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"Combustion Chemistry and the Carbon Neutral Future"

By Kenneth Brezinsky, Department of Mechanical and Industrial Engineering, University of Illinois, Chicago, IL, USA, Elsevier, USA, 2023, 639 pp, ISBN: 978-0-323-99213-8, £124.00

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NON-PEER REVIEWED FEATURE

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Introduction

"Combustion Chemistry and the Carbon Neutral Future: What Will the Next 25 Years of Research Require?" is part of the Developments in Physical & Theoretical Chemistry series by Elsevier. This book is composed of 17 chapters and provides readers with a variety of topics ranging from alternative fuels such as natural gas, hydrogen, ammonia and biofuels, to advances in combustion chemistry to influence emissions composition and utilisation for functional materials, as well as diagnosing and monitoring aspects. One would appreciate the technical detail and benefit from the plethora of references shared in each chapter, which points readers to the relevant information to delve deeper into each subject. Here is a synopsis of each chapter.

Reducing Emissions

The chapter by S. L. Kokjohn and A. Babu starts by stating internal combustion engines (ICE) fuelled by liquid hydrocarbons are estimated to remain a dominant form of carrier energy for the foreseeable future. Significantly higher energy density of these fuels compared to other sources such as batteries explains the continued interest. A system level assessment of vehicle weight and practicality of charging needed to handle various drive cycles is demonstrated for electrochemical storage as a disadvantage. In contrast, well-to-wheels CO_2 (a greenhouse gas) emissions of vehicles fuelled with conventional energy sources such as diesel fuel is demonstrated to be higher than a battery electric vehicle. The discussion then moves to the use of alternative fuels such as renewable diesel (soybean) or corn ethanol which might serve as a medium that could substantially reduce CO_2 emissions. Use of these alternative fuels may not be as straightforward for low-load operating conditions, for which the authors provide a few approaches from combustion mechanics and chemistry to make it work.

F. Carbone, K. Gleason and A. Gomez tackle the question whether soot research will remain relevant and a priority in the coming decades. Countries are heading towards carbon neutrality later this century; however, the authors assert that reliance upon fossil fuels will remain high, even through 2050. As a result, Carbone *et al*. suggest that there will remain a strong need for improved understanding of soot nucleation, which will become even more important as soot mass is reduced. They describe several diagnostic techniques available for intrusive sampling as well as several optical techniques, discussing some of the benefits and challenges of each. Carbone *et al.* compare several flame types, comparing options against their flame selection criteria. The authors conclude by suggesting the use of partially premixed laminar flames to simplify the study of soot formation, including the nucleation step. Additionally, they mention that the information needed requires the use of intrusive sampling techniques. Further, computational modelling will be key to a better understanding of soot nucleation.

Alternative Fuels

J. M. Mehta and K. Brezinsky draw attention to natural gas as an alternative fuel that could reduce the carbon footprint of transport; however, they highlight that the combustion chemistry of this fuel is not fully understood partly due to assumption of methane chemistry not being able to address the source-by-source compositional differences in absence of mandated standards, unlike other fuels. Contrasting conventional subsurface natural gas, biogas (requiring removal of CO_2) is demonstrated as a more sustainable supply of methane, also referred to as synthetic natural gas (SNG). The authors also touch briefly on a novel method to generate SNG *via* methanation (i.e. hydrogen is made to react with CO_2 to form SNG and water). Ongoing kinetic model development to understand parameters influencing purity of natural gas synthesis as well as cleaner engine combustion strategies are covered, recognising the gaps in current understanding that remain in the way of efficient utilisation of this fuel.

Charles Westbrook discusses sustainable bio-oxygenate fuels as potential alternative sources of energy for the combustion of hydrocarbon fuels. The author discusses the use of liquid biofuel candidates as a replacement for petroleum fuels, focusing on the combustion process for biofuels. Westbrook also discusses the use of alcohols such as methanol, ethanol and butyl alcohol, focusing on the impact of oxygen in the alcohol structure and its impact on soot formation in the combustion process. This has been incorporated into kinetic models for the combustion process. This information is also applied to kinetic modelling of methyl esters within biodiesel fuel. These detailed kinetic models will be very helpful in understanding and predicting the use of oxygenated fuels in the combustion process.

