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

PattiMichelle Sheaffer[1]

[1]The Aerospace Corp. (ret.)

February 6, 2023

Abstract

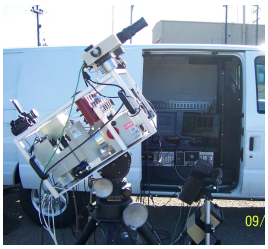
Although adequately detailed kerosene chemical-combustion Arrhenius reaction-rate suites were not readily available for combustion modeling until ca. the 1990's (e.g., Marinov [1998]), it was already known from mass-spectrometer measurements during the early Apollo era that fuel-rich liquid oxygen + 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 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 also need larger fuels loads to achieve the same launched 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.

1.00

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

PattiMichelle Sheaffer

USAF/SMC; Aerospace Corp. (retired)


PRESENTED AT:

INTRODUCTION

- New, low-Performance engines (Hanwah, SpaceX) source significant lower- and upper-atmospheric PAH and related pollutant species
- Chemistry known since the 1960's
- Upper atmosphere impacts not yet assessed
- GIGO invalidates existing Assessments and estimates of species deposition
- Significant contributions from film-coolants and open-cycle gas generators are ignored

Environmental and Atmospheric scientists are misled 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]

CHEMISTRY/MODELING 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 the last five decades[9-12]. The newer, complex technical advances have been primarily confined to the engineering of preburner (i.e., high-efficiency) engines.[16,35] On the other hand, recent cost-priority, privately-funded open-cycle rocket engines are decidedly low-tech and low-Performance (Figure 2, and see "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 climate cycles. This has not been discussed, primarily because published computer models of engine exhaust yields support only GIGO calculations which ignore PAH.* (*e.g., ref. [1-3,6-8]*) *The resulting lack of valid information presents a unique problem for upper-atmosphere chemists, physicists, engineers, and regulators. This document is intended to review known, crucial scientific information to fill the information vacuum.*

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 - even very complex reaction sets [3] have been used, but have nonetheless ignored PAH. The known PAH yields [4] of rocket combustion are thus left out of EPA documents and the recent scientific and technical literature, with the result of misleading scientists, engineers, and regulators about PAH in these new engines.

Example calculation of valid PAH estimate results are shown in the section: non-GIGO Calculations

---

Rocket engine *Performance* is tied to combustion chamber PAH yields in low-Performance LOX/RP-1 engines by incomplete fuel combustion (*low combustion efficiency*) and resulting nozzle inefficiency, which, in turn, requires higher fuel loads and hence larger atmospheric deposition of PAH and related species by the launch vehicle. High-energy injector atomization of low vapor pressure fuels (RP-1) is an enabling technology for increasing the efficiency internal combustion engines but is not possible with the pintle injector designs in these engines. 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 efficiency due to large fuel droplet average diameter (slow fuel evaporation/gasification rates).[14,15] This results in hot, high-*Cp* (*i.e., polyatomic hydrocarbons as PAH*) combustion-products entering the rocket nozzle, lowering the nozzle exaust velocity (*c*), and therefore Performance via, [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 thermodynamically requires a very low Cp in the $\boldsymbol{\eta}$ *equation - that is, monatomic and diatomic species. The presence of polyatomic species such as PAH rapidly lowers nozzle efficiency by decreasing the numerical value of the exponent of the (Pe/Pc) term.[11,12]*

Open-Cycle Gas Generators (OCGG) typically consume on the order of 1%-10% of total vehicle fuels 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*).

For film-coolants, due to temperatures and oxygen-starvation present (after the film-coolants have absorbed their latent heats and evaporated) the chemistry is similar, and 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 component of radial flame-front travel, pintle designs typically require extra "head-end' combustion-chamber film coolants to prevent excessive thrust chamber wall erosion.[10,15,16]

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, *but GIGO calculations present in public documents on these engines not include these reactions: The computer models are typically instructed not to include PAH*. [1-3,6-8,18,21] The results deprive atmospheric scientists and regulators of needed, critical data. Examples of public documents seen to date which present GIGO results are shown in the Tables. Typically it is asserted in the text of these documents that "soot is also present," ignoring the well-understood facts of soot-formation chemistry (see boxes ***Hydrocarbon Sources and ***non-GIGO Calculations***).[6,7]

Examples of GIGO calculations taken from existing engine documents are shown in the Tables.

