The molecular and isotopic composition of thirteen (13) natural gas samples from 13 producing wells of the "X" Field of the Niger Delta, Nigeria was used for this study. The study is aimed at establishing the genetic relationship between natural gases and classifying them into genetic families. The Gas chromatographic technique was used to determine the molecular composition of the natural gases using GPA 2286, as a standard test method. The carbon isotopic compositions for C1, C2, and C3 were computed using regression formulas. The results indicate that the natural gas is dominated by methane with an average dryness coefficient (C1/C1+C2+C3*100) of 95.61%, with minor amounts of CO2 = 1.48%, N2 = 0.22%. The H2S content of the samples was below the detection limit of 0.20 ppm. The δ13C1 values range from -43.63‰ to -37.64‰, with an average of -40.79‰. The average carbon isotopic composition for the heavy hydrocarbon gases: ethane (δ13C2) and propane (δ13C3) are -27.47‰ and -28.15‰ respectively. The results also indicate that 11 samples out of the 13 studied samples are genetically related, implying that they were generated by the same source rock at almost the same temperature and pressure conditions. The 2 samples S1 and S7 that showed a significant difference in the isotopic and molecular composition may be as a result of a flow barrier between these two wells and the other 11 wells within the reservoir. The natural gases are genetically related and were generated by the same source rock.

Contribution/Originality: This study is one of the very few studies which have investigated the genetic relationships between natural gases in the Niger Delta Basin of Nigeria. The study outlines how molecular and isotopic composition of natural gases are used in a natural gas correlation study.

1. INTRODUCTION

Natural gases are derived from biogenic and non-biogenic sources through diverse processes, including bacterial formation, catagenesis, hydrothermal/geothermal activity, and to an unknown degree, primordial or mantle emissions. Exploration for natural gas is aimed principally at accumulations of fossil fuel hydrocarbons, but other gas accumulations, notably those of noble gases, can also be economic targets (Whiticar, 1994). Natural gases are the least compositionally complex form of petroleum. Unlike crude oils that have a large number of geochemical characteristics for making interpretations, natural gases because of their simplicity are limited in the type and
amount of information that can be obtained from them. Only the composition of the gas and its isotopic signatures are available for use in making interpretations of the origins of the gas, its maturity, and making gas-to-gas and gas-to-source rock correlations (Dembicki-Jr, 2017). Gas-to-gas correlations attempt to find geochemical relationships between gases in two or more reservoirs or the same reservoir in two or more traps. These relationships suggest the gases were generated from the same source rock at approximately the same time or maturity (Dembicki-Jr, 2017). As mentioned early, the compositional simplicity of natural gas limits the geochemical characteristics that can be used for these endeavors. For both isolated gases and gases associated with oil, there are two avenues for comparison: one is based on the composition of the gas and the other utilizes carbon-isotopic signatures of the individual C1 through C2 components (Erdman & Morris, 1974).

According to Wikipedia (2019) Nigeria is Africa’s largest gas reserve nation and ranks 9th as the world’s proven natural gas reserves. Aturamu and Ojo (2015) indicated that abundant petroleum resources have accorded Nigeria a considerable influence, both domestically and internationally and have brought about sustained geosciences research on Nigeria’s petroleum resources from different views. This notwithstanding, there is still a gap in geosciences research on natural gas, despite that natural gas is an important source of energy for national development and it is averred to be the 21st-century fossil fuel. Opafunso (2007) pointed out that, the Niger Delta Basin is a productive petroleum province and currently the only basin in which commercial petroleum production thrives in Nigeria. Based on the petroleum system concept, the Niger Delta has a single active petroleum system, which is the tertiary Niger Delta (Akata–Agbada) petroleum system. Akinlua (2012) indicated that the Niger Delta is a hydrocarbon province with an ultimate recovery presently estimated at nearly 40 billion barrels of oil. This is about 70% of the overall hydrocarbon reserves of sub-Saharan Africa. The gas reserves are conservatively estimated at over 40 trillion cubic feet.

The study rest on the hypothesis that, natural gases that are genetically related will have the same or similar molecular and isotopic composition. This study has the objective of correlating and classifying the gases generated from the various wells in the "X" Field of the Niger Delta into genetic families.

