



# Autothermal reforming of Fischer–Tropsch diesel over alumina and ceria–zirconia supported catalysts

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## HIGHLIGHTS

- ▶ Full-scale Fischer–Tropsch diesel autothermal reforming for hydrogen generation.
- ▶ Two catalytic zones were used. Bimetallic RhPt catalysts supported on  $\delta$ -Al<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>–ZrO<sub>2</sub>.
- ▶ Catalytic monoliths were sequentially placed in the autothermal reformer.
- ▶ Higher reducibility of Rh<sub>x</sub>O<sub>y</sub> species in CeO<sub>2</sub>–ZrO<sub>2</sub> lead to 42% vol hydrogen after CeO<sub>2</sub>–ZrO<sub>2</sub>.
- ▶ Optimum operating conditions were determined at O<sub>2</sub>/C = 0.42 and H<sub>2</sub>O/C = 2.5.

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## ABSTRACT

Autothermal reforming (ATR) of synthetic Fischer–Tropsch diesel has been carried out to evaluate the fuel reformer and the catalyst performance at realistic operating conditions. Hydrogen was produced via ATR in a full-scale reformer (ID = 84 mm, L = 400 mm) at 650–750 °C. The two monolithic catalysts were sequentially located in the reformer and simultaneously tested. The catalysts were composed of 1:1 wt% Rh:Pt as active metals; CeO<sub>2</sub>, MgO, Y<sub>2</sub>O<sub>3</sub>, and La<sub>2</sub>O<sub>3</sub> were used as promoters. The first catalytic monolith was supported on  $\delta$ -Al<sub>2</sub>O<sub>3</sub> and the second on CeO<sub>2</sub>–ZrO<sub>2</sub>. Fresh samples were characterized by N<sub>2</sub>-BET, XRD and H<sub>2</sub>-TPR analyses. Catalyst activity was evaluated at O<sub>2</sub>/C ~ 0.34–0.45 and H<sub>2</sub>O/C ~ 2–3. Results show an increased catalyst activity after the second monolithic catalyst due to the effect of steam reforming, water–gas shift reaction (WGS) and higher catalyst reducibility of Rh<sub>x</sub>O<sub>y</sub> species on the CeO<sub>2</sub>–ZrO<sub>2</sub> mixed oxide as a result of the improved redox properties. Hydrogen concentrations of 42 vol% and fuel conversion of 98% after the CeO<sub>2</sub>–ZrO<sub>2</sub>-supported catalyst was obtained at O<sub>2</sub>/C = 0.42 and H<sub>2</sub>O/C = 2.5.

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## 1. Introduction

Use of alternative fuels and integration of fuel cell auxiliary power units (FC-APUs) in vehicles, have been considered for reduction of issues such as pollutant emissions, oil dependence and greenhouse emissions in the transport sector. FC-APUs can provide on-board auxiliary electricity in vehicles, in particular during stand-still mode when 60% of engine operating time is used inefficiently [1]. Commercialization of this technology is being promoted by several public and private pilot projects but also, due to the stricter legislation on emission limits in the US and Europe, such as the EURO VI directive and the anti-idling regulation, respectively [2]. Besides, use of FC-APUs on-board will overcome limitations such as storage and transport of hydrogen [3,4].

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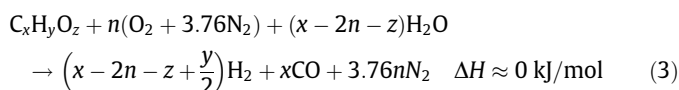
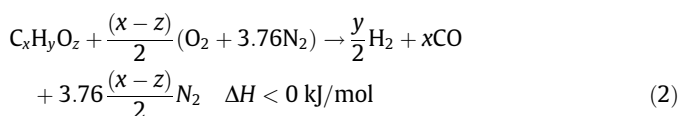
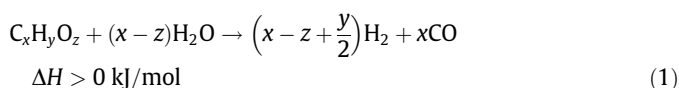
Commercialization of the FC-APU is linked with the viability of the system fuel flexibility, to cover a wider range of applications. In actual commercial fuel qualities i.e. European standard diesel (DIN 590), great challenges are found for hydrogen production. This is due to its sulfur and aromatic content. Recently, researchers have made significant progress in overcoming these limitations by decreasing diesel sulfur content and promoting usage of alternative fuels. For instance use of rapeseed methyl ester (RME) and Fischer–Tropsch (FT) diesel in the transport sector for reduction of pollutant emissions [5,6]. Specifically, FT diesel characteristics, i.e., high cetane number, low aromatic content, high paraffinic content, and low sulfur content represent the advantage of facilitating hydrocarbon oxidation and decreasing autothermal reforming (ATR) catalyst deactivation [1,7–9]. FT diesel properties are shown in Table 1.

