Evaluation of the Gross Heating Value of Natural Gas Sample from Soku Gas Plant

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Abstract
The gross heating value of natural gas sample obtained from Soku gas processing plant was determined using gas chromatographic technique. The gross heating value of the gas sample at standard conditions (60^0F/15 ^{0}C and 14.74Psia/1 atmospheric pressure) was determined using the molecular compositional analysis data and standard heating value data for pure hydrocarbon (Alkanes) gases usually found in natural gas mixtures. The composition of the natural gas sample was measured with a 500 series version thermal conductivity detector (TCD) gas chromatograph built by SHIMADZU Corporation, Japan. Chromatographic technique used for the measurement of gas sample composition was in accordance with (ASTM D 7164 -10) standard method. The values obtained falls within the range of natural gas gross heating value of (950 – 1150BTU/SCF). The calculated average gross heating value of the gas sample at standard conditions was (1,133BTU/SCF). It was observed that, the gross heating value of natural gas depends on the volume or molar fractions of constituents in the gas sample mixture.

Keywords: *Gross heating value, natural gas, BTU, chromatographic technique.*

1.1 Introduction

Natural gas is a fossil fuel formed when layers of decomposing plant and animal matter are subjected to great heat and pressure for over thousands of years. The energy that plants originally obtained from the sun is stored in form of chemical bonds in natural gas molecules (USDE, 2013). Natural gas is non-renewable resource because, it cannot be replenished on a human time scale. It consists primarily of methane which accounts for over 80% by volume, the rest includes varying amount of C_2 to C_6^+ and non-hydrocarbon components such as helium, N_2, CO_2, H_2S and moisture (Perderson, 1989). The composition of natural gas varies from one location to another.

Associated gases are found in association with crude oil and water in oil reservoirs. During production of crude oil to surface conditions, gases dissolved in crude oil are liberated as by–

product. The liberated gas from oil phase is known as associated gas. Non associated gases are found in dry gas well. Non associated gas may be dry gas (lean gas or wet gas (rich gas) (Perderson, 1989).

Oil producing companies, Refineries, Petrochemical plants, and Gas processing plants often burn fuel gases (associated and non-associated gases and refinery gases LPG) when there is no storage/treatment facilities in place. The burning of these fuel gases which are considered unusable waste gases or flammable gases are released by pressure relief valves during oil production, oil refining and unplanned over pressuring of gas plant is known as gas flare. Whenever the plant equipment items are over pressured, pressure relief valves actuate to automatically released gas (wet or dry gas and sometimes liquids). The released gases and/or liquid vapors are burnt as they exit the flare stack chimney. The size and the radiated heat and the brightness of the flame depend on the quantity of flammable gas and the heating value of the flammable gases (Bruno, 2007). Gases flared in refineries, oil production platform and gas processing plants are composed mainly of low molecular weight hydrocarbons with high heating value (NNPC, 2012).

The commercial value of natural gas to a consumer who uses it as heating fuel depends on its heating value, usually measured in British Thermal Unit (BTU) per standard cubic feet. BTU is the heat energy needed to raise the temperature of one pound of water by one degree Fahrenheit (1^0F). The heating value of natural gas supplied to consumers varies hence, its value is constantly measured in order to meet standard specifications set by gas utility/supply companies. Since the heating value (BTU) of natural gas varies with gas compositions, and the potential financial impact of BTU data is tremendous, it is imperative that we determine the BTU quality of gas we utilize and the quality of the data produced by laboratories using gas chromatographs for BTU determination is accurate (Joseph, 1989). The range of heating value of natural gas is 950 – 1150 BTU/SCF (Bruno, 2007). According to the United States Energy Information Administration, the heating value of natural gas delivered to consumers in the United States from 2009 to 2014 ranges from 958 to 1, 083 BTU/SCF (USEIA, 2016).
According to an on-line energy conversion platform, the BTU is related to electrical energy unit in kilo watt-hour (kwh). For instance, when one standard cubic meter (1.0 m^3) of natural gas is burnt in air at standard conditions, 37.3 kilo joule (kJ) of heat energy or 11.11 kilowatt-hour electric unit worth of energy is released (http://www.kylesconverter, 2016]. This makes natural gas attractive alternative source of clean, efficient and cheap energy. The market value placed on any fuel gas such as natural gas is the heating value (BTU/SCF).