2. MATERIALS AND METHODS

2.1. Study Area

The Cenozoic Niger Delta Figure 1. covers an area of about 256,000 km² which lies in the Gulf of Guinea in Equatorial West Africa between longitude 3°E to 8°E and latitude 4°N to 6°N (Opafunso, 2007). The Niger Delta Basin is a productive petroleum province and currently the only basin in which commercial petroleum production thrives in Nigeria. Based on the petroleum system concept, the Niger Delta has a single active petroleum system, which is the tertiary Niger Delta (Akata–Agbada) petroleum system (Opafunso, 2007). It is the youngest of the three large sediment bodies that filled the aulacogen formed after the separation of the African and South American plates. It was initially built out over a transgressive Paleocene pro-delta as river-dominated lobes which later coalesced and became high-energy, wave-dominated, and tide-influenced depo-belts. The delta grossly consists of three subsurface lithostratigraphic units Figure 2. namely the marine Akata Shale, the paralic Agbada Formation, and the continental Benin Formation. The Niger Delta is a hydrocarbon province with an ultimate recovery presently estimated at nearly 40 billion barrels of oil. This is about 70% of the overall hydrocarbon reserves of sub-Saharan Africa. The gas reserves are conservatively estimated at over 40 trillion cubic feet (Akinlua, 2012). The hydrocarbon was sourced from marine shales with land plant materials giving rise to mainly Types III and II/III organic matter within an oil window that varied in depth from 9,000 to 14,000 ft. The reservoirs are mainly shoreface, beach, channel sands bearing low sulfur/nickel, light waxy, nondegraded oils. light crude-bearing deeper reservoirs have also been substantiated in some inland blocks (York, Diego, & Francisco, 2017).
Figure 1. The general outline of the Niger Delta Petroleum Province, including shallow and deep offshore (York et al., 2017).

Figure 2. Stratigraphy of the Niger Delta (Doust and Omotsola, 1990)
2.2. Method

Thirteen (13) natural gas samples were collected from 13 producing gas wells in the “X” field of the Niger Delta using isotope tubes. The GC oven temperature was initially set at 30°C for 10 min and then elevated to the maximum temperature of 180°C at a rate of 10°C/min where it was held for 20-30 min. In accordance with ASTM D 4810, Gastec tubes were used to measure the hydrogen sulphide contents of the samples. The carbon isotopic compositions were computed using the regression formulas by Faber (1987). The analytical results were subjected to data treatment and interpretation.

3. RESULTS

The molecular and isotopic signatures of the 13 natural gas samples from the “X” Field of the Niger Delta are shown in Table 1.

Table 1. Molecular and isotopic composition of the natural gases from the ‘X’ Field of the Niger Delta.

| Well | C1 | C2 | C3 | n-C1 | i-C1 | n-C2 | i-C2 | N | Co | H2S | C2H6 | C2H4 | C2H2 | C3H8 | C3H6 | C3H4 | C4H8 | C4H6 | C4H4 |
|------|----|----|----|------|------|------|------|---|----|-----|------|------|------|------|------|------|------|------|------|
| S1   | 98.06 | 0.12 | 0.05 | 0.02 | 0.01 | 0 | 0 | 0.55 | 0.47 | BDL | 98.56 | -57.64 | -26.91 | -23.89 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 |
| S2   | 95.83 | 1.74 | 1.68 | 0.43 | 0.65 | 0.21 | 0.17 | 0.04 | 0.96 | BDL | 95.06 | -40.76 | -27.45 | -29.01 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 |
| S3   | 94.61 | 1.57 | 1.17 | 0.29 | 0.44 | 0.14 | 0.12 | 0.59 | 0.86 | BDL | 96.21 | -40.19 | -27.17 | -27.42 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 |
| S4   | 92.82 | 2.24 | 1.89 | 0.48 | 0.09 | 0.22 | 0.15 | 0.14 | 1.06 | BDL | 94.22 | -41.51 | -28.21 | -29.98 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 |
| S5   | 94.86 | 1.28 | 1.59 | 0.38 | 0.53 | 0.16 | 0.13 | 0.08 | 0.75 | BDL | 95.89 | -40.01 | -26.72 | -28.73 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 |
| S6   | 91.82 | 2.30 | 1.98 | 0.49 | 0.72 | 0.23 | 0.16 | 0.14 | 1.00 | BDL | 93.98 | -41.51 | -28.21 | -29.98 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 |
| S7   | 98.76 | 1.44 | 0.51 | 0.08 | 0.12 | 0.03 | 0.04 | 0.45 | 0.67 | BDL | 97.55 | -58.61 | -29.05 | -24.72 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 |
| S8   | 93.7 | 2.39 | 1.55 | 0.27 | 0.58 | 0.21 | 0.16 | 0.32 | 0.53 | BDL | 94.72 | -10.86 | -28.37 | -29.69 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 |
| S9   | 93.33 | 1.69 | 1.66 | 0.41 | 0.61 | 0.18 | 0.15 | 0.05 | 1.71 | BDL | 95.21 | -41.13 | -27.35 | -28.95 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 |
| S10  | 89.93 | 1.89 | 1.6 | 0.4 | 0.58 | 0.17 | 0.14 | 0.25 | 4.85 | BDL | 94.95 | -83.63 | -27.67 | -28.76 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 |
| S11  | 93.82 | 2.24 | 1.99 | 0.47 | 0.70 | 0.19 | 0.16 | 0.14 | 1.06 | BDL | 94.23 | -41.51 | -28.21 | -29.98 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 |
| S12  | 94.86 | 1.28 | 1.59 | 0.38 | 0.53 | 0.16 | 0.13 | 0.08 | 0.75 | BDL | 95.89 | -40.01 | -26.72 | -28.73 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 |
| S13  | 90.9 | 1.98 | 1.1 | 0.27 | 0.43 | 0.16 | 0.13 | 0.23 | 4.58 | BDL | 95.71 | -42.92 | -27.81 | -27.20 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 |

