

The analyses were carried out by gas chromatographic techniques. Separate determinations were done for C_1 - C_5 aliphatics and aromatics. Since the samples were taken at the end of the runs the results represented average yields and did not reveal changes during the experiment.

Preliminary work revealed that the oil shale feed rates had an effect on the yields. Yields increased with decreasing feedrates until they stabilized at around 0.1 gsec^{-1} . This phenomenon was also reflected in the temperature changes during pyrolysis; at higher feed rates temperature drops were 15-20% while with 0.1 gsec^{-1} they did not exceed 2-3%. Apparently heat transfer rates optimized only at low feed rates. (At higher feed rates the particles formed agglomerates which resulted in less favorable heat transfer conditions; therefore the yields were also unsteady.)

Results

Yields of pyrolysis products were investigated as functions of temperature, residence time and carrier gas. In order to estimate the proper range for the residence time, heat transfer calculations were carried out for a series of particle sizes assuming spherical shapes. The calculations showed that the expected residence times were less than 2 sec for particles between diameters of 5×10^{-5} and 2.5×10^{-4} m.

Our experimental strategy consisted of a two-level factorial and a quadratic model. The factors and their levels are depicted in Table 2. The yields of the major pyrolysis products at the proper combinations of the factor levels are shown in Table 3.

We also identified other products (propane, C_3 aliphatics, toluene, xylene, etc.) but did not determine amounts quantitatively. Inspecting the results for the two-level factorial design (Exp 1-8 in Table 3) revealed that this model was inadequate. This prompted us to augment it to a full quadratic design (Exp 9-14 in Table 3), which had the following general form:

$$\text{yield} = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_4x_1x_2 + a_5x_1x_3 + a_6x_2x_3 + a_7x_1^2 + a_8x_2^2 + a_9x_3^2$$

The precision of the data are reflected by experiment 15, 16 and 17 which were replicate runs. The relative errors were less than 10 percent for each product except propylene. The resulting equations were computer plotted as function of temperature (x_1) and residence time (x_2) at three levels of the carrier gas ($x_3 = 100\%N_2$, $50/50\% N_2/CO_2$, $100\% CO_2$).

These cross sections of the experimental space provided a visual representation of the yield distribution and showed the highest yield regions.

For ethylene the maximum yields (60.3-64.5 lbs/ton shale) were computed to be between 850 - 980°C with less than 0.8 sec residence time at 100%

nitrogen (Figure 3). We carried out two experiments in this region and confirmed the yields at 60.6 and 62.4 lbs/ton shale. Yields in the maximum region declined for the two other levels of the carrier gas by about 8 percent per level. The lowest yields were indicated at high temperatures and longer residence times in accord with experience that ethylene is consumed under such conditions.

For methane the highest yield region (52.3-55.4 lbs/ton shale) was between 880-1070°C with more than 0.9 sec residence time and at 100% nitrogen level. The yields decreased by only about 3 percent per level for the other levels of the carrier gas. The yields decreased toward lower temperatures and short residence times.

Ethane yields were highest (6.8-7.4 lbs/ton shale) at low temperatures (<720°C) and longer residence times (>1.2 sec). Ethane showed no change with respect to carrier gas. The lowest yield region was indicated at higher temperatures and longer residence times.

Maximum acetylene yields (7.8-8.5 lbs/ton shale) were computed for high temperatures (>1000°C) and short residence times (<0.6 sec). The yields - similarly to those of ethane - were not sensitive to the carrier gas. The yields changed linearly with temperature and residence time reaching minimum values at low temperatures and long residence times.

For propylene the highest yield region (27.0-28.7 lbs/ton shale) was at low temperatures (<720°C) and short residence times (<0.3 sec) at 100% nitrogen level. The yields declined only slightly for the other levels of the carrier gas (about 3% per level). The yields decreased with increasing temperature and residence time.

C₄ products showed a similar distribution pattern to that of propylene. Maximum yields (38.2-40.6 lbs/ton shale) were indicated at lower temperatures (<720°C) and short residence times (<0.3 sec).

Benzene displayed a bimodal plot with maximum yields above 900°C and at both short (~ 0.2 sec) and long (~ 1.5 sec) residence times. The highest yields (19.4-20.4 lbs/ton shale) were computed for the 50/50 mixture of nitrogen and carbon-dioxide and the yields declined by about 30 percent for the two other levels of the carrier gas.

Table 4 shows the conversion of kerogen to ethylene, total hydrocarbons and the conversion of carbonates. The highest conversion to ethylene was 17 percent and to hydrocarbons 42 percent (Exp. 4). Based on the H/C ratio of the feedstock (Table 1), theoretically 84 percent of it could be converted to ethylene. The highest measured yield corresponded to 20 percent of this limit.

To determine the extent of carbonate decomposition is important because in one-step pyrolysis raw oil shale is processed and carbonate (calcite, dolomite etc.) decompositions represent a heat sink which can adversely influence the economics of the process.

