DOCTORAL THESIS IN CHEMICAL ENGINEERING

Hydrogen Generation for Fuel Cells in Auxiliary Power Systems

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Live as if you were to die tomorrow
Learn as if you were to live forever

Mohandas K. Gandhi
ABSTRACT

Heavy-duty trucks are in idle operation during long periods of time, providing the vehicles with electricity via the alternator at standstill. Idling trucks contribute to large amounts of emissions and high fuel consumption as a result of the low efficiency from fuel to electricity. Auxiliary power units, which operate independently of the main engine, are promising alternatives for supplying trucks with electricity. Fuel cell-based auxiliary power units could offer high efficiencies and low noise. The hydrogen required for the fuel cell could be generated in an onboard fuel reformer using the existing truck fuel. The work presented in this thesis concerns hydrogen generation from transportation fuels by autothermal reforming focusing on the application of fuel cell auxiliary power units. Diesel and dimethyl ether have been the fuels of main focus. The work includes reactor design aspects, preparation and testing of reforming catalysts including characterization studies and evaluation of operating conditions. The thesis is a summary of five scientific papers.

Major issues for succeeding with diesel reforming are fuel injection, reactant mixing and achieving fuel cell quality reformate. The results obtained in this work contribute to the continued research and development of diesel reforming catalysts and processes. A diesel reformer, designed to generate hydrogen to feed a 5 kW_e polymer electrolyte fuel cell has been evaluated for autothermal reforming of commercial diesel fuel. The operational results show the feasibility of the design to generate hydrogen-rich gases from complex diesel fuel mixtures and have, together with CFD calculations, been supportive in the development of a new improved reformer design. In addition to diesel, the reforming reactor design was shown to run satisfactorily with other hydrocarbon mixtures, such as gasoline and E85. Rh-based catalysts were used in the studies and exhibit high performance during diesel reforming without coke formation on the catalyst surface. An interesting finding is that the addition of Mn to Rh catalysts appears to improve activity during diesel reforming. Therefore, Mn could be considered to be used to decrease the noble metal loading, and thereby the cost, of diesel reforming catalysts.

Dimethyl ether is a potential diesel fuel alternative and has lately been considered as hydrogen carrier for fuel cells in truck auxiliary power units. The studies related to dimethyl ether have been focused on the evaluation of Pd-based catalysts and the influence of operating parameters for autothermal reforming. PdZn-based catalysts were found to be very promising for DME reforming, generating product gases with high selectivity to hydrogen and carbon dioxide. The high product selectivity is correlated to PdZn interactions, leading to decreased activity of decomposition reactions. Auxiliary power systems fueled with DME could, therefore, make possible fuel processors with very low complexity compared to diesel-fueled systems.

The work presented in this thesis has enhanced our understanding of diesel and DME reforming and will serve as basis for future studies.

Keywords: autothermal reforming, auxiliary power unit, diesel, dimethyl ether, fuel cell, fuel-flexible reformer, hydrogen, PdZn alloy, reforming catalyst, reformer design, Rh
SAMMANFATTNING

Titel: Vätgasframställning för bränsleceller i hjälpkraftsystem


Arbetet som presenteras i avhandlingen har ökat vår kunskap om reformering av diesel och DME och kommer att utgöra en bas för fortsatta studier inom området.
PAPERS REFERRED TO IN THIS THESIS

The work presented in this thesis is based on the following papers, referred to in the text by their Roman numerals, and appended at the end of the thesis.


Contribution to the papers. The author of this thesis took active part in all stages of the work presented in the thesis and had the main responsibility in the planning, implementation and evaluation of the studies as well as in writing the papers. Co-authors have been responsible for the reactor design and CFD calculations in Paper I and the TEM analyses in Paper V.
OTHER PUBLICATIONS AND CONFERENCE/SEMINAR CONTRIBUTIONS

Manuscript


Publications in peer-reviewed journals


Conference/Seminar contributions


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CHAPTER 1

INTRODUCTION

1.1 Setting the scene

It is widely accepted that oil is a finite resource. Within a short period of human history, the world supplies of fossil fuels, that took nature hundreds of millions of years to create, are about to become exhausted. This period of time is often referred to as the “Golden age of oil” during which the welfare in the developed countries of the world escalated and a dependence on oil for heating, power generation, and transportation was created. The amount of oil that will be accessible in the future depends on technologies available for extraction of oil but also on political, economical, and environmental circumstances. We are facing a continuous decline in the global oil production, commonly referred to as “Peak Oil” [1, 2]. The oil consumption in the developed countries of the world is still increasing and at the same time, the energy needs in fast-growing countries such as China and India are rapidly growing. Existing oil reservoirs may not be capable of meeting this increasing world demand and technology development does not keep pace with the surging needs. Moreover, fossil fuel usage has led to global warming, rising levels of pollution, a growing instability in natural ecosystems, and an increasing gap between rich and poor. Radical measures will be needed to start a transition towards a more sustainable future and to address the issues of the link between oil, peace and security throughout the world.

The transportation sector is often argued to be the most difficult energy sector when it comes to sustainable development. The accessibility and flexibility that vehicle use has provided have made it indispensable for moving people, goods, and information. In Sweden, the Commission on Oil Independence has proposed a reduction of petroleum-based fuels used for road transport with 40-50 % by 2020 [3]. This is a challenging target. The phasing out of fossil fuels is suggested to be accomplished by using more energy-efficient transport, increasing the production of renewable fuels and by changing over to a fleet of vehicles that is not dependent on fossil fuels. Reaching upcoming emission targets and managing the transition to a renewable transportation system will place large demands on efficient energy use.

Hydrogen is by many envisioned to be an important energy carrier taking part in a future sustainable energy system. The planned hydrogen society includes the clean and efficient energy conversion of hydrogen in fuel cells. To reach the envisioned level of implementation for fuel cells, there are barriers that have to be addressed, including performance, cost, vehicle design boundaries, and competing alternatives. The step for fuel cells to reaching
competitiveness and diffusion into the automotive market could be realized by means of niche technologies. The fuel cell auxiliary power unit (APU) is one niche that is put forward as a strategy for introducing fuel cells, and thereby hydrogen, into the transportation sector. Since the distribution and on-board storage of hydrogen present technical problems, related to its low volumetric energy density, current focus is on fuel processing technologies as alternatives to supply the fuel cells with hydrogen during a transition period. These systems could present one of the first large market penetration opportunities for fuel cells and thereby contribute to developing more efficient energy converters. The catalytic reforming of transportation fuels into hydrogen for use in fuel cell auxiliary power units is the subject of this thesis.

1.2 Objectives of the work

The main objective of the work presented in this thesis has been to address the challenge of reforming transportation fuels, specifically diesel and dimethyl ether (DME), into hydrogen-rich gases for use in fuel cell auxiliary power units onboard trucks. Fossil-based diesel is considered a viable short-term alternative to feed fuel cells in auxiliary power units with hydrogen, whereas dimethyl ether is an interesting diesel fuel alternative that can be produced from renewable resources. Special emphasis has been placed on the development of reforming catalysts and on the identification of operating conditions for optimal performance during autothermal reforming of diesel and dimethyl ether, respectively.

During the research project, test facilities for experimental evaluation of reforming processes and catalysts have been built up at KTH. A system for evaluation of a full-scale (5 kW_{e}) diesel reformer was built with the aim to gain practical experience and a broader knowledge of the diesel reforming process. A small-scale test rig was built for study of DME reforming catalysts.

The thesis is based on five appended papers focusing on hydrogen generation from transportation fuels by autothermal reforming. In Paper I, a reformer designed to generate hydrogen for a 5 kW_{e} fuel cell was evaluated based on results from experiments and CFD calculations. Paper II presents results from the small-scale testing of diesel reforming catalysts. The effect of adding manganese to the catalysts as a means of reducing noble metal loading was investigated. In Paper III, a fuel-flexible reactor concept is evaluated. Paper IV addresses the evaluation of Pd-based catalysts as well as the mapping of operating conditions during DME autothermal reforming. In Paper V, the catalytic properties of Pd-based catalysts during DME autothermal reforming have been further investigated.

1.3 Research context

The work presented in the thesis is part of two different research projects. The studies on diesel reforming have been performed within the framework of the program “Energy Systems in Road Vehicles”, financed by the Swedish Energy Agency. The cluster “Innovative fuel reformer for heavy-duty truck APU” comprised representatives from the Royal Institute of Technology, Chalmers University of Technology, Luleå University of Technology and Volvo Technology Corporation. The overall vision of the cluster was to develop a diesel fuel reformer for a
fuel cell auxiliary power unit that significantly could reduce fuel consumption and emissions originating from idle operation of heavy-duty trucks. The development of the innovative reformer focused on the development of a diesel reforming process including an active and selective catalyst and a ceramic CO₂-selective membrane that would force the equilibrium of the water-gas shift reaction towards higher hydrogen production.

The studies related to dimethyl ether have been performed within the project “Aftertreatment and fuel upgrading system for DME-fueled diesel engines”, initiated by the Royal Institute of Technology, Chalmers University of Technology, and Volvo Technology Corporation and financed by the Swedish Agency for Innovation Systems, the Swedish Road Administration, and the Swedish Environmental Protection Agency. The vision of the project has been to develop a system meeting the future demands on alternative and sustainable transport solutions in Sweden. The system combines lean combustion of DME in a compression ignition (CI) engine with lean nitrogen oxide aftertreatment where the nitrogen oxides are reduced, either by hydrogen produced in a reformer or by DME directly. The hydrogen from the reformer can also be used in a fuel cell auxiliary power unit. Such a system could create a vehicle with low emissions of NOₓ, hydrocarbons, and particulate matter (PM) compared to existing technology.

The work included in this thesis has been conducted at the Division of Chemical Technology, Royal Institute of Technology (KTH) and Volvo Technology Corporation, Sweden. The research has been conducted in close cooperation with leading industrial teams in the area at Volvo PowerCell. The collaboration included participation in discussions and workshops as well as taking active part in the operation and evaluation of a 5 kW prototype diesel fuel processor (including gas cleanup and heat management) aimed for a truck fuel cell APU.

1.4 Thesis outline

Following this introduction, Chapter 2 provides a background to fuel cell technology and the use of fuel cells in auxiliary power units. Chapter 3 gives an overview of the topic of fuel processing, with special focus on diesel and dimethyl ether. Different reforming technology options are described and recent research in the area is outlined. Chapters 4-6 summarize the results from the appended papers. Finally, in Chapters 7 and 8, respectively, conclusions and final remarks are given, with the aim of trying to highlight the most important findings and the wider perspectives of the work.
CHAPTER 2

FUEL CELLS FOR AUXILIARY POWER UNITS

The principle of the fuel cell was first demonstrated in 1839 by the Welsh scientist Sir William Grove [4]. Despite major improvements that have taken place since then and despite the large potential of the technology for efficient energy conversion, the technology is still immature and in its early phases of development [5, 6]. The main challenges to fuel cell commercialization are cost and durability. In this thesis, heavy-duty truck auxiliary power units (APUs) are suggested as a niche strategy to stimulate the development and market diffusion of fuel cell technology in mobile applications. As the storage of hydrogen presents technical problems related to its low volumetric energy density, the focus is on fuel processing of the existing truck fuel to a reformate gas (a mixture of CO, CO₂, H₂, H₂O, and N₂) for providing the fuel cell with hydrogen. This chapter provides a basic introduction to the principle of fuel cells and the concept of fuel cell-based auxiliary power units with the aim to motivate their use and provide understanding of the requirements placed on the fuel processor.

2.1 Fuel cell technology

A fuel cell converts chemical energy into electrical energy by electrochemical oxidation of hydrogen into water [7]. The principle of a hydrogen-fuelled fuel cell is shown in Figure 2.1. The cell basically consists of an electrolyte medium between two electrodes. Hydrogen is fed to the negative anode, where it is ionized, creating electrons and protons (Eq. 2.1). The protons migrate through the electrolyte from the anode to the cathode, while the electrons are forced through an external circuit, generating an electric current on their way to the cathode. Oxygen is fed to the positive cathode, where it reacts with the protons and electrons forming water and heat (Eq. 2.2), thereby completing the total reaction (Eq. 2.3).

\[
\text{Anode reaction} \quad 2H_2 \rightarrow 4H^+ + 4e^- \quad (2.1) \\
\text{Cathode reaction} \quad 4H^+ + 4e^- + O_2 \rightarrow 2H_2O \quad (2.2) \\
\text{Total reaction} \quad 2H_2 + O_2 \rightarrow H_2O \quad (2.3)
\]
The electrodes, electrode catalysts and membrane together form the membrane electrode assembly, MEA. Bipolar plates are placed on each side of the MEA, allowing for a good electrical contact with the surface of the electrodes and providing channels for distribution of the gases and channels for cooling medium. The ideal potential for the H₂ - O₂ reaction is 1.23 V. However, due to losses in the MEA, a single cell usually operates at 0.5-0.8 V. By connecting several cells in series into a fuel cell stack (Figure 2.2), higher voltages can be achieved. Through the direct conversion of fuel to electrical energy, fuel cells offer high efficiency compared to other energy-converting technologies, especially at part load. The electrical efficiency of modern stacks is in the order of 40-70 %, based on the lower heating value (LHV) of the fuel [7, 8]; the remaining energy is released as heat. Practical fuel cell systems need to be supplied with more reactants than the stoichiometric amount required for the desired current production in order to avoid starvation at the end furthest away from the fuel supply. For fuel cells, the term stoichiometry represents the amount of reactant supplied per amount of reactant consumed in the fuel cell. At the anode side, the stoichiometry is typically around 1.1-1.3. Figure 2.3 shows the hydrogen consumption for a PEFC stack fed with pure hydrogen; running on reformate, the partial pressure of hydrogen will be lower, which means that a higher stoichiometry is needed. The cathode stoichiometry is usually 2 or higher.

The choice of electrolyte material governs the operating temperature of the fuel cell. For use in auxiliary power units, either low-temperature (70-90 °C) polymer electrolyte fuel cells (PEFC) or high-temperature (>600 °C) solid oxide fuel cells (SOFC) have been suggested [9-11]. PEFCs use a solid polymer as electrolyte, most commonly Nafion®, a sulfonated tetrafluoroethylene copolymer allowing the movement of cations through the membrane but not conducting electrons. The systems can be made light and compact. The short startup times and good response to transient operation are advantageous and make them more...
suitable than SOFCs in automotive applications. PEFCs operating on neat hydrogen at optimal conditions show good performance over a wide range of loads. However, they need platinum metal as catalyst, and if the fuel cell is fed with reformate, carbon monoxide will preferentially adsorb on the Pt sites at low temperatures, blocking sites active for the anode reaction (Eqs. 2.4 and 2.5) [12].

\[ CO + Pt \rightarrow Pt - CO_{ads} \]  \hspace{1cm} (2.4)
The impact of carbon monoxide on the power output of a PEFC increases with the concentration and will become significant already at ppm levels [13, 14]. Non-inert effects of CO\(_2\) have also been reported [13, 15]. The mechanism of CO\(_2\) poisoning of the Pt catalyst is believed to involve the reduction of CO\(_2\) by H\(_2\), either electrochemically (Eq. 2.6) [16] or through the reverse water-gas shift reaction (Eq. 2.7) [17], to CO that then poisons the catalyst.

\[
\begin{align*}
2CO + 2Pt - H_{ad} & \rightarrow 2Pt - CO_{ad} + H_2 \\
CO_2 + 2H^+ + 2e^- + Pt & \leftrightarrow Pt - CO_{ad} + H_2O \\
CO_2 + 2Pt - H_{ad} & \leftrightarrow Pt - CO_{ad} + H_2O + Pt
\end{align*}
\]  

(2.5)

The oxidation rate of H\(_2\) in the presence of CO can be improved by alloying the Pt catalyst with a second metal, such as Ru, Sn, Co, Fe, Ni, Pd, Mo etc. [18]. For PtRu catalysts, the alloying has been shown to modify the electronic properties, leading to a decreased CO binding energy on Pt sites and to a strong binding of OH on the Ru sites [19]. Other methods of handling CO and CO\(_2\) at the anode are to introduce a small amount of air into the anode fuel stream, so-called air bleeding [20], or purging a fraction of the spent anode gas to avoid build-up of impurities during recycling [13].