Natural gas dispensed from a simple table top gas cooker/burner or stove can generate temperature in excess of 1100^oC (2000^oF) making it a powerful domestic cooking and heating fuel (Zimmerman, 1995). However, the quantity of heat produced during combustion of any fuel gas depends on its heating value (BTU). Why the heating value of natural gas should be determined is due to the fact that, there are cases of compositional variations during transportation and at the point of delivery to consumers. Change in gas stream compositions seriously affect the value of BTU of gas supplied to consumers. Therefore, the heating value of natural gas must be determined from time to time to enable the updating of BTU conversion factor effectively. Gas companies have observed in practice that, the BTU of natural gas supplied to consumers varies from point to point across delivery system such that, some customers receive more energy than others even though they may consume the same volume of gas. One way to overcome the variation of BTU is to regularly update BTU conversion factor from time to time. This ensures the most accurate method of billing customers for the quantity of energy consumed.

The heating value of natural gas is important to consumers in that, it determines the energy content or quantity of heat energy per unit volume or mass supplied to the consumers. The consumers pay for the energy unit in BTU of fuel gas in volumes or mass. For instance, to boil 4 litres of water, customers in areas that receive natural gas with lower BTU content use a greater volume of gas than customers receiving natural gas with higher BTU content to boil the same amount of water. However, both customers use the same amount of energy (Columbia Gas Inc, 2016). The heat release rate of a burning natural gas from gas flare stack is calculated from the heating value (BTU) of the gas, (firenist.gov). Gas flare stacks design Engineers rely on the accurate value of the gross heating value of nature gas to be flared as an input parameter for simulation to optimize design cost. The total heat load of the gas flare stack or chimney depends on the gas composition and the gross heating value, hence, the accurate determination and update of BTU is imperative. This paper focuses on the accurate determination of the gross heating value (BTU/SCF) of natural gas sample from Soku gas processing/Treatment plant.

2.0 Materials and Method

2.1 Gas Sampling and Condition for Analysis:

Soku gas processing plant is located in souk in Rivers states of Nigeria. It is a gathering centre and also a processing plant where all gases from the oil and gas field are assembled and processed for industrial use and exportation. Two gas samples were obtained from the Soku gas processing plant for compositional analysis by Gas chromatograph. The two gas samples were heated to field temperature condition of 96^{o}F in an air bath thermostat oven for one hour to equilibrium gas sample temperature of 96^{o}F.

2.2 Gas Chromatograph Analysis

A 500 series variant Thermal Conductivity Detector (TCD) gas chromatograph which was built by SHIMADZU Corporation, Japan was used for gas sample composition analysis.

The gas chromatograph consists of five main units, namely, the thermostat controlled constant temperature oven column, the detector, the integrator, microprocessor and the output signal strip-chart pen plotter / recorder unit. These five main units are combined to form the complete gas chromatographic system with flow regulator manifold and other peripheral devices that ensure stable and error free operating environment of the system.

The carrier gas (Helium gas) cylinder manifold value was opened and flowing carrier gas line pressure was set at 450 Kpa. The oven column unit was switched on where temperature was set at 150^{o}c. the carrier gas circulated for at least 30 minutes through the oven column before the detector unit was switched on and detector filament current was set at 250mA in line with the operational guidelines. The entire system was conditioned for 24hours without power interruption. The gas chromatographic system (GC) has been calibrated previously with all process/operating parameters needed to run the system and analyze gas have been keyed into the database through the operator console/keyboard. The GC was put on standby for routine gas analysis throughout the duration of the analysis.

2.2.1 The Operating Parameters of Gas Chromatograph

Time Program 40 minutes

Carrier gas	High grade (99%) Helium gas
Carrier gas line constant flow pressure	450Kpa set point (80Psia)
Oven column temperature	150^{o}c
Detector filament bridge current	250-300 mA
Normal set point for detector current	250mA
Constant DC voltage	16.5 VDC
Power consumption	49.5 Watt
Thermal conductivity coefficient	$4.4x10^{-4}$ cal/ sec cm^{2} ^{o}C.
Detector filament material	Tungsten- Rhenium
Temperature coefficient ()	0.0033 $^{o}c^{-1}$
(Ro) Reference bridge resistance (at 0^{o}c)	25^{o}C
R+ Bridge resistance at 350^{o}c	55

Signal response factor for small sampling (TCD) 6000-7000 uvCm^{3}/ mg at 150^{o}c. Column material is made of 12 feet long stainless steel silicone column with 1/4 inch diameter packed with 42-60 mesh molecular sieve coated with Dow corning silicone fluid.

