

Garbage-In Garbage-Out (GIGO): The Use and Abuse of Combustion Modeling and Recent Spacelaunch Environmental Impacts

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Introduction

- New, lower-Performance engines (Hanwha, SpaceX) release significant PAH and related species into the lower- and upper-atmosphere
- Engine chemistry known since the 1960's
- Upper atmosphere impacts not yet assessed
- GIGO invalidates other Assessments and estimates of species deposition
- Significant contributions from film-coolants and open-cycle gas generators is ignored

Environmental and Atmospheric scientists are misinformed by a lack of reliable measurements and modeling.

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Hydrocarbon Sources

Nozzle efficiency (η) visual diagnostics (Fig 2)

Figure 2. Comparison of three similarly-sized launch vehicles. **Left:** brilliant visible afterburning of significant quantities of PAH/tars/soot discarded by engine, with predicted lower-Performance (LOX/RRP-13). **Middle:** minimal visible afterburning indicates high-Performance and primarily low Cp gases present (high- η , LOX/RRP-1). **Right:** non-hydrocarbon fuel with only minimal Cp species in the plume, obtaining maximal η (LOX/RRP-1).

The thermal cracking and oligomerization of large hydrocarbons in oxygen-starved hot environments was extensively studied in the condensed phase during the second half of the 20th century [22-28]. In the gas- and vapor-phase, the intermediate reaction pathways and products are essentially identical (except for the physically controlled, lower-temperature processes such as formation of the liquid carbonaceous mesophase). These cracking and oligomerization reactions occur at high

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Hydrocarbon Deposition

Afterburning and Afterburning Shutdown

Figure 5. Progression of afterburning (AB) shutdown with increasing altitude, showing transition to direct atmospheric and orbital PAH/tar deposition. **Upper left:** AB shutdown beginning. **Lower left:** nearly complete AB shutdown; **Upper right:** complete AB shutdown; **Lower right:** no AB in plume [ref. 13]

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Non-GIGO Calculations

Pyrolysis continually creates aromatics and PAH: the building blocks of carbon solids (i.e., coke & soot)

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SUMMARY/CONCLUSIONS

- High molecular weight hydrocarbons - e.g., aromatics, PAH, tars - are present when soot is formed in LOX/RRP-1 combustion chambers, gas generators, and film coolants, and may exceed soot yields
- GIGO calculations conceal PAH
- Non-GIGO chemical calculations support the observed presence of PAH
- Brilliant afterburning in a hydrocarbon rocket plume is diagnostic of large quantities of PAH
- The new low-Performance rocket engines produce large amounts of PAH

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Background: Garbage-In, Garbage-Out (GIGO) combustion calculations are defined here as the use of a detailed Arrhenius chemical-kinetic reaction/combustion suite for *some* of the chemical species which are present in real-world combustion, but the exclusion *by choice* of detailed reactions of other crucial chemical species known to be present. In the simplest instance, a detailed H_2+O_2+CO reaction suite combined with a single kerosene overall- or net-reaction (pseudoreaction) can produce valid LOX/RP-1 (kerosene) combustion chamber pressures and temperatures for engine-design purposes, but the results *cannot* produce data on hydrocarbons relevant to nozzle efficiency and mandated environmental assessments, because it ignores the complex hydrocarbon chemistry dependent upon trace- O_2 *hydrocarbon cracking and oligomerization reactions* (e.g., Christardo [2009], Seshardi [1982], VanKamp [1984], Speight [2003]) which ultimately produce legally regulated aromatic hydrocarbons, polycyclic aromatic hydrocarbons, and soot observed in real-world combustion (e.g., PM2.5). Non-GIGO chemistry for these key species in LOX/RP-1 combustion modeling has been available for decades (e.g., Marinov [1998]; see text), and reproduces known LOX/RP-1 measurements: Large quantities – *up to several percent of total fuels flow* – of complex hydrocarbons are typical: benzene, butadiene, and polycyclic aromatic hydrocarbons (PAH) such as anthracene, fluoranthene, etc. (Thompson, Rocketdyne[1966]). These hydrocarbons are the well-known soot-precursor species, and are therefore necessarily formed concomitantly with soot (e.g, Pugmire [2001]). The direct observation of large quantities of apparent soot in a rocket plume is thus *diagnostic of low combustion-efficiency and the presence of these toxic chemical species*, as well as diminished overall engine-efficiency due to rocket nozzle thermodynamics. The latter is due to the inherent inefficiency in extracting molecular vibrational energy from the expansion of large polyatomic molecules such as benzene and PAH (Clark [1972]). Examples are provided. Additionally, legal limits have since been established on the production of these class-1 carcinogens from internal combustion engines (e.g., rocket engines), and appropriate employee and civil protections established, making these species important to model and measure directly. These considerations apply to both the open-cycle fuel-rich gas generators and main engine combustion chamber fuels and film-coolants in LOX/RP-1 engines since the products distribution is largely thermodynamically controlled. During the decades of government-funded launch vehicle development, liquid fueled engines for space launch were typically designed for high efficiency to maximize, for instance, mass-to-orbit. To this end, pre-burners and high-energy fuels atomization (via high-energy swirl or impinging injectors) have been used to minimize fuel droplet starting size, maximizing gasification rate, and increasing gas-phase combustion efficiency and therefore engine/nozzle efficiency (Clark; Sutton; Sutton/Yang). Recent private LOX/RP-1 rocket engine development in the U.S. (SpaceX), and a strikingly similar Korean engine (Hanwha), favor particularly *low*-combustion-efficiency by eschewing fuel atomization in favor of Pintle-style injectors (Son [2016], Seedhouse; Springer[2013], Mueller [2012], Zarchan [2004]). The resulting low gasification rate of the characteristically large RP-1 fuel droplets maximizes the yield of large hydrocarbons (e.g. benzene, PAH, PM2.5, tars, and cokes), lowering gas-generator/nozzle/engine efficiency. Egregious GIGO errors can be seen, for instance, in recent U.S. Environmental Assessment/Impact documents (45thSpace Wing [2007], U.S. Army [2007], Nelson Eng. [2013], F.A.A. [2014], Sierra Eng. #2003-001 [2003], Song [2017]) wherein GIGO calculations de facto instruct computer combustion models *to ignore PAH formation known to be present*. Examples are provided. *Awareness of the above combustion science is essential knowledge for both environmental regulators and research personnel studying launch vehicle upper-atmospheric impacts on climate breakdown.*

Impacts: During flight in the Troposphere, a sufficient atmospheric partial pressure of O_2 is present to burn-off the PAH and soot generated by low-efficiency rocket engines, ignited by the hot rocket plume. This so-called “afterburning” of the excess hydrocarbons (PAH, tars, soot, etc.) gives rise to the *brilliant* appearance of an inefficient LOX/RP-1 rocket plume shortly after lift-off in these engines; however, above the troposphere, and on the launch stand during water-deluge, afterburning ceases and the predominant quantities of these species are directly deposited and persist. Examples are provided. Low-efficiency launch vehicles also need significantly larger liftoff fuels loads (a factor of >1.2) to achieve similar orbital mass, further increasing the per-launch yield of complex hydrocarbon tars and stable PAH free radicals (as do the reusability requirements on the combustion chambers of these engines). These hydrocarbons are deposited directly into launch trajectories, including the launch pad (impacting post-launch first-responders), the stratospheric ozone layer, mesosphere, and above. Increasing launch rates of these new, low-efficiency engines must therefore have an increasing cumulative impact on critical and poorly-understood upper-atmosphere chemistry systems (Ross/Sheaffer [2014]; Sheaffer [2016]). For instance; the ozone reactions of gas- or condensed-phase hydrocarbon tars combined with PM2.5 have not yet been studied, and potentially represent an unrecognized class of ozone-depleting compounds. The direct deposition of PAH tars during orbital transfer maneuvers into populated orbits and orbital stations is of potential concern to the satellite remote-sensing community. The solar absorption of these species at high altitudes is much higher than that of the background atmosphere, and converts UV/Visible insolation into upper-atmospheric heat.

