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SYNTHESIS OF ORGANIC GEOCHEMICAL DATA FROM THE EASTERN GAS SHALES

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ABSTRACT

Over 2400 core and cuttings samples of Upper Devonian shales from wells in the Appalachian, Illinois, and Michigan Basins have been characterized by organic geochemical methods to provide a basis for accelerating the exploitation of this unconventional, gas-rich resource. This work, sponsored by the United State's Department of Energy's Morgantown Energy Technology Center, was part of a program initiated to provide industry with criteria for locating the best areas for future drilling and for the development of stimulation methods that will make recovery of the resource economically attractive.

The geochemical assessment shows that the shale, in much of the Appalachian, Illinois, and Michican Basins is source rock that is capable of generating enormous quantities of gas. In some areas the shales are also capable of generating large quantities of oil as well. The limiting factors preventing these sources from realizing most of their potential are their very low permeabilities and the paucity of potential reservoir rocks.

Low permeability has prevented migration of most of the free hydrocarbons from their site of origin in the shale matrix into nearby reservoirs. This retention of generated hydrocarbons has retarded the further generation of hydrocarbons within the shale, particularly the liquid (oil) ones, over much of the basin. Where there is fracturing, the shales themselves provide both source rock and the reservoir, and allow generation to proceed. In some cases, contiguous or interbedded siltstones provide small reservoirs, and the fractures provide migration channels through which the hydrocarbons move for relatively short distances.

This geochemical data synthesis gives direction to future selection of sites for stimulation research projects in the Appalachian Basin by pinpointing those areas where the greatest volumes of gas are contained in the shale matrix.

Another accomplishment of the geochemical data synthesis is a new estimate of the total resource of the Appalachian Basin. The new estimate of 2,500 TCF is 25 percent greater than the highest previous estimates. This gives greater incentive to government and industry to continue the search for improved stimulation methods, as well as for improved methods for locating the sites where those improved stimulation methods can be most effectively applied.

INTRODUCTION

During the course of the Eastern Gas Shale Program (EGSP) sponsored by DOE's Morgantown Energy Technology Center (METC) more than 2400 individual core samples, as well as several hundred cuttings samples, were taken from Devonian Shale Wells drilled in the Appalachian Basin (Figure 1). These samples were submitted to a rather comprehensive suite of geochemical analyses (Figure 2). The analyses were performed 1) to identify the original hydrocarbon source potential of the dark shales, 2) to assess the source potential that has been realized, 3) to identify the nature of the product, i.e., dry gas, wet gas, oil, or any combination of these, that has been generated regionally and locally within the potential source rock, and 4) to ultimately estimate the gas in place.

This paper reviews the organic geochemical data, illustrates the interrelationships of the data and identifies the parameters which have exploration significance and which can be used for an assessment of gas in place. The identified diagnostic parameters, which include organic carbon content, biofacies and thermal alteration, are mapped to pinpoint the richest sediment wedges which could serve as future exploration targets.

Of course, the fact that a rock has hydrocarbon source potential does not necessarily mean that contiguous reservoirs will contain any oil or gas, but shows that the rock does satisfy one of the three major requirements for the presence of pooled hydrocarbons.

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The other requirements are the occurrence of some type of porous volume to serve as the reservoir, and the presence of some type of seal to confine the resource. If these two other requirements are met, migration of the hydrocarbons from the source to the reservoir must also take place. In classical reservoirs hydrocarbons may migrate many miles, but in the case of the dark shales, the same rock that generates the bulk of the hydrocarbon can also serve as the reservoir, i.e., where it is fractured or interbedded with thin silt stringers. An assessment of these requirements must be made to determine future drilling sites.

BACKGROUND

Total Organic Carbon

The source of virtually all the petroleum in all the sedimentary basins of the world is the remains of living organisms which were incorporated in the fine-grained rocks of those basins at the time they were deposited (1,2). The primary criteria in any basin assessment should be the amount and distribution of this material which is called "organic matter". The amount of this primary source material would be diminished by the fraction converted to mobile products that have moved or have been displaced from the rock by physico-chemical processes, called migration, but fortunately, the majority of the organic matter deposited in petroleum source rocks still reamins in the mineral matrix, i.e., rock within which it was deposited. It is estimated both empirically and in laboratory experiments that less than a third of the original organic carbon is converted to mobile products, oil and gas (3), and only a portion of this can move from the rock. Therefore, a measurement of the amount of organic matter in an unmetamorphosed sedimentary rock is a semiquantitative indicator of the amount of organic matter that was originally present.

Geochemists estimate the organic matter contents of rocks by determining the amount of organic carbon they contain. Organic carbon is defined as the carbon incorporated into the carbon-carbon and carbon-hydrogen structures of organic molecules, and excludes the carbon in mineral carbonates. These latter forms, which may be the remains of skeletons or protective shells of living organisms, are technically "organic", but are not so labeled by petroleum geochemists because they do not enter into the oil or gas-forming processes. In many studies, the amount of organic matter was calculated from organic carbon contents, using a conversion factor, but the experimentally determined factor varied so greatly from rock to rock (about 1.07 to 1.40) in the few rocks in which the detailed composition of the organic matter was measured (4), that organic carbon became the accepted reporting parameter.

As a first step in an exploration or basin assessment program, organic carbon data provide a means of high-grading the more favorable petroleum areas within the basin. Ronov (5) was the first to map organic contents regionally, and showed that on the Russian Platform, excellent potential reservoirs were filled or partially filled with oil and gas only if the nearby Devonian shales contained greater than 0.5 percent organic carbon. Large areas of the province, which were investigated, were found barren, and in all of these the organic carbon contents were beneath the minimum value.

Ronov's research also revealed that the amount of organic carbon was controlled to a large degree by the environment of deposition in various parts of the basin, but the major conclusion was that there was a minimum content of organic carbon that had to be exceeded before a rock could be a source, i.e., deliver commercial volumes of oil or gas to reservoirs, in any geological setting.

Subsequent studies of petroleum source relationships (6,7,8) confirmed this concept, i.e., that the organic carbon contents of rocks must exceed some threshold amount before they can begin to act as significant sources of petroleum hydrocarbons. Some geochemists feel that 0.4 percent represents the cutoff for shales. Others prefer 1.0 percent. For carbonates rocks, a lower limit was established, i.e., about 0.3 percent organic carbon (9). Beyond these lower limits, the general rule is, "other things equal, the greater the organic carbon content, the greater the potential a rock has to act as a petroleum source rock".

