydrogen:							
Initial pressure, p.s.i.g.....							1,710
Feed ratio:							
Percent of stoichiometric <sup>1</sup> .....							103.4
SCF/lb. of organic C+H.....							31.66
SCF/ton of shale.....							7,669
Operating results:							
Reactor temperature, ° F.....	950	1,025	1,075	1,200	1,300	1,300	1,300
Reactor pressure, p.s.i.g.....	4,255	4,430	4,705	5,125	5,540	5,630	5,720
Time above room temp., min.....	89	97	107	125	140	150	170
Time at nominal run temp. (1,300° F.), min.....					0	10	30
Product gas yield: <sup>2</sup>							
SCF/lb. organic C+H.....	30.81	30.45	31.28	31.50	32.11	32.65	33.21
SCF/ton of shale.....	7,462	7,376	7,577	7,630	7,778	7,908	8,044
Net B.t.u. recovery, M B.t.u./ton of shale <sup>3</sup> .....	234	912	3,228	5,019	4,688	4,639	4,424
Gasification of organic C+H in shale, percent of total <sup>2</sup> .....	5.2	20.6	68.4	110.0	104.2	105.0	100.3
Gasification of organic C in shale, percent of total <sup>4</sup> .....							95.7
Gaseous hydrocarbon space-time yield, SCF/cu. ft. reactor-hr.....			298.3	123.8	100.7	84.6	61.1
Thermal space-time yield, M B.t.u./cu. ft. reactor-hr.....			390.6	184.1	114.5	92.3	64.9
Spent shale, weight percent of shale charged.....							77.2
Material balance, percent.....							97.1
Product gas properties, composition, mole percent:							
N <sub>2</sub> +CO.....	2.1	4.0	6.4	7.0	6.0	4.5	4.3
CO <sub>2</sub> .....	1.3	1.4	2.1	4.7	8.0	11.1	13.1
H <sub>2</sub> .....	94.4	86.5	58.9	23.1	6.1	3.1	3.1
CH <sub>4</sub> .....	0.9	3.5	15.7	40.0	70.6	77.6	77.6
C <sub>2</sub> H <sub>6</sub> .....	0.4	1.9	8.8	22.8	8.6	2.3	1.0
C <sub>3</sub> H <sub>8</sub> .....	0.3	1.0	5.3	0.5	0.2	0.1	0.1
Higher paraffins.....	0.2	1.1	1.9				
C <sub>2</sub> H <sub>4</sub> .....		0.1	0.3	0.2			
Higher olefins.....	0.4	0.5	0.6	0.1	0.5		
Benzene.....				1.5		1.2	0.7
Toluene.....				0.1		0.1	0.1
Total.....	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Heating value, B.t.u./SCF.....	350.0	446.0	739.9	969.4	908.4	887.3	845.6
Specific gravity (air=1).....	0.130	0.214	0.447	0.687	0.674	0.704	0.705

