THERMAL CONVERSION OF OIL-SHALE KEROGEN IN THE PRESENCE OF CARBON MONOXIDE AND WATER

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INTRODUCTION

The decrease in the world's oil supply must be supplemented by alternate energy resources. One of these alternate energy resources is oil shale. Oil shale is composed of insoluble organic material (kerogen), soluble organic material (bitumen), and inorganic minerals. Although oil shale contains no oil, the insoluble organic kerogen can be converted to oil by heat.

Both aboveground and underground retorting techniques (7, 11, 12, 16,)[1] have been used to process oil-shale kerogen. Some of these processes utilize solvent, hydrogen, and steam (3, 6, 8, 9, 14); however; present technology can be improved relative to increased yields of products with less environmental impact (13). The CO-H_2O reaction to be discussed in this report is a method by which oil-shale kerogen is converted to gaseous and soluble products in the presence of molecular or reactive hydrogen formed during the water shift reaction shown below:

$$CO + H_2O \rightleftharpoons H_2 + CO_2$$

The converted products can be recovered along with water-soluble minerals. The major advantage of this reaction is that more of the insoluble kerogen is converted to gaseous and soluble products in the presence of CO and H_2O than is converted by conventional methods at the same temperature. Also removal of the water-soluble minerals would make the shale residue inert to water leaching on disposal and the water-soluble minerals would be available for commercial use.

In recent years the CO-H_2O reaction has been used to convert organic wastes to oil (1), to hydrogenate coal (2, 4, 10), to liquify coal or lignite (5, 7, 17) and to degrade oil-shale kerogen (13). Since high yields of soluble products are obtained from carbonaceous materials at low-temperatures, study of the CO-H_2O reaction and its application to oil-shale kerogen conversion to soluble products is continuing at the Laramie Energy Research Center.

The present paper describes the effects of seven variables on the CO and water reaction. The seven variables are temperature, heating time, CO pressure charged, presence and absence of carbonates, shale particle size, shale grade, and water to shale ratio. In addition, the conversion of kerogen in the presence of water only, the composition of some soluble products and the effect of the CO-H_2O reaction on some oil-shale minerals will be described. Other processes utilize steam or steam and recycle gas but none have duplicated the conditions of this study. For this reason only limited comparisons with other kerogen conversion methods will be discussed.

EXPERIMENTAL

All of the oil-shale samples came from the Piceance Creek Basin of the Green River Formation. Most of these samples for this research were ground to

[1] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

pass through a minus 100 mesh screen. To determine the effect of different grades of oil shale on kerogen conversion, four grades namely 8, 18, 23, and 65 gallons of oil per ton of shale were selected for this investigation. To determine the effect of shale particle size on kerogen conversion, some large pieces of 65 gallon per ton shale were crushed and screened to the following sizes: 0.01, 0.015, 0.029, 0.125, 0.25, and 0.50 inches. In addition, some 1-1/4" cube shale blocks were cut from a 35 gallon per ton piece of oil shale to determine if the kerogen in a block of shale of this size could be converted by the $CO-H_2O$ reaction.

Some minus 100 mesh 65 gallon per ton oil-shale sample was leached with 10 percent hydrochloric acid to remove the natural carbonates. The sample was then washed free of acid and dried under reduced pressure at 60° C. This sample was used to study the effect of the presence and absence of mineral carbonates on kerogen conversion in the presence of $CO-H_2O$.

An American Instrument Company[2] 1-liter reaction vessel constructed of inconel - 600 metal and mounted in a rocking assembly was used for all reactions. The reaction vessel was externally heated with electrical heaters enclosed in a metal jacket. The heating elements were controlled by a Love Controls Corporation model 49 proportioning controller.

Prior to each test a weighted amount of oil-shale sample and a selected amount of water were placed in the pressure vessel. When sodium carbonate was used, it was added at this time. The pressure vessel was then sealed and charged to the selected CO pressure. The oil-shale samples were then heated in the presence of CO and H_2O at the predetermined conditions. On completion of each test the pressure vessel was allowed to cool to room temperature after which a gas sample was taken for mass spectral analysis. The reaction vessel was opened and the heated residue and water were recovered.

The heated oil-shale residue was separated from the water by filtration. The water was extracted in a separatory funnel with diethyl ether. The heated oil-shale residue was air-dried at room temperature and then extracted with a methyl alcohol-benzene mixture overnight to recover the soluble product from the oil-shale residue. The ether-soluble product and methyl alcohol-benzene soluble products were combined to represent the total soluble product.