A. Viggiano and V. Magi summarise the use of syngas and its surrogates as promising fuels for engines. This literature review begins with an overview of syngas and how its chemical–physical properties and energy content can be beneficial to combustion. The authors contrast several different methods of syngas use in engines: dual-fuel (diesel-syngas) compression ignition (CI) engines, homogenous charge spark ignition (HCSI) engines, and direct injection spark ignition (DISI) engines. They summarise the impacts on performance, efficiency and emissions for dual-fuel, as well as syngas-fuelled HCSI and DISI engines. The authors suggest that, with proper tuning of engine operating parameters, greenhouse gases and unburned hydrocarbon emissions could be reduced with syngas. There remain challenges associated with syngas use in dual fuel engines (for example fuel supply lines), HCSI engines (such as reduced power) and DISI engines (for example, lack of understanding of optimal injection and injection timings and duration). The authors conclude that syngas technology has reached a level of maturity which would now allow optimisation to be carried out, to further drive research and development efforts in this area.

J. M. Mehta, F. N. Egolfopoulos and K. Brezinskya evaluate hydrogen as a zero-carbon fuel. Combustion (identified as a yet to be well-understood area) and fuel cell routes are explored with a relatively more feasible outlook than battery electrification would require. The authors touch on an interesting angle with the introduction of 'hythane' (a mixture of hydrogen and methane) that could help improve carbon neutrality. An overview of attempts to develop kinetic mechanisms to aid hydrogen engine development is provided. The authors conclude with an assessment of research areas to be focused on in the near future, including prevention of lubricant contamination, ways to improve heat recovery, definition of flame characteristics, prediction of hydrogen and oxygen kinetic mechanism, safe and practical hydrogen storage.

J. A. Mayoral Chavando *et al.* open their chapter with the various 'colours' of ammonia production depending on the source of hydrogen used in the synthesis process. They highlight its potential beyond its main use for fertilisers as an alternative fuel that might be more practical to store and has a well-established distribution network. Globally, it has not been produced or made commercially available uniformly across the seven continents. Due to its carbon-free combustion and significant energy density, compatibility of ammonia with existing CI or spark ignition (SI) engines are discussed for potential use in ICE. Even if it cannot be utilised as a complete switch, blending it with conventional hydrocarbon-based fuels is suggested as a good balance.

C. Saggese, T. Chatterjee and W. J. Pitz consider the status and needs of using small alcohols as biofuels. They discuss methanol, ethanol, propanols, butanols and pentanols in turn, summarising the current level of understanding for each as a fuel feedstock. In particular, the authors focus on the availability and maturity of kinetic models for each alcohol discussed. However, further development and refinement of kinetic models is needed for the various alcohols discussed. The authors suggest that, since there exists a vast amount of data for methanol and ethanol, the focus of future work should be on discrepancies between experimental and predicted results. Butanol models are progressing but need some mechanism validation efforts to be refined further. Other alcohols such as propanols and pentanols require much more effort on model development, refinement and validation.

M. Alam, K. Yehliu, C. Sun and A. L. Boehman provide a background on Fischer-Tropsch (FT) and other synthesised hydrocarbon fuels. The chapter begins by summarising how the FT process recycles CO_2 to diesel fuel. The authors compare the fuel properties between FT and conventional diesel fuels, then focus on the impacts of FT fuels on diesel engine performance and emissions. They discuss how the higher cetane number and lower aromatic content of FT fuel can impact diesel combustion. Specifically, changes in start of injection (SOI) can lead to reduced NOx formation, and reduction in aromatics and sulfur can lead to reductions in soot generation. Further, the use of FT fuels can also lead to reduced CO and THC emissions. The authors support these assertions *via* summarising a series of engine evaluations, where BP15 baseline fuel, FT fuel and B100 biodiesel were compared. Alum *et al.* also characterise the soot particles generated in these experiments, *via* Brunauer–Emmett–Teller, high-resolution transmission electron microscopy, thermogravimetric analysis, X-ray diffraction and X-ray photoelectron spectroscopy, indicating differences in the nanostructure of the soot, which would suggest higher reactivity of the soot.

Cleaner Combustion

Y. Ju and Z. Wang prepare a detailed literature review of various low-temperature combustion (LTC) concepts for advanced internal combustion engines. They point towards homogeneous charge CI, pre-mixed charge CI and reactivity-controlled CI engines as beneficial, as they simultaneously reduce NOx and soot emissions. The authors provide a background on cool and warm flames and discuss how the chemistry of these occur within LTC. They also discuss the various aspects of low-temperature flames comparing premixed and non-premixed cool and warm flames. Further, the authors summarised LTC chemistry at high pressure, discussing how temperature and pressure can dictate the reaction pathways during the LTC process. Ju and Wang close by emphasising that there are many opportunities for further understanding of combustion at extreme pressure and low temperature, as there are large discrepancies between experiments and model predictions at present.