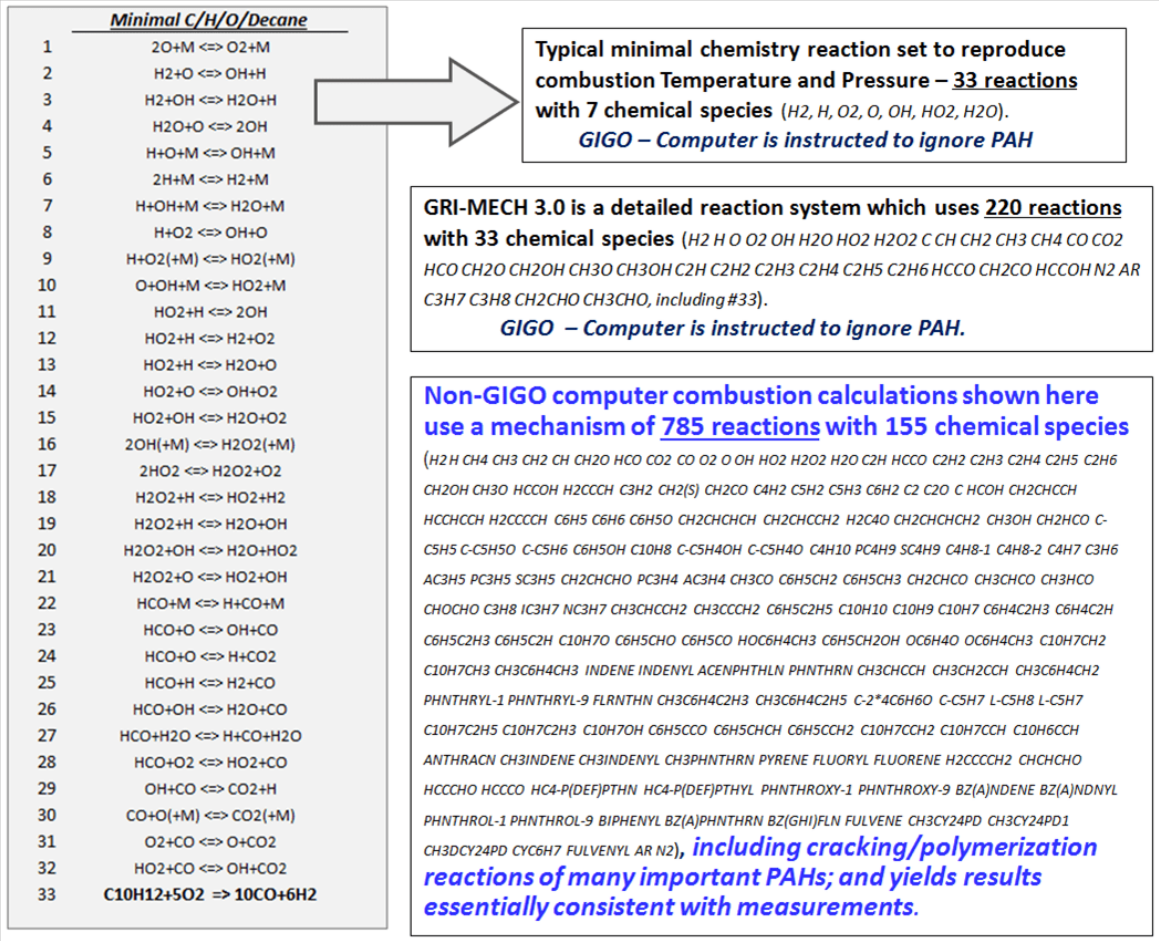


Figure 1. Three progressively larger computer combustion models. All will reproduce engine pressure and temperature, but only the largest model (155 species) is non-GIGO for PAH species. (Pseudo-reactions such as #33 allow RP-1 to be added without PAH in GIGO reaction models.) However, even some very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

