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Current Opinion in Chemical Engineering

Integrated design of renewable fuels and their production processes: recent advances and challenges

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Rational design of renewable fuels for advanced internal combustion engines aims at enabling CO_2-neutral road transportation with low pollutant emissions. It requires identifying species/mixtures with favorable fuel properties and designing sustainable production processes. We have discussed opportunities and challenges of integrating fuel and production process design in 2012 [9]. The present article reviews the progress made since then. Importantly, the field has moved from single-molecule fuel evaluation and mass-based production pathway screening to multi-species fuel design and energy-based pathway assessment. Integrated methods now simultaneously optimize fuel composition and production pathways. We discuss challenges in incorporating more detailed modeling and give perspectives on well-to-wheel optimization.

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Current Opinion in Chemical Engineering 2019, **27**:45–50

This review comes from a themed issue on **Frontiers of chemical engineering**

Edited by **Rafiqul Gani** and **Lei Zhang**

For a complete overview see the Issue and the Editorial

Available online 25th December 2019

https://doi.org/10.1016/j.coche.2019.11.001

Introduction

Road transportation accounts for a large share of global oil demand and thus significantly contributes to climate change. One option to defossilize road transport is the development of fuels from renewable energy sources and feedstocks, predominantly renewable electricity and biomass, for advanced internal combustion engine (ICE) concepts [1••].

To maximize combustion efficiency and minimize pollutant emissions, today's conventional fuels likely need to be replaced by (multi-species) fuels tailored to specific needs of future engine concepts [2,3]. Model-based fuel design, a special case of computer-aided molecular design (CAMD) [4], first translates engine requirements into a set of physico-chemical fuel properties and their corresponding target values or ranges, and then uses predictive property models to screen existing or designed molecular structures with regard to their suitability as a fuel (species) [2].

To achieve CO_2 neutrality, rationally designed fuels must also be efficiently produced from renewable resources. To this end, novel production routes need to be assessed and compared already at an early stage of process design. To determine the optimal pathway or process configuration based on economic and/or environmental objectives, in early-stage process design, mathematical programming is often applied to a network of possible reaction pathways or a superstructure of unit operations [5••].

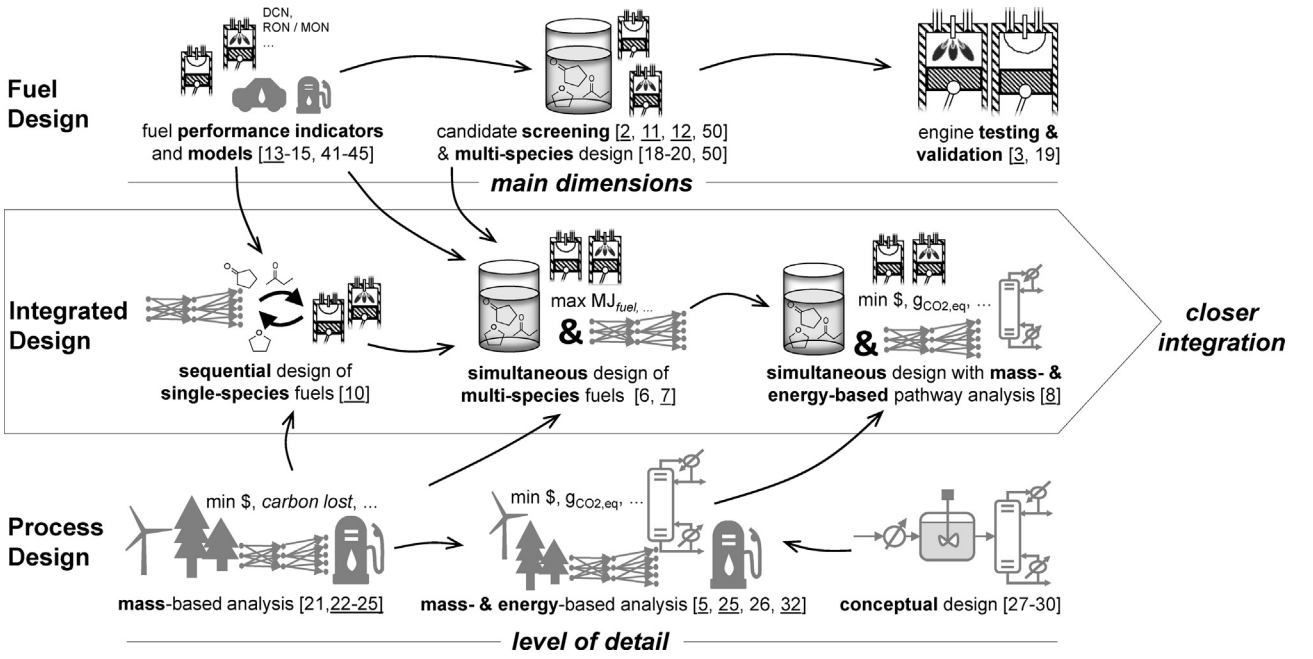
These two design problems, that is, fuel and process design, can be treated sequentially or iteratively in case of single-species fuels. However, if the objective is to produce a multi-species fuel from a common feedstock in a single plant, for example, a lignocellulosic biorefinery, fuel and process design are deeply interwoven, because the fuel's molecular composition becomes a design degree of freedom also in pathway optimization [6,7••]. Hence, to fully capture nonlinear co-production benefits occurring, for example, by efficiently combining fuel species produced from different biomass fractions, simultaneous process and fuel design is required [8••].

