PROCESS DESIGN AND DEVELOPMENT

PIPELINE GAS FROM OIL SHALE BY DIRECT HYDROGASIFICATION

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The rate of hydrogasification of the organic matter in a Colorado oil shale was measured in a laboratory semiflow reactor at temperatures from 1100° to 1400° F. and pressures up to 2000 p.s.i.g. The kerogen hydrogenolysis reaction sequence was shown to involve initial formation of intermediates at least partially recoverable as liquids at very short residence times and/or low temperatures, followed by pyrolysis, hydrogenation, and hydrogenolysis reactions leading to gaseous aliphatic hydrocarbons of decreasing molecular weight. At sufficiently long gas residence times, the primary gaseous hydrocarbons were methane and ethane. Continuous operation at 1200° to 1400° F. was simulated in tests conducted at 1000 p.s.i.g. and at hydrogen–oil shale ratios ranging from 100 to 250% of the stoichiometric requirement for complete conversion of the organic matter to methane. At average oil shale residence times of about 5 minutes, the instantaneous organic carbon gasification averaged 63 to 64%.

T HE gas industry has been studying methods for the production of natural gas substitutes from coal and petroleum oils. Processes for direct conversion of these fossil fuels to high heating value gases consisting largely of methane are in an advanced stage of development (6, 7). In the case of oil shale, existing technology would involve a preliminary retorting step to produce crude shale oil, and refining to prepare a suitable feed for continuous destructive hydrogenation (hydrogasification). It was reasoned that a direct oil shale hydrogasification process might be preferable because of potentially higher conversion of the organic matter to gas, and elimination of a number of process steps.

Feasibility was shown for direct hydrogasification of the organic matter in Green River oil shale. High heating value gases were produced (1, 8, 11) in batch reactor tests at 1300° F., at 1200 to 5500 p.s.i.g., and with 100% of the stoichiometric hydrogen requirement for complete conversion of the organic matter to methane. About 90% or more of the organic carbon plus hydrogen content of the oil shale was converted to methane and ethane.

In these tests, the path of the hydrogenolysis of kerogen was only partially indicated at the long heatup times and long gas residence times encountered in the batch reactor. Only the slower final breakdown of higher gaseous paraffins to methane and ethane could be observed. It was also not possible to measure over-all reaction rates and precisely determine the effects of temperature. Pressure effects were obscured by changes with temperature and degree of conversion.

The present work was conducted in a reactor system in which oil shale heatup times and exit gas holdup times in the heated portion of the reactor were of the order of a few seconds. After leaving the reactor, the reaction products were cooled rapidly to minimize further reactions.

The scope of this study was rather broad and three separate test programs are described. The objective of the first test series was to show the mechanism of the hydrogasification of oil shale kerogen, and to measure the rates of kerogen conversion to gaseous hydrocarbons and of mineral carbonate decomposition. In these first tests, product residence times in the heated portion of the reactor were small, so methane and ethane were not the only major gaseous products. The second test series was conducted over a range of hydrogen space velocities with a bed of inerts downstream of the oil shale

charge to simulate conditions conducive to vapor-phase hydrogenolysis of heavier hydrocarbons to methane and ethane in hot spent oil shale in a cocurrent flow reactor. Once the conditions necessary for producing primarily methane and ethane were found in the second test series, a third test series was conducted to show the effects of a major design parameter, hydrogen–oil shale ratio, on product distribution. Tests were made with continuous feeding of oil shale to simulate continuous operation and to provide data for pilot plant reactor design.

Experimental

Apparatus. A schematic diagram of the semiflow reactor system is shown in Figure 1.

The reactor contained a self-sealing, modified Bridgman closure at each end and was 2 inches in inside diameter, 4 inches in outside diameter, and 60 inches in inside length. The reactor barrel, constructed of Uniloy N-155 super alloy, was rated for operation at a maximum temperature of 1700° F at 1500 p.s.i.g. The closures were rated for a maximum temperature of 1400° F. at 1500 p.s.i.g. Satisfactory closure operation was obtained with both 16-25-6 and Inconel-X seal rings. A boundary lubricant of molybdenum disulfide, applied in aerosol form, was used on all closure threads and on the seal rings to prevent galling. This reactor has been completely described (9), along with design details of the use of externally heated reactors at combined high temperatures and high pressures.

An Inconel-X thermowell of $^3/_8$-inch outside diameter, with a 12-gage wall thickness and 58 inches long, was mounted axially in the bottom closure. The thermowell could contain up to five 0.040-inch outside diameter thermocouples. Thermocouples were Chromel-Alumel, magnesium oxide insulated, and enclosed in a swaged Inconel sheath. To provide for complete containment and recovery of the oil shale residue, the reactor was provided with a removable stainless steel insert, $1^5/_8$ inches in inside diameter by 1.990 inches in outside diameter and containing a $^1/_2$-inch outside diameter thermowell sleeve.

The reactor was heated by means of an electric resistance furnace containing four separately controlled heating zones, consisting of four rectangular heating elements, 7 inches wide and 12 inches long. Temperatures were controlled manually during tests but by pyrometric controllers during reactor heatup. Each temperature was recorded at approximately 3-second intervals by means of a high-speed potentiometric temperature recorder during the test period.