In many cases, organic carbon determinations are made on rocks extracted exhaustively with organic solvents to remove the soluble organic matter, called "bitumen". The values, thus determined will be as much as 17 percent low (10). Nevertheless, the geographic and stratigraphic contrasts in the amounts of organic carbon are extremely useful in exploration. The residual organic matter that cannot be extracted has been labeled by petroleum geochemists as "kerogen". This term expands the earlier definition in which the term only included those kinds of organic matter which gave up significant quantities of liquid hydrocarbons upon heating. Under the new usage, the term includes more inert forms.

Biofacies

Organic carbon is usually the first parameter determined in a geochemical evaluation of the oil and gas potential of a basin, play, or formation. It is often used as a screening step because it gives a relative picture of the potential of a rock, and it is an inexpensive and rapid analysis. The next step is usually to determine whether that organic matter is of the correct type to produce gas and/or oil under subsurface conditions.

Very early in the development of organic geochemistry, the nature of the organic matter was recognized as being equally as important as the amount. It was obvious from coal chemistry that bituminous coal contained more liquid hydrocarbons, and would produce more on heating, than anthracite coal (12).

The organic matter of fine-grained rocks, i.e., the kerogen, could be similarly divided into more and less bituminous types, which have been called sapropelic and humic, respectively (13). With time, these types have been further subdivided and defined. Current descriptions include identification and estimation of relative proportions of structured or cellular material, called "woody", or shiny, angular opaque material, called "coaly", or spores, pollen, plant cuticle fragments. All other membraneous plant remains are described by the term "herbaceous", remains of algae, called "algal", and nondescript, fluffy material, "amorphous". These distinctions are made by examination, under the microscope, or mineral acid-insoluble residues from fine-grained rocks being studied for their source potential.

Organic matter of the algal and amorphous types has a greater potential to generate hydrocarbons than that derived from plants which grow in the shallow water near the shore line or on land masses surrounding the seas and lakes where the host rocks are deposited (14). The materials from plants, the herbaceous type, has greater potential to generate gas than does the woody-coaly types. Not only does the potential quantity of associated hydrocarbon decrease in order from the amorphous type, through the algal, herbaceous, and woody varieties, to the coaly types, but the tendency to generate liquid hydrocarbons (oil) also decreases in the same sequence, i.e., the amorphous kerogen has the greatest tendency to generate hydrocarbons, the coaly types, virtually none. Moreover, oil derived from these kerogen types tends to be more napthenic with algal, amorphous kerogen, more paraffinic with herbaceous-woody types, and more aromatic with coaly types.

Another method of classifying sediments according to their relative hydrocarbon potential and their relative oil vs gas-generating potential is provided by the palynologist. Palynology is the study of pollen, spores and other microfossils in the acid-insoluble rock residues. Microfossils exist in many different shapes and forms (called their morphology) which have been classified and cataloged, they are so different and distinctive that they can be used for age determination, for stratigraphic correlation, and for identifying the nature of the environment of deposition that existed at the time the host rock was deposited. This environmental interpretation is called the paleoenvironmental analysis. The determination of the most abundant type of organic matter is known as biofacies analysis.

Maturity

Organic matter laid down at the time of deposition contains only traces of free petroleum hydrocarbons, far too little for even an organic-rich rock to act as a source rock without further change. Some changes, such as oxidation destroy some or all of the source potential, but in a normal source-producing environment, the bulk of the organic matter is preserved because the conditions at or shortly after deposition are anerobic, or reducing.

Organic matter in potential source rocks undergoes a sequence of changes that converts as much as 30 to 35 percent of its original mass to petroleum hydrocarbons. The first process, a low temperature one, is called diagenesis. This term refers to the combined effects of biological, physical, and chemical alteration before heat begins to "crack" the organic matter. The only potential petroleum-producing reaction operating during diagenesis is the microbial formation of methane, large quantities of which may form and be trapped in reservoirs that are formed early. It is estimated that 20% of the world's gas reserves are made up of this biogenic gas (16). This gas can be identified by its carbon isotopic composition (i.e., it is enriched in the lighter isotope).

When the temperature of a rock rises to above about 50°C, the chemical bonds of the contained organic matter begin to break in response to the heat, and the stage called thermal maturation or catagenesis begins. The great majority of the petroleum hydrocarbons of the world is formed by this process which continues until the temperature of the rock reaches about 150 to 200°C. At higher temperatures, the process, now called metamorphism, begins to destroy petroleum hydrocarbons.

Temperature estimates for the onset and completion of petroleum hydrocarbon production are only approximate because the rock organic matter system is so variable and complex. Moreover, because the organic matter is a chemical system, the rate of reactions must increase with temperature. Therefore, there should be a trade-off of temperature for time, i.e., rocks buried for longer periods at lower temperature should experience the same degree of catagenesis as those buried at higher temperatures for shorter periods of time.

In an exploration venture, it is important to know whether the organic matter has undergone sufficient catagenesis to produce commercial quantities of petroleum, but not so much alteration that the hydrocarbon has been destroyed. This is not always easy to determine from the present day geological setting of the rock or its present temperature because the rock may have had a complex history of several episodes of burial, uplift, and erosion of the overlying rocks.

Fortunately, the kerogen itself, immobilized in the rock matrix since deposition, carries a record of its own time-temperature history. The degree of thermal alteration, catagenesis, can be estimated from the color of spores, pollen, or plant cuticle fragments (13), or from the optical reflectivity of specific carbonized particles, called virtinite (17).

Kerogen coloration is reported on a scale of from 1 to 5. These values are also called Thermal Alteration Index (TAI) values. Fresh, unaltered pollen, spores and cuticle fragments are light yellow or light greenish yellow, this unaltered kerogen is assigned a TAI of 1. Such a rating indicates that the rock has not been exposed to temperatures above 50°C. Rocks with this low a TAI are sometimes associated with methane gas of biogenic origin.

The onset of catagenesis, between 50 and 100°C, is detected by the loss of the greenish tinge and a slight intensification of the yellow coloration of the appropriate type of herbaceous kerogen. TAI's of rocks with kerogen exhibiting this coloration are rated at 1+. These rocks are associated with dry (methane only) gas and sometimes with heavy oil. Rocks with these very light colors are said to be "immature".

