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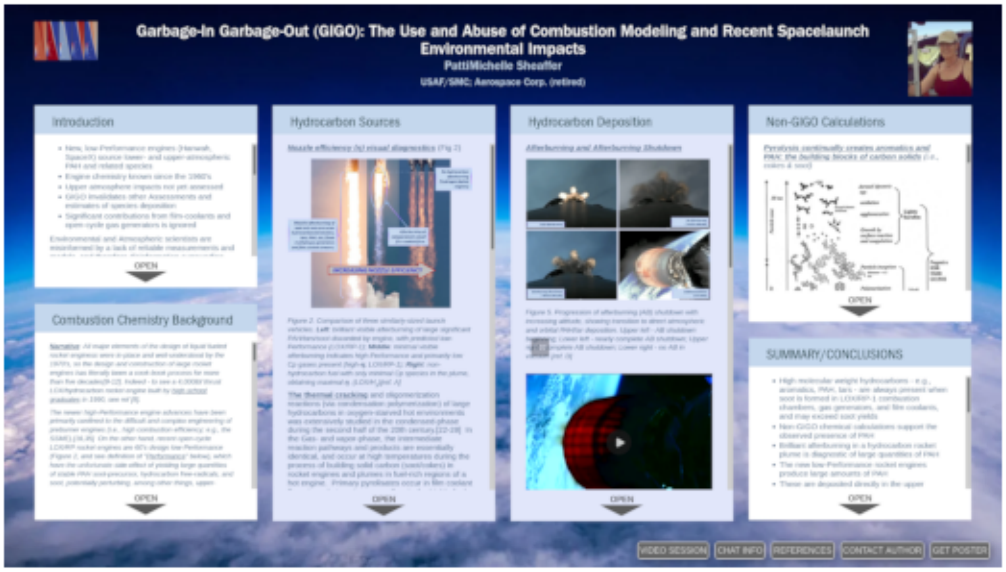
Garbage-In Garbage-Out (GIGO): The Use and Abuse of Combustion Modeling and Recent Spacelaunch Environmental Impacts



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PRESENTED AT:

INTRODUCTION

- New, lower-Performance engines (Hanwah, SpaceX) source novel lower- and upper-atmospheric PAH and related species
- 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 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 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 launch vehicles.[1-7]

The background science draws from a number of separate 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 lower-Performance (Figure 2, and see definition of "Performance" below), which have the unfortunate side-effect of yielding large quantities of stable PAH soot-precursor, 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 well-known interdisciplinary scientific information in carbon science and rocket plume combustion in order to fill the information vacuum for climate and atmospheric scientists and other non-specialists.

GIGO Calculations: Computer models of rocket engine combustion typically have involved simplified reaction[13] sets - examples are shown in Figure 1. However, these ignore PAH, providing highly distorted results. GIGO is sometimes very subtle - recently, even very 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 at a 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 ($\boldsymbol{\eta}$) 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 engines. Resulting poor fuel atomization, and therefore poor gasification, results in incomplete fuel combustion (low combustion efficiency). This, in turn, requires higher fuel loads and larger tankage, and hence larger atmospheric deposition of PAH and related species by the launch vehicle.

Two general sources of PAH are considered:

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

$$c^2 = [\text{Enghalpy Terms}] * \boldsymbol{\eta}$$
$$\boldsymbol{\eta} = \text{Nozzle Efficiency} = 1 - (Pe/Pc)^{R/Cp}$$

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

Maximizing nozzle-efficiency, and therefore engine *Performance*, thus thermodynamically requires a very low Cp in the $\boldsymbol{\eta}$ equation - 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 ***η*** equation.[11,12]

Thermodynamically, this inefficiency occurs because the partitioning of energy quanta into internal molecular modes of polyatomic species, which is largely not extracted by exhaust gas expansion in the rocket nozzle.

Open-Cycle Gas Generators (OCGG) typically consume on the order of 1%-10% of total vehicle fuels [16] but provide no thrust, decreasing launch capacity of a launch vehicle. 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.

For film-coolants, due to temperatures and oxygen-starvation present (after the film-coolants have absorbed their latent heats and evaporated), have a nearly identical chemistry to OCGG. Film-coolants, though required, also do not contribute to engine thrust. The amount of film coolant required 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 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!*

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

A diagram of typical chemistry omissions invalidating computer model results with respect to PAHs, and 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, outdated 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 results are typically similar to measurements.

The only known examples of public documents on these engine exhausts present GIGO results, and 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).