Besides CO and CO\(_2\), other impurities may be present in the reformate feed that can influence the fuel cell performance. Sulfur may be present as H\(_2\)S in anode feeds originating from reformed fuels, which could severely poison the Pt catalyst, or as SO\(_x\) present in the air feed, which can lead to potential problems related to depression of the MEA pH [14]. When it comes to possible contamination effects of hydrocarbons or additives present in transportation fuels, published information is scarce.

Lately, there has been enhanced interest in operating PEFCs at temperatures \(>100 \, ^\circ\text{C}\), commonly referred to as HT-PEM fuel cells [21]. Operation at higher temperature decreases the effect of carbon monoxide impurities in the feed gas since the adsorption is less favored at higher temperatures [22]. In addition, higher temperature will simplify water management and enhance reaction rates, which means the noble metal loading can be decreased. Conventional membranes will, however, dehydrate and lose conductivity at high temperature and low humidity operation. Much effort is being put into developing membranes that can tolerate these conditions. Acid-base polymer membranes with enhanced CO tolerance, that can be operated in a stable manner at temperatures up to \(200 \, ^\circ\text{C}\) have been suggested [23]. While conventional membranes operating at \(80 \, ^\circ\text{C}\) could be significantly poisoned at CO concentrations above 10 ppm (transient CO peaks up to a few hundred ppm could be tolerated [24]), HT-PEM technology could allow operation with CO concentrations of up to a few percent in the feed [21].

SOFCs use electrolytes made of ceramic material, usually yttria-stabilized zirconia. The mobile ion is O\(^2-\) and the water is formed at the anode. SOFCs operate at temperatures between 600 and 1000 \(^\circ\text{C}\). This means that high reaction rates can be achieved and that
reforming reactions can be performed internally. The SOFC is more tolerant to poisons than the PEFC and does not need noble metal catalysts, an expensive component of the PEFCs. Negative aspects of SOFCs are long startup times, low response and low power density. Another problem is the frequent start-ups and shutdowns during operation in automotive systems, which will cause thermal stress of the membrane. For this reason, stationary power generation may be a more suitable application for SOFCs.

In summary, each fuel cell type has the possibility to solve some problems, but brings other problems itself. For use in auxiliary power units, the PEFC is considered to be the most feasible technology at present and is therefore in focus in the present work, even if others may see the SOFC technology as the obvious winner.

2.2 Truck idling and auxiliary power units

There are clear economic and environmental incentives for developing more efficient solutions to providing trucks with electricity for non-propulsion needs during driver rest periods, replacing the common practice of engine idling. American studies suggest that diesel trucks, used for long-haul, overnight travel, operate in idling mode during 20-40 % of the time the engine is running [25]. This is a consequence of an increased utilization of just-in-time production, increasing the time the drivers spend in the truck. At the same time, the demands on driver comfort systems are growing. Truck drivers idle their engines to cool or heat the cab, to keep the fuel and engine warm during cold weather and to power electrical equipment in the sleeper. The electrical demand of a parked commercial truck is typically around 1-5 kW, a requirement that currently cannot be met by the batteries alone. An average of 6 hours of idling per day has been reported [25]. A significant quantity of fuel is consumed in this way and considerable amounts of nitrogen oxides, hydrocarbons, carbon oxides and particulates are emitted [26]. In the US, there are 450 000 long-haul trucks, consuming more than 3000 million liters of diesel every year, without the truck even moving [25]. Furthermore, the energy efficiency when generating electricity via the alternator at standstill can be as low as a few percent [27, 28].

An alternative to idling of the truck engine is to install an auxiliary power unit. Auxiliary power units, APUs, are systems providing electricity to trucks operating independently of the main engine. APUs consisting of a small internal combustion engine are commercially available today [26] but have drawbacks in terms of weight, noise and emissions. By using fuel cells in heavy-duty truck auxiliary power units, commercialization of fuel cells could be possible in the near term. They provide lower noise and less vibrations (few moving parts, the compressor is an exception) compared to existing technology. In addition, higher electrical efficiencies are expected compared to an APU based on a small combustion engine. For a fuel cell APU including fuel processing of diesel, an efficiency of 34-38% has been predicted [29]. Using fuel cell APUs, truck drivers could meet impending legislation concerning idling and emission levels. Even taking total life cycle emissions into account, the amount of pollutants from a fuel cell APU will be up to 99 % lower compared to idle operation of diesel engines [30]. At the same time, the fuel economy can be improved and the need for vehicle maintenance lowered. Figure 2.4 shows a CAD model of the packaging of a fuel cell APU. The packaging and integration of the APU is important considering
durability and safety as well as customer acceptance. An effective packaging will increase the efficiency and minimize the weight and volume of the APU [31]. The package is to be placed on the frame rails of the truck.

System development targets for truck fuel cell APUs based on a PEFC fueled with diesel reformate are given in Table 2.1 [32]. While efficiency targets are likely to be met, the main technological challenges for market diffusion of fuel cell APUs has been identified to be volume and startup time requirements [33], but lifetime should probably also be mentioned as a concern. As the drivers are able to plan their stops, the startup problems can be circumvented. A large issue is the vehicle boundary conditions, placing high demands on the volume of the system. In the case of a successful market introduction of fuel cell APUs, it is likely that the design of the trucks will be affected, including the vehicle/APU interface but also the possibilities the presence of an extra power source onboard result in [6, 33]. In addition, the cost of fuel cells is still higher than the market is willing to pay. The cost of fuel cells today is generally stated to be between € 3000 and 5000 per kW [34, 35]. In a study where the cost was set to between ~€ 800 and 2000 per kW, the payback period for fuel cell APUs was estimated to be between 2.6 and 4.5 years, which is close to the 2-year requirement desired by fleet owners, but being highly dependent on fuel price and amount of fuel consumed during idle operation [27]. Future cost reductions driven by scale and learning effects are difficult to predict. The cost of mass-produced SOFC-based APUs have been estimated to vary between € 275 and 520 per kW, excluding costs for packaging, assembly and installation [36]. Governmental incentives and regulations could help the technology adapt to the market at a faster rate.

**Figure 2.4** An auxiliary power unit for heavy-duty trucks ([37] © PowerCell)
Table 2.1 Development targets for truck PEFC-APUs [32]

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<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Peak power</td>
<td>3-6</td>
<td>[kW]</td>
</tr>
<tr>
<td>System cost</td>
<td>400-800</td>
<td>[€/kW]</td>
</tr>
<tr>
<td>Specific power</td>
<td>50-100</td>
<td>[W/kg]</td>
</tr>
<tr>
<td>Volumetric power density</td>
<td>30-50</td>
<td>[W/dm³]</td>
</tr>
<tr>
<td>Lifetime</td>
<td>10 000</td>
<td>[h]</td>
</tr>
<tr>
<td>System efficiency</td>
<td>&gt;35</td>
<td>[%]</td>
</tr>
<tr>
<td>Ambient temperature</td>
<td>- 25 to + 45</td>
<td>[°C]</td>
</tr>
<tr>
<td>Number of cold starts</td>
<td>2000</td>
<td></td>
</tr>
</tbody>
</table>

2.2.1 Anti-idling incentives and regulations

In the US, a number of measures have been taken to address the issue of idling trucks. At regional level, more than 50% of the states have anti-idling regulations [38]. In California, the permitted idling time is limited to 5 minutes, sleeper trucks are no longer allowed to idle during periods of sleep and rest and new trucks (2008 models and later) are required to be equipped with systems that automatically shut down the engine after 5 minutes of idle operation [39]. The California Air Resources Board also provides grant incentives for the incremental cost of cleaner-than-required engines and equipment, including auxiliary power units [40]. At national level, the Energy Policy Act of 2005 (EPAct) permits a 400-pound weight exemption for APUs [41]. The Safe, Accountable, Efficient Transportation Equity Act (SAFETEA) allows idle-reduction facilities to be placed in rest or recreation areas, and in safety rest areas located on the interstate highway system [42]. Further, tax exemptions for installation of idle-reducing devices have been proposed in the US congress, e.g. the Idling Reduction Tax Credit Act of 2007, which suggests a 25% tax credit of the cost of a qualifying idle-reducing device, up to $1000, for diesel-powered on-highway vehicles [43].

2.2.2 Other markets

Even if the focus of this thesis is on the use of fuel cell APUs in long-haul trucks, it should be mentioned that there are a number of other applications, which have been pointed out as interesting markets, e.g. aircrafts [44], leisure yachts, recreational and luxury vehicles [45, 46], and military applications [47, 48]. For onboard power generation on commercial aircraft, fuel cell/gas turbine hybrid APU systems could offer greatly improved efficiency and fuel economy compared to today’s turbine-powered APUs [44]. The leisure market is particularly interesting during the commercialization phase, as the end users typically are willing to spend more money for the latest technology providing them higher comfort. Campervan developers have started offering fuel cell APUs running on methanol either as standard or optional equipment [46]. Most caravan parks provide electricity plugs so these systems rely on the customers being willing to pay or on customers wanting to stop wherever they wish to. In the military, advances in battlefield sensing, targeting and communications equipment have created a growing demand for power sources with high power density. Fuel cell APUs
could be employed to provide electricity with low acoustic and infrared signature during a tactical mode of operation termed “Silent Watch” [47]. Although the military market is limited, its importance for diffusion of new technologies has been emphasized [33]. Another application where fuel cell APUs have been suggested is in transit buses. However, during normal operation the main engine is never shut off, and fuel cell APUs cannot offer higher fuel efficiency while the main engine is running [49]. In this case, it would be more efficient to use the engine to supply all auxiliary power (3-14 kW) and the APU market for transit buses therefore appears limited [33].

2.2.3 Competing alternatives

To reduce diesel engine idling of trucks, several alternatives could be considered in addition to fuel cell APUs [25]. *Automatic engine stop-start controls*, which function by sensing sleeper temperature and turning the engine on if the sleeper is either too hot or too cold, could save fuel but will result in additional engine wear. Another method of saving fuel is *cylinder deactivation*, which will limit the combustion to part of the engine. Separate *direct-fired heaters* [50, 51] can be used to provide the engine and cab with heat. These systems are small and lightweight and offer significant fuel savings but they cannot provide cooling, will cause emissions, noise and vibrations and require retrofitting of the truck. *Thermal storage systems* make use of a material that stores thermal energy during main engine or air conditioning operation. A negative aspect is that large space is required for the storage medium.

If electricity is desired, none of the aforementioned techniques can be used. *Auxiliary power units* based on small internal combustion engines provide electricity and are commercially available [52-55] but have not been adopted onboard trucks to any large extent. State-of-the-art technology is, however, heavy, expensive and noisy, and will not decrease emissions considerably [25]. *Truck stop electrification* has been pointed out as the major competitor to fuel cell auxiliary power units [33]. Instead of using an onboard power supply, truck drivers can plug in to outlets at the truck stop. It could be either stand-alone [56] or shore power (onboard) [57] systems. The stand-alone systems are owned and maintained by private companies that charge an hourly fee. Heating, ventilation and air conditioning are contained in a structure above the truck parking spaces. For the onboard systems, the truck has to be equipped with an inverter, an electrical system for heating, ventilation and air conditioning and hardware to plug in to the electrical outlet. The main problem with truck stop electrification is limited availability, as the busiest routes often become overcrowded. In comparison, APUs provide more flexibility for the driver to stop wherever desired. Also, large investment costs are required for truck stop electrification. There are currently around 130 truck stops in the US offering idle-reduction facilities [58].

2.2.4 Developers of FC-APU technology

If truck stop electrification establishes a market before fuel cell auxiliary power units have become commercially available, the market introduction and diffusion of fuel cell APUs will be challenging [33]. In other words, the timing of the launch will be important. A number of R&D groups in industry, research organizations and universities, creating networks and
partnerships, are presently involved in the development of fuel cell auxiliary power systems [33, 59]. The key market players have optimistic time frames, having reported a start in the commercialization process in 2009-2011 [60, 61]. Some of the currently major developers of FC-APU technology are listed here [59, 62].

- Ballard/Voller Energy Group
  - LPG-fueled PEFC-APU for leisure, marine and construction markets
- BMW/Delphi/Renault
  - SOFC-APU for luxury cars, military and recreational vehicles
- Cummins/Protonex
  - SOFC-APU for trucks
- Daimler Chrysler/Freightliner
  - Hydrogen-fueled PEFC-APU
- Delphi/Battelle
  - Multifuel SOFC-APU for trucks
- Fraunhofer ISE/DLR
  - Kerosene-fueled SOFC-APU for Boeing aircraft
- MAN/Hydrogenics
  - Hydrogen-fueled PEFC-APU for urban bus with H2-ICE
- PowerCell (Volvo)
  - Diesel-fueled PEFC-APU
- Ricardo/Technology Management Inc.
  - Multifuel SOFC-APU for trucks
- SFC Smart Fuel Cell
  - Sold >4000 DMFC-APUs for recreational vehicles in 2007
- Staxera (HC Starck, Webasto and IKTS Research)
  - Gasoline or diesel-fueled SOFC-APU
- Topsoe Fuel Cell/Wärtsilä
  - Fuel-flexible SOFC-APU for marine and transportation markets
- Volkswagen/IdaTech
  - Diesel-fueled PEFC-APU
- ZBT
  - LPG-fueled PEFC-APU for leisure applications

The addressable market potential for truck fuel cell APUs in the US has been estimated to around 100 000 units annually [32]. The key drivers and barriers for FC-APUs are summarized in Table 2.2.
### Table 2.2 Drivers and barriers for FC-APUs

<table>
<thead>
<tr>
<th>Drivers</th>
<th>Barriers</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ Increasing auxiliary power requirements</td>
<td>- Investment cost</td>
</tr>
<tr>
<td>+ Anti-idling incentives and regulations</td>
<td>- Durability</td>
</tr>
<tr>
<td>+ Increasing fuel cost</td>
<td>- Reliability requirements</td>
</tr>
<tr>
<td>+ Lower noise and less vibration</td>
<td>- Fuel flexibility</td>
</tr>
<tr>
<td>+ Lower emissions</td>
<td>- Sulfur tolerance</td>
</tr>
<tr>
<td>+ Benefits of early market creation</td>
<td>- Heat management</td>
</tr>
<tr>
<td></td>
<td>- Volume requirements</td>
</tr>
<tr>
<td></td>
<td>- Competing alternatives</td>
</tr>
</tbody>
</table>

### 2.3 Fuelling fuel cells

As described in Section 2.1., PEFC systems operate on hydrogen or a hydrogen-rich gas. In a sustainable transport system, the hydrogen should preferably be produced from inexhaustible, democratically distributed resources (e.g. solar or wind). The fuel cell systems will then have the possibility to provide zero local and global emissions. The storage of hydrogen in a safe, reliable, and cost-effective manner is one of the major technical challenges for realization of the envisioned use of hydrogen in the transport sector. The difficulties result from the fact that hydrogen is not a natural resource, but an energy carrier, and therefore has to be produced from other resources. Further, the volumetric density of gaseous hydrogen is very low (0.084 kg·m⁻³ at NTP compared to ~820-840 kg·m⁻³ for diesel \[63\]). This makes the storage and distribution of hydrogen difficult, particularly within the size and weight boundaries of a vehicle. Energy transformations will enable distribution of limited amounts of hydrogen energy and are always associated with energy losses \[64\]. Currently considered alternatives for hydrogen storage include compression in gas cylinders (@ 350-750 bar), storage as a cryogenic liquid (@ -253 °C), and storage in advanced materials (e.g. metal hydrides) \[7\]. However, limitations due to the absence of a refueling infrastructure, logistic problems associated with refueling, safety issues, as well as high energy demand, cause these technologies not yet to be viable for use in automotive applications. To reduce energy use and cost related to distribution, the most preferable method is probably to produce the hydrogen locally, which for trucks means onboard the vehicle. This can be done by means of electrolysis or fuel processing \[7\]. In electrolysis, water is split into hydrogen and oxygen using an electric current passing through two electrodes, i.e. the reverse of the fuel cell process. Electrolysis provides high-purity hydrogen but is energy intensive and expensive and the need for water and electricity makes it unsuitable for use onboard trucks. The most realistic solution to generating fuel cell anode feeds presently may therefore be onboard hydrogen generation by processing the existing truck fuel. Designing the system around a fuel that is readily available to the end user is considered very important for market uptake, and differentiates the APU from other applications. Today, trucks are generally run on fossil diesel but eventually, diesel can be replaced with biomass-derived fuels, such as Fischer-Tropsch diesel or DME, as the production capacities of those fuels are increasing. The fuel processing of transportation fuels into hydrogen-rich gases is addressed in the following chapter.
CHAPTER 3

FUEL PROCESSING FOR FUEL CELLS IN AUXILIARY POWER UNITS

Fuel processing technologies are used to extract hydrogen from a hydrogen carrier, which for fuel cell auxiliary power units will be a transportation fuel. The fuel processor typically comprises a reformer, which is used to convert the fuel into a hydrogen-rich gas, and a number of gas cleanup steps, whose task is to remove impurities prior to entering the fuel cell. The nature of the truck fuel will affect the complexity of the fuel processor. This chapter covers reforming processes and catalysts for fuel processors in FC-APU systems. Cleanup steps are briefly mentioned at the end of the chapter. As a background, the fuels in focus are described.