Orange colors indicate that the rock's organic matter is moderately altered, it has probably been exposed to temperatures in the range 100 to 150°. Light orange kerogen (TAI = 2) is sometimes associated with gas with a large percentage of ethane, propane, the butanes and some light hydrocarbon liquids. TAI's of 2 generally indicate that the rock is in its most prolific oil generating stage.

Brown colors (TAI = 3) indicate that the organic fractions of the rock have been strongly altered, probably haveing experienced temperatures above 150°C. At these temperatures, kerogen has realized most of its potential to give up hydrocarbons, the free hydrocarbons have been converted to light liquid and gaseous hydrocarbons. Deep brown or brownish black (TAI = 4) coloration denotes severly altered kerogen with dry methane gas the only associated hydrocarbon.

When the kerogen is black (TAI = 5), the rock has been exposed to relatively high subsurface temperatures (200°C) and there is little possibility of associated hydrocarbon except for a small amount of methane.

These colorations are not always clear cut. Different spores and pollen grains from the same rock sample may have somewhat different colorations. Therefore, ratings should be made with other samples from the same well or outcrop so that subtle trends and relative colorations can be detected. The colors should be checked frequently against standard kerogen slides. Of course, the method is also somewhat subjective because of the different perception of color by different individuals, but it has the advantage of being rapid and requiring only a microscope.

Vitrinite reflectance is measured with a photomultiplier detector capable of accurately measuring the percent of a collimated beam light that is reflected from a polished surface of a minute vitrinite particle imbedded in a plastic matrix. While the measurement can be done accurately on a single particle, one of the drawbacks is that is it not always easy to recognize vitrinite. Other macerals, or kerogen types, that can be confused with vitrinite have quite different reflectance values at the same stage of thermal alteration. Another limitation is that even vitrinite particles that have experienced exactly the same histories may vary in reflectance because of small variations in the method of sample preparation, oxidation of the surface, texture, etc. Therefore, the reflectance of a large number of particles must be measured to derive a statistically significant estimate of alteration. In cases where the vitrinite is very uniform, this may require only 30 readings, in other cases where the rock has a heterogeneous organic population, it may require over a hundred. In addition, the procedure is time-consuming and expensive relative to determination of TAI's.

Skillful interpretation of the data not only gives an estimate of extent of thermal maturation, but also may provide valuable information on possible unconformities in the section, on the amount of reworked kerogen introduced into the basins from eroding older rocks, and on the proportion of cavings in the well (14).

ASSESSMENT PROGRAM

Over 2400 core and cuttings samples from wells drilled as part of the Eastern Gas Shale Program were subjected to geochemical analyses. Most of these were selected at 30 or 10 foot intervals from the cored sections of wells in the Appalachian Basin. The overall core was examined, its lithology described, the fracture distribution noted, and the gamma radiation measured. After the examination a 3 to 6 inch cylinder of core is broken from the core and sealed in a gas-tight container to retain the released gas while the samples are transported to the laboratory for further analyses.

A flow chart for the sequence of analyses is given in Figure 2. Generally, at any level in the chart, the determination on the left was the first one performed.

Gas volume and composition in the free-gas space was determined first. A correction is made for the gas pressure in the container. Then, the volume and composition of the gas still retained in the core was measured, and total gas volume calculated. The sample was then dried and its detailed lithology recorded before subdividing into samples for the analytical determinations scheduled. The analyses were performed using standard organic geochemical procedures which are widely used in industry.

From regional plots and cross correlations of the various parameters it became apparent that the three previously discussed were the most useful ones for geochemical assessment of the Eastern Gas Shale Basins: 1) The amount of total organic carbon; 2) The nature of the organic matter as described in the biofacies determinations; and 3) The degree of thermal alteration as described by the visual thermal alteration index. These three could be combined for an estimate of maximum indigenous gas expected in a zero-permeability shale. Another supporting parameter, but of more limited utility, was the residual gas determined in the initial screening analysis of the overall analytical scheme.

Total Organic Carbon

From the beginning in the Eastern Gas Program, it was apparent that the organic carbon content varied widely from one ten-foot interval to the next in many of the wells. This was not surprising considering that the environment of deposition of sediments can change abruptly with changes in sea level, with tectonism, with circulation, etc., and that a ten-foot section of Devonian shale might represent the sediments deposited over 5,000 to 10,000 years. The distribution of organic carbon in the samples analyzed is shown in histogram form in Figure 3. The range of values measured was from less than 0.10 to greater than 27 percent, with a mean value of 2.13 percent. Superimposed on the data from the Eastern Gas Shale samples are the data from various source shales from around the world, and the generally accepted source potential rating associated with various ranges. It is obvious that, based on this criterion alone, much of the dark Devonian shale must be considered an exceptional potential source of hydrocarbons. Orginally it was intended to map the values of organic carbon to show the regional trends. However, with the observation of the rapidly changing values, the average value for a unit was misleading, particularly if there were only a few analyses in a thick section. Therefore, it was decided to supplement the mapping with a series of cross sections on which the stratigraphic and regional distribution of the organic carbon would be illustrated.

To prepare the cross sections, strip logs of total organic carbon vs depth were prepared for each well. The appropriate value of organic carbon was plotted at the appropriate sampling depth. The tops of stratigraphic intervals identified from well logs or palynology were also recorded on each of the strip logs. Then each of these logs were positioned so that some stratigraphic marker common to two neighboring logs was aligned horizontally.

Because the data were so highly variable, it was not possible to correlate the detailed layers of alternating rich and lean organic carbon; however, general wedges of rich and very rich potential source rocks were outlined on each of the sections.

The rich organic carbon wedges bore a striking resemblance to the dark shale zones delineated in the stratigraphic column shown in Figure 4 and with the dark shale units presented in summary form in Potter's summary report (11). This correspondence was anticipated. However, the organic carbon data show that the "dark shale zones" are not necessarily uniformily dark they just contain more consistent and more closely spaced layers rich in organic carbon.

The organic carbon cross sections did show that there probably is rich gas potential over virtually the entire Appalachian Basin. Along the Cincinnati and Findlay Arches almost the entire section is very rich in organic carbon. Eastward and southeastward, there is still abundant gas source rock, but it occurs in progressively thinner zones that tend to become less rich and more widely separated by poor source quality intervals.

