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Discussion

Comments on "A new gaseous and combustible form of water," by R.M. Santilli (Int. J. Hydrogen Energy 2006: 31(9), 1113–1128)

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1. Introduction

The author of "A new gaseous and combustible form of water," (Int. J. Hydrogen Energy 2006:31(09);1113–1128) purports to present evidence for a "new combustible form of water"—"HHO gas." In this article, the author invites or requests of the "chemistry community (for) its independent verification (of)...HHO gas..." The following comments are submitted in this spirit.

Anyone seriously attempting to establish the existence of any new form of matter, such as "HHO gas" is claimed to be, especially in a mixture of such common gases as hydrogen, oxygen, and water vapor, would have to be extremely meticulous and detailed in the appropriate selection and application of analytical techniques, and in the interpretation of the resultant data, in order to have any hope of convincing the scientific community. However, as presented, the author demonstrates that he does not have an elementary grasp of the analytical techniques that were used, and/or the proper interpretation of the resultant data. Indeed, crucial experimental details are omitted so that it is not possible for anyone to reproduce the data (which is a basic tenet of the "scientific method"), and/or to accurately interpret what amounts to the cursory data that are presented.

2. Specific comments

There are many serious misinterpretations, and misunderstandings of the "data" presented in this manuscript. Below are just some of the most obvious that I encountered in the author's efforts to establish "HHO gas" as a new form of matter. Most of the correct interpretations of the data are quite straightforward, and certainly do not require the invocation of any new form of matter.

p. 1114, line 56 *et seq*.: "Feature 1 of HHO gas:" The author begins with the so-called "efficiency" of the electrolyzer, E. The study of the physical behavior of water and water vapor has been the subject of countless experiments over almost a century, culminating in, among other things, the International Steam Tables (1936). The latter include the energy required to vaporize liquid water, or the enthalpy change of vaporization of water. These values are very well known, and can also be accurately measured in the laboratory with a calorimeter.

55 SCF (@ 60°F, 1 atm) of water vapor is about 1.18 kg. The energy required to vaporize 1.18 kg of saturated liquid water at 25 °C is $1.18 \text{ kg} \times 2442.3 \text{ kJ/kg}$ (enthalpy change of vaporization of water @ 25 °C) =2882 kJ. To take it to saturated water vapor (or steam) at 35 psig requires about another 184.5 kJ/kg, or an additional 218 kJ for 1.18 kg of water, for a total of about 3.1 MJ. The author states that the electrolyzer requires 5kWh or 18 MJ to vaporize the same amount of water. However, the author does not recognize that most of the energy input into the electrolyzer does not go into just vaporizing water, but rather into electrolytically decomposing water into hydrogen and oxygen via electrochemical reaction. The energy required to electrolyze water is given by the negative of the enthalpy change of formation (i.e., heat of formation) of water vapor (-241.83 kJ/mol @ 25 °C, 1 atm). This is an order of magnitude greater than that required for just vaporization, which, from the preceding, is about 47.3 kJ/mol. So, for every mol of water decomposed to hydrogen and oxygen, approximately only 16% of the energy input goes into evaporating water. Since commercial evaporators do not decompose water, but just evaporate or vaporize it, the entire argument about comparisons of efficiencies is meaningless. It is quite telling that the author never actually

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calculates an electrolyzer efficiency, but rather just states that it is "... an efficiency that is at least 10 times the corresponding efficiency of conventional water evaporation ...". In fact, if an actual comparison were to be made, it would have to show that the electrolyzer has an extremely low efficiency for just evaporating water. In addition, the vaporization of water with the electrolyzer is accomplished with one of the highest cost energy sources available—electricity. Most industrial evaporators operate with much cheaper thermal sources from waste heat or process steam, so they are much less costly to operate—again, if the objective were just to vaporize water, which does not apply to the electrolyzer.

p. 1114, line 66: Consequently, the ensuing statement, "The above efficiency establishes the existence of a transition of water from liquid to the gaseous state that is not caused by evaporation" has no basis in fact. The remainder of the paragraph then jumps to the totally unsupported conclusion that "HHO" must be another novel form of gas.