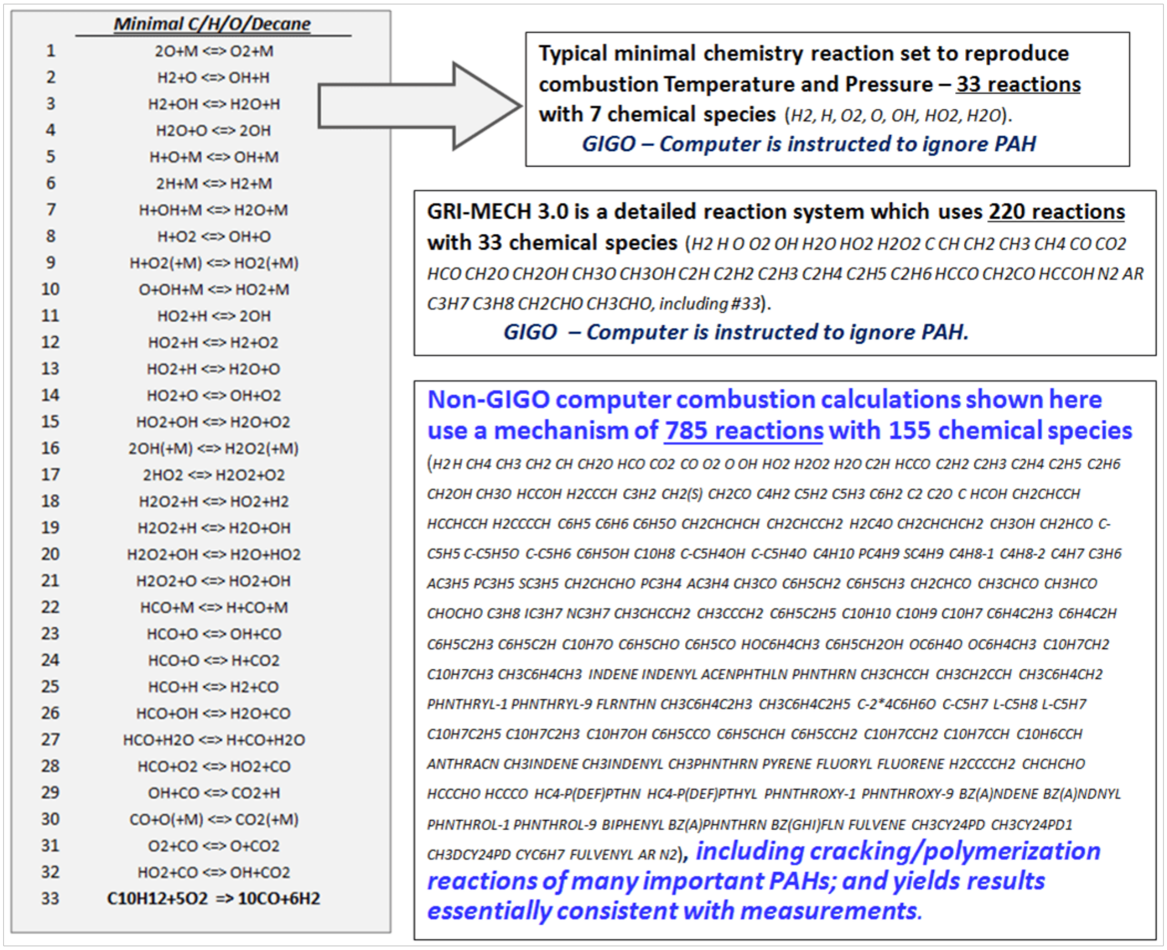


Figure 1. Three progressively larger computer combustion models. All will reproduce in a model the engine pressure and temperature, but only the largest model (155 species) is non-GIGO for PAH species. Pseudo-reactions such as #33 allow RP-1 to be added without PAH in GIGO reaction models. However, even some very large models are GIGO for PAH.[3] Besides the combustion chamber, 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 [2] using a model which is even simpler than the simplest model shown in Figure 1.

Pexit (psia) 82

Texit (R) 3351

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

HYDROCARBON SOURCES

Nozzle efficiency (η) visual diagnostics (Fig 2)