Note: *BDL = Below Detection Limit.*

Figure 3. Comparison of C1–C4 gas composition for use in gas-to-gas correlation (Dembicki Jr., 2017).
Figure 4. Comparison of C₂–C₄ gas composition for use in gas-to-gas correlation (Dembicki-Jr, 2017).

Figure 5. Cross-plot of natural gas ratios in gas-to-gas correlation (Dembicki-Jr, 2017).

Figure 6. Cross-plot of i-C₄/n-C₄ against C₂/C₃ in gas-to-gas correlation (Dembicki-Jr, 2017).
4. DISCUSSIONS

The natural gases from the “X” Field of the Niger Delta have dominance in alkane gases as shown in Table 1, with C1-5 gases ranging from 94.97% to 99.18%, with an average of 98.09%. The concentration of methane ranges from 89.93% to 98.08%, with an average of 93.79%. The concentration of heavy hydrocarbon gases (C2-5) is relatively low, varying from 1.10% to 5.88% with an average of 4.31%. All the natural gases are dry and of thermogenic origin (C1/C1-5 *100 <100) having gas dryness coefficients (C1/C1-5*100) ranging from 94.23% to 98.89% with an average of 95.61% (Bernard, Brooks, & Sackett, 1978; Golding, Boreham, & Esterle, 2013). For the non-hydrocarbon gases, the carbon (iv) oxide (CO2) has a very low concentration ranging from 0.47% to 4.83% with a mean value of 1.48%; the concentration of nitrogen is lower than CO2, ranging from 0.04% to 0.59%, with a mean value of 0.22%. The hydrogen sulphide concentration in all the natural gases was below the detection limit of 0.20 ppm, indicating a sweet gas. The stable carbon isotopes of methane (δ13C1) differ from -43.63‰ to -37.64‰, with an average value of -40.79‰ Table 1. The average carbon isotopic composition for the heavy hydrocarbon gases; ethane (δ13C2) and propane (δ13C3) are -27.47‰ and -28.15‰, respectively Table 1.

Gas-gas correlation is accomplished in several ways by comparing the composition of two or more gases. Most obvious among this is to plot the relative concentration of the hydrocarbons gases as shown in Figure 3. These direct comparisons are useful, but not always very informative. This is because natural gases are dominated by methane as shown in Table 1, making it hard to see the difference in the ethane, propane, and butanes (Dembicki-
The plot of the relative composition of the hydrocarbon gases excluding methane, as shown in Figure 4, provided more insights into the difference and similarities between the natural gases than that of Figure 3. According to Dembicki-Jr (2017) cross-plot of some of the hydrocarbon gas ratios is important to illustrate similarities and differences between the gases, as indicated in Figure 5. The cross plot of C1/C3, against % wet gas ([Σ %C3-2] / [Σ %C1-2]) as indicated in Figure 5, show that 11 samples out of the 13 gas samples have similarities in chemical composition, this implies that those gases are genetically related and can be said to have been generated by the same source rock at similar/same conditions of pressure and temperature. Sample S1 and S7 are widely spaced from the 11 other samples, this may likely be attributed to the presence of a baffle preventing communication with the other 11 wells within the reservoir.

The cross-plot of iC4/nC4 against C3/C4 indicated in Figure 6 also corroborates the findings in Figure 5. According to James (1983) a comparison of carbon isotope (C1-C4) data from the individual gas components is an important tool in gas-to-gas correlations. The plot of carbon isotopic data from the 13 natural gas samples as indicated in Figure 7, shows similar patterns for 11 samples except for S1 and S7. The similarities in patterns for the 11 samples denotes that they are genetically related. This further confirms the initial findings that all the natural gases from the ‘X’ Field of the Niger Delta are genetically related and can be classified into one genetic family. This denotes that the natural gases were generated by the same source rock. Samples S1 and S7 have molecular and isotopic compositions very different from the rest of the samples, this may be attributed to the presence of an impermeable layer within the reservoir preventing fluid communication between wells S1, S7 and the rest of the wells within the “X” Field. Dembicki-Jr (2017) indicated that the non-hydrocarbon gases (CO2, N2, H2S) can be useful in gas-to-gas correlation. The plot of the concentration of the non-hydrocarbon gases in Figure 8 showed dissimilar patterns for all the samples. The absence of H2S may impede the use of the non-hydrocarbon gases in this study.