All gas analyses were performed on a CEC 21-620 mass spectrometer capable of analyzing low-molecular-weight polar and hydrocarbon materials. All soluble products, all oil-shale residues and the original oil-shale sample were analyzed for carbon, hydrogen, nitrogen, and sulfur by the standard methods used at this Center for oil shale and oil-shale products. Mineral carbonate contents were determined for the oil-shale sample and all heated residues. The organic carbon contents of the oil-shale sample and the heated residues equalled the total carbon content minus the mineral carbon content. Kerogen conversion was calculated from the amount of organic carbon present in the oil-shale sample before and after heating.

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2 Reference to specific trade names or manufacturers does not imply endorsement by the Energy Research and Development Administration.

RESULTS AND DISCUSSION

Effects of Variables

Time and temperature series

The conversion of oil-shale kerogen in the presence of $CO-H_2O$ at temperatures from 300° to 450° C for heating times from 0.25 to 6 hours was investigated. The kerogen conversions relative to time are plotted in figure 1. Kerogen conversion increases 3.7 times from about 26 to 98 percent with increased temperatures. Kerogen conversion does not increase consistently with increased heating time and only at 400° C does the conversion increase with increase in heating time. Heating time has a minor effect on kerogen conversions at the heating time selected for study. Kerogen conversion results obtained at 350° C and 400° C by Hubbard and Robinson (11) using dry heat and no hydrogen at atmospheric pressure are included for comparison with the $CO-H_2O$ reaction results. Generally, conversions using the $CO-H_2O$ reaction at the same temperature show little increase in conversion with increase in heating time. In contrast, data presented by Hubbard and Robinson (11) at 350° and atmospheric pressure show a gradual increase in conversion with increase in heating time. Also, kerogen conversions at 350° and 400° C using the $CO-H_2O$ reaction exceed the conversion obtained by Hubbard and Robinson (11) by 200 and 125 percent respectively with 98 percent of the kerogen being converted to either a soluble or gaseous product at 450° C.

Effect of varying pressure of CO charged

The effect of varying pressure of CO charged on oil-shale kerogen conversion while being heated at 375° C for 2 hour was investigated and the results appear in figure 2. The five charge pressures appear at the bottom of the figure and approximate operating pressures appear at the top of the figure. Oil-shale conversion decreases from about 80 to 60 percent as the CO charge pressure increases from 200 to 1000 psig and the operating pressure increases from 3000 to 6000 psig. These results suggest that no benefit in conversions results from increasing charged CO pressure above 200 psig and an adverse effect on conversion does result at higher CO charged pressures. Some additional tests at varying pressures will be made in a bench scale reactor at a later date to confirm these results.

Effect of varying mineral carbon content

The effect on oil-shale kerogen conversion of the absence of natural oil-shale carbonates and the addition of sodium carbonate to shale samples prior to the tests was investigated and the results appear in figure 3. Kerogen conversion increased with increase temperature in the presence or absence of carbonates. Almost the same amount of kerogen was converted in the presence and absence of added sodium carbonate when raw shale was heated in the presence of $CO-H_2O$. A decrease in kerogen conversion was obtained when the oil-shale natural carbonates were removed at each temperature except at 375° C. Addition of sodium carbonate did not increase the yield equal to that obtained with the natural carbonates present in the raw oil shale.

In general, the results show that more kerogen is converted in the presence of the oil-shale carbonates (raw oil shale over HCl leached shale) and that the addition of sodium carbonate does not benefit kerogen conversion during $CO-H_2O$ reaction.

Effect of varying particle size of oil shale

The effect of oil-shale particle size on kerogen conversion during the $CO-H_2O$ reaction was studied and the results appear in figure 4. About 70 to 80 percent of the kerogen is converted when less than 0.1 inch shale particle sizes are reacted. Kerogen conversion decreases to about 50 percent as the particle size increases to .5 inches and increases to 60 percent as the particle size increases to the 1.25 inch cubes. The cubes became pliable, soft, and even spongy as the result of the reaction. Generally these results show that the $CO-H_2O$ process will be more useful in converting finely ground oil shales to soluble products; however, particle sizes up to at least 1.25 inches can be satisfactorily converted.

