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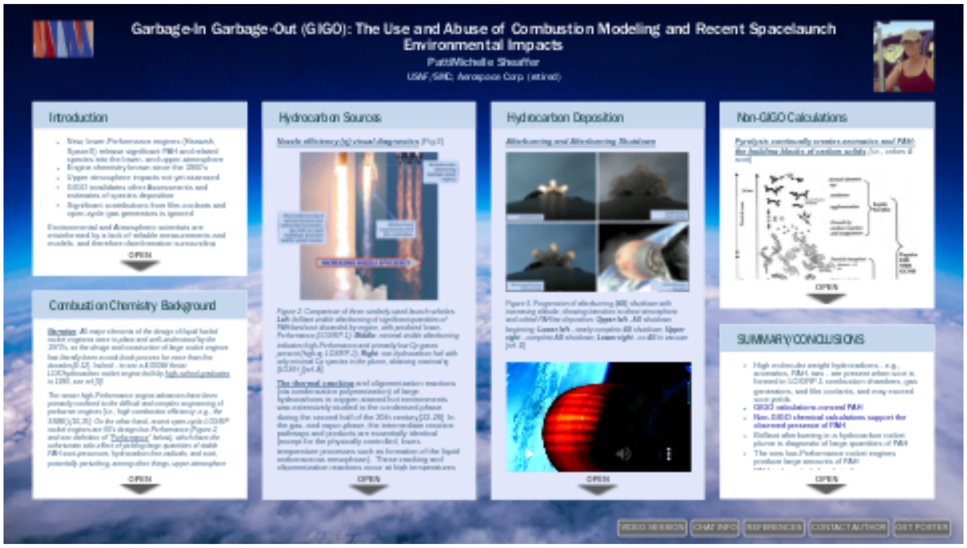
Garbage-In Garbage-Out (GIGO): The Use and Abuse of Combustion Modeling and Recent Spacelaunch Environmental Impacts



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PRESENTED AT:

INTRODUCTION

- New, lower-Performance engines (Hanwah, 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
- Use of 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 models, and therefore disinformation surrounding new open-cycle LOX/RP-1 rocket engines. Most available information relies on GIGO combustion calculations which ignore, by design, the known significant amounts of important large-hydrocarbon products such as *benzene*, polycyclic aromatic hydrocarbons (PAH), tars, cokes, etc., dumped by these engines directly into the lower- and upper-atmosphere and orbital stations. Yet these GIGO calculations have been nearly the only (unreliable) source of information for atmospheric scientists and regulators on the impacts of these new, large space launch engines.[1-7]

The background science presented herein draws from a number of disciplines. The details are somewhat complex, but are provided to give a complete story of the scientific understanding amassed in the 20th century and relevant to these rocket engines.

All rocket engine relevant details, 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 of liquid fueled rocket enginess 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 4,000lbf thrust LOX/hydrocarbon rocket engine built by high-school graduates in 1990, see ref [9].*

The newer high-Performance engine advances have been primarily confined to the difficult and complex engineering of preburner engines (i.e., high combustion efficiency; e.g., the SSME).[16,35] On the other hand, recent open-cycle LOX/RP rocket engines are 60's design low-Performance (Figure 2, and see definition of "Performance" below), which have the unfortunate side-effect of yielding large quantities of stable PAH soot-precursors, hydrocarbon free-radicals, and soot, potentially perturbing, among other things, upper-atmosphere chemistry cycles. This has not been discussed because published computer models of engine exhaust yields of these engines support only GIGO calculations, which ignore PAH. (e.g., ref. [1-3,6-8]) No known discussion of this appears in the technical or scientific literature and 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 from the fields of carbon science, gas phase combustion, internal combustion engine mechanics, and finite-volume chemical kinetic combustion modeling. The goal of this work is to fill-in the information vacuum on these new, low-Performance engines for climate and atmospheric scientists and other non-specialists. *(Many of the listed references, and the references* they *contain, are effectuve entry points into each of these listed fields.)*

GIGO Calculations: Chemical kinetic finite-volume computer models of rocket engine combustion typically have involved simplified reaction[13] sets - examples are shown in Figure 1. For various reasons, these models[8] have not evolved much in the last 40 years and remain heritage models (see Tables). These ignore PAH, providing highly distorted results. (These are discussed in contrast to non-GIGO models below and in Figure 1 and the Tables.)

GIGO is sometimes quite subtle - very recently, even highly complex reaction sets [3] have been used which nonetheless ignore PAH. The PAH yields of these types of rocket engines, known since the 1960's [4], are thus left out of EPA documents and the recent scientific and technical literature, with the result of disinforming a generation of scientists, engineers, and regulators about chemically active effluents of these new engines, even at this critical time in the Holocene → Anthropocene handover.

Example calculations of valid PAH estimating results are shown in the section: ***non-GIGO Calculations***

Rocket engine Performance is tied, via the rocket engine nozzle efficiency (***η***), to combustion chamber *PAH yields* in these new LOX/RP-1 engines. High-energy injector atomization of low vapor pressure fuels (i.e., RP-1) has been the *primary enabling technology* for increasing the efficiency of internal combustion engines, and was used in Apollo-era engines. However, such injectors are not compatable with the pintle designs in these new LOX/RP-1 engines. The poor fuel atomization, and therefore poor gasification, results in incomplete fuel combustion (low combustion efficiency). This feeds back into the requirement for higher fuel loads and larger tankage, larger lift-off mass, and hence larger atmospheric deposition of PAH and related species by the launch vehicle.

Two general sources of PAH are considered with regard to engine *Performance*:

- The dumping-overboard of uncombusted and partially-combusted fuel during engine operation (as open-cycle gas generator exhaust and significant film-coolant flows)
- 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-*Cp* combustion-product gases (i.e., polyatomic hydrocarbons as PAH) entering the rocket nozzle, lowering the *exaust velocity* (*c*), and therefore *Performance*: [10,11,16]

c^2 = [Enghalpy Terms] * $\boldsymbol{\eta}$

$\boldsymbol{\eta}$ = Nozzle Efficiency = $1 - (Pe/Pc)^{R/Cp}$

...where *Pe* = exhaust pressure; *Pc* = chamber pressure, *R* = gas constant, *Cp* = heat capacity at constant pressure

Maximizing nozzle-efficiency, and therefore engine *Performance*, thus is *thermodynamically* constrained to a very low *Cp* in the $\boldsymbol{\eta}$ equation above - that is, *monatomic and diatomic species only*. The presence of polyatomic species such as PAH rapidly lowers nozzle efficiency, and therefore engine efficiency, by decreasing the numerical value of the exponent of the (*Pe/Pc*) term in the $\boldsymbol{\eta}$ equation.[11,12]

Thermodynamically, this inefficiency occurs as a result of the partitioning of molecular energy quanta into *internal* molecular modes of the polyatomic species rather than translational molecular velocities (i.e., gas temperature). This energy is largely *not extracted* by the exhaust gas expansion produced by the rocket nozzle, and thus is lost from the production of thrust by the nozzle. Hence, low $\boldsymbol{\eta}$.