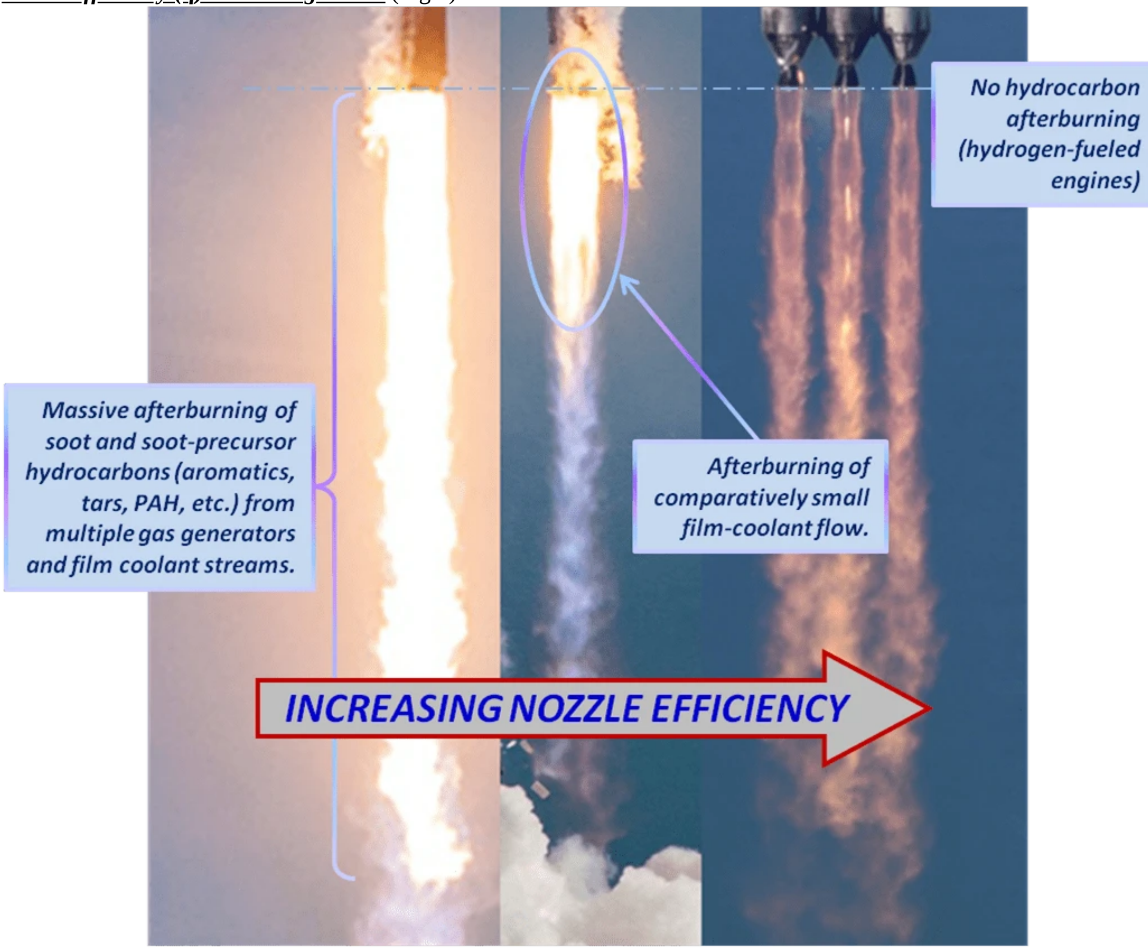


Figure 2. Comparison of three similarly-sized launch vehicles. ***Left****: brilliant visible afterburning of large significant PAH/tars/soot discarded by engine, with predicted low-Performance (LOX/RP-1);* ***Middle****: minimal visible afterburning indicates high-Performance and primarily low Cp gases present (high-****η****; LOX/RP-1);* ***Right****: non-hydrocarbon fuel with only minimal Cp species in the plume, 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, and occur at high temperatures during the process of building solid carbon (soot/cokes) in rocket engines and plumes in fuel-rich regions of a hot engine. Primary pyrolisates 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.

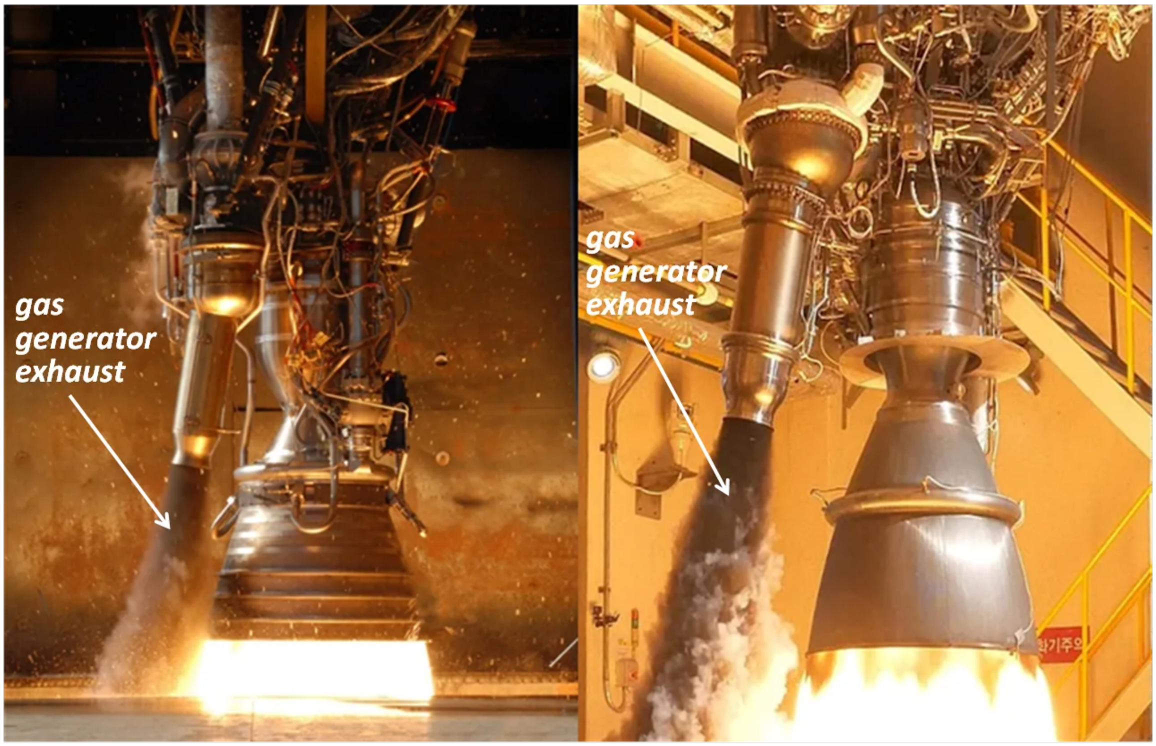


Figure 3. SpaceX (left) and Hanwha (right) gas generator exhaust and afterburning film-coolants (brilliant engine-nozzle exhausts), viewed on the test-stand, above the water deluge which protects the "flame bucket" but also suppresses PAH afterburning on the test-stand. [ref. B]

Figure 4. Static firing - deluge water below vehicle prevents facility damage by the hot plume - but deluge water also shuts-down tropospheric 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 - 5). 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, 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. 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