The present article shows the progress made since our 2012 article was published in this journal [9]. Back then, we laid out our vision of integrating model-based fuel and process design as part of fuel value chain optimization [9]. Since then, the field has advanced rapidly leading to fully integrated, simultaneous design methods. In this article, we review the most important advancements with some focus on our own contributions. We also discuss remaining challenges and give our perspectives on rational design of renewable fuels in a well-to-wheel approach.

Recent advances in model-based design of fuels and their production processes

Figure 1 gives an overview on how fuel, process, and integrated design methods have evolved towards

Figure 1



Overview of the advances in integrated production process and fuel design methods achieved by combining methods/aspects of process and fuel design. Process design methods differ in level of detail whereas fuel design methods differ with respect to the investigated dimension/research question. References to our contributions are underlined.

multi-species fuel design, energy-based pathway analysis, and simultaneous design methods in recent years. In the following, we first briefly review important advances in both fuel design and early-stage process design; we then assess the progress made in integrating the two fields to co-optimize fuel production and combustion.

Fuel design

Early fuel design approaches relied on evaluation of basic physico-chemical properties such as lower heating value or normal boiling point which are easy to predict from molecular structure [10–12]. Only recently models have advanced to the point where *in silico* combustion kinetics related performance indicators, for example, derived cetane number (DCN) [13,14], research and motor octane number [14,15], can be predicted for a broad range of oxygenated candidate structures (cf. upper left part of Figure 1).

Using such a novel DCN model [13], we have predicted, among other properties, the auto-ignition quality of computer-generated, bio-based molecular structures and identified a wide range of oxygenated fuel candidates for future spark-ignition (SI) and compression-ignition (CI) engines [2]. Such single-species fuel screenings have been advanced towards the design of multi-species fuels (cf. upper middle part of Figure 1). Specifically, methods from fuel blending in refineries [16] and computer-aided mixture design [17] have been successfully applied to the formulation of biofuel-gasoline blends [18], biofuel-diesel blends [19•], and diesel surrogate fuels [20]. First rationally designed fuels have recently been validated in experimental engine tests [3,19•] (cf. upper right part of Figure 1). In particular, we have collaborated with engine researchers to investigate the performance of tailor-made fuels in a highly-boosted single-cylinder research engine, realizing efficiency gains of up to 20% over conventional RON95 gasoline [3].

Early-stage process design

In the past, optimization-based screening methods for early-stage process design relied on material balances (cf. lower left part of Figure 1). Such pathway evaluation requires only basic reaction information, for example, stoichiometry and yield. Examples are given by the shortcut method of Bao *et al.* [21] and reaction network flux analysis (RNFA), a method proposed [22] and extended [23–25] by our group. Recently, more detailed process evaluation methods have been developed to analyze heat integration [26], complex reactions [27], separation networks [28], and comprehensive superstructures based on simulation results [29,30] (cf. lower right part of Figure 1). The latter, however, often require rather extensive data acquisition [5••]. To evaluate novel fuel production pathways on an intermediate level of detail, we have further developed RNFA into process network

flux analysis (PNFA) [5••] (cf. lower middle part of Figure 1). In addition to reaction pathways, PNFA also considers associated separations of solvents and (by-) products. To avoid the need for conceptual process design on a level of individual unit operations, the minimum energy demands of separations are estimated using thermodynamically-sound reduced-order separation models [31]. By extending the mass-based analysis of RNFA with energy-based assessment criteria, PNFA is capable of estimating process utility costs and emissions, while preserving a rapid screening character [5••,32•].