INTRODUCTION

- ❖ Recent commercial low-Performance engines (Hanwha, SpaceX) generate significant aromatic (e.g., benzene) and PAH species into the lower- and upper-atmosphere and orbital environments
- ❖ *This aspect of engine chemistry has been known since the 1960's*, but is absent and misrepresented by available documentation, including Environmental Assessments.
- ❖ Upper atmosphere impacts of these chemical releases have not yet been studied and is potentially disruptive
- ❖ *The prevailing use of GIGO rocket combustion chemistry codes invalidates existing Assessment documents and estimates of species deposition for these engines*
- ❖ Three sources of PAH in these engines:
 - open-cycle gas generator exhausts
 - substantial thrust chamber, throat, and nozzle film-coolant requirements
 - low-efficiency primary combustion in the thrust chamber
- ❖ *Non-GIGO* rocket combustion chemistry calculations easily estimate the lower-molecular-weight fractions of PAH yields.

Environmental and Atmospheric scientists are currently misinformed by a lack of reliable measurements and irrelevant engine chemistry model results/studies on new large open-cycle LOX/RP-1 rocket engines. The only documented information available for these engines relies on GIGO combustion calculations which ignore, *by design*, the well-known, significant amounts of important large-hydrocarbon products such as benzene, polycyclic aromatic hydrocarbons (PAH), tars, cokes, etc., dumped by engines of this design directly into the lower- and upper-atmosphere and orbital stations. Restating, GIGO calculations in available documents have been the only (unreliable) source of information for atmospheric scientists and regulators on the impacts of these newly designed, low-Performance, high-wastage, large space launch engines.[1-7]

To amend this lacuna, the relevant science is presented herein and draws from a number of disciplines including the older rocket engine literature. The problem with low-Performance, high-wastage open-cycle LOX/kerosene engines, including PAH formation, has been well-understood for many decades (i.e., since before the Apollo era). The interdisciplinary study of *Plume Science* is somewhat complex, but relevant details are outlined herein in order to give a complete picture of the scientific understanding amassed in the 20th century relevant to two similar rocket engine designs. All rocket-engine-relevant details, measurements, combustion chemistry, and hydrocarbon pyrolysis science are drawn from the open scientific literature, public documents, and public record USAF/SMC documents (i.e., Aerospace Corp. Technical and Technical-Operating Reports).

COMBUSTION CHEMISTRY BACKGROUND

Narrative: *All major elements of the design and chemistry of liquid-fueled rocket engines were in-place and well-understood by the 1970's, so the design and construction of large rocket engines has literally been a cook-book process for more than five decades[9-12]. Indeed – to see a 4,000 lbf thrust LOX/hydrocarbon rocket engine that was home-built by **high-school graduates** in 1990, see ref [9].*

Modern government-funded high-Performance engine advances have been primarily confined to the difficult and complex engineering of high-efficiency preburner-style engines (i.e., high combustion efficiency; e.g., the Space Shuttle Main Engine - SSME).[16,35] For the privately-funded rocket engines discussed herein, the fuel-rich open-cycle LOX/RP pintle-injector rocket engines are basically 1960's-era design low-Performance, high-wastage engines (Figure 2, and see definition of "Performance" below). These have the unfortunate side-effect of yielding large

quantities of stable PAH soot-precursors, polycyclic hydrocarbon stable free-radicals, and soot; toxic yields that, among other issues, deposit in populated areas and potentially perturb upper-atmosphere chemistry cycles. This has not been discussed because all published computer models of exhaust yields from these two engines are either hearsay or supported by only GIGO engine calculations, which by design ignore real-world PAH yields. (e.g., ref. [1-3,6-8]) No known discussion of this appears in relevant Environmental Assessment documents or the scientific/technical literature, in part, presumably, because the design of these two engines had been essentially abandoned for large spacelaunch systems decades ago due to low-Performance, not to mention toxicity. The resulting lack of valid information presents a unique problem for upper-atmosphere chemists, physicists, engineers, and regulators.

This document reviews "**plume science**," a well-understood but highly interdisciplinary scientific knowledge pool drawing in widest interpretation from the fields of carbon science, gas phase combustion, internal combustion engine mechanics, and finite-volume detailed chemical-kinetic combustion modeling. The goal of this paper is to fill-in the existing information vacuum on these low-Performance engines for climate and atmospheric scientists and other non-specialists. Note that many of the listed references, and the references contained therein, are effective entry points into each of these listed fields for the interested reader.

Several important concepts must be introduced:

GIGO Calculations: Detailed chemical-kinetic finite-volume computer models of rocket engine combustion typically have involved overly-simplified reaction sets – examples are shown in Figure 1.[13] For various reasons, these models have not evolved much in the last ~30 years and remain, essentially, heritage or legacy models.[8] *By design*, these models ignore PAH (see Tables), providing highly distorted representations of real-world combustion chemistry, although more than adequate for their originally intended purposes, which did NOT include faithful reproduction of rocket plume chemical effluents. These are discussed in contrast to non-GIGO models below and in Figure 1 and the Tables.

The GIGO process itself is sometimes quite subtle – very recently, even highly complex reaction sets have been used to model these engines, *but which nonetheless ignore PAH*. [3] The PAH yields of these types of rocket engines, understood since the 1960's [4], are thus left out of U.S. EPA documents and the recent scientific and technical literature, with the result of misinforming a generation of scientists, engineers, and regulators about reactive effluents of these engines, even at this critical time in the Holocene → Anthropocene climate breakdown. It is shown here that calculations of valid PAH-estimating (non-GIGO) results have been possible since *ca.* 1990 – see section: **non-GIGO Calculations**. The results reproduce actual measurements on these engines.

Rocket engine Performance is the key engine parameter that is tied; via the rocket engine nozzle efficiency factor (η), to combustion chamber PAH yields in these LOX/RP-1 engines. *High-energy injector atomization* of low vapor pressure fuels (i.e., RP-1/kerosene) has been the primary enabling technology for increasing the efficiency of *all internal combustion engines* in the last 5 decades. However, high-energy atomization is not compatible with the pintle designs in these LOX/RP-1 engines. The resulting poor fuel atomization, and therefore slow fuel gasification, results in much slower and incomplete fuel combustion – yielding relatively low combustion efficiency and hence, via the detailed chemistry, to low η . This, along with engine reusability design considerations, feeds back into the requirement for higher fuel loads and larger tankage, larger lift-off masses, and hence a larger net atmospheric deposition of PAH and related species by these launch systems.

