Carbon Dioxide in view of Geochemical Characterization of Natural Gases using GC

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ABSTRACT

Sixty eight natural gas samples were collected from four different formations in the northern Western Desert from different depths and their composition was correlated with age and depth of the formations. An organic geochemical characterization of the collected natural gases was achieved by determining carbon dioxide via gas chromatography connected with thermal conductivity detector (TCD) and flame ionization detector (FID). The mol percent of CO_2 increases as a function of both the depth and the age of the formation of the bearing reservoir, its presence suggest organic origin of the gases and CO_2 presents as a by-product of thermal maturity of the kerogen.

Key word:- Natural Gas, northern Western Desert, carbon dioxide, Gas chromatography, Thermal conductivity detector, Geochemical characterization.

Introduction

Natural gases are an important source of fuel, clean source of energy and the production of high value chemicals. natural gas supply chain was investigated using concepts related to natural gas industry [1]. The characteristics of natural gases are dependent on the carbon dioxide contents and hydrocarbons distribution in the gases. Thus, the calculation of calorific value, hydrocarbon dew point, specific gravity and other physical properties requires detailed analysis of the gases as

can be provided by gas chromatography [2]. Also, the gas compression flow rates through pipes, and therefore shape of flames, design of gas holders and the most other gas handling equipments [3, 4]. The correct decision about the most profitable petrochemical products to be made from natural gases is essentially dependent on the hydrocarbons distribution in the gases.

Carbon dioxide content in natural gases was employed to evaluate the geochemical aspects of the natural gases. As a significant by-product of Kerogen maturation, CO_2 is considered of organic origin, this is primarily due to decomposition of carbonyl (C=O), methoxyl (-OCH~), phenolic hydroxyl (-OH) and perhaps other oxygen groups. Its content in natural gases varies systematically with both the reservoir age and temperature [5-7]. The percent of CO_2 in natural gases may suggest the origin of these gases. When CO_2 content is less then 15%, it strongly suggests the organic origin of the gases and the bearing basins are probably tectonically stable. Inorganic C~ as well as organic C~ can be generated in the oil and gas bearing basins or areas that are tectonically active (e.g. with active faults, magnetism and seismic activity [8]. On the other hand the primary agent responsible for carbonate dissolution in the subsurface is carbonic acid (H_2CO_3) formed by generation of carbon dioxide during the thermal maturation of organic matter in sediments [9]. This study aims to evaluate the natural gases from different formations from Western Desert in view of CO_2 content. In addition the geochemical aspects of the studied gases can be discussed on the bases of CO_2 ratios in these areas.

Experimental

Sampling

For surface sample: The gas sample container was heated to the temperature at which the sample was collected and stabile for two hours with shaking to revalorize any liquid. With the cylinder in the vertical position the bottom valve was cracked carefully to check for liquids and then the opening pressure was determined. This pressure was equal to or slightly greater than the pressure at the time of sampling.

Gas sample preparation for analysis

Separator gas samples were collected by using a previously evacuated sample cylinder of the correct size according to the API method [10]. The gas from subsurface and well head pressurized liquid samples was separated according to the following procedure.

The sample was placed in a stand and the lower valve connected to a high pressure mercury pump. Mercury is injected and the sample agitated until it is in single phase at 5000 psig. A volume of this oil is then carefully pumped out of the cylinder through an atmospheric separator connected to a gas collection device, in order to see how much gas and oil were liberated from a measured volume of pressurized oil.. The volume of gas and its temperature were measured along with the weight of oil and its density [11]. The hydrocarbon and non hydrocarbon components in the collected gas are then analyzed by gas chromatography according to ASTM (D 1942-91) [12].

