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Hydrogen generation system for ammonia–hydrogen fuelled internal combustion engines

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ABSTRACT

Ammonia is a well known hydrogen carrier which can be effectively utilized as a fuel in internal combustion engines (ICEs) when a small percentage of other fuels are added as combustion promoters. Among them, hydrogen is certainly the most valuable since it is carbon free and has opposed and complementary characteristics to those of ammonia.

In this work, a Hydrogen Generation System (HGS) capable of supplying up to 1.4 $Nm^3 h^{-1}$ of H_2 from ammonia was successfully developed and coupled to an ICE fuelled with ammonia. The main component of the HGS is a cracking reactor housing a ruthenium based catalyst. This system is capable of working both in a stand-alone mode (as required in vehicular applications for the cold start) and in combination with a spark ignited (SI) ICE (i.e. using the combusted gases exhausted by the engine). Beside the cracking reactor, an integrated system was designed and realized in order to allow system cold start and increase overall efficiency during steady state operations.

The engine experimental activity confirmed the reactor performance, which was previously verified on a dedicated test bench. Although a lower hydrogen flow rate could be used to achieve satisfactory engine operation, a greater value was used during engine experimentation with benefits for fuel economy and engine cyclic variability. On the other hand, this choice led to higher NO_x emissions.

Introduction

The wide and distributed utilization of fossil fuels over the last century have resulted in harmful effects both on human health and on the environment [1,2]. Therefore, sustainable alternatives should be identified and progressively implemented in the world fuel strategy utilization [3].

In this scenario, hydrogen is often considered as a promising fuel and energy carrier. However, the implementation of

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Abbreviations

CA	crank angle
CNG	compressed natural gas
COV	coefficient of variation
DI	direct injection
EBTE	engine brake thermal efficiency
ECU	electronic control unit
GHSV	gas hourly space velocity
HGS	hydrogen generation system
ICE	internal combustion engine
imep	inlet mean effective pressure
LHV	lower heating value
MBT	maximum brake torque
NL	normal litre
NO_x	oxides of nitrogen (NO and NO_2)
ppm	parts per million
PWM	pulse width modulation
rpm	revolution per minute
SCR	selective catalytic reactor
SI	spark ignited
TDC	top dead centre
TOF	turnover frequency
UEGO	universal exhaust gas oxygen

a hydrogen based economy is not foreseeable unless a suitable storage medium could be found [4].

Ammonia with its high content of hydrogen per unit of weight and volume, could be considered as a transitional solution bridging the present to a foreseeable hydrogen society. In fact, ammonia contains 1.5 molecule of hydrogen which is equivalent to a hydrogen content of 17.8 wt. %. In other terms, 108 kg of H_2 are embedded in one m^3 of liquid ammonia at 20 °C and 8.6 bars [5].

Ammonia can be used as a clean energy carrier and fuel for several reasons: (a) can be easily converted to hydrogen and nitrogen resulting in a CO_x free hydrogen source [6]; (b) can be combusted or oxidized in an environmentally benign way, exhausting only water and nitrogen [6–8]; (c) can be synthesized without using fossil fuels as feedstock [9]. Some additional advantages of ammonia, still in respect to hydrogen, are commercial availability and viability, the global distribution network, handling experience, etc. Its toxicity may be seen as a challenge but this drawback could be mitigated by using modern control and storage technologies.

Ammonia was investigated as alternative to fossil fuels for transportation vehicles already in the 20th century. In this respect, for example, a fleet of ammonia fuelled buses was operated in Belgium during World War II in conjunction with a shortage of fossil fuels [10]. Then, after a period of little interest, experimental investigations on this field received a renewed interest starting from the mid of the1960's to the beginning of 1970's [11–15]. These showed that ammonia could be used as a primary fuel or in conjunction with a pilot fuel or spark source in either spark-ignition (SI) or compression-ignition (CI) engines.

In the last years, as a consequence of a quickly increasing oil price and of an improved environmental awareness, ammonia is receiving renewed attention. Primary investigation fields are related to the use of ammonia as CO_x free hydrogen carrier [16] and as an alternative fuel for combustion devices [17–19], especially Internal Combustion Engines (ICE) [7,8,20–24]. However, in conventional ICE, ammonia should be co-fed together with a combustion promoter. In fact, ammonia combustion is characterized by low flame temperature, low laminar burning velocity, high ignition energy and narrow flammability limits which would strongly hinder satisfactory engine performance. Several works demonstrated that hydrogen is a suitable combustion promoter [15,23,25]. In particular, small amount of hydrogen added to air-ammonia mixture (ca. 1 wt. %, or equivalently 8 vol. % H_2/NH_3), were found to be effective to speed combustion up allowing satisfactory engine running [8].

It is noteworthy that hydrogen can be obtained directly from ammonia by cracking with the aid of a solid catalyst [5,6]. Thus, in case of vehicular applications hydrogen could be synthesized on board and directly injected into the ICE together with ammonia (i.e. expensive and space consuming hydrogen tanks are not required). Moreover, two additional advantages make on-board ammonia cracking very suitable to vehicular applications. Ammonia cracking is an endothermic reaction ($\Delta H_r = -46.22$ kJ/mol) requiring thus a heat source capable of maintaining the catalyst at the proper cracking temperature and thus delivering the required reaction enthalpy. Compatible gas temperature and power in vehicular application could be available by utilizing the combusted gases exhausted by the engine, resulting in a strong increase of overall efficiency. Last but not least, ammonia cracking is an equilibrium reaction [26]. Consequently, there are always traces of ammonia in the H_2–N_2 mixture exiting the cracking reactor. This fact might be a drawback in case the produced hydrogen is fed into Proton Exchange Membrane Fuel Cell (PEMFC), but does not represent a limitation in ICE, since ammonia traces are burned into the engine cylinder.

Many metals, alloys and compounds of noble metals have been tested for ammonia cracking, as for instance, Fe, Ni, Pt, Ru, Ir, Pd, Rh, Ni–Pt, Fe-MeO_x (where Me = Ce, Al, Si, Sr and Zr), and consequently, many reports are available in the literature [27–32]. Studies devoted to the identification of the most suitable support for the active phase dispersion are available as well [26]. Generally speaking, conversion and TOFs of metal supported on carbon or alumina was found to decrease in the order Ru > Rh ≈ Ni > Pt ≈ Pd > Fe [24]. More recently, attention has been paid to the use of metal nitrides and carbides as well as alloys as active components for this decomposition reaction [33]. However, although some metal nitrides and carbides have similar qualitative properties as those of noble metals, they were found to be much less suitable for ammonia decomposition, since small amounts of O_2 or H_2O were found to be responsible for fast catalyst deactivation [34].

Several ammonia cracking reactors have been developed and are described in the open literature. However, most of them were devoted to the delivery of hydrogen to fuel cell [35–41], and to the best of our knowledge only few examples of reactors and systems developed for vehicular applications are available [42].

In this work a Hydrogen Generation System (HGS) capable of supplying up to 1.4 $Nm^3\ h^{-1}$ of H_2 was successively developed and will be described. This unit was built within a