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A Review of the Isotopic Data for Gas Samples from the Napoleonville Well NS #1 and Bayou Corn Gas Samples

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I have been asked to review and comment on the isotopic data from two gas samples collected in the Gulf Coast region. One sample was from a gas storage cavern and the second was collected from a bayou in the area. The initial problem was to determine whether the gas collected from the bayou was biogenic or thermogenic. Secondly if the gas was determined to be thermogenic, then could it be demonstrated that the gas was, or was not, related to the gas from the Napoleonville Well NS#1.

In the initial investigation two gas samples were collected and sent to Isotech, Illinois, for stable isotope analyses of the individual gas components plus their compositional analyses. Prior to discussing the results a brief overview of stable isotopes will be given.

Stable Isotopes

The hydrocarbon constituents of natural gas consist of 2 atoms, carbon and hydrogen. Each atom is comprised of a heavy and light isotope with the lighter isotope generally being the most abundant and dominating the heavier isotope. The relative proportions of the two isotopes are measured relative to an international standard and expressed using the δ notation in parts per thousand. Therefore a compound that has a $\delta^{13}C$ value of -33 per mil is depleted in 33 parts per thousand of the heavier isotope relative to the standard. Isotope values of individual components in different gas samples can vary as a result of numerous factors such as source and maturity. Through the use of the combined gas chromatograph-isotope ratio mass spectrometer (GCIRMS) it is now possible to determine both the C and H isotope composition if the individual compounds in natural gas samples without having to physically separate the compounds prior to analysis. For C these values can be measured with a precision of +/- 0.3 per mil and for H the precision is generally +/- 5 per mil.

When comparing two samples as in the current study, the results are relatively easy to interpret. If the samples are isotopically distinct from each other that suggests they are not related or from the same source. If the samples are isotopically very similar then the result is somewhat ambiguous since it may mean they are related and from the same source or it could be a coincidence.

The second question is whether or not the gas is of thermogenic or biogenic origin. Again this is generally a relatively easy question to address. Basically biogenic gas is

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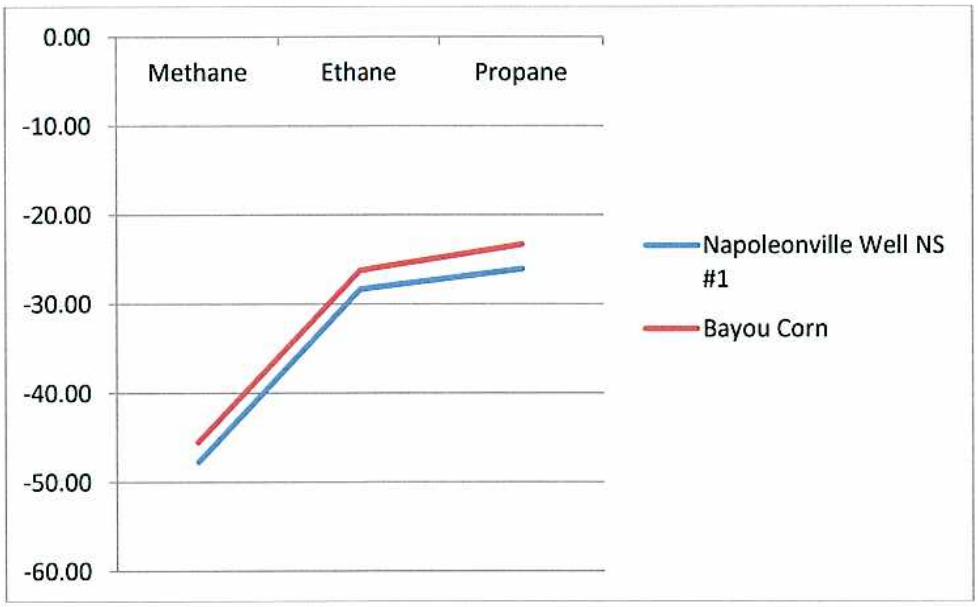
isotopically light meaning that their values will be isotopes values will be very negative, i.e. C values for biogenic gas will be in the range -60 to -80 per mil and H values in the range -200 to -300 per mil. Thermogenic methane will be heavier and have C isotope values in the range -48 to -35 per mil.

Discussion

The data for the two samples analysed by Isotech for Chevron in this study are presented in Table I. The results are best presented in a plot of carbon number against isotope values for C and H as shown in Fig. 1a and b. Bearing in mind the precision given above, the differences between the two samples is much greater than the precision and therefore one can confidently say that the samples are isotopically distinct. Examination of the relative proportions of other components in the two samples such as the iC4/nC4 ratios support these two samples being different from each other. Therefore one can conclude that the gas in the Napoleonville Well NS#1 is not the source of the Bayou gas sample. To complete this investigation samples of gases from other potential sources in the area should be collected and characterized isotopically and quantitatively.