Open-Cycle Gas Generators (OCGG) typically consume on the order of 1%-10% of total vehicle fuels [16] but provide no thrust and incomplete combustion products are simply discarded (see Figure 3), thereby decreasing launch capacity of a launch vehicle (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 measured. (Combustion products of these fuels does not change with motor technology.) This also is consistent with straightforward, non-GIGO combustion calculations and measurements [17-20] (also see section ***non-GIGO Calculations***, Figure 7). These exhaust products are dumped overboard into the atmosphere from the launch vehicle during engine operation; the exhaust burns up in the troposhpere *but not at highel altitudes nor under launch- and test-stand stand deluge water*.

For film-coolants, due to very high temperatures and oxygen-starvation present (after the film-coolants have absorbed their latent heats and evaporated), have a nearly identical chemistry to species produced in OCGG; that is, dominated by hydrocarbon cracking and oligomerization reactions. Film-coolants, though required to prevent combustion chamber damage, also do not contribute to engine thrust since the free LOX is consumed by gas-phase combustion near the injector, leaving only radical species, such as OH, and in very high temperature regions, O and H.

The *amount* of film coolant required in a rocket engine combustion chamber depends strongly on the *dynamics* of the combustion chamber flame-front. Due to a strong radial component of flame-front travel, pintle designs typically require significant extra "head-end' combustion-chamber film coolants to prevent excessive thrust chamber wall-erosion.[10,15,16] *This is an especially critical consideration for a reliable, reusable engine.* Thus, even more film-coolant derived PAH is deposited into the upper atmosphere by reusable engine designs, due to increased reliability considerations. No information currently appears to be available in the open literature on the film coolant rates of these two engines.

Non-GIGO computer models of oxygen-starved RP-1 combustion must include cracking and polymerization reactions between large, unburned hydrocarbon molecules in order to approximate real-world values of PAH. The GIGO calculations present in available public documents for these engines do not include these reactions.

A diagrammatic illustration of the typical chemistry omissions invalidating computer model results with respect to PAHs, including a minimally-complete PAH chemistry suite, is provided in Figure 1. GIGO computer models are literally instructed not to include PAH.[1-3,6-8,18,21] This is largely done by rocket modelers to facilitate rapid calculations; however, the overly-simplified (i.e., *sans* PAH) results *deprive atmospheric scientists and regulators of needed, critical data*. Additionally, heritage computer models are often not capable of the complex chemistry required to reproduce PAH results.[8] More modern and capable codes exist are therefore required. Note also that direct plume measurements are quicker, more reliable and more accurate than rocket combustion chamber code results; however, carefully coded non-GIGO model results are typically similar to measurements for the species they include. (see box ***non-GIGO Calculations***)

Only GIGO results are presented in the known public documents on these engine exhausts, and excerpts are shown and referenced in the Tables. These documents assert textually that "soot is also present," ignoring known science of the soot-formation chemistry (*see also the boxes **Hydrocarbon Sources** and **non-GIGO Calculations***).[5-7] These documents provide researchers no valid information on the chemistry deposited in the lower and upper atmosphere by these engines (Figures 3-6).

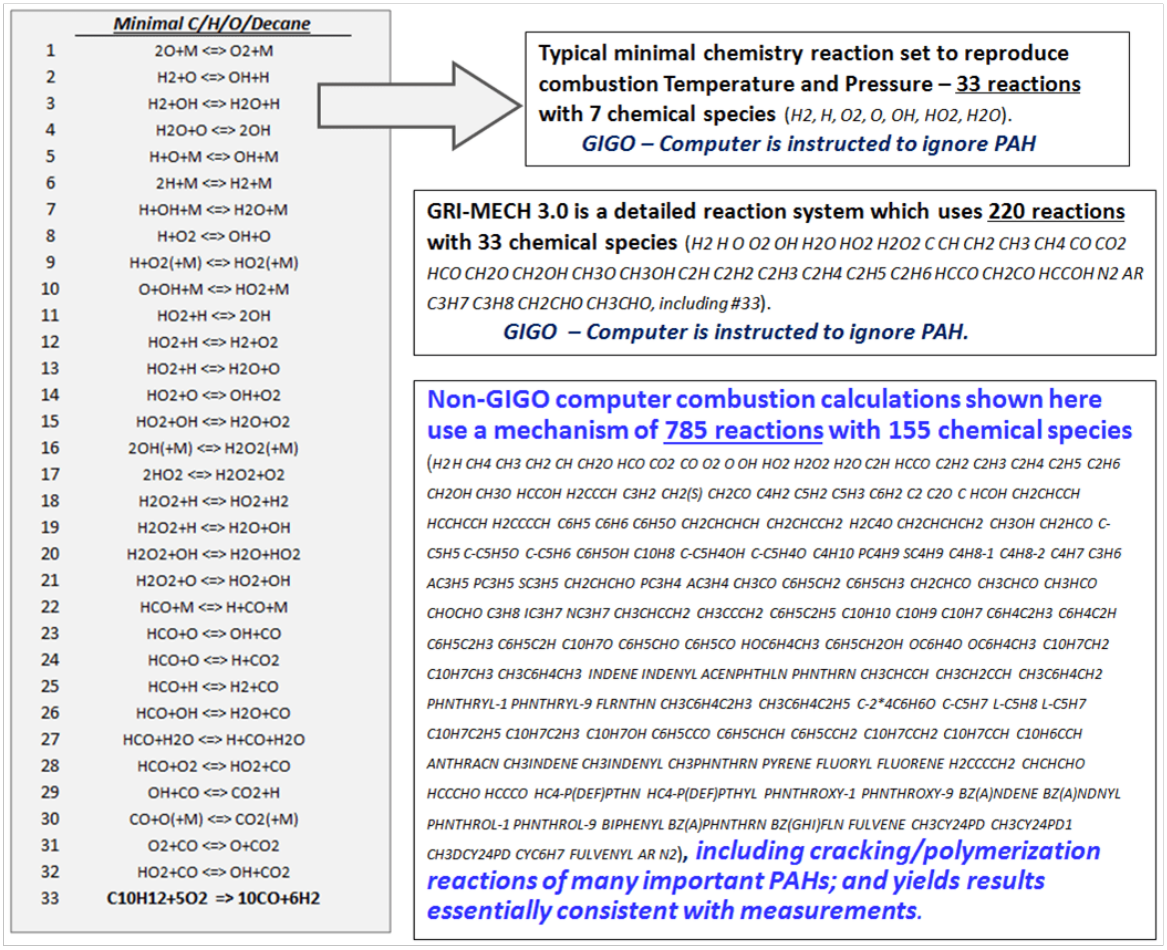

Figure 1. Three progressively larger computer combustion models. All will reproduce in a model the engine pressure and temperature, but only the largest model (155 species) is non-GIGO for PAH species. (Pseudo-reactions such as #33 allow RP-1 to be added without PAH in GIGO reaction models; however, even some very large models are GIGO for PAH.[3]) No known documents validly includes the PAH contributions from film-coolants or open-cycle gas generators - a significant omission for this engine design. Direct measurements would therefore be required since PAH is known to exist whenever soot exists (and from previous measurement).