The integrated FC-APU contains a fuel reformer, where fuel is converted over a catalyst to obtain a H<sub>2</sub>-rich gas via ATR. Studies

**Table 1**  
Fischer–Tropsch diesel properties.

Properties	Unit	FT
Density	kg/m <sup>3</sup>	800
Viscosity at 40 °C	mm <sup>2</sup> /s	2.5–4
Flash point	°C	75
Boiling point	°C	180–360
Self-ignition temperature	°C	Above 200
Lower heating value	MJ/kg	47
Sulfur content	ppm	0
C mass fraction	wt%	85
H mass fraction	wt%	15

on ATR of diesel have described it as the most viable process for hydrogen production in mobile applications such as trucks [10]. The ATR combines endothermic steam reforming (SR), see Eq. (1), and partial oxidation (POX), Eq. (2); where ATR, Eq. (3), is the global reaction of the process [1,11,12]



In ideal ATR adiabatic operation heat generated by the exothermic reaction is used to supply the endothermic steam reforming reaction. Which takes place together with reactions such as the water–gas-shift reaction (WGS) in the catalytic zone [13]. However, in realistic conditions, as is the objective of the present study, the system presents heat losses resulting in incomplete adiabatic operation; thus excess of air is used [14] for practical operation of the FC-APU.

Despite of many advances in catalyst optimization and process performance i.e., introduction of zone-coating catalysts, new fuel evaporation systems such as injectors and nozzles [14–17], issues such as fuel flexibility, use of alternative fuels for hydrogen production and the amount of noble metal loading required for complete fuel conversion still remain to be solved [1,7]. As a continuation of previous research at our group, in this study is reported the ATR of FT diesel in a 5 kWe-scale reformer as well as the effect of using two different catalyst compositions sequentially located and simultaneously tested.

Noble metal catalysts (Rh:Pt) were used as active metals for both catalytic monoliths. Active metals and promoters were supported on Al<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>–ZrO<sub>2</sub>, for the first and second monoliths, respectively. The monolith location was chosen depending on the reaction conditions to which the catalyst was subjected. That is oxidation reactions (exothermic) and steam reforming (endothermic) [13]. Results show an increased catalyst activity after the second monolithic catalyst due to the effect of steam reforming, the water gas shift reaction (WGS) and higher catalyst reducibility on CeO<sub>2</sub>–ZrO<sub>2</sub> mixed oxide. Hydrogen concentrations of 42 vol% and fuel conversion of 98% after the CeO<sub>2</sub>–ZrO<sub>2</sub>-supported catalyst was obtained at O<sub>2</sub>/C = 0.42 and H<sub>2</sub>O/C = 2.5.

### 1.1. ATR catalyst selection

Catalyst optimization for autothermal reforming conditions has been reported previously, describing systems with different sup-

ports, which demonstrate the superiority of Rh over Pt and Pd, for reforming of high sulfur-content fuels [9,18,19]. Similar results were also shown by Nilsson et al. [20] and Ferrandon et al. [21]. As example, Sigarov et al. [22] studied the performance of Co, Mn, Rh, BaO, La<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> in diesel ATR in a reactor with two cylindrical metallic monoliths. Maximum hydrogen yield of 18 mol/mol (fuel) was achieved at O<sub>2</sub>/C = 0.5, H<sub>2</sub>O/C = 1.5–1.7, GHSV = 2000–10,000 h<sup>-1</sup> and at temperatures of 840–880 °C. The authors showed that the most active catalysts were the combination of Co<sub>3</sub>O<sub>4</sub>/MnO<sub>4</sub>–BaO in the first zone of the reactor and Rh/MnO<sub>4</sub>–BaO in the second zone, with a product composition of H<sub>2</sub> = 32%, CH<sub>4</sub> = 1%, CO<sub>2</sub> = 12%, CO = 11%, N<sub>2</sub> = 44%.