Effect of varying grade of oil shale

The effect of varying grade of oil shale on kerogen conversion was studied and the results appear in figure 5. Oil-shale kerogen conversion, increases from 50 to more than 70 percent as the grade of oil shale increases from less than 10 to more than 60 gallon of oil per ton of shale. These results suggest that all grades of oil shale could be satisfactorily converted, but the conversion tends to increase with increase in the richness of the oil shale. Very rich oil shales, which cause considerable problems with some retorting operations, would be converted very successful with the $CO-H_2O$ reaction.

Effect of varying amount of water

The effect of the amount of water on kerogen conversion was investigated. The amount of water was varied from .25 to 3 milliliters water per gram of oil shale. Kerogen conversions varied some but at 350° C and water to shale ratios greater than 0.25 kerogen conversion appears to be independent of the amount of H_2O present. These results show that only small amounts of water are needed to convert kerogen using the $CO-H_2O$ process as the 0.25 water to shale ratio represents only the amount of water needed to wet the oil shale.

Conversion in Presence of Water Only

Kerogen was converted in the presence of water only to determine the amount of kerogen converted at temperatures from 350° to 450° C for heating times from .25 to 6 hours. The conversion results are compared with some of the results obtained in the presence of $CO-H_2O$ and appear in table I. The operating

TABLE I. - Effect of varying the temperature and heating time on oil-shale kerogen conversion in the presence of $CO-H_2O$ and H_2O only

		Kerogen converted, wt percent			
		$CO-H_2O$		H_2O	
Heating time, hrs	Temperature °C	Gas product	Soluble product	Gas product	Soluble product
2.0	350	1.1	39.7	4.5	36.4
6.0	350	0.1	39.0	6.5	46.4
0.25	400	2.0	66.3	12.7	57.6
1.0	400	1.9	75.0	19.5	69.3
1.0	450	18.7	79.2	63.4	22.7

pressures ranged from 2400 psig to 3600 psig in the presence of H_2O only and from 4800 psig to 6000 psig in the presence of CO-H_2O. About 3 to 9 times more gas is formed when water alone was used over that obtained with water and carbon monoxide. Some carbon residue was evident in the sample heated at the highest temperatures when water alone was used.

Relative to results obtained using CO and H_2O more kerogen is converted to the soluble product at the lower temperatures and less kerogen is converted to soluble products at the higher temperatures in the presence of H_2O alone. Conversely, significantly greater amounts of gaseous products are produced in the presence of H_2O only. The composition of the residual gases generated at 450° C in the presence of water only consists of about 29 percent saturate and 10 percent unsaturate C_1 to C_6 hydrocarbons and in the presence of CO-H_2O consists of about 19 percent methane. Hydrogen content of the gas from the test using water only was 29 percent and the gas from CO-H_2O test was 44 percent. These results show that 3 to 9 times more kerogen is converted to gas in the presence of water only than in the presence of water and carbon monoxide.

Composition of Soluble Products

The average atomic ratios calculated from the elemental analysis of the soluble products appear in figure 7. In all cases the atomic hydrogen-to-carbon ratio (X 10) for the soluble extracts exceeded the 154 ratio obtained for kerogen. All of the O/C, N/C, and S/C ratios are less than the O/C of 5.40, the N/C of 2.56, and the S/C of 0.47 ratios obtained for the kerogen. Using Stanfield's (15) elemental analyses of composite Fischer Assay oils, the following atomic ratios were calculated for a representative retorted shale oil: H/C ratio of 164, O/C of 1=0, N/C of 2.0, and S/C of 0.3. With the exception of oxygen amounts, the soluble extracts from the CO-H_2O reaction appear to have average compositions similar to that of a representative Fischer Assay oil. The presence of more oxygen in the extracts indicates a less severe thermal history than the usual retorted oil.

Generally the results show that some hydrogen is probably added to the soluble products during the CO-H_2O process. Also the elemental composition of the soluble products is similar to the elemental composition of the Fischer Assay oils except the oxygen content which is 3 to 5 times more. This higher oxygen content (14) occurs because the soluble products are formed 50° to 200° C below the normal 500° C retorting temperature at which Fischer Assay oil is formed. These oxygen values (17) do not exceed the amount of oxygen present in the kerogen. The soluble products should be suitable feedstock for hydrocracking and refining operations.