p. 1114, line 74 *et seq*.: "Feature 2 of HHO gas:" The argument about "oxygen depletion" is specious. The global oxygen cycle is very well-known, and it maintains the concentration of oxygen at sea level at a constant 21 mol%. Thus, it is quite an exaggeration to imply that "oxygen depletion" is an environmental problem.

p. 1114, line 84 *et seq.*: "Feature 3 of HHO gas:" The author states that liquid water can be condensed out of "HHO gas" at about 150 psi, while a much greater pressure is required to do the same from "conventional gases." I really have no idea what this means, but apparently the author has not considered the phenomenon of rain. Water vapor in the atmosphere condenses into liquid water at a total pressure of about an atmosphere at sea level. It is all a question of humidity (or water content or vapor pressure), and is very well-known. But, once again, the author's incorrect statement and misunderstanding lead him to conclude that "HHO gas" "does not possess a conventional structure." Well, if that is so, then air must not possess a "conventional structure" either. Once again, the argument is specious, and the conclusions that the author jumps to are completely unsupported.

p. 1114, line 93 et seq.: "Feature 4 of HHO gas:" The author cites "anomalous adhesion (adsorption) to gases, liquids, and solids ...," presumably of "HHO gas." I cannot even begin to speculate on what "adhesion" of a gas to another gas means, since adhesion requires the interaction of a species with a bulk phase. However, vapor or liquid water is well-known to "adhere" and adsorb onto many solids, which makes it an ubiquitous contaminant in many such instances because of this property. With respect to liquids, water can be absorbed in to the bulk liquid phase of certain compounds, and can even concentrate at liquid interfaces when surfactants are present. Since the "adhesion" properties of "HHO gas" do not appear to be any different than water vapor, how does this confirm a "novel chemical structure" for "HHO gas," as claimed by the author? Once again, the author cites a phenomenological observation, misinterprets it, and comes up with an unwarranted conclusion.

p. 1114, line 101 et seq.: "Feature 5 of HHO gas:" The author states that "HHO gas" has "a widely varying thermal

content..." This is such imprecise language that it does not convey any real meaning. Apparently, however, it is related to the observation that an "HHO gas" flame is cool in ambient air, but can transfer large amounts of energy upon contacting solid objects. Once again, due to the lack of calculations, "hard numbers," and specifications characterizing the gas mixture composition and the flow rates, temperatures, pressures of the produced gas, etc., it is difficult to make accurate calculations. However, I can think of at least one alternative explanation for this behavior that just involves water.

A pure hydrogen flame (i.e., from a dry gas mixture) is very hot (3080 K for hydrogen in oxygen). However, in the current case, the "HHO gas" from the electrolyzer is undoubtedly saturated with water, and, depending on the details of the electrolyzer design (which I do not know), may actually have a significant amount of entrained liquid water as very fine droplets. These droplets can be quite small-their size, amount, etc., is a function of the fluid mechanics of the gas jet produced from the electrolyzer. In air, which has a low thermal conductivity, the heat transfer from the flame will be very low. However, liquid water has a large heat of vaporization and a much higher heat capacity than air. To heat liquid water from 25 to 150 °C (as cited on p. 1115, line 1 in the article) and vaporize it will take about 2.6 MJ/kg. Burning hydrogen produces about 242 kJ/mol hydrogen. Thus the amount of liquid water required to absorb the entire energy of the combustion reaction by evaporating liquid water is about 0.09 kg water/mol hydrogen burned. At 150 °C the volume of the gas is about 34.7 l/mol, while the volume of liquid water is about $1 \text{ cm}^3/\text{g}$. If the composition of the "HHO gas" is about 95% hydrogen and oxygen in stoichiometric ratio, and 5% water vapor (as mentioned in the article; see below), then the amount of hydrogen in the gas would be about 0.633 mol H₂/mol "HHO gas." Complete combustion of this amount of hydrogen would produce about 153 kJ/mol "HHO gas." This amount of energy would heat and volatilize about 0.059 kg, or about 59 cm^3 of liquid water/mol "HHO gas." Thus, on a volumetric basis, all you would need is 0.0591/34.71 or about 0.17% by volume of liquid water droplets in the "HHO gas" to "absorb" all the energy from the combustion of the hydrogen in the gas. This very low volume fraction of liquid water would be difficult to observe in the gas flow, especially as fine droplets. However, when the flame is brought to bear on a solid object with thermal conductivities several orders of magnitude greater than air, the heat transfer would be extremely good (in comparison to the heat transfer in air), and thus the solid object would have to heat up to very high temperatures, just as observed.