Two general sources of PAH can be considered with regard to the engine Performance:

- The dumping-overboard of un-combusted and partially-combusted fuel as open-cycle gas generator exhaust and large film-coolant flows during engine operation
- As mentioned above, the lack of combustion-chamber high-energy fuel atomization resulting in low combustion chamber efficiency due to large fuel droplet average diameter (slow fuel evaporation/gasification rates).[14,15] This results in hot, high- C_p combustion-product gases

(i.e., polyatomic hydrocarbons and PAH) entering the rocket nozzle, lowering the exhaust velocity (c), and therefore Performance, since for a given exhaust mass the exhaust velocity is the primary determinant of thrust, as follows: [10,11,16]

$$c^2 = [\text{enthalpy terms}] * \eta$$

$$\eta = \text{Nozzle Efficiency} = 1 - (P_e/P_c)^{R/C_p}$$

...where P_e = exhaust pressure; P_c = chamber pressure, R = gas constant, C_p = heat capacity at constant pressure

Maximizing nozzle-efficiency (i.e., the exhaust velocity c), is thus required to maximize engine Performance, and is thermodynamically constrained to the requirement for a very low C_p in the η equation above. This is equivalent to the requirement that *monatomic* and *diatomic* species must *predominate* in the exhaust flow in the engine throat/nozzle. The presence of polyatomic species such as PAH rapidly lowers nozzle efficiency (η), and therefore exhaust velocity and engine Performance, by decreasing the numerical value of the exponent of the (P_e/P_c) term in the η equation.[11,12]

Thermodynamically, this inefficiency occurs primarily as a result of combustion-generated thermal energy absorbed as molecular-vibration quanta in polyatomic molecules. Monatomic and diatomic gases have significantly fewer vibrational modes than polyatomic species hence less thermal energy can be carried in vibrational modes – therefore more energy is present as molecular *translational velocity* (i.e., gas temperature) in monatomic and diatomic species.[41] Because molecular vibrational energy is not efficiently extracted by the *exhaust gas expansion* occurring in the rocket nozzle, internal energy of polyatomic species is lost from the production of exhaust velocity (*thrust*) by the nozzle. This results in the comparatively low value of η in these engines. Note: this is historically why highly-efficient rocket engines are operated slightly fuel-rich – to favor monatomic and diatomic exhaust products over tri-atomic (and larger) gas species. As mentioned, legacy rocket-engine *models* (Fig. 1, Table I & II) ignore larger molecular species and hence ignore real-world chemistry – yet these have been invalidly cited in documents for these engines.

Open-Cycle Gas Generators (OCGG) typically consume on the order of 1%-10% of total vehicle fuels [16] depending on design, but provide no thrust, with incomplete combustion products simply discarded overboard (PAH, etc., see Figure 3), and thereby decreasing vehicle launch capacity (although these engines are simple and cheap to design and build). This has been known for decades: highly fuel-rich, OCGG exhaust chemistry was characterized by Rocketdyne [4] to be 1% - 5% *benzene* – higher molecular weights were present but not easily measured with available online mass spectrometer equipment at the time.[30] (Note that combustion products of these fuels largely do not change among similar motor technologies due to essentially identical combustion conditions required of operational rocket engines of this fuel type.[11]) This also is consistent with straightforward, **non-GIGO** combustion calculations and measurements, as well as decades of soot-formation research results [17-20] (also see the section: **non-GIGO Calculations**, and Figure 7). These exhaust products are dumped overboard into the atmosphere from the launch vehicle during engine operation. The discarded high-temperature exhaust efficiently burns-up *only in the troposphere*, but not at high altitudes nor under the launch- and test-stand protective water deluge.

Combustion chamber and nozzle film-coolants (FC); due to the very high temperatures and oxygen-starvation present after the FC have absorbed their latent heats and evaporated, nearly identical high-temperature cracking/oligomerization chemistry occurs to that present in OCGG chemistry; that is, dominated by high-temperature hydrocarbon cracking and oligomerization reactions which produce PAH. FC, though *required* to prevent combustion chamber and throat/nozzle erosion, also do not contribute to engine thrust since the free LOX is fully consumed by gas-phase combustion near the injector, leaving only relatively small quantities of reactive but high-temperature-stable radical species

such as OH, O, and H. These post-combustion reactive species are separated by wall-flow dynamics from the bulk of FC flows, so little combustion is possible.[39] Indeed this is the required function of film coolants, that is, to keep combustion and hot/reactive gases *away* from the engine/nozzle walls. (This problem is exacerbated in reusable engines; below.) Additionally, traces of combustion radical species enter the interface of the FC flow, are not present in sufficient quantity to support combustion of the relatively large amounts of FC hydrocarbons, but they *can and do* support increased rates of cracking and oligomerization of FC hydrocarbons in the formation of PAH species.[21-28]

An additional design issue specifically present in these types of engines (i.e., the pintle design) is that the *amount* of FC required in a rocket engine combustion chamber depends strongly on the mean flow dynamics of the *primary combustion flame-front* in the combustion chamber. The inherently strong radial component of flame-front travel characteristic of pintle engine designs causes the flame front to be oriented toward direct impingement on the combustion chamber sidewalls, typically requiring a significant amount of extra “head-end” combustion-chamber FC in order to prevent excessive thrust-chamber wall-erosion from flame-front impingement.[10,15,16] This need for increased head-end FC is an especially critical consideration for *reusable engines*, such as in the subject engines. Thus, even more FC-derived PAH is deposited into the upper atmosphere *due to the reusability requirements* calling for an additional safety margin of FC in these engines. No information appears to be available in the open literature on the FC mass-flow rates of these two specific engines, but typical values can be estimated based on publicized engine design parameters. [15,16]

Non-GIGO computer chemistry models of oxygen-starved RP-1 combustion must include cracking and polymerization reactions between large, unburned hydrocarbon molecules in order to approximate real-world yields of PAH, which are the raw building-blocks of soot. The GIGO calculations present in available public documents (i.e., Figure 1 and Tables) for these engines do not include these reactions and hence cannot yield real-world chemistry (although claimed to support assessment of real-world environmental impacts in US EPA documents).

Figure 1 provides a diagrammatic illustration of typical GIGO chemistry used in heritage rocket engine combustion models to predict operational parameters, such as combustion chamber pressure and nozzle throat species and temperature. However, the GIGO chemistry, while able to provide reasonable estimates of operational parameters, ignores real-world combustion for hydrocarbons, including PAH. An example of a minimally-complete PAH chemistry suite for non-GIGO calculations is also provided. Again, GIGO computer models *are programmed not to include PAH*. [1-3,6-8,18,21]

Ignoring PAH is often done by rocket and rocket-plume modelers to facilitate rapid calculations; however, the overly-simplified (i.e., *sans* PAH) results deprive atmospheric scientists and regulators of needed, critical data. Additionally, older heritage computer models are often simply not capable of the complex chemistry required to reproduce PAH results.[8] More modern and capable codes exist and are required for non-GIGO calculations. Note also that direct plume measurements are quicker, more reliable and more accurate than rocket combustion chamber computer model code results; however, carefully coded non-GIGO model results are typically similar to engine measurements for the species they do include, and thus can provide valuable guidelines for as to which engine chemistry measurements must be undertaken. (see section: **non-GIGO Calculations**) Both considerations show the extreme need for more careful study of these engines and valid information.

