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

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Abstract

Although adequately detailed kerosene chemical-combustion Arrhenius reaction-rate suites were not readily available for combustion modeling until ca. the 1990's (e.g., Marinov [1998]), it was already known from mass-spectrometer measurements during the early Apollo era that fuel-rich liquid oxygen + kerosene (RP-1) gas generators yield large quantities (e.g., several percent of total fuel flows) of complex hydrocarbons such as benzene, butadiene, toluene, anthracene, fluoranthene, etc. (Thompson [1966]), which are formed concomitantly with soot (Pugmire [2001]). By the 1960's, virtually every fuel-oxidizer combination for liquid-fueled rocket engines had been tested, and the impact of gas phase combustion-efficiency governing the rocket-nozzle efficiency factor had been empirically well-determined (Clark [1972]). Up until relatively recently, spacelaunch and orbital-transfer engines were increasingly designed for high efficiency, to maximize orbital parameters while minimizing fuels and structural masses: Preburners and high-energy atomization have been used to pre-gasify fuels to increase (gas-phase) combustion efficiency, decreasing the yield of complex/aromatic hydrocarbons (which limit rocket-nozzle efficiency and overall engine efficiency) in hydrocarbon-fueled engine exhausts, thereby maximizing system launch and orbital-maneuver capability (Clark; Sutton; Sutton/Yang). The rocket combustion community has been aware that the choice of Arrhenius reaction-rate suite is critical to computer engine-model outputs. Specific combustion suites are required to estimate the yield of high-molecular-weight/reactive/toxic hydrocarbons in the rocket engine combustion chamber, nonetheless such GIGO errors can be seen in recent documents. Low-efficiency launch vehicles (SpaceX, Hanwha) therefore also need larger fuels loads to achieve the same launched/transferred mass, further increasing the yield of complex hydrocarbons and radicals deposited by low-efficiency rocket engines along launch trajectories and into the stratospheric ozone layer, the mesosphere, and above. With increasing launch rates from low-efficiency systems, these persistent (Ross/Sheaffer [2014]; Sheaffer [2016]), reactive chemical species must have a growing impact on critical, poorly-understood upper-atmosphere chemistry systems.

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INTRODUCTION

❖ New, lower-Performance engines (Hanwha, SpaceX) release significant PAH and related species into the lower- and upper-atmosphere

❖ This aspect of engine chemistry has been known since the 1960's

❖ Upper atmosphere impacts have not yet been assessed

❖ *The prevailing use of GIGO rocket combustion chemistry codes invalidates other Assessment documents and estimates of species deposition*

❖ Three sources of PAH:

➢ *low-efficiency primary combustion in the thrust chamber*
➢ *thrust chamber, throat, and nozzle film coolants*
➢ *open-cycle gas generators*

❖ *Non*-GIGO rocket combustion chemistry calculations easily estimate PAH yields

Environmental and Atmospheric scientists are misinformed by a lack of reliable measurements and engine chemistry models, and thus by the disinformation surrounding new open-cycle LOX/RP-1 rocket engines. The only recently 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. These GIGO calculations have been the only (unreliable) source of information for atmospheric scientists and regulators on the impacts of these new, large space launch engines.[1-7]

To amend this lack, the background science presented herein draws from a number of disciplines, including the older rocket engine literature. The interdisciplinary details are somewhat complex, but are provided herein in order to give a complete story of the scientific understanding amassed in the 20th century relevant to these new (old-style) 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 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 built by high-school graduates in 1990, see ref [9].*

Newer, high-Performance engine advances have been primarily confined to the difficult and complex engineering of high-efficiency preburner engines (i.e., high combustion efficiency; e.g., the SSME).[16,35] On the other hand, recent fuel-rich open-cycle LOX/RP rocket engines are basically 1960's-era 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, polycyclic hydrocarbon stable 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 by definition ignore real-world PAH yields. (e.g., ref. [1-3,6-8]) No known discussion of this seems to appear in available documents or the scientific/technical literature, in part, presumably because the design of these new engines had been an essentially abandoned low-Performance design. 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 chemical-kinetic combustion modeling. The goal of this work is to fill-in the existing information vacuum on these new, 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.

GIGO Calculations: Chemical-kinetic finite-volume computer models of rocket engine combustion typically have involved 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 models.[8] These ignore PAH (see Tables), providing highly distorted representations of the realities of combustion chemistry. (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 have been used which nonetheless ignore PAH.[3] 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 misinforming a generation of scientists, engineers, and regulators about reactive effluents of these new engines, even at this critical time in the Holocene $\rightarrow$ Anthropocene handover. Example calculations of valid PAH-estimating (non-GIGO) results are shown in the section: ***non-GIGO Calculations***.

Rocket engine *Performance* is tied, via the rocket engine nozzle efficiency factor ($\boldsymbol{\eta}$), 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 engines. However, such injectors are not compatible with the pintle designs in these new LOX/RP-1 engines. The resulting poor fuel atomization, and therefore poor gasification, results in incomplete fuel combustion, yielding relatively low combustion efficiency and hence, low $\boldsymbol{\eta}$. This feeds back into the requirement for higher fuel loads and larger tankage, larger lift-off mass, and hence a larger net atmospheric deposition of PAH and related species by these launch systems.

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

- The dumping-overboard of un-combusted 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-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 mass of exhaust, the exhaust velocity is the primary determinant of thrust: [10,11,16]

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

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

...where Pe = exhaust pressure; Pc = chamber pressure, $\boldsymbol{R}$ = gas constant, Cp = heat capacity at constant pressure

Maximizing nozzle-efficiency, and therefore engine Performance, thus is thermodynamically constrained to requiring a very low Cp in the $\boldsymbol{\eta}$ equation above – that is, *monatomic* and *diatomic* species must dominate in the exhaust flow at the engine throat. The presence of polyatomic species such as PAH rapidly lowers nozzle efficiency ($\boldsymbol{\eta}$), 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 combustion-generated heat into molecular energy quanta in 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* occurring in the rocket nozzle, and thus is lost from the production of *thrust* by the nozzle. Hence, low η and therefore low overall engine efficiency at turning fuel mass into usable thrust.