Without knowing many more details about the electrolyzer design, the gas jet and its composition, the preceding alternative explanation is just conjecture at this point. However, the important point here is that it certainly does not require the postulation of "HHO gas." Before a new form of matter can be established, all known, conventional explanations must be explored and ruled out. Obviously, this has not been done.

p. 1115, line 8 *et seq*.: The author states the "anomalous" apparent measured molecular weight of "HHO gas" as 12.3 g/mol (line 14). The author also states that the molecular weight of

a stoichiometric mixture of H_2 and O_2 gas resulting from the decomposition of water is 11.3 g/mol (line 17). It is not. The molecular weight of a stoichiometric mixture of completely decomposed water (i.e., 2/3 H_2 , 1/3 O_2) is:

$$(2/3)2 + (1/3)32 = 36/3 = 12 \text{ g/mol}.$$

The author even writes the equation "(2 + 2 + 32)/3 = 11.3"! The answer is obviously 12; his arithmetic is incorrect. (What is the compound P₂? (line 15) I guess it should be O₂—typo? What is HBN₂? (line 16) Another typo?)

All you need to obtain an apparent molecular weight of 12.3 g/mol is to have some water vapor present, as there must be since the product gas originates from the electrolysis of liquid water. In fact, all it takes is 5% water vapor to increase the apparent molecular weight of the gas mixture to 12.3 g/mol from 12 g/mol. At atmospheric pressure this corresponds to about 38 mm Hg of water vapor, which would be the equilibrium vapor pressure of water in a warm (near ambient) gas mixture (33 °C).

p. 1115, line 27: This line actually contains one of the very few correct observations in the entire manuscript—there *is in-deed* an "additional *heavier* species" in the gas mixture (than hydrogen, that is)—it is just water vapor. Thus, this simple molecular weight determination does not at all suggest any new, anomalous gaseous molecular forms other than just normal water vapor.

p. 1115, line 37: Here the author is attempting to refer to a "gas chromatograph" not a "Gas Chromatographer" (Fig. 1). Even if it was referred to as a gas chromatogram it would still be totally wrong. Fig. 1 is not a gas chromatogram at all (i.e., it is not a plot of retention times of various species through a chromatographic column, as measured by a detector)—it is a mass spectrum, most probably obtained with a quadrupole mass spectrometer. The spectrum appears to be a normal one of hydrogen and oxygen gas together with some water vapor and other background species that are typically present in vacuum chambers. The ordinate is labeled incorrectly-it should be "Faraday Cup Current (1E-11 A)"-and the abscissa should be "m/e-mass-to-charge ratio." How can the author not know that Fig. 1 is a mass spectrum, especially since he includes additional mass spectra in Figs. 10-12? This creates some doubt as to whether he actually knows the difference between a gas chromatograph (GC) and a mass spectrometer (MS).

p. 1115, line 47 *et seq*.: The author talks about a "new species" at m/e=33 of "nonmolecular nature." How could any chemical species be of "nonmolecular nature?" What does this term even mean? Even radicals, ions, dimers and clusters have a "molecular nature." In any case, m/e = 33 is probably just HO_2^+ formed by ion-molecule reactions in the MS ion source; e.g.,

$$O_2^+ + H_2 \rightarrow HO_2^+ + H.$$

None of the MS operating parameters is reported, but I would venture to guess that the background pressure in the ion source was high enough to cause significant ion-molecule reactions. All you have to do is vary the ion source pressure and you would see the 33 signal vary with pressure. What about the much larger m/e = 28 peak, which the author ignores?—Is it also another new "nonmolecular" species? No—as anyone who has ever looked at background mass spectra knows fully well, it is either just residual N_2^+ in the vacuum chamber, or background CO (CO⁺) outgassing from the vacuum system walls. And what about the very large "negative peaks" like at m/e=34? How can you get peaks of negative ion currents? Why are they negative? It looks like either an electrometer problem or a classical baseline problem.