3.1 Fuels

In the search for alternative solutions in the transport sector, available and novel technologies are competing in terms of well-to-wheels climate effects, energy efficiency, and land use effectiveness. Other factors of importance are versatility, infrastructure, safety and economics as well as the use of non-fossil feedstocks. Figure 3.1 shows liquid fuel pathways from different resources for internal combustion engines (spark ignition and compression ignition engines), and fuel cell or hybrid vehicles.

Due to their beneficial fuel economy, long-haul trucks are generally operated by compression-ignition engines, which use the heat of highly compressed air to ignite a spray of fuel introduced after the start of the compression stroke. In this thesis, diesel and dimethyl ether have essentially been the fuels in focus for reforming in fuel cell auxiliary power systems. Diesel, because it is the most commonly used fuel in trucks today, and DME, because it has been identified as a possible diesel fuel alternative. The following sections provide a background to the characteristics of diesel and DME, respectively. In addition, gasoline, ethanol, E85, and methanol were used in the fuel-flexible reactor concept, which is further described in Chapter 5.
3.1.1 Diesel fuel

The diesel combustion process, patented in 1892 by Rudolf Diesel, requires a fuel that will ignite easily. The ignition quality is determined by the nature of the hydrocarbons present in the fuel mixture and is defined by the cetane number. A high cetane number will not only improve ignition characteristics but also lead to lower emissions and noise. Diesel fuel constituents have to decompose easily at high pressure and temperature. This means that straight-chain paraffins are ideal fuel components that will increase cetane number, whereas (in contrast to gasoline) olefins and aromatics are not. Diesel fuel is obtained by refining of crude oil (fractional distillation at \( \sim 200-350 \, ^\circ\text{C} \)) or produced synthetically through gas-to-liquid (GTL), biomass-to-liquid (BTL) or transesterification processes. Diesel fuel mixtures consist of a complex mixture of hundreds of different hydrocarbons, the average chemical formula can be described by \( \sim \text{C}_{14}\text{H}_{26} \). The composition of fossil diesel fuels varies considerably worldwide. Swedish diesel fuel typically contains 50-70 % paraffins, 30-45 % cycloparaffins, and 3-5 % aromatics (Table 3.1) [65] while US diesel may contain up to 35 % aromatics [66]. The quality of the fuel depends largely on the nature of the crude oil. Fossil diesels will also contain sulfur compounds, which could cause corrosion and affect
Table 3.1 Examples of diesel hydrocarbon components (adapted from Liu et al. [67]) and typical composition of Swedish diesel fuel

<table>
<thead>
<tr>
<th>Compound type</th>
<th>Composition</th>
<th>Representative structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffins</td>
<td>50-70 %</td>
<td><img src="image" alt="Paraffins structure" /></td>
</tr>
<tr>
<td>Cycloparaffins</td>
<td>30-45 %</td>
<td><img src="image" alt="Cycloparaffins structure" /></td>
</tr>
<tr>
<td>Aromatics</td>
<td>3-5 %</td>
<td><img src="image" alt="Aromatics structure" /></td>
</tr>
</tbody>
</table>

1Alkyl benzenes 2Indans 3Tetralins 4Indenes 5Alkynaphthalenes 6Biphenyls

emissions and exhaust aftreatment systems negatively. Lately, more stringent emission regulations have led to decreased sulfur content in diesel fuels and the adoption of so called “sulfur-free” (<15 ppm) fuels in many countries. In addition, diesel fuels typically contain additives such as ignition quality improvers, detergents, cold flow additives, flow improvers, lubricity additives, antifoam additives, antioxidants, antistatic additives, biocides etc. [63].

The high energy density and existing infrastructure make diesel suitable as a hydrogen carrier for truck APUs. On the other hand, one might realize that the complex and unspecified nature of the fuel brings challenges to the reforming process.

3.1.2 Dimethyl ether as a diesel fuel alternative

DME, with the chemical formula H₃C-O-CH₃, is a colorless, gaseous compound at room temperature and atmospheric pressure. It is biologically degradable and considered non-hazardous from a health point of view. The key physical properties and combustion characteristics of DME are summarized in Table 3.2 and compared to diesel fuel.

The possible application areas for DME are several and make it attractive in a long-term perspective. Today, the major application of DME is as an aerosol propellant, for example in hairsprays and paintsprays, where it has replaced the formerly used ozone-destroying chlorofluorocarbons (CFCs). Other possibilities are to use DME for power generation (in turbines or stationary fuel cells), as a cooking gas (substitute or blend for liquid petroleum gas, LPG), for industrial use (as a chemical feedstock, solvent or refrigerant), and for transportation applications (in compression ignition engines or fuel cell vehicles).

The first use of DME in transportation applications was as an ignition improver for methanol in compression ignition engines [68, 69]. But rather than regarding DME as
improving the methanol combustion characteristics it may have been more correct to look on methanol as a contaminant deteriorating the ignition of DME. DME was at that time synthesized through methanol dehydration in an expensive process and was therefore not considered a potential fuel. In the 90’s, the use of DME as a fuel achieved renewed attention. A low cost synthesis route was developed [70]. DME could now be produced directly from synthesis gas, instead of via a first methanol synthesis step. DME can be produced from numerous feedstocks including natural gas, coal, and biomass, at lower energy input and greenhouse gas emissions than other GTL or BTL fuels [71].

As a compression ignition engine fuel, DME could offer high efficiency from well to wheels [71]. It is an interesting diesel fuel candidate from several points of view. The cetane number is very high, which means that the ability to autoignite is good. Diesel fuel generally has a cetane number of around 50 while for DME it has been estimated to be above 65 [72]. A high cetane number is desirable since it gives rise to shorter ignition delays, which is advantageous as the NOx emissions can be reduced. It has also been shown that DME can be operated with high exhaust gas recirculation (EGR) allowing for further lowering of nitrogen oxides [73-75]. No carbon-carbon bonds and high oxygen content (35 wt%) minimize the tendencies to producing particulates during combustion and, therefore, the NOx/particulate trade-off problem in a diesel engine will not exist for DME [75]. Furthermore, DME can be used as a NOx-reducing agent in exhaust aftertreatment systems with high conversion over a wide range of temperatures (~275 - 450 °C) [76, 77]. To be able to run a diesel engine on neat DME, the injection system has to be adapted. The lower heating value of DME is 29 MJ/kg (compared to 42 MJ/kg for diesel [78]) and the density is 666 kg/m³, meaning that it is necessary to inject a larger volume of fuel into the engine. This leads to long injection periods, which could lead to increased combustion temperature.

### Table 3.2 Key properties of DME compared to diesel [66]

<table>
<thead>
<tr>
<th>Property</th>
<th>DME</th>
<th>Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>CH₃OCH₃</td>
<td>~ C₁₄H₂₆</td>
</tr>
<tr>
<td>Molecular weight [g/mol]</td>
<td>46.1</td>
<td>~ 194</td>
</tr>
<tr>
<td>Carbon content [wt%]</td>
<td>52</td>
<td>86</td>
</tr>
<tr>
<td>Hydrogen content [wt%]</td>
<td>13</td>
<td>14</td>
</tr>
<tr>
<td>Oxygen content [wt%]</td>
<td>35</td>
<td>0</td>
</tr>
<tr>
<td>Boiling point @ 1 bar [°C]</td>
<td>-24.8</td>
<td>~ 150 – 380</td>
</tr>
<tr>
<td>Vapor pressure @ 20°C [bar]</td>
<td>5.1</td>
<td>–</td>
</tr>
<tr>
<td>Liquid density @ 20°C [kg/m³]</td>
<td>666</td>
<td>800 – 840</td>
</tr>
<tr>
<td>Relative density, gaseous (air=1)</td>
<td>1.59</td>
<td>–</td>
</tr>
<tr>
<td>Liquid viscosity @ 25°C [kg/m·s]</td>
<td>0.12 – 0.15</td>
<td>2 – 4</td>
</tr>
<tr>
<td>Lower heating value [MJ/kg]</td>
<td>29</td>
<td>42</td>
</tr>
<tr>
<td>Autoignition temperature [°C]</td>
<td>350</td>
<td>206 a</td>
</tr>
<tr>
<td>Flammability limits in air [vol%]</td>
<td>3 – 17</td>
<td>0.6 – 6.5</td>
</tr>
<tr>
<td>Cetane number</td>
<td>&gt;&gt;55</td>
<td>40 – 55</td>
</tr>
<tr>
<td>Sulfur content [wt-ppm]</td>
<td>0</td>
<td>10 – 500</td>
</tr>
</tbody>
</table>

* n-cetane
and consequently increased NO\textsubscript{x} emissions, requiring advanced injection strategies. However, the low boiling point and surface tension of DME allows very fast evaporation of the fuel.

The physical characteristics of DME are similar to those of LPG, a proven commercial product stored and transported globally. Disadvantages arise from the low viscosity and low lubricity of DME, leading to problems with leakages and with lubrication of moving parts. DME is also a good organic solvent, which could lead to problems with gaskets and sealings. In addition, due to the lower energy content, lower liquid density and the need for a vapor space above the fuel in the tank, running a compression ignition engine on DME will require a tank twice the size to drive the same distance compared to diesel fuel [79].

A number of test vehicles have already been developed, demonstrating the feasibility of DME for use in CI engines. In Sweden, a field test with 14 third generation BioDME trucks will start at the end of 2009 [80]. The project will demonstrate the whole technology chain, from biomass to fuel in the trucks, including distribution and filling stations for DME. The fuel will be produced via black-liquor gasification at a Swedish pulp mill [81].

As a hydrogen carrier for fuel cells, DME requires a lower reforming temperature than diesel, with the possibility to obtain low concentrations of CO and high hydrogen yields.

3.2 Reforming chemistry

3.2.1 Principal reactions

There are three major reforming technology options for producing hydrogen-rich fuel cell feeds from fuels: steam reforming (SR), partial oxidation (POX), and autothermal reforming (ATR). In steam reforming, the fuel is reacted with steam into hydrogen and carbon oxides. Partial oxidation is the conversion of fuels with oxygen in fuel-rich conditions. During autothermal reforming, thermally neutral conditions are obtained by combining the endothermic steam reforming and the exothermic partial oxidation reaction. Maximum energy efficiency for the fuel processing system can be obtained during autothermal reforming, where the heat needed for the steam reforming is supplied by partial oxidation. In practice, it is common that autothermal systems require the addition of a small amount of heat to compensate for heat losses and to obtain a more dynamic system; they are therefore operated at slightly exothermic conditions. The term autothermal is used more generally for processes where steam reforming is combined with partial oxidation and can also be referred to as oxidative steam reforming or combined reforming. Steam reforming can yield high concentrations of hydrogen but the main drawbacks are that the reaction is comparatively slow and needs an external heat supply. Partial oxidation is fast but the amount of hydrogen generated is lower and there is a risk of hot spot formation in the catalyst due to the exothermicity of the reaction. Automotive fuel processors have to be able to operate during both transient and steady state operation and with frequent startups and shutdowns. The more dynamic and energy-efficient ATR process is hence considered advantageous over SR and POX for transportation applications [82].

ATR is a very complex process and the overall reaction comprises a series of different reaction pathways. The major products formed during reforming are CO, CO\textsubscript{2}, and H\textsubscript{2}. CO\textsubscript{2}
is formed through the water-gas shift reaction, which also increases the hydrogen concentration. In addition, the reformate will contain steam and nitrogen. Methane or other light hydrocarbons may also be formed during ATR conditions. The principal reactions occurring during ATR conditions can be generalized as follows, for a hydrocarbon and DME, respectively (enthalpies reported for gaseous species):

### Steam reforming:

\[
C_xH_y + xH_2O \rightarrow xCO + \left( x + \frac{y}{2} \right)H_2 \quad \Delta H > 0 \text{ kJ/mol (3.1)}
\]

\[
CH_3OCH_3 + 3H_2O \rightarrow 2CO_2 + 6H_2 \quad \Delta H = 122 \text{ kJ/mol (3.2)}
\]

### Partial oxidation:

\[
C_xH_y + \frac{x}{2}(O_2 + 3.76N_2) \rightarrow xCO + \frac{y}{2}H_2 + \frac{x}{2} \cdot 3.76N_2 \quad \Delta H < 0 \text{ kJ/mol (3.3)}
\]

\[
CH_3OCH_3 + 1/2(2O_2 + 3.76N_2) \rightarrow 2CO + 3H_2 + 1.88N_2 \quad \Delta H = -38 \text{ kJ/mol (3.4)}
\]

### Total oxidation:

\[
C_xH_y + x(O_2 + 3.76N_2) \rightarrow xCO_2 + \frac{y}{2}H_2O + x \cdot 3.76N_2 \quad \Delta H < 0 \text{ kJ/mol (3.5)}
\]

\[
CH_3OCH_3 + 3(O_2 + 3.76N_2) \rightarrow 2CO_2 + 3H_2O + 11.3N_2 \quad \Delta H = -1330 \text{ kJ/mol (3.6)}
\]

### Water-gas shift:

\[
CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H = -41 \text{ kJ/mol (3.7)}
\]

### Carbon (coke) formation:

\[
C_xH_y \rightarrow \xi C + C_{x-\xi}H_{y-2\xi} + \xi H_2 \quad \Delta H \text{ hydrocarbon dependent (3.8)}
\]

\[
2CO \rightarrow C + CO_2 \quad \Delta H = 172 \text{ kJ/mol (3.9)}
\]

### Methanation:

\[
3H_2 + CO \rightarrow H_2O + CH_4 \quad \Delta H = -254 \text{ kJ/mol (3.10)}
\]

### DME decomposition:

\[
CH_3OCH_3 \rightarrow CO + H_2 + CH_4 \quad \Delta H = -1 \text{ kJ/mol (3.11)}
\]

#### 3.2.2 Thermodynamic considerations

During ATR operation, the oxygen-to-carbon (O\textsubscript{2}:C) and steam-to-carbon (H\textsubscript{2}O:C) ratios have to be optimized for the system under consideration in order to control the reaction temperature and product gas composition and at the same time prevent the formation of coke. The heat integration is unique for every system and should preferably be experimentally evaluated. Guidelines for where the desired operating conditions are likely to occur can be obtained by means of thermodynamic equilibrium calculations. However, equilibrium calculations do not take the kinetics of the reactions into account. The reactions
are assumed fast enough to reach chemical equilibrium at the end of the reactor. Furthermore, the types of catalyst and reactor used are ignored. Figure 3.2 shows equilibrium compositions of the product gas at varying operating conditions for autothermal reforming of diesel \((\text{C}_{14}\text{H}_{26})\) and DME, respectively, obtained by minimizing Gibb’s free energy using MATLAB® and the NASA CEA software [83]. For the equilibrium calculations, the reactants were assumed to be ideal gases, the reaction rates were assumed infinite and the process isothermal.