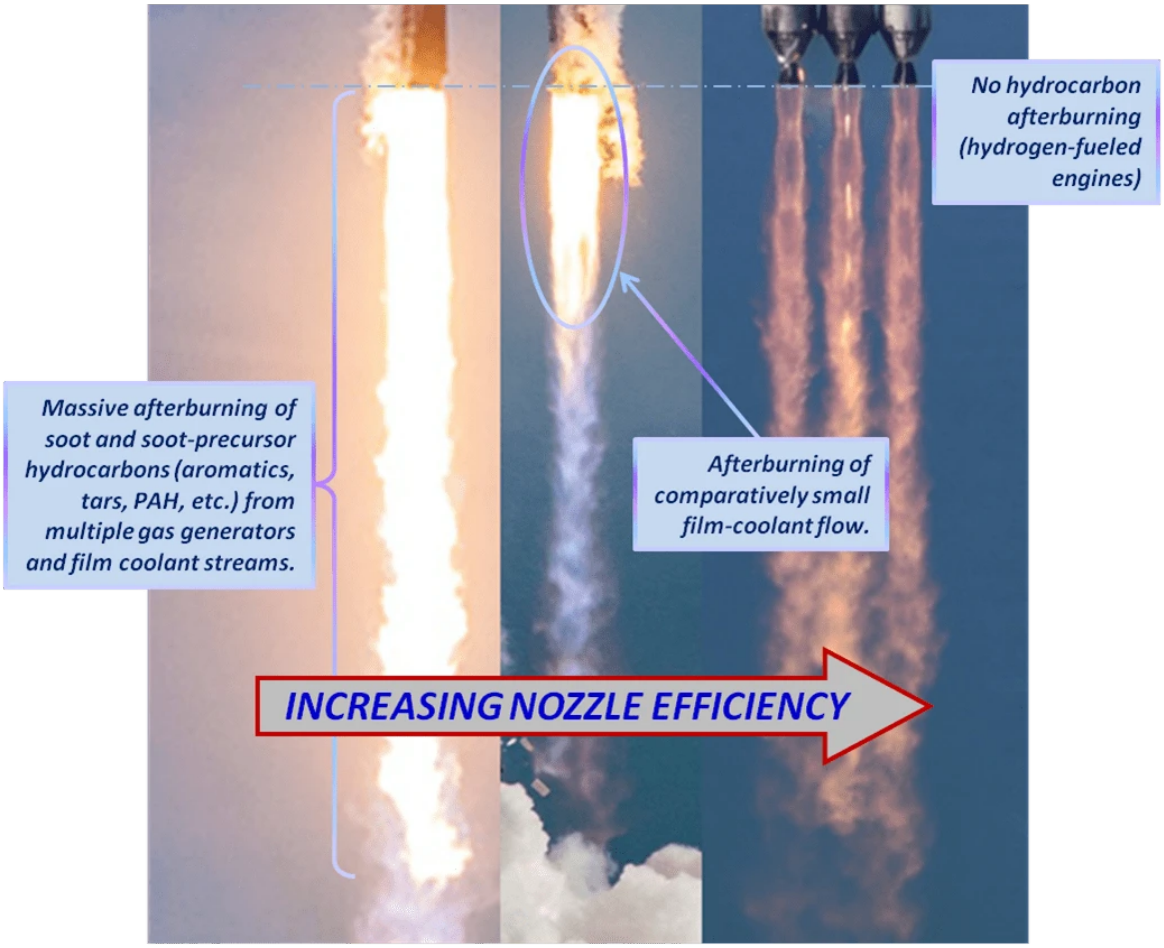


Figure 2. Comparison of three similarly-sized launch vehicles. ***Left****: brilliant visible afterburning indicates large amounts of PAH/tars/soot discarded by engine with predicted low-Performance (LOX/RP-1);* ***Middle****: minimal visible afterburning indicates high-Performance and primarily low 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]*

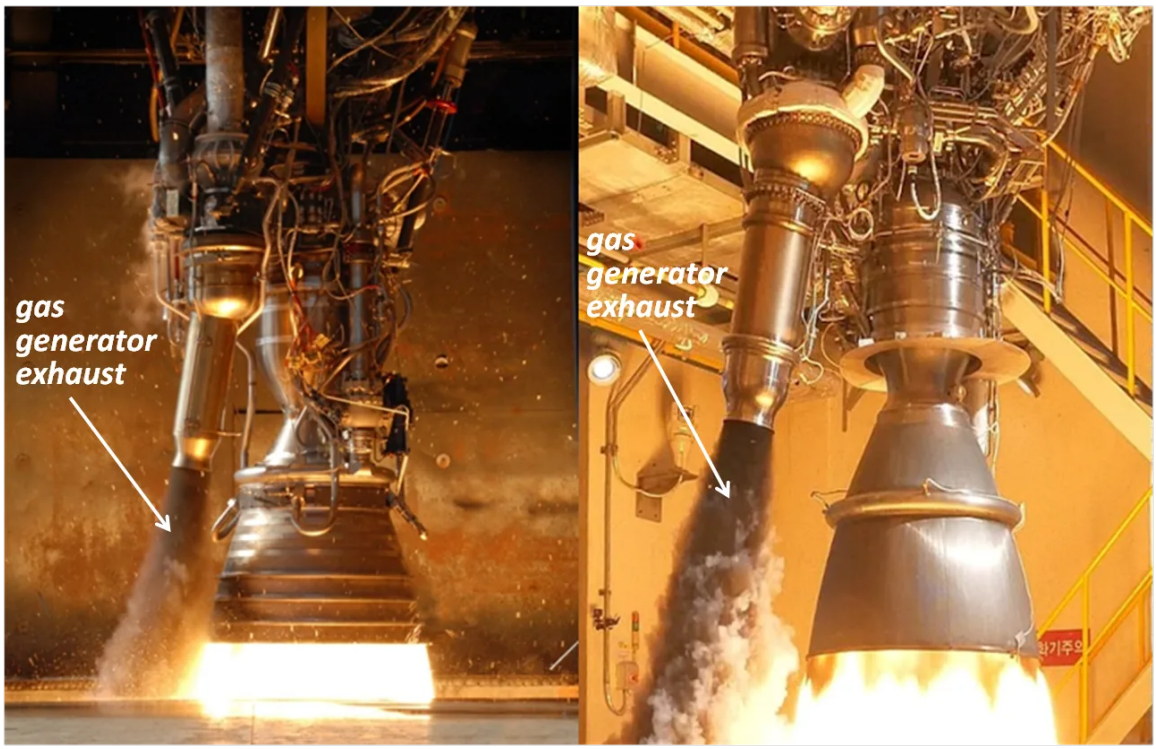


Figure 3. SpaceX (left) and Hanwha (right) gas generator exhaust and afterburning film-coolants (brilliant engine-nozzle exhausts), viewed on the test-stand, above the water deluge which protects the "flame bucket" but also suppresses PAH afterburning. [ref. B]

Figure 4. Static firing - deluge water below vehicle prevents facility damage by the hot plume - **but** *deluge water also shuts-down tropospheric afterburning of the soot, aromatics, PAH, tars, etc. created by the gas generator and film coolant flows, which then form the large dark cloud (PM2.5, PAH, aromatics, etc., left). [ref. C]*