Renewable fuel production no longer targets biomass raw materials only but also considers renewable electricity and CO_2. Several recent studies have assessed the performance of electro-fuels (e-fuels) [33,34] and possible combination with biomass feedstocks [26,35]. In particular, we have recently adapted RNFA and PNFA to optimization-based bio-fuel and e-fuel assessment to analyze synergies of a combined use of multiple feedstocks [25].

Integrated fuel and production process design

Optimal renewable fuels do not only need to meet engine requirements but also need to be efficiently produced. To co-optimize aspects of both product and production process design, we had previously combined CAMD methods with RNFA-based pathway screening into an iterative design cycle for single-species fuels [10] (cf. left part of integrated design in Figure 1). Since then, Ng and co-workers have proposed a sequential method for *in silico* design of multi-species fuels and their associated production processes [36] and Huo *et al.* [37] have presented a 'fuel property first' approach that combines computer-aided fuel property estimation with experimental pathway development and experimental property validation. However, both methods [36,37] lack a feedback loop from process design back to fuel design.

To rigorously account for the interdependence of fuel composition and production pathway configuration in case of multi-species fuels, simultaneous product and pathway design methods have been developed that apply mass-based pathway evaluation [6,7••] (cf. middle part of integrated design in Figure 1). The method of Daoutidis and co-workers couples mass-based pathway analysis with linear mixing rules for the fuel properties to generate optimal gasoline-biofuel blends based on automatically-generated reaction networks [6]. Using thermodynamically-sound nonlinear property models, for example, a differential-algebraic model for the fuel distillation curve, we have later presented a method for simultaneous design of multi-species biofuels and corresponding production pathways [7••]. We have proposed a simultaneous design method [8••] that integrates the energy-based pathway evaluation of PNFA [5••] (cf. right part of integrated design in Figure 1). This method enables direct optimization of fuel production cost and global warming impact under explicit consideration of process energy demands. As the optimization problems resulting from simultaneous fuel and process design are computationally demanding, we have also proposed a sequential, iterative solution approach, which greatly reduces computational solving times, however, may deliver suboptimal designs that disregard some co-production benefits [8••].

Challenges and perspectives on integrated design of renewable fuels

Integrated design methods need to be improved regarding process modeling (cf. Section 'Process modeling') and fuel performance assessment (cf. Section 'Fuel performance assessment'). Moreover, future integrated design methods should aim at a holistic well-to-wheel optimization (cf. Section 'Well-to-wheel optimization/assessment') rather than considering product and process only.

Process modeling

Previous studies have demonstrated that for multi-species fuels co-production benefits can arise by efficiently combining fuel species produced from different biomass fractions [7••,8••]. In principle, similar benefits can be expected for any route yielding a mixture of useful species. Assessment of complex mixtures, however, is often hindered by imprecisely quantified molecular compositions. Even if the composition is known, a large number of species complicates estimation of minimal separation energy demands based on shortcut methods. We have therefore abstracted such mixtures by few representative molecules [25]. However, even for a moderate number of such pseudo-components, it can become too difficult to generate *a priori* meaningful options on how to split a given mixture. These cases will necessitate inclusion of separation energy demand as a function of mixture composition in optimization.

Another major concern relates to investment cost estimation in current early-stage process screenings. While PNFA [5••] uses an empirical function [38] that correlates process investment cost to the number of processing steps thus disregarding differing throughputs of pathways, our integrated design method [8••] uses an investment cost correlation based on the total process energy transfer duty [39]. Though the latter correlation has yielded decent investment cost estimates for ethanol and biodiesel biorefineries [40], energy transfer duties are not inherently linked to apparatus costs. Thus, for novel fuels, we expect the current investment cost correlations to be characterized by significant uncertainty. To improve early-stage cost estimation, a shortcut method for estimating investment costs of each processing step is required, especially for non-standard, for example, biochemical and electrochemical, pathways.

Fuel performance assessment

Engine-out pollutant emissions are typically addressed indirectly in fuel design by fuel oxygen content and basic physico-chemical fuel properties related to in-cylinder mixture formation such as viscosity and surface tension [2,7••,8••]. Group additivity models have been derived for the threshold sooting index (TSI) [41] and the yield sooting index (YSI) [42,43], two measures for the intrinsic sooting tendency of a fuel molecule. However, as both TSI and YSI are based on flame experiments, it is unclear to which degree they correlate with engine-out soot emissions of practical automotive engines. The oxidation potential number (OPN) has recently been proposed as a more advanced measure of a fuel's influence on the in-cylinder mixture formation process [44]. Its calculation, however, requires expensive computational fluid dynamic engine simulations that currently hinder integration into simultaneous process and fuel design.