For diesel fuel (Figures 3.2a-c), maximum hydrogen concentration is obtained thermodynamically at around 700-750 °C. The CO concentration increases and the \(\text{CH}_4\) concentration decreases with the temperature, while the \(\text{CO}_2\) concentration is slightly decreased. Methane formed by methanation (Eq. 3.10) is thermodynamically favored at lower temperature, but methane could also be formed by cracking of hydrocarbons, which may be promoted by the reforming catalyst. Oxygen in the feed will decrease the hydrogen concentration (and nitrogen in the air will dilute the gas) and should therefore be kept at a minimum. Oxygen is used to provide heat for the steam reforming reaction, but also to reduce coke formation on the catalyst. The steam-to-carbon ratio reaches a maximum in hydrogen concentration at \(\text{H}_2\text{O}:\text{C}=1\). Reforming of higher hydrocarbons, such as diesel, is usually performed with higher amounts of steam in order to suppress coke formation and decrease the CO content by inducing the water-gas shift reaction. However, excess steam will dilute the reformate and decrease the overall efficiency of the fuel processor.

For DME (Figures 3.2d-f), similar trends can be observed, but a lower reforming temperature can be utilized. It is apparent that DME ATR conditions thermodynamically can generate high concentrations of hydrogen (~40-50 %) in combination with low CO concentrations (< 5 %) over a wide range of operating conditions. The maximum hydrogen concentration is obtained at the lowest temperature and lowest oxygen feed rate. The conversion of DME is not thermodynamically limited at temperatures \(\geq 200 \, ^\circ\text{C}\). Possible byproducts during DME ATR are methane (\(\text{CH}_4\)), methanol (\(\text{CH}_3\text{OH}\)) and formaldehyde (\(\text{HCHO}\)). \(\text{CH}_4\) may be formed via CO methanation (Eq. 3.10) or decomposition of DME (Eq. 3.11) and is thermodynamically favored. However, the rate of methane formation has been shown to be comparatively slow during experiments, and the catalysts normally used for DME ATR are considered unlikely to promote methane formation to any large extent.
Figure 3.2 Thermodynamic equilibrium compositions of the product gas during reforming of diesel (left column) and DME (right column) at varying operating conditions obtained by minimizing Gibb’s free energy (p=1 bar)
3.2.3 Prereforming of hydrocarbons

While the conversion of DME during reforming may be considered comparatively straightforward, the reforming of liquid hydrocarbons is more complex. During steam reforming of higher hydrocarbons, the hydrocarbon is adsorbed onto the catalyst surface, and the terminal C-C bonds are broken until the hydrocarbon is converted into C1 components [84]. This is a general mechanism, but the reaction rate can be assumed to increase with the carbon number for individual hydrocarbons. However, the longer hydrocarbons are also more prone to thermal cracking. Therefore, reforming of higher hydrocarbons may require a low-temperature prereforming step, where the fuel is broken down to shorter hydrocarbons to facilitate the subsequent catalytic ATR step. Prereforming will decrease cracking reactions and subsequently prevent coke formation, because cracking produces olefins and aromatics, which are precursors of carbon [85]. The prereforming process may be catalytic or based on homogeneous reactions. Lately, some studies focusing on the use of cool flames for use in diesel fuel reforming for fuel cells have been performed [86, 87]. During low-temperature oxidation, the heat release follows an Arrhenius behavior, rising exponentially with temperature. Whether ignition will occur depends on the heat losses from the system. Some fuels (including diesel) exhibit a certain temperature interval where a deviation from the Arrhenius curve occurs. This region is characterized by a decrease in the reaction rate with increased temperature and is termed NTC (negative temperature coefficient). In order to stay in the cool flame regime, and avoid ignition of the fuel, heat losses from the system are required. The cool flame occurs in a narrow temperature and pressure interval. The temperature where the cool flames are initiated decreases with increasing number of carbon atoms in the alkane used as fuel [88]. The occurrence of cool flames can kinetically be described by the competition between the formation of active OH• radicals and the splitting to R• + O2. In this way, periodically oscillating flames can occur. By using cool flame partial oxidation as a prereforming step in fuel cell fuel processors, the long hydrocarbon chains of diesel fuel can be broken down without being completely combusted.

3.3 Reforming reactor design

Industrial reformers are often large and bulky in order to overcome mass and heat transfer limitations. In onboard fuel cell applications, the design of the reformer is an important issue, because of the requirements considering cost, weight, volume, complexity and efficiency. The types of reformer designs are basically four, specifically fixed catalyst beds, monolith-based reactors, heat exchangers and membrane reactors. Catalysts used in automotive applications must be able to withstand mechanical stress caused by vibrations and frequent changes in load and operating conditions. Fixed bed catalysts may therefore not be suitable in automotive environments since they could easily be damaged by means of attrition. Furthermore, the higher thermal mass of e.g. pellets could cause problems with dynamic operation of the reformer [89]. Catalyst monoliths offer the robustness required in vehicular applications. Monoliths are extruded blocks of ceramics or metals containing straight parallel channels. Figure 3.3 shows examples of monolith substrates. The catalyst powder is
Figure 3.3 Catalyst monolith substrates. Left: Cordierite (2MgO·5SiO₂·2Al₂O₃) honeycomb structure. Right: Structure based on alternately flat and corrugated metal foils.

deposited onto the walls of the channels. A well-known application of monoliths is the three-way catalyst used for reduction of emissions in the exhaust from spark-ignition engines. The major advantage with monoliths is the high open frontal area providing a low pressure drop. A significantly lower Reynold’s number compared to a fixed bed will lead to decreased mass and heat transfer, which could be a drawback. Furthermore, since there is no mass transfer in the radial direction, the conversion could be negatively affected. It is therefore of great importance to obtain a high loading of catalyst and a uniform distribution of active material on the walls of the monolith. A Microlith® substrate has been developed recently, consisting of a series of short-channel-length, low thermal mass, catalytically coated metal meshes with very small channel diameters, with greatly improved mass and heat transfer characteristics [90]. Other types of microstructured reformers have also been developed, e.g. [91, 92]. In catalyst-coated plate heat-exchanger reactors, steam reforming can be effectively coupled with oxidation, allowing for a very compact design [93]. Future reformer designs are likely to comprise microstructured plate heat exchangers due to their potentially superior performance [94]. Finally, membrane reactors, which combine reforming with membrane separation, can be used. The most commonly suggested technology is Pd membranes for H₂ separation [95]. Another possibility is to use CO₂-selective membranes, based on ion-exchanged zeolites, in order to remove CO₂ from the reformate and in that way force the equilibrium of the water-gas shift reaction in the reformer towards higher hydrogen production [96].

3.4 Reforming catalysts

The catalytic reformer is the heart of the fuel processor and, therefore, high demands are placed on the reforming catalyst. Industrial steam reforming, typically of natural gas or naphtha, is performed over fixed bed Ni-based catalysts, where the catalyst utilization often is below 20 % due to diffusion limitations [97]. The poor utilization of the catalyst is circumvented by using excess catalyst, which is feasible due to the comparatively low cost of nickel. Further, the Ni-based catalysts promote coke formation and need regeneration. For
onboard fuel cell applications, a much better utilization of the catalyst is necessary. The catalyst should be highly active and selective in order to obtain a compact and light fuel processor with low complexity. The catalyst should also be thermally resistant, survive potential poisons in the fuel and be able to withstand the harsh conditions on the frame rails of the truck. Another difference from large-scale industrial reformers is that the system will operate during transient conditions and for numerous startups and shutdowns. An additional problem with Ni, which usually not is brought up in conjunction with catalysts, is its allergenic properties. Consequently, Ni is in many companies often a restricted substance [98].

This section provides a brief introduction to reforming catalyst technology followed by an outline of state-of-the art of diesel and DME ATR catalyst development for fuel cell applications.

3.4.1 Reforming catalyst technology

The reforming catalyst typically comprises a substrate, a support, and an active material. The role of the substrate is to give structure to the catalyst and to facilitate the transport of reacting molecules between the gas phase and the catalyst surface. The substrate may be e.g. pellets or monoliths, as previously described in Section 3.3. The support, also termed washcoat, is used as a carrier to disperse the active material. The active material is a metal or a metal oxide. It is often important to disperse the active material on a large surface area in order to maximize the number of active sites, especially if expensive noble metals are used. The support could also function by increasing the activity and stability of the active components, by providing metal-metal or metal-support interactions. In some cases, the support directly participates in the reforming reactions. It is important that the support be stable at the specific operating temperature considered. Undesired phase transformations of the support could cause sintering and encapsulation of active material and, subsequently, loss of activity. One of the most commonly used washcoat materials is γ-alumina (γ-Al₂O₃). The surface area of γ-Al₂O₃ is high, typically around 200 m²/g. However, at elevated temperatures other transitional phases with lower surface area are formed, termed δ, θ and α, respectively. The δ and θ phases are formed at ~ 900 and 1000 °C, respectively, whereas the α phase is formed at ~1200 °C and has a surface area of only a few m²/g [99].

There are many different methods for preparation of heterogeneous catalysts, the two most common, and the ones used in the work in this thesis, being impregnation and coprecipitation. In impregnation techniques, a solution of a metal salt is added onto a support. Incipient wetness impregnation is a very straightforward method, where incipient wetness indicates that the volume of the solution should be just enough to fill the pores of the support. After drying, the material is calcined, which means thermal treatment in order to generate the active phase (metal or metal oxide) on the surface of the catalyst, to get rid of chemically bound water and to stabilize the mechanical properties. For large-scale industrial preparation of catalysts, wet impregnation is a preferred technique. Here, a larger volume of solution than required to fill up the pores is used. The excess liquid is then removed prior to drying and calcination. Coprecipitation means the simultaneous precipitation of more than
one component, which could make possible a close interaction between the various components.

The performance of reforming catalysts is usually evaluated in terms of conversion, selectivity and yield. Conversion is defined as the amount of fuel reacted divided by the amount of fuel fed to the reactor. Selectivity is a measure of the distribution of the converted species to the different products whereas the yield is the conversion times the selectivity, which can be used to express the ratio of the amount of a specific product to the amount of fuel normalized by the stoichiometric factors. Besides activity and selectivity, reforming catalysts need to be proven to have high durability.

3.4.2 Diesel reforming catalysts

The complex and varying composition of diesel fuel, poses difficulties when it comes to quantification of reactant and product gas composition and evaluation of reforming catalysts. Therefore, relatively few experimental studies have been performed using real diesel fuel mixtures. Some studies, though, have been performed dealing with reforming of road transport diesel [100-102] as well as military [103-106] and jet fuels [107-110], although the more common approach is to use a model compound, such as n-hexadecane (C_{16}H_{34}) [105, 111-115] or n-dodecane (C_{12}H_{26}) [116, 117], or alternatively a simulated fuel mixture comprising a few hydrocarbons [117-121]. The different components in diesel fuel vary largely in reactivity and the reactivity of one component could affect the reactivity of others, i.e. the reforming performance using a fuel mixture is not simply the sum of the separate components [121]. The composition of the fuel mixture will not only affect the overall reaction rate but also carbon formation and deactivation by sulfur poisoning. For these reasons, the importance of studying real fuel mixtures, and developing a catalyst for the conditions at hand, need to be emphasized. Further, most catalyst studies consider materials in the form of powders. More effort is needed to study catalyst performance using engineered substrates suitable for real-life applications.

For diesel ATR, a catalyst active for both steam reforming and partial oxidation of hydrocarbons is required. The fast partial oxidation reaction is considered to occur at the catalyst entrance followed by steam reforming downstream the bed [122]. Therefore, different catalyst materials could be used in different parts of the reactor. The catalysts that have been studied for autothermal reforming of diesel or surrogate fuels for diesel can be divided into base and noble metal materials. The metals are usually dispersed or incorporated into an oxide support, such as alumina, ceria, zirconia, magnesium aluminate, or perovskites. The supports can be further promoted or doped with other metals in order to improve activity or thermal stability of the catalyst. The operating temperature of a diesel reforming catalyst is typically between 700 and 900 °C.

3.4.2.1 Base metal catalysts

Base metal catalysts may typically be Ni, Co, or Fe. Unmodified Ni-based catalysts tend to deactivate rapidly as a result of both carbon deposition and sintering. Ni-based catalysts are therefore normally modified with some promoter, in order to limit coke deposition, or
incorporated into a coke-resistant lattice. Promoters are typically alkali oxides, such as K$_2$O, which function by neutralizing the acid sites supposed to be responsible for coke formation [123]. Sulfur present in hydrocarbon fuels is also a source of deactivation of Ni catalysts. Sulfur adsorption causes excessive coke deposition by blocking reforming reactions while C-C and C-H bond cleavage can continue to occur. Due to the tough requirements on reforming catalysts in fuel cell applications, noble metal catalysts may be required and the major part of the studies found in the literature is focused on noble metal-based catalysts. There are, however, cases where base metal oxide catalysts are suggested to be a viable option. For example, Ni supported on a La/Ce-modified alumina have been shown to be more active than Pt on the same support and more selective towards hydrogen production for ATR of pure hexadecane, decalin and tetralin, respectively [124]. This was explained by a greater Ni-ceria interface, leading to enhanced significance of the ceria promoter by increasing the rate of the reaction of steam (enhanced water adsorption) with both reactant molecules and surface carbon. Ni supported on ceria-zirconia has been reported to give “relatively high” conversion for autothermal reforming of jet fuel surrogates without significant deactivation [125]. Another group has tested NiO/MgO/La$_2$O$_3$/Al$_2$O$_3$ catalysts in a process for hydrogen generation from light-distillate Fischer-Tropsch fuel. By using catalytic steam reforming at low temperature as a prereforming step followed by ATR, coke formation could be minimized [126].

3.4.2.2 Perovskites

Oxygen ion-conducting perovskites have also been suggested as diesel ATR catalysts, being another low-cost alternative to noble metals. Perovskites consist of a rare earth element A and a first row transition metal B in the form ABO$_3$. The perovskites can also be doped with other transition metals in order to increase stability. LaNiO$_3$ and LaCoO$_3$ have been reported to exhibit high hydrogen yields during autothermal reforming of hydrocarbons but these catalysts generally have insufficient structural stability. Partial substitution of the A and B sites into a material comprising La$_{0.8}$Sr$_{0.2}$B$_{0.9}$Ni$_{0.1}$O$_3$, where B=Cr, Mn or Fe, was shown to improve the structural stability without decreasing the hydrogen yield [127]. Sr-doped perovskites have also been tested for low-sulfur diesel fuels. La$_{0.5}$Sr$_{0.5}$CoO$_3$ and La$_{0.5}$Sr$_{0.5}$FeO$_3$ were designed to contain oxygen anion vacancies for rapid diffusion of oxygen in the bulk, allowing for efficient oxidation of adsorbed surface carbon from beneath [101]. The materials were tested for reforming of commercial diesel fuel in a membrane reactor and showed good activity although the reaction of sulfur with lanthanum and strontium was pointed out as a concern. The perovskite catalysts were deactivated already at 5 ppm sulfur in the feed. Another study has demonstrated high sulfur tolerance of perovskites where the B site is partially substituted by Ru during autothermal reforming of a simulated fuel mixture containing 50 ppm sulfur [128]. The highest hydrogen yield was obtained with a LaCr$_{0.5}$Ru$_{0.5}$O$_3$ catalyst. Ru is suggested to participate in the ATR reaction through a redox mechanism. ZrO$_2$-supported LaCoO$_3$ has also been reported to be very active and stable for oxidative reforming of diesel (12 ppm sulfur) [102].
3.4.2.3 Noble metal catalysts

As noble metals are highly active and have the ability to inhibit coke formation, they are more commonly adopted in studies found in the literature. Pt, Ru, Rh and Pd are noble metals that have been reported to be active for diesel ATR. Pt supported on alumina or ceria-based supports are commonly suggested materials for reforming of longer hydrocarbons [120, 129-131]. Sulfur-tolerant catalysts based on a group VIII metal and an oxide ion-conducting support have been patented for use in reforming of a large variety of hydrocarbons [132]. An analogous catalyst formulation, Pt supported on Gd-doped ceria, has been reported to exhibit significantly improved performance compared to conventional reforming catalysts, although the hydrogen yield during ATR of a commercial sulfur-containing diesel fuel was considerably lower than for hexadecane [114]. Ru on ceria-doped alumina was shown to operate in a stable manner during 8000 h using desulfurized kerosene [110]. Rh/γ-Al₂O₃ catalysts have been successfully tested for autothermal reforming of JP-8 fuel in millisecond contact time reactors [105]. Bimetallic catalysts have been shown to be superior to their monometallic counterparts in terms of activity and thermal stability during diesel ATR [100, 133]. The enhanced performance is explained by strong metal-metal and metal-support interactions, i.e. structural and electronic effects, rather than the degree of metal dispersion. Pt-Pd and Pt-Ni supported on ceria were reported to be stable running on JP-8 fuel, whereas the monometallic catalysts lost activity during time on stream [133]. Improved sulfur resistance has also been shown for Rh-Pt bimetallic catalysts tested for commercial low-sulfur diesel fuel [134].