During the CO-H_2O reaction numerous changes occur to the oil-shale minerals. If sufficient water is present the water-soluble minerals, which are mainly alkali carbonates, are solubilized. In addition, the crystalline forms of the quartz minerals are altered and if dawsonite (an aluminum containing mineral) is present it is converted to another mineral form. The removal of the readily water-soluble minerals could prove to be an environmental advantage because these materials may contaminate surface and ground waters when stored with the remainder of the oil-shale residue as is commonly done with other conversion processes.

Effect on Mineral Compositions

A dawsonitic oil shale and the dawsonitic shale residue heated at 400° C in the presence of CO-H_2O were X-rayed. The peak intensities of five minerals

(dolomite, feldspar, quartz, analcime, and dawsonite before and after heating at 400° C in the presence of $CO-H_2O$) are plotted in figure 8. Three minerals (dolomite, quartz, and dawsonite) present in the original oil-shale sample are not detected in the shale residue after heating at 400° C. Apparently the dolomite decomposes into calcium and magnesium carbonate with the formation of calcite. The dawsonite probably reacts to form analcime and carbon dioxide in the presence of $CO-H_2O$ at 400° C. All the quartz loses its crystalline structure upon being heated at 400° C and is converted to an amorphous form not detectable by X-ray. Feldspar appears to be fairly stable in the presence of $CO-H_2O$ at 400° C. Unfortunately the aluminum present in dawsonite is converted to a more insoluble form during the $CO-H_2O$ reaction. To remove the aluminum for commercial use, it would be necessary to degrade the dawsonite to a soluble form prior to the $CO-H_2O$ reaction or devise a technique which would prevent the formation of analcime during the reaction. An environmental advantage is gained with the removal of the water-soluble minerals because the oil-shale residue would become essentially inert to leaching of the salts by atmospheric or ground water moisture. However, more research needs to be done in this area.

SUMMARY

Using the $CO-H_2O$ reaction more kerogen is converted to soluble products and and gas at lower temperatures than is obtained by dry retorting at near atmospheric pressure.

Pressure does not appear to be a significant variable for kerogen conversion in the $CO-H_2O$ reaction

Natural carbonates present in the oil shale are adequate to promote kerogen conversions and additional sodium carbonate does not increase kerogen conversion.

The $CO-H_2O$ reaction is suitable for use with either finely ground or extremely rich oil shales, materials that create difficulties for some oil-shale conversion processes.

Only small amounts of water are needed to convert oil-shale kerogen to a soluble product during the $CO-H_2O$ reaction.

More kerogen is converted to gaseous products in the presence of water alone than in the presence of both carbon monoxide and water.

Soluble products formed in the presence of carbon monoxide and water should be satisfactory materials for refining to needed energy fuels.

Some of the oil-shale minerals undergo major changes during the $CO-H_2O$ reaction for example dawsonite being converted to analcime.

REFERENCES

1. Appell, H. R., Y. C. Fu, S. Friedman, P. M. Yavorsky, and I. Wender. Converting Organic Wastes to Oil. A Replenished Energy Source. BuMines RI 7560, 1971, 20 pp.

2. Appell, H. R., and I. Wender. The Hydrogenation of Coal with Carbon Monoxide and Water. Preprints, Div. Fuel Chem., ACS, v. 12, No. 3, 1968, p. 220.

3. Burwell, E. L., and I. A. Jacobson, Jr. Concurrent Gasification and Retorting of Oil Shale - A Dual Energy Source. Preprints, Rocky Mt. Regional Meeting, Soc. Petr. Eng., Paper number SPE 5335, 8 pp.

4. Fisher, F., and H. Schrader. Hydrogenation of Coal with Carbon Monoxide. Brenstoff-Chem., v. 2, 1921, pp. 257-261.

5. Handwerk, J. G., R. M. Baldwin, J. O. Golden, and J. H. Gary. Co-Steam Coal Liquefaction in a Batch Reactor. Preprints, Div. Fuel Chem., ACS v. 20, No. 1, 1975, pp. 26-46.

6. Hartley, F. L. High Recovery Proves Out for Shale-Oil Process. Chem. Eng. News, July 1, 1974, pp. 15-16.

7. Henderson, T. A. Oil-Shale Processing Methods. Quart. Colo. School Mines, v. 69, No. 3, 1974, pp. 45-69.

8. Hendrickson, T. A. Oil-Shale Processing Methods. Quart. Colo. School Mines, v. 69, No: 2, 1974, pp. 45-69.

9 Jensen, H. B., W. I. Barnet, and W. I. R. Murphy. Thermal Solution and Hydrogenation of Green River Oil Shale. BuMines Bulletin 533, 1953, 42 pp.