In addition to mixture formation and combustion processes, fuel performance indicators must be defined for material compatibility and exhaust gas aftertreatment efficiency, two important aspects in practical application. To consider such novel indicators in fuel design, predictive structure-property relationships with broad applicability must be first derived.

More accurate mixture property models are required in multi-species fuel design. For instance, the research octane number (RON), which is strongly related to SI engine efficiency, may exhibit significant nonlinear blending effects [45]. Nevertheless, predictive mixture RON models are yet unavailable for the vast majority of interesting species.

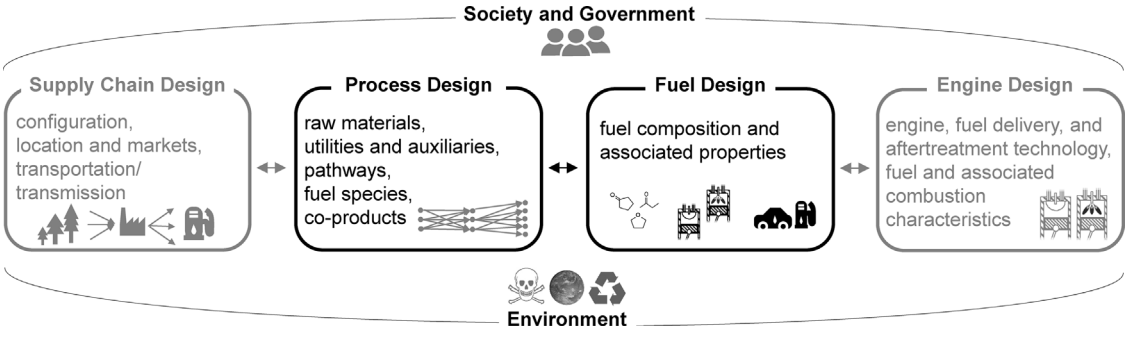
Well-to-wheel optimization/assessment

Figure 2 depicts our perspective on well-to-wheel assessment integrating fuel and process design with supply chain and engine design under consideration of the political, societal, and environmental framework conditions.

Linking process and supply chain design allows optimizing conversion technology while accounting for logistics, supply, and demand considerations. This is particularly important for renewable feedstocks and utilities that are produced regionally or intermittently, or are expensive to transport. Integration of supply chain and process design for bio-products has been achieved with varying degrees of detail [46]. In particular, PNFA has been coupled with biomass supply chain design [32•]. With the successful integration of PNFA and fuel design [8••] (cf. right part of integrated design in Figure 1), the groundwork is laid to integrate the three design problems in one method (cf. Figure 2). The performance of advanced engine concepts not only depends on the fuel but also on engine-related variables [3]. To better capture complex fuel/engine interactions, fuel performance indicators and their fixed target ranges should thus be substituted by ICE models that integrate those engine-related degrees of freedom. This enables direct optimization for engine efficiency and emissions, thus performing model-based co-design of fuel and engine. Such closer integration of product design and product-use process design has already been achieved in other domains, for example, in solvent design [47,48]. As a first step in this direction, Gschwend *et al.* [49,50•] have evaluated molecular structures using CAMD approaches and a low-complexity ICE model. However, more detailed analysis of combustion system performance typically requires rather complex reaction kinetics and fluid simulations [1••]. Recently, the computational effort of such simulations has been reduced by data-driven surrogate modeling techniques from the machine learning domain [51,52]. Further approaches towards solving integrated fuel and engine design problems might exploit high-performance computing.

Holistic fuel performance assessment must also consider societal, political, and environmental framework conditions. To this end, the interdependencies between different sectors and resources, for example, electricity, food, water, and land-use, must be analyzed. Rationally

Figure 2



Integrated fuel and process design as part of well-to-wheel optimization/assessment.

designed ICE fuels must also be compared to, for example, battery electric and fuel cell electric vehicles, in a well-to-wheel approach to assess their role in a world of post-fossil mobility. First studies in this direction include life cycle assessments [53•], scenario reviews [54], and comprehensive quantitative and qualitative comparisons [55]. However, these analyses do not yet include rationally designed fuels.

Finally, given the strong CO_2 reduction targets for the next decades [56] and the large efforts required to establish the necessary production facilities and infrastructure, tailor-made renewable fuels and associated engine designs must be identified and implemented quickly. In particular, it must be shown whether the efficiency increases enabled by tailor-made fuels outweigh the emissions of required fleet and infrastructure changes on a reasonable time horizon or if instead integrated design should focus on fast drop-in solutions achievable with minimal implementation time and effort.

Conflict of interest statement

Nothing declared.

Acknowledgements

This work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy — Cluster of Excellence 2186 'The Fuel Science Center'.

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