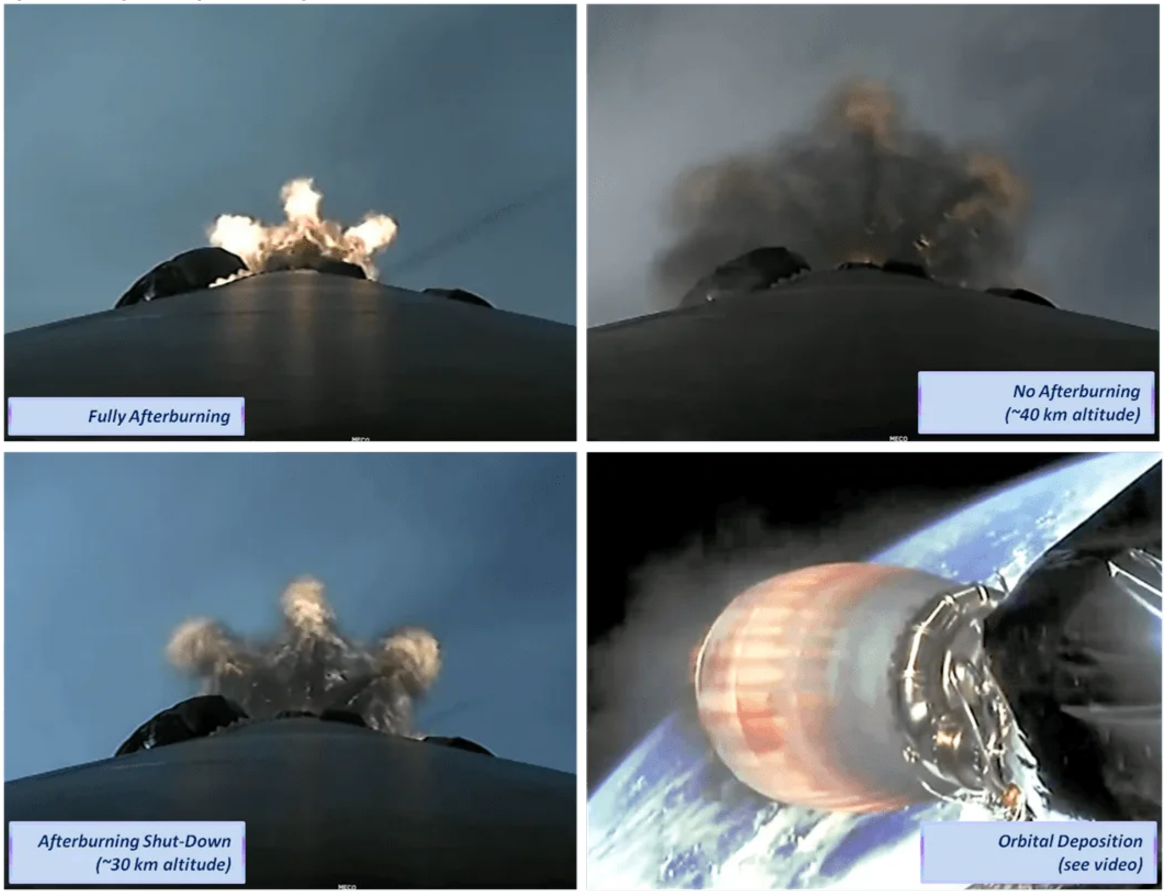
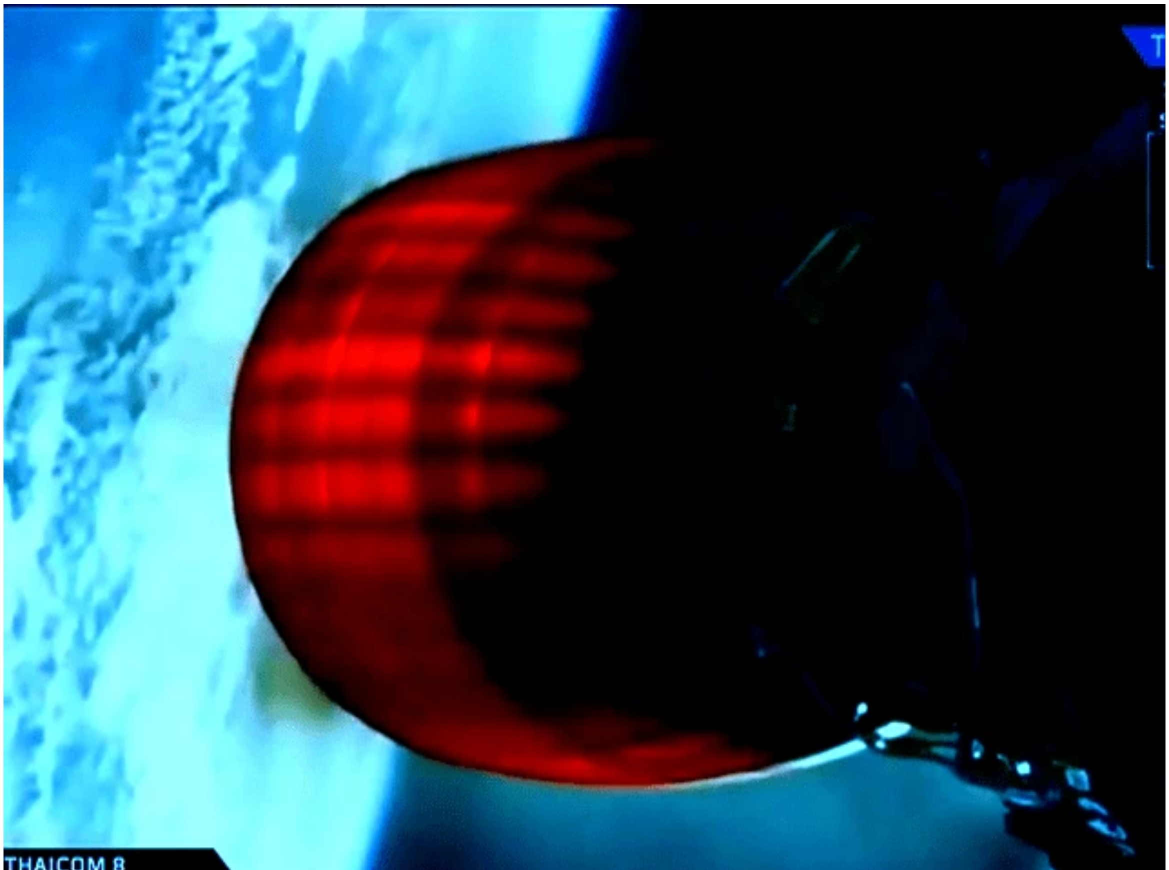