In this assessment of exploration potential and gas-in-place, several parameters, including the organic carbon, had to be crossplotted. This could only be done on maps of the area. It is difficult to summarize the potential based on organic carbon and show it geographically on but one map of the basin or even on single maps for single formations since the organic carbon is quite variable within the formation. Therefore, the stratigraphic column was divided into seventeen separate units chosen because of their somewhat greater uniformity in organic carbon contents throughout. These seventeen units are identified on the generalized stratigraphic column in Figure 4.

The average values of organic carbon in each of these map units were then contoured across the basin study area.

Biofacies

In the Eastern Gas Shale geochemical study, it was found that the kerogen was made up of more of the algal forms west of the Appalachian Basin axis, and more of the woody/coaly forms east of that axis. Herbaceous matter was ubiquitous. The relative quantities of the major kerogen types varied so widely from sample to sample within single rock units, that average composition of thick sequences of rock was obviously not a useful parameter for showing regional contrasts in organic contents or sequence potential.

In this study, the most useful method for showing regional and stratigraphic contrasts was the palynology. Although this technique revealed four distinctly different assemblages, or facies, or acid-resistant microfossils (15), the three major ones were selected as the primary parameters to be used for the assessment phase of the project.

The most important facies that emerged from palynological examination was one labeled "Tasmanites". It is characterized by very large numbers of the green algae, Tasmanites, in many cases to the exclusion of other marine forms such as acritarchs (algal origin), scolecodonts (polychaete worm teeth), and chitinozoans (flask-shaped forms of indeterminate origin). Because in many of the samples the distribution of palynomorphs was limited, or restricted, entirely or almost entirely to Tasmanites, the term "restricted marine" was also used to describe this facies. This was intended to imply only that the kerogen forms were restricted to Tasmanites. However, since the term restricted marine has other connotations in consideration of the environment of deposition, namely in referring to depositional areas or basins with restricted water circulation, that term was dropped in favor of the more descriptive term, Tasmanites facies.

Tasmanites obviously were deposited in a marine environment, but their presence apparently hindered or even prevented the growth of other marine algae. Perhaps like present-day red tides, their metabolism may have produced toxic products that were lethal to other life forms. Meanwhile, detrital material such as the herbaceous matter, particularly saccate and zonate spores, were transported to the area by prevailing winds, were dropped on the surface of the sea, sank, and were incorporated into the sediment.

The second major facies is a "marine" facies which implies a normal assemblage of marine microfossils that are found in marine Devonian shales elsewhere in the world. Among the forms found in sediments deposited in this environment in the Eastern Gas Shale basins are chitinozoans (which became extinct in the Upper Devonian), acritarchs, scolecodonts, leisospheres, and spaeromorphs (distinctive, thin-walled sperical palynomorphs), a few Tasmanites, and the usual herbaceous material.

The third major facies is labeled "terrestrial" because of the predominance of nonmarine or terrestrial debris and a very small or insignificant contribution of marine palynomorphs to the organic matter. The terrestrial kerogen is made up of both fresh woody debris and oxidized and reworked woody material. There are also small quantities of normal marine forms, as well as the ever-present herbaceous kerogen. The description as terrestrial refers to the predominant source of the organic material deposited with the mineral matter in these rocks, and not to the environment of deposition.

There is little question but that all of the Upper Devonian sediments of the Appalachian Basin were deposited in a normal, albeit relatively shallow marine environment. However, the organic matter varied in both biological and geographic origin. There were times and areas where normal marine forms grew, died, and their remains were incorporated into the sediments. There were other times when the green algae, Tasmanites, flourished and at periods of maximum growth, actually crowded out other marine organisms. When erosional slopes of the emergent land masses and their stream gradients were steep enough, large quantities of particulate woody material from primitive forests would flood portions of the basin, particularly the eastern parts, to such an extent that the marine forms were virtually obscured. And, superimposed on all possible combinations of these organic-matter types, herbaceous material, primarily in the form of saccate and zonate spores, was transported, probably wind-borne, across the entire basin.

As in the case of the organic carbon, the facies changed so rapidly from formation to formation, and within single formations that the first analysis was done on cross sections, the same ones on which organic carbon was presented. To assist in plotting the facies, each sample was labeled depending on its position on a triangular diagram corresponding to its relative content of each of the three major facies types of organic matter.

In order to present the biofacies data in map form, the appropriate data for each of the seventeen units chosen for presentation of the organic carbon data (discussed earlier) were placed on separate maps. These maps revealed a sequence of events in the deposition of organic matter from which local tectonism and direction of drainage could be inferred.

Maturity

The Thermal Alteration Index (TAI) measurements on the samples from the Eastern Gas Shale Program appear to be more useful for the purposes of assessment than reflectance estimates. TAI data more closely parallel the geology and show trends from top to bottom in some wells in which reflectance values were inexplicably uniform from top to bottom. Therefore, in this assessment, the TAI's are the factor used in the calculations and mapping.

To show regional trends in maturity, TAI values were spotted on the appropriate map (of the seventeen subdivisions selected for this study). Comparison of these maps showed that some of the TAI contours of adjacent intervals were identical and the maps could be combined into five maps.

These maps reveal that not all portions of the basin are as favorable for the generation of hydrocarbons as others. Some sediments are too immature to have realized a significant fraction of their enormous potential and some have experienced such extensive thermal cracking that the hydrocarbon is probably destroyed. The former case probably applies to the extreme northwestern and western portions of the study area where TAI's are less than 2. In spite of thick sections rich in organic carbon, the rocks can only be considered poor to fair sources of gas, and much of this may be microbially, not thermally, produced.

Source shales located in the areas where TAI's are between 2 and 3+ are in the optimum range for hydrocarbon generation, and this will be reflected in the hydrocarbon potential maps that will be presented later. Rocks exposed to temperatures such that their TAI's are 3+ or greater, are considered too mature. Most of their hydrocarbon has probably been dissipated or destroyed.

REGIONAL HYDROCARBON SOURCE POTENTIAL

The next step of the assessment was to combine the data on the organic carbon content, the biofacies (organic) type, and the thermal alteration index into a rating system that shows the relative source character of each of the seventeen study intervals as well as for the Appalachian Basin as a whole. This then was combined with the thickness of each unit to give the source potential of each unit, and a combined potential for the entire Upper Devonian.