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) 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] *However - note that these species are* always *present in "sooty" internal combustion engine exhausts unless specifically removed, by, for example, catalytic converters or specially-designed afterburners.*

In the absence of the **tropospheric plume afterburning** shown in Figure 2, these species are directly deposited into the

atmosphere (Figures 3 - 5). This deposition occurs during pre-launch water deluge of the flame bucket *and at high altitudes*, after afterburning shuts down. *Of particular concern for this work is upper-atmosphere (above ~30km) deposition of reactive stable free-radicals, and PAH (Figures 5 and 6), which have unknown impacts at high altitudes, and have yet to be recognized or assessed*.[29-31] 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 an 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. Additionally, UV-B photodegradation of the larger PAH molecules [37,38] 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

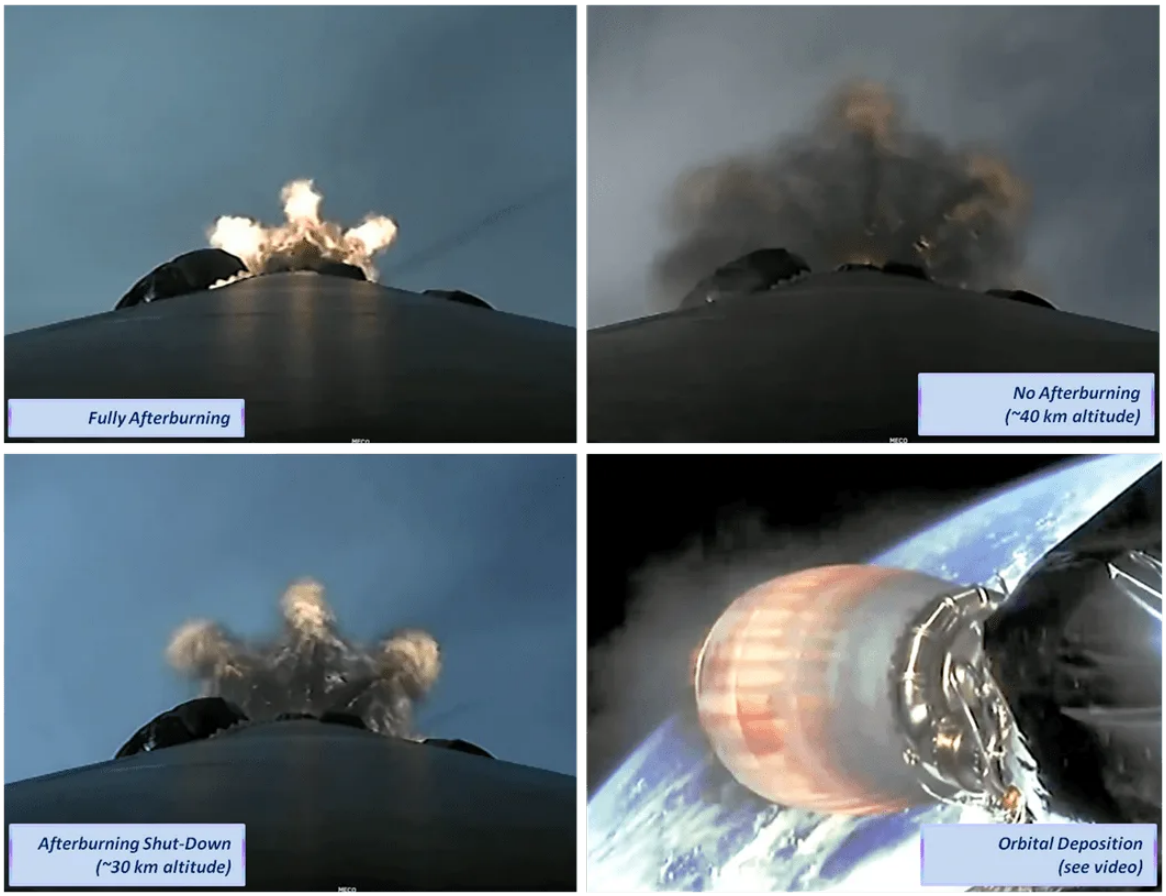


Figure 5. Progression of afterburning (AB) shutdown with increasing altitude showing transition to direct atmospheric and orbital PAH/tar deposition. ***Upper left*** *- AB shutdown beginning;* ***Lower left*** *- nearly complete AB shutdown;* ***Upper right*** *- complete AB shutdown;* ***Lower right*** *- 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

Figure 6. PAH/tar deposition during orbital-transfer burn. Note: nozzle is highly underexpanded in vacuum, so PAH is observed to spread out laterally from the nozzle. [ref. D]

[Fig. 6 ((video)) (http://video: https://pattimichelle.com/OUT_lfp1ym.mp4)]

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. The **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.[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

Combustion chamber pyrolysis continually creates aromatics and PAH - the building blocks of stable carbon solids