Table I. Example GIGO calculation documented for rocket motor exit plane exhaust chemistry [5] using a chemistry model similar to the simplest model shown in Figure 1.

Species	Chamber	Exhaust
H	0.14%	0.00%
HO2	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%

Table II. Example GIGO calculation documented for rocket motor exit plane exhaust chemistry [1,2] using a model which is even simpler than the simplest model shown in Figure 1.

Pexit (psia) 82

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Species	Exhaust
CO	34%
CO2	17%
H2O	33%
H2	16%

HYDROCARBON SOURCES

Nozzle efficiency (η) visual diagnostics (Fig 2)

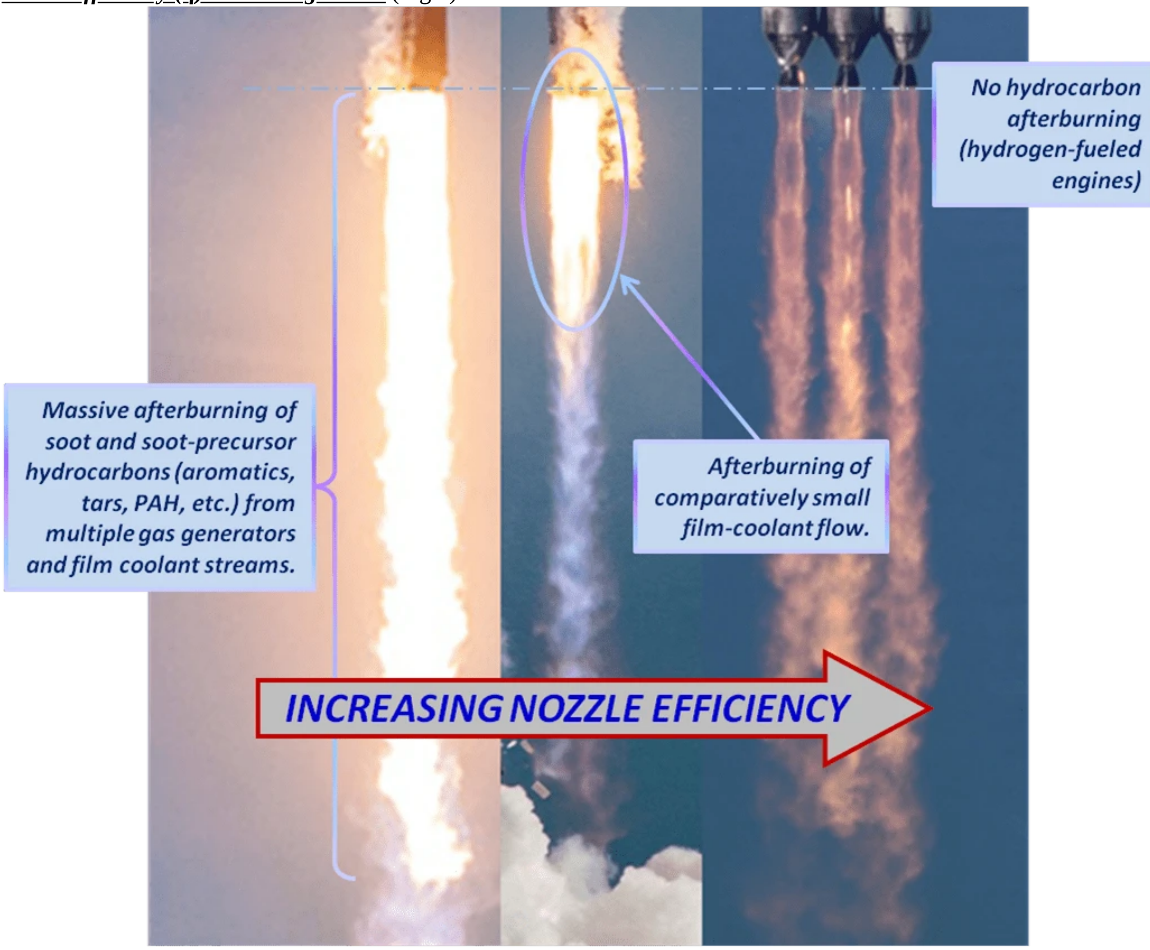


Figure 2. Comparison of three similarly-sized launch vehicles. ***Left****: brilliant visible afterburning of significant quantities of PAH/tars/soot discarded by engine, with predicted lower-Performance (LOX/RP-1);* ***Middle****: minimal visible afterburning indicates high-Performance and primarily low Cp gases present in the nozzle (high-****η****; LOX/RP-1);* ***Right****: non-hydrocarbon fuel with only minimal Cp species in the nozzle, obtaining maximal* ***η****. (LOX/H_2)[ref. A]*

The thermal cracking and oligomerization reactions (via condensation polymerization) 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 temperatures during the process of building solid carbon (soot/cokes) in rocket engines in fuel-rich regions of a hot engine. Primary pyrolisates (e.g., PAH) occur in 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 afterburners.

