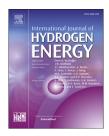
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## Comparative assessments of two integrated systems with/without fuel cells utilizing liquefied ammonia as a fuel for vehicular applications

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#### ABSTRACT

In the current study, two different integrated systems for vehicular applications are presented and thermodynamically analyzed. The first system consists of liquefied ammonia tank, dissociation and separation unit (DSC) for decomposition of ammonia and an internal combustion engine (ICE) to power the vehicle. The second system is a hybrid system consisting of liquefied ammonia tank, DSC unit, a small ICE and a fuel cell system. In the second system, the main power unit is fuel cell and a supplementary internal combustion engines is also utilized. The exhaust gasses emitted from the ICE are used to provide the required heat for the thermal decomposition process of ammonia. The ICE is fueled with a mix of ammonia and hydrogen generated from the DSC unit that is installed in the two systems. Hydrogen generated from DSC unit will be utilized to operate fuel cell installed in system 2. The proposed systems are analyzed and assessed both energetically and exergetically. A comprehensive parametric study is carried out for comparative assessments to determine the influence of altering design and operating parameters such as the amount of ammonia fuel supplied to the two systems on the performance of the two systems. The overall energy and exergy efficiencies for system 1 and system 2 are found to be 61.89%, 63.34%, 34.73% and 38.44% respectively. The maximum exergy destruction rate in the two systems occurred in the ICE.

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#### Introduction

The transportation sector extensively utilize fossil fuels as a potential source of energy and consumes about 61.2% of the world oil reserves, resulting in the production of greenhouse gas (GHG) emissions predominantly CO<sub>2</sub> emissions that affect the global climate significantly [1]. World CO<sub>2</sub> emissions generated by transportation sector are estimated at 23% from

fuel combustion in 2014 [2]. Therefore, alternatives fuels for vehicle powering should be introduced and applied [3]. Hydrogen uniquely appears to be a promising fuel particularly if it is generated from renewable sources, it can be utilized in internal combustion engines (ICEs) and fuel cells (FCs). Additionally, it is burned in an environmentally way generating no greenhouse gas emissions and emitting water vapor. However, hydrogen storage is a vital and critical issue that need to be solved to achieve an adequate hydrogen economy [4].

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Ammonia can easily be used to be obtained by using both hydrogen and nitrogen and improve the qualities of hydrogen for direct use without changing the existing infrastructure in a more efficiency manner because of its high content of hydrogen per unit of weight and volume, it is able to solve the problem of hydrogen storage in a cheaper way since storing ammonia is three times cheaper than storing hydrogen. Ammonia supply structure is already existing, and ammonia can be burned in clean way, emitting typically water vapor and nitrogen. Moreover, any leakage can be noticed by a nose as long as the concentration is less than 5 ppm [5].

Using ammonia as a fuel in the transportation sector was, in fact, implemented seventy years ago during world war II due to the lack of fossil fuels supplies, Belgium had to run an entire fleet of busses running on ammonia [6]. Many recent studies discussed ammonia usage in the ICEs. For instance, Grannell et al. [7] investigated mixing ammonia with gasoline in spark ignition ICE, they concluded that using only ammonia as a fuel resulted in poor engine performance, while mixing ammonia with gasoline at percentages of 70% and 30% respectively results in an adequate engine performance. They recommend a compression ratio of 10:1 for the ammonia and gasoline blended engine. Frigo and Gentili 8 burned ammonia directly in the 4-stroke twin-cylinder SI engine of 505 cm<sup>3</sup> using hydrogen as a promoter. Results assure that using hydrogen along with ammonia enhance mixture ignition and augment combustion velocity. Reiter and Kong [9] studied the combustion and emissions features of a compression-ignition engine utilizing a blend of ammonia and diesel fuel. Results displayed that carbon monoxide and hydrocarbon emissions using the ammonia/diesel blend were higher than carbon monoxide and hydrocarbon emissions when utilizing pure diesel fuel for similar power output and increasing the ratio of the ammonia in the mixture will result in longer ignition delays, and mitigate the peak combustion pressure. Mørch et al. [10] investigated the use of metal ammine complexes as ammonia storage and the use of a hydrogen/ammonia mixture as a dual fuel for the spark ignition ICE. The results prove that a fuel blend with 10 vol% hydrogen achieved the best performance represented in the efficiency and power. The highest NO<sub>x</sub> emissions recorded with an excess air ratio between 1.1 and 1.4. Ezzat and Dincer [11] introduced an integrated energy system comprising of PEM fuel cell, photovoltaic, AEC unit and an additional Li-ion battery. The photovoltaic subsystems are utilized to operate an ammonia electrolyte cell to produce hydrogen onboard from liquefied ammonia and then supply it to the fuel cell to reduce hydrogen consumption from the compressed hydrogen tank and increase the mileage of the proposed vehicle.