Figure 5. Progression of afterburning (AB) shutdown with increasing altitude, showing transition to direct atmospheric and orbital PAH/tar deposition. Upper left - AB shutdown beginning; Lower left - nearly complete AB shutdown; Upper right - complete AB shutdown; Lower right - no AB in vacuum [ref.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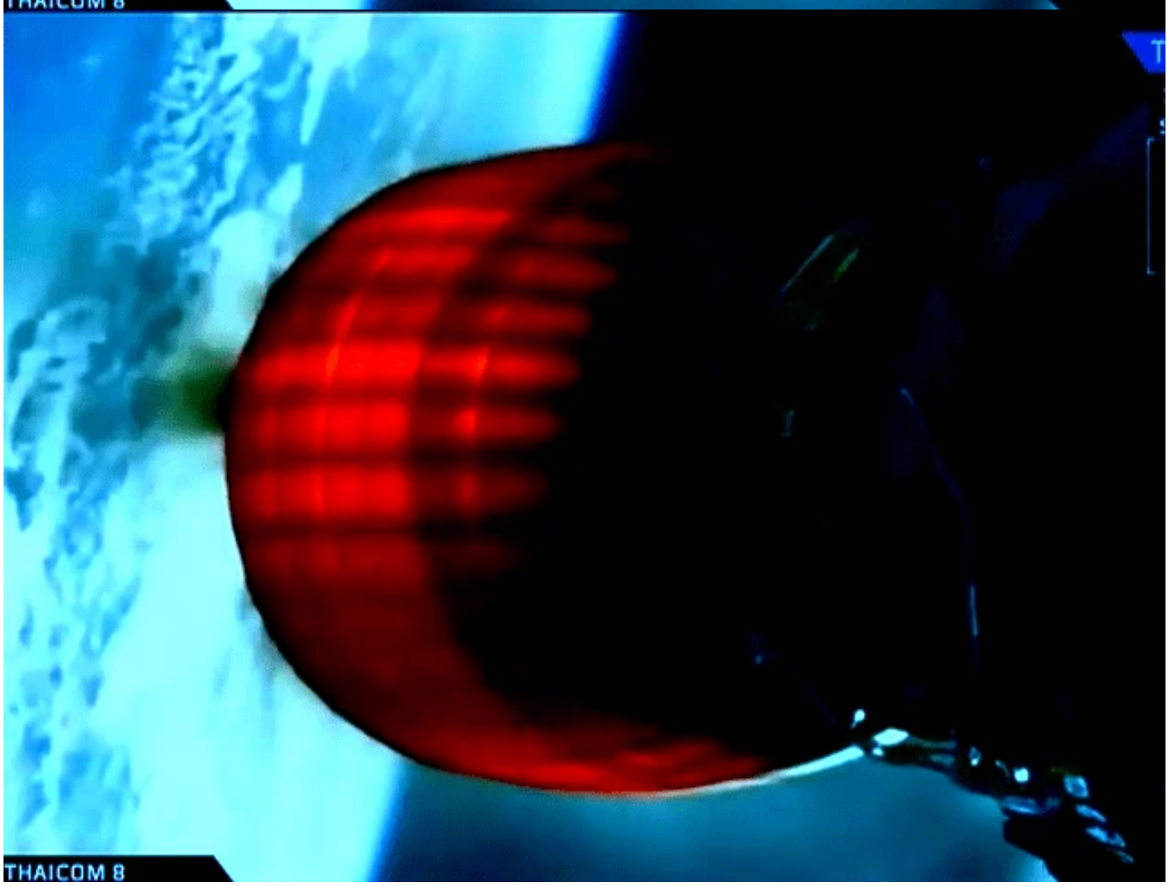
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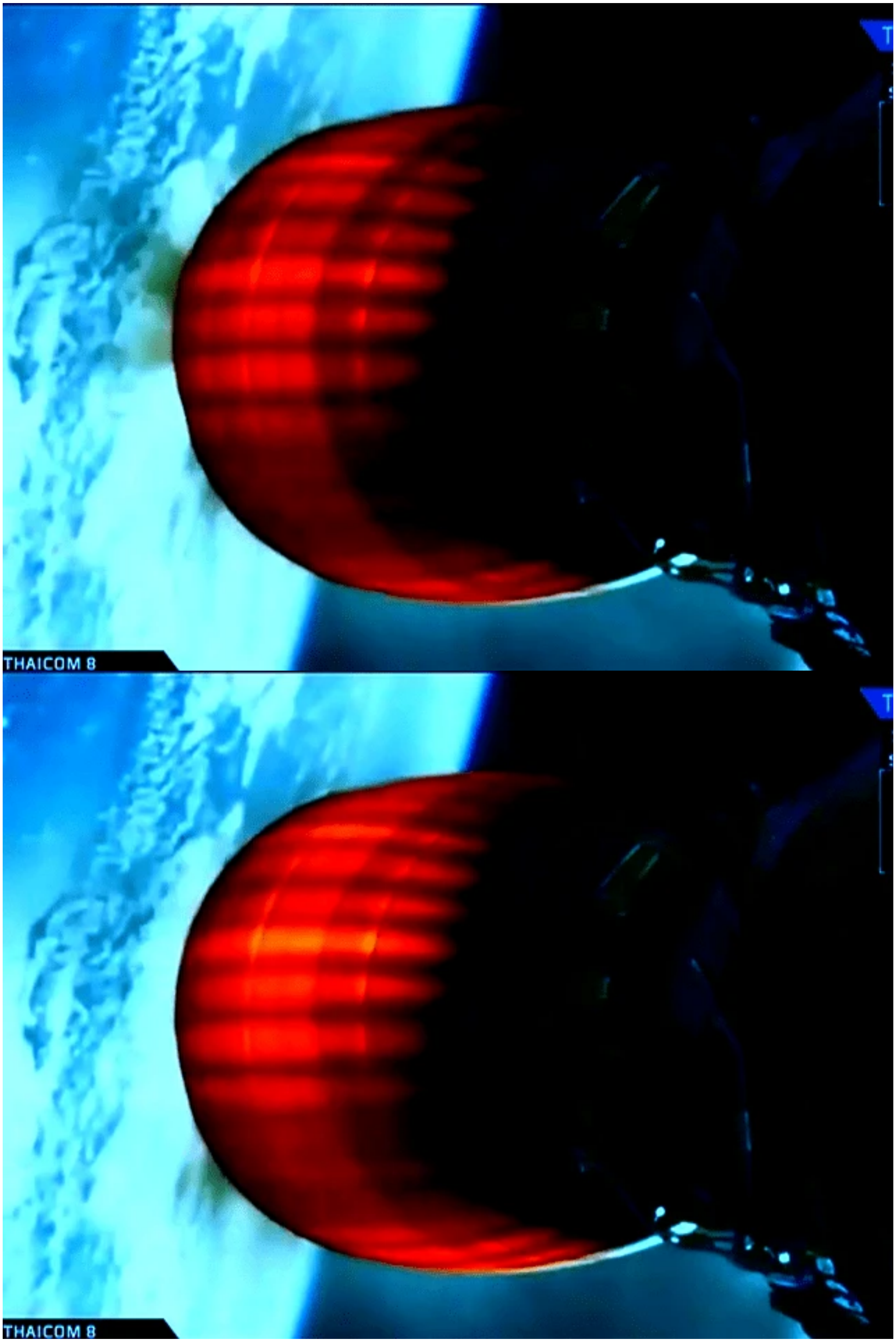