Gas chromatographic analysis

The analysis was performed using a Varian vesta 402 gas chromatograph equipped with thermal conductivity detector (TCD) and flame ionization detector (FID) under the following conditions: The instrument is fitted with three columns, the first is 13x molecular sieve to separate O_2 N_2 and Methane, the second is porapak to separate CO_2 and light gases, the third is OV 101 column to separate the remaining hydrocarbons. The analysis occurs under two

programmed of temperatures, the first initial temperature 50°C at 7 min initial time with 20 degree min^{-1} till reached to the first final temperature 120°C which heated with 10 degree min^{-1} till reached to second final temperature 240°c and final time 10 min. Helium was used as carrier gas for TCD with flow rate 25 ml min"} and Nitrogen was used as carrier gas for FID with flow rate 30 ml min-t. The injector temperature was 220°C and both the detector temperatures were 300 ºC. The instrument was connected with the board data handling system for computing the peak area and mol percent. The quantitative analysis was conducted by analyzing standard reference samples of natural gas containing CO_2 of mol percent ranging from 1 % to 100%.

Results and Discussion

Sixty eight gas samples were collected from four locations representing different formations. The distribution of CO_2 was determined by gas chromatography according to the recent procedures applied in this field. The result of the analysis of CO_2 may represent an important source of data on the chemistry of gases in Western Desert. In this paper, the abundance and distribution of CO_2 content of the natural gases from the studied samples was evaluated from geochemical point of view. In this concern, CO_2 content exhibits some trends, geographic depth and age. Moreover,

the percent volume of CO_2 may suggest the origin of the gases and the temperature decline at which the CO_2 content increases markedly.

(i) Distribution and abundance of CO_2 in natural gases, Western Desert.

Tables (1, 2) and Figure 1 represent the average CO_2 content (as mole %). In natural gas samples collected (recovered) from four formations. It is clear that the average CO_2 content increases from the youngest to the oldest Formation i.e. CO_2 content in formation 1 varies from 0.14 to 2.74 mol % and in formation 4 the content ranges from 5.58 to 7.97 mol %

Table 1 Depths and carbon dioxide contents of the studied natural gas samples from the different four formations

Age	Formation	No. of Wells	Avg. Depth FT	Avg. CO_2 mol %
Upper Cretaceous	Formation 1	17	8621	1.52
Upper Cretaceous	Formation 2	18	6713	1.39
Lower Cretaceous	Formation 3	19	10623	4.46
Jurassic	Formation 4	20	12474	7.56

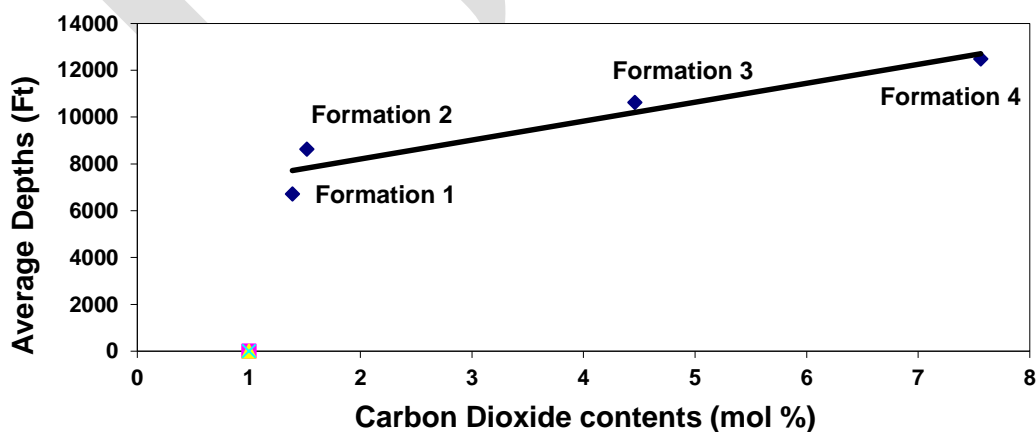Fig 1.