For this purpose an arbitrary rating system, shown in Table 1, was set up. In this chart, relative ratings of source and potential were assigned to various combinations of organic carbon contents and thermal alteration indices. The absolute values were based on petroleum geochemical considerations, biased somewhat by the observation that in this basin, the low permeability Devonian shales apparently retain most of the gas that they generate, and because of this, maximum generation of hydrocarbons, and particularly of liquid hydrocarbons (oil), is held back until higher temperatures are reached (i.e., at higher alteration indices).

The qualifying footnotes at the bottom of the Table are based on the facts that algal and amorphous kerogens begin to crack at lower temperatures than terrestrial organic matter, and that algal and amorphous kerogen gives up more hydrocarbon liquids (oil or condensate) than does the terrestrial types.

A set of source quality maps was derived by first cross plotting TAI against organic carbon content to obtain a relative numerical ranking in each small uniform field on the map. This map was then superimposed on the biofacies map of the same interval, and the qualifying statements at the bottom of Table 1 were used to label the relative nature of the hydrocarbon expected from the kerogen in each field.

The next step in determining the relative source potential of each unit and of the basin involved the cross plotting of the relative source quality values, with the thickness of each unit. The numerical value of the relative source potential is the product of the source quality value for each individual unit times its thickness in feet. Thus, a very thin rock unit with exceptional source quality would not have very much potential. But a thick rock unit with only moderate source character would have an excellent potential.

First it was necessary to construct isopach maps for the limited stratigraphic units into which the Upper Devonian was divided for this study. The stratigraphic data interpreted from well logs from each of the study wells was used, and the contours were smoothed by referring to the published isopach maps of the basin (18, 19, 20).

Next, to show overall source potential for gas and for oil in the basin, the numerical rating from each of the areas for each of the seventeen maps was transferred to a grid with lines spaced about 9 miles apart both north-south and east-west. The values at each grid coordinate on each map were totaled with those at the same grid point on all the other maps, and the total was placed on similar grid for the entire Upper Devonian section. This process was done individually for each grid point in an area identified as having gas potential, and again for each grid point in any area identified as having oil potential. The data on the composite grids were contoured, and the absolute values reduced by a factor of ten, to produce the two overall source quality maps shown in Figure 5 and 6.

It is important to keep in mind that all of the areas within the 1 or 2 contour lines contain what would be considered good to exceptional oil sources in other basins of the world. If the shales themselves were fractured and/or interbedded with thin siltstone stringers, or if there were more typical sand or carbonate reservoir rocks in formations immediately above or below the rich source units, commercial production would be expected.

This exercise in geochemistry testifies to the face that the primary control on oil and gas occurrence in the Upper Devonian (in the portion of the basin studied) is something other than the distribution of source rocks. Obviously, the paucity of porosity and permeability in the Upper Devonian rocks has kept the dark shale units from sourcing one of the greatest oil and gas-producing provinces of the world.

GAS CONTENTS

One of the most recent estimates of the magnitude of the resource in the Eastern Gas Shale Basins has been based on the thickness of the dark and the gray shale, the relative proportions of which in turn were based on the gamma-ray log response, and the estimated average volumes of gas associated with each of these (21). It was an either-or situation and no intermediate values of gas contents for shales with intermediate organic contents was considered. Another estimate is based on pyrolysis yields of a handful of samples (22); others seem to be even more subjective (23).

The geochemical program has made it possible to make more accurate estimates of gas-in-place in the shales because one of the analyses is a direct measurement of gas contained in freshly taken cores from different parts of the basin. The measurement, as originally applied to well samples in the early part of the program, gave low estimates of the gas in place, because gas was lost as the core was brought out of the hole, and while the core was being measured and described, however quickly, before samples were sealed in gas-tight containers.

However, as part of this program, a controlled off-gassing procedure was developed, and the accuracy of the gas-in-place estimates derived from it were correlated with the pressure-retaining core barrel (24). These accurate estimates, together with the kerogen, biofacies and thermal alteration index data were then used to develop algorithms from which indigenous gas contents have been calculated for each rock unit at each well location.

The term "indigenous gas" means the gas produced by kerogen during the entire natural thermal evolutionary process before natural migration or loss during core retrieval and sample handling. These values are probably the most accurate estimates of gas-in-place available today.

The indigenous gas contents values calculated from the algorithms were described in map form. These maps gave a more accurate picture of the richness of the undisturbed shale, and the regional distribution of that richness. These values are also presented as MCF/A-F).

The next step in the assessment was to combine the richness of the rock in each interval with the thickness of each interval to obtain the distribution of the total quantities of gas in each unit.

With the data and maps available, the total acreage contained within each contour area on each of the maps of indigenous gas was integrated into one interval and the total gas in-place in that interval was computed. The total resource for that unit was expressed on each map as TCF (trillion cubic feet).

The maps provided the basis for a new assessment of the resource in the basin. The total resource from these units is approximately 2,500 TCF of gas. The distribution of the gas for the entire unit basinwide is shown in Figure 7. This map was prepared by summing the values on 9-mile grid lines for each of the 17 units. The matrix of totals for each of the grid intersections, over 1000 in number, were then contoured to produce the final map shown here.

The trend of greatest gas volumes is along an arcuate line extending from TENN - 9 through western Kentucky, southeastern Ohio, northwestern Pennsylvania, and to the area of the New York wells. The areas with the greatest volumes of gas are in Eastern Ohio and extreme west south-central New York where gas volumes reach 80 MMCF per acre dispersed through the entire upper Devonian.

CONCLUSIONS

From the perspective of petroleum geochemistry, the Upper Devonian rocks of the Appalachian Basin have exceptionally good potential to generate (i.e., source) large volumes of oil and gas. There is an abundance of algal organic matter, either Tasmanites or other marine algae as well as large quantities of herbaceous organic derivatives. In other basins, the former type of kerogen has been used as a promising sign in the search for oil and gas, and the oil is usually of the naphthenic type. The latter type, while not as encouraging as the algal kerogen, is still often associated with large commercial oil and gas fields, the oil usually being of a more paraffinic type.

Various amounts of more woody terrestrial organic matter also characterized parts of many of the units. And, while this type of organic matter is not as encouraging a sign, it can still generate significant quantities of gas, and small quantities of oil which tends to be of a more aromatic or paraffinic nature.

Based on the geochemical data, and particularly the algorithms for the calculation of in-place gas contents (which also make use of the controlled off-gassing results), a new estimate of total gas-in-place, both in matrix and porosity of the Upper Devonian shales of the Appalachian Basin, is set at approximately 2,500 TCF.