10. Nguyen, D. Reduction of Subbituminous Coal with Carbon Monoxide and Water. Ph.D. Thesis, Montana State University, 1973, 83 pp.

11. Hubbard, A. B., and W. E. Robinson. A Thermal Decomposition Study of Colorado Oil Shale. BuMines RI 4744, 1950, 24 pp.

12. Ridley, R. D. In Situ Processing of Oil Shale. Quart. Colo. School Mines, v. 6, No. 2, 1974, pp. 21-24.

13. Robinson, W. E., and J. J. Cummins. An Oil-Shale Conversion Process Using Carbon Monoxide and Water. E.R.D.A. Technical Progress Report 75/1, 1975, 14 pp.

14. Robinson, W. E., and J. J. Cummins. Composition of Low-Temperature Thermal Extracts from Colorado Oil Shale. J. Chem. Eng. Data, v. 5, No. 1, 1960, pp. 74-80.

15. Stanfield, K. E., I. C. Frost, W. S. McAuley, and H. N. Smith. Properties of Colorado Oil Shale. BuMines RI 4825, 1951, 27 pp.

16. Weichman, B. The Superior Process for Development of Oil Shale and Associated Minerals. Quart. Colo. School Mines, v. 69, No. 2, 1974, pp. 25-43.

17. Smith, J. W. Ultimate Composition of Organic Material in Green River Oil Shale. BuMines RI 5725, 1961, 16 pp.

18. York, W. J. Reduction of Subbituminous Coals and Lignite Using Carbon Monoxide. Ph.D. Thesis, Montana State University, 1971, 83 pp.

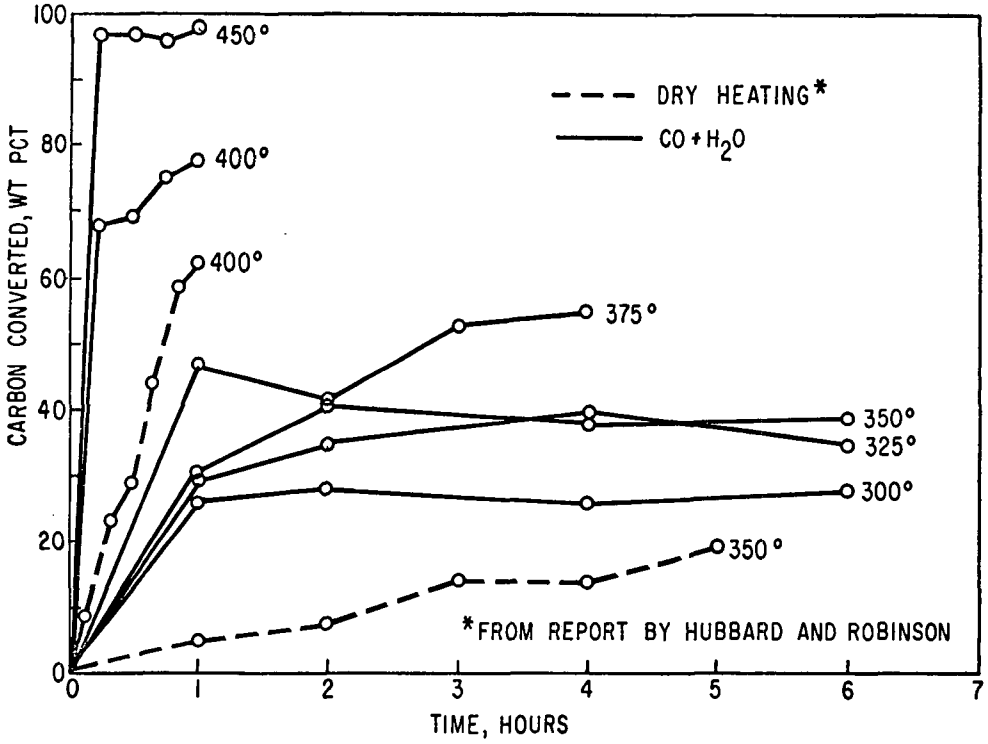

FIGURE I.-KEROGEN CONVERTED TO SOLUBLE PRODUCTS & GAS AT 300 TO 450 °C IN THE PRESENCE OF CO AND H_2O.