Open-Cycle Gas Generators (**OCGG**) typically consume on the order of 1%-10% of total vehicle fuels [16] but provide no thrust, with incomplete combustion products simply discarded overboard (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. (Note that combustion products of these fuels largely do not change among similar motor technologies.) This also is consistent with straightforward, non-GIGO combustion calculations and measurements as well as decades of soot-formation research [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 exhaust burns up in the troposphere but not at high altitudes nor under launch- and test-stand stand protective 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), a nearly identical cracking/oligomerization chemistry occurs in film-coolant flows to that creating the species produced in OCGG; that is, dominated by hydrocarbon cracking and oligomerization reactions which produce PAH. 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. These species are separated by flow dynamics from the bulk of film coolant flows, so little combustion is possible [39] – indeed this is the required function of film coolants, to keep hot/reactive gases *away* from the engine/nozzle walls. Also, traces of these reactive species which enter the film-coolant flow cannot support combustion of the relatively large amounts of film-coolant, although they *can and do* support increased rates of cracking and oligomerization of film-coolants to form PAH species.[21-28]

Additionally, the *amount* of film coolant required in a rocket engine combustion chamber depends strongly on the dynamics of the combustion chamber injector flame-front. Due to an inherently strong radial component of flame-front travel in pintle designs, they typically require significant extra "head-end" combustion-chamber film coolant in order to prevent excessive thrust-chamber wall-erosion.[10,15,16] The need for additional film-coolant is an especially critical consideration for *reusable engines*, such as in these engines. Thus, even more film-coolant-derived PAH is deposited into the upper atmosphere due to the reusability requirements of these engines in terms of required increased film-coolants. No information currently appears to be available in the open literature on the film coolant mass-flow rates of these two engines.

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. The GIGO calculations present in available public documents for these engines do not include these reactions and hence do not represent real-world chemistry.

A diagrammatic illustration of the typical chemistry omissions invalidating GIGO computer model results, with respect to PAHs, and including a minimally-complete PAH chemistry suite, is provided in Figure 1. GIGO computer models are *literally told not to include PAH*.[1-3,6-8,18,21] This is often 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, older 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

computer model code results; however, carefully coded non-GIGO model results are typically similar to measurements for the species they include and thus can provide valuable guidelines for those studying engine chemistry. (see section: **non-GIGO Calculations**)

The known public documents on these engine exhausts present only the results of GIGO calculations, and examples/excerpts are shown and referenced in the Tables. These documents assert textually statements such as "soot is also present," in contradistinction to the known science of the soot-formation chemistry, which *necessarily* includes PAH (see also the sections **Hydrocarbon Sources** and **non-GIGO Calculations**).[5-7] These documents therefore provide researchers no valid information on the chemistry deposited in the lower and upper atmosphere by these engines (Figures 3-6).

	Minimal C/H/O/Decane
1	2O+M <=> O2+M
2	H2+O <=> OH+H
3	H2+OH <=> H2O+H
4	H2O+O <=> 2OH
5	H+O+M <=> OH+M
6	2H+M <=> H2+M
7	H+OH+M <=> H2O+M
8	H+O2 <=> OH+O
9	H+O2(+M) <=> HO2(+M)
10	O+OH+M <=> HO2+M
11	HO2+H <=> 2OH
12	HO2+H <=> H2+O2
13	HO2+H <=> H2O+O
14	HO2+O <=> OH+O2
15	HO2+OH <=> H2O+O2
16	2OH(+M) <=> H2O2(+M)
17	2HO2 <=> H2O2+O2
18	H2O2+H <=> HO2+H2
19	H2O2+H <=> H2O+OH
20	H2O2+OH <=> H2O+HO2
21	H2O2+O <=> HO2+OH
22	HCO+M <=> H+CO+M
23	HCO+O <=> OH+CO
24	HCO+O <=> H+CO2
25	HCO+H <=> H2+CO
26	HCO+OH <=> H2O+CO
27	HCO+H2O <=> H+CO+H2O
28	HCO+O2 <=> HO2+CO
29	OH+CO <=> CO2+H
30	CO+O(+M) <=> CO2(+M)
31	O2+CO <=> O+CO2
32	HO2+CO <=> OH+CO2
33	C10H12+5O2 => 10CO+6H2

Typical minimal chemistry reaction set to reproduce combustion Temperature and Pressure – 33 reactions with 7 chemical species (*H2, H, O2, O, OH, HO2, H2O*).
GIGO – Computer is instructed to ignore PAH

GRI-MECH 3.0 is a detailed reaction system which uses 220 reactions with 33 chemical species (*H2 H O O2 OH H2O HO2 H2O2 C CH CH2 CH3 CH4 CO CO2 HCO CH2O CH2OH CH3O CH3OH C2H C2H2 C2H3 C2H4 C2H5 C2H6 HCCO CH2CO HCCOH N2 AR C3H7 C3H8 CH2CHO CH3CHO, including #33*).
GIGO – Computer is instructed to ignore PAH.

