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Perspective

Clean combustion: Chemistry and diagnostics for a systems approach in transportation and energy conversion

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This perspective article intends to show opportunities and provide food for discussion regarding some specific developments in the field of combustion. It reflects the author's views and makes no claim to be exhaustive. It is hoped that aspects and problems addressed in this article will stimulate intensified communication and collaboration toward more efficient processes and reduced combustion emissions. In the author's view, combustion science as a multidisciplinary field connecting chemistry, fluid dynamics, metrology, and high-performance computing with a variety of practical applications in energy, transportation, and industrial production is well positioned to help developing technologies for an integrated, sustainable future energy system.

1. Combustion's role? Some reflections on the status quo

Emissions from combustion processes have a large influence on air quality, environment, climate, and health [1,2]. They cause concerns about severe air pollution in cities and contributions to anthropogenic carbon dioxide [3,4]. Today, more than 80% of global primary energy consumption relies on fossil energy carriers [1,2,5]. High-energy-density liquid fuels are indispensable for transportation, with trends noted toward bringing in fuels of non-fossil origin. A fully renewable energy supply based on wind, water, and sun is suggested as technically viable [6] with the largest concern being temporal fluctuations. Also, research toward harvesting and storing renewable energy with chemistry is accelerating [7]. Nevertheless, global CO_2 emission has risen from about 22 Gt in 1990 to 36 Gt in 2015 [3]. With increasing global energy demand, anthropogenic fossil-fuel contributions to CO_2 emissions (of near 94% in 2015 [3]) are not expected to change rapidly [1,2,4]. Carbon dioxide, however, is only one pertinent issue regarding combustion emissions. Black carbon, for example, – particulate matter or soot from open burning and controlled combustion – is associated with significant climate impact [8] and reported to be among the most prominent global health hazard factors [9–12], contributing notably to risks such as diseases of the respiratory and cardiovascular systems.

It is too short a perspective, although quite common in public debate, to target only combustion emissions from ground transportation: Combustion is not synonymous with combustion engine. Introducing enough electric cars, so one rationale, would supersede combustion and eliminate its emissions. This perception, however, neglects not only that electric propulsion is not yet independent of fossil energy [13], but disregards also the multitude of combustion processes and devices in use, including aero-engines, stationary gas turbines and boilers, waste incinerators, household appliances, and industrial furnaces and processes for the production of glass, ceramics, steel, cement, and other major products. The CO_2 burden from cement making alone was approximately 2 Gt in 2015 or 5.6% of global CO_2 emissions [3]. Approximately half of this amount was generated in China [3], where further significant CO_2 contributions for some high-temperature industrial products (metals, plate glass, and chemicals) were recently evaluated [14]. A wide spectrum of such thermochemical energy conversion processes must thus be targeted with the aim of enhancing efficiency and reducing emissions while bringing in renewable energy sources, a large-scale transformation that will take enormous time and effort. Promising concepts and strategies will need interdisciplinary knowledge on fuels, energy conversion processes, systems, and infrastructure – knowledge in part available from combustion scientists and engineers.

- Combustion processes dominate today's energy and transportation systems to an extent that substantial changes will take time, especially with growing population and energy demands.
- Combustion science and technology can assist in the transformation of energy conversion systems toward efficient processes with low emissions.

2. Good fuels? Informed choices toward a future fuel portfolio

Future transportation fuels are discussed with today's liquid petroleum-based fuels as the benchmark. The question of tomorrow's best fuels, however, is not settled, and solutions will depend on many factors, including scientific understanding of their use and impact, energy density, toxicity, water solubility, emissions, availability, economic viability, adaptation to existing infrastructure, ease of end use, and a viable lifecycle analysis, with carbon neutrality and sustainability as key factors. Biomass-based fuels beyond first generation are often considered promising [15–18], but challenges include sufficiency of resources, large-scale energy-efficient, economic production, and the availability of “green” hydrogen for deoxygenation of feedstock with too high oxygen content.

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Improvements in process technology and integration are reported [17,18], with research needs including, for example, higher efficiency for catalytic conversions. Biomass-based fuel additives offer chances to tailor fuel properties, but complications with such multi-component mixtures can arise for *e.g.*, mixture formation, ignition timing, and reaction chemistry. Fuel design from biomass should strive for suitable propulsion and emission performance of the fuel–engine system and then develop a viable and sustainable fuel production strategy [19].