SOA-650P

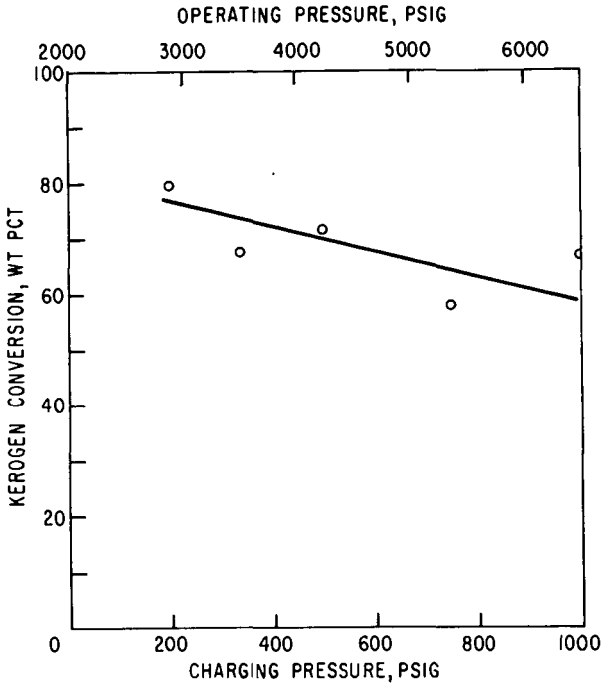

FIGURE 2.-EFFECT OF VARYING PRESSURE ON KEROGEN CONVERSION AT 375°C FOR TWO HOURS.

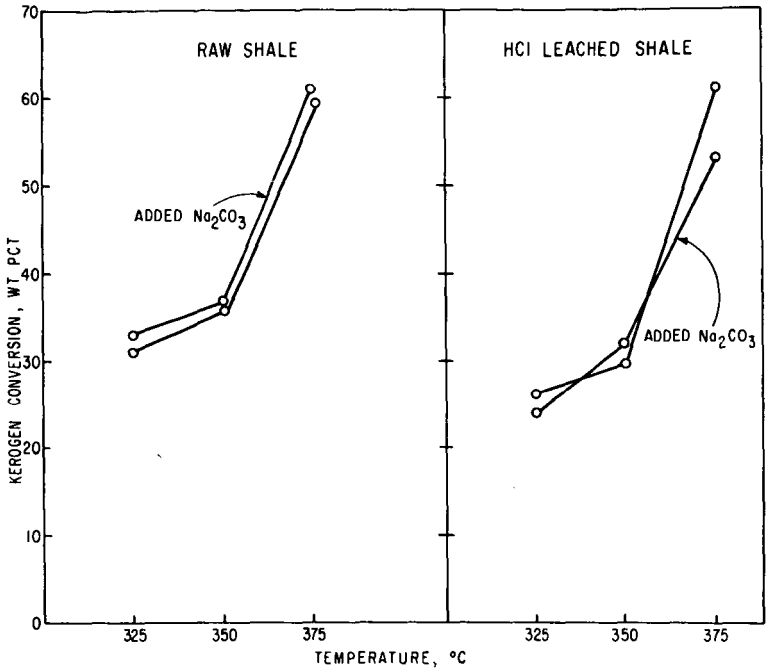

FIGURE 3.-EFFECT OF PRESENCE OR ABSENCE OF CARBONATE ON KEROGEN CONVERSION AT 325 TO 375 °C FOR TWO HOURS IN THE PRESENCE OF CO AND H_2O.