The mass peaks at 16 (O^+) and 17 (OH^+) are classical "fragment ions" PRODUCED from neutral water vapor in the ion source of the mass spectrometer. They will be present whenever neutral water vapor is present; i.e., they are "fingerprints" of neutral water vapor. *They are definitely not present as radicals in the neutral sampled gas.* The author apparently does not understand how a mass spectrometer ion source functions. He concludes that O and OH radicals are present in the "HHO gas." Even if they were, they would certainly disappear by homogeneous and heterogeneous processes (reactions) well before they could be ionized and reach the detector. The companies that obtained the data for the author could have told him that. Consequently, he probably either did not discuss his conclusions with them, or if he did, he ignored what they told him.

In Fig. 12, the author shows a relatively large *positive* peak at m/e = 34. What is the difference between the data in Fig. 1 (negative 34 peak) and Fig. 12 (large positive 34 peak)? There is no explanation. What about the unexplained peak at m/e = 40, which is labeled as 100% (which is customarily reserved for the largest peak in the spectrum)? What is it, and where does it come from? Once again, there is absolutely no explanation. A large m/e = 40 peak is usually indicative of a large air leak. This peak originates from argon (Ar⁺) in the air. Argon is the next most abundant species in dry air, after N₂, O₂, and CO₂. However, the author does not show the entire spectrum, so one does not know if the "telltale" m/e = 28, 32, and 44 peaks for air were present as well.

Line 57 and the caption of Fig. 12 also mentions the absence of a m/e = 35 peak, that was "detected in other tests..." (Fig. 1?). What happened to it? There is no explanation. The author does not understand that processes which occur in the ion source of a mass spectrometer have a significant effect on the resultant observed spectra. However, this misunderstanding may certainly be expected since he did not even realize that he was talking about a mass spectrum, at least insofar as Fig. 1 is concerned.

Figs. 10 and 11, which the author does acknowledge as mass spectra, exhibit bizarre, unexplained features that cast doubts on their validity and interpretation. In Fig. 10 there is a peak at m/e = 5 that is 75% of the hydrogen signal, but in Fig. 11 which is also supposed to be another spectrum of "HHO gas" there is absolutely no hydrogen (m/e = 2) (How can that be? By the author's own claims, hydrogen makes up the majority of "HHO gas."). There is also no m/e = 5 for that matter. The author never even attempts to explain these very disturbing anomalies. All the other peaks in Fig. 11 are also common background vacuum chamber peaks. They show 15 (CH₃⁺),

12 (C⁺) (so there is obviously some background hydrocarbon contamination, which is very common), and 14 (either CH_2^+ and/or N^+ or N_2^{++}). It is quite apparent that the author does not understand how to properly interpret such data. However, once again, the important conclusion here is that there is nothing in these data that justify the postulation of, or support the existence of any such thing as "HHO gas."

p. 1115, line 61 *et seq*.: The "anomalous adhesion" attributed to "HHO gas" is nothing more than the very well-known, normal behavior of water vapor in all sorts of GC columns.

p. 1115, line 70 et seq.: Figs. 2 and 3 are supposed to be "IR signatures" of H₂ and O₂. However, as anyone who has taken freshman chemistry knows, homonuclear molecules like H₂, O₂, and N₂ are transparent to IR radiation. Thus, the absorption features in Figs. 2-4 are due to other species. Once again, there is no information on the sources of the gas samples, how they were prepared, etc., under what conditions (temperature, pressure, etc.) the spectra were taken, what the cell window was, whether the spectra were corrected for the humidity of the outside air in the beam path, etc. Therefore, it is almost impossible to unambiguously interpret the spectra. However, some absorption is evident between 2800 and 3000 cm^{-1} that may be due to water vapor. The absorption coefficient of water vapor in this region is not very large, but significant. The fact that the "IR signature of "HHO gas" in Fig. 4 has the largest absorption in this region is consistent with the much larger amount of water vapor that may be expected in "HHO gas" than in the dry hydrogen or oxygen gases.