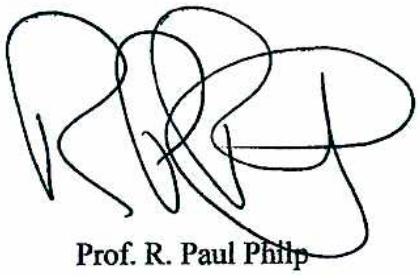
It is also important to note that analyses of gas samples by GC and GCMS where all the volatile gaseous components simply elute with the solvent peak is a total waste of time. You have to characterize gas samples through the use of gas chromatography using a temperature program that will actually resolve individual components in the C1-C5 range and then secondly the samples have to be characterized isotopically.

The question as to whether the bayou gas is biogenic can also be readily answered from the isotopic data. The value of -45.49 for the C isotope composition of methane is isotopically too heavy for this gas to be biogenic. In addition it is not possible to have a mixture of the biogenic gas and gas from the Napoleonville well to produce a value of -45.49 for the bayou gas. Biogenic gas would be expected to have a C isotope value in the range -55 to -80 and mixing that with a sample that is -47.73 would produce a value that would be isotopically lighter than -47.73

for the C isotope value of the methane. It should also be noted that there is no evidence for the presence of ethylene and propylene that may be expected if biogenic gas was present. Finally ratios of C1/C2+C3 for the Napoleonville well sample and bayou sample were 58.1 and 39.7, respectively, typical of values expected for thermogenic gas.

Summary

Based on the isotopic and compositional analyses of these two samples a number of conclusions may be reached. First the bayou gas sample is not biogenic and is dominated by thermogenic gas. Secondly the two samples are isotopically and compositionally distinct from each other. It would appear unlikely that the Napoleonville gas is the source of the bayou gas. These conclusions are based on the data available from these two samples and of course if additional data become available from other samples I reserve the right to revise my opinions based on the additional results.



Prof. R. Paul Philp
Wednesday, July 11, 2012

ISOTECH
ISOTECH LABORATORIES INC

ANALYSIS REPORT

Lab #: 252843 Job #: 18596
Sample Name: Napoleonville Well NS #1 Co. Lab#:
Company: ChevronTexaco
Date Sampled: 6/26/2012
Container: 300 ml stainless
Field/Site Name:
Location:
Formation/Depth:
Sampling Point:
Date Received: 6/28/2012 Date Reported: 7/10/2012

Component	Chemical mol. %	$\delta^{13}C$ ‰	δD ‰	$\delta^{15}N$ ‰
Carbon Monoxide	nd			
Hydrogen Sulfide	na			
Helium	0.0033			
Hydrogen	0.0012			
Argon	nd			
Oxygen	nd			
Nitrogen	0.25			
Carbon Dioxide	0.97	-4.81		
Methane	96.93	-47.73	-174.3	
Ethane	1.48	-28.38	-124.4	
Ethylene	nd			
Propane	0.211	-26.05		
Propylene	nd			
Iso-butane	0.0505			
N-butane	0.0470			
Iso-pentane	0.0192			
N-pentane	0.0125			
Hexanes +	0.0221			

Total BTU/cu.ft. dry @ 60deg F & 14.73psia, calculated: 1020
Specific gravity, calculated: 0.576

nd = not detected. na = not analyzed. Isotopic composition of hydrogen is relative to VSMOW. Isotopic composition of carbon is relative to VPDB. Calculations for BTU and specific gravity per ASTM D3588. Chemical compositions are normalized to 100%. Mol. % is approximately equal to vol. %.

ISOTECH
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ANALYSIS REPORT

Lab #: 252844 Job #: 18596
Sample Name: Bayou Corn Co. Lab#:
Company: ChevronTexaco
Date Sampled: 6/26/2012
Container: Cali-5-Bond Bag
Field/Site Name:
Location:
Formation/Depth:
Sampling Point:
Date Received: 6/28/2012 Date Reported: 7/10/2012

Component	Chemical mol. %	$\delta^{13}C$ ‰	δD ‰	$\delta^{15}N$ ‰
Carbon Monoxide	nd			
Hydrogen Sulfide	na			
Helium	0.0018			
Hydrogen	nd			
Argon	0.257			
Oxygen	4.54			
Nitrogen	19.26			
Carbon Dioxide	1.70	-3.58		
Methane	72.21	-45.49	-161.3	
Ethane	1.54	-26.26	-113.1	
Ethylene	nd			
Propane	0.328	-23.32	-101.4	
Propylene	nd			
Iso-butane	0.0742	-24.12		
N-butane	0.0520			
Iso-pentane	0.0196			
N-pentane	0.0092			
Hexanes +	0.0102			

Total BTU/cu.ft. dry @ 60deg F & 14.73psia, calculated: 773
Specific gravity, calculated: 0.690

nd = not detected. na = not analyzed. Isotopic composition of hydrogen is relative to VSMOW. Isotopic composition of carbon is relative to VPDB. Calculations for BTU and specific gravity per ASTM D3588. Chemical compositions are normalized to 100%. Mol. % is approximately equal to vol. %.