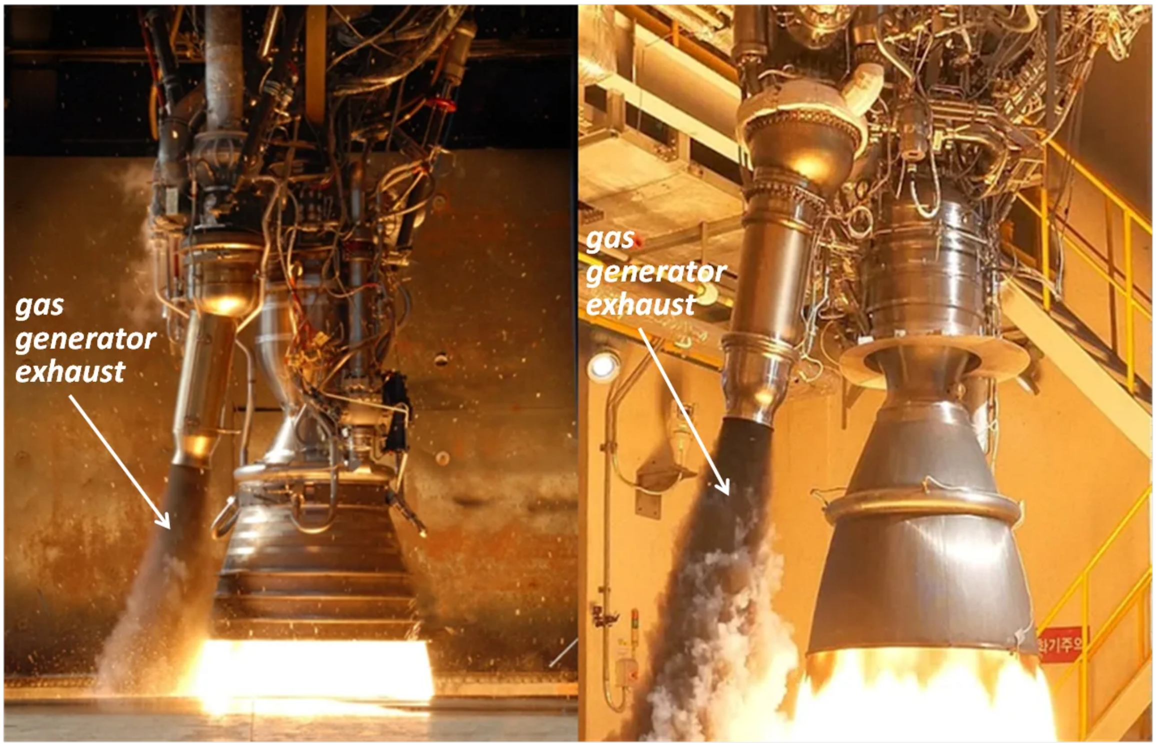


Figure 3. SpaceX (left) and Hanwha (right) gas generator exhaust and afterburning film-coolants (brilliant engine-nozzle exhausts), viewed on the test-stand, above the water deluge which protects the "flame bucket" but also suppresses PAH afterburning on the test-stand. [ref. B]

Figure 4. Static firing - deluge water below vehicle prevents facility damage to the test-stand by the hot plume - but deluge water also quenches after-burning of the soot, aromatics, PAH, tars, etc. created by the gas generator and film coolant flows, seen as the large dark cloud (PM2.5, PAH, aromatics, etc., left). Compare this with Figure 5 post-AB shutdown (upper right). [ref. C]

In the absence of the ***tropospheric rocket-plume afterburning*** shown in Figure 2, these 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 and *at high altitudes after plume afterburning shuts down*.