Figure 6. Video (and video excerpts) of PAH/tar deposition during orbital-transfer burn. Note: nozzle is highly underexpanded in vacuum, so film-coolant PAH is observed to spread out laterally from the nozzle. [ref. D]

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 low partial pressure of atmospheric O_2 at altitudes above 30km-40km. AB shutdown with the 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 - so PAH/tars are likely 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 estimated that on the order of 2 metric tons of PAH/soot/tars/etc. 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

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

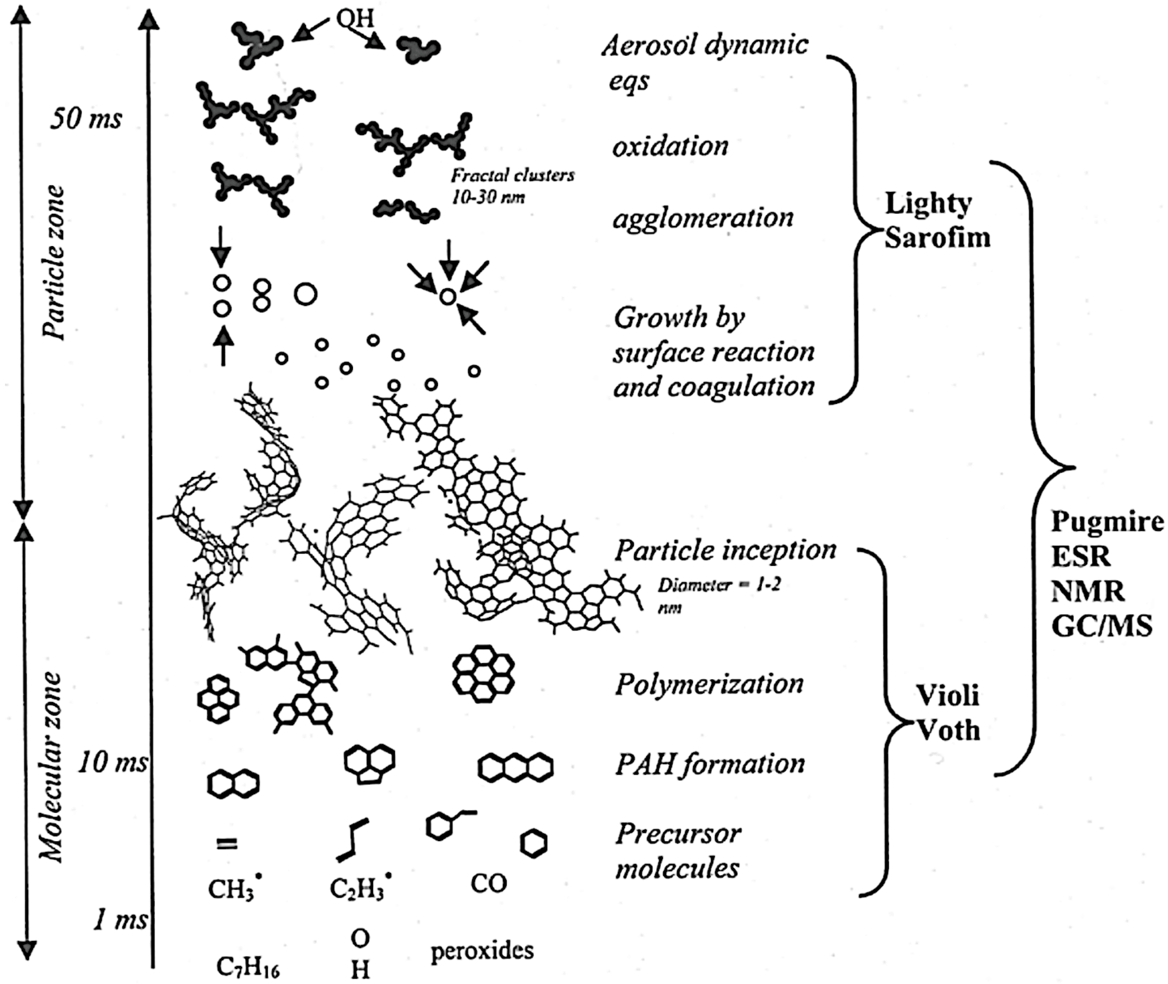
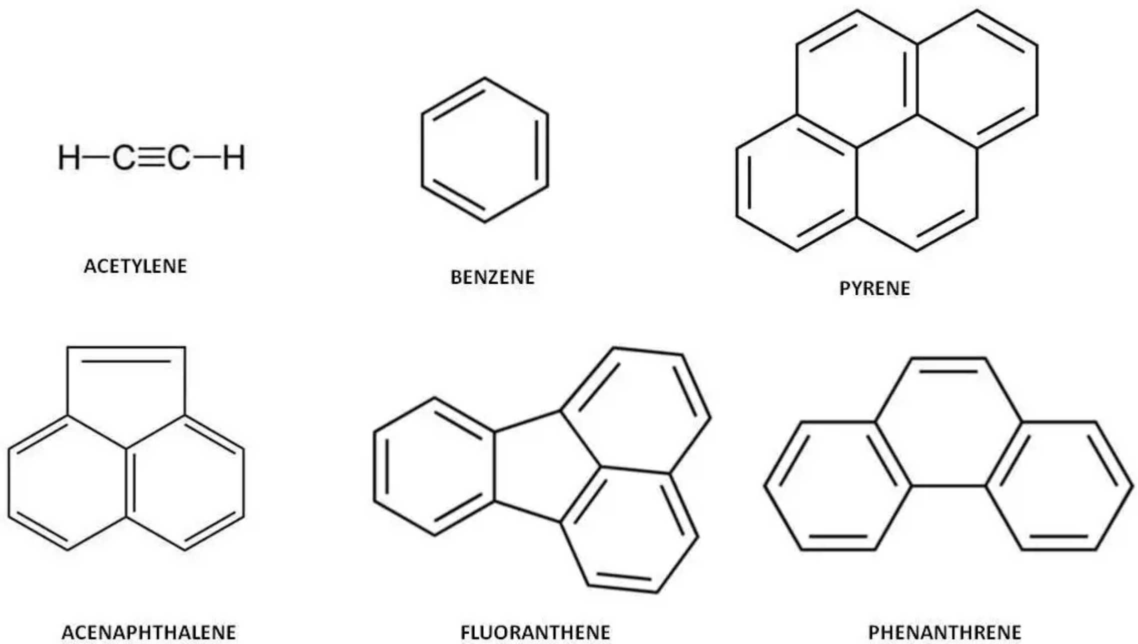