Non-GIGO computer combustion calculations shown here use a mechanism of 785 reactions with 155 chemical species (*H2 H CH4 CH3 CH2 CH CH2O HCO CO2 CO O2 O OH HO2 H2O2 H2O C2H HCCO C2H2 C2H3 C2H4 C2H5 C2H6 CH2OH CH3O HCCOH H2CCCH C3H2 CH2(S) CH2CO C4H2 C5H2 C5H3 C6H2 C2 C2O C HCOH CH2CHCCH HCCHCCH H2CCCCH C6H5 C6H6 C6H5O CH2CHCHCH CH2CHCCH2 H2C4O CH2CHCHCH2 CH3OH CH2HCO C-C5H5 C-C5H5O C-C5H6 C6H5OH C10H8 C-C5H4OH C-C5H4O C4H10 PC4H9 SC4H9 C4H8-1 C4H8-2 C4H7 C3H6 AC3H5 PC3H5 SC3H5 CH2CHCHO PC3H4 AC3H4 CH3CO C6H5CH2 C6H5CH3 CH2CHCO CH3CHCO CH3HCO CHOCHO C3H8 IC3H7 NC3H7 CH3CHCCH2 CH3CCCH2 C6H5C2H5 C10H10 C10H9 C10H7 C6H4C2H3 C6H4C2H C6H5C2H3 C6H5C2H C10H7O C6H5CHO C6H5CO HOC6H4CH3 C6H5CH2OH OC6H4O OC6H4CH3 C10H7CH2 C10H7CH3 CH3C6H4CH3 INDENE INDENYL ACENPHTHLN PHNTHRN CH3CHCCH CH3CH2CCH CH3C6H4CH2 PHNTHRYL-1 PHNTHRYL-9 FLRNTHN CH3C6H4C2H3 CH3C6H4C2H5 C-2*4C6H6O C-C5H7 L-C5H8 L-C5H7 C10H7C2H5 C10H7C2H3 C10H7OH C6H5CCO C6H5CHCH C6H5CCH2 C10H7CCH2 C10H7CCH C10H6CCH ANTHRACN CH3INDENE CH3INDENYL CH3PHNTHRN PYRENE FLUORYL FLUORENE H2CCCCH2 CHCHCHO HCCCHO HCCCO HC4-P(DEF)PTHN HC4-P(DEF)PTHYL PHNTHROXY-1 PHNTHROXY-9 BZ(A)NDENE BZ(A)NDNYL PHNTHROL-1 PHNTHROL-9 BIPHENYL BZ(A)PHNTHRN BZ(GHI)FLN FULVENE CH3CY24PD CH3CY24PD1 CH3DCY24PD CYC6H7 FULVENYL AR N2*), *including cracking/polymerization reactions of many important PAHs; and yields results essentially consistent with measurements.*
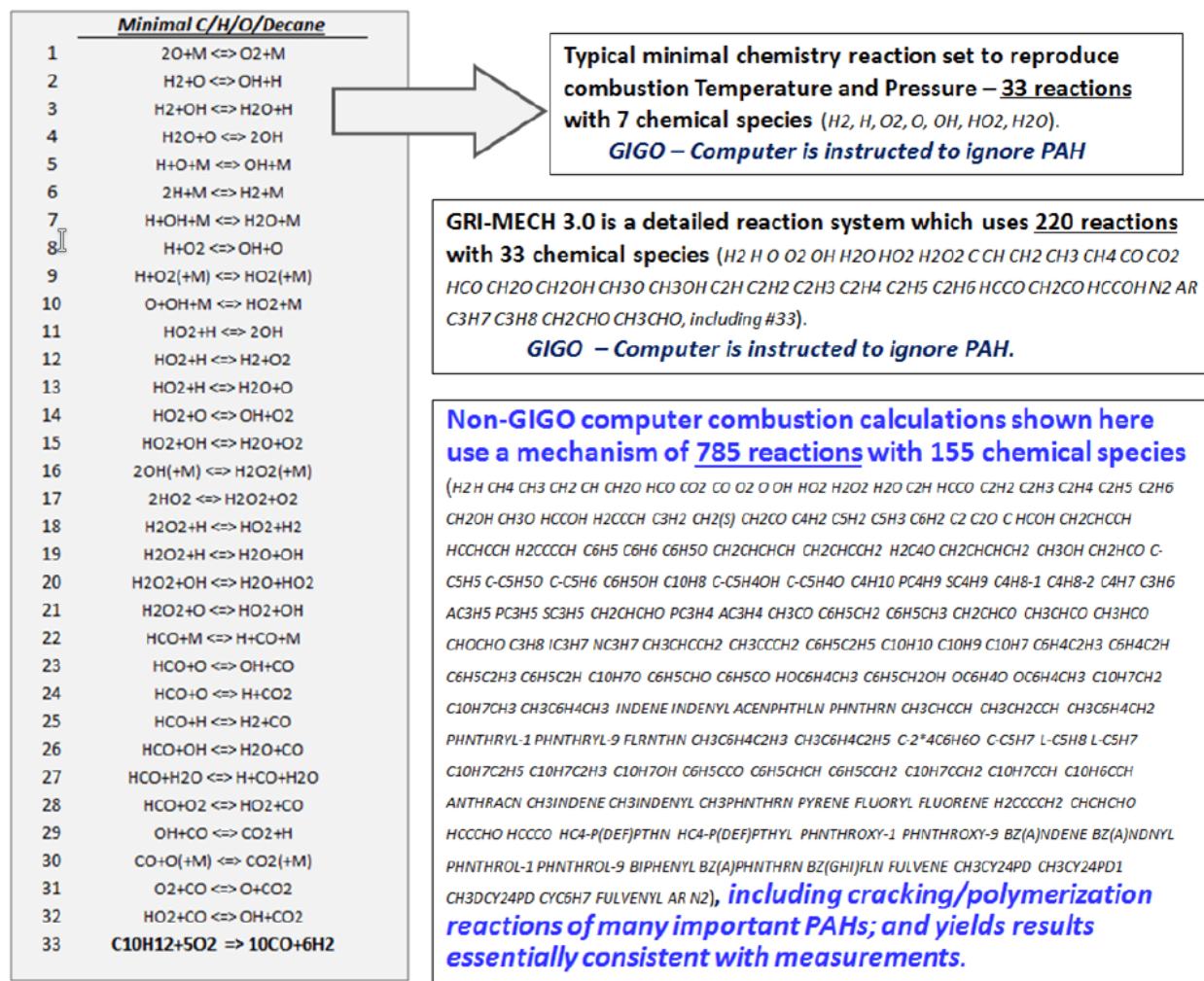