Of particular concern for this work is upper-atmosphere (above ~30km) deposition of reactive and stable polycyclic free-radicals, and PAH (Figures 5 and 6), which 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 may present a larger UV/VIS/IR cross-section to incoming insolation than the equivalent mass of carbon contained in a small-radius soot particle which interact with insolation only via MIE scattering. PAH species typically have many strong absorption bands in LWIR and UV/Vis.

The rates for PAH decomposition reactions with ozone are low, suggesting these species may persist and build-up with time and number of launches.[37,38] 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 with time and number of launches.

As mentioned, these high-molecular-weight species are the building blocks of observed soot, and therefore are always present following afterburning shut-down (next section).

HYDROCARBON DEPOSITION

Afterburning and Afterburning Shutdown

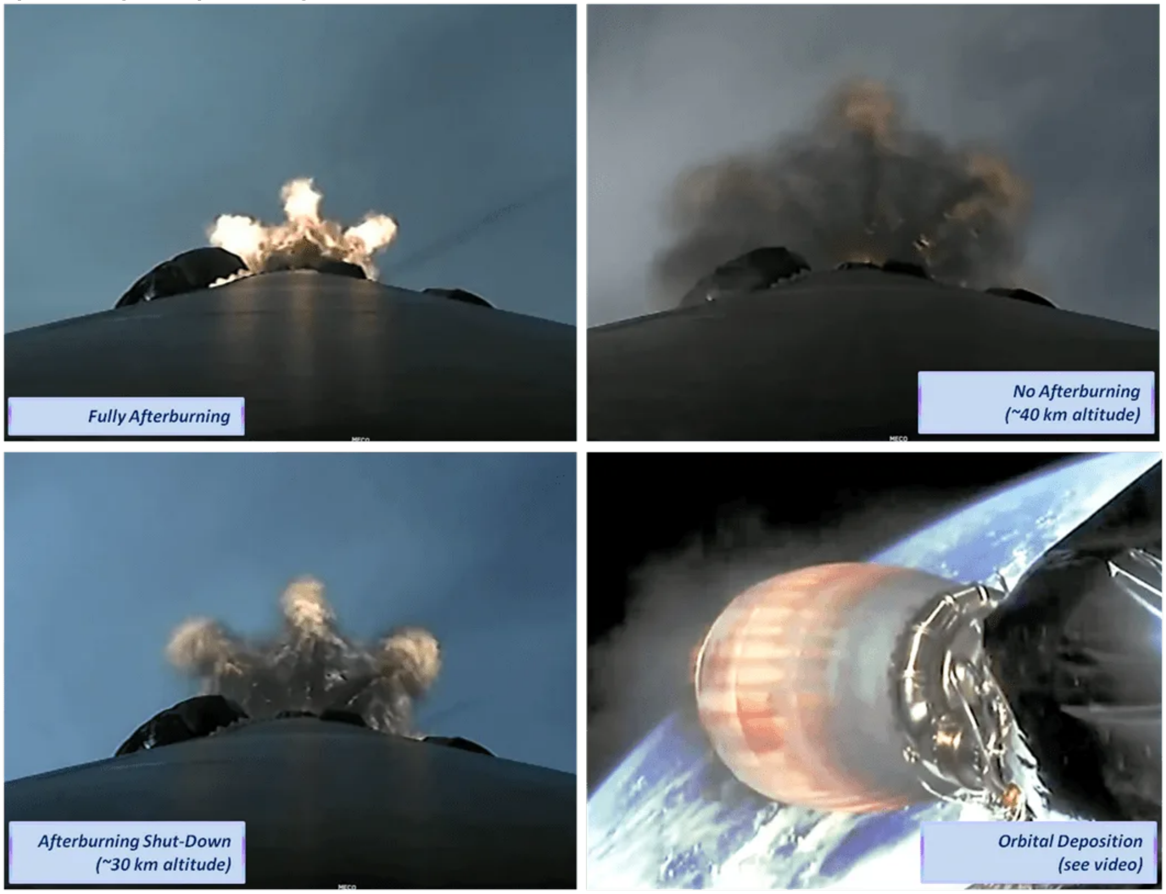
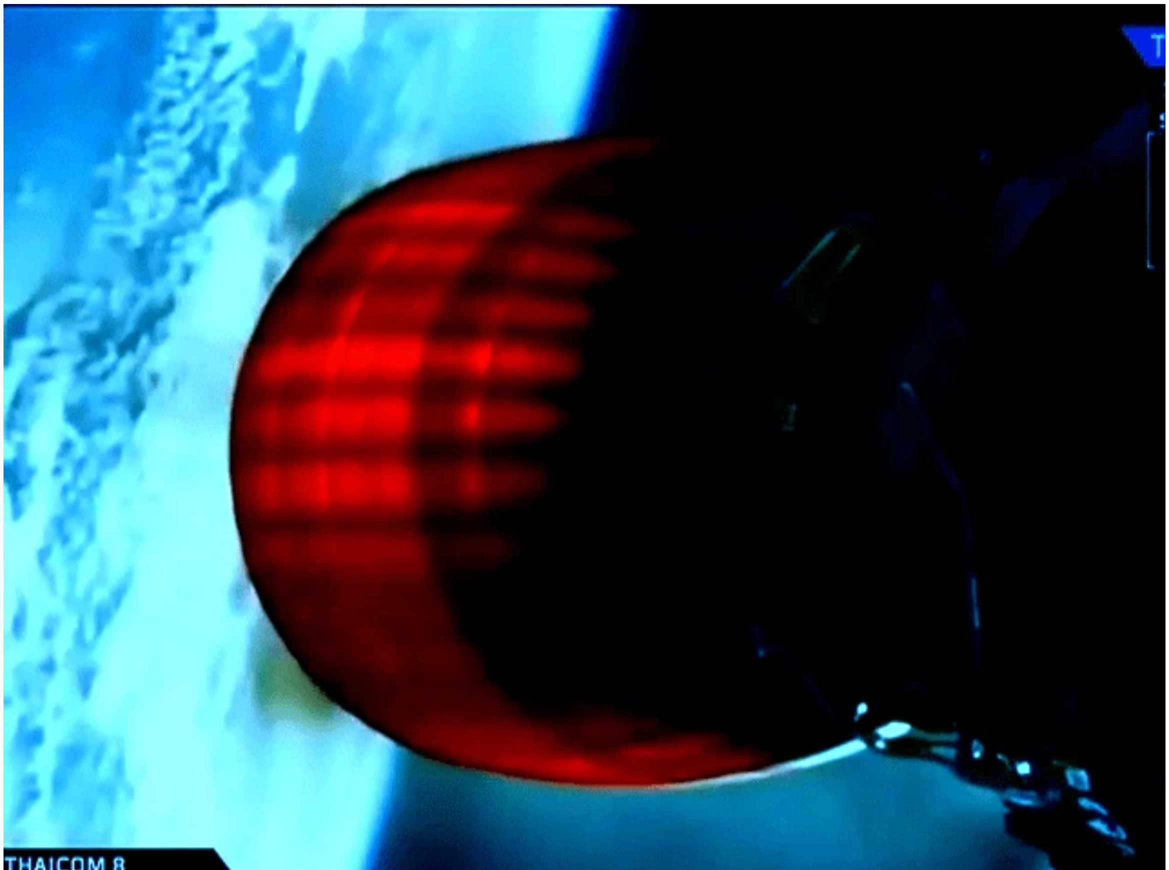