Table I. Example GIGO calculation claimed for rocket motor exit plane exhaust chemistry [1,2] using a chemistry model which is simpler than the simplest model shown in Figure 1. See also *textual attributions of PAH-free engine chemistry* quoted in items [6] and [7] of the **References** section.

Pexit (psia)	82
Texit (R)	3351
<u>Species</u>	<u>Exhaust</u>
CO	34%
CO2	17%
H2O	33%
H2	16%

Table II. Example GIGO calculation claimed for rocket motor exit plane exhaust chemistry [5] using a chemistry model similar to the simplest model shown in Figure 1. See also *textual attributions of PAH-free engine chemistry* quoted in items [6] and [7] of the **References** section.

<u>Species</u>	<u>Chamber</u>	<u>Exhaust</u>
H	0.14%	0.00%
H2O	0.01%	0.00%
H2	1.01%	1.24%
H2O	25.40%	26.33%
H2O2	0.00%	0.00%
O	0.48%	0.00%
OH	3.29%	0.00%
O2	1.07%	0.00%
HCO	0.00%	0.00%
CO	44.55%	37.84%
CO2	24.05%	34.59%

HYDROCARBON SOURCES

Nozzle efficiency (η) visual diagnostics (Fig 2)

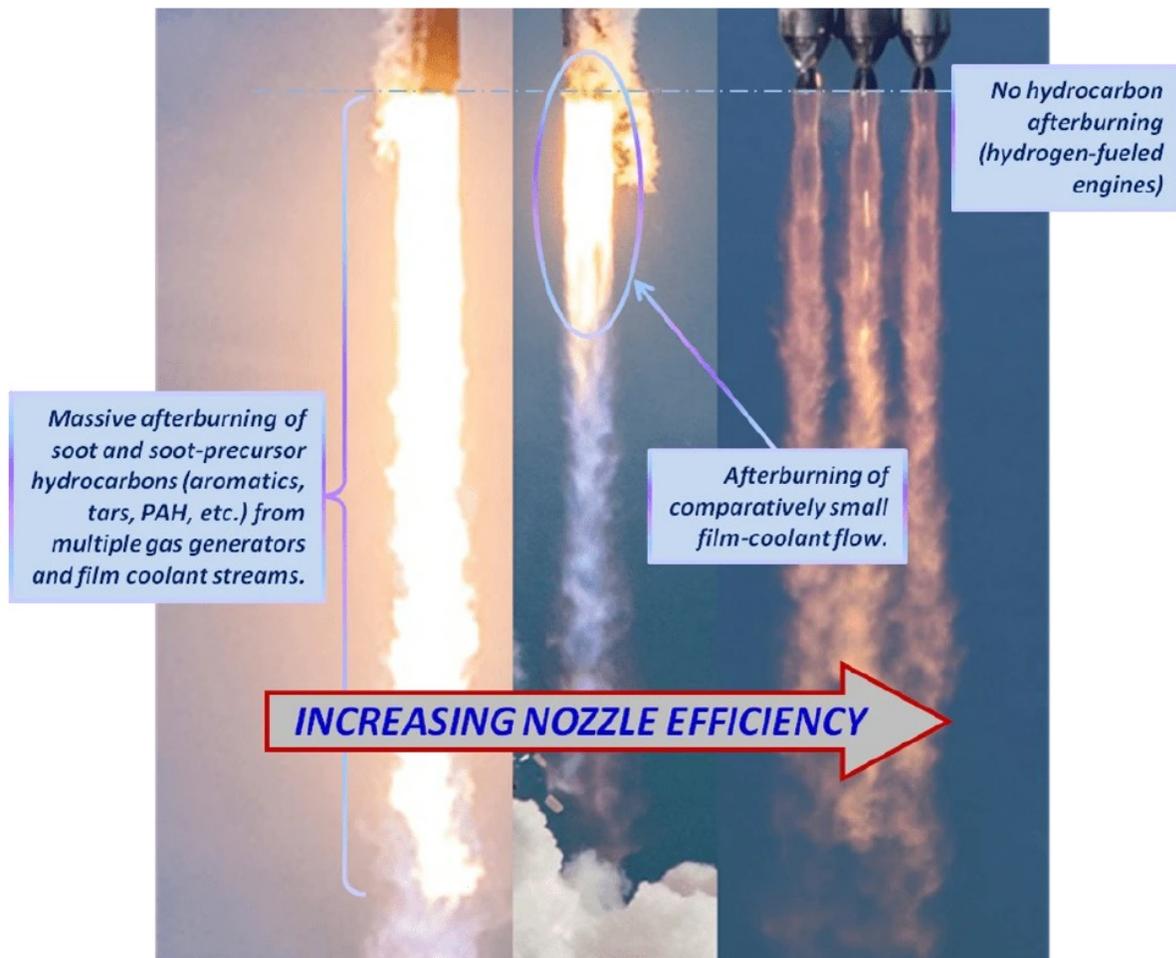


Figure 2. Comparison of **afterburning** in three similarly-sized launch vehicle plumes. **Left:** brilliant, visible afterburning of large amounts of wasted, very high- C_p hydrocarbons PAH/tars/soot, significant quantities of which are present in the engine nozzle, with predicted lower-Performance (LOX/RP-1); **Middle:** minimal visible afterburning of comparatively small amount of film-coolant hydrocarbons indicates high-Performance and primarily low- C_p gases present in the nozzle (high- η ; LOX/RP-1); **Right:** non-hydrocarbon fuel with *only* low- C_p species in the nozzle, thereby obtaining maximal η . (LOX/H₂)[ref. A]

Hydrocarbon thermal cracking and oligomerization reactions (condensation polymerization) of large hydrocarbons in oxygen-starved hot environments was studied in detail during the second half of the 20th century.[22-28] In the gas- and vapor-phase, the intermediate reaction pathways and products are essentially identical (except for the physically controlled, lower-temperature processes such as formation of the liquid carbonaceous mesophase). The necessary cracking and oligomerization reactions occur at high temperatures during the process of building solid carbon (soot/cokes) in fuel-rich regions of a hot engine (cf. Figure 6). These reactions are actually accelerated by residual *traces* of ligand oxygen and oxygen-containing small radicals. Primary pyrolysates (e.g., PAH) therefore occur in all film-coolant flows in rocket engines as well as in the highly-fuel-rich, lower-temperature flows of gas generators; and a few measurements exist.[4,17,19,20]

Note that these PAH building-block species are always present in "sooty" internal combustion engine exhausts unless specifically removed by, for example, catalytic converters or specially-designed exhaust afterburners.