Carbonate decompositions seemed to depend on all three factors and varied from 2.3% (Exp. 9) to 74.2% (Exp. 3). The data also show that in those runs where carbon dioxide was the carrier gas (Exp. 5,6,7 8 and 14) less decomposition took place than in runs carried out with nitrogen (Exp. 1,2,3,4 and 13.) This can be explained by the excess concentration of carbon dioxide which shifted the carbonate decomposition equilibria back toward the reactants. In the accompanying economic analysis we assumed conservatively that all carbonate was decomposed.

Economics

The experimental results provided the input for an economic evaluation focusing on ethylene as the main product. The basis for the cost estimate and the breakdown of the economics are shown in Table 5 and Table 6. In the process we envisage to apply Occidental's patented pyrolysis system (13).

The total capital investment was estimated to be \$737 MM for the plant producing 871 MM lbs ethylene/year. The byproduct credits were projected for mid 1982 from present market prices.

In the evaluation mined shale was considered at zero cost. The reason was that we assumed that the process will be associated with Occidental's modified in situ retorting technology requiring that 20-25% of the oil shale has to be mined out.

In our analysis we assumed 29¢/lb ethylene price and this gave 20% DCF-ROI. With 25¢/lb ethylene price the DCF-ROI is 18%, still an attractive value.

As a final comment, we realize that a more realistic economic evaluation should consist of a comparative analysis including two-step pyrolysis, aboveground retorting, and direct utilization of oil shale in energy production (such as fluidized bed combustion).

Conclusions

Short residence time pyrolysis of finely ground oil shale produces low molecular weight aliphatics and aromatics. An experimental design study successfully determined the optimum yield regions for several pyrolysis products as function of temperature (700-1100°C), residence time (0.2-1.5 sec) and two carrier gases (nitrogen and carbon dioxide). The economics of a plant based on one-step pyrolysis was also evaluated and suggested attractive profitability.

Acknowledgement

The authors express their gratitude to Ms. V. Kobayashi and Mr. J. Colanino for their competent work in the experimentation.

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Table 1

ORGANIC CONTENT OF THE FEEDSTOCK (wt %)

Carbon	13.03
Hydrogen	1.82
Sulfur	0.23
Nitrogen	0.58
H/C (atomic)	1.68
Kerogen (excluding oxygen)	15.7
Fischer Assay	28 gallon/ton

Table 2

FACTORS AND LEVELS ESTABLISHED FOR THE EXPERIMENTAL MODELS

Factors	Levels	
	Low	High
Temperature (x_1)	700	1100 (°C)
Residence Time (x_2)	0.2	1.5 (sec)
Carrier Gas (x_3)	N ₂	CO ₂

Table 3
REACTION CONDITIONS AND PRODUCT YIELDS

Exp.	Temp. (°C)	Residence Time (sec)	Carrier Gas	Yields (lbs/ton)								
				CH ₄	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₄ H ₁₀	C ₆ H ₆	H ₂	CO
1	825	.2	N ₂	22.2	1.2	50.3	5.2	19.5	23.7	7.0	1.7	8.6
2	815	1.5	N ₂	49.0	.7	53.6	6.0	7.1	4.6	10.4	3.6	17.2
3	989	1.5	N ₂	50.2	5.5	30.7	1.0	7.1	1.9	13.9	9.9	110.6
4	1013	.2	N ₂	39.8	9.8	58.4	1.4	16.9	3.9	14.9	6.1	71.9
5*	796	0.2	CO ₂	22.8	0.9	36.2	4.6	21.5	26.5	6.3	1.2	15.9
6*	829	1.5	CO ₂	34.9	0.7	45.5	5.9	14.5	11.3	11.0	2.3	14.5
7	992	1.5	CO ₂	47.5	5.4	28.3	.9	8.3	1.9	15.9	9.2	112.1
8	1015	.2	CO ₂	36.3	12.8	41.6	.6	15.3	4.3	10.0	5.1	121.2
9	699	.7	N ₂ /CO ₂	13.9	.1	26.6	5.6	18.5	25.8	4.1	.6	13.4
10	910	1.5	N ₂ /CO ₂	54.4	2.3	43.3	1.7	1.8	2.8	22.2	5.6	60.1
11	1090	.7	N ₂ /CO ₂	42.6	5.9	7.9	.1	2.9	.4	14.5	13.5	204.7
12	904	.2	N ₂ /CO ₂	26.1	3.0	54.7	3.7	15.8	19.6	20.0	2.2	27.7
13	915	.7	N ₂	45.2	3.1	59.2	2.5	3.3	5.3	7.3	4.4	30.1
14	903	.7	CO ₂	46.0	3.0	51.6	2.0	4.0	6.1	12.4	4.7	33.6
15	910	.85	N ₂ /CO ₂	49.8	3.2	55.8	1.7	1.4	4.7	13.1	5.3	41.2
16	908	.85	N ₂ /CO ₂	50.1	2.9	55.1	2.1	3.0	4.4	12.5	5.0	42.0
17	913	.85	N ₂ /CO ₂	52.7	3.2	56.6	1.9	2.3	4.2	12.7	5.4	44.0