In light of the widespread occurrence of such excellent oil and gas source rocks, the production history of these rocks has been extremely disappointing. The major reason for this disappointment is the paucity of reservoirs associated with the organic-rich Upper Devonian shales. Most giant oil and gas fields of the world are produced from thick porous sands or limestones in juxtaposition with, or fluid continuity with, good petroleum source rocks, but source rocks with no better, and sometimes less, potential than that of the Upper Devonian of the Appalachian Basin.

These more typical geological relationships do not occur in the geological setting of interest. Therefore, the future likelihood of exploitation of this resource depends on two improvements in technology. The first of these will require the sharpening of our ability to locate naturally occurring porosity within the rich shale deposits themselves. This porosity is made up of networks of natural fractures and/or thin silt stringers, the location of which may be facilitated by detailed lithofacies studies, improved well log analysis, structural geology, and aerial photo analysis.

The second technological improvement that will increase the realization from this vast resource will be in stimulation methodology. Industry needs a documented stimulation program for every situation encountered in the shale; i.e., what current methods should be employed and what modifications need to be made for shale depth, thickness, lithology, mineralogy, physical and mechanical properties, organic richness, gas content, etc. The very magnitude of the resource itself justifies a continuing effort toward these ends.

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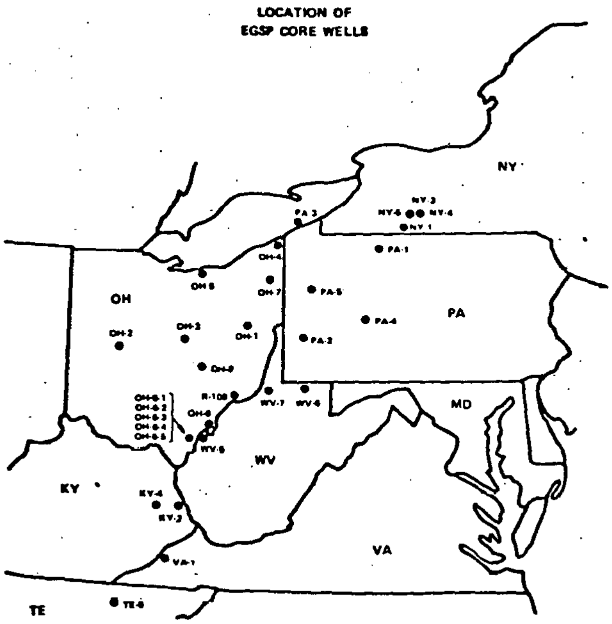