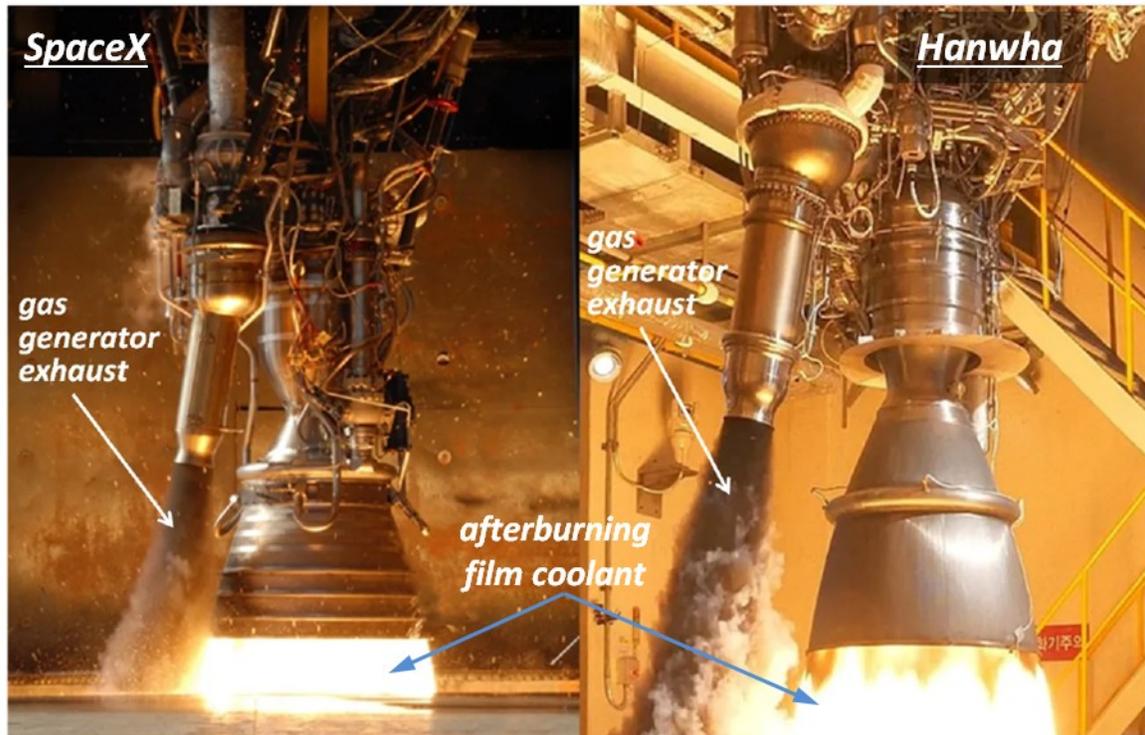


Figure 3. Example SpaceX (left) and the remarkably similar Hanwha (right) gas generator exhaust (labeled) and *afterburning film-coolants* (brilliant engine-nozzle exhausts), as viewed on the test-stand – above the water deluge which protects the "flame bucket" – but which simultaneously suppresses atmospheric PAH afterburning on the test-stand, allowing troposphere deposition of aromatics, PAH, etc., as in Figure 4. [ref. B]



Figure 4. Exhaust from static-firing of full launch vehicle. The test-stand deluge water injected below the engine nozzles prevents damage to the test-stand by the hot plume during static firing, but the deluge water also *quenches after-burning of the soot, aromatics, PAH, tars, etc. created by the gas generator and film coolant flows.* The residual is present as the black cloud (PM2.5, PAH, aromatics, etc., left), about half way through the test-stand firing sequence for this vehicle. Compare this with the deposition of these effluents shown in Figure 5 (upper right) of the high-altitude afterburning shutdown sequence. [ref. C]

In the absence of low-altitude tropospheric rocket-plume afterburning illustrated in Figure 2, these exhaust species are directly deposited into the atmosphere (Figures 3 - 6). This deposition occurs in the troposphere during the pre-launch water deluge of the flame bucket, as well as at high altitudes where plume afterburning has shut down. (see section: ***Hydrocarbon Deposition***)

Of particular concern for this work is upper-atmosphere (above ~30km) deposition of reactive and π -delocalized, stabilized polycyclic free-radicals, and stable PAH species (Figures 5 and 6), which radicals are often stabilized by unpaired-electron delocalization among the many sp² orbital π -bonds present in PAHs. These stabilized radicals and PAH have unknown impacts at high altitudes, and have yet to be recognized or assessed.[25-31] It is hypothesized here that, at a minimum, gas-phase PAH/tar species deposited at these altitudes present a larger UV/VIS/IR cross-section, per unit carbon mass, than the equivalent mass of carbon contained in a small-radius soot particles which interact with light only via MIE scattering: PAH species typically have strong absorption bands in LWIR and UV/Vis. Stable PAH radicals may also participate catalytically in the ozone destruction cycle. The rates for PAH decomposition reactions with ozone are low, suggesting these species may persist and build-up with time and number of rocket launches. Additionally, UV-B photodegradation of the larger PAH molecules appears to decrease with increasing molecular weight, also tending toward upper-atmospheric build-up of higher molecular weight PAH molecules.[37,38]

It should be re-emphasized that, as mentioned, these high-molecular-weight aromatic (e.g, benzene) and PAH species are the chemical building blocks of soot, and therefore are *always present* following afterburning shut-down (next section).