Figure 1. Three progressively larger computer combustion models. All will model the engine pressure and temperature with reasonable accuracy, but only the largest model shown here (155 species) is non-GIGO for PAH species. (*Pseudo-reactions such as #33 allow RP-1 to be added without PAH in GIGO reaction models; however, even some very large models are GIGO for PAH*.[3]) No known documents validly include 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 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.

```
Pexit (psia) 82
Texit (R) 3351
Species     Exhaust
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.

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%

HYDROCARBON SOURCES
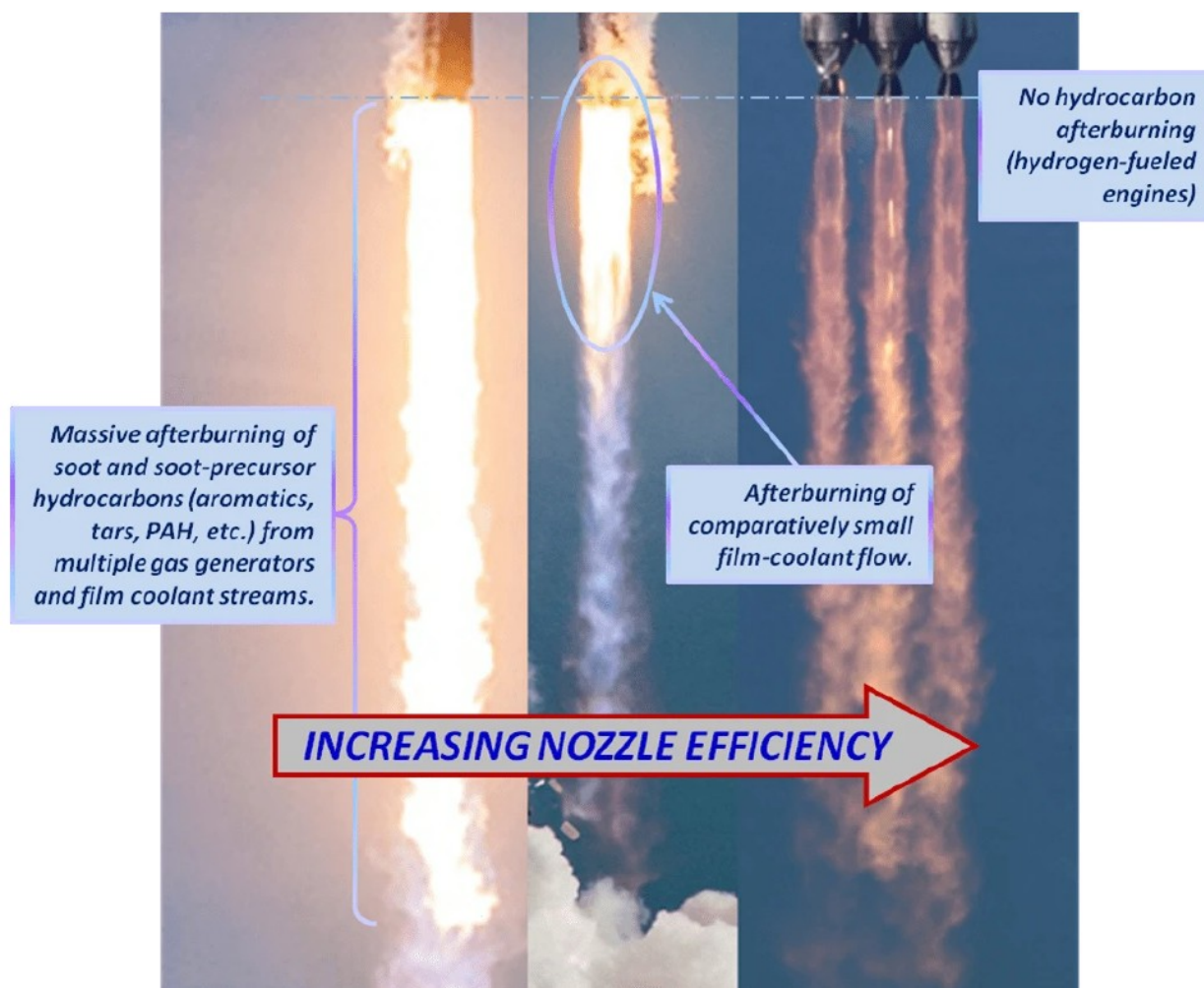
Nozzle efficiency (η) visual diagnostics (Fig 2)

Figure 2. Comparison of three similarly-sized launch vehicle plumes. *Left*: brilliant visible afterburning of large amounts of very high-Cp PAH/tars/soot, significant quantities of which are present in the engine nozzle, 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* low-Cp species in the nozzle, thereby obtaining maximal *η*. (LOX/H2)[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, and these reactions are accelerated by *traces* of oxygen. 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.*
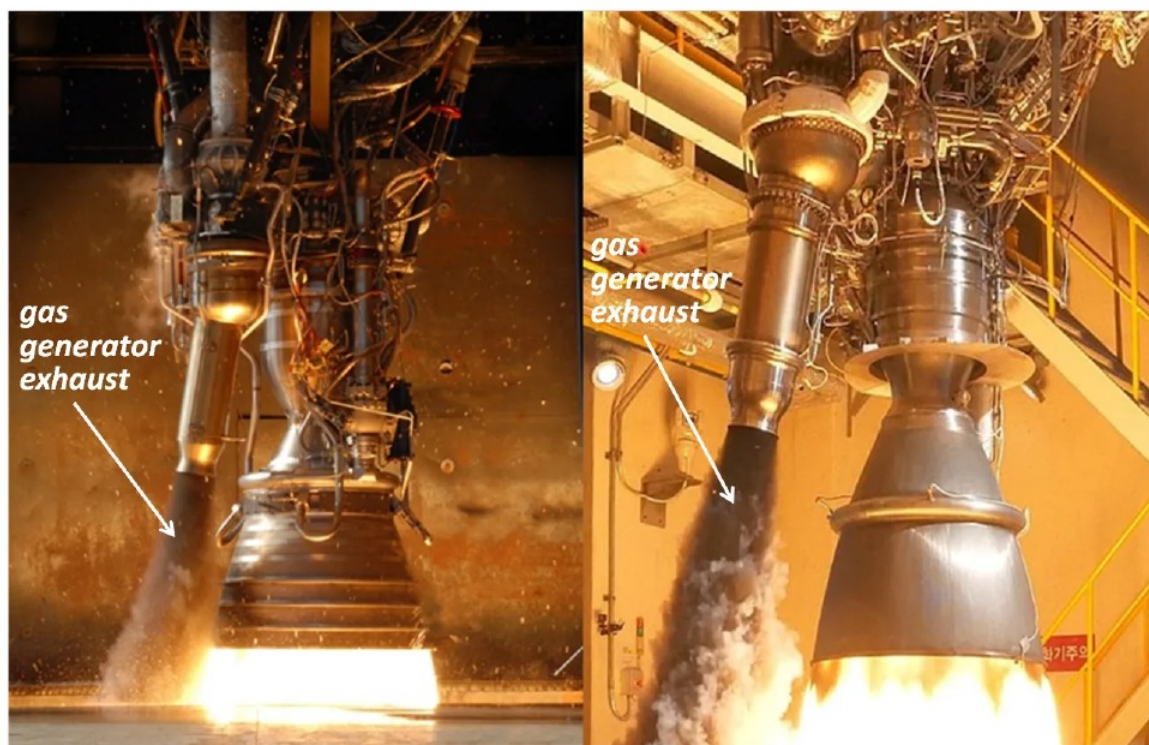
Figure 3. SpaceX (left) and Hanwha (right) gas generator exhaust (labeled) and afterburning film-coolants (brilliant engine-nozzle exhausts), as viewed on the test-stand above the water deluge which protects the "flame bucket" – but which simultaneously suppresses PAH afterburning on the test-stand. [**ref. B**]

Figure 4. During static firing the deluge water below vehicle prevents facility damage to the test-stand by the hot plume, but the 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 low-altitude, 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. (see section: ***Hydrocarbon Deposition***)