R. K. Rahman, K. R. V. Manikantachari and S. S. Vasu provide a background summary of the use of supercritical CO_2 (sCO_2) combustion to simultaneously reduce greenhouse gas emissions as well as assist in supporting additional energy demands. The authors lay out the need for a better understanding of the fundamental properties of supercritical fluids. Rahman *et al.* discuss the equation of state model and its importance in simulating thermal, transport and kinetic properties during combustion. Additionally, the authors delve into the compressibility factor, specific heat capacity, viscosity and thermal conductivity predictions as they apply to sCO_2 combustion. The authors conclude that additional modelling and experimental validation is greatly needed as sCO_2 combustion at high temperatures and pressures is considered.

V. Palma, G. Iervolino and E. Meloni prepare a chapter on catalytic oxidation of soot generated by ICEs fuelled by liquid HCs. Conventionally, platinum group metal-based catalyst coatings are utilised on monolithic filter substrates for particulate matter abatement in automotive emissions. Non-platinum group metal-based catalysts such as metal oxides (for example ceria, perovskite, hydrotalcite) are highlighted for their potential to provide lower cost synthesisable alternatives. Coupling non-thermal plasma with the abovementioned catalysts appears to open a new avenue to explore to push the boundaries of soot oxidation to even lower temperatures.

A. Joshi *et al*. provide a literature review of the chemical looping combustion (CLC) concept. CLC is a technology which seeks to address CO_2 capture during electricity generation from hydrocarbons. This process generates a pure CO_2 stream as a byproduct over the reducer, which can be sent directly for sequestration. Joshi *et al.* focus their review on the oxygen carrier options, reactor design and process simulation and analysis for CLC as well as for chemical looping hydrogen generation.

Diagnostics and Sensors

K. Kohse-Höinghaus *et al.* cover an extensive set of niche applications for characterisation techniques aiding the carbon-neutral future. Some practical examples are the use of infrared spectroscopy to analyse sustainable aviation fuel to identify not only its physical-chemical properties but also its combustion chemistry and the detection of hydrogen *via* laser absorption spectroscopy. This chapter provides a multi-author perspective on the present use and future potential of various diagnostic techniques.

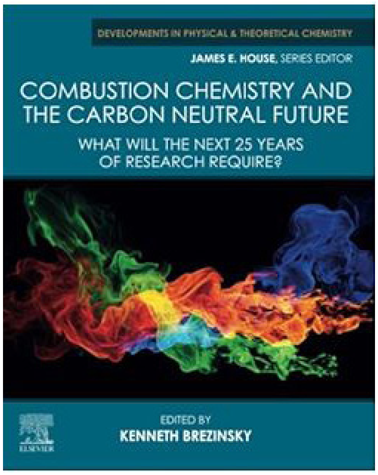
R. M. Spearrin and C. S. Goldenstein compare and contrast several different options for high-pressure diagnostic capability for high-efficiency combustion systems. The authors outline the challenges that exist with using current laser diagnostic methods in the high-pressure environment commonly found in modern internal combustion engines. Approaches to improve the capabilities of laser absorption spectroscopy are discussed; however, the authors also emphasise that further improvements are needed in the coming decades. Improved spectroscopic models are needed, as well as additional light source development for use in a high-pressure environment. New sensing strategies need to be developed to target specific molecules.

Bio-derived Fuels

In the penultimate chapter, M. Tomar *et al*. provide a lengthy review of bio-derived sustainable aviation fuel (BSAF) and its prospects. The authors begin the conversation by discussing the importance of BSAF amongst the various energy supply options due to cost, sustainability and emissions. Tomar *et al.* provide detailed reviews of the various production pathways and the feedstocks to be used in them. Additionally, the authors discuss the fuel properties of BSAF and the impacts on combustion chemistry. The authors present an in-depth discussion of current trends and future opportunities associated with BSAF, focusing on potential feedstocks, production pathway optimisation and fuel property impacts (for example additives, ignition quality). Tomar *et al.* wrap up their review by stressing the importance of BSAF as an aviation fuel in the global economy and its ability to help drive towards long-term net-zero carbon emission goals.

Carbon Utilisation

This final chapter by S. D. Tse and H. Hong covers a unique aspect of utilising emissions generated by combustion of fuels for synthesising novel materials. Flame synthesis could be used to produce structures such as carbon nanotubes or nanowires or cultivate graphene growth up to a few layers. These unique structures could be grown on metal or metal oxide substrates. Combustion chemistry could be engineered to influence the type of functional structures synthesised as well as the oxidation and reduction environment during the synthesis.



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The Reviewers

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