HYDROCARBON DEPOSITION

Afterburning and Afterburning Shutdown

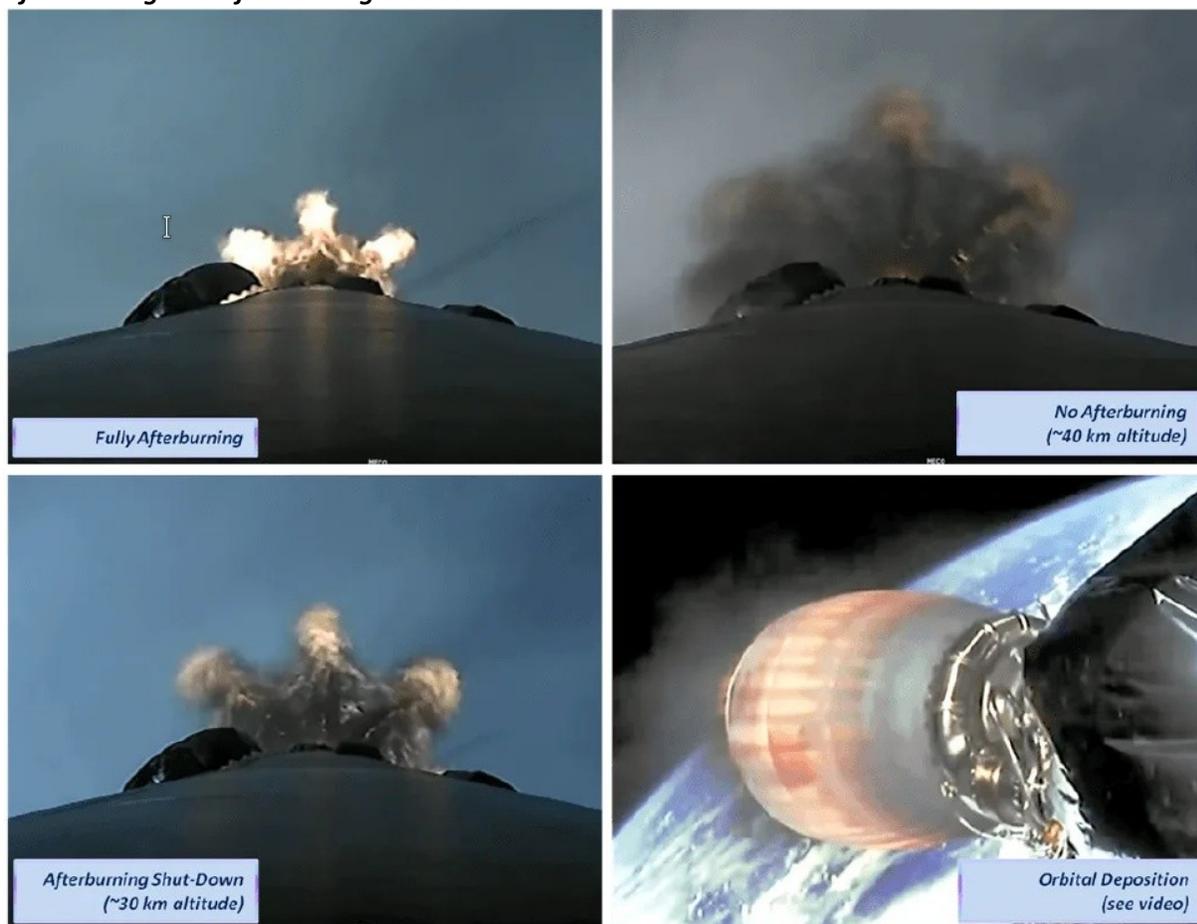


Figure 5. Progression of afterburning (AB) shutdown with increasing altitude, showing the *transition to direct atmospheric and orbital PAH/tars deposition*. **Upper left:** AB shutdown beginning; **Lower left:** nearly complete AB shutdown; **Upper right:** complete AB shutdown; **Lower right:** lack of any AB in vacuum [ref. D]

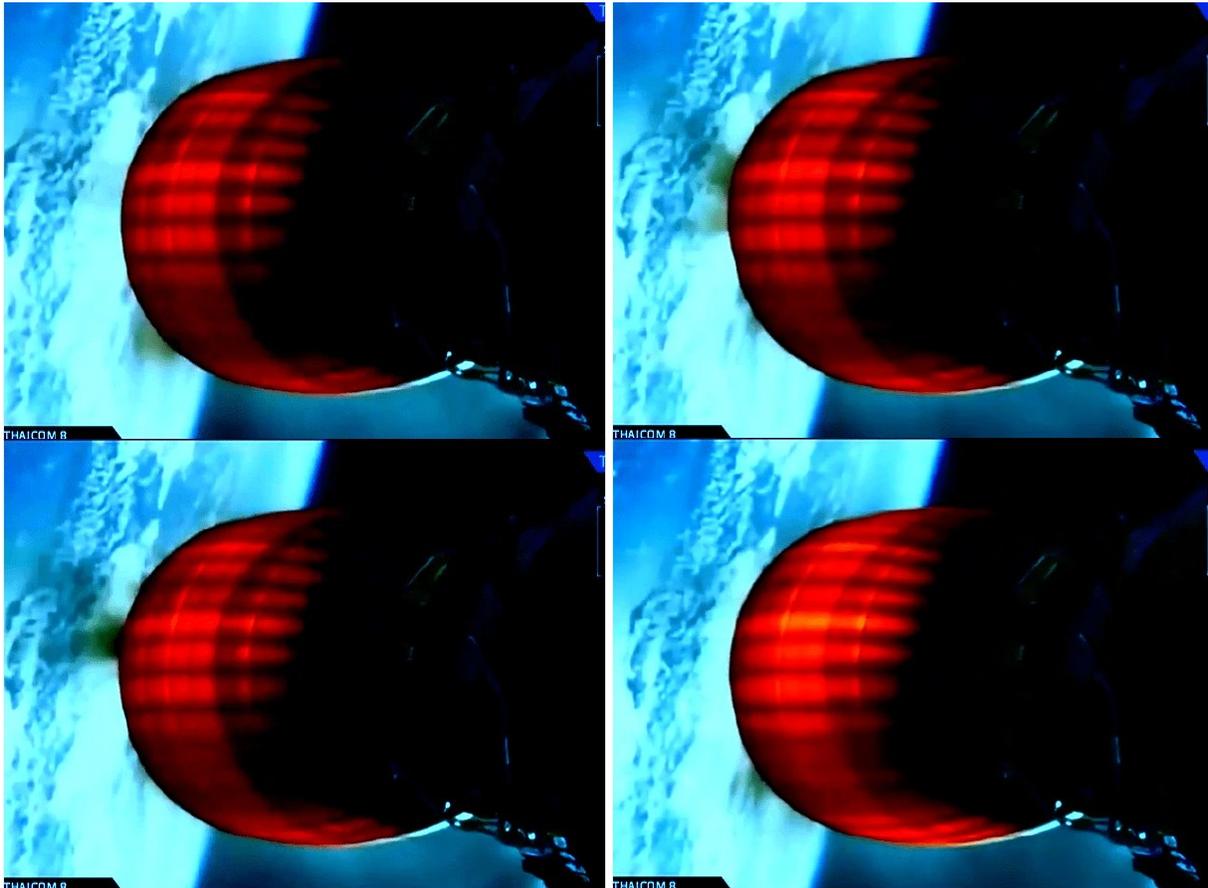


Figure 6. Excerpts from video (*see link*) of PAH/tar deposition during orbital-transfer burn. Note: the nozzle is highly *underexpanded* in vacuum, so the film-coolant PAH is observed to spread out *laterally* from the nozzle and is therefore much more tenuous to observe in vacuum, but is nonetheless clearly observable in video. [ref. D] https://www.essoar.org/cms/asset/2b4b21ae-3752-470c-91f4-a85f87b5a92c/out_2.mp4 and http://yavapaiweathertracks.org/OUT_lfp1ym.mp4

A typical launch-vehicle trajectory involves quickly vertically traversing the troposphere, then pitching over to accelerate toward orbit. Afterburning (**AB**) destruction of the soot/PAH/tars by the hot plume is has been widely known to plume science to shut-down due to rapidly decreasing partial pressure of atmospheric O₂ at altitudes above ~30 km.[32] AB shutdown, with the concomitant deposition of *unburned* soot/PAH/tars/etc., can be clearly observed in Figure 5. Afterburning shutdown and the decreased rate of climb act together to increase the relative burden of upper-atmospheric soot/PAH/tars from launches with these engines.

Since no afterburning is possible in space, deposition continues above the von Karman line from a single orbital-transfer engine and can be observed in Figure 6. The short-term fates of these PAH tar-mixture species at these altitudes is unknown, but was studied for another similar-molecular-weight aliphatic mixture, RP-1, and the liquid phase was found to be unexpectedly persistent in hard vacuum – suggesting PAH/tars are likely similarly persistent *in vacuo*.[33]

An example mass-deposition rate estimate can be made as follows.[16,34] Assuming afterburning suddenly shuts off at 40 km altitude (conservative), and assuming two 30-second burns (first stage, then second stage) above the afterburning shut-down and below the von Karman line (100 km), a fuels flow rate of ca. 250 kg/sec, and about 3% of fuels converted to PAH, then it can be somewhat conservatively estimated that on the order of 2 metric tons of PAH/soot/tars/etc., and possibly more, are deposited into the upper atmosphere per launch (ignoring first-stage-return engine operation). A more precise estimate would require knowledge of the actual film-coolant and gas-generator flows, as well as

PAH→soot conversion rates, although it appears that the overall conversion yield of PAH→soot is low, so the PAH yield likely dominates.[19,20]

It is currently unknown if any other public documents exist which present valid information on the presence of the soot building-block species (i.e., carcinogens such as benzene, PAH, etc.) in the Merlin/Hanwha engine exhausts. Hence, the estimates provided here, perhaps with some valid refinements, should be adopted immediately by the atmospheric science community. Of particular importance would be future measurements, if they could be made by experienced and unbiased third-parties, although this seems unlikely given the recent economics of U.S. spaceflight. Nonetheless, and as a key test, the results of such measurements must corroborate, extend, and refine the large and well-understood body of science and data presented and referenced herein.

