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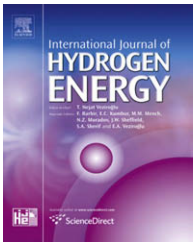

Diesel fuel reformer for automotive fuel cell applications

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ABSTRACT

Fuel economy and emission abatement are issues, which are highly prioritized areas in the automotive industry of today. The debate about climate change has in recent years even more emphasized the importance of these issues and has increased the search for finding sustainable technical solutions. This paper describes an effort to develop an innovative and environmentally-benign hydrogen generation system operating on commercial diesel fuel to avoid running the engine to supply electricity at stand-still. The use of a fuel cell-based auxiliary power unit (APU) has the potential of delivering electricity at high efficiencies independent of the heavy-duty truck engine. During the reformer development phase, spray formation and mixing of reactants proved to be crucial to obtain high reforming efficiencies and low diesel slip. The diesel is being injected through a nozzle creating a spray of fine droplets of a size which can establish rapid evaporation. Air and steam are being pre-heated and injected into the mixture chamber and subsequently mixed with the evaporated diesel fuel. Depending on the operating parameters, a part of the fuel is being oxidized and produces heat. Autothermal reforming was chosen to circumvent the heat transfer problem in catalytic steam reforming. By supplying heat directly to the catalyst surface by an oxidation reaction the heat demand of the strongly endothermic steam reforming reaction can be fulfilled. We employed CFD calculations, which revealed the importance of avoiding large recirculation zones leading to a prolonged residence time of the hydrocarbon molecules and causing auto-ignition and excessive temperatures in the catalyst. Five different reformer generations are being described and discussed in detail in this publication. The first one was based on a fixed bed reactor, while the other four all relied on catalytic monoliths enabling low pressure drops. The early reactor designs all suffered from auto-ignition and instability problems. The latter generations exhibited a considerably more stable temperature profile in the reformer. The conversion of diesel and the reformer efficiencies are significantly higher than the early generation diesel reformers.

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Nomenclature

A	Area
C_nH_m	Generic hydrocarbon
CFD	Computational Fluid Dynamics
CO	Carbon monoxide
CO_2	Carbon dioxide
C_p	Heat capacity
E_A	Activation Energy
h	Enthalpy
H_2	Hydrogen
H_2O	Water
kW_{th}	kW thermal
L	Length
LHV	Lower Heating Value
m	Mass, kg
N_2	Nitrogen
NMHC	Non Methane Hydrocarbon
Nm^3	Normal-m^3, 1 atm, 273.15 K
O_2	Oxygen
p	Pressure
PEM	Polymer Electrolyte Membrane
PrOX	Preferential Oxidation
R	Gas constant
SCR	Steam-to-Carbon-Ratio, mol H_2O/mol C
T	Temperature
t	Time
t_{id}	Ignition delay time
u	Velocity, m/s
WGS	Water–gas shift reaction
Δ	Change
η	Efficiency
λ	Air-to-fuel ratio
τ	Residence time
ϕ	Fuel-to-air ratio
$\dot{m}$	Mass flow, kg/s
Subscript	
flue	Flue gas
m	Mixture
rea	Reactor

1. Introduction

This work is part of a program to develop a diesel fueled fuel cell auxiliary power unit (APU) for heavy duty trucks. The project mission was to design and construct a dynamic low temperature fuel cell system which would use the main engine fuel, rather than a model fuel like hydrogen or methanol.

The combination of rapidly increasing fuel costs (Fig. 1) [1], and stringent environmental legislation has created the need for new and innovative transport solutions. Heavy duty trucks operate in the idling mode 20–40 % of its operating time. Idling has increased significantly in recent years, partly due to the utilization of just in time production methods. In essence this is a way to keep the storage of goods on the road instead of at the production site. This leads to an increased demand for comfort systems (air condition, microwave ovens, etc) for both the driver and goods. By operating these comfort systems from an energy source independent of the internal combustion engine, better energy utilization can be achieved.

Fuel Cell systems have the potential to increase the efficiency of modern vehicles while simultaneously decreasing emissions and particulates. However, in order to make use of the existing infrastructure, a system for converting a commercially available fuel into hydrogen must be developed.

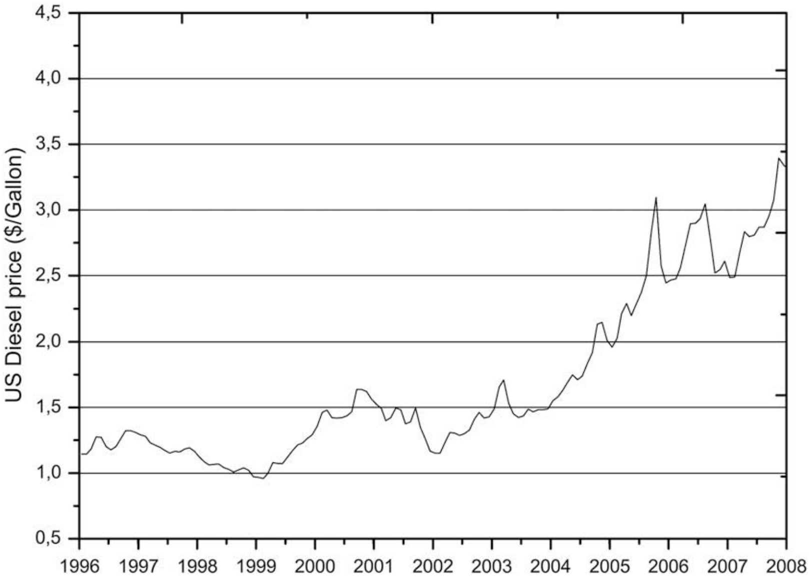

Fig. 1 – Diesel fuel price development. Adapted from [1].

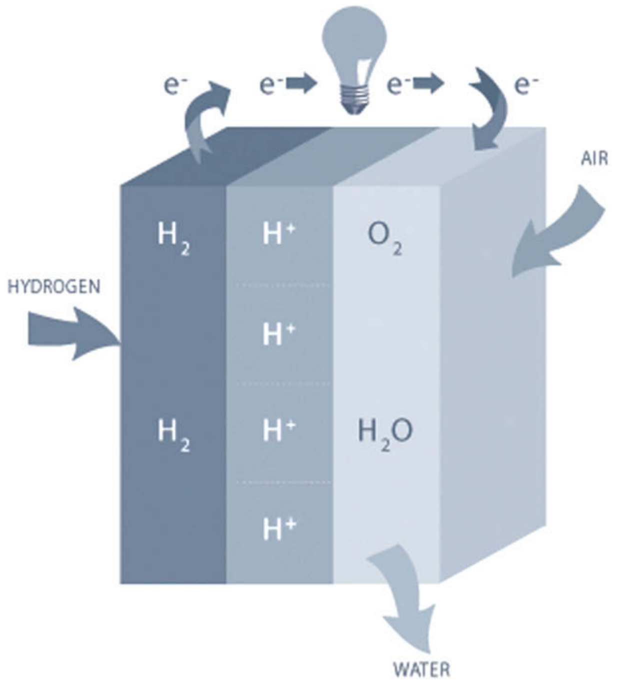

Fig. 2 – Fuel cell stack principle.

Industrial scale production of hydrogen has been operational in the oil and gas industry for more than a century and forms the base of the modern chemical industry. The hydrogen rich gas produced in modern refineries is a mixture of hydrogen (H_2), carbon dioxide (CO_2) and carbon monoxide (CO). The mixture, known as synthesis gas (syngas), is a key reagent in the chemical industry.

A modern plant has the capacity of producing more than 100 000 Nm^3 a year, providing the large scale production of ammonia, methanol and a variety of specialty chemicals [2].

The development of portable fuel processors has however for several years received significant attention in relation to the increase in worldwide fuel cell activities. The bulk of these activities have however been on simple singular fuels such as alcohols and methane. Diesel is a complex mixture of hydrocarbons, with a wide boiling point range, making both the evaporation and reforming of the fuel a difficult challenge.

The prime challenge in designing a diesel reformer is creating a perfect mixture of fuel and oxidant before contact with the catalysts, while preventing autoignition of the mixture. In recent years, several methods, such as cool flame or direct evaporation in preheated steam, have been proposed to resolve this problem [3]. These methods have however been shown to produce large amounts of soot or unstable reformers with high risk for autoignition due to prolonged residence times in the reactor. In this paper several concepts for mixture homogenization have been studied and evaluated.

The diesel fuel processor developed at PowerCell is based upon the Autothermal reforming concept for the cracking of the hydrocarbon fuel and both the water–gas shift (WGS) and preferential oxidation (PrOX) reactions for purifying the gas to a quality that is compatible with a PEM fuel cell. This paper focuses on the design and operation of the diesel autothermal reformer.

2. Fuel cell power systems

Fuel Cell systems generate electrical power through an electrochemical reaction of air and hydrogen. The only by-product from the reaction is water and heat (Fig. 2). The current production in the stack exists as long as the fuel is fed to the electrolytes in the cell and contrary to a battery – the electrolytes in a fuel cell are unchanged by the reaction.