Some fossil fuel options may continue to be relevant both in the short-term as well as in the more distant future, where their use will depend on the potential of re-activating CO_2. Currently, a cleaner fuel of choice for a range of applications might be natural gas (compressed or liquefied to simplify transportation). The fuel portfolio can also include more unconventional fossil sources such as shale gas and, potentially, methane hydrate. However, leakage of the potent greenhouse gas methane could lead to adverse effects that should be considered. With a future perspective of carbon capture [20] and recycling, *i.e.* using the waste product CO_2 as a renewable C1 building block in organic synthesis [21], liquid compounds can be accessed such as methanol, usable directly or upgradable to further useful chemicals such as dimethyl ether (DME), ethene, and fuels with a longer carbon chain [22]. As further synthetic fuel candidates, oxymethylene ethers (OMEs) receive attention [23,24] that are accessible from methanol and formaldehyde [24,25], itself a C1 energy carrier. Also, ammonia is being discussed as an energy vector [26]. Solar and wind power will be important for producing electricity renewably, but owed to their intermittent nature, energy storage issues will need attention: The current storage capacity, almost exclusively from pump-storage hydroelectricity, is estimated to be about 1% of the energy consumed worldwide [13], not suggesting, however, that long-term buffering could be achieved with this capacity. It could be extended beneficially by using liquid hydrogen-rich compounds – fuels.

It should not be overlooked that aviation fuels must adapt to specific criteria, including foremost high energy density. Also, combustion for stationary purposes, from household heating to gas-fired turbines for power generation, might consume similar energy as in the transportation sector. Here the challenge for new fuels lies in the hundreds of millions of consumers, with a vast diversity of combustion equipment that is adapted to a specific range of fuels, *i.e.* natural gases. Drastic changes in fuel properties, for example by introducing hydrogen, imply large-scale changes in equipment. Fuel-flexible devices would thus be a useful option.

Which fuel, for which purpose is a complex issue, and predictions are not easy. Ultimately, fuels should have a neutral carbon footprint and be derived from a source in infinite supply. To reduce particle formation, options may include compounds with only C1 chains such as OMEs, especially when they are liquid, not toxic, and can be sustainably produced. Process integration providing multiple conversion options between heat, electric power, chemical storage, and transportation fuels will be advisable [27,28]. Thermochemical energy conversion processes are valuable building blocks for future energy systems, where combustion specifically provides links between high-energy-density liquid carriers from different sources and thermal energy at the needed high temperature and pressure levels. Inherent complexity and yet unclear challenges regarding suitable interfaces of future energy conversion systems demand an interdisciplinary scientific approach. Revealing the physics and chemistry controlling these processes for real fuels and pertinent thermodynamic conditions can rely prominently on expertise gained from combustion.

- Whilst future's "best" fuel is not yet decided, high-energy-density liquid compounds are always useful for energy conversion and storage.
- Since change of fuels can entail large changes in infrastructure for production, delivery, handling, and conversion, such processes are best optimized jointly, considering a viable lifecycle analysis.

3. Cleaning up? Research needs for emission reduction and aftertreatment

Combustion emissions are composed of a diverse spectrum of chemical species of which only some are regulated so far [29]. These include gaseous species such as oxides of carbon, nitrogen, and sulfur, for which measurement procedures are available to control compliance with regulations. The chemical composition of emissions depends on both, fuel and combustion process. Understanding and controlling particulate matter or soot emission from combustion counts among the most pressing issues [9,11,30]. In terms of disability-adjusted life years (DALYs), ambient particulate matter (PM) pollution is estimated for 2015 to exhibit up to 16% influence on tracheal, bronchial, and lung cancer in almost all regions of Africa and Southeast Asia, and household air pollution from solid fuel burning a contribution of 4–8% on all health risks in most of the same regions [10]. A crucially important target is therefore to accurately assess black carbon impacts on the global atmospheric radiative energy balance, on human health, and air quality [30]. Further research to systematically understand the relationships between fuel, combustion process, soot formation mechanism, resulting particle properties, as well as soot emission and oxidation characteristics is highly needed [31,32]. Relevant details are lacking in the understanding of influences on soot mass and number concentration, size distribution, morphology, optical properties, chemical composition, active surface area, and reactivity [33]. Such properties must be reliably determined, especially for nanometer-size particles, requiring advances in measurement techniques. Furthermore, secondary organic aerosol (SOA), organic matter that forms in the atmosphere by oxidation from gas-phase precursors including aromatics and larger alkanes, may be a potentially underestimated combustion-related emission [29]. Research focusing on such aspects is the more acute since particulates from combustion are one of the best targets to alleviate climate forcing impacts and human health risks simultaneously.