Figure 5. Progression of afterburning (AB) shutdown with increasing altitude, showing transition to direct atmospheric and orbital PAH/tar deposition. ***Upper left*** *- AB shutdown beginning;* ***Lower left*** *- nearly complete AB shutdown;* ***Upper right*** *- complete AB shutdown;* ***Lower right***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

[VIDEO] https://res.cloudinary.com/amuze-interactive/video/upload/vc_auto/v1637268793/agu-fm2021/AF-F1-FB-A2-17-7D-5C-7A-A9-FC-E6-FC-23-86-5D-53/Video/OUT_lfp1ym.mp4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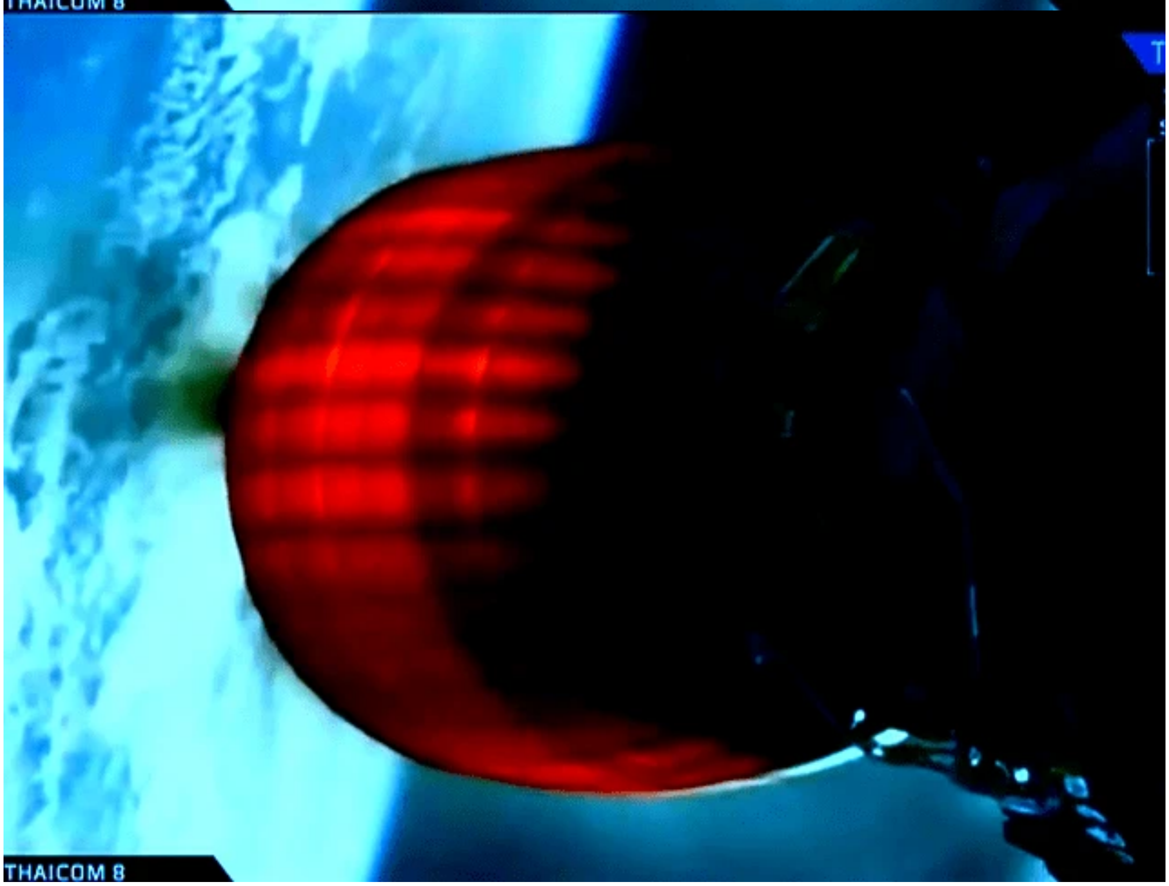
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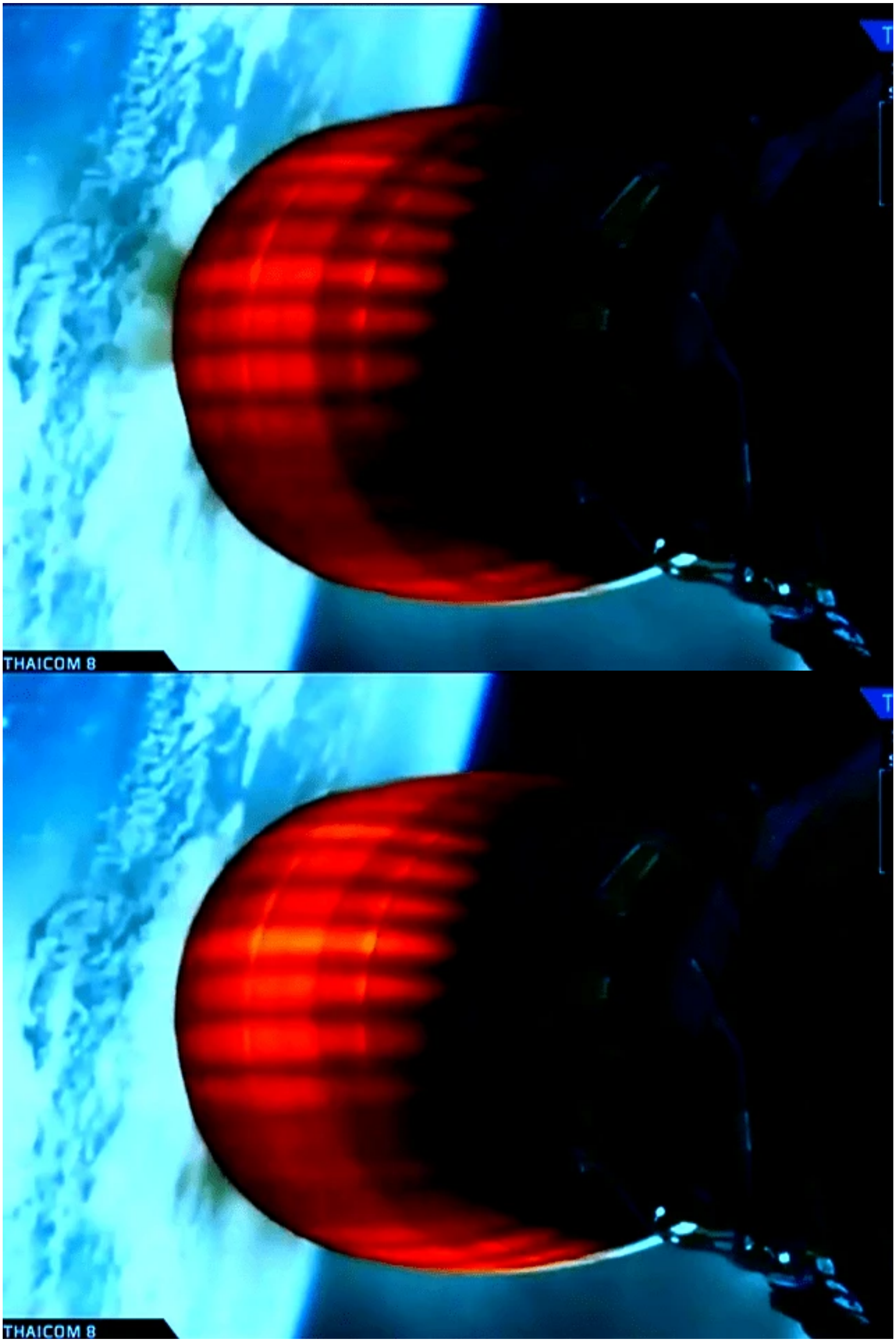


Figure 6. Video (and video excerpts) of PAH/tar deposition during orbital-transfer burn. Note: the nozzle is highly underexpanded in vacuum, so the film-coolant PAH is observed to spread out <u>*laterally*</u> *from the nozzle and is therefore much more tenuous to observe in vacuum, but is clearly observable in the video. [ref. D]*

A typical launch vehicle trajectory involves quickly traversing the troposphere, then pitching over to accelerate toward orbit. Shortly after launch, the rocket enters the stratosphere and pitches over to fly more tangentially to the surface of the earth while continuing to gain altitude. Afterburning (AB) destruction of the soot/PAH/tars by the hot plume is widely known to shut-down due to rapidly decreasing partial pressure of atmospheric O_2 at altitudes above ~30km. AB shutdown, with the concomitant deposition of unburned soot/PAH/tars/etc., can be clearly observed in Figure 5.[32] 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 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 [33], and the liquid phase was found to be unexpectedly persistent in hard vacuum - suggesting PAH/tars may be similarly persistent in vacuo.

An example mass-deposition rate estimate might 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), and a fuels flow rate of ca. 250 kg/sec, then it can be somewhat conservatively estimated that on *the order of* 2 metric tons of PAH/soot/tars/etc., and possibly more, are released into the upper atmosphere per launch (ignoring first-stage-return firings). A more precise estimate would require knowledge of film-coolant and gas-generator flows, as well as PAH→soot conversion rates, although it appears that the overall conversion yield of PAH→soot may be low, so the PAH yield may dominate.[19,20]

It is unknown if any documents exist which present valid information on the presence of the soot building-block species (i.e., benzene, PAH, etc.) in the Merlin and Hanwah engine exhausts. Hence, the estimates provided above, perhaps with valid refinements, should be adopted by the atmospheric science community. Of particular importance would be future measurements if they could be made by experienced and objective third-parties. Crucially, these measurements must corroborate, extend, and refine *known* data and science understanding.