For automotive applications, the hydrogen can either be stored in pressurized tanks or produced on-board from the vehicle fuel. The complexity of the fuel cell system depends on both fuel used and the type of fuel cell used (Table 1). The selection of fuel cell type depends strongly on the application and operating conditions that the stack will be exposed to. The principal difference between the types is in the composition of the material used in the electrolytes.

The PEM type technology used in the PowerCell system requires a high grade hydrogen gas and therefore a complete gas cleanup unit must be integrated into the system. The hydrogen rich gas can be produced in a fuel reformer, by cracking the hydrocarbon fuel into syngas (1).

$$C_nH_m \overset{ox}{\rightarrow} H_2 + CO + CO_2 \tag{1}$$

2.1. *Fuel reforming*

There are three established methods for reforming fuels: Steam Reforming (SR), Catalytic Partial Oxidation (CPO) and Autothermal reforming (ATR). All of the described methods produce a syngas mixture; however the difference in reaction

Table 1 – Fuel cell type.

Fuel cell class	Operating temp.	Mobile ion	Dynamics	Tolerance to poison			Cost	Power density
				CO	CO_2	S		
Alkaline (AFC)	60–120 °C	OH^-	High	Low	Low	Low	Med.	Med.
Molten Carbonate (MCFC)	600–1000 °C	CO_3^{2-}	Low	Med.	High	High	Med.	Low
Polymer Electrolyte (PEFC)	50–100 °C	H^+	High	Low	High	Low	High	High
HT-Polymer Electrolyte (HT-PEFC)	150–200 °C	H^+	High	High	High	Med.	High	High
Phosphoric acid (PAFC)	175–220 °C	H^+	Med.	Med.	High	High	High	Med.
Solid Oxide (SOFC)	600–1000 °C	O^{2-}	Low	High	High	Med.	Med.	High

Table 2 – US fuel properties.

Fuel property	Unit	Specification	
		Grade 2-D (1993)	Upgrade (2006)
Cetane Number		40 (min)[a]	
Either (1) Cetane Index		40 (min)	
Or (2) Aromatics	% (vol.)	35 (max)	
Cloud Point	°C	[b]	
Distillation 90% (vol.)	°C	282–338[c]	
Total Sulphur	% (wt.)	0.05 (max)	15 ppm[d]
Flashpoint	°C	52 (min)	
Kinematic Viscosity @ 40 °C	mm^2/s	1.9–4.1	
Water & Sediment	% (vol.)	0.05 (max)	
Ramsbottom Carbon on 10% Residue	% (wt.)	0.35 (max)	
Ash	% (wt.)	0.01 (max)	
Copper Strip Corrosion		No. 3 (max)	
Lubricity limit	μm	–	520

a – Low temperatures and high altitude operation may require use of fuels with higher cetane.
b – in most cases, satisfactory operation is assured with the cloud point specified 6 °C above the tenth percentile minimum ambient temperature for the area in which the fuel will be used.
c – if cloud point of less than – 12 °C is specified, the minimum viscosity should be 1.7 mm^2/s and the 90% distillation point should be waived.
d – Complete compliance from 1st Jan 2010.

temperature and oxidants yields different CO concentrations in the syngas mixture (Equations (2–4)).

$$C_nH_m + nH_2O \rightarrow nCO + (n + m/2)H_2 \tag{2}$$

$$C_nH_m + 1/2nO_2 \rightarrow nCO + m/2H_2 \tag{3}$$

$$C_nH_m + n/2 * \lambda(O_2 + 3.76N_2) + n(1-\lambda)H_2O \rightarrow nCO + [m/2 + n(1-\lambda)]H_2 + 3.76 * n/2 * \lambda N_2 \tag{4}$$

Selecting the most suitable reforming technology depends on both the application requirements and the available design options. For our application the autothermal reforming technology was considered as we required a relatively dynamic system with high fuel efficiency.

2.2. *Reformer efficiency*

The efficiency of the reformer is defined as the ratio of the usable energy produced to the energy of the fuel used in the process. In the reformer both hydrogen and carbon monoxide are considered usable as nearly all of the carbon monoxide, can be converted into hydrogen in the water gas shift reactors ($CO + H_2O \rightarrow H_2 + CO_2$). The amount of H_2 and CO produced in the reformer limits the amount of H_2 that can be generated in the fuel processor. In this paper the efficiency is defined as:

$$\eta_{fp} = \frac{\dot{h}_{prod}}{\dot{h}_{diesel}} = \frac{(n_{CO} + n_{H_2}) \cdot h_{H_2-LHV}}{n_{diesel} \cdot h_{diesel-LHV}} \tag{5}$$

Table 3 – Properties of diesel fuel used in experiments.

Properties	Results	Units	Ref. Test methods
Appearance at 20 °C	BRIGHT AND CLEAR		ASTM D 4176-93 (1997)
Ash content	0.001	% m/m	ASTM D 2274
Carbon residue (10% dist. res)	0.03	% m/m	ASTM D 189
Carbon/Hydrogen ratio	6.42	CH	API
Cetane Index	51.7	–	ASTM D 4737
Cetane Number	52.6	–	ISO 5165:1998
Cloud point	−8	°C	ASTM D 2500
Cold Filter Plugging Point	−15	°C	EN 116:1997/AC:1999
Conductivity	690	pS/m	ISO 629
Cu strip corrosion(3 h at 50 °C)	1A		ASTM D 130
Density at 15 °C	835.1	kg/m3	ISO 3675
Dist. IBP	192.0	°C	ISO 3405:1988
Dist. 10% Evap.	216.0	°C	ISO 3405:1988
Dist. 50% Evap.	261.0	°C	ISO 3405:1988
Dist. 90% Evap.	327.0	°C	ISO 3405:1988
Dist. 95% Evap.	347.0	°C	ISO 3405:1988
Dist. FBP	365.0	°C	ISO 3405:1988
Flash point	76.0	°C	ASTM D 93
Lubricity (wsd1.4)at 60 °C	355	μm	ISO 12156-1:1997
Net heat of combustion	42.94	MJ/kg	SS 15 51 38:1992
Oxidation stability	1.0	mg/100 ml	ASTM D 2274
Polycyclic aromatic content	4.2	% m/m	IP 391/95
Sulphur content	10	mg/kg	ISO 8754:1992
Total Acid number	0.03	mg KOH/g	ASTM D 664
Water content	30	mg/kg	ASTM D 1744-92
Viscosity at 40 °C	2.62	mm2/s ISO	3104:94/COR.1:97
MW	191	g/mol	UOP Method 375-86

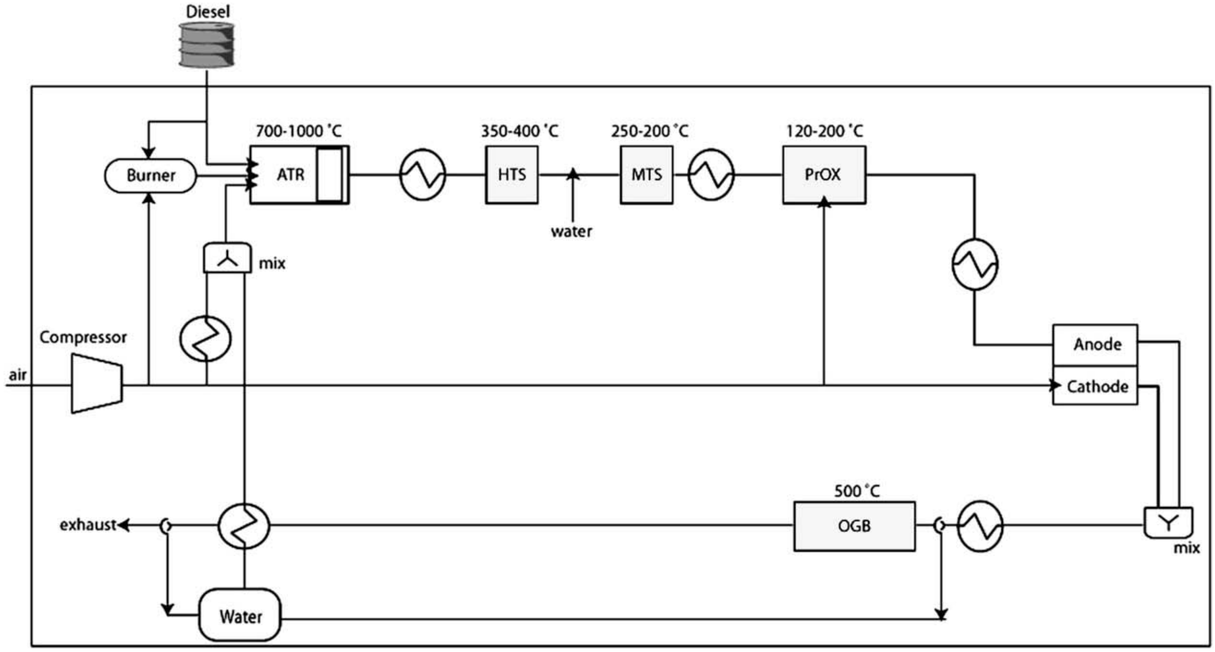

Fig. 3 – Fuel cell system design.

