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# Hydrogen production by partial oxidation of ethanol/gasoline blends over $Rh/Al_2O_3$

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ABSTRACT

The catalytic partial oxidation (CPOX) of ethanol-blended fuels is studied over rhodium/alumina coated monoliths with ethanol/iso-octane mixtures as model systems. Blends containing 5–85 vol.% ethanol are investigated, as well as the pure substances. All mixtures show a hydrogen yield of over 80% in millisecond contact times, with the highest yield for a blend with 10 vol.% ethanol. For a high ethanol concentration in the blend, generally a high by-product formation is observed already at fuel lean conditions. The product yields cannot be linearly interpolated from the yields of the pure substances. In addition, the commercial fuels 95 RON gasoline and E85 are studied, revealing similar product yields in CPOX of the commercial fuels and the corresponding ethanol/iso-octane blends. Thus, two-component mixtures can be proposed as model system for the complex compositions of commercial fuel.



## 1. Introduction

The use of auxiliary power units (APU) – consisting of fuel reformer and fuel cell – is a promising possibility to reach an efficient way of power generation for mobile applications [1,2]. Hydrogen production based on fuel reforming has already been extensively studied in the past [3–14]. Steam reforming (SR), catalytic partial oxidation (CPOX) or the combination of both, autothermal reforming (ATR) are the most common paths to convert logistic fuels to hydrogen. For mobile applications, CPOX is a very promising option [7,15,16], because no additional steam and no heat supply device are required. Furthermore, fast start-up procedures and transient responses on load changes can be realized in CPOX reformers [17].

The general advantage of on-board hydrogen production is the utilization of commercially available fuels, e.g. gasoline or diesel, with an already existing retail infrastructure [1,18]. The investigation of the performance of these fuels is mainly based on simple surrogates such as iso-octane (2,2,4-trimethyl pentane) [7,8,19,20] and iso-octane blended with toluene [9,21] for gasoline. These rather simple surrogates are especially useful to achieve a fundamental understanding. On the other hand, commercially available fuels are studied for evaluation of the overall performance of the reformer [5,22,23]. The increasing use of biomass-derived fuels and fuel blends in vehicles, e.g. ethanol and E10 (gasoline blended with 10 vol.% ethanol), respectively, led to intense research activities concerning these biomass-containing fuels [16,23–32]. Even though the use of ethanol as fuel is controversial, it may present a promising alternative to fossil fuels when derived from efficient sources and processing [28,33].

In the work presented, the conversion of ethanol-blended gasoline toward hydrogen (with carbon monoxide) is studied in a CPOX reformer using rhodium/alumina-coated honeycomb monoliths. First, a model system, consisting of ethanol and iso-octane, is investigated to gain a deeper understanding of the otherwise complex fuel composition in the reformer. The global reaction route of direct partial oxidation of ethanol and iso-octane are

$$2C_2H_5OH_{(g)} + O_{2(g)} \rightarrow 4CO_{(g)} + 6H_{2(g)}, \quad \Delta_R H^\circ = +43.88\,\mathrm{kJ\,mol^{-1}} \tag{1}$$

$$i\text{-}C_8H_{8(g)} + 4O_{2(g)} \rightarrow 8CO_{(g)} + 9H_{2(g)}, \quad \Delta_R H^\circ = -660.14\,\mathrm{kJ\,mol^{-1}} \tag{2}$$

Ethanol/iso-octane blends with ethanol concentrations varying from 5 to 85 vol.% are studied for several operating conditions

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ranging from fuel lean to fuel rich conditions. In addition, the pure substances ethanol and iso-octane are studied. Thus, the performance of the blends cannot only be compared with each other but also with the performance of the pure substances.

Commercial gasoline is composed of several hundreds of different hydrocarbons, belonging to the different families of *n*-alkanes, branched alkanes, cyclo-alkanes, alkenes, aromatic compounds, and oxygenated hydrocarbons [34]. This high complexity of the commercial fuel leads to an even more complex reaction system in the reformer. Furthermore, the composition of commercial fuels depends on geographical and seasonal factors. Substitution of commercial fuels with model systems that consist of a limited number of hydrocarbons and reproduce the general behavior of the commercial fuel is advantageous not only for mechanistic and kinetic understanding but also for optimization of reformer design and operating conditions [35]. Therefore, the reformer is also operated with commercial fuels 95 RON gasoline (gasoline blended with 5 vol.% ethanol) and E85 (gasoline blended with 85 vol.% ethanol) directly taken from German gas stations, and the resulting reformate composition is compared with that of the model fuel surrogates.

## 2. Experimental set-up

The study is carried out in a flow reactor containing the catalyst and which is housed in a furnace used for light-off and thermal insulation. The liquid fuel is mixed with an inert gas and evaporated in a pre-evaporator. The gaseous reactants and the evaporated fuel are mixed at the reactor inlet by using a tube in tube system, which allows for a rapid mixing below auto-ignition temperature. Thus, a homogeneous, pulse-free inlet flow is ensured. The product stream is analyzed by a combination of FT-IR and MS for time-resolved monitoring of the product stream and GC–MS for steady-state analysis of further hydrocarbon components of the product stream. A detailed description of the experimental set-up can be found elsewhere [6,8].