LOCATION OF
EGSP CORE WELLS

FIGURE 1

FLOW DIAGRAM FOR GEOCHEMICAL ANALYSIS

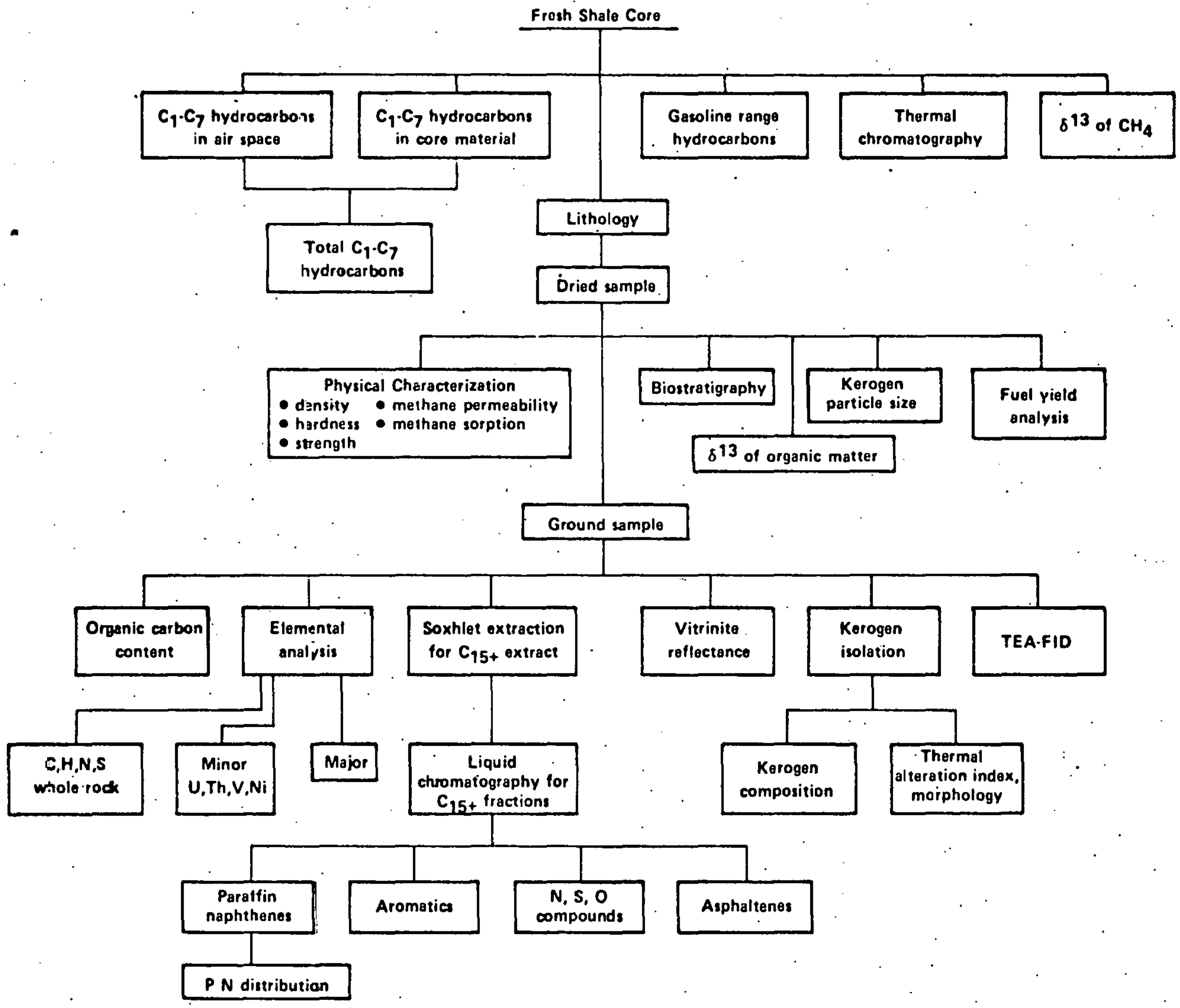


FIGURE 2

FLOW DIAGRAM FOR FUEL YIELD ANALYSIS

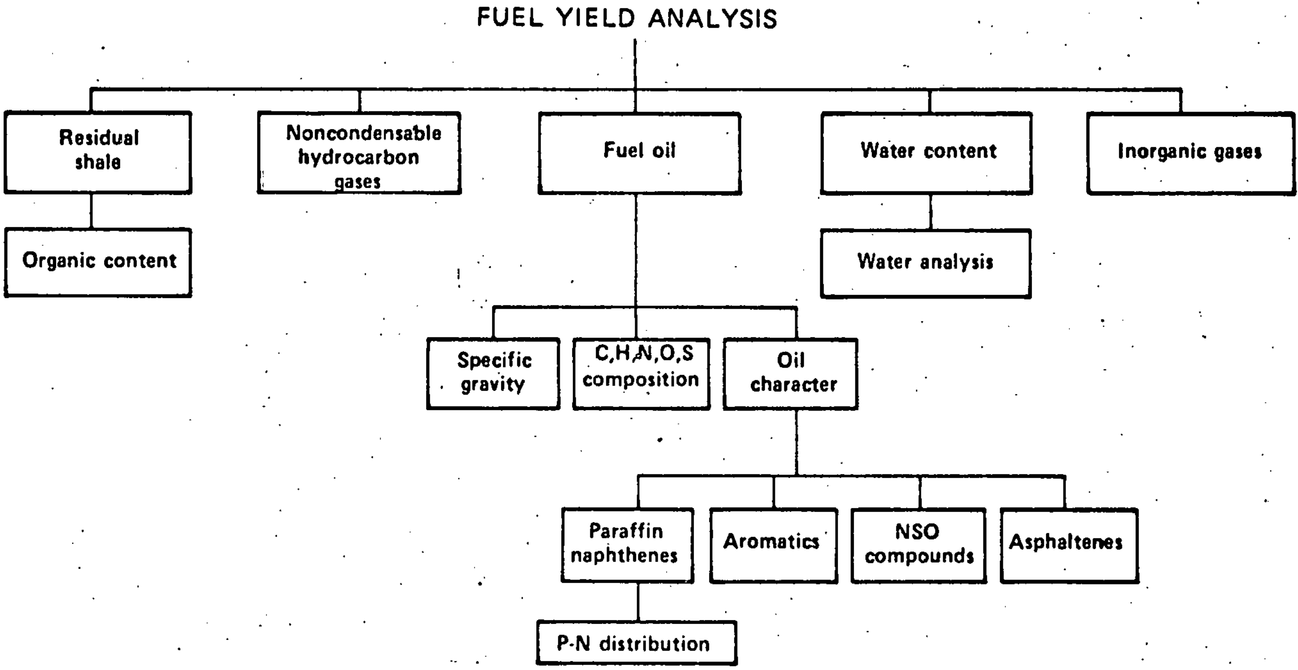
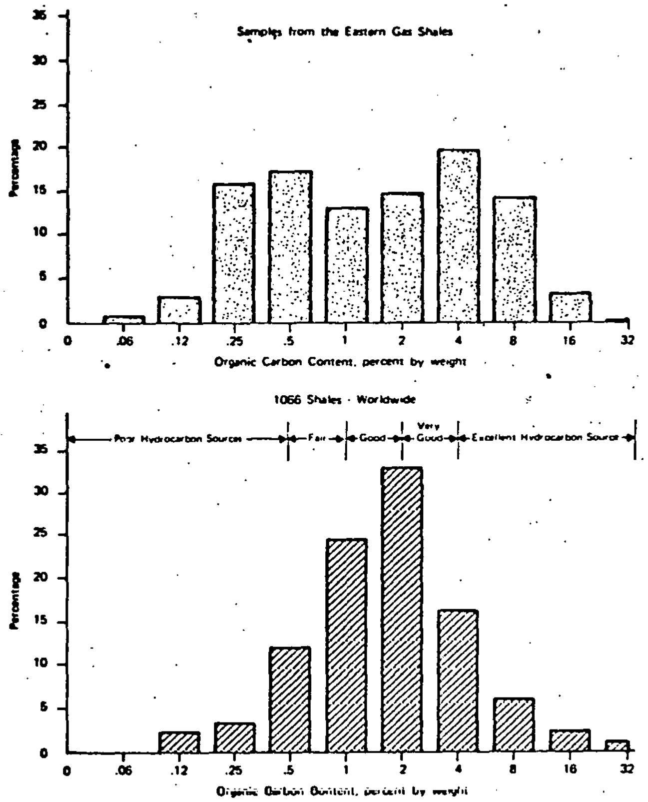


FIGURE 2A


Samples from the Eastern Gas Shales

1066 Shales - Worldwide

Organic Carbon Content of the Eastern Devonian Shales from the Appalachian Basin Compared with Other Shales.