2.3. *Reformer startup*

In automotive applications, a fast start up sequence is essential as the end user usually requires immediate power from a generator. The fuel processor requires both elevated temperatures and steam for normal operation.

The amount of energy required to achieve full power in the fuel processor can be expressed as a function of the thermal mass of the fuel processor ($m_{rea} \cdot C_{p,rea} \cdot \Delta T_{rea}$; $\Delta T_{rea} =$ temperature rise in the reactors). The energy can be supplied either by indirect heating (electrical) or by direct heating, using a start-up burner that feeds the reactors directly with the hot flue gas.

The use of a burner is the most effective method for fast startups and is the method utilized in our system. The startup time of such a system is dependent of the calorific value of burner gas ($\dot{m}_{flue} \cdot C_p \cdot \Delta T_{flue}$; ΔT_{flue}: temperature difference between inlet and outlet) [4].

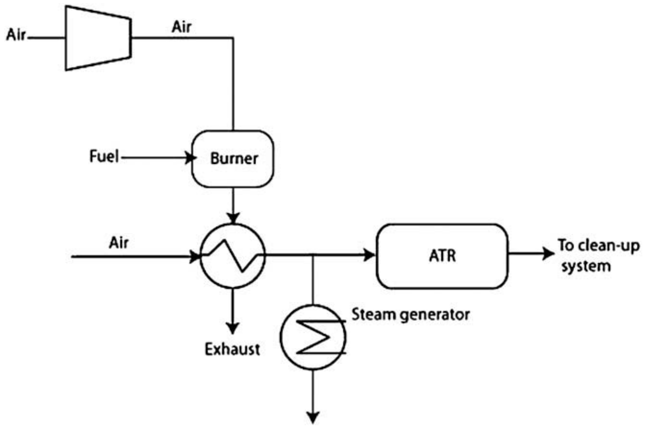

Fig. 4 – System startup concept.

The startup time can be derived from the ratios of the thermal mass of the reactor and the thermal mass supplied by the burner:

$$t = \frac{m_{rea} \cdot C_{p,rea} \cdot \Delta T_{rea}}{\dot{m}_{flue} \cdot C_p \cdot \Delta T_{flue}} \tag{6}$$

Following the above logic, it is clear that it is possible to optimize the startup times by decreasing the thermal mass of the reactors as well as by integrating heat exchangers with the burner and reformer.

2.4. *Diesel fuel*

Diesel and Jet Aviation (Jet-A) are petroleum based fuels, principally produced in refineries from crude oil. The physical

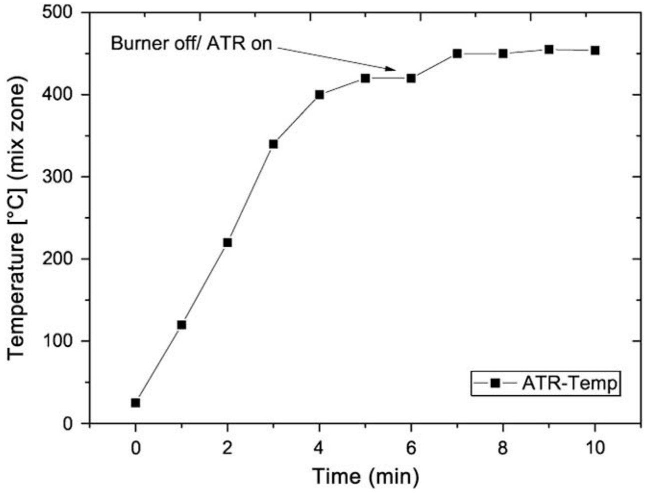

Fig. 5 – Reformer startup time.

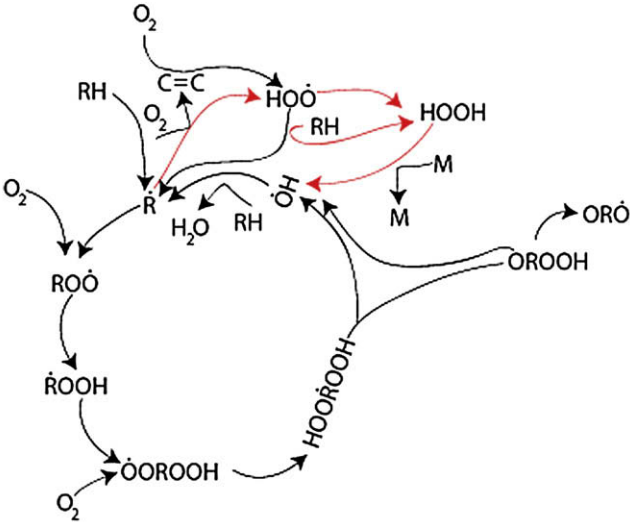

Fig. 6 – Generic fuel reactions [7].

and chemical properties of these fuels vary from region and refinery and are essentially a mixture of different hydrocarbons fuels. There is no predominant compound in the fuel and the governmental regulations focus primarily on the overall property of the fuel [5].

The fuel reformer was developed for the North American and European markets, and tests have mainly been performed on US standard diesel, as this fuel has a higher aromatic and sulphur content than European (Table 2 and 3) and poses more of a challenge to reform.

For non-road markets, such as the marine, the implementation of lower sulphur diesel is not mandated until 2012.

A detailed analysis of the fuel used is shown in Table 3. From the measured molecular mass and the carbon-to-hydrogen ratio it is possible to calculate the approximate molecular formula of the fuel as proposed by Van Gerpen [6]. With the measured fuel molecular weight of 191 g/mol and the C/H mass ratio of 6.42 the approximate formula for the diesel used in the experiments is:

$C_{13.883}H_{24.053}$

This approximation is used for all calculations in this paper.

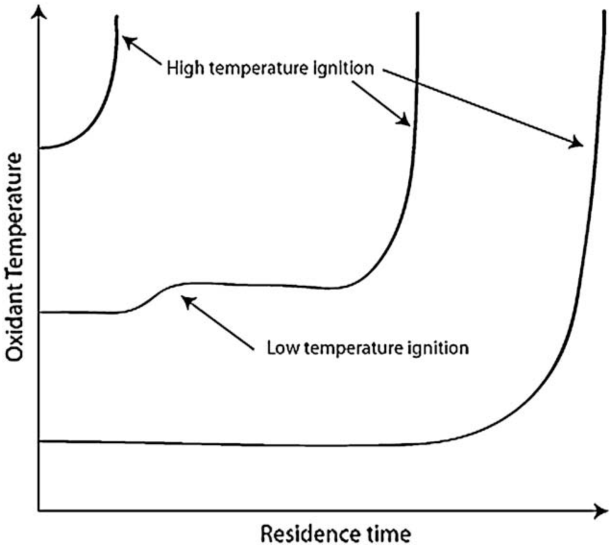

Fig. 7 – Typical ignition delay times for different starting temperatures.

Table 4 – Reaction data n-heptane [7].

#	Reaction	E_A [kJ]
Initiation		
1	$RH + O_2 \rightarrow \dot{R} + HO\dot{O}$	201
Low Temperature Oxidation mechanisms		
2	$\dot{R} + O_2 \rightarrow RO\dot{O}$	0
3	$RO\dot{O} \rightarrow \dot{R}OOH$	44.97
4	$\dot{R}OOH + O_2 \rightarrow \dot{O}OROOH$	0
5	$\dot{O}OROOH \rightarrow HOO\dot{R}OOH$	44.78
6	$HOO\dot{R}OOH \rightarrow \dot{O}H + 1/16O_2 + RH + 7/8CO + ROOH$	31.40
7	$\dot{O}H + RH \rightarrow \dot{R} + H_2O$	3.42
High Temperature oxidation mechanisms		
8	$\dot{R} + O_2 \rightarrow 7/16O_2 + 7/8CO + HO\dot{O}$	25.10
9	$HO\dot{O} + HO\dot{O} \rightarrow O_2 + HOOH$	−5.20
10	$RH + HO\dot{O} \rightarrow \dot{R} + HOOH$	70.77
11	$HOOH + M \rightarrow \dot{O}H + \dot{O}H + M$	206.80
12	$\dot{O}H + RH \rightarrow \dot{R} + H_2O$	3.42

2.5. *System design and operational description*

The fuel cell system design, employed by PowerCell (Fig. 3), utilizes an autothermal reformer in combination with a PEM-based fuel cell stack. The system has been optimized for quick start-up and durability.

2.5.1. *Startup sequence*

The system starts by igniting the diesel burner and using the off-gasses from the burner to heat up a separate air-stream that is used to supply heat directly in the reformer. By constructing the indirect heating system, shown in Fig. 3, it is possible to heat the reformer without risking contamination by particulate matter formed in the burner during cold start. Albeit the startup time is longer than for a direct heated reformer, the life expectancy of the system is much higher, as

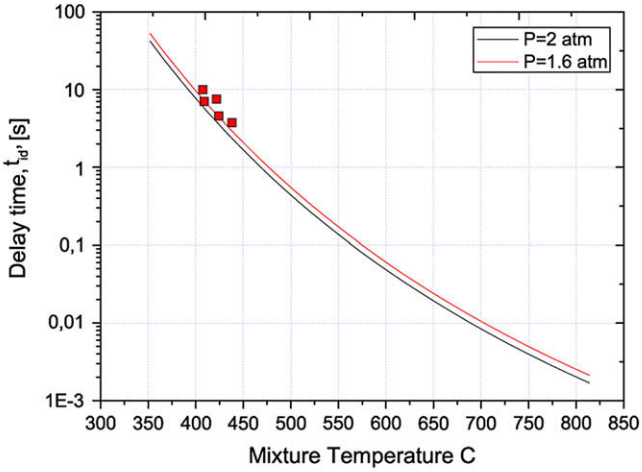

Fig. 8 – Autoigniton delay time in ATR-M2/M3.