3.4.3 DME reforming catalysts

The interest in using DME as hydrogen carrier for fuel cells started in the late 90s’, after the development of the low-cost DME synthesis process [135]. The studies on hydrogen generation from DME performed since then concern, with a few exceptions, the steam reforming process. Steam reforming of DME is generally considered to proceed via two succeeding reactions [136-139]. The first step is hydrolysis of DME into methanol (Eq. 3.12) and the second step is steam reforming of methanol (Eq. 3.13).

\[
\text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \rightarrow 2\text{CH}_3\text{OH} \quad (3.12)
\]

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}_2 \quad (3.13)
\]

The common approach is to use a solid acid catalyst for the hydrolysis of DME to methanol, e.g. H-mordenite, ZSM-5, Zeolite Y, ZrO₂ or γ-Al₂O₃ [140-143], combined with a methanol reforming catalyst, among which Cu is the most commonly adopted material. It could be either a physical mixture of a DME hydrolysis catalyst and a methanol steam reforming catalyst or a single dual-function catalyst. DME hydrolysis is thermodynamically limited (see Figure 3.4) but when methanol steam reforming occurs simultaneously, high DME conversions can be achieved [144].
Acid site density, strength of the acid sites, and hydrophobicity have been suggested to influence the activity of the hydrolysis catalyst [141, 145]. The hydrolysis of DME to methanol over $\gamma$-Al$_2$O$_3$ occurs in the temperature range of 300-400 °C [145] with high product quality and stability. For zeolites, equilibrium may be reached at 200-300 °C [145]. However, zeolites could generate long-chain hydrocarbons through the methanol-to-gasoline (MTG) reaction, especially at temperatures above 300 °C [141, 143, 145]. The higher temperature required for equilibrium over $\gamma$-Al$_2$O$_3$ has been explained by the potentially inhibiting effect of adsorbed water [146]. ZrO$_2$ has also been tested for DME hydrolysis but did not reach predicted equilibrium conversions of DME during experiments [144].

Copper catalysts are widely known to have high activity for steam reforming of methanol. This reaction occurs at temperatures of 200-300 °C [147], but the durability of copper will be a concern if $\gamma$-Al$_2$O$_3$ is used as support. Copper catalysts are prone to sintering at temperatures above approximately 300-350 °C [148] leading to loss of activity. Therefore, they must be made thermally stable for use in reforming of DME. Copper-based spinel oxides (CuMn$_2$O$_4$ and CuFe$_2$O$_4$) have been reported to suppress sintering of copper at temperatures up to 400 °C during DME steam reforming [149, 150].

Palladium catalysts have also been shown to exhibit high activity for DME steam reforming, however associated with the formation of large amounts of CO [137, 138]. This is not surprising, since Pd is known to be selective for methanol decomposition (Eq. 3.14) [151, 152]. For use in methanol steam reforming, zinc can be incorporated with the palladium to promote the selectivity to CO$_2$ and H$_2$ [153-155]. The similar catalytic properties of Cu and PdZn during methanol steam reforming have been ascribed to the similar electronic structures of the two, which is different from that of metallic Pd [156].

$$CH_3OH \rightarrow CO + 2H_2 \quad (3.14)$$

Figure 3.4 Thermodynamic equilibrium composition and DME conversion during DME hydrolysis as a function of temperature at H$_2$O:DME=3 and p=1 bar
Partial oxidation of DME has been studied over various metal catalysts supported on Al₂O₃ and over nickel on different supports [157, 158]. Ni supported on LaGaO₃ and Rh supported on Al₂O₃ have been reported as active and selective catalyst materials. The reaction has been suggested to proceed through the oxidation of methyl (-CH₃) or decomposition of methoxy (-O-CH₃) species formed by dissociative adsorption of DME [158]. The autothermal reforming process will require a catalyst active for both steam reforming (i.e. both DME hydrolysis and MeOH steam reforming) and partial oxidation of DME. As for the diesel reforming catalyst, it could be possible to use separate catalyst segments for partial oxidation and steam reforming.

### 3.5 Gas cleanup

#### 3.5.1 CO cleanup

The aim of the CO cleanup steps downstream the reformer is to reduce the CO content in the reformer product gas to levels where the losses in fuel cell performance are negligible. As described in Chapter 2, this level will depend on the operating temperature of the fuel cell. Water-gas shift (WGS) (Eq. 3.7) and preferential oxidation (PrOx) (Eq. 3.15) are the two main processes used for removing CO from the reformer product gas.

\[ CO + \frac{1}{2}O₂ \rightarrow CO₂ \]  

(3.15)

**Figure 3.4** Fuel processor for a fuel cell auxiliary power unit. Diesel fuel is converted into a hydrogen-rich gas in the reformer, the hydrogen content is optimized using water-gas shift (WGS) and the CO content is reduced to a level the PEFC can tolerate by preferential oxidation (PrOx). (© PowerCell)
Water-gas shift is thermodynamically favored at low temperatures and is therefore often separated into two steps with cooling in between, one operating with fast kinetics at 300-400 °C (HTS - high-temperature shift) and another operating at 200-300 °C (LTS – low-temperature shift). The concentration of CO after the shift steps is typically 0.5-1 % [159]. The gas can then be fed to a PrOx reactor, where CO is selectively oxidized resulting in an expected CO concentration below 50 ppm [160]. The main drawbacks with this process are that hydrogen oxidation will be a competing reaction and that the addition of nitrogen via air will further dilute the fuel cell feed gas. A fuel processor for a fuel cell APU is shown in Figure 3.4 and as part of a typical APU system in Figure 3.5.

3.5.2 Sulfur removal

A major challenge in reforming logistic fuels is the inherent sulfur content, which will deactivate the catalysts in the fuel processor. Besides poisoning the catalyst, increased carbon formation has been reported during reforming of sulfur-containing feeds [120, 161]. The sulfur content varies considerably between different fuels. In many countries, more stringent regulations for diesel fuel standards have been adopted lately (<50 ppm in the EU [66] and < 10 ppm in Sweden [65] for road transport diesel), while other diesel fuels may contain 300-3000 ppm sulfur or more. Sulfur may be removed from the fuel by deep desulfurization using hydrotreating catalysts or adsorptive desulfurization [162]. Sulfur-free diesel (e.g. Fischer Tropsch diesel) is currently not widely available and, therefore, onboard desulfurization and sulfur-tolerant catalysts are needed. Sulfur compounds may be removed either prior to or after the reformer.
Figure 3.5 A typical FC-APU system comprising fuel processing, air supply, water and heat management systems and fuel cell stack (adapted from Bodén [62])
CHAPTER 4

HYDROGEN GENERATION FROM DIESEL FUEL (PAPERS I-II)

The first part of this thesis has described the context of the work in the appended papers and motivated the use of fuel cell auxiliary power systems onboard heavy-duty trucks. Also, a literature survey covering recent research in reforming catalyst technology has been provided. Challenges associated with the systems have been identified and resulted in a number of technology choices, which have led us to autothermal reforming of the onboard fuel supply over a monolith-type catalyst based on noble metals to generate hydrogen-rich anode feeds for polymer electrolyte fuel cells in truck auxiliary power units. The following part of the thesis will present results from the appended papers. The work includes reactor design considerations, preparation and testing of reforming catalysts including characterization studies and evaluation of reaction conditions during operation.

This chapter summarizes the results from Papers I-II, addressing hydrogen generation from diesel fuel by autothermal reforming. The studies have been focused on the development of an appropriate reformer design, including an active and selective catalyst. A kW-scale reformer was designed and experimentally evaluated (Paper I). Reactor design considerations as well as the impact of operating conditions on the activity and product composition is discussed. Also, computational fluid dynamics (CFD) is used as a tool to try to explain the major characteristics of the reactant mixing. The work resulted in a new improved reformer design. In addition, a small-scale reactor has been used to test Rh and Ru-based catalysts for diesel ATR (Paper II). The potential of adding manganese as a means of reducing precious metal content is considered.

4.1 Important issues in diesel fuel reforming

Reforming of liquid hydrocarbon mixtures, such as diesel, is accompanied by a number of challenges, which remain to be solved before a large-scale production of diesel fuel processors in FC-APUs could be realized. As described in Chapter 3, diesel fuel is a middle distillate of crude oil comprising a mixture of hydrocarbons with a boiling point interval between \(~200\) and \(350\) °C. The hydrocarbons are primarily n-paraffins and cycloparaffins but also aromatics and polyaromatics. The complex and often poorly specified composition of the fuel gives rise to challenges to obtain complete fuel conversion and to prevent coke formation. Compared to idealized diesel-like model fuels, such as n-hexadecane and
n-dodecane, reforming of commercially available fuels results in additional difficulties. The activity and selectivity depend largely on the fuel properties. During reforming of individual compounds, the $H_2$ production rate has been shown to decrease in the order n-paraffins > cycloparaffins >> aromatics [119, 121]. Olefinic and aromatic hydrocarbons in diesel are known to be precursors of coke and need to be minimized [85, 122]. For these reasons, a highly active and selective catalyst is required. Also, the catalyst should be durable considering metal vaporization and agglomeration as well as stability of the support at higher temperatures, and considering poisoning by impurities in the fuel.

Other challenges with diesel ATR are fuel injection and evaporation. A poor fuel spray could result in wetting of the reactor walls and catalyst. If a homogeneous mixture of reactants is not obtained, a non-uniform distribution of fuel and temperature will create risks of incomplete fuel evaporation and formation of hot spots. Furthermore, heavier hydrocarbons may react pyrolytically in fuel-rich areas, resulting in coke formation. These issues calls for an appropriate reactor design and optimization of the reforming process.

4.2 Reformer design

4.2.1 Description of the ATR

The diesel reformer was designed considering a hydrogen production to feed a 5 kW$_e$ PEFC, taking into account a fuel cell system efficiency of 0.4 and an anode stoichiometry of 1.5. The reactor is shown schematically in Figure 4.1. The key design factors considered were compactness, robustness and simplicity. The reactor is made of stainless steel and operates at atmospheric pressure. It consists of two different parts. In a first section, the fuel is evaporated and mixed with air and steam and homogeneous prereforming reactions partially break down the fuel. In a subsequent section, the mixture is reacted over a monolithic catalyst (78 mm diameter, 100 mm length) into a hydrogen-rich gas. Air and steam are mixed outside the reformer and preheated to 300 °C. The air/steam mixture is then fed via a mantle covering the reactor, allowing for indirect heat exchange with the inside of the reformer, and then enters the reactor through holes perpendicular to the reactor flow direction (see Figures 4.1 and 4.2). The fuel is injected to the reformer through a single-fluid swirl nozzle and evaporated in the air/steam mixture. The nozzle generates a hollow cone of fuel, which breaks up into droplets and can provide good atomization at relatively low pressures.

The simple direct-injection concept for evaporation of diesel has been reported as advantageous for control over a wide range of operating conditions without the formation of coke [59, 104]. However, the more common approach is to use a dual-fluid nozzle, where the fuel spray is assisted by air or steam. These nozzles give finer sprays at low fuel pressure but may give increased penetration and result in the formation of coke on the nozzle tip. There are no available components dedicated for these systems and there is definitely a need for the development of nozzles, which operate at low pressure over a wide range of operating conditions. For more details on the reformer design, see Paper I.
Figure 4.1 Schematic drawing of the reformer design. T# shows the axial positions of the thermocouples (L - length of unit, x/L – relative position in the reactor)

Figure 4.2 Left picture: Flange seen from the inside showing the nozzle and the thermocouple inlets. Right picture: Inlet of reformer showing the holes where the air/steam mixture enters the reactor

Rh supported on Ce/La-doped Al₂O₃ was chosen as reforming catalyst. Alumina was used because of its high surface area and stability and ceria and lanthana were added to the support as structural and textural promoters. Ceria has high oxygen-storage capacities resulting in a number of advantages for reforming catalysts, such as oxidation/reduction reversibility of the active metal, stabilization of metal dispersion, support of the mechanism of carbon removal from the metal surface and increased sulfur resistance [110, 163, 164]. Moreover, ceria promotes reforming reactions and water-gas shift by enhancing the adsorption and dissociation of water molecules [165, 166]. Lanthana is known to stabilize alumina towards temperature-induced phase transitions [167]. The catalyst was deposited on
cordierite monolith substrate. Further information on the preparation procedure is outlined in Paper I.

4.2.2 Mixture formation

As already mentioned, mixture formation is an important factor in the diesel reforming process. CFD modeling was used to study the mixing process in the reformer. The calculations were performed in the program STAR-CD (see Paper I for details). Figure 4.3 shows the velocity field distribution in the mixing section of the reactor. As can be seen in the figure, the model suggests that stagnant zones of recirculated air/steam mixture are formed adjacent to the nozzle. These findings indicate that the mixing is insufficient and that hot spots may be formed. Such a flow profile would also be favorable for the formation of coke on the nozzle and reactor wall [168]. Further, an inhomogeneous reactant mixture will lead to less efficient utilization of the catalyst. During the experiments, no coke was found, either on the catalyst or on the inside of the reactor, during any of the experiments. However, small amounts of carbonaceous material were found in the reactor effluent condensate. Even if the results from the computational analyses are associated with discrepancies regarding assumptions, especially due to insufficient nozzle characteristics, the approach could be used to explain some of the major characteristics during operation of the reformer and has been supportive for optimization of a new reactor design. The poor reactant distribution in the mixing section was explained by the design of the air/steam injection. A more favorable flow profile could be obtained by placing the inlet holes further upstream the reformer.

Figure 4.3 Velocity profile in the mixing section of the reformer at 400 ms obtained from CFD calculations (mean fuel droplet diameter: 50 μm)
4.3 Influence of operating parameters

The heat integration is unique for every reactor design and needs to be experimentally evaluated. The temperature profile was studied during reforming by measuring the temperature with thermocouples (K-type) at different radial and axial positions (see Figure 4.1). The reforming performance was studied by varying the oxygen-to-carbon ratio ($O_2:C$) and the steam-to-carbon ratio ($H_2O:C$). Considering the $O_2:C$ ratio, it is important to have enough oxygen in the feed to generate heat for the steam reforming reaction, but too much oxygen will result in loss of efficiency due to complete combustion of the fuel as well as dilution with nitrogen. Regarding the $H_2O:C$ ratio, there are two options in a fuel processor. Either, steam is added in several steps, first in the reformer and then in the water-gas shift units. Alternatively, all of the steam is added directly to the reformer. A surplus of steam in the reformer is advantageous for suppression of CO and coke, but at the expense of the cost to superheat a large amount of steam. Considering the volume and weight of the vaporizer and the condenser recovering the water from the fuel cell, a low $H_2O:C$ ratio would be preferable. Furthermore, additional water could be needed to lower the temperature in the WGS steps; thus it is unfavorable to add all of the steam directly into the reformer. This is especially the case when using fuels requiring high temperatures to be converted, such as diesel.