RUN 5.—0.025 LB. ORGANIC C+H, 200% OF STOICHIOMETRIC

Feed shale:							
Charge weight, lb.....							0.2064
Organic C+H, lb.....							0.0250
Feed hydrogen:							
Initial pressure, p.s.i.g.....							700
Feed ratio:							
Percent of stoichiometric <sup>1</sup> .....							206.2
SCF/lb. of organic C+H.....							63.18
SCF/ton of shale.....							15,300
Operating results:							
Reactor temperature, ° F.....	950	1,025	1,075	1,200	1,300	1,295	1,298
Reactor pressure, p.s.i.g.....	1,755	1,845	1,870	2,010	2,120	2,080	2,040
Time above room temp., min.....	88	97	100	120	135	145	165
Time at nominal run temp. (1,300° F.), min.....					0	10	30
Product gas yield: <sup>2</sup>							
SCF/lb. organic C+H.....	59.82	59.18	58.02	57.66	57.34	56.42	55.22
SCF/ton of shale.....	14,486	14,331	14,050	13,963	13,885	13,662	13,372
Net B.t.u. recovery, M B.t.u./ton of shale <sup>3</sup> .....	358	1,887	2,223	3,849	4,442	4,348	4,366
Gasification of organic C+H in shale, percent of total <sup>2</sup> .....	12.0	45.6	56.0	89.7	103.8	104.0	107.8
Gasification of organic C in shale, percent of total <sup>4</sup> .....							100.0
Gaseous hydrocarbon space-time yield, SCF/cu. ft. reactor-hr.....			111.8	32.3	25.8	22.9	18.5
Thermal space-time yield, M B.t.u./cu. ft. reactor-hr.....			412.8	66.1	42.5	33.5	23.7
Spent shale, weight percent of shale charged.....							73.8
Material balance, percent.....							98.6
Product gas properties, composition, mole percent:							
N <sub>2</sub> +CO.....	0.9	1.3	2.0	5.5	8.1	8.6	8.7
CO <sub>2</sub> .....	0.9	1.0	3.3	1.8	3.1	4.1	5.4
H <sub>2</sub> .....	95.5	87.4	81.0	62.1	47.9	41.2	31.9
CH <sub>4</sub> .....	1.0	3.7	5.3	17.9	29.7	38.5	50.7
C <sub>2</sub> H <sub>6</sub> .....	0.5	2.5	3.8	11.7	11.0	7.4	3.2
C <sub>3</sub> H <sub>8</sub> .....	0.4	1.9	2.8	0.6	0.1		
Higher paraffins.....	0.4	1.1	1.1	0.2			
C <sub>2</sub> H <sub>4</sub> .....		0.5	0.3			0.1	
Higher olefins.....	0.3	0.6	0.3	0.1			
Benzene.....	0.1		0.1	0.1	0.1	0.1	0.1
Toluene.....							
Total.....	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Heating value, B.t.u./SCF.....	362.1	472.7	506.1	625.7	671.9	676.0	692.0
Specific gravity (air=1).....	0.120	0.202	0.269	0.360	0.440	0.466	0.504

<sup>1</sup> Stoichiometric for complete conversion of organic C+H in shale to methane.<sup>2</sup> Calculated from observed reactor pressure and temperature, and initial reactor free volume, assuming ideal gas law.<sup>3</sup> Product of gas yield and heating value, less thermal input of feed hydrogen.<sup>4</sup> Calculated from carbon analysis of residue.<sup>5</sup> Value doubtful.



Thus, in the embodiment of the present invention carried out for the purpose of producing an ethane-rich stream in high yields from the specified fossil fuels, the reaction conditions are adjusted to lower temperatures and gas residence times, and to higher pressures and hydrogen to shale feed ratios, so as to favor ethane over methane formation. As illustrated in FIGURE 2, with results obtained with the oil shale and Gilsonite previously described, optimum ethane yields were realized at the lower end of the preferred 1200° to 1300° F. range. It can also be seen that increases in feed ratio from 50% to 200% of stoichiometric, and increases in pressure from 1000 to over 5000 pounds per square inch gauge, significantly increase ethane formation. We find that the temperature specified is especially critical and that the product gas must be withdrawn from the reaction zone immediately upon attainment of the specified temperature if processing in a batch reactor or the ethane product will be decomposed to methane by reaction with hydrogen. Processing with a moving or fluid bed also requires close control of residence time, with values toward the lower end of the 0.5 to 10 minute range set forth above. In this manner, ethane yields of 1100 to 1700 standard cubic feet per ton of shale, with mole percentages of 12% to 23% have been produced from the oil shale described above at hydrogen feed ratios of about 100 to 200 percent of stoichiometric requirements. Table II, below, is supplied to set forth specific examples of the operating conditions and results obtained in practicing the modification of the present invention for the production of ethane. These data provided the basis for the integrated processing schemes illustrated in FIGURES 3 and 4. The examples given utilize as charging materials the previously described 22.9 gallon per ton oil shale, and Gilsonite.