Table 5 – ATR generations.

Generation	Catalyst	Reforming technology	Residence time [s]	T_{mix}
ATR-M2	Monolith	Cool flame	>7	350–800
ATR-M3	Monolith	Modified cool flame	>3 s	350–800
ATR-M4	Monolith	ATR	0.12–0.65	∼460
ATR-M5	Monolith	ATR	0.11–0.63	∼480

soot deposition deactivates the catalysts and produces hot-spots during startup (Fig. 4).

The flue gases are also used to heat the steam generator, enabling a faster startup of the reforming process.

When the gas temperature in the ATR was above 300 °C, the heating circuit was broken and the air/steam mixture (preheated to 350 °C) was introduced in the reformer – and after a time delay of 1 s, diesel was injected into the oxidation zone and mixed with the oxidants. Light off was immediate and normal operating conditions in the reformer was obtained within one minute from light off (Fig. 5-start up time). The ATR operates within a temperature interval of 700–1000 °C, depending on the air-to-fuel ratio used in the reformer.

2.5.2. *Normal operation*

The syngas mixture produced in the reformer is quickly cooled down to the operating temperature of the high temperature shift reactor (HTS). The shift reactors convert the bulk of the CO to CO_2 and H_2, thus increasing the efficiency of the reforming process. It is critical to cool down the mixture quickly before the syngas comes into contact with the shift catalyst, to kinetically prevent coke formation through the Boudouard reaction ($2CO \rightarrow C + CO_2$).

Before entering the second shift step, the gas is cooled down to 300 °C in which the CO is reduced to approximately 0.5%. Further reduction of CO is achieved in the preferential oxidizer (PrOX) where the CO is oxidized by direct injection of air into the reactor ($CO + 1/2\ O_2 \rightarrow CO_2$). The oxidation reaction usually suffers from a 50% selectivity, which leads to a small loss of hydrogen in the reactor. The CO content after the PrOX is usually in the range of 1–50 ppm, depending on the operating conditions and catalyst performance.

The purified hydrogen gas is cooled down to 80 °C before entering the stack, ensuring that liquid water does not condense inside the stack. In the fuel cell, approximately 80% of the hydrogen is converted into electricity and heat.

The flue gas from the fuel cell is used in a catalytic off-gas burner (OGB) to provide heat for the fuel cell system. The water produced in the fuel cell and catalytic burner is recycled into the water tank and reused in the reforming process.

The reactor design and operating conditions in the fuel cell system can be varied in numerous ways and the degree of integration of the components strongly affects the complexity and cost of the system.

3. Mixture homogenization

The prime challenge with a diesel based fuel cell system is to achieve a clean conversion of the fuel into a hydrogen-rich gas. Diesel is a complex mixture of inhomogeneous hydrocarbons, with a broad distillation range, that readily forms soot and undesirable byproducts when evaporated, mixed and reacted with the oxidants in the reformer.

The establishment of a homogeneous mixture of vaporized fuel and oxidants before contact with the catalyst is essential for the complete reformation of diesel and the protection of the catalysts from rapid thermal stress and degradation.

3.1. *Fuel evaporation and homogenization*

In order to avoid the characteristic soot formation, associated with rich diesel oxidation at elevated temperatures, system must be designed so that the evaporated mass is mixed rapidly to homogeneity avoiding rich zones. This can be achieved by injecting the fuel into a preheated oxidant(s) and allowing for a rapid evaporation.

In the case where air or air/steam mixtures are used as oxidants, a set of complex chemical reactions will be initiated when the hydrocarbon species come into contact with the preheated air resulting in more than 10 000 reactions and heat release from the oxidation in the mixing zone [7].

The oxidation reactions of the fuel and air must however be controlled as it can lead to autoignition as well as the complete consumption of oxygen in the mixture prior to contact with the catalyst, leading to a lower fuel conversion in the catalyst.

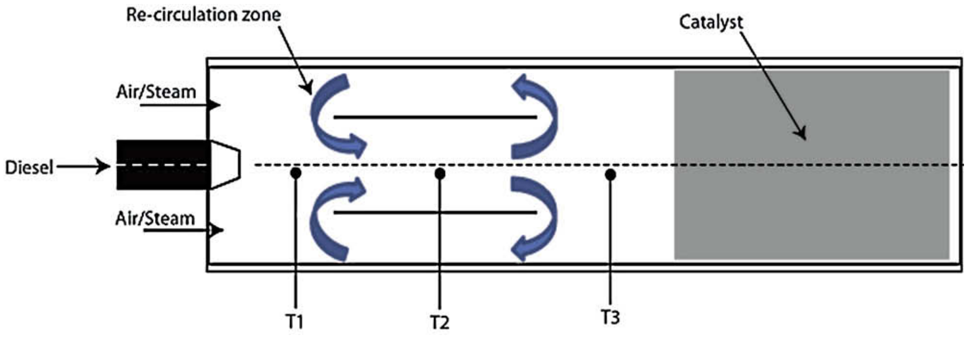

Fig. 9 – ATR-M2 reactor.

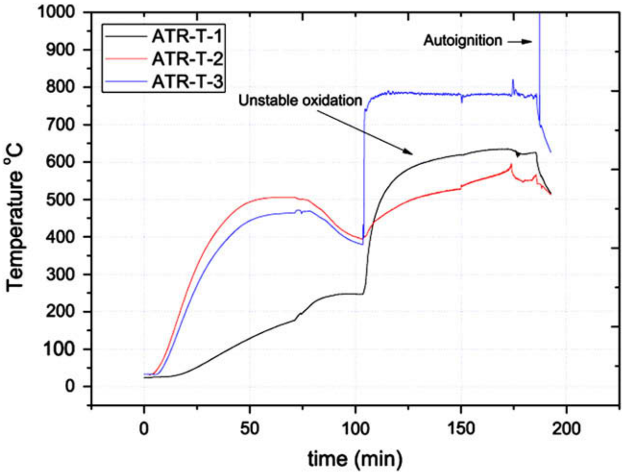

Fig. 10 – Temperature profile in ATR-M2 reactor.

The chemical reactions between the air and fuel in the reformer start immediately upon contact, however initially the reactions proceed at a limited rate and consequently the amount of fuel consumed is low and the rise in temperature insignificant compared to complete oxidation [8]. Earlier studies have shown that two main mechanisms can occur during the oxidation of hydrocarbons [8,9].

The first is a low temperature mechanism that involves the formation of peroxides and the cracking of the molecule into a series of radicals (Fig. 6). The second is a high temperature mechanism, initiated by the ignition precursors formed in the low temperature reactions that without quenching will lead to autoignition (Fig. 7).

From generic reaction data, for n-heptane (Table 4), its evident that the activation energies (E_a) for the primary oxidation processes are significantly lower than for the high temperature cycle, where the reaction $HOOH + M \rightarrow OH + OH + M$ has a significant limiting effect, and it is only after the oxidation temperature and residence time exceed the kinetic limitation of the high temperature mechanisms that the secondary oxidation reaction can initiate (Fig. 7).

The low temperature oxidation reaction that take place at temperatures below 400 °C are known as cool flame, a phenomenon that is associated with a negative temperature coefficient of reaction rate. A distinct property that results in a decrease in the reaction rate with an increase in temperature [10–12] The cool flame phenomena should not be confused with the blue flame that forms in the products of the cool flame in the temperature range of 400–800 °C. In the cool flame there is no formation of soot precursors and only a fraction of the fuel is consumed.

Cool flames properties are not observed for all fuels, since the initiation process is influenced by several factors such as carbon chain length and C–H type [13]. The formation of ketohydroperoxides (OROOH) is instrumental in the heat release process in cool flames. The heat release is coupled to the structure of the fuel and the reaction conditions in the reformer. Generally straight-chain alkanes show cool flame behaviour under the conditions present in a diesel reformer. The easiest C–H bond to break is a tertiary C–H bond since the carbon atom in this case is bound to three other carbon atoms [14].

Hartmann et al. [3] have proposed to actively utilize the cool flame phenomenon to create a homogeneous mixture for the reforming reaction. This is achieved by prolonging the residence time in the reactor by recirculation of the fuel/oxidant mixture in the oxidation zone while maintaining a temperature below 400 °C in the oxidation zone.