Swedish Environmental Class 1 diesel fuel, purchased from a public fuelling station, was used in the experiments. This fuel contains a maximum of 10 ppm sulfur and less than 5% aromatics [65]. Using a commercial fuel helps in gaining understanding of how the real fuel mixture affects conversion, product gas composition, carbon formation and deactivation by sulfur. During the experiments, a flow rate of 12 g/min of diesel fuel was fixed as design value and the oxygen-to-carbon ratio was varied between 0.3 and 0.45 and the steam-to-carbon ratio between 2 and 3. The catalyst volume was 0.5 dm$^3$ implying a gas hourly space velocity (GHSV) over the catalyst of between 7600 and 9200 h$^{-1}$. The product gas was analyzed using gas chromatography (GC). The GC instruments were equipped with thermal conductivity and flame ionization detectors (TCD and FID). The TCD was used for detection of CO, CO$_2$, H$_2$, N$_2$, and O$_2$. As it was not possible to calibrate the GC with all different kinds of plausible reactants and products, the responses from the FID were assumed to be proportional to the number of carbon atoms for all hydrocarbon structures. All products > C$_8$ were assumed to be unconverted diesel fuel reactants, similarly to previous studies reported in the literature [169]. The FID responses were then converted to C$_{14}$ equivalents and the fuel conversion was calculated by representing the inlet fuel with C$_{14}$H$_{26}$.

The reformer was successfully operated at $O_2:C$ values between 0.3 and 0.4. Temperature profiles at varying $O_2:C$ are shown in Figure 4.4. At $O_2:C=0.45$, large temperature fluctuations were observed, suggesting hot-spot formation resulting from insufficient mixing of reactants. Changes in the $H_2O:C$ ratio did not have a significant effect on the product composition and no coke was observed on the surface of the catalyst. Therefore, the reformer was operated at $H_2O:C=2$. 
Figure 4.4 Temperature profile in the reformer (T1-T9 in Figure 4.1) for O₂:C ratios of 0.3-0.45 at H₂O:C=2 (Diesel fuel flow rate: 12 g/min)

Figure 4.5 shows the product gas concentration of the key reforming products, H₂, CO₂, and CO and Figure 4.6 of C₁-C₄, C₅-C₈ and >C₈ hydrocarbons. The conversion of the fuel ranged from 99 to nearly 100 % (increasing with the O₂:C) at measured catalyst outlet temperatures of 675 °C. However, comparison to thermodynamic equilibrium concentrations indicate that the actual reforming temperature inside the monolith is substantially higher (~775 °C), shown in Figure 4.7 as product yields for O₂:C=0.4.

Improvements are needed to increase the activity for conversion of the hydrocarbons observed in the product gas in order to optimize the process in terms of efficiency as well as economics. A possible option could be to combust the hydrocarbons in an afterburner to generate heat for the fuel processor. However, the fuel cell performance is likely to be affected by the hydrocarbons.

Figure 4.5 Concentration of H₂, CO₂, and CO in the product gas at O₂:C=0.3-0.45 and H₂O:C=2
4.4 Reforming development

Following characterization of the reformer, the next generation reformer was developed [170]. A picture of the new reactor is shown in Figure 4.8. The same concept was used, but a number of measures were taken so as to address the limitations of the first reformer. In order to obtain a more favorable flow profile in the mixing section, as predicted by the CFD calculations, the air/steam inlet holes were placed further upstream the reformer. In addition, the nozzle was replaced; the new nozzle yielded a spray with finer droplets than the previous one. The new system also allows the possibility to preheat the liquid fuel prior to injection in order to facilitate the fuel evaporation.
To overcome the drawbacks with hydrocarbons in the product gas, two catalyst segments were utilized. The catalysts were supplied from a catalyst manufacturer and were noble metal-based and supported on 900-cpsi cordierite monoliths. A ceramic foam was placed prior to the catalysts to further enhance the radial mixing of the reactants. Gas sampling is possible after each monolith and prior to the first one to study the effect of using two catalyst segments. Further, thermocouples have been placed prior to and after the catalysts as well as inside the monolith channels in the new setup.

The reformer is currently under investigation and has shown very promising results [171]. As expected, significantly improved operational stability has been obtained. No local hot spots could be detected and a diesel slip of less than 10 ppm (measured by FTIR) has been obtained (at O₂:C=0.5, H₂O:C=2.5, GHSV=7700 h⁻¹). The second monolith was found to be essential to obtaining the high hydrocarbon conversion. The hydrogen concentration was similar to the results from the previous reformer but the CO concentration was slightly higher. The temperature was ~730 °C after the first monolith and ~675 °C after the second at a load of 13 g diesel/min, while the temperatures measured inside the monolith channels ranged between 750 and 775 °C (measured at the front part of each monolith). CH₄ concentrations were around 500 ppm.

The operational stability of the reformer and the nearly complete fuel conversion strongly indicate that the new design ensures complete evaporation of the fuel and a homogeneous mixture of the reactants.

### 4.5 Evaluation of diesel reforming catalysts

In Paper II, Rh and Ru catalysts supported on CeO₂-ZrO₂ were tested for autothermal reforming of a standard reference diesel fuel (Euro III/IV, 10 ppm sulfur [66]) in a small-scale reactor setup. Ceria-zirconia mixed oxides are widely used in three-way catalysts for
automotive pollution abatement [172] and have also been reported to exhibit features suitable for reforming applications. Besides the recognized advantages of ceria, described in Section 4.2.1, zirconia provides high thermal stability and comparatively low acidity. The obvious drawback with precious metals, such as Rh and Ru is the cost. The potential of adding manganese to the catalysts was investigated, with the aim to try to reduce the precious metal loading.

4.5.1 Experimental setup

Catalyst materials were prepared by incipient-wetness impregnation of aqueous metal salt solutions of the CeO$_2$-ZrO$_2$ support; 400-cpsi cordierite monolith samples (20 mm diameter, 35 mm length) were used as substrate. A washcoat layer corresponding to 20 wt% of the total catalyst structure was applied onto the monoliths by means of dip-coating. Catalyst powder samples were characterized by liquid nitrogen adsorption, temperature-programmed reduction (TPR) and X-ray diffraction (XRD).

The lab-scale reactor consists of a stainless steel tubular reactor operating at atmospheric pressure, placed in a vertically mounted furnace. The reactor setup is shown schematically in Figure 4.9. Diesel is injected together with nitrogen as carrier gas and mixed with air and steam just prior to the catalyst. A porous quartz plate is placed at the reformer inlet to distribute the reactants evenly over the cross section of the reactor. Product gases were analyzed by FTIR, NDIR and TCD techniques and temperatures were measured with K-type thermocouples.

**Figure 4.9** Small-scale reactor setup for testing of diesel reforming catalysts (MFC - mass flow controller, $T_x$ - thermocouple)
4.5.2 Effect of manganese addition to Rh and Ru catalysts on diesel reforming activity

Figure 4.10 shows the results from the catalyst tests at an inlet temperature of 650 °C and a GHSV of 15 000 h⁻¹ as fuel conversion, hydrogen yield, CO₂/(CO₂+CO) product ratio, and hydrocarbon selectivities. It can be seen that both Rh and Ru exhibit high activity for diesel reforming reactions. The activity of Ru was highest initially but the conversion decreased continuously during time on stream, while the activity of Rh was stable. The CO₂/(CO₂+CO) product ratio was higher compared to the Ce/La-doped alumina catalyst used in Paper I. This indicates that the oxygen-storage capacity and water-gas shift activity of ceria-zirconia are beneficial during diesel reforming. A high CO₂/(CO₂+CO) product ratio is desirable because it means the complexity of the CO cleanup system can be reduced.

![Figure 4.10](image)

**Figure 4.10** Results from autothermal reforming of diesel fuel over CeO₂-ZrO₂-supported Rh and Ru catalysts (Reaction conditions: O₂:C=0.45; H₂O:C=3; temperature at catalyst inlet=650 °C; GHSV=15 000 h⁻¹): (a) Fuel conversion, (b) hydrogen yield, (c) CO₂/(CO₂+CO) product ratio, and (d) C₁-C₃ selectivities

Manganese was demonstrated to increase the activity of the Rh catalyst. The activity of a catalyst containing 1 wt% Rh and 9 wt% Mn was comparable to that of a 3 wt% Rh catalyst. The same effect was not observed for Ru. The role of the manganese could be related to its
stabilizing or promoting abilities. Manganese is known to be a good sulfur sorbent and has been shown to prevent carbon formation at the metal-support interface by adsorbing sulfur that otherwise would have had the potential to block reforming reactions [127]. Manganese has also been postulated to exhibit steam reforming or partial oxidation activity in contact with noble metals [173]. The effect could also be related to the oxygen-storage capacity of Mn, which has been shown to be greater than that of ceria [173]. The findings were correlated to TPR experiments. TPR profiles are shown in Figure 4.11. For the Mn-containing Rh catalyst, the reduction peak of Rh appeared to be shifted to higher temperature, whereas the reduction of Mn was easier in the presence of Rh. The ability of a noble metal oxide to increase the reducibility of a metal oxide can be explained by an intimate contact between the two species [174]. Metallic Rh adsorbs and dissociates hydrogen with very low activation energy. This means that if Mn oxide species are in close contact with the Rh sites, they can be reduced at a lower temperature than if they were to react with molecular hydrogen by themselves. Based on the TPR results, synergistic effects between Mn and Rh are suggested to be responsible for the increased performance. In summary, manganese has the potential to be used to reduce the loading of expensive Rh metal of diesel reforming catalysts.

![Figure 4.11 TPR profiles of the CeO$_2$-ZrO$_2$-supported Rh catalysts](image)

Figure 4.11 TPR profiles of the CeO$_2$-ZrO$_2$–supported Rh catalysts
CHAPTER 5

THE FUEL-FLEXIBLE REFORMER CONCEPT
(PAPER III)

An efficient and reliable reformer that can operate on any truck fuel available on the market would obviously be a big advantage for the APU application. However, relatively few studies have been reported on reformers with fuel-flexible capabilities [175-178]. Paper III has been focused on investigating whether the diesel reformer developed in Paper I has the flexibility to be used with various fuels. Both logistic fuels (diesel, gasoline, and E85) and alternative fuel candidates (methanol, ethanol, and dimethyl ether) were tested in the reformer. For more information about the properties of each fuel, see Paper III:

5.1 Practical feasibility of the concept

The key criterion for evaluation of the fuel-flexible reformer concept was practical feasibility. The aim of the studies was not to optimize the process for each fuel but to evaluate which fuels could have the possibility to be used in the reformer design. A practically feasible ATR process was defined as self-sustaining and stable, where the main part of the fuel is converted into a hydrogen-rich gas.

Each fuel has its own optimal operating conditions, which have to be adjusted for different reactor designs depending on the heat integration of the system. The parameters used in this study are shown in Table 5.1. Those were obtained from own experience or collected from literature data and then adjusted during experiments to allow control of the reforming reactions in the specific design. The reformer and experimental setup are described in Chapter 4 (Section 4.2.1) and Paper I. The liquid fuels were delivered with a piston pump and DME, the only gaseous fuel tested, was fed to the reformer through a tube from the flange at the inlet after removal of the nozzle. The experiments were run with an amount of fuel that theoretically would generate the same amount of hydrogen as with 12 g diesel/min (reference point from Paper I). Due to this fact, and that different oxygen-to-carbon and steam-to-carbon ratios were used, different GHSVs were obtained. The same catalyst composition was used for all fuels, Rh supported on Ce/La-doped Al₂O₃.
Table 5.1 Operating conditions for the different fuels used in the study

<table>
<thead>
<tr>
<th>Fuel used</th>
<th>Flow rate (g fuel-min⁻¹)</th>
<th>O₂:C (mol:mol)</th>
<th>H₂O:C (mol:mol)</th>
<th>GHSV (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dieselᵃ</td>
<td>12.0</td>
<td>0.40</td>
<td>2</td>
<td>8700</td>
</tr>
<tr>
<td>Gasolineᵇ</td>
<td>14.4</td>
<td>0.40</td>
<td>2</td>
<td>10900</td>
</tr>
<tr>
<td>DMEᶜ</td>
<td>20.4</td>
<td>0.25</td>
<td>2</td>
<td>8800</td>
</tr>
<tr>
<td>Ethanolᵈ</td>
<td>15.8</td>
<td>0.35</td>
<td>3</td>
<td>9500</td>
</tr>
<tr>
<td>E85</td>
<td>18.6</td>
<td>0.40</td>
<td>3</td>
<td>12900</td>
</tr>
<tr>
<td>Methanolᵉ</td>
<td>22.7</td>
<td>0.20</td>
<td>1.7</td>
<td>6900</td>
</tr>
</tbody>
</table>

Operating parameters obtained from: aown results breference [179], cown results, dreference [180], ereference [181]. fSwedish Environmental Class 1 (MK1), g85 vol % bio-ethanol/15 vol % MK1 gasoline

5.2 Evaluation of the fuel-flexibility

Figure 5.1 compares the fuels in terms of conversion and selectivity to hydrogen and carbon dioxide and Figure 5.2 shows representative temperature profiles in the reformer after stabilization of the reactions for the various fuels. For diesel, gasoline and E85, the conversion is calculated by atomic carbon balances and only CO, CO₂, and CH₄ is considered to be converted fuel. It was concluded from the study that the reformer design was suitable for reforming of diesel, gasoline and E85, but that it worked less satisfactorily with DME, ethanol and methanol. The hydrocarbon fuels (but not the oxygenates) can be successfully pre-reformed in the mixing section of the reformer without large losses in efficiency.

Figure 5.1 Comparison of the different fuels in terms of H₂ selectivity, CO₂ selectivity, and conversion during autothermal reforming
Figure 5.2 Temperature profiles in the reactor during autothermal reforming of the various fuels, (L - length of reformer, positions of the thermocouples are shown in Figure 4.1)

The oxygenated fuels need lower temperature for conversion, and are generally easier to reform than the hydrocarbon mixtures. However, the oxygenates have lower energy densities and, therefore, larger volumetric flows of fuel are needed to obtain the same amount of hydrogen. This led to problems with part of the fuel penetrating the monolith before being sufficiently mixed with the air/steam mixture. This problem was especially observed for DME and methanol and resulted in low fuel conversions (78 and 73 % for DME and
methanol, respectively. During DME reforming, oxidation reactions in the mixing section resulted in a high extent of total combustion of the fuel and a subsequent loss in efficiency. This was shown by a hydrogen selectivity of less than 50%. Also, the Rh catalyst promoted the direct decomposition of DME (Eq. 3.11) [182], which was indicated by high concentrations of CO and CH₄. Coke was observed on the catalyst after reaction, but was not found to result in any decline in activity with time during the experiments. The methanol reforming experiments were characterized by poor fuel evaporation and difficulties with the reactant mixing. Further, a high concentration of CO suggests that Rh catalyzes decomposition of methanol into CO and H₂ [152].

For ethanol, the major negative aspect was the formation of byproducts. The byproducts were coke (found in the reactor effluent), methane (~4 %) and other C₂ components. Byproduct formation during ethanol reforming over Rh/Al₂O₃ has been shown to result from insufficient Rh loading [183]. Still, the Rh catalyst was selective for hydrogen generation from ethanol; a reformer that can perform well with both hydrocarbon mixtures and ethanol should therefore not be considered unattainable.

In summary, the reformer design could most likely be optimized to run on (at least) diesel, gasoline and E85, and possibly also with ethanol. The results are expected to improve with further optimization of the reactor design as well as the operating parameters for each fuel. Rh catalysts appear to be very promising candidates for fuel-flexible reformers.
CHAPTER 6

HYDROGEN GENERATION FROM DIMETHYL ETHER
(PAPERS IV-V)

As described in Chapter 3, a catalyst for DME autothermal reforming should be active for partial oxidation, DME hydrolysis and methanol steam reforming. The most common material used for methanol steam reforming is Cu. Due to the higher thermal stability of Pd compared to Cu, Pd-based catalysts were tested for autothermal reforming of DME. Alumina, or mixtures of alumina, zinc oxide and zinc aluminate, was used as support for Pd and to provide DME hydrolysis activity.