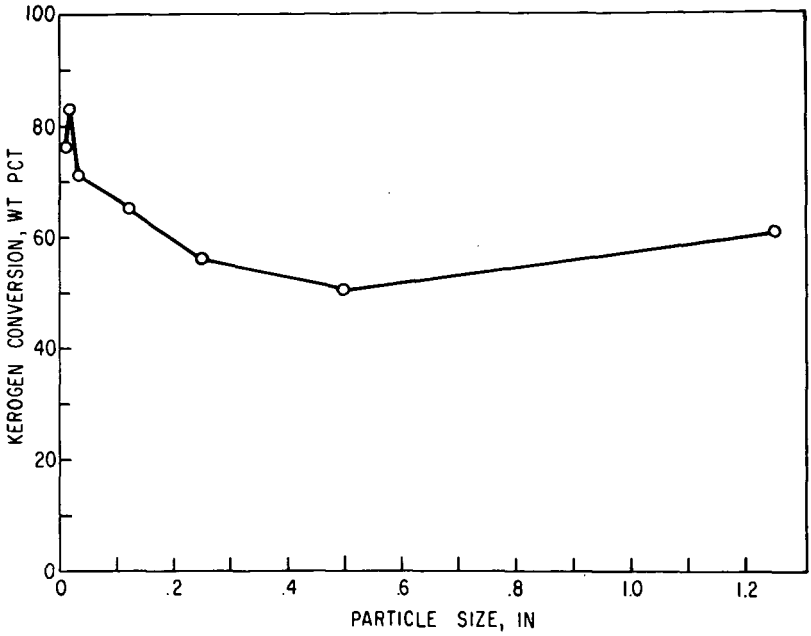

FIGURE 4.-EFFECT OF VARYING OIL SHALE PARTICLE SIZE ON KEROGEN CONVERSION AT 400 °C FOR ONE HOUR.

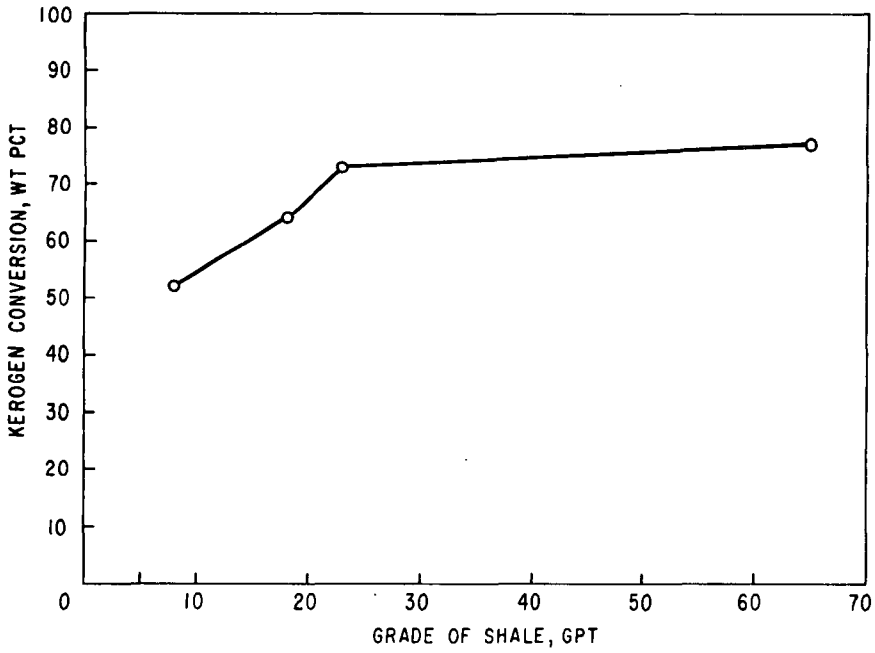

FIGURE 5.-EFFECT OF VARYING THE GRADE OF SHALE ON KEROGEN CONVERSION AT 400°C FOR ONE HOUR.

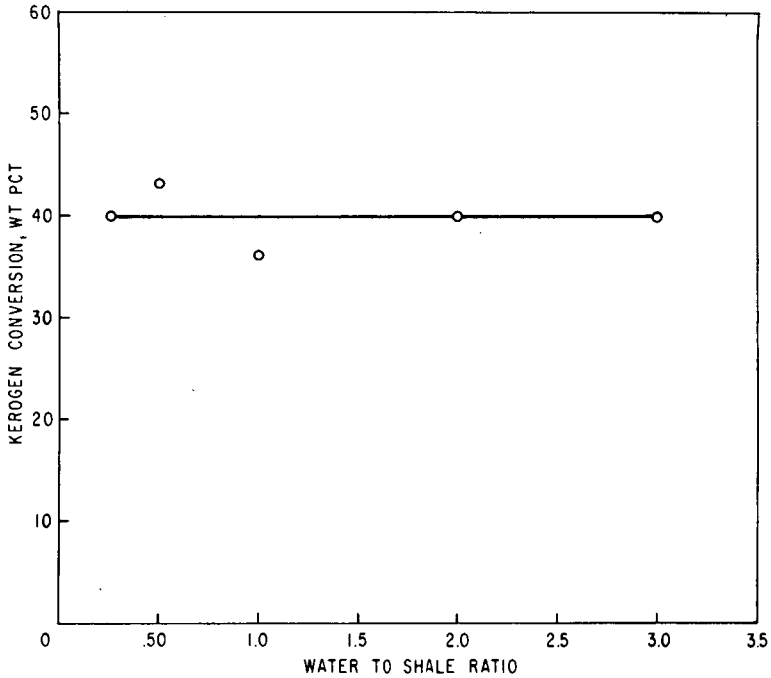

FIGURE 6.-EFFECT OF VARYING THE AMOUNT OF WATER ON KEROGEN CONVERSION AT 350°C FOR TWO HOURS.