5. CONCLUSION

The natural gases from the “X” field of the Niger Delta have dominance in alkane gases as shown in Table 1, with C1-3 gases ranging from 94.97% to 99.18%, with an average of 98.09%. The stable carbon isotopes of methane (Δ13C1) differ from -43.63‰ to -37.64‰, with an average value of -40.79‰. The average carbon isotopic composition for the heavy hydrocarbon gases; ethane (Δ13C2) and propane (Δ13C3) are -27.47‰ and -28.15‰, respectively. The natural gases are of thermogenic origin. The study concludes that the gases produced from the wells within the “X” Field are genetically related due to the existence of similarities among their molecular and isotopic compositions, except for samples from wells S1 and S7 which shows different isotopic and molecular composition compared to the remaining 11 samples. This probably could be attributed to an impermeable layer within the reservoir that impedes communication between wells S1, S7 and the rest of the wells within the “X” Field of the Niger Delta. The natural gases of the “X” Field of the Niger Delta are said to have been generated by the same source rock hence belonging to the same genetic family.

Funding: This work was supported by the World Bank Africa Centre of Excellence, Centre for Oilfield Chemicals Research, University of Port Harcourt, Nigeria.

Competing Interests: The authors declare that they have no competing interests.

Acknowledgement: Management and staff of Louis Max petroleum fluids laboratory, Port Harcourt, Nigeria are appreciated for their support in the laboratory work.

REFERENCES

Akinlua, A. (2012). Analytica chimica acta the role of analytical Chemistry in Niger Delta petroleum exploration: A review. Analytica Chimica Acta, 730, 24–32. Available at: https://doi.org/10.1016/j.aca.2011.10.067.

Aturamu, A. O., & Ojo, A. O. (2015). Integrated biostratigraphic analysis of the Agbada formation (Nep-1 Well) Offshore, Eastern Niger-Delta Basin, Nigeria. Australian Journal of Biology and Environment Research, 2(1), 1-14.
Bernard, B. B., Brooks, J. M., & Sackett, W. M. (1978). Light hydrocarbons in recent Texas continental shelf and slope sediments. *Journal of Geophysical Research: Oceans, 83*(C8), 4053-4061. Available at: https://doi.org/10.1029/jc083ic08p04053.

Dembicki-Jr, H. (2017). Petroleum geochemistry for exploration and production. In *Practical Petroleum Geochemistry for Exploration and Production*.

Doust, H, Omatsola, E. (1990). Niger-Delta. In: Edwards JD, Santogrossi PA (eds) Divergent/passive margins basins: AAPG Memoir, vol 48, pp 201–238

Erdman, J., & Morris, D. (1974). Geochemical correlation of petroleum. *AAPG Bulletin, 58*(11), 2326-2337. Available at: https://doi.org/10.1306/83d91ba5-16c7-11d7-8645000102c1865d.

Faber, E. v. (1987). Zur isotopengeochemie gasförmiger Kohlenwasserstoffe. *Erdöl, Erdgas, Kohle, 103*(5), 210-218.

Golding, S. D., Boreham, C. J., & Esterle, J. S. (2013). Stable isotope geochemistry of coal bed and shale gas and related production waters: A review. *International Journal of Coal Geology, 120*, 24-40. Available at: https://doi.org/10.1016/j.coal.2013.09.001.

James, A. T. (1983). Correlation of natural gas by use of carbon isotopic distribution between hydrocarbon components. *AAPG Bulletin, 67*(7), 1176-1191.

Opafunso, Z. (2007). 3D formation evolution of an oil field in the Niger delta area of Nigeria using schlumbeger petrol workflow tool. *Journal of Engineering and Applied Sciences, 2*(11), 1651-1660.

Whiticar, M. J. (1994). Correlation of natural gases with their sources, in L. B. Magoon and W. G. Dow, eds., *The petroleum system—From source to trap* (pp. 261–283): AAPG Memoir 60.

Wikipedia. (2019). List of countries by natural gas proven reserves - Wikipedia.Retrieved from: https://en.wikipedia.org/wiki/List_of_countries_by_natural_gas_proven_reserves.

York, N. E. W., Diego, P. S. A. N., & Francisco, S. A. N. (2017). Cenozoic foraminifera and calcareous nannofossil biostratigraphy of the niger delta (O. S. Adegoke, A. S. Oyebamiji, J. J. Edet, P. L. OSterLOff, & O. k. ULU, eds.) (pp. 570): Elsevier.