* Average of two experiments

Table 4
CONVERSION OF KEROGEN AND CARBONATES

Exp. #	Conversion %		
	To Ethylene	To Total Hydrocarbons*	Carbonate Conversion
1	14.6	37.4	21.7
2	15.5	38.1	54.0
3	8.9	32.0	74.2
4	17.0	42.1	57.5
5	10.5	34.4	20.3
6	13.2	35.9	19.0
7	8.2	31.4	66.2
8	12.1	35.1	50.4
9	7.7	27.4	2.3
10	12.6	37.3	48.9
11	2.3	21.5	41.1
12	15.9	41.4	30.4
13	17.2	36.5	47.9
14	15.0	36.3	33.2
15	16.2	37.6	46.5**
16	16.0	37.7	
17	16.4	38.7	

*Hydrocarbons from Table 3.

**Average of Exp. 15, 16 and 17.

Table 5

BASIS FOR PRODUCTION COST ESTIMATION

Start-up:	Mid-1982
Plant Capacity:	40,000 tons oil shale/day 871 MM lb ethylene/year
Shale Grade:	28 gallons per ton
Operating time:	7920 hours per year
Project life:	15 years
Construction period =	3 years
Federal Tax =	50%
Tax credit =	10%
Depreciation method =	Sum of year digits, 11 years
Construction period =	3 years
Sales Build-up =	3 years, initial fraction of full capacity = 60%

Table 6

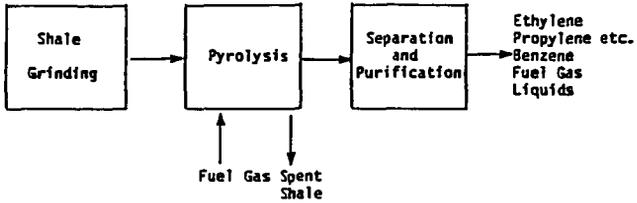
ETHYLENE FROM OIL SHALE, PRELIMINARY ECONOMIC DATA

Estimated Fixed Capital Investment	\$ 737,000 M
Annual Fixed Costs	
Operating Labor (24 shift positions)	\$ 5,590 M
Maintenance (4.5% Fixed Capital)	\$ 33,330 M
Plant Overhead	\$ 5,472 M
Local Tax and Insurance (2.5% Fixed Capital)	\$ 18,425 M
Annual Variable Costs	
Electricity (5¢ per kWh)	\$ 19,031 M
Mined shale (30.3 lb shale/lb ethylene)	----
Annual Byproduct Credit	
Propylene (64.5 MM lb, 25¢/lb)	-\$ 16,125 M
Fuel Gas (3.9 x10 ⁶ MM BTU, \$5/MM BTU)	-\$ 19,550 M
C ₄ Stream (56.6 MM lb, 18¢/lb)	-\$ 10,188 M
BTX (331 MM lb, 23¢/lb)	-\$ 76,130 M
Heavy Fuel Oil (218 MM lb, 6¢/lb)	-\$ 13,080 M
Sales, General and Administrative (2% sale)	\$ 5,052 M
Gross Ethylene Revenue (871 MM lb, 29¢/lb)	\$ 252,590 M
Annual Capital Charges	\$ 300,763 M
Profitability (Discount Cash Flow-Return on Investment)	20%

Figure 1

WAYS TO CONVERT OIL SHALE TO CHEMICALS

1) One-Step Pyrolysis



2) Two-Step Pyrolysis

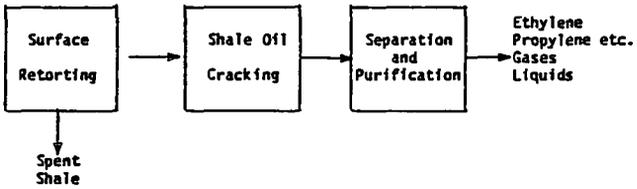


Figure 2

PYROLYSIS APPARATUS

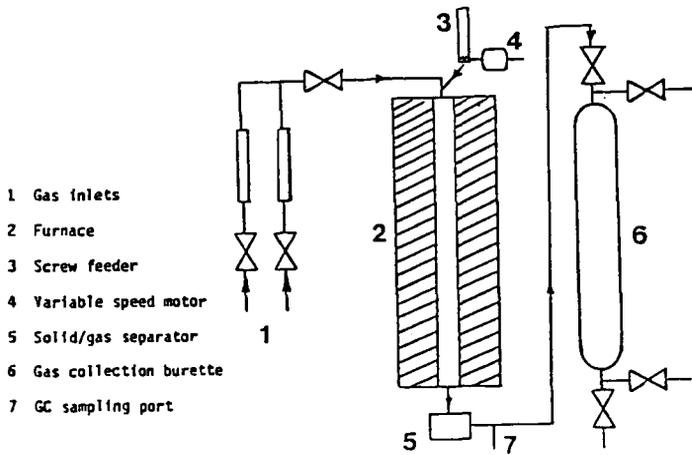


Figure 3