Hydrogen can be generated directly through thermal decomposition of ammonia using solid catalyst [3]. For instance, Liu et al. [12] stated that using nano-sized Ni/SBA-15 catalyst at 650 °C is able to achieve 99.2% conversion efficiency for the dissociation reactor and produce 33.2 mmol of hydrogen per minute per gram of catalyst loaded (mmol/min/g). This concept would be very useful if it is implemented in vehicular applications to produce hydrogen on board and inject it with ammonia in the ICE. Ammonia synthesis is an endothermic reaction which means that it requires heat to proceed the separation reaction, this heat can be provided

using the high temperature exhaust gasses resulting from fuel combustion inside the ICE. Recovering the exhaust gasses heat will definitely enhance the overall system efficiency.

Ammonia is recognized as a thermodynamically stable and reliable substance. It normally starts to crack thermally at elevated temperatures typically 200 °C, and the cracking process is depending on the temperature and the catalyst. At 425 °C ammonia can be converted to hydrogen and nitrogen with conversion efficiency reaching 98-99% [13], and at temperatures above 500 °C ammonia can be cracked thermally without any catalysts [14]. Using the thermal ammonia dissociation unit in vehicular application to generate hydrogen on board is mentioned in the literature. For instance, Kojima et al. [15] filed a patent proposing the utilization of ammonia in ICEs, they exploited the exhaust heat to generate hydrogen from ammonia and the generated hydrogen is stored so that it can be supplied to the ICEs along with the ammonia to be combusted inside the burning chamber. Dincer and Zamfirescu [16] established a new system with DSU to separate hydrogen so that it can be combusted in the ICE. They also suggested using ammonia as a refrigerant for vehicle air conditioning based on ammonia-water absorption refrigeration systems. Moreover, they suggested utilizing ammonia as a reduction agent of NO<sub>x</sub> emission of internal combustion engine. Comotti and Frigo [17] established a system for hydrogen production feeding 1.4 Nm<sup>3</sup> h<sup>-1</sup> of hydrogen separated from ammonia to be utilized in operating ICEs resulting in better system efficiency due to the utilization of the exhaust gasses in operating the ammonia thermal cracker. However, combusting hydrogen leads to an increase in the combustion temperatures resulting in higher  $NO_x$  emissions. Frigo et al. [18] claim that the addition of hydrogen to ammonia-air mixture will lead to an improve in the ignition features and make the combustion faster. This is due to the fact that combusting ammonia is notable by its narrow flammability range, low flame temperature and slow flame speed. Ryu et al. [19] assured that combusting hydrogen, which produced from ammonia dissociation, along with ammonia in the ICE caused an enhancement in the engine performance and a reduction in the exhaust emissions compared to an ICE combusting only ammonia. A higher power is obtained from the dual fuel engine and a decrease in the consumption of the fuel is observed.

Lee et al. [20] investigated the potential of burning and reforming ammonia as a carbon-free fuel in hydrogen generation. Their study results displayed a significant enhancement in the laminar burning velocities when increasing the amount of the supplied hydrogen, specifically under fuel rich condition. In addition, estimated flame structures demonstrate that substitution of hydrogen reduced the formation of nitrogen oxide (NOx) and nitrous oxide (N<sub>2</sub>O), and the aggregation of the added hydrogen shows an improvement in the stretching of the flame sensitivity. Joo et al. [21] examined the influence of partial NH3 substitution on burner-stabilized premixed H<sub>2</sub>-air flames. They found that improving the NH<sub>3</sub> substitution the combustion steadiness limits are significantly decreased, displaying that the mixture tube exit velocity at both the lower and upper stability limits reduced. This supports the potential of NH<sub>3</sub> as a carbon-free, green additive in premixed H<sub>2</sub>-air flames for enhancing the safety of H<sub>2</sub> utilization. Li et al. [22] studied the possibility of using  $NH_3$  and  $H_2$ 

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