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 per unit carbon mass to incoming insolation than the equivalent mass of carbon contained in a small-radius soot particles which interact with insolation only via MIE scattering. PAH species typically have 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. 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.[37,38]

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

HYDROCARBON DEPOSITION

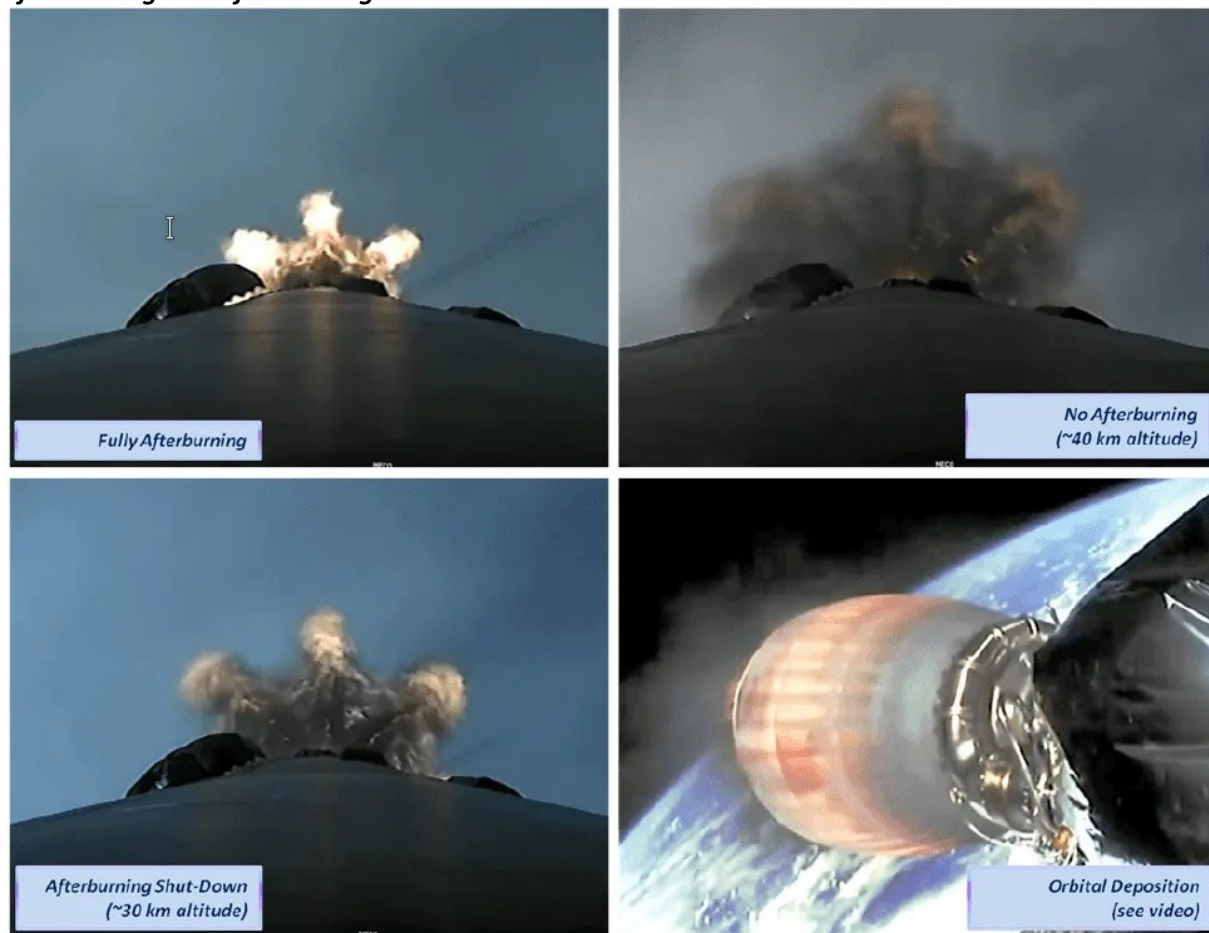### *Afterburning and Afterburning Shutdown*

Figure 5. Progression of afterburning (**AB**) shutdown with increasing altitude, showing the *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**]
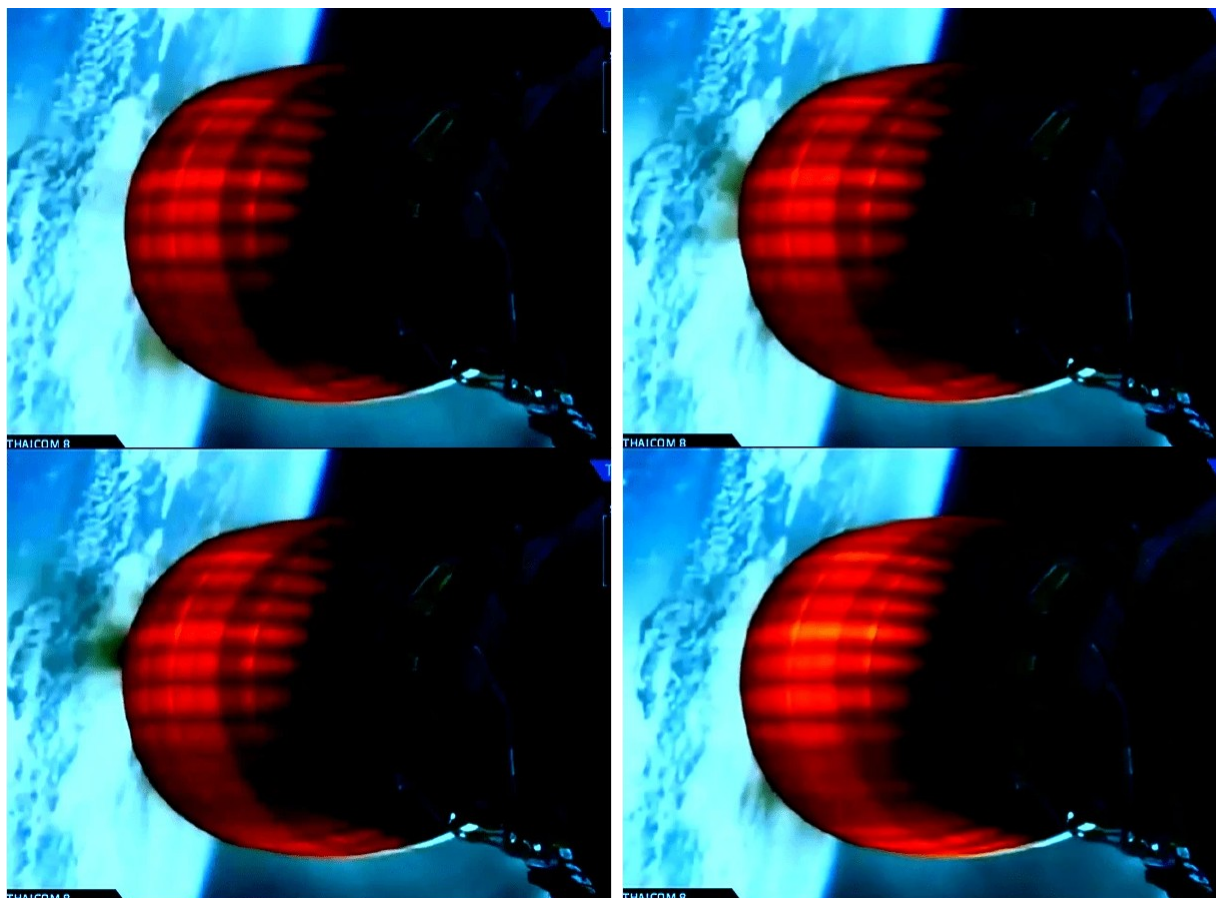
Figure 6. Video excerpts of PAH/tar deposition during orbital-transfer burn. Note: the nozzle is highly *underexpanded* in vacuum, so the film-coolant PAH is observed to spread out *laterally* from the nozzle and is therefore much more tenuous to observe in vacuum, but is nonetheless clearly observable in video. [**ref. D**] *https://www.essoar.org/cms/asset/2b4b21ae-3752-470c-91f4-a85f87b5a92c/out_2.mp4*

A typical launch vehicle trajectory involves quickly vertically traversing the troposphere, then pitching over to accelerate toward orbit. Shortly after launch, the rocket enters the stratosphere and pitches over to fly in an increasingly parallel aspect 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 ~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 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. 