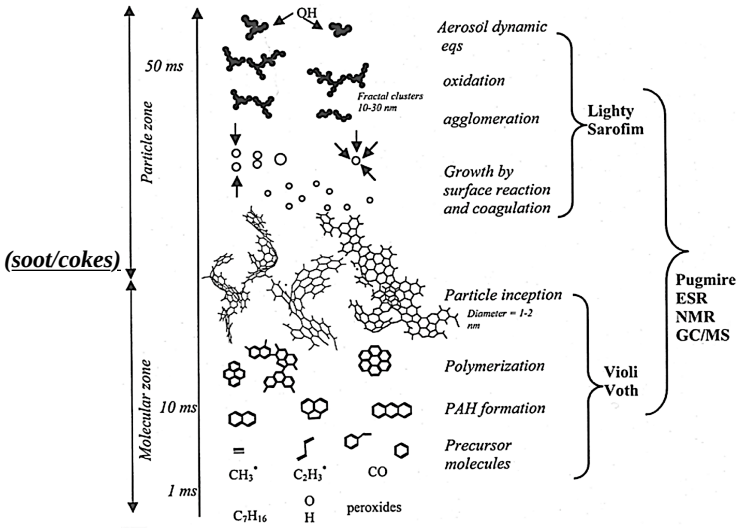


Figure 6. PAH molecules are continually created during sooty combustion, and grow by cracking and oligomerization reactions (via condensation polymerization) to form larger PAH - the thermodynamically favored form of carbon - which are in turn the building blocks of the soot particles. [18,21,30] These 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 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. (see, for example, [1] and [2], as well as other Environmental Assessment/Impact documents, such as [5-7]) ***The primary importance of non-GIGO PAH calculations is to reveal the significant presence of PAH and related species which are routinely deposited into the atmosphere, and show the need for full quantification.*** *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 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.

Accurate, non-GIGO calculations reveal the typical combustion products obtained, as shown in Figure 7. These calculations are relatively straightforward using high quality solvers, such as OpenFOAM, even in a simple flow condition.[36] They typically 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). All of these are absent from available documentation.[1-3,5-7]