TABLE II

Charging material.....	Gilsonite		Oil shale	
Run No.....	105		25	
Feed ratio:				
Percent of stoichiometric <sup>1</sup>	78.1		276	
SCF/ton of charge.....	55,980		20,500	
Temperature, ° F.....	1,230		1,200	
Pressure, p.s.i.g.....	3,225		2,010	
Time above room temp., min.....	123		120	
Conversion of org. C to ethane, weight percent.....	34.0		48.4	
Conversion of org. C+H to gas, weight percent.....	78.9		89.7	
Product gas yields:	SCF/ton Gil.	SCF/ton org. C+H	SCF/ton Shale	SCF/ton org. C+H
N <sub>2</sub> +CO.....	50	52	768	6,342
CO <sub>2</sub> .....	343	359	251	2,073
NH <sub>3</sub> .....	19,433	20,366	13,871	114,540
H <sub>2</sub> .....	19,143	20,062	2,499	20,636
CH <sub>4</sub> .....	9,253	9,698	1,634	13,493
C <sub>2</sub> H <sub>6</sub> .....	50	52	84	694
C <sub>3</sub> H <sub>8</sub> .....	50	52	28	231
Higher paraffins.....	50	52	14	116
Higher olefins.....	343	359	14	116
Benzene.....	147	154		
Toluene.....	98	103		
Higher aromatics.....				
Total.....	48,960	51,309	19,163	158,241
Product gas properties, composition, mole percent:				
N <sub>2</sub> +CO.....			4.0	
CO <sub>2</sub> .....	0.1		1.3	
NH <sub>3</sub> .....	0.7			
H <sub>2</sub> .....	39.7		72.5	
CH <sub>4</sub> .....	39.1		13.0	
C <sub>2</sub> H <sub>6</sub> .....	18.9		8.5	
C <sub>3</sub> H <sub>8</sub> .....	0.1		0.4	
Higher paraffins.....	0.1		0.1	
Higher olefins.....	0.1		0.1	
Benzene.....	0.7		0.1	
Toluene.....	0.3			
Higher aromatics.....	0.2			
Total.....	100.0		100.0	
Specific gravity (air=1).....	0.488		0.281	

Since, in the production of ethane, increases in hydrogen feed will increase ethane yields, and there is no limitation on the product gas heating value in this embodiment of the invention, the hydrogen rate can be increased to considerably in excess of 100% of the stoichiometric requirements for conversion to methane. In a preferred form of the process of this invention as applied to production of ethane-rich gas from oil shale, a charging material characterized in practice by an ash content of over 50 weight percent, advantage can be taken of this wider range of practical hydrogen feed rates. In this embodiment of the invention, if the mineral matter content of the charging material is so great that the heat recoverable from the hot spent charging material leaving the reaction zone is greater than that required to preheat the minimum amount of process hydrogen required on the basis of ethane yield considerations, it may be preferable to use excess hydrogen as a means of heat recovery from the spent charging material. This heat can then be given up to the incoming fresh charging material, and the excess hydrogen recycled. Thus, with high mineral matter content feedstocks such as oil shales, which are also characterized by remaining in a solid, non-agglomerated state at reaction conditions, the following steps must be provided for:

(1) The fresh shale must be raised to reaction threshold temperature (approximately 1000° to 1050° F.), preferably by heat exchange with the hot product gases moving countercurrent thereto as shown in FIGURE 3. The entering hydrogen flows counter to the spent shale having the reactor to recover the heat therefrom.

(2) The preheated shale and hot hydrogen must be reacted under conditions insuring that exothermic heat of reaction raises the temperature of the reacting system preferably not about 1300° F. in the case of pipeline gas production, and preferably not above 1250° F. in the case of ethane production.

(3) The hydrogen feed rate must be at least 50% of the stoichiometric requirements for methane formation, and preferably sufficient to recover the sensible heat from the spent shale so as to insure fuel economy of the process, but not in excess of the amount which will reduce product gas ethane content to less than 5 mole percent.

Below, a heat balance is given for the case in which a typical Colorado oil shale with a Fisher assay of 22.9 gallons of oil per ton is processed at approximately 2000 pounds per square inch gauge, 1200° F. and a hydrogen feed rate equivalent to 276% of the stoichiometric requirements for methane formation.

Hydrogasifier heat balance

Heat supplied, B.t.u./ton shale fed:	
(1) Heating of shale from 77° to 1200° F (includes sensible heat, heats of decomposition, heats of vaporization) .....	810,000
(2) Sensible heat of hydrogen fed (20.6 M s.c.f./ton shale fed) .....	421,000
(3) Heat losses .....	50,000
<b>Total heat supplied .....</b>	<b>1,281,000</b>
Heat recovered, B.t.u./ton shale fed:	
(1) Heat of hydrogasification (at 1200° F.) of hydrocarbon constituents .....	376,000
(2) Sensible heat of spent shale from 1200° F. to 390° F. outlet temperature .....	421,000
(3) Sensible heat of gaseous products from 1200° F. to 150° F. outlet temperature .....	484,000
<b>Total heat recovered .....</b>	<b>1,281,000</b>

<sup>1</sup> Stoichiometric for complete conversion of organic C+H to methane.  
<sup>2</sup> Based on experimental data for a test with 206.2% of stoichiometric hydrogen requirements (15,300 SCF/ton).