200 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 currently unknown if any public documents exist which present valid information on the presence of the soot building-block species (i.e., benzene, PAH, etc.) in the Merlin and Hanwha engine exhausts. Hence, the estimates provided above, 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 objective third-parties. Crucially, these measurements must corroborate, extend, and refine the known data and science presented and referenced herein.

NON-GIGO CALCULATIONS

Pyrolysis continually creates aromatics and PAH, the building blocks of carbon solids (i.e., cokes & soot)
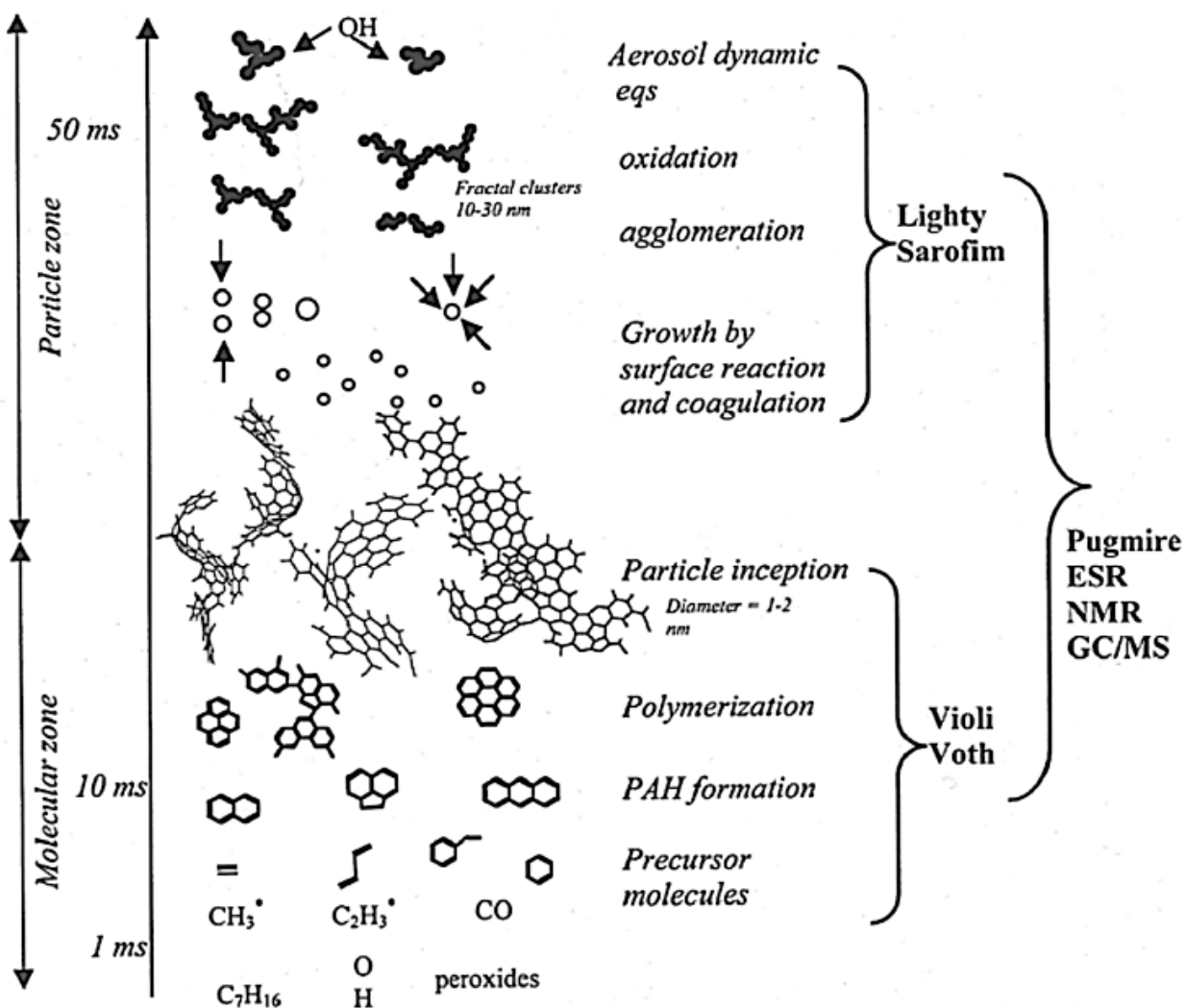
Figure 6. PAH molecules are continually created during fuel-rich, sooty combustion, and grow by cracking and oligomerization reactions (via condensation polymerization) to form larger PAH – which is the thermodynamically favored sp2 carbon hybridization state under combustion conditions – and which are in turn the building blocks of 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.*

Current computer combustion models still cannot fully 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 new low-Performance spacelaunch vehicles. This is fundamental because 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 data beyond the capabilities of current models – that is, very large PAH species.