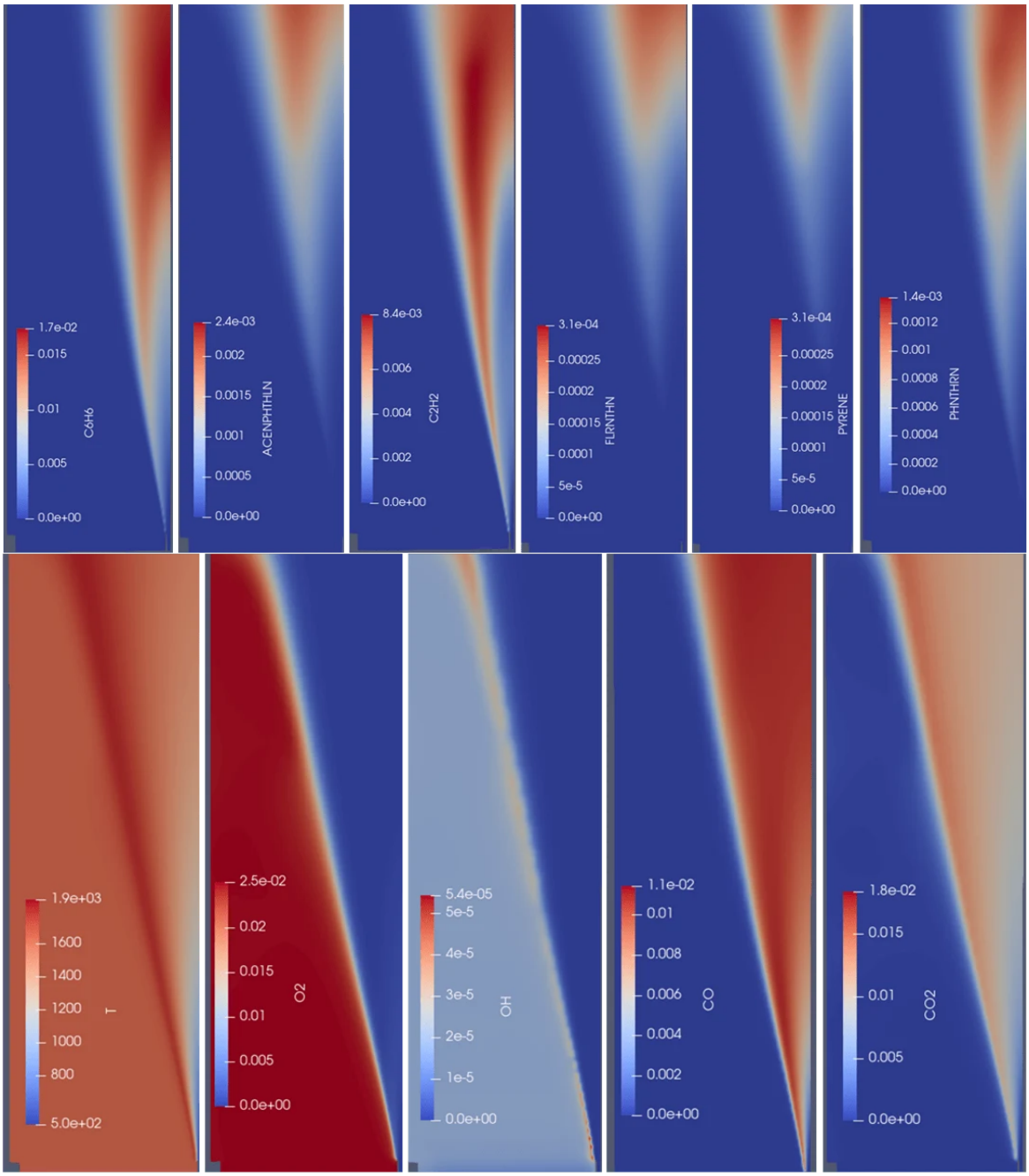


Figure 7. Non-GIGO calculation. Oxygen-starved hydrocarbon combustion using 155-species chemistry model shown in Figure 1, representing high-efficiency combustion of fully-gasified fuel. Significant quantities of benzene and PAH are nonetheless generated. (P = 100 atm.; yields are insensitive to perturbations in temperature and pressure. Low combustion efficiency is expected to generate significantly more PAH, tars, and soot than are generated by this fully-gasified model. Nonetheless, non-GIGO models are consistent with known measurements and clearly demonstrate 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, atmospheric scientists and regulators.

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 persist and 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.*

DISCLOSURES

No conflict of interest or funding disclosures.

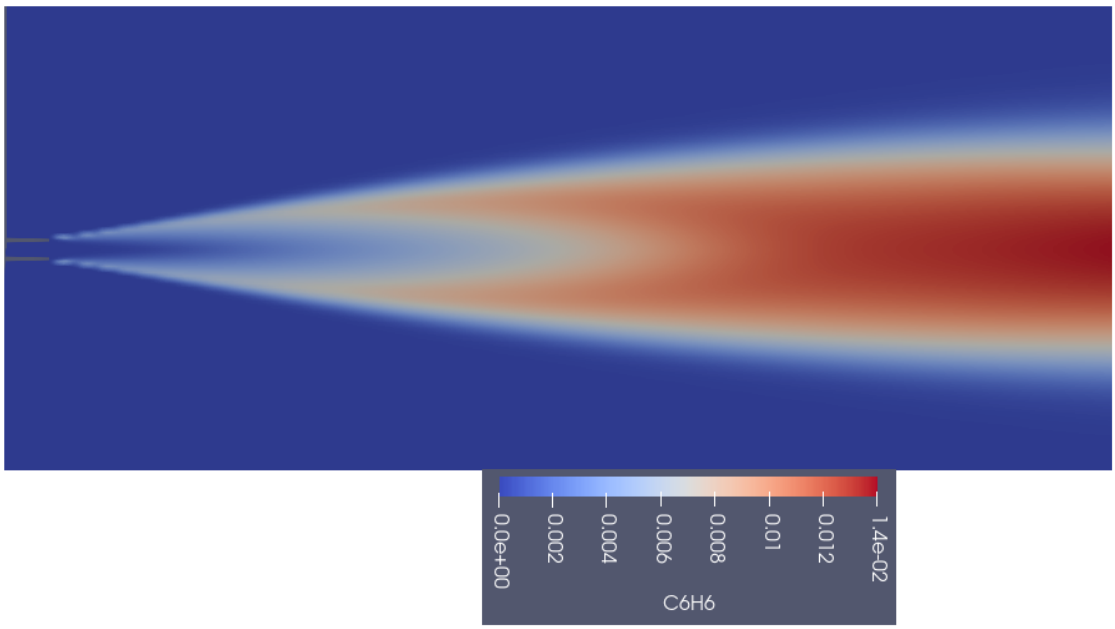
AUTHOR INFORMATION

Patricia Michelle Sheaffer is a retired Level-II chemical physicist and materials scientist for the US Air Force Space and Missile Systems Center under contract with The Aerospace Corporation at the Ivan A. Getting Research Laboratories, having a 36 year career in multidisciplinary science there. Her research included designing laboratory and remote sensing equipment to research the chemical species present in rocket jet-engine plumes, including operating a 4,000 LOX/hydrocarbon rocket engine. Her early career involved research in carbon pyrolysis materials science, in both the gas and condensed phases. Her work also includes studying the impacts of anthropogenic emissions on climate change via global climate models.

Her multidisciplinary research also included an important contribution to the NASA DebriSat Hypervelocity Impact experiment including designing and building Debris-LV - which simulated one of the 100+ launch vehicle upper stages still on orbit. In this experiment, she discovered the process which creates highly-destructive "space flakes" which result from hypervelocity impacts against metallic vehicles, such as upper stages. Public outreach included presentation on a BBC science special on orbital debris: https://www.bbc.co.uk/programmes/p02yvrtq

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 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 also need larger fuels loads to achieve the same launched 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.