2.3 Gas Compositional Analysis.

The gas sample after conditioning at the constant temperature air bath oven for one hour to equilibrium temperature of 96^{o}f was flashed to standard atmospheric conditions. The flashed gas without liquid drop out was passed through the Gas chromatograph for compositional analysis. For any gas sample composition to be analyzed, a reference standard gas chromatogram must first be obtained. Thus a reference standard gas cylinder was connected to the gas sampling loop valve of the gas chromatograph flow manifold. The whole manifold system including sampling loops was evacuated for about 30 minutes to ensure that, all loops, control valves and oven column were air tight and leak proof. Thereafter the whole system was flushed with high grade Helium gas and evacuated for another 15-30 minutes. The standard gas cylinder valve was carefully opened and purged the gas flow line with the standard gas. The metering needle value was carefully opened to admit the reference standard gas. The solenoid valve was manually operated to actuate the sampling loop valve to place the standard gas sample in the column. The time programmed was set at 40 minutes. At the end of 40 minutes, the strip chart pen plotter/recorder produced a profile of triangular peak areas over elution time period, this profile or chart is the chromatogram for the reference standard gas. Table 1 below shows the peak area of composition of reference standard gas and the absolute response factor (RF) for TCD.

3.0 Results and Discussion

Table 1: Peak Area and Composition of Reference Standard gas sample

Component 1	Reference Standard (mole%)2	Peak area 3	Absolute response factor 4 =(2÷3)
N_2	3.54	6224	0.0005688
CO_2	2.24	4397	0.0005094
C_1	72.40	92053	0.0007865
C_2	7.96	16432	0.0004844
C_3	5.54	14292	0.0003876
i C_4	2.53	7854	0.0003221
nC_4	3.67	11335	0.0003238
iC_5	1.00	3409	0.0002933
nC_5	1.00	3487	0.0002868
C_6^+	0.12	2627	0.0000457
TOTAL	100.00	162110	

The response factor (RF) compares the peak area with the composition. The relative response factor (RRF) compares the detector response of all compounds or components of gas sample to that of the reference compound. A data base of reference compound was held when a reference standard gas was first analyzed. The microprocessor comparator was able to compare data base in the system with any new data from other gas sample different from the reference standard gas.

$$Absolute\ response\ factor\ (ARF)\ = \frac{Reference\ Standard}{Peak\ area} \qquad (1)$$

The peak areas from the chromatogram of Soku field natural gas sample chromatographic analysis is shown in table 2.

Table 2: Peak Area of Soku Gas sample

Component	Peak Area
N_2	141
CO_2	909
C_1	115119
C_2	8553
C_3	6818
i C_4	1688
nC_4	2664
iC_5	830
nC_5	678
C_6+	6252
TOTAL	143652

The composition of each component of Soku gas sample was determined by multiplying the absolute response factor for the reference standard with the peak area for each component.

$$Molar\ composition\ of\ unknown\ gas\ sample = Absolute\ response\ factor\ (Ref.Standard)\ x\ Peak\ area\ of\ unknown\ gas\ sample \qquad (2)$$

Table 3: Peak area of Soku gas sample converted to known composition from absolute response factor of reference standard

Gas Components	Reference Standard(mole %) (1)	Reference Peak area (2)	Standard Absolute response factor (3)	Soku gas sample Peak area (4)	Comp. (mole %) 5= (3) x (4)
N_2	3.5400	6224	0.0005688	141	0.0802
CO_2	2.2400	4397	0.0005094	909	0.4630
C_1	72.4000	92053	0.0007865	115119	90.5411
C_2	7.9600	16432	0.0004844	8553	4.1431
C_3	5.5400	14292	0.0003876	6818	2.6427
iC_4	2.5300	7854	0.0003221	1688	0.5437
nC_4	3.6700	11335	0.0003238	2664	0.8626
iC_5	1.0000	3409	0.0002933	830	0.2434
nC_5	1.0000	3487	0.0002868	678	0.1945
C_6+	0.1200	2627	0.0000457	6252	0.2857
TOTAL	100.0000	162110		143652	100.0000

Table 4: The composition of Soku Field natural gas sample from chromatographic analysis result

Molar composition			
Gas Component	**Weight %**	**Mole %**	**Molecular weight**
N_2	0.1212	0.0802	28.02
CO_2	1.0986	0.4630	44.01
C_1	78.3022	90.5411	16.04
C_2	6.7171	4.1431	30.07
C_3	6.2822	2.6427	44.09
iC_4	1.7038	0.5437	58.12
nC_4	2.7031	0.8626	58.12
iC_5	0.9468	0.2434	72.15
nC_5	0.7566	0.1945	72.15
C_6+	1.3684	0.2857	88.84
TOTAL	100.0000	100.0000	

Standard conditions 60^{0}F/15^{0}C and
Average molecular weight 18.5417g/mole
Gas gravity (Air = 1.0000) 0.6402.