NON-GIGO CALCULATIONS

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

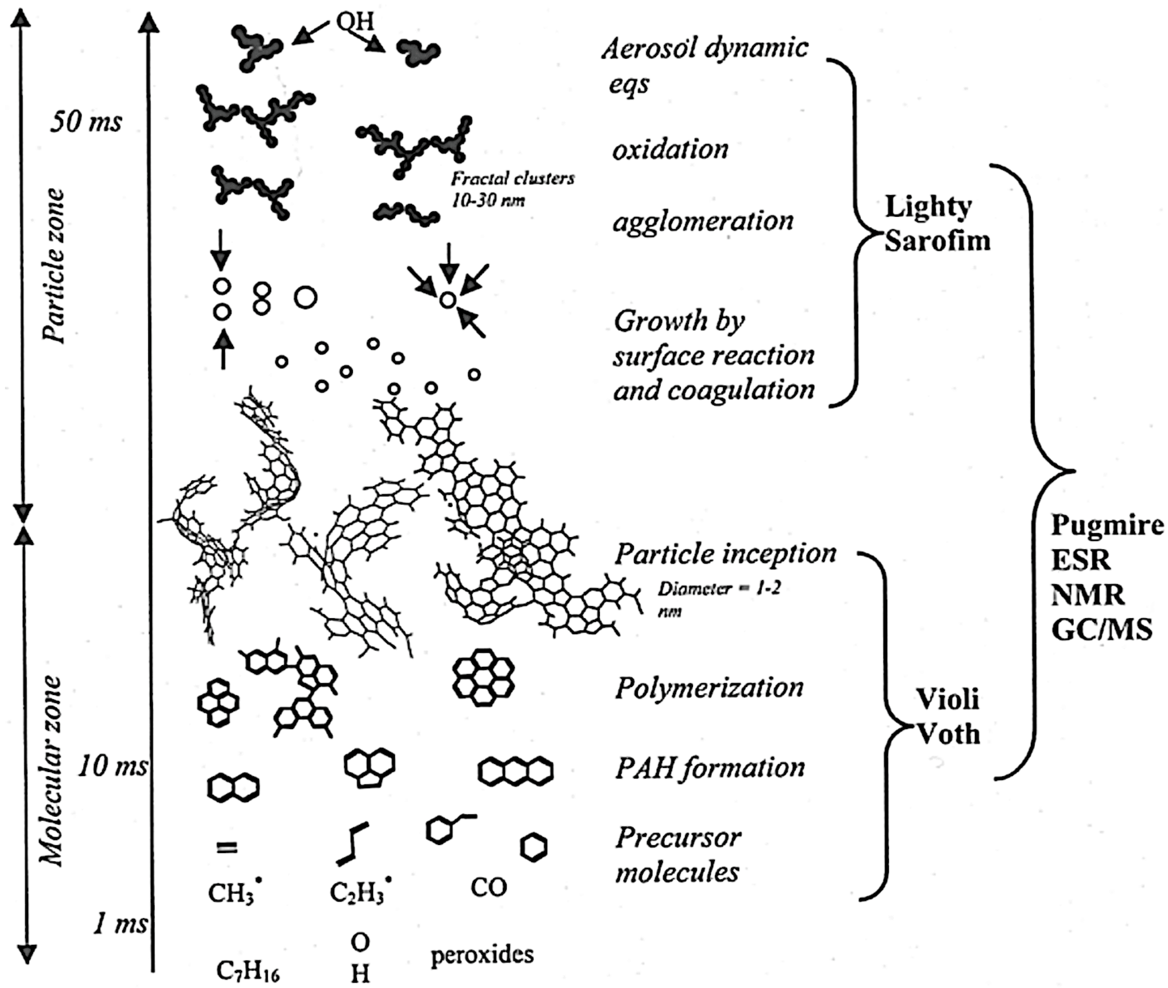
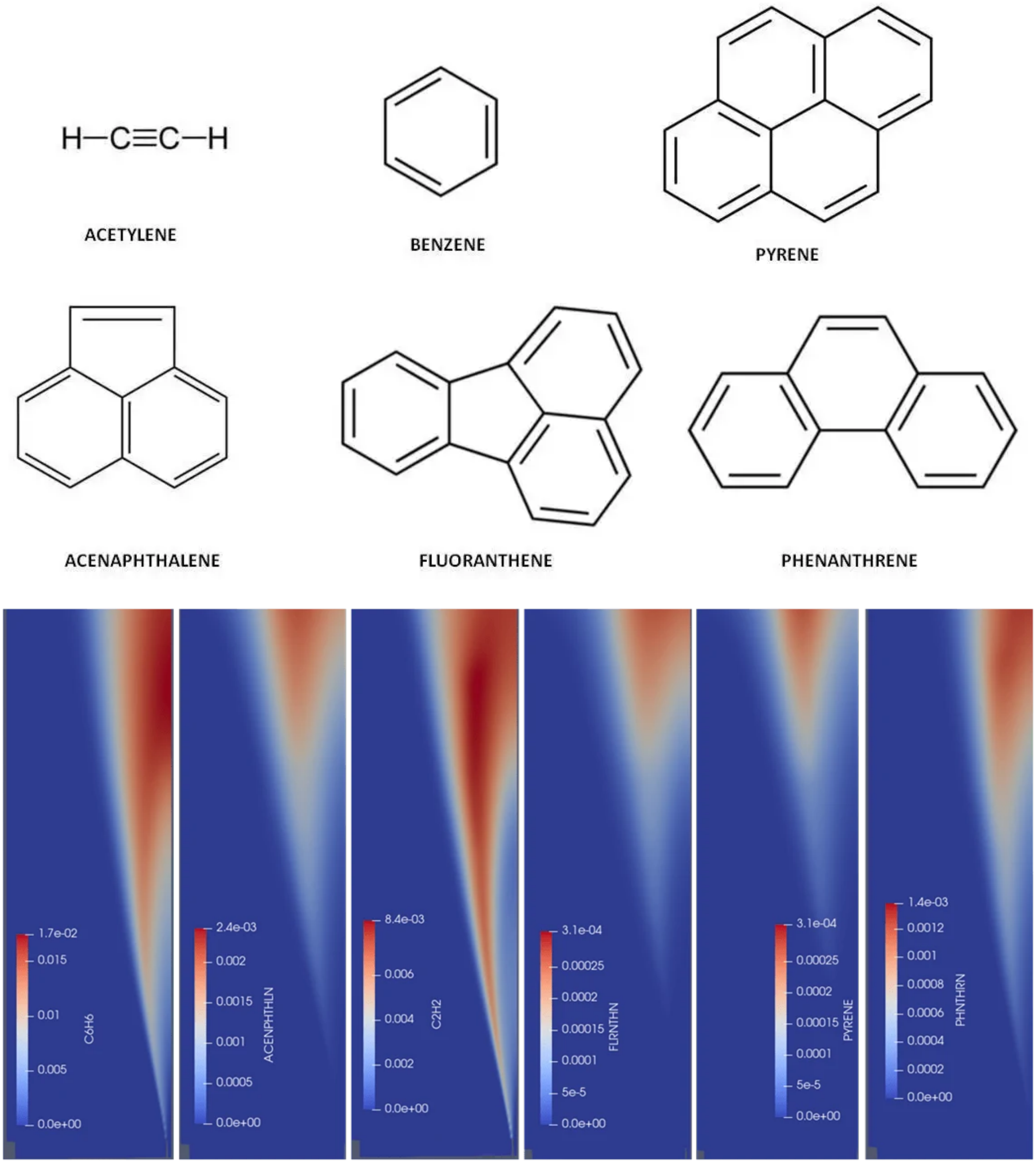


Figure 6. PAH molecules are continually created during sooty combustion, and grow by cracking and oligomerization reactions (via condensation polymerization) to form larger PAH - the thermo-dynamically favored sp2 form of carbon - which are in turn the building blocks of cokes and soot particles. [18,21,30] These are always present in significant quantity unless specifically removed, e.g., by catalytic converters, etc.