It can be seen that when gaseous products are dis-

charged at 150° F. and spent shale is discharged at 390° F., no external heat would be required upon assumption of heat losses of 50,000 B.t.u. per tone of shale. After bringing the reaction zone of the reactor to above threshold temperature for the hydrogenolysis reactions, the process takes place under a balanced or autothermic condition. The initial heating of the shale in the retort to reaction temperature can be accomplished by preheating hydrogen and passing it directly into the reaction zone.

When richer shale is used, that is, shale containing less mineral matter, the heat requirements for retorting per unit quantity of ethane produced, as well as the heat recoverable from the spent shale, is decreased. In contrast, the heat released as a result of the exothermic hydrogasification reactions remains approximately constant per unit quantity of ethane produced. As a result, insufficient hot spent shale may remain to preheat the required amounts of hydrogen, and insufficient mineral matter may be fed in the raw shale to provide a heat sink for the exothermic hydrogenolysis reactions.

In the event that an exceedingly lean shale is to be processed, it may not be economical to use a correspondingly greater amount of hydrogen to recover the heat contained in the spent shale to provide a means for preheating the fresh shale to reaction threshold temperature. Instead, it may be preferred to limit the amount of hydrogen feed so as to avoid excessive dilution of the product gas and attendant increase in ethane recovery costs and gas handling costs. Spent shale would then be rejected at relatively high temperature and heat content. The heat loss from the process in this manner would have to be supplied from an external source.

In case that a relatively low ash content material such as an asphaltite is used as a charging material, a reactor system based on countercurrent flow of solids and gas may not be feasible since the charging material may soften, agglomerate or liquefy. In this case, conventional fluid or moving bed reactors involving the use of solid heat transfer media will be most suitable. For example, melted Gilsonite may be introduced onto a stream of preheated solids and contacted with hydrogen either in a fluid or moving bed. Reactor temperatures could be adjusted by control of the temperatures of the entering heat transfer solids, the hydrogen and the charging material. If, under given reaction conditions, the over-all process requires additional heat, it could be supplied, in a separate vessel, by combustion of carbonaceous material deposited on the heat transfer solids, with possible introduction of an external source of fuel, if required. In addition, the feed hydrogen could be preheated, such as by heat exchange with the gaseous products. In case the over-all process releases more heat than required to maintain the desired reactor temperature, heat could, for example, be removed by steam generation in a suitably constructed separate vessel through which the heat transfer solids circulate.

Many other embodiments of apparatus and methods of processing, designed to be specifically suited for the charging material under consideration, will be apparent to those skilled in the art.

The examples given in FIGURES 3 and 4 of the embodiments of the present invention for production of an ethane-rich gas from solid fuels belonging broadly to the classes of oil shales and asphaltites, are similar in respect to the method of hydrogen supply and the method of product recovery. They differ only in respect to the modifications in the hydrogasification step which must be made to process these two different classes of charging materials. In FIGURE 3, which illustrates the conversion of a material of relatively high mineral matter content, which has the additional property of forming a non-agglomerating residue, countercurrent contact of hydrogen and charging material is the preferred method. This permits the greatest heat economy since it allows recovery

of the sensible heat in the spent shale with feed hydrogen, and recovery of the sensible heat in the product gas by heat exchange with the raw shale. In the example given in FIGURE 4, where Gilsonite is the charging material, the residue from the hydrogasification step does not contain a significant amount of sensible heat. Furthermore, a contacting method must be selected which will permit effective handling of a material which will soften and liquefy and may tend to agglomerate. Thus, conventional moving bed or fluid-bed techniques utilizing a suitable heat transfer solid could be employed. These techniques do not necessarily require countercurrent contacting of hydrogen and charging material.