3.1 Calculation of the gross heating value of the Soku gas sample

The molar composition of the gas sample obtained from chromatographic analysis in Table 4 was used for the calculation of the heating value (BTU) of the gas sample. Since the natural gas sample is a mixture of hydrocarbon gaseous components, mainly Alkanes, it is calculated by the summation of the product of each component gross heating value (BTU/SCF) and the molar fraction of each component in the gas sample.

The gross heating value (BTU/SCF) data for pure component gaseous alkanes and vapors' are presented in Table 5.

Table 5: The gross heating value of pure hydrocarbons (Alkanes)

Gas Component	Gross heating value (Hi) (BTU/SCF)
N_2	-
CO_2	-
CH_4	1010.0
C_2H_6	1769.7
C_3H_8	2516.1
i C_4H_{10}	3251.9
nC_4H_{10}	3262.3
iC_5H_{12}	4000.9
nC_5H_{12}	4008.9
Hexanes plus	4943.0
Vol. 83,419,1978	

Source: F.E. Jones, J.R., National Bureau of Standard [11]

Table 6: Calculated Gross heating value of Soku Field Natural Gas Sample

Component (1)	**Composition gross heating values (BTU/SCE) (2)**	**Component/ Composition Mole fraction (3)**	**Calculated component gross heating value (yiHi) 4=(2)x(3)**
N2	-	0.0802	-
CO2	-	0.4630	-
C1	1010.0	90.5411	914.4651
C2	1769.7	4.1431	73.3204
C3	2516.1	2.6427	67.4930
i C4	3251.9	0.5437	17.6806
nC4	3262.3	0.8626	28.1406
iC5	4000.9	0.2434	9.7382
nC5	4008.9	0.1945	7.7973
C6+	4943.0	0.2857	14.1222
		100.0000	1,132.7574 BTU/SCF

Table 7: Summary of Result

Component	Composition		Pure component gross heating value BTU/SCF	Estimated gross heating value (BTU/SCF)
	Weight	Molar weight		
N2	0.1212	0.0802	28.02	-
CO2	1.0986	0.4630	44.01	-
C1	78.3022	90.5411	16.04	914.4651
C2	6.7171	4.1431	30.07	73.3204
C3	6.2822	2.6427	44.09	67.4930
i C4	1.7038	0.5437	58.12	17.6806
nC4	2.7031	0.8626	58.12	28.1406
iC5	0.9468	0.2434	72.15	9.7382
nC5	0.7566	0.1945	72.15	7.7973
C6+	1.3684	0.2857	88.84	14.1222
Total		100.0000	28.02	1,132.7574

$$Average\ molecular\ weight = 18.5471\ g/mokle$$

$$Gas\ gravity\ (Air = 1.00) = 0.6402$$

$$Gas\ Gross\ heating\ value = 1{,}132.7574\ BTU/SCF$$

$Standard\ conditions\ \left(60\ \ ^{0}F\right)$ = (60^{o}F/15^{o}C, 14.74psia)

The result of molecular compositional analysis of the gas sample is shown in Table 4. The BTU data of pure hydrocarbon gases (Alkanes) obtained from National Bureau of standard hand book used for the calculation of the gross heating value of the natural gas sample is shown in table 5.0.

The calculation steps used to arrive at the heating value of the gas sample is also shown in Table 6, while Table 7 shows the overall summary of result.

The compositional analysis showed that, the major component of the gas sample is methane which accounts for 90.5%. The gas contains small but significant amount of carbon dioxide and nitrogen gases which necessitated treatment at Soku gas treatment plant. The gas sample also contains appreciable intermediate fractions C2 – C5 which may be recovered as compressed natural gas liquids (CNGL) during treatments. It is lighter than air with average molecular mass of 18.5 gram/mole and gas gravity of 0.64 (Air = 1.00) respectively.

Its calculated average gross heating value at standard conditions is in the range of (950 – 1150) BTU/SCF as reported in literature.

Conclusion

The gross heating value of natural gas sample obtained from Soku gas processing plant has been determined, the calculated average gross heating value at standard conditions is within the recommended value range by National Bureau of Standard (1978) and reported in literature. The Soku gas is classified as good source of thermal energy for electric power generation because of its high BTU valued of 1,132.8BTU/SCF. It is also a good source of compressed natural gas liquid (CNGL) and extractable C3 – C4 for LPG for export and domestic use. This result obtained will guide oil and gas industry, upstream and downstream sector in the design, construction and operation of gas flare stacks, venting/safety procedures.

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