NON-GIGO CALCULATIONS

Pyrolysis continually creates aromatics and PAH, the building blocks of carbon solids (i.e., cokes & soot)

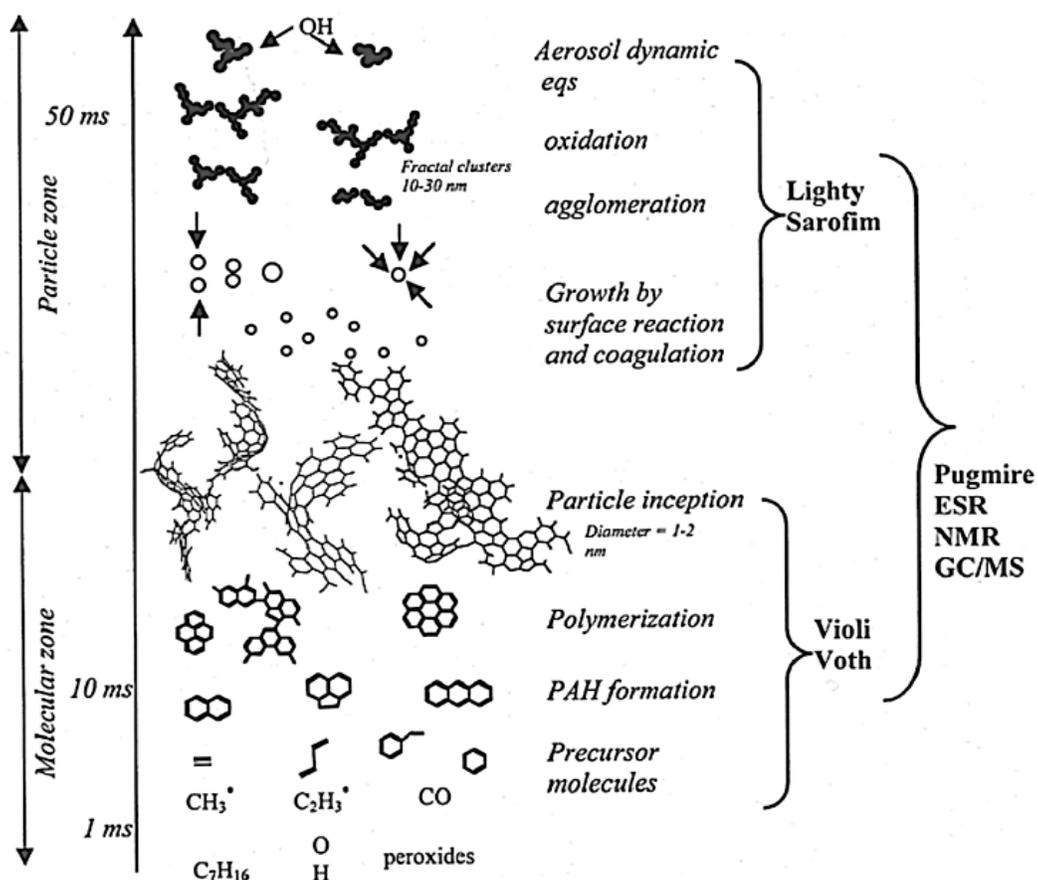


Figure 6. PAH molecules are continually created during fuel-rich, sooty combustion, and grow by cracking and oligomerization reactions (via condensation polymerization) to form larger PAH – which is the thermodynamically favored sp² carbon hybridization state under combustion conditions – and which are in turn the building blocks of tars, cokes, and soot particles.[18,21,26,30] *Aromatic and PAH species are therefore always present in significant quantity unless specifically removed, e.g., by catalytic converters, etc. (not possible in rocket engines).*

Current computer combustion models still cannot fully simulate the formation of large soot particulates from published sets of *elementary, detailed* chemical reactions. *However, models have existed since the 1990's which can validly model key PAH components of the soot-formation process* [18,21,30] and

should be used to introduce and guide scientists in understanding the impacts of these low-Performance space-launch vehicles. This is fundamental because the existence of these pollutants are currently hidden from atmospheric researchers by misleading and invalid documentation.[1,2,5-7] The primary importance of non-GIGO PAH calculations is to *demonstrate the significant presence of benzene, PAH, and related species requiring further clarification/measurement*. Objective measurements under real-world conditions would reveal the concentrations of very large PAH species.

Non-GIGO Combustion Calculations. Although non-GIGO rocket engine calculations are difficult under *multiphase* combustion conditions present in these rocket chambers, it is nonetheless easy to form a good estimate of the typical and expected chemical species products in *targeted regions* of gas-phase rocket engine combustion – providing a good measure of expected yields. The chemistry of oxygen-starved hydrocarbon combustion and pyrolysis in the post-combustion region of a highly fuel-rich gas generator, or of a LOX/RP-1 engine film-coolant after evaporation, can be simulated using simple geometries to reveal the underlying chemistry.[18,21] At a minimum, non-GIGO calculations serve as accurate guides to required measurements as well as reasonably estimating many species yields.

Although it is currently difficult to model PAHs beyond C18 hydrocarbons, such non-GIGO calculations correctly model some the typical lower molecular weight PAH combustion products obtained, as shown in Figures 7 and 7a, up to the limits of the available chemical mechanisms.[18] These calculations are relatively straightforward using high quality solvers in simple flow conditions.[36] These calculations produce the expected large yields of benzene, *exceeding the yield of acetylene*, a known significant rocket plume constituent.[40] Substantial yields of stable PAH species are shown, consistent with the required building blocks of easily-observed soot/PM2.5 yields (Figures 2 and 4).

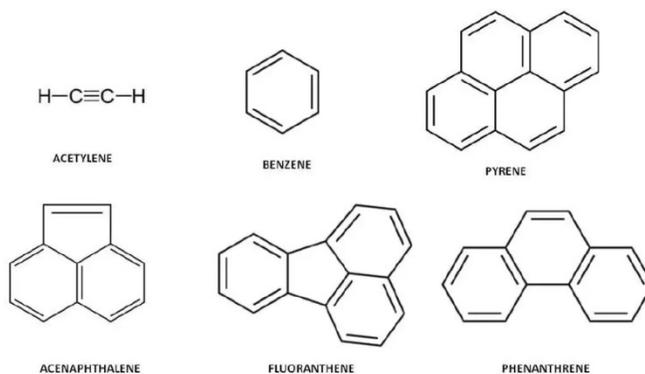


Figure 7. Some species solved-for using the non-GIGO combustion chemistry suite shown in Fig. 1. Much larger PAH species are present in the real world, as required in soot formation during fuel-rich LOX/hydrocarbon combustion (Fig. 6). The results obtained (Fig. 7a) are consistent with both the combustion literature and published measurements. Of special interest is the large quantities of benzene generated, which is one of the most stable hydrocarbon pyrolysis products at fuel-rich combustion temperatures, and is also a class-I carcinogen.