Distribution of Average carbon dioxide contents with depths of the studied formations

(ii) Depth trends

The distribution of average CO_2 content with depth of the four studied formations was given in Table (2). Correlation of CO_2 content of the studied gases shows a very systematic relationship with depth especially in the Formations 1 and 2. In these two areas, there is a fairly low and constant level of CO_2 at shallow depths (<1 mole percent) down to a point at which the CO_2 content increases markedly. Depth corresponding to the increase of CO_2 mole percent is shallower in Formation 1 (6200-8000) than in Formation 2. This difference may be due to the difference in geothermal gradients between the two locations. The thermal gradients range between 28.2 °F/Km. If the surface temperature is assumed to be 23.3 °C then the temperature of rapid increase in carbon dioxide is 103°C in Formation 2. This is in good agreement with in 100°C peak of CO_2 generation. The inflection near 100°C suggests that the gases have not been influenced by vertical migration.

From another point of view CO_2 content of gases from formation 4 is relatively high. The formation is presents at deep depths and gases collected of depth starting from (11017 ft.). This depth corresponds to the peak generation of CO_2 ranging from (II 01717798 ft).

However, the CO_2 mole percent in formation 3 not correlate with depth. This may be due to the variation of carbonaceous matter in this formation, thus the CO_2 content varies not systematically. The gases may suffer vertical migration at different depths.

(iii) Age Trend:

There is an overall increase in CO_2 content from stratigraphically top most formation 2 to relatively bottom most formation 4. Higher CO_2 content in formation 4 and occasionally in formation 3 is possibly related to higher content of carbonaceous matter in these formations. Both the formations 3 and 4 comprise significant quantities of carbonaceous claystones, coaly shales and coal seams.

(iv) Hydrocarbon Origin

The CO_2 content of the analyzed samples suggests the organic origin mainly of the gases as a byproduct of Kerogen maturation. The occurrence of carbonaceous matter in formations 3 and 4 suggest the contribution of inorganic origin of the gases.

Table 2. Distribution of Average carbon dioxide contents with depths of the studied formations

Formation 1		Formation 2		Formation 3		Formation 4	
Depths FT	CO_2 Mol %	Depths FT	CO_2 Mol %	Depths FT	CO_2 Mol %	Depths FT	CO_2 Mol %
2580	0.14	5514	0.42	8456	2.18	11017	5.59
3800	0.69	5600	0.88	8549	6.37	11127	6.67
4000	0.39	5880	0.98	8882	6.92	11291	7.05
5325	0.40	5900	0.93	8906	4.35	11501	7.09
3770	1	6614	1.2	9027	2.48	11546	7.33
5880	1.03	7200	1.2	9373	3.21	11788	7.08
5984	1.08	7395	0.74	9374	5.28	11930	7.15
5989	1.45	9217	1.2	9445	3.99	12046	7.66
6043	1.27	9371	1.29	9449	4.31	12261	8.16
6101	1.01	9734	1.6	10160	2.05	12332	7.91
6174	1.23	9740	1.7	10847	7.59	12436	7.79
6236	0.81	9747	2.55	11682	4.79	12538	7.94
6285	1.31	9978	1.8	11848	4.24	13120	7.64
8187	2.23	10219	1.94	12242	5.09	13200	7.71
8893	2.39	10661	2.07	12329	5.59	13250	7.51
10827	2.66	11515	2.53	12344	4.59	13300	7.89
11099	2.74	12275	3.25	12431	2.3	13310	7.97

Conclusion

- CO_2 content in natural gases from Western Desert varies from 0.14 to 7.97 mol percent. The CO_2 mol percent correlates systematic with depth, age in the following formations, 1, 2, 4 and 3. Formation 3 is the only formation which shows no trend for CO_2 with depth this due to the heterogenic nature of the lithofacies.

- The geothermal gradients range between 28.2 of to 51.8 °f/Km. the gases in Western Desert may be of organic origin, however in case of formations 3 and 4 CO_2 of inorganic origin may contributes in the content of the gases.

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