In Paper IV, the objectives were to find a catalyst that could generate a high concentration of hydrogen accompanied by high selectivity to carbon dioxide and then to investigate the effect on the product gas composition of varying operating parameters for this catalyst. First, a screening of Pd-based catalysts was performed, where different supports, Pd loading, and preparation methods were assessed. Thereafter, a PdZn-based catalyst was chosen for study of the operating characteristics of the process. In Paper V, the catalytic properties of PdZn-based catalysts were further studied.

6.1 Catalyst materials for dimethyl ether autothermal reforming

6.1.1 Experimental setup

All experiments for evaluation of DME ATR catalysts were performed in small-scale laboratory reactors, similar to the one used for testing of diesel ATR catalysts (see Section 4.4.1). The catalyst materials were deposited onto 400-epsi cordierite monolith substrate with 20 mm diameter and 35 mm length. DME was mixed with steam, air and nitrogen before the preheater. In the screening study, gas chromatography was used for product gas analyses, whereas in the other tests, FTIR, NDIR and TCD analyses were used. See Papers IV and V, respectively, for more details.
6.1.2 Material screening

Nine different Pd-based materials, shown in Table 6.1, were tested for autothermal reforming of DME; γ-Al₂O₃, ZSM-5, and a Zn-Al hydrotalcite-like compound were compared as supports for Pd. The addition of Zn and of Pt to Pd was evaluated and the effect of changing the Pd content and Pd:Zn ratio was tested for the Zn-containing catalyst. Two different preparation methods were used, incipient wetness (IW) impregnation and coprecipitation. A “hybrid” catalyst was also prepared, by physically mixing alumina and coprecipitated Pd and Zn before coating of the monolith, trying to separate the sites active for DME hydrolysis from the ones active for reforming. Prior to reaction, the catalysts were activated in a flow of hydrogen. More details on the preparation procedure for the catalysts in Table 6.1 can be found in Paper IV.

All Pd-based catalyst materials tested in the experimental study were active for DME autothermal reforming at an O₂:DME of 0.4 and a H₂O:DME of 2.5. The catalysts were compared in terms of hydrogen concentration and CO₂ selectivity in the product gas. Table 6.2 summarizes the results from the screening study at a temperature of 400 °C. Al₂O₃ was found to be the most suitable support considering activity and hydrogen generation. The zeolite and the Zn-Al hydrotalcite exhibited selectivity for the MTG reaction (methanol-to-gasoline), i.e. higher molecular weight compounds were formed. Hydrocarbons were observed in the condensate obtained in the cold trap as well as in the gas analysis. The MTG reaction has been shown to be favored by strong acid sites on catalyst surfaces at temperatures above 300 °C [184, 185]. The Pd(1)/γ-Al₂O₃ catalyst generated large amounts of carbon monoxide. As previously described, Pd is known to be active for decomposition of methanol (\( CH_3OH \rightarrow CO + 2H_2 \)), which is generated via the hydrolysis of DME. Incorporation of zinc oxide with Pd promotes the methanol steam reforming reaction, producing mainly CO₂ and H₂. In this study, Zn was added to Pd with the objective to examine if there was a comparable trend during autothermal reforming of DME over alumina-supported catalysts. The difference from methanol steam reforming is not only the reactants but also the fact that alumina is supposed to act both as a support and to
participate in the reactions by converting DME to methanol. It was found that the addition of Zn to Pd increased the selectivity for the DME reforming reactions. This feature was improved by preconditioning of the catalyst in hydrogen. For the Pd(1)/Zn(9)/γ-Al₂O₃ catalyst, a CO₂ selectivity of 82 % was achieved. Further increasing the amount of Pd resulted in increased activity but decreased CO₂ selectivity for the same amount of Zn. The effect of the Pd:Zn ratio on the CO₂ selectivity and of the Pd loading on the activity during autothermal reforming of DME is illustrated in Figure 6.1. By adding 9 % Zn to the 1 % Pd/γ-Al₂O₃ catalyst, the CO₂ selectivity was increased from 17 to 82 %. The activity was found to increase with the Pd loading but since the concentration of Zn was kept constant, the CO₂ selectivity decreased. This phenomenon could be attributed to the presence of a larger amount of metallic Pd, catalyzing decomposition reactions and leading to poorer reforming activity. It is assumed that the interaction of Zn with Pd on the alumina surface changes the selectivity towards carbon dioxide. This hypothesis was evaluated by means of X-ray diffraction (XRD) and temperature-programmed reduction (TPR). XRD revealed that pretreatment of the catalyst samples in hydrogen at 400 °C resulted in the formation of Pd-Zn species. The lower reduction temperature and higher degree of hydrogen consumption for the PdZn/γ-Al₂O₃ compared to the Pd/γ-Al₂O₃ catalyst (shown by TPR, see Figure 6.2) suggest that Pd and Zn interact. ZnO is not an easily reducible oxide, but in the presence of Pd, hydrogen spillover can reduce the ZnO at lower temperatures [186, 187]. This feature is believed to influence the selectivity to CO₂ during autothermal reforming of dimethyl ether over PdZn/γ-Al₂O₃ catalysts.

The PdZn-based catalyst prepared using the impregnation technique was more selective compared to the coprecipitated one. This could possibly be explained by a large fraction of micropores in the coprecipitated catalyst (shown by liquid nitrogen adsorption, BET surface areas presented in Table 6.1), leading to encapsulation of sites necessary to reach high selectivity. The hybrid catalyst exhibited a low activity, which indicates that the Pd loading

### Table 6.2 Results from the screening of various Pd catalysts: DME conversion, product gas concentration (H₂O and N₂ not shown), and CO₂ selectivity

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>DME conv. [%]</th>
<th>Product gas concentration [%]</th>
<th>CO₂ selectivity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H₂</td>
<td>CO</td>
</tr>
<tr>
<td>Pd(1)/γ-Al₂O₃</td>
<td>80</td>
<td>40</td>
<td>14</td>
</tr>
<tr>
<td>Pd(1)/ZSM-5</td>
<td>44</td>
<td>8</td>
<td>3.0</td>
</tr>
<tr>
<td>Pd(1)/HTlc</td>
<td>40</td>
<td>20</td>
<td>n.d.</td>
</tr>
<tr>
<td>Pd(1)Zn(9)/γ-Al₂O₃</td>
<td>76</td>
<td>46</td>
<td>3.8</td>
</tr>
<tr>
<td>Pd(2)Zn(9)/γ-Al₂O₃</td>
<td>78</td>
<td>43</td>
<td>6.0</td>
</tr>
<tr>
<td>Pd(5)Zn(9)/γ-Al₂O₃</td>
<td>94</td>
<td>49</td>
<td>9</td>
</tr>
<tr>
<td>Pd(1)Zn(9)-Al₂O₃</td>
<td>85</td>
<td>42</td>
<td>20</td>
</tr>
<tr>
<td>Pd(1)Zn(9)+γ-Al₂O₃</td>
<td>57</td>
<td>31</td>
<td>12</td>
</tr>
<tr>
<td>Pd(1)Pt(0.5)/γ-Al₂O₃</td>
<td>58</td>
<td>38</td>
<td>14</td>
</tr>
</tbody>
</table>
could be lower than the target loading for this catalyst. This would lead to lower DME conversion due to thermodynamic limitations of the DME hydrolysis reaction as a result of low methanol-reforming activity. Alternatively, the active sites need to be in closer proximity than in the hybrid catalyst, as the reactions occur simultaneously. This was not further evaluated in this study.

The addition of Pt to Pd resulted in a higher concentration of CH₄ associated with a high CO concentration, suggesting that the DME is decomposed over Pt generating CH₄, CO, and H₂ (Eq. 3.11).

Based on the catalyst screening results, taking into account the concentration of hydrogen in the product gas and the selectivity to carbon dioxide, a PdZn/γ-Al₂O₃ catalyst prepared by
incipient wetness impregnation was selected for use in the study of the operating parameters, outlined in Section 6.2.

6.2 Effect of operating conditions

The parameter study was performed using a Pd(3)Zn(27)/\(\gamma\)-Al\(_2\)O\(_3\) catalyst. The influence of oxygen-to-DME ratio and steam-to-DME ratio on the conversion and selectivity to hydrogen and carbon dioxide was evaluated.

6.2.1 Influence of oxygen-to-DME ratio

The O\(_2\):DME ratio was varied from 0.4 to 0.9 with the temperature ranging from 350 to 400 °C. The results are shown in Figure 6.3. The conversion of DME was found to increase at increasing oxygen feed as a result of the higher reaction rate of the oxidation compared to the steam reforming and the increase in temperature. Considering the hydrogen concentration, an optimum could be identified at O\(_2\):DME values between 0.5 and 0.7 for a temperature of 400 °C. At an O\(_2\):DME of 0.7, the concentration of hydrogen amounted to 48 %. At a further increase of the oxygen feed, the hydrogen concentration decreased accompanied by a slight increase in the CO\(_2\) and H\(_2\)O (not shown) concentrations.

The values of CO\(_2\) selectivity for the Pd(3)Zn(27)/\(\gamma\)-Al\(_2\)O\(_3\) catalyst were comparable to those of the Pd(1)Zn(9)/\(\gamma\)-Al\(_2\)O\(_3\) catalyst tested in the screening study but the activity was higher at increased Pd loading. That is, the selectivity for PdZn/\(\gamma\)-Al\(_2\)O\(_3\) catalysts is mainly dependent on the Pd:Zn ratio whereas the conversion can be increased by increasing the Pd content. The CO\(_2\) selectivity was not considerably affected by changes in the oxygen feed.

The influence of the temperature was larger at the lowest O\(_2\):DME ratio, since this is where the conversion is affected the most. It is evident from this study that an oxygen-to-DME ratio higher than 0.4, which was used in the catalyst screening, might be necessary in order to supply sufficient heat for the steam reforming reaction (but this will of course depend on heat losses and heat integration of the system).

6.2.2 Influence of steam-to-DME ratio

The H\(_2\)O:DME ratio mainly affected the CO\(_2\) selectivity, while the impact on the hydrogen yield was small. The H\(_2\)O:DME ratio was varied from 1 to 3 at an oxygen-to-DME ratio of 0.7 and a catalyst inlet temperature of 400 °C (Figure 6.4). A H\(_2\)O:DME ratio of 1 gave a high DME conversion, but more steam will be needed to induce the water-gas shift reaction and suppress carbon formation. The highest CO\(_2\) selectivity was found at the highest steam-to-DME ratio. However, at higher H\(_2\)O:DME ratios, the diluting effect of the steam will come into play, decreasing the concentration of hydrogen. The effect of steam on the CO\(_2\) selectivity was more pronounced at the lower H\(_2\)O:DME ratios. A low temperature will be favorable for the water-gas shift reaction, resulting in higher selectivity to CO\(_2\).
Figure 6.3 CO$_2$ selectivity, DME conversion, and H$_2$ concentration as a function of O$_2$:DME for catalyst inlet temperatures of 350, 375, and 400 °C (H$_2$O:DME=2.5)

Figure 6.4 CO$_2$ selectivity, DME conversion, and H$_2$ concentration as a function of H$_2$O:DME for catalyst inlet temperatures of 350, 375, and 400 °C (O$_2$:DME=0.7)

6.3 Activity and selectivity of PdZn-based catalysts

Following the parameter study, new catalyst materials were prepared with the aim to further study the activity and selectivity during DME ATR. Three different materials were prepared, with the same contents of Pd, Zn and Al, but with different chemical composition, acidity, and textural properties. Mixtures of ZnO/ZnAl$_2$O$_4$/Al$_2$O$_3$ were prepared by thermal treatment of a ZnO-Al$_2$O$_3$ support. The materials were impregnated with Pd followed by reduction treatment. During methanol reforming, the presence of ZnAl$_2$O$_4$ and ZnO on Al$_2$O$_3$ has been shown to inhibit interactions between Pd and Al$_2$O$_3$, thus avoiding the
Table 6.3 Composition, surface area, CO uptake, and acidic properties of the DME ATR catalysts

<table>
<thead>
<tr>
<th></th>
<th>Pd/ZA(400)</th>
<th>Pd/ZA(700)</th>
<th>Pd/ZA(1000)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phases identified(^a)</td>
<td>γ-Al(_2)O(_3), ZnO, PdZn</td>
<td>Al(_2)O(_3), ZnO, ZnAl(_2)O(_4), PdZn</td>
<td>ZnAl(_2)O(_4), ZnO, Al(_2)O(_3), PdZn</td>
</tr>
<tr>
<td>Pd content [wt%](^b)</td>
<td>3.8</td>
<td>3.7</td>
<td>3.5</td>
</tr>
<tr>
<td>Zn content [wt%](^b)</td>
<td>35</td>
<td>36</td>
<td>34</td>
</tr>
<tr>
<td>BET surface area [m(^2)-g(^{-1})](^c)</td>
<td>112</td>
<td>93</td>
<td>26</td>
</tr>
<tr>
<td>CO uptake [μmol·g(^{-1})](^d)</td>
<td>20</td>
<td>21</td>
<td>17</td>
</tr>
<tr>
<td>Acid amount [μmol·g(^{-1})](^e)</td>
<td>37</td>
<td>29</td>
<td>17</td>
</tr>
<tr>
<td>Density of acid sites [μmol·m(^{-2})](^e)</td>
<td>0.33</td>
<td>0.31</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Estimated by \(^a\)XRD, \(^a\)TEM, \(^b\)ICP-OES, \(^c\)liquid nitrogen adsorption, \(^d\)CO chemisorption, \(^e\)NH\(_3\)-TPD

formation of metallic Pd on Al\(_2\)O\(_3\) [188]. The properties of the different materials are shown in Table 6.3; the catalysts are denoted Pd/ZA(400), Pd/ZA(700) and Pd/ZA(1000), where the number in parenthesis corresponds to the temperature at which the support was treated. Physical mixtures of the catalysts with alumina were also evaluated. The materials were characterized by CO chemisorption, liquid nitrogen adsorption, temperature-programmed desorption of ammonia (NH\(_3\)-TPD), temperature-programmed reduction (TPR), transmission electron microscopy (TEM), and X-ray diffraction (XRD) and tested for activity and selectivity during DME ATR. The XRD analyses revealed the 1:1 PdZn alloy with similar intensity for all samples. The composition of the material changed from mixtures of Al\(_2\)O\(_3\) and ZnO in Pd/ZA(400) to mainly ZnAl\(_2\)O\(_4\) in Pd/ZA(1000), see Table 6.3. Figure 6.5 shows results from XRD at 2θ angles between 54 and 64°.

Figure 6.5 X-ray diffraction patterns displaying the difference of the supports. (a) Pd/ZA(400), (b) Pd/ZA(700), (c) Pd/ZA(1000)
Figure 6.6 shows TEM images of the catalysts. The Pd/ZA(400) catalyst support comprised mainly a mixture of ZnO and Al₂O₃ with a 2:1 Al:Zn ratio, see Figure 6.6a. The dark spots are Pd-containing crystals with sizes of 3-7 nm. In some parts of the material, agglomerates of ZnO (50-150 nm) were found, whose surfaces were free from Pd, see Figure 6.6b. In the Pd/ZA(700) catalyst, the support had partly reacted into ZnAl₂O₄. Again, Pd particles were only found on alumina-containing material; pure ZnO did not contain any Pd. The distribution of Pd on ZnAl₂O₄ in this catalyst is shown in Figure 6.6c. In the Pd/ZA(1000)
catalyst, the main part of the material comprised ZnAl₂O₄, supporting faceted particles, see Figure 6.6d. The inset shows a high-resolution image of a Pd-containing particle. The observed lattice distances could be associated to a PdZn particle of 1:1 composition. The extent of alloy formation in the various catalysts could not be quantified; it was found that the materials comprised mixtures of Pd, PdZn and Pd₂Zn. PdZn alloy formation was also confirmed by TPR, see Paper V.