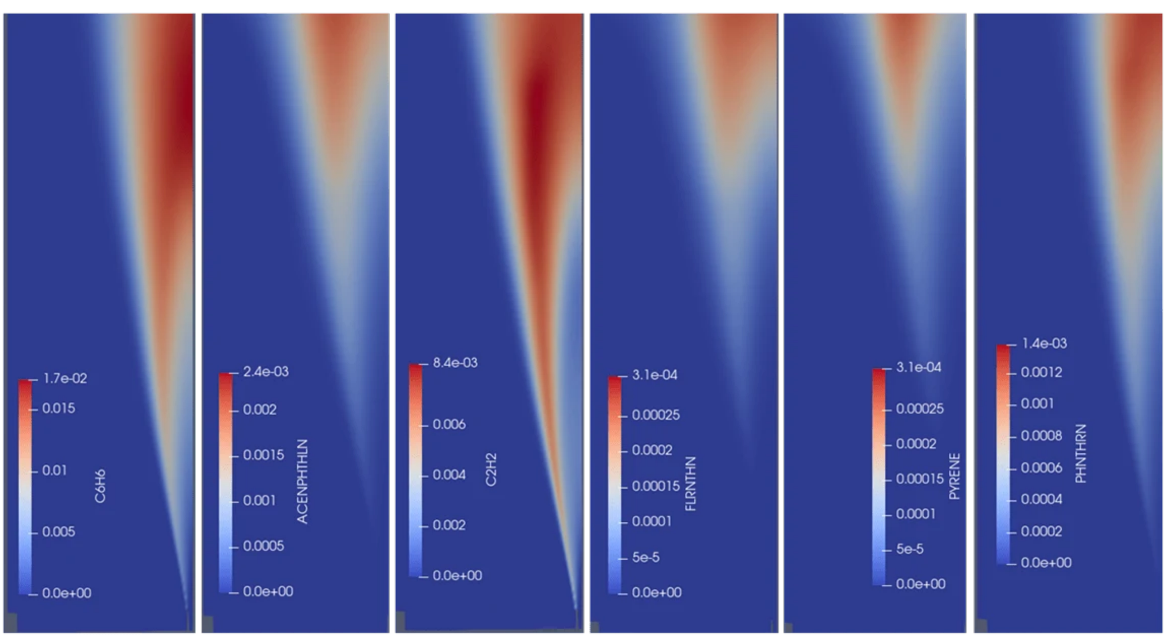
Figure 6. PAH molecules are continually created during sooty combustion, and grow by cracking and oligomerization reactions (via condensation polymerization) to form larger PAH - the thermo-dynamically favored sp2 form of carbon - which are in turn the building blocks of cokes and soot particles. [18,21,30]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

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 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. The chemistry of oxygen-starved hydro-carbon 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]





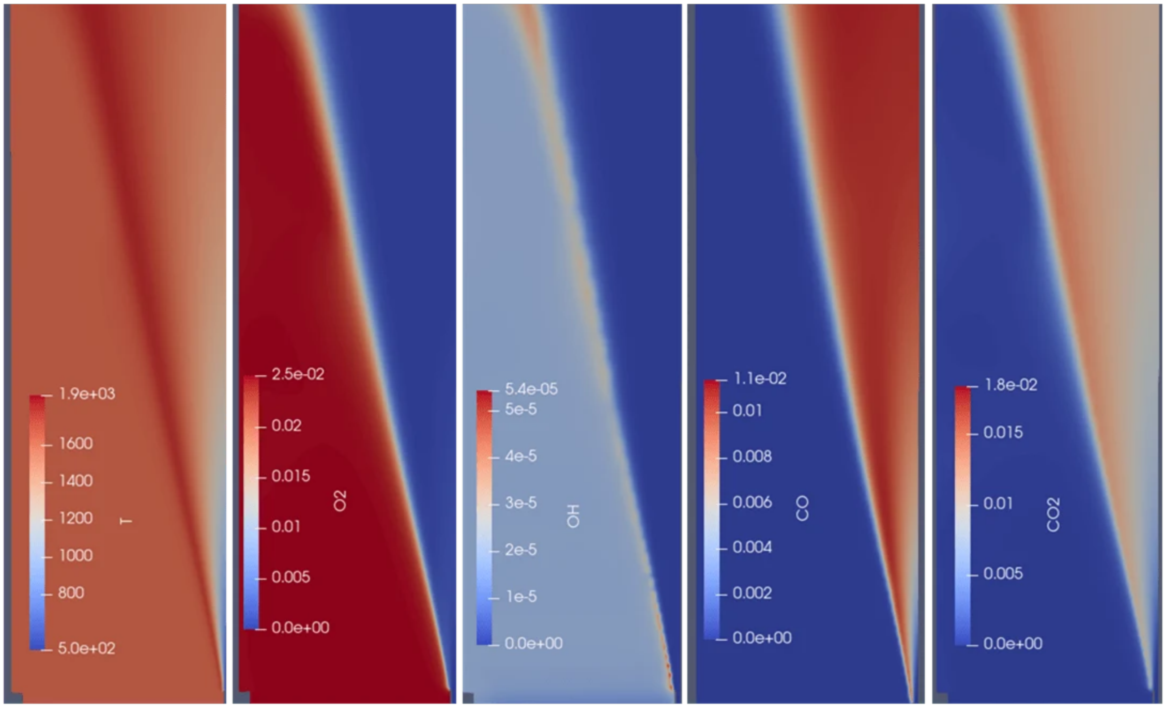


Figure 7. Some results of a non-GIGO calculation: An oxygen-starved hydrocarbon combustion case using the 155-species chemistry model shown in Figure 1, representing high-efficiency combustion of fully-gasified fuel. Even under these highly-efficient combustion conditions, significant quantities of benzene 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.

Combined with existing measurements, these 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 always present when soot is formed in LOX/RP-1 combustion chambers, gas generators, and film coolants, and may exceed soot yields
- 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
- These are deposited directly in the upper atmosphere and on the launch stand
- Reactions between ozone/UV and larger PAH species appear to be slow, suggesting these species may persistand accumulate, *requiring 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...
- 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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