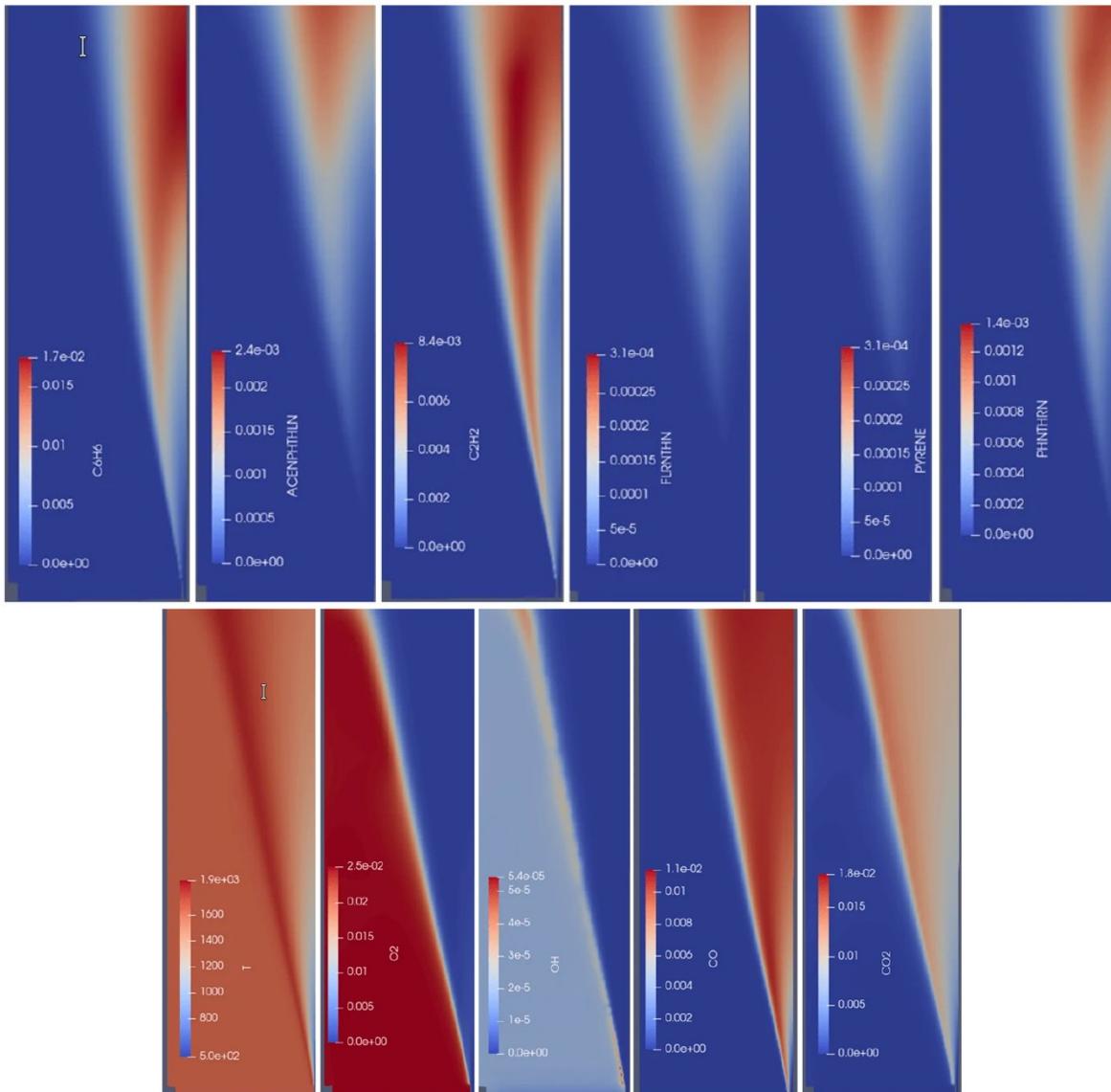


Figure 7a. Some results of a **non-GIGO** calculation: An oxygen-starved hydrocarbon combustion case using the 155-species chemistry model [18], shown in Figure 1 and representing high-efficiency (i.e., gas-phase) combustion of fully-gasified fuel. (The free O_2 is nearly completely consumed in the initial combustion at the injector flame-front.) Even under these highly-efficient combustion conditions, significant yields of benzene and PAH are observed. ($P = 100$ atm.; yields are largely insensitive to perturbations in temperature and pressure). Although not modeled here, the added presence of liquid-phase fuel would be expected to generate additional PAH due to increased localized O_2 starvation at the evaporating liquid interface. This nonetheless demonstrates that non-GIGO models are consistent with known measurements, and *supports the need for characterization of low-Performance LOX/RP-1 engines for valid atmospheric impact assessments.*

Even under highly-efficient gas-phase combustion conditions used here and shown in Figure 7a, significant quantities of benzene and PAH are generated. This is consistent with the fact that the sp^2 hybridized carbon contained in these species is the kinetically- and thermodynamically-preferred state of the hydrocarbon-recombination (oligomerization) products of oxygen-starved pyrolysis, and are thus important targets for precise measurement and documentation for scientists. Delocalization of unsaturated electrons across the π -bond network of large PAH radicals also increases the stability of these species (so called *stable free radicals*), possibly supporting increased effective lifetimes and reactivity in the upper atmosphere. It is noted that the benzene yield dominates the acetylene yield – the latter a known major rocket plume constituent under the conditions being discussed.[40] Combined with existing measurements, such *non-GIGO* results underscore the need for accurate information and documents to support regulators, engineers, and climate and atmospheric scientists.

SUMMARY/CONCLUSIONS

- ❖ High molecular weight *sp*²-cyclic hydrocarbons – including butadiene, aromatics (e.g., benzene, toluene), PAH, and petroleum tars – are present whenever ‘soot’ is diagnosed in fuel-rich LOX/RP-1 combustion chambers, gas generators, and film coolants
- ❖ GIGO combustion calculations *completely* conceal the presence of aromatic and PAH species in the subject engines of this paper (*SpaceX; Hanwha*)
- ❖ Non-GIGO chemical calculations readily reproduce the observed presence of benzene and lower molecular weight PAH species
- ❖ Brilliant low-altitude afterburning in a hydrocarbon rocket plume is diagnostic for the presence of large quantities of PAH and related species in the plume
- ❖ Aromatics, PAH, and hydrocarbon tars are deposited directly in the upper atmosphere and on the launch stand due to the cessation or inhibition of afterburning for these types of rocket engines
- ❖ UV/Vis decomposition rates of larger PAH species are low, suggesting these species may persist and accumulate in the upper atmosphere – this requires further study
- ❖ The LOX/RP-1 internal- and external-combustion scientific assessments outlined herein are based on decades of hydrocarbon combustion science and are highly reliable.
- ❖ The current lack of valid documentation on PAH/aromatic yields of these engines presents a unique challenge to upper atmospheric and climate scientists, engineers, and regulators; thus *the PAH yield estimates provided herein should be immediately adopted by the scientific community*

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Note: *Some of these references are specific to the text and some are intended primarily as starting-points for entry into the relevant Carbon literature, Chemistry Modeling literature, Combustion literature, Rocket Design literature, etc., and hence the reader is also referred to many of the references contained within those listed below.*

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