The concept was tested by PowerCell in two early rector designs (ATR-M2/M3). The results were initially promising; however prolonged test showed that the conversion of aromatics was low (see Results and discussion), and that the heat release in

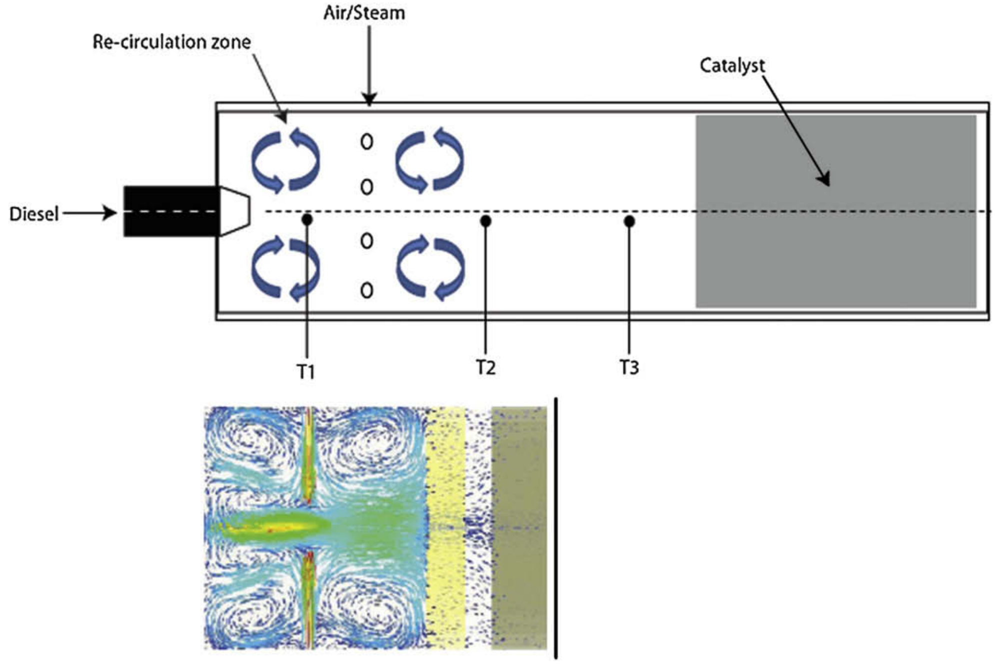

Fig. 11 – ATR-M3 design.

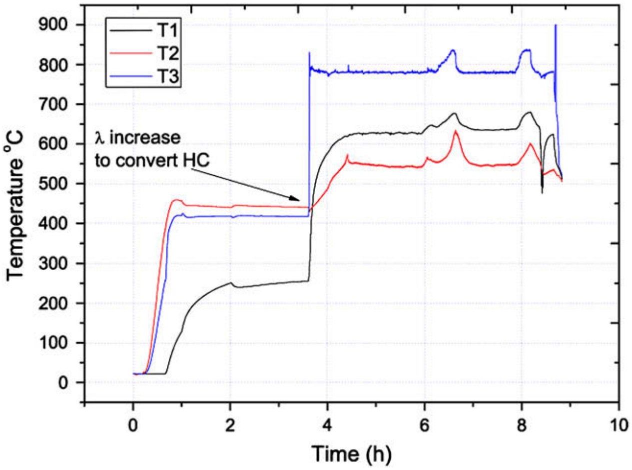

Fig. 12 – Temperature profile in ATR-M3 reactor.

the post mixing zone was high, indicating a high conversion of oxygen before contact with the catalyst (see next section on reactor design). Additionally we observed polymerization on the fuel nozzle due to condensation of recirculated hydrocarbons.

During stable operation ($t > 20$ min) a continued increase in reaction temperature was observed for the cool flame reactors, which inevitably led to autoignition.

Autoignition is the spontaneous oxidation of the fuel and oxidant in the absence of an external source of ignition. Autoignition occurs when the residence time of the oxidant–fuel mixture is greater than the delay time to ignition. The delay time taken to reach autoignition in an oxidation chamber depends on temperature, pressure, fuel/oxygen concentration.

The delay time is composed of two components: Physical and chemical delay times. The physical delay predominates in the early part of the autoignition process and is described as the time taken for the fuel drops to form, heat up, evaporate and mix with the oxidant. The chemical delay occurs after the physical delay and is dependent on the chemical kinetics.

The residence time is defined as the ratio between the tube length (L) and the educt flow velocity (u):

$$\tau = \frac{L}{u} \tag{7}$$

The flow velocity can be calculated, under the assumption of ideal gas conditions, by:

$$u = \frac{\dot{m}_m R_m T_m}{p A_p} \tag{8}$$

Lefebvre et al. [12] have studied the influence of the delay parameters for a diesel fuel and showed that temperature and pressure had the greatest influence on the ignition delay time. Furthermore, the authors showed that the activation energy for the autoignition process was 29.6 kcal/mol and that the pressure and fuel concentration exponents were 0.98 and 0.37 respectively.

$$t_{id} \propto e^{\left[\frac{E_A}{RT}\right]} [\text{Fuel}]^{-m} p^{-n} \tag{9}$$

Fig. 8, shows the theoretical correlation for ignition delay times according to Lefebvre versus actual measurements in ATR-M2/M3 where autoignition was observed in the reformer. The added use of steam as an oxidant in the mixture increases the heat capacity of the oxidant/fuel mixture and the resistance to autoignition.

4. Reactor design solutions and mixture zone properties

In the process of developing a diesel fuel cell system, five generations of fuel reformers were developed (Table 5). Onboard hydrogen generation from commercial liquid fuels is a challenging task including advanced heat-integrated reformer design and catalyst development. In the literature examples of studies can be found regarding reforming of hydrocarbon fuels covering subjects such as the influence of diesel fuel properties on reforming efficiency [15,16] and catalysts and reactor design considerations using catalytic partial oxidation [17–19].

The first generation in this study (ATR-M1) was a simple packed bed reactor that generated large amounts of soot and fuel deposits in the reactor. The results from ATR-M1 are limited as the design was flawed and that inhomogeneous mixture was obtained under all tested operating conditions.

The second and third generations (ATR-M2/M3) were based upon the cool flame concept, described in the previous section (Fig. 9). The ATR-M2 reactor employed a forced recirculation zone to increase the residence time in the reactor to allow the formation of cool flames – to partially break down the fuel and to control the oxidation.

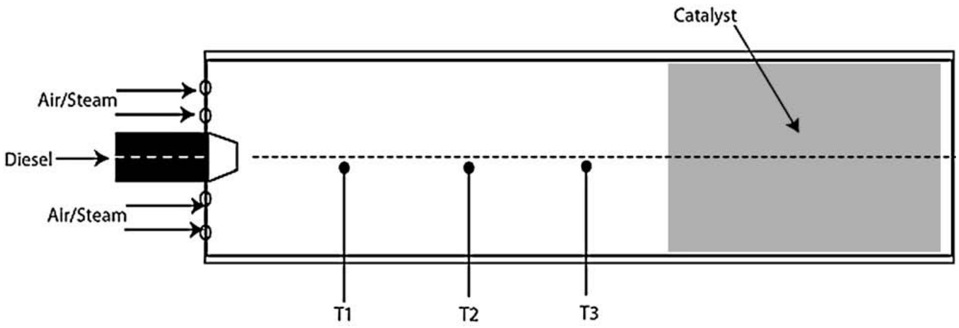

Fig. 13 – ATR-M4 Design.

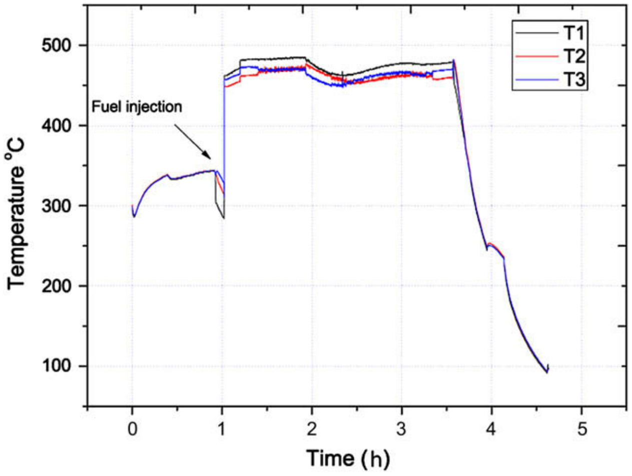

Fig. 14 – Temperature profile in ATR-M4 reactor.

Initial tests on the reactor were promising and the conversion of a gas-to-liquid (GTL) fuel was successful. However, when operated on standard diesel, the conversion of aromatics was low and the system was difficult to control as autoignition occurred due to a constant temperature rise in the reactor (Fig. 10).

The oxidation zone was inhomogeneous and a significant amount of heat was released downstream from the recirculation zone due to the formation of a blue flame from the products of the cool flame.

The increased heat in the post cool flame zone (T3), resulted in a rapid increase in the temperature of the cool flame to a temperature >400 °C and thereby changing the chemistry of the reaction – leading to autoignition.

In an attempt to reduce the residence time, while maintaining the positive effects of the cool flame, a modified reactor was built – without the forced recirculation tube (Fig. 11).

This reactor was more stable. However the aromatics in the diesel fuel could only be reduced at high air-to-fuel ratios ($\lambda > 0.34$), which in combination with the recirculation increased the temperature in the oxidation zone >400 °C (Fig. 12) and the formation of a blue flame, causing an unstable condition in which autoignition occurs.