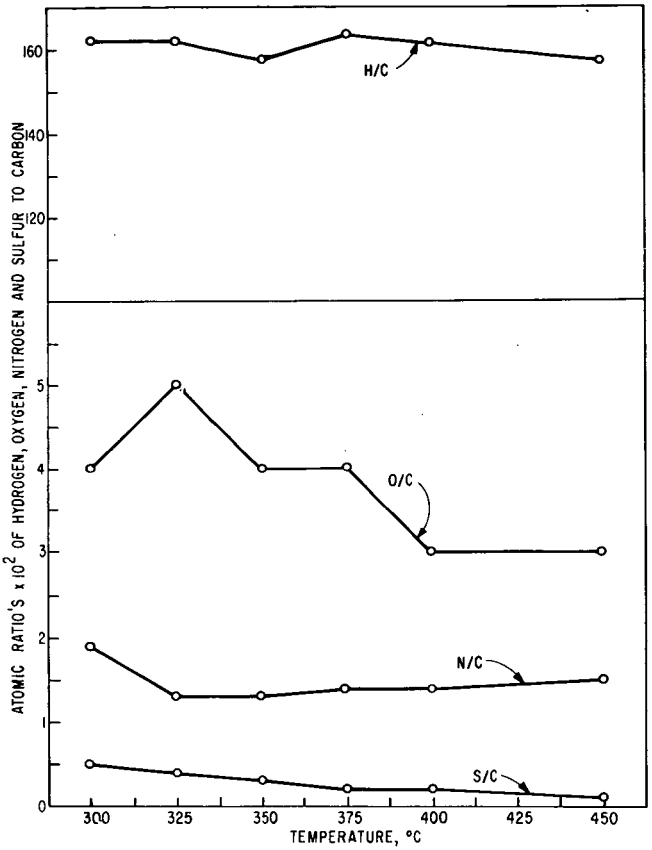

FIGURE 7.- AVERAGE ATOMIC RATIO'S OF THE SOLUBLE PRODUCTS FORMED IN PRESENCE OF CO-H_2O AT VARIOUS TEMPERATURES.

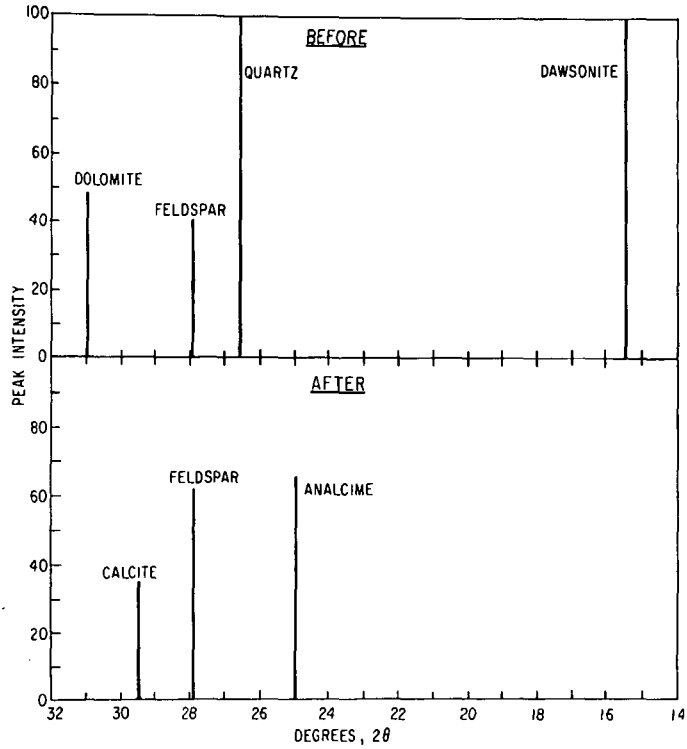

FIGURE 8.-EFFECT OF CO-H_2O ON MINERALS IN DAWSONITE CONTAINING OIL SHALE AT 400 °C.