Non-GIGO Model Estimates. Although non-GIGO rocket engine calculations are difficult under the multiphase combustion conditions present in rocket chambers, it is nonetheless relatively easy to form a good estimate of the typical and expected chemical species products in targeted regions of rocket engine combustion. 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 non-GIGO geometries.[18,21] To obtain high-accuracy data on the PAH burdens, careful measurements must 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 the required measurements and estimated 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 Figure 7, up to the limits of the available chemical mechanisms.[18] These calculations are relatively straightforward using high quality solvers in a simple flow condition.[36] These calculations show large yields of benzene, even exceeding the yield of acetylene which is a known significant rocket plume constituent.[40] Substantial yields of PAH, consistent with the required building blocks of easily-observed soot/PM2.5 yields (Figures 2 and 4) are present.
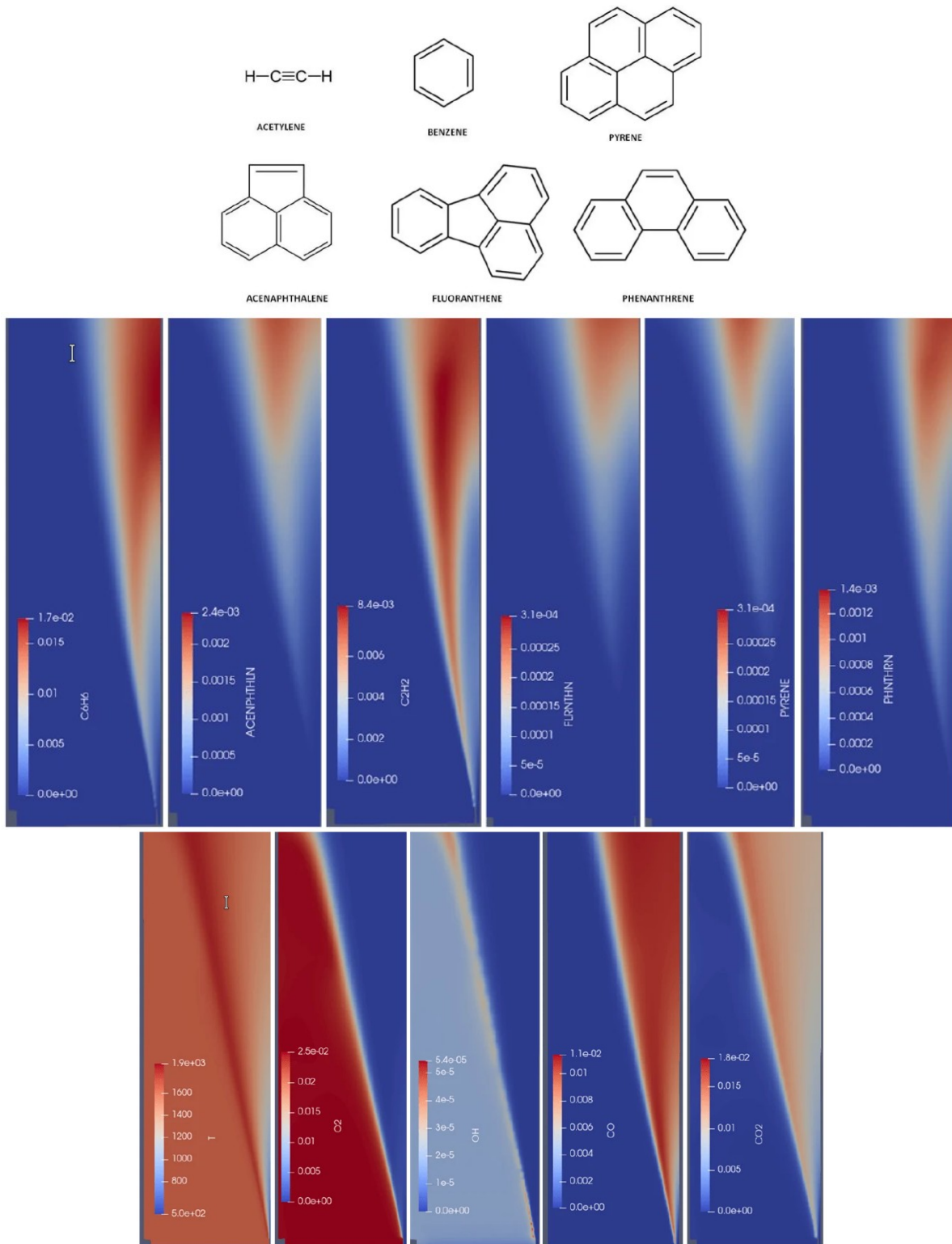
Figure 7. Some results of a non-GIGO calculation: An oxygen-starved hydrocarbon combustion case using the 155-species chemistry model [18], shown in Figure 1 and representing high-efficiency combustion of fully-gasified fuel. Even under these highly-efficient combustion conditions, significant quantities of benzene and PAH are generated. (P = 100 atm.; yields are largely 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 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 is consistent with the fact that the sp2 hybridized carbon contained in these species is the kinetically- and thermodynamically-preferred state of the hydrocarbon recombination products of oxygen-starved combustion, and are thus important targets for precise measurement and documentation for scientists. (It is again noted that benzene yield dominates acetylene, the latter a known major 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 engineers as well as climate and atmospheric scientists.

SUMMARY/CONCLUSIONS

❖ **High molecular weight hydrocarbons – e.g., aromatics, PAH, tars – are present when soot is formed in fuel-rich LOX/RP-1 combustion chambers, gas generators and film coolants, and yields may exceed soot yields**

❖ **GIGO combustion calculations conceal the presence of PAH**

❖ **Non-GIGO chemical calculations reproduce the observed presence of benzene and PAH**

❖ **Brilliant afterburning in a hydrocarbon rocket plume is diagnostic for the presence of large quantities of PAH in the plume**

❖ **For these types of engines, PAH is deposited directly in the upper atmosphere and on the launch stand due to the cessation/inhibition of afterburning**

❖ **Reaction rates between ozone/UV and larger PAH species appear to be low, suggesting these species may persist and accumulate in the upper atmosphere – this requires further study**

❖ **The current lack of valid, relevant documentation on 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 atmospheric scientists***

❖ **Careful measurements by trusted agents are indicated to document the yields of these important species with improved accuracy as the Anthropocene deepens, in order to facilitate understanding of upper atmospheric impacts.**

➢ ***New measurements must corroborate and refine the known combustion science referenced and presented herein.***

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