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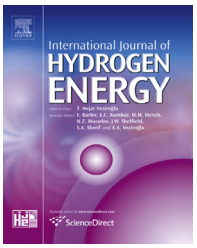

Numerical optimization and reaction flow analysis of syngas production via partial oxidation of natural gas in internal combustion engines

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ABSTRACT

The production of hydrogen is studied numerically under uncatalyzed partial oxidation and homogeneous charge compression ignition (HCCI) conditions in an internal combustion engine fueled by natural gas. The HCCI process is modeled by a single-zone variable volume reactor using a global heat transfer model and elementary-step reaction mechanisms. Numerical optimization is applied to maximize the hydrogen yield at the end of the expansion stroke by varying the equivalence ratio, engine speed and initial pressure for a fixed initial temperature. Suitable constraints were defined, including peak pressure and bounds to the optimization variables. From these results, maximum hydrogen yield profiles and the associated operating parameter profiles as functions of initial temperature were obtained. The profiles exhibit strong linear dependency with initial temperature. Reaction flow analysis was performed to gain detailed insight into the chemical processes involved when the engine is run under optimal conditions for a maximum hydrogen yield. The integral reaction flow analysis shows that substantial amounts of hydrogen are produced from precursors, which are also valuable products, such as methanol, formaldehyde and ethylene.

Introduction

Internal combustion engines (ICEs) can be viewed as highly dynamic high temperature/pressure reactors. Therefore, ICEs can possibly be an attractive alternative to conventional reactors for certain chemical synthesis applications. Depending on the operating parameters, reaction conditions are attainable that can hardly be achieved in conventional reactors. For example, ICEs posses the intrinsic feature to quench the reaction, which stems from the piston motion.

An interesting idea is outlined by Atakan [1], where he proposes to operate gas turbines as polygenerators in order to produce gaseous base chemicals together with mechanical power. When operated under fuel-rich conditions with methane as fuel, the process has been shown to be thermodynamically more favorable. In other words, the production of useful chemicals such as syngas and olefins simultaneously with mechanical energy shows potential to increase the energetic efficiency of the process viewed as a whole. The produced syngas could be fed to a gas-to-liquid process, the

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mechanical energy converted to electricity and the excess heat used for preheating the fuel or in other nearby industrial processes. Although gas turbines were the focus of the work in the publication by Atakan [1], similar considerations hold for ICEs, which are addressed in this study. The use of ICEs to produce more useful products instead of CO_2 and H_2O is thus motivated by two different aspects: Firstly, the potential to increase overall process efficiency and secondly, the possibility to achieve conditions that are not feasible in conventional reactors arising from the piston motion. In addition, piston engines can be operated very flexibly and react promptly to changes in controls. This poses another advantage that can possibly also be exploited for a variety of further chemical processes.

There is a growing interest to use methane as chemical feedstock, as the long-term availability of oil reserves is not guaranteed. Furthermore, natural gas has recently become more available due to the widespread usage of hydraulic fracturing (fracking). It is therefore worthwhile to explore new ways to exploit natural gas reserves.

Homogeneous charge compression ignition (HCCI) is a relatively new concept for operating an ICE that can be viewed as a hybrid between spark ignition (SI) and compression ignition (CI). A premixed and homogeneous fuel-oxidizer mixture is induced into the cylinder, as done in a SI engine. However, the mixture is then brought to ignite solely by the compression heat without external influence, a situation that reflects CI operation [2]. A key difference between SI or CI and HCCI combustion mode is that, in the latter case, the combustion process is believed to occur at many points simultaneously [3]. From a modeling point of view, the HCCI operating mode poses the advantage that, depending on the subject of interest, the process can be adequately described by a simple single-zone. This is considerably simpler than having to consider flame propagation or droplet mixing and evaporation, processes that affect the combustion in SI and CI modes. The autoignition characteristics make it evident that chemical kinetics plays the most significant role in the system, making detailed modeling of the chemistry a necessity. Besides being easier to implement than more sophisticated models such as multi-zone models [4,5] or even CFD codes coupled with chemical kinetics [6], the single-zone approach involves much lower computational times. This is a critical issue, especially in light of optimization. With the optimization we aim to point out important trends and promising operating regions to produce hydrogen. The determination of exact ignition timings, for example, is not the aim of this work.

Internal combustion engines (ICE) have previously not often been the target of research regarding their use for the production of chemicals. Modeling work concerning ICEs has therefore essentially been done to investigate operating characteristics under conventional conditions, i.e. to produce mechanical energy. Examples include work relating to ignition timing control under HCCI conditions and alternate fuels [7–9]. Only few studies have dealt with the use of an engine as a reactor, e.g. Refs. [10–14]. In these publications, the production of syngas by partial oxidation, i.e. under fuel-rich conditions, of hydrocarbon fuels was studied. In particular, methane and natural gas as fuels were examined. In summary, the research which has been conducted so far represents a number of feasibility studies. The experimental results show that the production of synthesis gas via partial oxidation of methane in the most common engine types is possible. In addition, many of these reports state that the engine was also capable of simultaneously delivering power to the shaft. However, it took some effort to ensure stable engine operation in the experiments.

In this study, we investigate the production of syngas under uncatalyzed partial oxidation and HCCI conditions in an internal combustion engine fueled by natural gas. We apply numerical optimization to propose optimal operating conditions for the production of syngas. This is advantageous since the possible combinations of engine operating parameters that influence the outcome of reactions are abundant. An analysis of syngas production solely by trail-and-error methods or empirical experiments is therefore impractical.

Numerical optimization methods are successfully applied in many fields, ranging from optimization of complex geometries such as airplanes to homogeneous and heterogeneous reacting systems. Previous work from our group includes the optimization of product yields by the variation of operating conditions and catalyst loading in catalytic monoliths [15]. Another example is the optimal control problem described in Ref. [16], where conversion of methane to ethylene in a short contact time reactor was optimized by varying the temperature profile. Since the use of ICEs to produce H_2 is only sparsely documented in the literature, a meaningful comparison with experimental data as to whether the optimization improves the situation is not possible. However, the results presented herein provide further indications as to which operating parameters favor partial oxidation of the fuel instead of full combustion.

The purpose of this paper is to conduct a fundamental study employing numerical optimization to identify promising operating regions for the production of syngas from natural gas in an ICE. The optimization is carried out using the derivative-free algorithm COBYLA [17,18] to vary initial pressure, engine speed and equivalence ratio at various constant initial temperatures ranging from 473 K to 773 K. The peak pressure during the simulation is constrained to below 250 bar. Any power produced by the engine was not considered in the optimization. A second point of interest is to gain detailed insight of the combustion process which can guide further work. To this end, a reaction flow analysis based on the GRI 3.0 mechanism [19] is conducted which provides further insight into the simulation results. Hydrogen, being the more valuable product of the syngas mixture, is the focus of this work. Hence, the optimization is carried out to maximize the H_2 yield and the reaction flow analysis is focussed on the reaction pathways from methane to hydrogen.

Modeling approach and fundamental definitions

Description of the reactive system

A new computer code DETCHEM^{ENGINE} [20] was developed, which calculates time-dependent concentration profiles for the compression and expansion strokes of a four-stroke engine using detailed gas-phase reaction mechanisms. The

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