The results from the activity measurements for DME ATR are shown in Figures 6.7 and 6.8 as DME conversion and selectivity to CO₂. It can be concluded from the tests that the decreasing surface areas and number of acid sites at higher calcination temperature of

![Figure 6.7](image1.png)

**Figure 6.7** Activity of the catalysts for autothermal reforming of DME
Operating conditions: O₂:DME=0.7, H₂O:DME=2.5

![Figure 6.8](image2.png)

**Figure 6.8** CO₂ selectivity of the catalysts for autothermal reforming of DME
Operating conditions: O₂:DME=0.7, H₂O:DME=2.5
Figure 6.9 Concentration of CH₄, CO, and CH₃OH in the product gas during DME ATR

Operating conditions: O₂:DME=0.7, H₂O:DME=2.5, T=450 °C

the support did not affect the activity negatively. The highest DME conversion was achieved with the Pd/ZA(1000) catalyst, in which the support comprised mainly ZnAl₂O₄. By physically mixing the catalysts with γ-Al₂O₃, the conversion increased although the selectivity to CO₂ was decreased. The CO₂ selectivity has been correlated to PdZn alloy formation. A reasonable effect of decreased surface area would be decreased metal dispersion. Results from CO chemisorption measurements show similar CO uptakes for all samples. However, the CO chemisorption ability of Pd has been shown to be affected in the presence of strong Pd-Zn interactions [189], which could explain this feature. This could mean a higher extent of PdZn formation in Pd/ZA(400) and Pd/ZA(700) compared to Pd/ZA(1000), which correlates with the higher CO₂ selectivity for the former ones. This theory is strengthened by estimating the particle sizes by taking the reciprocal of the measured metal dispersion [190, 191]. The values obtained are higher than the ones observed in the TEM analyses (3-7 nm) and point towards a higher metal dispersion. Nevertheless, the CO₂ selectivity was high for all materials, with CO concentrations in the product gas below 5 %, see Figure 6.9. The CO is suggested to originate primarily from decomposition reactions, either from DME as for the Pd/ZA(400) and Pd/ZA(700) (CH₄:CO close to 1), or from methanol (alternatively POX) as for the other catalysts (low CH₄ concentrations). By coupling the ATR with a WGS reactor, CO concentrations of 0.5-1 % can be obtained (unpublished results [192]). The product gas from the WGS unit could then possibly be fed directly to a HT-PEM fuel cell. This means that the overall complexity of the DME fuel processor will be low compared to a diesel-fueled fuel processor.
CHAPTER 7

CONCLUSIONS

Fuel cells have potential to contribute to meeting future energy demands. However, the fuel cell technology is immature and has in many areas still much to prove. Nevertheless, early market niches could provide further development of the technology, which in turn potentially could lead to competitiveness and diffusion of the technology into other markets. One such niche is auxiliary power units in heavy-duty trucks. In the absence of a hydrogen infrastructure, the hydrogen required for the fuel cell could be generated onboard by reforming of the existing truck fuel. This research project was undertaken to design and evaluate reforming processes and catalysts for hydrogen generation from diesel and DME. The research has enhanced our understanding of diesel and DME reforming and will serve as a base for future studies.

A significant outcome of the studies is that it is highly feasible to generate hydrogen-rich product gases from commercial diesel fuel. By coupling the reformer with a number of cleanup steps, fuel cell quality reformate could be obtained and, hence, auxiliary power units could be considered to have potential to become one of the first widespread applications for fuel cells in transportation applications.

Diesel fuel reforming is most commonly studied using model compounds or surrogate fuels for diesel. In the work presented in this thesis, the challenge of reforming real diesel fuel mixtures into hydrogen-rich gases has been addressed. A compact 5 kW<sub>e</sub> reactor, consisting of a mixing/prereforming section and a catalytic reforming section, was designed and evaluated. Experiences from operation of the reformer in addition to CFD calculations have contributed to the development of existing systems and have been supportive in the development of a new improved reformer design. The fuel flexibility of the reactor was also investigated. The results from the study support that the reactor concept and catalyst can be optimized to run on several fuels. The reformer was shown to work successfully running on diesel, gasoline and E85. Fuel flexibility is considered advantageous to provide robustness and simplicity to the APU systems and to meet requirements considering regional differences in fuel supply.

In addition to the studies on reactor design, catalytic materials for diesel reforming were evaluated. The feasibility of Rh to generate hydrogen-rich gases from commercial diesel was demonstrated both in the kW-scale reactor (supported on Ce/La-doped Al<sub>2</sub>O<sub>3</sub>) and in a small-scale laboratory reactor (supported on CeO<sub>2</sub>-ZrO<sub>2</sub>). Importantly, no coke was
observed on the surface of the Rh catalyst, even at comparatively low steam-to-carbon-ratios (H₂O:C=2), which has been identified as a big issue in diesel reforming. An important finding was that the addition of Mn to Rh catalysts was shown to increase the activity for diesel reforming. This result was explained by synergistic effects between Rh and Mn. Hence, Mn could be used to decrease the loading of Rh metal in the diesel reforming catalyst, an expensive component of the reforming system.

Dimethyl ether is a potential diesel fuel alternative and has lately been considered as hydrogen carrier for fuel cells in truck auxiliary power units. In the present work, the feasibility of generating hydrogen by autothermal reforming of DME has been demonstrated. To the author’s knowledge, this is the only work performed so far considering hydrogen generation from DME by ATR. Alumina-supported Pd-based catalysts were shown to be active for DME autothermal reforming, yielding hydrogen-rich product gases at temperatures between 350 and 450 °C. PdZn-based catalysts were superior among the evaluated Pd catalysts with respect to obtaining high CO₂ selectivity. The increased CO₂ selectivity with the addition of Zn was ascribed to interactions between Pd and Zn, leading to higher reforming activity and lower activity for decomposition reactions. Pd supported on Zn-Al mixed oxides was found to exhibit improved activity during DME ATR compared to γ-Al₂O₃-supported PdZn. Despite the recognized importance of acid sites for conversion of DME, no decline in activity was observed even though the surface area and number of acid sites were significantly lower for the Zn-Al mixed oxide supports. A catalyst where the support comprised mainly ZnAl₂O₄ exhibited the highest activity for DME conversion.

The operating conditions were found to have large impact on the reformer performance during DME ATR. Increasing the oxygen-to-DME ratio affected both the reactor temperature and the reformer efficiency. The highest efficiency will be obtained for conditions with sufficient supply of heat to the steam reforming reaction but without the loss of hydrogen. The efficiency is strongly dependent on the product gas composition and side reactions such as total combustion and methane formation will influence the hydrogen yield negatively. The work in the present thesis has been helpful in obtaining a broad understanding on hydrogen generation from dimethyl ether by autothermal reforming. Knowledge has been built up considering operating characteristics and catalyst materials for the process.
CHAPTER 8

FINAL REMARKS

Fossil fuel usage in transportation vehicles throughout the world contributes to environmental deterioration and greenhouse gas emissions. Increases in energy usage are driven by population growth and economic development. Consequently, due to the predicted increase in population and economic progress in the future, the world is facing serious environmental issues. Given these problems, the current transportation system could be considered unsustainable, calling for the need of a radical change. There is no formal definition of sustainable transportation; those found in the literature are usually derived from the definition of sustainability. The most widely adopted definition of sustainability is probably the one from the Brundtland commission, saying “development that meets the needs of the present without compromising the needs of future generations to meet their own needs” [193]. There is a number of more or less similar definitions available in the literature, although they have slightly different perspectives. Sustainability is commonly used in terms where a comparison is made with the present solution using different indicators and suggests policies that will push the development towards a system, which is less unsustainable. Other viewpoints on sustainable development do not fit together with the current solution, which is doing more with less by retrofitting existing systems, and instead suggest that we should follow nature’s design principles [194]. Regardless of the perspective, steps towards a more sustainable transportation system will likely include

- reducing the need for transport (local production, mobility management, urban planning, telecommunication etc.),
- improving efficiency and reducing the impact of vehicles (minimized fuel consumption, decreased emissions – if possible zero, replacement of fossil fuels with renewable resources), and
- using green transport modes (e.g. human-powered vehicles, public transportation).

The research in this thesis has covered the second point. Concerning the replacement of fossil transportation fuels it is still not clear which alternative is the preferred choice. Therefore, it is considered important that measures are directed towards various alternatives in order to prevent an early lock-in. There are significant uncertainties related to the use of biofuels, regarding efficiency, supply, ecological sustainability of production, and competition with food production. Biomass will likely play a large role in the future and it is
important that purposes such as food production and preservation of biodiversity be satisfied. Even though the biomass resources, in the long run, most likely will not be sufficient to supply the total amount of energy needed for transport, the conversion of biomass to liquid fuels is by many considered to represent a step in the right direction towards a more sustainable use of energy in the transport sector. Biomass-derived DME offers one route in heavy-duty vehicle applications in society’s effort to replace fossil fuels.

When it comes to using our resources more efficiently, it will not only be necessary to replace fossil fuels; we also need to call attention to the importance of achieving high energy efficiency onboard vehicles. In this context, fuel cells are often pointed out as “the energy converter”, being highly efficient as well as having the possibility to provide zero emissions both on the local and global scales. However, fuel cell technology is today not a widely preferred alternative for the transportation sector. Instead, electric vehicles appear to be the most favored long-term strategy. If the hydrogen required for the fuel cell is produced from electricity, electricity from the grid will evidently be less expensive than electricity from hydrogen and fuel cells. Consequently, based on what we know today, it will be difficult for fuel cells to compete with electricity for propulsion of vehicles, with the exception of cases where longer driving ranges are required or the time for refueling is restricted. Circumstances that could help the fuel cell technology towards a wider implementation include the availability of inexpensive hydrogen, for example with a breakthrough of photovoltaics, biological hydrogen production or CO2 sequestration, in addition to limited availability of bioenergy. Of course, the technical and economical limitations of the technology also need to be solved.

Still, research and development of the fuel cell technology is considered important in order to stimulate different technologies and prevent a lock-in to technologies that later might prove not to be a good option. In fact, the present commitment to hybrid vehicles might provide a path towards a completely electric platform, thereby supporting a future adoption of fuel cells. Furthermore, one should take into account that it is often the highly improbable events that turn out to have the highest impact on the future [191]. In this context, it is possible that we have underestimated the potential of the fuel cell technology and leave an additional application out, the one for unpredicted future uses. Other benefits related to a continued development of fuel cells, e.g. buildup of knowledge, spillover to other markets and the creation of early markets could also be identified as positive.

There are, however, niches where fuel cells could have the possibility to be competitive today. This thesis has been devoted to fuel cell auxiliary power units, which are suggested to have the potential to become the first widespread commercial application for fuel cells in vehicles. The market potential for APUs is continuously increasing, as policy incentives to reduce emissions from idling trucks are being implemented. Fuel cell auxiliary power units must provide sufficient added value to the customers to compensate for a high investment cost. The outcome of niche developments of advanced technologies has been shown to be highly dependent on positive expectations and visions by developers and end users. Furthermore, the APUs probably need to be commercialized in the near future, in order not to be hindered by competitors. The work in the present thesis contributes to the development of existing systems, showing that diesel can be used as a short-term alternative
to supply fuel cells with hydrogen onboard trucks. Fueling fuel cells with diesel, however, is associated with losses and still has a negative environmental impact. A diesel-fueled APU only seeks to decrease emissions and deplete natural resources more slowly and may therefore not be considered truly sustainable. A first step could be to replace the fossil diesel with a renewable fuel, such as DME. DME is easier to reform than diesel, which may increase the potential for fuel cells in APUs. In the future, if hydrogen is to take part in a sustainable transportation system, losses associated to production, distribution, storage and end use of hydrogen, need to be accentuated. Hydrogen and fuel cells are at the moment not considered likely to solve all problems, but may possibly contribute to part of the solution.
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*Stockholm, February 2009 – Marita Nilsson*
## NOMENCLATURE

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>a.u.</td>
<td>Arbitrary unit</td>
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<tr>
<td>APU</td>
<td>Auxiliary power unit</td>
</tr>
<tr>
<td>ATR</td>
<td>Autothermal reforming</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller (method for surface area measurement)</td>
</tr>
<tr>
<td>BTL</td>
<td>Biomass-to-liquids</td>
</tr>
<tr>
<td>CAD</td>
<td>Computer-aided design</td>
</tr>
<tr>
<td>CFD</td>
<td>Computational fluid dynamics</td>
</tr>
<tr>
<td>CIDI</td>
<td>Compression ignition direct injection</td>
</tr>
<tr>
<td>CNG</td>
<td>Compressed natural gas</td>
</tr>
<tr>
<td>Cpsi</td>
<td>Cells per square inch</td>
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<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DME</td>
<td>Dimethyl ether</td>
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<tr>
<td>EGR</td>
<td>Exhaust gas recirculation</td>
</tr>
<tr>
<td>F</td>
<td>Molar flow</td>
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<tr>
<td>FC</td>
<td>Fuel cell</td>
</tr>
<tr>
<td>FID</td>
<td>Flame ionization detector</td>
</tr>
<tr>
<td>FT diesel</td>
<td>Fischer Tropsch diesel</td>
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<tr>
<td>FTIR</td>
<td>Fourier-transform infrared (spectrometer)</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatograph</td>
</tr>
<tr>
<td>GHSV</td>
<td>Gas hourly space velocity</td>
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<tr>
<td>GTL</td>
<td>Gas-to-liquids</td>
</tr>
<tr>
<td>HAADF</td>
<td>High-angle annular dark field</td>
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<tr>
<td>H$_2$O:C</td>
<td>Steam-to-carbon ratio</td>
</tr>
<tr>
<td>H$_2$O:DME</td>
<td>Steam-to-DME ratio</td>
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<tr>
<td>HTlc</td>
<td>Hydrotalcite-like compound</td>
</tr>
<tr>
<td>HT-PEM</td>
<td>High temperature proton exchange membrane</td>
</tr>
<tr>
<td>HTS</td>
<td>High temperature water-gas shift</td>
</tr>
<tr>
<td>ICE</td>
<td>Internal combustion engine</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively coupled plasma – optical emission spectroscopy</td>
</tr>
<tr>
<td>IW</td>
<td>Incipient wetness</td>
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<tr>
<td>kW$_e$</td>
<td>kW electric</td>
</tr>
<tr>
<td>L</td>
<td>Length</td>
</tr>
<tr>
<td>Lambda ($\lambda$)</td>
<td>Air/fuel equivalence ratio</td>
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<tr>
<td>LHV</td>
<td>Lower heating value</td>
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<td>LNG</td>
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<tr>
<td>LPG</td>
<td>Liquefied petroleum gas</td>
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<tr>
<td>LTS</td>
<td>Low temperature water-gas shift</td>
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<td>MEA</td>
<td>Membrane electrode assembly</td>
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<td>MFC</td>
<td>Mass flow controller</td>
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<tr>
<td>MTG</td>
<td>Methanol-to-gasoline</td>
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<tr>
<td>NDIR</td>
<td>Nondispersive infrared</td>
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<td>Abbreviation</td>
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<td>-------------</td>
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<tr>
<td>NTP</td>
<td>Normal temperature and pressure</td>
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<td>PEFC</td>
<td>Polymer electrolyte fuel cell</td>
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<tr>
<td>PEM</td>
<td>Proton exchange membrane</td>
</tr>
<tr>
<td>PM</td>
<td>Particulate matter</td>
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<tr>
<td>POX</td>
<td>Partial oxidation</td>
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<tr>
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<td>Preferential oxidation</td>
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<tr>
<td>S</td>
<td>Selectivity</td>
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<tr>
<td>Sₘₐ</td>
<td>Surface area</td>
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<tr>
<td>SI</td>
<td>Spark ignition</td>
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<td>SOFC</td>
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<td>SR</td>
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<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
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<td>STY</td>
<td>Space-time yield</td>
</tr>
<tr>
<td>SV</td>
<td>Space velocity</td>
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<tr>
<td>T</td>
<td>Temperature</td>
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<td>TEM</td>
<td>Transmission electron microscopy</td>
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<td>TCD</td>
<td>Thermal conductivity detector</td>
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<td>TPD</td>
<td>Temperature-programmed desorption</td>
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<td>Temperature-programmed reduction</td>
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<td>XRD</td>
<td>X-ray diffraction</td>
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<td>WGS</td>
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REFERENCES