From the tests performed on the M2/M3 systems it was evident that the long residence times in the cool flame zone led to autoignition in the post-recirculation zone. In an attempt to achieve complete homogenization of the mixture without using the recirculation method – a completely new design was developed using CFD calculations and ignition delay tests.

The improved ATR-M4/M5 designs were shown to have a stable oxidation zone (Fig. 13) with a shorter residence time (<0.7 s) than the designs used in the cool flame reformers. The M4/M5 generations also showed complete conversions of all hydrocarbons (see Section 5).

The mean temperature in the new reaction oxidation zone was higher than in the recirculation zone used in the cool flame reactor, nonetheless the unstable oxidation which was observed in the cool flame reactors have not been detected in the M4/M5 reformers (Fig. 14).

5. Experimental

5.1. *Experimental setup*

Five generations of diesel fuel reformers have been developed and tested in our laboratory (Figs. 9, 11 and 13). The setup included a diesel fired burner for quick start up and a system for controlled mixing and pre-heating of the oxidants. A schematic diagram of the set-up including the location of the thermocouples is shown in Fig. 15. The pressure in all experiments was 1.6 atm.

All components in the system were insulated and the burner was operated near adiabatic conditions during system

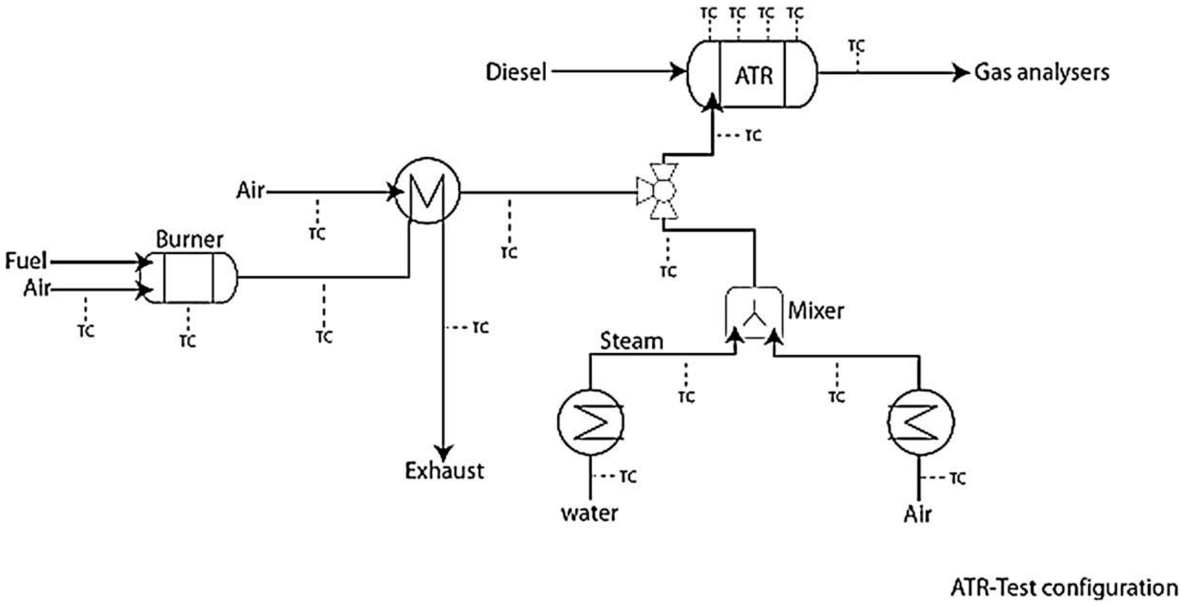

Fig. 15 – ATR test configuration.

Table 6 – Design parameters at maximum power.

Flow rate (g/s)	
Diesel	0.39
Air	1.71
Air – ATR-M3	1.93
Water	1.55
Ratios	
λ (ϕ)	0.3 (3.33)
λ (ϕ) – ATR-M3	0.34 (2.94)
O2/C (ATR-M3)	0.43 (0.49)
Steam-to-carbon	3

start-up. The catalysts in the ATR were in the ATR-M2–M5 generations commercial catalysts – coated on ceramic monoliths. For the ATR-M1 a pellet catalyst manufactured at KTH was used.

The reformers were designed to operate at a maximum power of 17 kW_{th}, with a turndown ratio of 1:10. A practical APU system would have a maximum electric power of 5 kW. Assuming a system efficiency of 30% means an input of 17 kW_{th}. Table 6, shows the experimental design parameters for full power conditions (17 kW_{th}).

5.1.1. *Startup sequence*

The system starts by igniting the diesel burner and using the off-gasses from the burner to heat a separate air-stream that is used to supply heat directly in the reformer. By constructing the indirect heating system, shown in Fig. 15, it is possible to heat the reformer without risking contamination by particulate matter formed in the burner during cold start. Albeit the startup time is longer than for a direct heated reformer, the life expectancy of the system is much higher. The impact of soot deposition was observed in an early set-up in which we used the burner off-gases directly in the reformer.

When the temperature in the ATR was above 300 °C, the heating circuit was broken and the air/steam mixture (pre-heated to 350 °C) was introduced in the reformer – and after a time delay of 1 s, diesel was injected into the oxidation zone and mixed with the oxidants. Light off was immediate and normal operating conditions in the reformer was obtained within one minute from light off (Fig. 5).

5.1.2. *Gas quality analysis*

Complete control over all species exiting the reformer is a necessary requirement, when developing a fuel reformer for PEM-fuel cells as these are particularly sensitive to both by-products from the reforming as well as the traces of the diesel fuel itself.

In our experimental setup, we have utilized the following measurement equipment, as shown in Fig. 16:

- FTIR analyser (wet measurement)
- FID (Signal, Hydrocarbon analyser, Model 3000, wet measurement)
- Maihak, (S700, dry measurement)
- H_2 mass spectrometer

5.1.2.1. *FID*. FID – the Signal Model 3000 Hydrocarbon analyser is based on the Flame Ionization Detector. This detector ionizes carbon atoms, in hydrogen flame. Normally a hydrogen flame produces a negligible amount of ions, any hydrogen carbon bounded compounds carried into the flame results in the formation of carbon ions.

Combustion exhaust gases normally contain some hydrocarbons which would be liquid under normal temperature and pressure. The Signal Model 3000 Hydrocarbon analyser incorporates a heated sample system and detector which maintains a sample temperature of up to 200 °C while carrying out the analysis. Therefore gases with a lower boiling point than 200 °C can be measured. Heated sample line back to the high temperature sources is necessary to maintain this high temperature throughout the gas sample tubing.

5.1.2.2. *FTIR*. The FTIR analyser uses Fourier transform Infrared (FTIR) spectrometry and is manufactured by Temet Instruments. The controlling and monitoring is done using the Windows based program ‘‘Calcmet’’ provided by the equipment manufacturer. The spectra generated by the analyser can be stored and/or processed in real time. The signals detected by the gas analyser are digitalised and Fourier transformed by a computer in order to get the infrared spectrum of the sampled gas. All gas molecules (except for

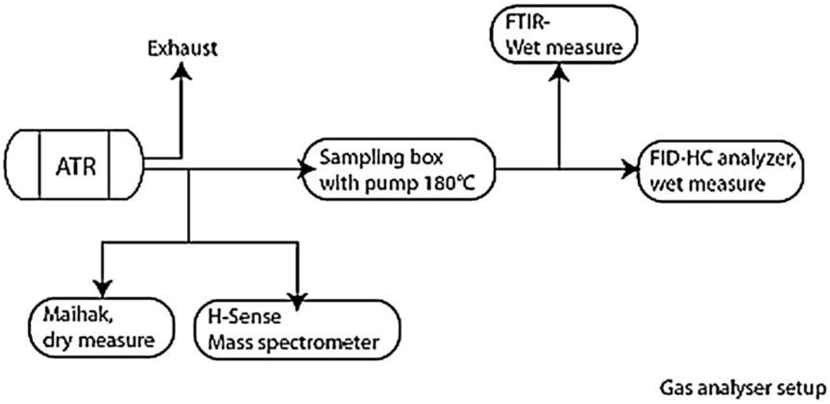

Fig. 16 – Gas analysis setup.

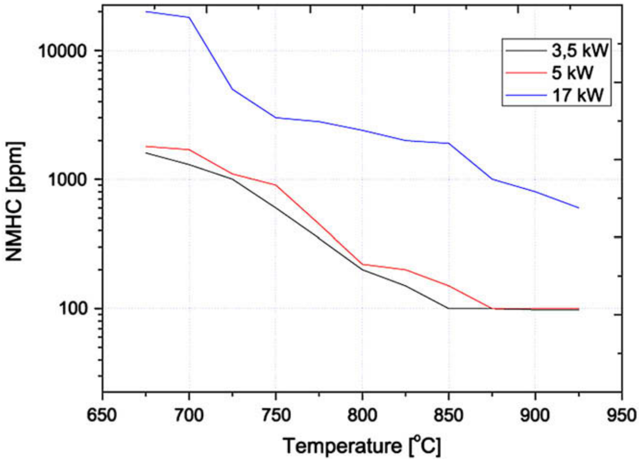

Fig. 17 – Diesel slip in ATR-M2.

non-polar gases) have a unique infrared spectrum. It is possible to identify the different gas components from the sample spectrum using a reference spectrum.