The important feature of the specific embodiments of the present invention disclosed herein, as illustrated in FIGURES 3 and 4, is the great economy in raw material requirements which results from utilizing the hydrogen streams remaining after separation of ethane, and of the pyrolysis products of ethane, in the production of an ethane-rich stream by hydrogasification of the specified solid fossil fuels under the critical conditions specified herein. Alternate prior methods of processing these fossil fuels, such as high temperature retorting and pyrolysis in the absence of hydrogen and at pressures ranging from one to two or three atmospheres, will produce significant quantities of ethylene, but will not result in the very high yields attainable when practicing the present invention.

In the preferred method of operation illustrated in FIGURES 3 and 4, namely, utilization of available tail gas streams for production of the hydrogen-rich gas needed in the hydrogasification step, these tail gas streams are obtained in two separation steps:

Separation I in which ethane and higher molecular weight hydrocarbon constituents are separated from the product gas, leaving a tail gas stream consisting of hydrogen, methane, and sometimes carbon monoxide, which is used as part of the feed gas to the catalytic reforming unit in which the hydrogen is produced; the remainder of this stream is available as fuel. In separation I, carbon dioxide, sulfur compounds and ammonia are also removed from the product gas stream; nearly quantitative conversion of the nitrogen content and sulfur content of the charging material to hydrogen sulfide and ammonia, respectively, is normally obtained in the hydrogasification step, although as a result of the limits of accuracy of the gas analyses no hydrogen sulfide was actually detected in the product gases of the examples given in FIGURES 3 and 4, and ammonia was detected only in the example given in FIGURE 4.

Separation II in which pyrolysis products of ethane are separated into (1) a tail gas stream which is very rich in hydrogen, (2) the ethylene product which also is associated with minor amounts of acetylene under the pyrolysis conditions given in the examples of FIGURES 3 and 4, (3) an ethane recycle stream which is combined with the fresh ethane feed to the pyrolysis step and (4) heavy ends consisting of C<sub>3</sub> and higher molecular weight hydrocarbons. Because of the high hydrogen content of the tail gas from separation II, it is conserved in its entirety as a feed gas to the reformer. Thus, it is apparent that in the operations shown in FIGURES 3 and 4 no process feed other than the solid fossil fuel charging material is required. Further, a significant portion of all of the fuel requirements of the process can be met with the portion of the tail gas stream from separation I not required for hydrogen production. The hydrogasification step will not normally require an external source of fuel except during start-up; however, as shown, it is convenient to use some fuel to melt an asphaltite where this is the charging material.

The purity of the hydrogen used in the hydrogasification reaction is not critical and may be as low as, say 90%. Even lower purity would not be a critical limitation to the process except that unnecessary dilution with un-

reacted constituents is equivalent to a reduction of the total pressure during the hydrogasification step. Any suitable process for producing hydrogen from tail gases is satisfactory. Similarly, one of any number of well known schemes may be used in separations I and II.

The ethylene pyrolysis step is also conventional; higher yields of ethylene can be obtained by adding a portion of the hydrocarbons recovered as heavy ends in separations I and II to the ethane feed, or by pyrolyzing them separately. The pyrolysis step can be conducted over a considerable range of temperatures, pressures and steam to hydrocarbon ratios fully disclosed in the prior art. It is also possible to significantly alter the product distribution of the ethane pyrolysis step so as to produce significant quantities of acetylene, or to produce acetylene predominantly. This method of processing is also fully described in the prior art.

One unexpected result when practicing the hydrogasification step of this invention was the relatively high ethane yields obtained from Colorado oil shale and Gilsonite compared to those obtained from petroleum oils and hydrocarbons with similar organic carbon to organic hydrogen weight ratios. This is illustrated in the table below:

TABLE III

Material	Weight ratio, org. C/org. H	Run No.	Feed ratio, percent of stoichiometric	Temperature, ° F.	Pressure, p.s.i.g.	Ethane yield, s.c.f./ton org. C+H
Oil Shale.....	1 6.62	10	102.9	1,200	2,240	11,544
Do.....	1 6.62	4	103.4	1,200	5,125	14,368
Gilsonite.....	8.16	105	78.1	1,230	3,225	9,698
Red. Crude Oil.....	7.04	14	93.6	1,200	3,380	9,220
Bunk. "C" Fuel						
Oil.....	8.51	42	95.9	1,207	4,380	7,820
n-Hexane.....	5.107	134	120.5	1,230	4,050	11,580
Cyclohexane.....	5.958	96	98.9	1,195	3,535	12,720
Do.....	7.149	135	84.3	1,190	3,140	8,140
n-Decane.....	5.416	101	112.0	1,213	3,835	13,590
Decalin.....	6.620	97	90.3	1,255	3,405	9,420

<sup>1</sup> Value may be low, due to presence of mineral water.