FIGURE 3

IDENTIFICATION OF SUBDIVISIONS USED IN ORGANIC
GEOCHEMICAL ASSESSMENT MAPPING

WEST — EAST

<table>
<tr><td colspan="5">APPALACHIAN BASIN</td><td></td></tr>
<tr><td colspan="2">OHIO</td><td>PENN.</td><td colspan="2">NEW YORK</td><td rowspan="3">ASSESSMENT MAP NUMBER</td></tr>
<tr><td colspan="2"></td><td></td><td colspan="2"></td></tr>
<tr><td colspan="2">BEDFORD SH.</td><td>POCONO FM.</td><td colspan="2">KNAPP FM.</td></tr>
<tr><td colspan="2">CLEVELAND SH.</td><td rowspan="6">CATSKILL</td><td colspan="2">CATTARAUGUS FM.</td><td>17</td></tr>
<tr><td colspan="2">CHAGRIN SH.</td><td colspan="2">CHADAKOIN FM.</td><td>16</td></tr>
<tr><td rowspan="6">OHIO SHALE</td><td rowspan="2">UPPER HURON SHALE M.</td><td rowspan="6">CANADAWAY GROUP</td><td rowspan="4"></td><td>15</td></tr>
<tr><td>14</td></tr>
<tr><td rowspan="2">MIDDLE HURON SHALE M.</td><td>13</td></tr>
<tr><td>12</td></tr>
<tr><td rowspan="2">LOWER HURON SHALE M.</td><td rowspan="2">DUNKIRK SH.</td><td rowspan="2">DUNKIRK SH. M.</td><td>11</td></tr>
<tr><td>10</td></tr>
<tr><td colspan="2">UPPER OLENTANGY SHALE</td><td>JAVA FM. (HANOVER SH.)</td><td colspan="2">JAVA FM. (HANOVER SH.)</td><td>9</td></tr>
<tr><td colspan="2">MIDDLE OLEN.</td><td></td><td rowspan="3">WEST FALLS FM.</td><td>ANGOLA SH. M.</td><td>8</td></tr>
<tr><td colspan="2" rowspan="2">LOWER OLENTANGY SH.</td><td rowspan="2">RHINESTREET SH.</td><td rowspan="2">RHINESTREET SH.</td><td>7</td></tr>
<tr><td>6</td></tr>
<tr><td colspan="2" rowspan="6">ONONDAGA LS.</td><td>MIDDLESEX SH.</td><td colspan="2">SONYEA GROUP MIDDLESEX SH.</td><td>5</td></tr>
<tr><td>HARRELL SH.</td><td colspan="2">GENESEE GROUP GENESEO SHALE</td><td>4</td></tr>
<tr><td>TULLY FM.</td><td colspan="2">TULLY FM.</td><td rowspan="2">3</td></tr>
<tr><td>MAHANTANGO FM.</td><td colspan="2">HAMILTON GROUP</td></tr>
<tr><td rowspan="2"></td><td colspan="2" rowspan="2">MARCELLUS</td><td>2</td></tr>
<tr><td>1</td></tr>
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FIGURE 4

OVERALL GAS SOURCE POTENTIAL

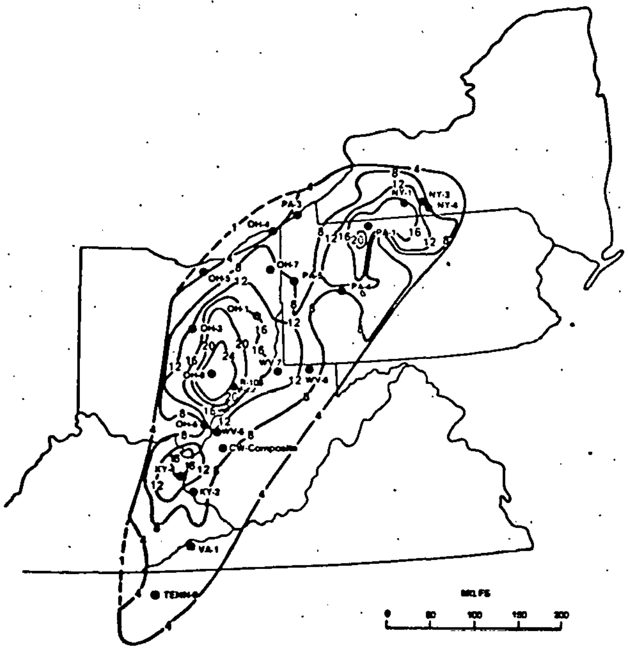

FIGURE 5

UPPER DEVONIAN SHALES

Prepared by Mound Facility

OVERALL OIL SOURCE POTENTIAL

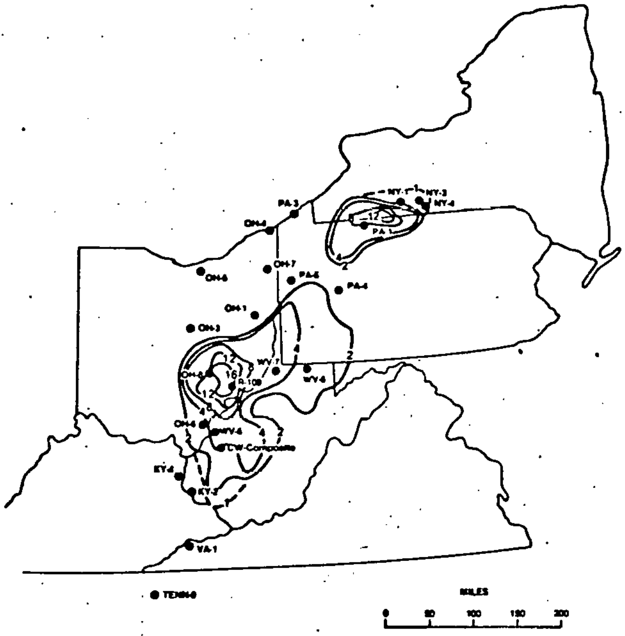

FIGURE 6

UPPER DEVONIAN SHALES

Prepared by Mound Facility

TOTAL UPPER DEVONIAN SHALE INDIGENOUS GAS IN PLACE

$$\left(\frac{\text{MCF Gas/Acre}}{1000}\right)$$

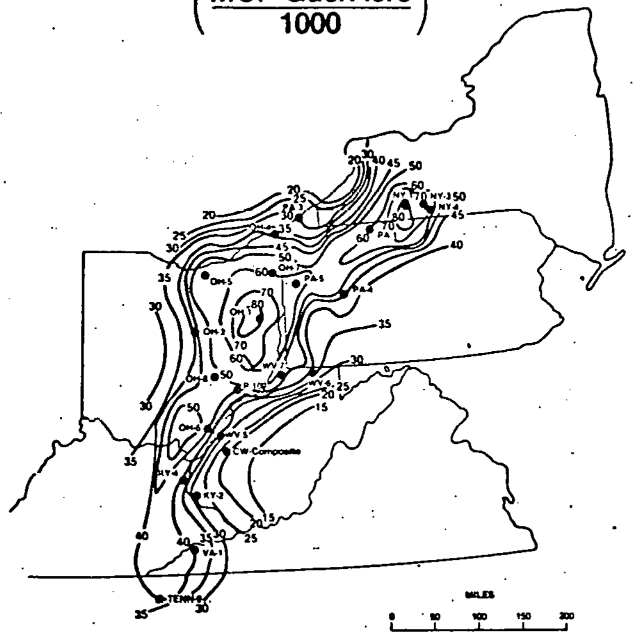

FIGURE 7

TOTAL 2579 TCF

Prepared by Mound Facility