### 2.1. Catalyst

The catalyst used is an industrially manufactured honeycomb monolith with rhodium (catalyst loading: 1.48 mg cm$^{-3}$) dispersed in a $\gamma$-$Al_2O_3$ washcoat. The monolith is 19 mm in diameter and 8 mm in length with 900 cpsi (channels per square inch). The position of the catalyst in the quartz glass reactor tube ($L$ = 500 mm, inner diameter = 19.5 mm, outer diameter = 21.5 mm) is 200 mm downstream of the mixture inlet. As heat shields, an uncoated $\gamma$-$Al_2O_3$ foam monolith (85 ppi (pores per inch)) and an uncoated honeycomb monolith (600 cpsi) are placed directly upstream and downstream the catalyst, respectively. Both heat shields, also serving as fixation for thermocouples, have a diameter of 19 mm and a length of 10 mm. The upstream uncoated foam monolith is used as a flow homogenizer as well. To prevent by-passing and for insulation, heat shields and catalyst are wrapped in ceramic fiber paper.

### 2.2. Fuel mixtures

Blends of ethanol and iso-octane containing 5, 10, 50, and 85 vol.% ethanol are investigated. The exact concentrations are determined by NMR spectroscopy. Also, the pure substances ethanol and iso-octane are investigated. In addition to the investigation of the model system consisting of ethanol/iso-octane blends, commercial fuels were examined. Commercial 95 RON gasoline and E85 were purchased from a German gas station (ZG Raiffeisen Tankstation Karlsruhe). To be able to calculate the C/O ratio for the commercial fuels, C/H/O content of the fuels was determined by elemental analysis.

Ethanol (purity: 99.9%, absolute p. A., Merck) and 2,2,4-trimethyl pentane (purity: 99%, Alfa Aesar), iso-octane, were used without further purification. The applied gases argon (5.0), carbon dioxide (4.5), helium (5.0), hydrogen (5.0), nitrogen (5.0), and oxygen (4.8) were obtained from Air Liquide. The purities of the gases are given in parentheses.

### 2.3. Measurement procedure

The measuring conditions are defined by the C/O ratio, which is the ratio of the total number of carbon atoms and the total number of oxygen atoms in the reactant feed. In the calculation of the C/O ratio (Eq. (3)), the oxygen atom present in the ethanol molecule is included in the amount of oxygen atoms in the inlet flow.

$$\frac{C}{O} = \frac{2n(\text{ethanol}) + 8n(\text{iso-octane})}{n(\text{ethanol}) + 2n(O_2)} \quad (3)$$

Measurements are performed from fuel lean (C/O = 0.6) to fuel rich (C/O = 1.5) conditions by gradual variation of the inlet mixture. To ensure reproducibility, each measurement was performed twice. The results for the measurements were compared and averaged as there were only slight differences observable. For the measurements, the feed is constantly diluted with 80 vol.% nitrogen. A total flow rate of 4.5 SLPM (standard liters per minute, referring to standard conditions: 298 K, 1.013 bar) is used for each measurement, corresponding to a gas hourly space velocity (GHSV) of 115 000 h$^{-1}$. The light-off is initiated by preheating the reactor with a furnace to 250 °C and by preheating the catalyst to approximately 300 °C by hydrogen oxidation. After light-off, the reactor is operated autothermally. For each C/O ratio, experimental data were collected for at least 15 min. By addition of a known amount of carbon dioxide to the product stream behind the reactor outlet, an increase of carbon dioxide concentration is detected, from which the total flow rate is determined. This method is derived from the method of internal standard [21]. One sample is analyzed by GC-MS for each C/O ratio. After one set of measurements reaching from fuel lean to fuel rich conditions the catalyst is regenerated. The regeneration is conducted by temperature programmed oxidation with synthetic air, in particular to burn off carbon deposits on the catalyst surface. Additionally, the amount of carbon deposited on the surface is quantified by monitoring the CO and $CO_2$ flux.

Additionally, a long-term measurement was conducted for a blend containing 10 vol.% ethanol, for which a C/O ratio of 0.72 is maintained for 24 min, then it is switched to C/O = 0.63 for 30 min, and afterwards back to C/O = 0.72 for another 100 min.

## 3. Results

First of all, ethanol/iso-octane blends with concentrations ranging from 5 to 85 vol.% ethanol were investigated under varying operating conditions. In addition, the pure substances ethanol and iso-octane were tested under the same conditions. A comparison of the blends and the pure substances revealed the differences in behavior of these fuels. Some variations were detected between measurements of blends with similar concentrations. For the ethanol/iso-octane blend containing 10 vol.% ethanol, three batches of blend were produced. The precise concentrations were determined to be 9.10, 9.44 and 10.37 vol.% ethanol. The results for these three blends were averaged to gain arithmetic mean values and standard deviation for this example. To determine the time dependence of the performance of the blends, a 2 h measurement at a constant C/O ratio for a blend containing 10 vol.% ethanol was accomplished. The measurements with the commercial fuels 95 RON gasoline and E85 were performed under conditions directly comparable to those employed for the blends.