(https://agu.confex.com/data/abstract/agu/fm21/6/9/Paper_792196_abstract_749941_0.png)

REFERENCES

1. *Sierra Eng. Report #2003-001*, prepared for T. Mueller (SpaceX) [2003]

2. Environmental Assessment – SpaceX Falcon 1 and 9 Launch Programs at CCAFS, Nov. 2007, prepared by Aerostar Environmental Services, Inc. Orlando, FL [2007] Appendix D, "Air Data"

3. Song and Song, Advances in Mechanical Engineering, Vol. 9(7) 1–11 DOI: 10.1177/1687814017711388 [2017]

4. Thomson, J. D., *A Study of Radiative Properties and Composition of the Turbine Exhaust Products of F-1 Engine*, Rocketdyne Report R-6743, 20 Sept., 1966

5. Supplemental Environmental Assessment SpaceX Falcon9 V1.1 vehicle launch at CCAFS August 2013, Section 4.5 Air Quality, Table 4-2

6. *SPACEX FALCON PROGRAM ENVIRONMENTAL ASSESSMENT, U.S. ARMY SPACE AND MISSILE DEFENSE COMMAND/U.S. ARMY FORCES STRATEGIC COMMAND,* P.O. Box 1500, Huntsville, AL 35807-3801, [2007] pp 7 "*Since the Falcon launch vehicles use LOX and kerosene propellants, the emission products (carbon monoxide, carbon dioxide, hydrogen, and water) lack hazardous materials and would consist primarily of steam.*"

7. *Falcon Heavy Vehicle Operations and Launch at SLC-40 on CCAFS, Environmental Assessment prepared for 45th Space Wing*, Patric AFB, FL, by Nelson Engineering Co., Merritt Island, FL [2013] pp 71 "B*ecause these launch vehicles use only LOX and RP-1 propellants, the exhaust cloud would consist of steam and minor amounts of hydrocarbon combustion products.*"

8. JANNAF Interagency Propulsion Committee, ***Propulsion Computer Codes (https://www.jannaf.org/node/35)***, https://www.jannaf.org/products/codes, retrieved Nov. 2021

9. EPG-Space 4,000 lbf Thrust LOX/hydrocarbon Rocket Engine [2010] https://youtu.be/wHLvlm72cMc

10. Huezel and Hwang, *The Design of Liquid Propellant Rocket Engines*, https://ntrs.nasa.gov/api/citations/19710019929/downloads/19710019929.pdf [1967]

11. Clark, J. D., https://archive.org/details/ignition_201612, Rutgers U. Press [1972]

12. Altman, et al., *Liquid Propellant Rockets*, Princeton Aeronaut. (Sect.B. eq. 3-1a) [1960]

13. Finlayson-Pitts/Pitts, *Atmospheric Chemistry*, J. Wiley & Sons [1987]

14. *see, for example*: Fraser, et al., *Droplet Formation from Liquid Sheets*, A.I.Ch.E Journal, Vol. 8, No. 5 [1962]

15. Yang, et al., Liquid Thrust Rocket Chambers, AIAA Vol. 200 [2004] ISBN 1-56347-223-6

16. Sutton, *A History of Liquid Propellant Rocket Engines*, AIAA Press, ISBN-10: 1563476495, ISBN-13: 978-1563476495 [2005] - - Sutton/Biblarz, *Rocket Propulsion Elements*, John Wiley & Sons, ISBN-10: 1118753658 ISBN-13: 978-1118753651 [2017]

17. Aerospace Corp., Technical Operating Report TOR-2016-01560 [2016] The Aerospace Corp., El Segundo, CA, SMC - USAF Space Command, Contract FA8802-14-C-001

18. Marinov, et al., *Aromatic and Polycyclic Aromatic Hydrocarbon Formation...*, Combustion and Flame, Volume 114, Issues 1–2 [1998]

19. Aerospace Corp. Report No. TOR-2016-02213, [2016] The Aerospace Corp., El Segundo, CA, SMC - USAF Space Command, Contract FA8802-14-C-001

20. Aerospace Corp. Report No. TOR-2016-02636, [2016] The Aerospace Corp., El Segundo, CA, SMC - USAF Space Command, Contract FA8802-14-C-001

21. Richter, et al., *Detailed modeling of PAH and soot formation...*, Proceedings of the Combustion Institute 30 (2005) 1397–1405

22. Van Camp, Van Damme, and Froment, *Thermal Cracking of Kerosine*, Ind. Eng. Chem. Process Des. Dev. 1984, 23, 1, 155–162 [1984]

https://doi.org/10.1021/i200024a026 (https://doi.org/10.1021/i200024a026)

23. Cristadoroa, et ql., Structural Ccharacterization of the Oligomeric Constituents of Petroleum Pitches, Carbon, Volume 47, Issue 10 [2009] https://doi.org/10.1016/j.carbon.2009.04.027 (https://doi.org/10.1016/j.carbon.2009.04.027)

24. Thies, *Fractionation and Characterization of Carbonaceous Pitch Oligomers: Understanding the Building Blocks for Carbon Materials*, Polymer Precursor-Derived Carbon, Chapter 5, ACS Symposium SeriesVol. 1173 ISBN13: 9780841229662eISBN: 9780841229679 [2014]

25. Lewis/Singer, *Further Electron Spin Resonance Studies of the Pyrolysis of Aromatic Hydrocarbons*, Carbon Volume 5, Issue 4 [1967]