Achieving lower emission levels, for existing and novel boundary conditions regarding fuel choice and combustion process, to meet tighter regulations or to reduce yet unregulated or "new" pollutants, will require a dedicated interdisciplinary approach. Developing lower-emission combustion systems demands improved scientific understanding of fuel- and condition-specific pollutant formation mechanisms, including the complex pathways of soot formation and oxidation. Development of new combustion concepts could be favorably coupled with research on suitable aftertreatment systems, involving the catalysis and materials science communities. Scientific evidence to inform policymakers, and affordable aftertreatment systems potentially suitable for retrofits might assist in speedy introduction of abatement measures in regions where this may be most needed. Similarly, efficient and affordable, potentially portable sensors must be available for local emission control. Reducing combustion emissions must focus on many applications, including ground and air transportation [29,34] but should not overlook the impact of low-tech devices such as rural cookstoves [35]. A wide research field thus continues to demand attention.

- Cleaner combustion concepts will profit from fundamental understanding and joint design of fuels, combustion and aftertreatment systems.
- Affordable technology, potentially for retrofits, is the key for fast improvements.

4. Too many reactions? Chemistry requirements to predict performance of real-world applications

With high-power computing, predictive simulation of combustion systems, including appropriate chemical reaction mechanisms, has become feasible. It plays an increasing role in systems design and optimization. Combustion models should describe the interplay of all relevant physical and chemical processes in necessary detail, such as mixture formation, turbulent motion, chemical reaction, and emission. The multi-scale four-dimensional (4D) space–time behavior of the system must be suitably captured across scales, from macroscopic dimensions to the molecular level. Modeling the fluid dynamics of a practical system is a challenge of its own, and further complexity arises from flow field–chemistry interaction. To keep a simulation manageable, it is often necessary to describe the relevant fluid mechanics aspects across scales with suitably reduced chemistry, or to choose idealized combustion situations with respect to the flow field so that the desired chemical details can be included. The focus here will be only on the gas-phase reactions that determine ignition, energy release, and pollutant formation. In this context it should be appreciated that chemical mechanisms for realistic transportation fuels can feature hundreds of species and thousands of reactions [36]. Additional complexity arises in the low-temperature oxidation regime [37] or when pollutant chemistry, especially polycyclic aromatic hydrocarbon (PAH) and particle formation is targeted. Mechanism construction can follow systematic rate rules for relevant reaction classes [38,39] and include valuable information from theory [40]. The most extensive knowledge on reaction pathways and emissions to date is probably available for methane. While scientific model development strives for comprehensive fundamental information, engineers need usable and compact models for practical purposes. Conceptually, a different perspective is thus assumed in "scientific" modeling approaches from "engineering" ones.

Any model application demands a good definition of the problem. Usable engineering models should be as large as needed and derived in a systematic fashion from a scientific one, concentrating on the relevant fundamental backbone and leaving out all insignificant detail for the application in question. Systematic model reduction and uncertainty analysis regarding large chemical mechanisms is an active research field [41–43]. Automated *ab initio* calculations of many relevant parameters could play an increasing role in mechanism development. However, even a "scientific" model will never include all possible pathways, and large systems are often heavily under-determined. High value must thus be placed on the quest for "correct" thermodynamics, transport, and kinetics data, not only for the comprehensive model, but also as a prerequisite for meaningful model reduction. Decisive progress toward highest quality should rely on collegial collaboration between modelers, experimentalists, and theoreticians. Beyond the existing fragmented knowledge, a common fundamental model and an extensive, reliable, well-documented database for model validation would be valuable. This basis could be continuously extended by collaborative efforts, to include a larger regime of relevant and challenging conditions, *e.g.*, reactions at high pressure or at surfaces and walls. It must be noted that currently there are too many combustion models and individual mechanisms, often reporting marginal changes to fit specific datasets. Exponential growth of incremental changes will not offer guidance, neither for research, nor for practitioners. Disagreement of model and experiment is a chance to improve, not discard, mechanisms. Systematic multi-scale modeling approaches based on molecular-level understanding cannot only benefit the combustion field itself but also assist research or application more generally in energy conversion and process engineering. For such purposes, generic modules would be favorable that can be used in various systems to describe particular conversion processes or interfaces.

- Combustion models, designed to predict multi-scale complex systems behavior in space and time, could favorably be transferred to other problems, especially with a modular approach.
- Compact practical models for specific real-world applications can be systematically obtained from fundamental ones that should be suitably extended and validated by collaborative effort.