5.1.2.3. *Maihak S700*. Gas analysers in the S700 series measure the volumetric portion (concentration) of a particular gas in a gas mixture (sample gas). The Maihak uses both NDIR and thermal conductivity modules in the measurements.

The Maihak system used the following measurement ranges:

- CO low range 0–20 ppm
- CO high range 0–2 vol%
- CO_2 range 0–30 vol%
- H_2 range 0–75 vol%

5.1.2.4. *H_2-sense mass spectrometer*. The mass spectrometer is based on the Electron Pulse Ionization (EIMS) Mass Spectrometer principle optimized to measure H_2 at high frequencies. The system has mainly been employed to verify the hydrogen measurements from the Maihak.

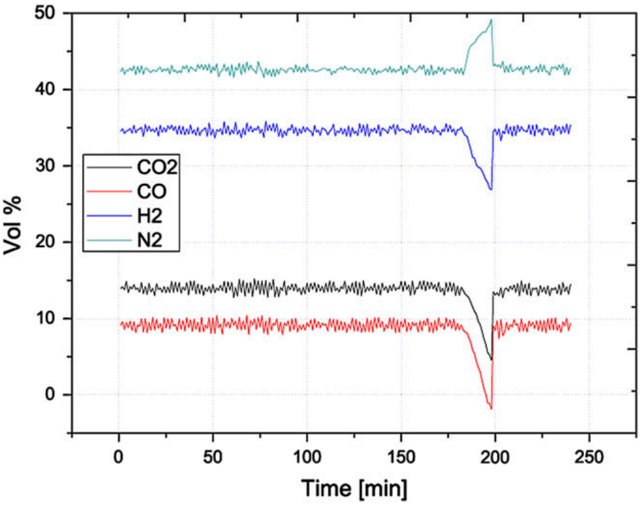

Fig. 18 – Gas composition ATR-M2.

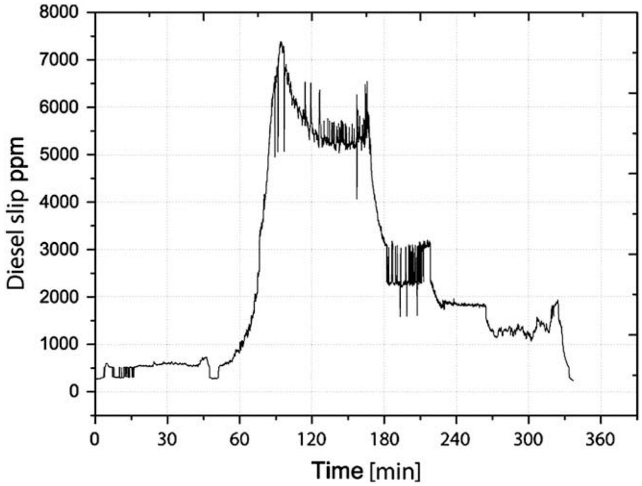

Fig. 19 – Variation in hydrocarbon slip over time for ATR-M2.

5.2. *Results and discussion*

The reformer reactors were initially tested at steady state conditions, at variable load points to determine performance and sensitivity to a wide turn-down ratio. In all design cases except for the fixed bed reactor a commercial catalyst was used, designed for autothermal reforming of diesel type fuels.

5.2.1. *M1-ATR reactor*

A fixed bed reformer was designed and constructed based on a cylindrical stainless steel reactor. Various catalysts were prepared and evaluated based on spherical γ-Al_2O_3 pellets with a diameter of 2.5 mm and a nominal BET surface area of 200 m^2/g. The pellets were supplied by Sasol Germany. Using a fixed bed reactor for automotive applications leads to problems with pressure drop and durability.

One severe problem is the mismatch in thermal expansion between the stainless steel reactor and the aluminium oxide

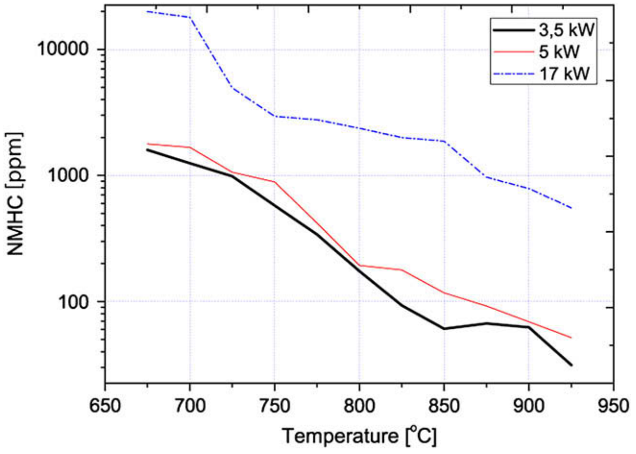

Fig. 20 – Diesel slip in ATR-M3.

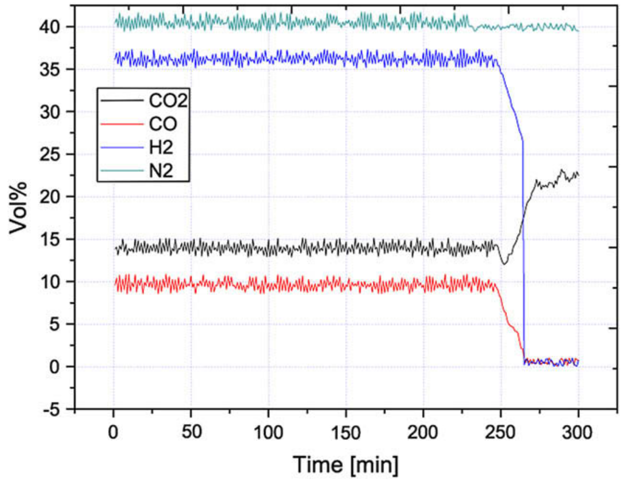

Fig. 21 – Gas composition ATR-M3.

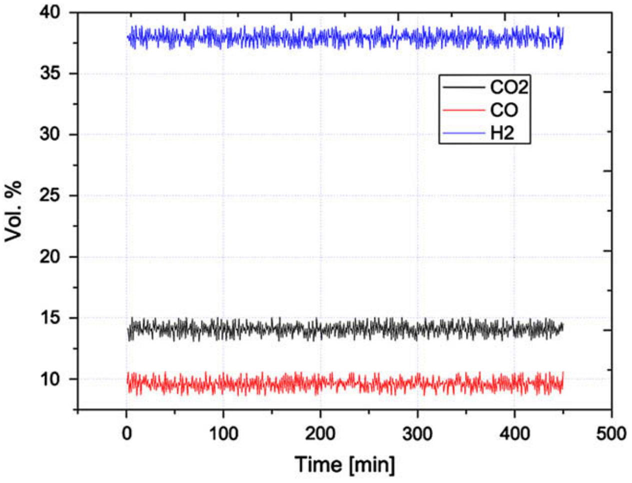

Fig. 23 – Gas composition ATR-M4.

pellets, which can lead to crushing of pellets at shut-down. Another problem is the attrition of the bed due to vibrations in the vehicle, which also can lead to mechanical damage of the reactor material.

On the other hand, one advantage is the possibility to achieve a high metal loading per unit volume compared to a monolith. Another advantage is the turbulent flow in the fixed bed resulting in favourable mass transfer characteristics.

The experimental results from this part of the programme were highly unrewarding, due to severe coking, especially when using nickel and platinum as active materials. This led to a decision to change track in the catalyst development and to use monolithic structures as catalyst substrates.

5.2.2. *M2-ATR (Cool flame design 1)*

Initial tests on the first cool flame reformer (ATR-M2) was tested by our development partner with a GTL fuel from Shell Oil (Sol-D), with promising results. The cool flame reformer was operated at low air/fuel ratios with a high fuel conversion.

However when tested in our laboratory with a standard European diesel (590 EN), the impact of the natural hydrocarbon mixture and aromatics, decreased the performance of both the hydrogen selectivity and conversion of hydrocarbons (Fig. 17). The temperature illustrated in this figure and the following ones is measured downstream the catalyst in the reformer.

The ‘‘diesel-slip’’ at the cool flame temperatures used with the GTL fuel produced hydrocarbon slips of more than 10 000 ppm, which would have detrimental effects on the fuel cell as well as on the shift catalysts. Efforts to decrease the slip, by increasing the λ, were done. However, at full loads the slip was in the range of 1500 ppm with catalyst exit temperatures greater than 900 °C, temperatures that would potentially decrease the lifetime of the catalyst in the reformer.

The reformer was also highly unstable and autoignition related mechanisms resulted in sudden decreases of hydrogen contents (Fig. 18) and increased hydrocarbon content in the reformer gas (Fig. 19).