26. Singer/Lewis, *Applications of ESR to Carbonaceous Materials*, Applied Spectroscopy Vol. 36, Issue 1, pp. 52-57 [1982]

27. Livingston, et al., ESR of Transient Radicals During Pyrolysis, J. Am. Chem. Soc. 1979, 101, 15, 4312–4319 [1979] https://doi.org/10.1021/ja00509a044

28. Yamada, et al., An Electron Spin Resonance Study of the Carbonization of Acenaphthylene, Bulletin of the Chemical Society of Japan 46.11 [1973]

29. Ross/Mills/Toohey, *Potential Climate Impact of Black Carbon Emitted by Rockets*, Geophys. Res. Lett., Vol. 37, Issue 24, https://doi.org/10.1029/2010GL044548 [2010] https://doi.org/10.1029/2010GL044548 (https://doi.org/10.1029/2010GL044548)

30. Pugmire, R. J., Yan, S., Ma, Z., Solum, M. S., Jiang, Y. J., Eddings, E. G., et al., The Soot Formation Process. Department of Chemical & Fuels Engineering, Department of Chemistry, University of Utah. Retrieved from http://acerc.byu.edu/News/Conference/2003/Presentations/Pugmire.pdf

31. Ross, *Comparative Analysis of Climate Forcing and Ozone Depletion Caused by Emissions from Two Different Suborbital Launch Systems*, AIAA 2020-4056 Session: Remote Sensing, Weather, Climate and Related Technology Issues, https://doi.org/10.2514/6.2020-4056 [2020]

32. *see, for example*: Calhoon, W.H., *Evaluation of Afterburning Cessation Mechanisms in Fuel-Rich Rocket Exhaust*, 34th AIAA/ASME/SAE/ASEE Joint Prop. Conf., Cleveland, OH [1998]

33. Sheaffer, Maghsoudy-Louyeh, Zittel, Conway, and Dinkleman, *The Impacts of Soot and Soot Precursors in LOX/Hydrocarbon Plumes*, The Aerospace Corporation, El Segundo, CA 90245, AIAA-2017 ITAR Restricted Session [2017]

34. http://www.b14643.de/Spacerockets_2/United_States_1/Falcon-9/Merlin/index.htm *retrieved Nov. 2021*

35. Biggs, *SSME; the First Ten Years*, http://www.enginehistory.org/Rockets/SSME/SSME1.pdf retrieved Nov. 2021 [1989]

36. Weller, H. G., Tabor, G., Jasak, H., Fureby, C., *A Tensorial Approach to Computational Continuum Mechanics Using Object-Oriented Techniques*, COMPUTERS IN PHYSICS, VOL. 12, NO. 6 [1998] http://dx.doi.org/10.1063/1.168744 https://openfoam.org/ (http://dx.doi.org/10.1063/1.168744) https://openfoamwiki.net/index.php/Main_Page

37. Nadal, et al., *Influence of UV-B Radiation and Temperature on Photodegradation of PAHs*, Journal of Atmospheric Chemistry volume 55, pages 241–252 [2006]

38. NIST Chemical Kinetics Database, Standard Reference Database 17, Version 7.0 (Web Version), Release 1.6.8 Data Version 2015.09 https://kinetics.nist.gov/kinetics/index.jsp

---------- Internet-Available Image/Movie Sources ----------

A. https://upload.wikimedia.org/wikipedia/commons/thumb/4/41/NROL-71_Wide_%28cropped_alt%29.jpg/390px-NROL-71_Wide_%28cropped_alt%29.jpg
https://scontent-sjc3-1.xx.fbcdn.net/v/t1.6435-9/115578714_1655222707982950_6086744189271211423_n.jpg?_nc_cat=109&ccb=1-5&_nc_sid=730e14&_nc_ohc=wmwO7N60cJEAX-7xjUP&_nc_ht=scontent-sjc3-1.xx&oh=acad15949cbad6a4fc96bcd92db40ff9&oe=61C7BD05
https://24liveblog.tradingfront.cn/event/2359719590513108760/20200518010912_831118.jpeg

B. https://www.google.com/imgres?imgurl=https://archive.vn/Ebu70/3c701235b9dcc1ca81be70e71233f360315713db/scr.png&imgrefurl=https:

//www.orbiter-forum.com/threads/the-south-korean-space-program-thread.32354/&h=768&w=1024&tbnid=j9f1swDQDqp1HM&tbnh=194&tbnw=259&usg=AI4_-kQdauQ2f9wKcfSmuoYLa7pTjiFrHw&vet=1&docid=mAo-5pIpv5eKUM&itg=1&hl=en
https://upload.wikimedia.org/wikipedia/commons/4/44/SpaceX_Testing_Merlin_1D_Engine_In_Texas.jpg

C. https://www.youtube.com/watch?v=SZQY902xQcw
https://youtu.be/SZQY902xQcw *retrieved [2016]*

D. https://www.youtube.com/watch?v=Lenl7QYT8o8 https://youtu.be/Lenl7QYT8o8 *retrieved [2016]*
https://www.youtube.com/watch?v=_S99962hthY https://youtu.be/_S99962hthY *retrieved [2021]*