Other modifications of the invention will be evident to those skilled in the art without departing from the scope and spirit of the invention.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. A process for making an ethane-rich gas which comprises hydrogenating a fossil fuel taken from the group consisting of oil shales, torbanites, cannel coals and asphaltites in a reaction vessel in the presence of at least 50% of the stoichiometric quantity of hydrogen required to convert all of the organic carbon and hydrogen in the fossil fuel to methane at a reaction temperature of 1100° to 1300° F. and a pressure of over 1000 pounds per square inch gauge, removing the product gas from the vessel upon attaining reaction temperature, and separating ethane from the product gas.

2. The process of claim 1 wherein said hydrogen is supplied from the tail gas remaining after removal of ethane from the product gas.

3. A continuous process for converting oil shale characterized by a mineral matter content of more than 50 weight percent to an ethane-rich gas which comprises subdividing said shale, introducing said subdivided shale into a reaction vessel, heating said shale to a temperature of 1100° to 1300° F. while maintaining said vessel at a

pressure of 500 to 5000 pounds per square inch gauge and feeding hydrogen into said vessel in a quantity of at least 50% of the stoichiometric quantity required to convert all of the organic carbon and hydrogen in said shale to methane and at a rate that will provide a gas residence time of from 0.5 to 10 minutes, said shale being moved through said vessel at a rate which provides a mean residence time of from 5 minutes to one hour.

4. A process for making ethylene which comprises hydrogasifying a fossil fuel taken from the group consisting of oil shales, torbanites, cannel coals and asphaltites at a temperature of 1100° to 1300° F. and a pressure in excess of 1000 pounds per square inch gauge to produce a product gas rich in ethane, methane and hydrogen, separating the ethane from said product gas, recycling part of the tail gas for reformation to hydrogen for supplying a portion of the hydrogen requirements for said hydrogasification reaction, pyrolyzing said ethane to convert it to an ethylene-rich gas, separating said ethylene from the other gaseous products of said pyrolyzing step and recycling said gaseous products for reformation with said part of the tail gas to supply the remaining hydrogen requirements for said hydrogasification reaction.

5. The process of claim 4 wherein said fossil fuel is Gilsonite.

6. The process of claim 4 wherein the portion of said tail gas not required for reformation to hydrogen is used to meet a portion of the fuel requirements.

7. A process for making an ethane-rich gas from an asphaltite which comprises melting said asphaltite and contacting it with preheated hydrogen to convert the molten material to an ethane-rich gas, said conversion being carried out at a temperature of 1100° to 1300° F., and a pressure of at least 1000 pounds per square inch gauge, the quantity of said hydrogen being equivalent to at least 50% of the stoichiometric amount required to convert all the organic carbon and hydrogen in the asphaltite to methane, and separating the ethane from said ethane-rich gas.

8. The process of claim 7 wherein said hydrogen is produced from the tail gas remaining after separation of said ethane.

9. A process for making an ethane-rich gas which comprises hydrogenating a fossil fuel taken from the group consisting of oil shales, torbanites, cannel coals, and asphaltites in a reaction vessel in the presence of at least 80% of the stoichiometric quantity of hydrogen required to convert all the organic carbon and hydrogen in the fossil fuel to methane at a reaction temperature of 1100° to 1300° F. and a pressure of over 500 pounds per square inch gauge to convert organic carbon and hydrogen in said fossil fuel to a product gas consisting predominantly of methane, ethane, and hydrogen and low in carbon monoxide and nitrogen, said hydrogen having a purity of at least 90%.

10. The process of claim 9 which includes the additional steps of removing the product gas from the vessel upon attaining the reaction temperature and separating the ethane from the product gas.

## References Cited in the file of this patent

## UNITED STATES PATENTS

2,174,196	Rogers .....	Sept. 26, 1939
2,595,234	Eastman .....	May 6, 1952
2,609,283	Kalbach .....	Sept. 2, 1952
2,687,950	Kalbach .....	Aug. 31, 1954