5.2.3. *M3-ATR (Cool flame design 2)*

In an effort to suppress the autoignition mechanisms, and the consumption of oxygen in the mixing zone, which in turn

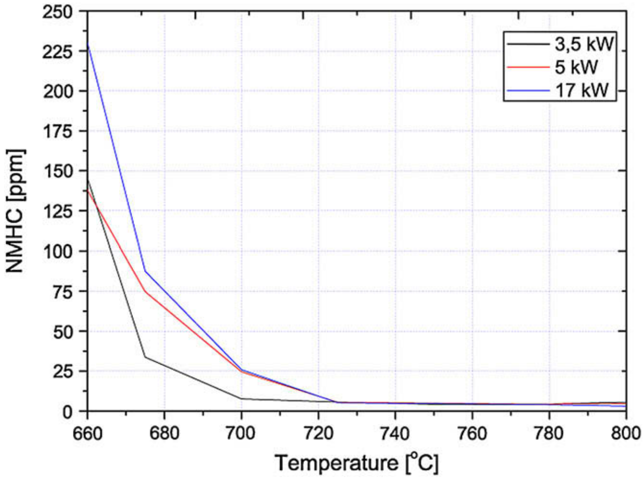

Fig. 22 – Diesel slip in ATR-M4.

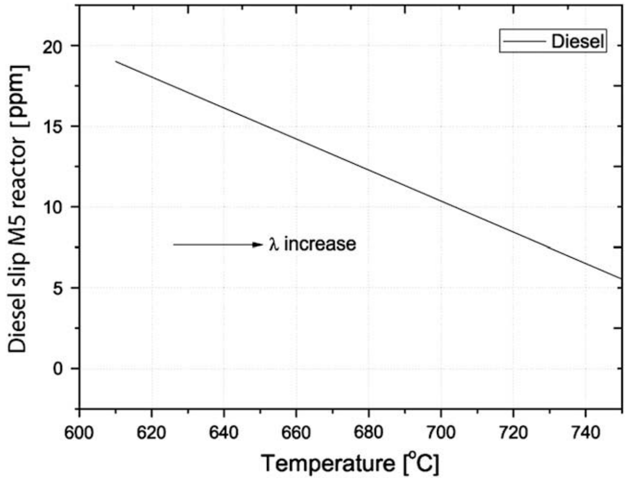

Fig. 24 – Influence of air-fuel ratio on diesel slip.

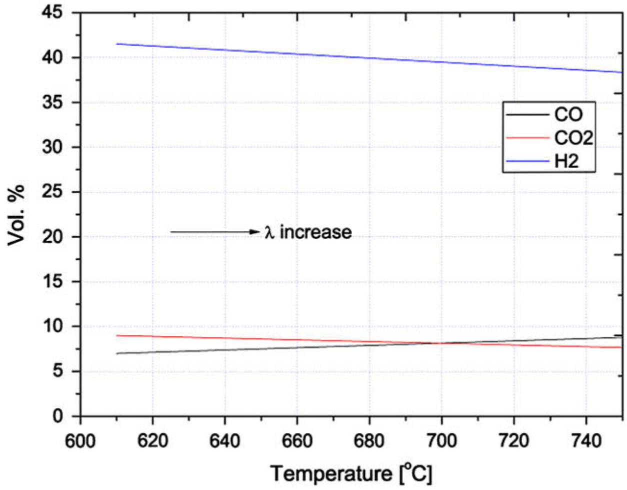

Fig. 25 – Influence of temperature and air-to-fuel-ratio on product gas composition in reformer.

decreased the cracking of aromatics in the catalyst, a new cool flame design was developed with the intention of decreasing the residence time of the cool flames.

The performance of the ATR-M3 was an improvement, over the M2 design as autoignition occurred at a lower frequency, however the conversion of diesel, was even in this design low (Fig. 20). The reformer, also showed a tendency to autoignite after operating times exceeding four hours (Fig. 21) and a careful analysis of the temperature profiles in the reactor showed a steady increase of temperature in the mixing zone (~0.1 °C/min) – which eventually led to reaction conditions that allowed autoignition of the mixture.

5.2.4. *M4-ATR*

Following the failure of the cool flame concept, a new approach was made, abandoning the cool flame design and selecting a more innovative solution. The M4-ATR design was developed using CFD and solutions previously used in diesel engine design at Volvo. The approach was to design a mixing chamber that allowed for homogeneous mixing of the reactants while significantly lowering the residence time and thereby hindering the autoignition process.

The results from tests with the new design were a significant improvement from ATR-M2/M3 and the diesel slip was at temperatures >730 °C less than 15 ppm, compared to the 1000 ppm of the previous design (Figs. 22 and 23).

The ATR-M4 was also more stable and autoignition has not been reported over the entire load range (Fig. 23). The hydrogen concentrations were also higher for the M4 compared to the previous designs.

Table 7 – Experimental results.

Component	M2	M3	M4	M5
Diesel slip (NMHC)	800 ppm	700 ppm	<15 ppm	<10 ppm
Operating temperature	925 °C	900 °C	750 °C	750 °C
Hydrogen content	33%	35%	38%	38.5%
Efficiency	75%	77%	82%	83%
Steam-to-carbon ratio	2.5	3	3	3
λ	0.3	0.34	0.3	0.29

5.2.5. *M5-Design*

The ATR-M5 is an improvement of the M4 design, with changes only to fuel injection system and the thermal management during start-up. The improved fuel injection system decreased the diesel slip further and the total content was with this design less than 10 ppm (Fig. 24). The diesel slip in the ATR-M5 could easily be controlled with variations in the air/fuel ratio, however as can be seen in Fig. 25 this results in a small decrease in the hydrogen content.

6. Conclusions

Comparing the results from the reformer generations (Table 7), we see that in addition to the improved stability reported earlier, the conversion and efficiency of the improved M4/M5 designs are significantly higher than for the cool flame reformers. The catalyst operating temperature required for operation at the highest conversion is also lower for the improved designs – which will significantly improve the lifetime of the reformer.

It is evident from the results presented herein that the reaction zone design and mixture homogeneity is the determining factor when designing a diesel fuel reformer.

REFERENCES

[1] US Census Bureau. US Energy Information Administration. Annu Energy Rev 2007.
[2] Docter A, Lamm A. Gasoline fuel cell systems. J Power Sources 1999;84:194–200.
[3] Hartmann L, Lucka K, Köhne H. Mixture preparation by cool flames for diesel-reforming technologies. J Power Sources 2003;118:286–97.
[4] Goebels SG, Miller DP, Pettit WH, Cartwright MD. Fast starting fuel processor for automotive fuel cell systems. Int J Hydrogen Energy 2005;30(4):953–62.
[5] Brown LF. A comparative study of fuels for onboard hydrogen production for fuel-cell-powered automobiles. Int J Hydrogen Energy 2001;26:381–97.
[6] Van Gerpen JH. The origins of fuel economy. Diesel Engine Technology Engineering Academy, SAE Engineering Academies; 2000.
[7] Karlsson JAJ. Modeling auto-ignition, flame propagation and combustion in non-stationary turbulent sprays. PhD thesis, Chalmers University of Technology; 1995.
[8] Spadaccini LJ, Tevelde JA. Autoignition characteristics of aircraft-type fuels. NASA contract report 159886; 1980.
[9] Zabetakis MG, Furno AL, Jones GW. Minimum spontaneous ignition temperatures of combustibles in air. Ind Eng Chem 1954;46(10):2173–8.
[10] Affens WA, Carhart HW. Ignition Studies. Part VII. The determination of autoignition temperatures of hydrocarbon fuels. Naval Research Laboratory report no. 7665; 1974.
[11] Sheinson RS, Williams FW. Cool flames: use of the term in combustion chemistry and analytical chemistry. Anal Chem 1975;47(7):1197–8.
[12] Lefebvre A, Freeman W, Cowell L. Spontaneous ignition delay characteristics of hydrocarbon fuel/air mixtures. NASA contract report 175064; 1986.

[13] Risberg P. Describing the auto-ignition quality of fuels in HCCI engines. PhD thesis, KTH-Royal Institute of Technology ISRN/KTH/MMK/R-06/07-SE; 2006.
[14] Westbrook CK. Chemical kinetics of hydrocarbon ignition in practical combustion systems. Proc Combust Inst 2000;28: 1563–77.
[15] Pereira C, Bae J-M, Ahmed S, Krumpelt M. Liquid fuel reformer development: autothermal reforming of diesel fuel. Presented at the U.S. DOE 2000 hydrogen program technical review. San Ramon, CA, May 9; 2000.
[16] Ahmed S, Krumpelt M. Hydrogen from hydrocarbon fuels for fuel cells. Int J Hydrogen Energy 2001;26:291–301.
[17] Krummenacher JJ, West KN, Schmidt LD. Catalytic partial oxidation of higher hydrocarbons at millisecond contact times: decane, hexadecane, and diesel fuel. J Catal 2003;215:332–43.
[18] Aicher T, Griesser L. Novel process to evaporate liquid fuels and its application to the catalytic partial oxidation of diesel. J Power Sources 2007;165:210–6.
[19] Cheekatamarla PK, Finnerty CM. Synthesis gas production via catalytic partial oxidation reforming of liquid fuels. Int J Hydrogen Energy 2008;33:5012–9.