Current computer combustion models still cannot completely simulate the formation of large soot particulates from known basic 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 spacelaunch vehicles. The existence of these pollutants are currently hidden from atmospheric researchers by existing invalid documentation.[1,2,5-7] The primary importance of non-GIGO PAH calculations is to reveal the significant presence of PAH and related species. Objective measurements under real-world conditions are required to obtain more accurate data.

Non-GIGO Model Estimates Although non-GIGO rocket engine calculations are difficult under multiphase combustion chamber conditions, it is easy to estimate typical and expected chemical species products in targeted regions of combustion. The chemistry of oxygen-starved hydrocarbon combustion and pyrolysis of a highly fuel-rich gas generator, or of a LOX/RP-1 engine film-coolant after evaporation, can be simulated using simple non-GIGO geometries.[18,21] To obtain high accuracy data on the PAH burdens, careful measurements must nonetheless be made of engine effluents from low-Performance open-cycle LOX/RP-1 rocket engines.[17,19,20] The non-GIGO calculations serve as guides to needed measurements.

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 Figure 7, up to the limits of the available chemical mechanism.[18] These calculations are relatively straight-forward using high quality solvers, such as OpenFOAM, even in a simple flow condition.[36] These calculations show large yields of benzene, consistent with known measurements, as well as substantial yields of PAH, consistent with the required building blocks of easily-observed soot/PM2.5 yields (Figures 2 and 4). However, even these simpler PAHs are absent from available documentation.[1-3,5-7]



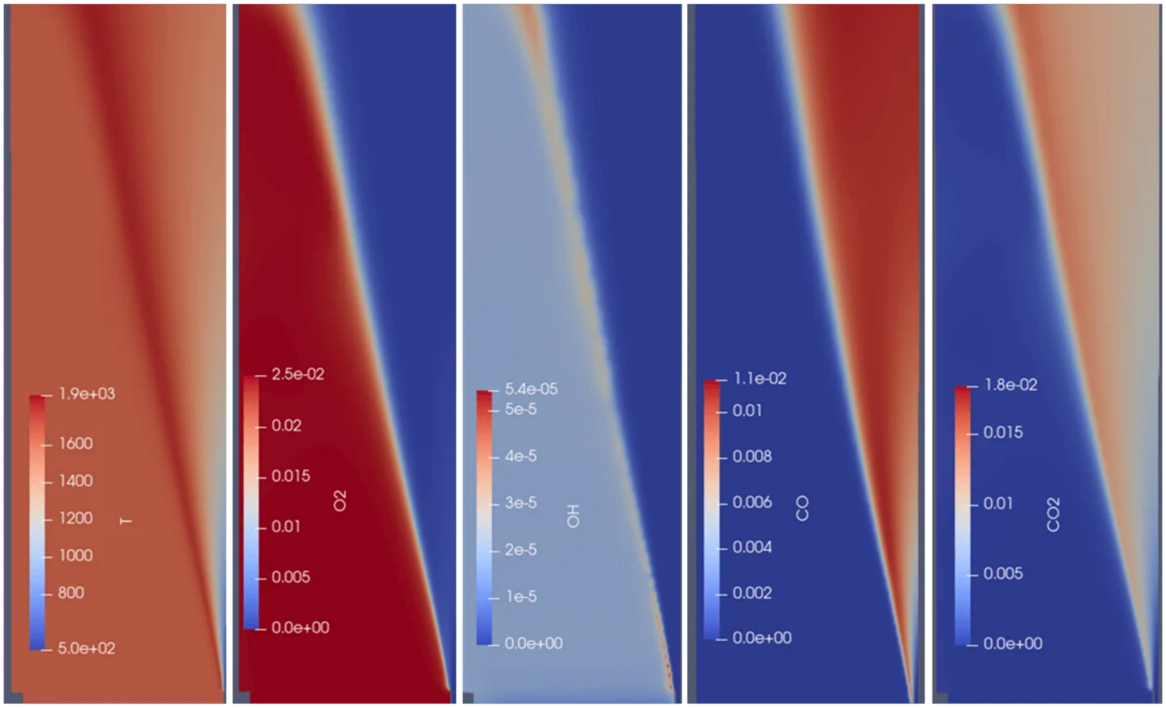


Figure 7. Some results of a non-GIGO calculation: An oxygen-starved hydrocarbon combustion case using the 155-species chemistry model[18] shown in Figure 1, representing high-efficiency combustion of fully-gasified fuel. Even under these highly-efficient combustion conditions, significant quantities of benzene and PAH are nonetheless generated. (P = 100 atm.; yields are insensitive to perturbations in temperature and pressure). Low combustion efficiency is expected to generate significantly more PAH, tars, and soot than are generated by these fully-gasified (high combustion efficiency) model conditions. This demonstrates that non-GIGO models are consistent with known measurements, and support the need for characterization of low-Performance LOX/RP-1 engines for valid atmospheric impact assessments.

Even under the highly-efficient combustion conditions shown in Figure 7, significant quantities of benzene and PAH are nonetheless generated. This shows that these species are kinetically- and thermodynamically-preferred products of oxygen-starved combustion, and are thus important targets for precise measurement and documentation for scientists. Combined with existing measurements, such non-GIGO results underscore the need for new, valid information and documents to support engineers, climate and atmospheric scientists.

SUMMARY/CONCLUSIONS

- High molecular weight hydrocarbons - e.g., aromatics, PAH, tars - are present when soot is formed in LOX/RP-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
- These two low-Performance rocket engines produce large amounts of PAH
- PAH is deposited directly in the upper atmosphere and on the launch stand
- Reaction rates between ozone/UV and larger PAH species appear to be low, suggesting these species may persist and accumulate, *requires further study*
- The currently lack of valid documentation on these engines presents a unique challenge to upper atmospheric and climate scientists, engineers, and regulators - *PAH yield estimates provided herein should be immediately adopted and improved, by...*
- Careful measurements by trusted agents are indicated to document the yields of these important species as the Anthropocene deepens, in order to facilitate understanding of upper atmospheric impacts.
    - *These measurements must corroborate and refine the known combustion science presented herein.*

REFERENCES

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, etc., and hence the reader is also referred to many of the references contained within the numbered references below.

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