p. 1116, line 9: Based on his incorrect interpretation of the IR spectra, the author concludes that the m/e = 18 peak observed in the mass spectra "... is not water vapor as conventionally understood in chemistry." However, the 18 peak is most certainly nothing but "conventional" water vapor. How could the "HHO gas" NOT contain water vapor?—It is produced from liquid water and thus is undoubtedly saturated with water vapor.

p. 1116, line 13 et seq.: The author apparently does not understand what bubbling an insoluble gas through a liquid hydrocarbon fuel like diesel does. It is called stripping. Diesel fuel is composed of many hydrocarbon compounds of varying volatility. By bubbling "HHO gas" (which is primarily insoluble hydrogen and oxygen) through the liquid diesel fuel, there is preferential stripping (i.e., removal into the gas phase) of the more volatile (i.e., higher vapor pressure) constituents from the diesel fuel. Obviously, the flash point of the resultant liquid fuel must then increase. So the result is anything but anomalous—it is what would normally be expected. In fact, the author concludes in a comparison of the data from the original fuel and that after stripping, that there is "a bigger elution time, and, above all, a shift of the peaks toward bigger amu values." (p. 1117, lines 31, 32). He also goes on to say (p. 1118, line 5) that the stripped diesel fuel clogged "the GC feeding lines." This is all very good proof that the resultant hydrocarbon mixture becomes heavier after stripping, which means that the flash point must have increased. Thus the author does not interpret the data properly, even when it shows the correct expected behavior!

Thus, these data provide no basis whatsoever for hypothesizing "the existence of an anomalous bond between the diesel and the HHO gas...". The data behave as expected. A similar result would have been obtained if the diesel had been stripped with any insoluble gas, such as nitrogen, argon or helium.

The article is replete with "pseudo-science" descriptions and explanations. One particular example appears in the caption of Fig. 9:

Fig. 9. One of the anomalous blanks of the GC-MS scans made by Toxic LTD Laboratories following the tests of the HHO. The blank is firstly anomalous because only the background should have been detected, thus indicating a bond between the HHO gas and the walls of the instrument, whose most plausible explanation is the magnetic polarization by induction of said walls by a form of magnetic polarization of the species composing the HHO gas. The second reasons for the anomalous nature of the blank is that the substances detected cannot possibly exist in the HHO gas produced from distilled water, thus showing an accretion of bonds to the instrument walls.

What does this even mean? Scientific and technological language should be precise. However, this language is obfuscatory—perhaps even intentionally so. The instrument was obviously contaminated by a previous sample or samples. This proves absolutely nothing about the nature of "HHO gas."

The remainder of the manuscript is a discussion of the author's theory of "magnecules" as related to "HHO gas." "Magnecules" are evidently supposed to be something like radicals bound to stable species by "opposing magnetic polarities originating from toroidal polarizations of the orbitals of atomic electrons." This is "pseudo-science" as well. H, O, OH, CH, as well as a number of other radicals, are present in all sorts of reacting systems. In flames they are the "chain carriers" for the hundreds of chain reactions that occur. The kinetics of these reactions has been studied in considerable detail and there are very robust flame kinetics models available that predict flame chemistry quite well. Due to the very reactive nature of these radicals, they react very rapidly with stable molecules, usually with little or no activation energy barrier. There is absolutely no evidence presented that they could form long-lived "cluster" species with stable molecules like water. If the author wishes to establish the existence of such "radical cluster" species, he should avail himself of the many laser spectroscopic techniques that have been so well developed for the study of radical species in combustion environments. Resultant spectra of "radical cluster" species would be a good start in attempting to establish the existence of anything like "HHO gas."

3. Conclusion

In conclusion, the author provides *absolutely no scientific* evidence that supports the existence of a new form of matter called "HHO gas." From the data presented, the gaseous product from the electrolyzer behaves in the same manner as would be expected of a mixture of hydrogen, oxygen, and watervapor.