Kaila and Krause [23] studied ATR of simulated gasoline and diesel fuels using catalysts composed of Rh and Pt as active components in monometallic and bimetallic form with zirconia as support. They found that Rh/ZrO<sub>2</sub> catalyst showed high ATR activity and selectivity. Additionally, it was confirmed less coke formation with Rh/ZrO<sub>2</sub> than for a nickel catalyst in the same application. In addition, Kaila et al. [24] found that the bimetallic prepared catalyst presented better performance than the monometallic catalyst.

As reported by Kang et al. [25] the role of the support in a reforming catalyst is not only determined by its mechanical or structural characteristics, but it can also affect the catalyst activity, selectivity, thermal stability, carbon and sulfur tolerance with a chemical role in formation of oxygen vacancies. This is possible due to the oxygen storage capacity (OSC) of materials such as CeO<sub>2</sub>. The addition of oxygen, facilitates the reaction by regenerating the oxide species of the surface belonging to the promoters and by oxidizing surface carbon species and carbon-containing products as is reported by Srisiriwat et al. [26]

Ceria presents a fluorite structure in which it is possible to substitute Ce<sup>4+</sup> ions for Zr<sup>3+</sup> or Gd<sup>3+</sup> producing oxygen vacancies and metal sites on the surface of the substrate. Other example is CeO<sub>2</sub>–ZrO<sub>2</sub> or ZrO<sub>2</sub> stabilized with yttrium [24,26]. Research on the oxygen storage behavior of CeO<sub>2</sub>–ZrO<sub>2</sub> mixed oxides has reveal that CeO<sub>2</sub>, ZrO<sub>2</sub> and Mn are sulfur adsorbents and decrease catalyst deactivation by sulfur poisoning and carbon deposition [27]. Sulfur adsorption on CeO<sub>2</sub>–ZrO<sub>2</sub> is accomplish through formation of a stable sulfide at the temperature range of ATR [28]. This species can partially being removed after vacuum treatment at high temperatures. However, under reducing conditions the CeO<sub>2</sub>–ZrO<sub>2</sub> facilitates desorption of sulfur species as H<sub>2</sub>S [29].

During ATR, the catalyst is subjected to oxidizing, partial oxidation (POX) and reducing conditions, steam reforming (SR). Therefore, CeO<sub>2</sub>–ZrO<sub>2</sub> with its oxygen storage capacity (OSC) could increase oxidation reactions under reducing conditions (SR) while presenting superior sulfur resistance than δ-Al<sub>2</sub>O<sub>3</sub> at the same conditions.

Alumina is the most common support material for environmental catalysis due to its high surface area, low cost and thermal stability. The Al<sub>2</sub>O<sub>3</sub> is thermally stabilized by CeO<sub>2</sub> or La<sub>2</sub>O<sub>3</sub> to avoid sintering of the active metal [30].

## 2. Experimental

### 2.1. Catalyst preparation

Catalyst samples were prepared by the incipient wetness impregnation procedure. Powders of δ-Al<sub>2</sub>O<sub>3</sub> (prepared by calcining γ-Al<sub>2</sub>O<sub>3</sub> supplied by Sasol GmbH Germany with a specific surface area of 105 m<sup>2</sup>/g) and CeO<sub>2</sub>–ZrO<sub>2</sub> (supplied by MEL Chemicals with a specific surface area of 241 m<sup>2</sup>/g) were used as supports. The δ-Al<sub>2</sub>O<sub>3</sub> was impregnated with an aqueous solution of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Alfa Aesar, 99.99%), and La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Alfa Aesar, 99.99%), and finally impregnated with an aqueous solution of Rh(NO<sub>3</sub>)<sub>3</sub> (Sigma Aldrich) and (NH<sub>3</sub>)<sub>4</sub>Pt(NO<sub>3</sub>)<sub>2</sub> (Alfa Aesar), dried

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