5. Beyond 4D? Diagnostics targets, tools, and expectations

Understanding combustion processes would not be possible without diagnostics. Direct inspection of combustion systems provides important information on phenomena or properties such as spray injection, evaporation, mixing, ignition, flame speed, reactivity, and product and pollutant formation. Combustion diagnostics gives access to quantities such as temperature, pressure, species concentration, and flow velocity as well as to their spatial distribution and development in time. Multiple techniques have been employed in laboratory and practical systems [44–46], often using variants and combinations of optical diagnostics and mass spectrometry. Advantages for the community are presented by the existence of some well-defined standard burner configurations as well as advanced method developments at highly instrumented user facilities [47–50]. Specific diagnostic challenges include high pressures, high temperatures, high time resolution, large gradients, and high accuracy. Rapid time series, multi-quantity, and multi-dimensional measurements up to 4D [51] have become feasible. Combustion diagnostics is successfully applied in challenging environments such as in engines [52] or in sprays at high pressures [53,54], revealing supercritical phase formation and needs to study new mixing phenomena [55]. Interesting chemistry has been discovered with previously undetected compounds [56], in low-temperature oxidation [57,58], and high-mass soot precursor formation [59]. However, advanced and costly combinations of techniques needed to study the interplay of all pertinent variables in a practical combustion environment, in 4D and across scales, are available only in few dedicated centers. These diagnostics capabilities might be valuably complemented with well-maintained, open-access-to-all test beds defining "standard" conditions, such as generic engines or combustors that could serve as validation targets for the community. Model development and critical inspection by experiment could go hand in hand using the results and insights from such collaborative approaches and shared facilities.

From an application engineering perspective, the wish list for combustion diagnostics includes low-cost sensors for real-time process monitoring and control. These should permit optimization of the system's performance, *e.g.*, to decrease pollutant emissions, maximize combustion efficiency, or counteract instabilities. Crucial to the success in developing such sensors is a clear understanding of the exact requirements – which quantity, how fast, how accurately must be measured? As part of the design process, scientific progress may still be needed to understand diagnostics challenges and implications in relevant domains, *e.g.*, at high pressures, in dense sprays [60], particle-laden flows, fast mixing areas, at phase boundaries, near surfaces and in hard-to-access or otherwise difficult environments. Sensor design should thus profit from close interaction with combustion research and applications. It is obvious that the diagnostics approaches from combustion can be migrated to other domains, as demonstrated in catalysis [61] and syngas conversion [62]. Further targets may include, but not be limited to, atmospheric and environmental processes, materials synthesis [63], and process engineering and control. Meanwhile, combustion diagnostics should continue to remain open for advances from other fields, such as from biological imaging, surface and interface science techniques, and chemically sensitive microscopy.

- Combustion diagnostics serves multiple purposes: it provides fundamental insight relying on cutting-edge advances in methods and instruments, it serves to examine and validate models, and it can enable real-time process optimization and control, with needs for reliable, fast and inexpensive sensors.
- The multitude of diagnostics techniques and approaches can be beneficially applied to questions beyond combustion.

6. Useful combustion knowledge? Improving systems

Combustion science and engineering offer knowledge and technology to understand, handle, model, design, and optimize complex multi-scale systems of reactive fluids. The field makes use of an established and continuously extended toolbox, in which those aspects discussed here – fundamental physical chemistry, multiple diagnostics techniques, mechanism development and simulation, systematic model reduction and uncertainty analysis, are only some ingredients. Similar methodological approaches may be in part useful in other domains such as in materials synthesis and process technology, or in atmospheric science and astrochemistry.

Not only tools from combustion can be shared, but intrinsic combustion knowledge is indispensable for applications that require integration of high-energy-density carriers, fuel and energy flexibility, and process control. Future energy systems will use a variety of energy carriers such as fossil, biomass-derived, and synthetic fuels, for energy conversion and efficient storage beyond batteries [64]. Such compounds will be available in varying amounts depending on time and location. Combustion processes, integrated into the energy system, can convert these energy carriers to release energy on demand for different purposes. System components such as combustion engines, chemical reactors, fuel cells, stationary gas turbines, and others, of different sizes, must be integrated, and complex and highly dynamic system behaviors may be expected. Characterization methods, process models, prediction tools, and hardware and software interfaces must be developed to assess and control integration and timing, efficiencies of different components, and energy and materials fluxes, including pollutants. Coupling fluctuating energy fluxes that are characteristic for many renewable sources into the system requires high flexibility of the various thermo-chemical conversion processes. Conversion options include polygeneration [27,28], *e.g.*, by using a single device that is capable to supply energy in different forms, as heat, mechanical energy, or chemicals. Interesting strategies include bidirectional chemical reaction processes that are reversible by moderate changes of temperature or pressure. The endothermic reaction can be performed with energy supply of the system, and consumers will utilize the exothermic step that could be combustion. For such concepts, process models must become available that can describe and adapt the dynamic response of each component to changes in operating conditions, ensuring optimum efficiency, minimum emissions, and safe operation, requiring real-time control and optimization. Existing combustion knowledge can deliver valuable input and be extended to assist in solving such problems.

- Transportation and energy needs can be quite different from a global or regional perspective, but with a common denominator of striving for sustainable processes, renewable resources, and low emissions.
- Progress toward this goal can build upon combustion knowledge, especially for integration and optimization of energy conversion systems with high-density energy carriers.

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