Ammonia and conventional engine fuels: comparative environmental impact assessment

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Abstract. Ammonia has recently attracted great attention as a fuel for internal combustion engines. The aim of this study was to compare the environmental impact caused by the production processes of ammonia and conventional engine fuels – gasoline and diesel oil. Present fuel technology, commonly used in Europe, was investigated. Haber-Bosch process for ammonia synthesis was considered, coupled with steam methane reforming (SMR) and partial oxidation of heavy oils (POX) as sources of hydrogen. Fuel technology was evaluated with the use of Life Cycle Assessment (LCA), based on a total emission of selected pollutants, including greenhouse gases, total consumption of water and primary energy, as well as Eco-indicator 99 score. LCA results indicated that current industrial methods for ammonia production have unambiguously more negative impact on the environment, compared to fossil fuel technologies, when energy content of the fuel is taken into account. The environmental load of ammonia production process depends strictly on the method of hydrogen obtaining. SMR has lower negative impact on the environment than POX. In order for ammonia to be considered as a potential transportation fuel, the use of hydrogen generation pathways that are less burdensome to the environment should be promoted.

1 Introduction

Fossil fuels have been extensively used to supply internal combustion engines for over a century. In fact, modern road transportation depends almost solely on diesel oil and gasoline, which are derived from petroleum. Yet fossil fuels have finite, though probably large reserves and their production as well as use have negative environmental impacts [1]. Because of this, alternative fuels are currently a topic of growing interest and importance. So far there have already been many successful attempts to substitute conventional fuels in vehicle and stationary applications with other energy carriers, both renewable (e.g. biogas [2], bioethanol [3]) and non-renewable (e.g. compressed natural gas – CNG [4], liquefied petroleum gas – LPG [5]). Ammonia (NH_3), despite its toxicity, was used occasionally in the past for power generation [6].

Ammonia is one of the major inorganic chemicals produced worldwide. Its synthesis has a significant impact on the environment on a global scale, contributing to almost 1.2% of total primary energy consumption and about 1% of global greenhouse gases emissions

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[7]. 80% or more of the ammonia produced is utilized in agriculture for fertilizing, while the rest is used as a substrate for the production of: nitric acid, explosives, plastics, fibres, dyes and pharmaceuticals.

The reasons for using ammonia as a fuel for combustion engines are thoroughly discussed in literature, i.e. as referenced in [8]. From the environmental point of view, the biggest benefit of burning ammonia instead of gasoline and diesel oil is the avoidance of carbon dioxide emission, since the only products of ammonia combustion are nitrogen and water [9]. Furthermore, ammonia can be produced from water, biomass, organic waste and air using any primary energy source, including all kinds of fossil fuels, such as coal, oil, natural gas, as well as nuclear, solar, wind, geothermal and hydro energy [10].

Fair comparison of the environmental impact of ammonia and conventional fuels should consider not only their combustion during the operation of an internal combustion engine, but also the production process. Taking into account a great variety of possible ammonia production paths, this is not an easy task. One of the solutions to this problem is the use of Life Cycle Assessment (LCA). During the last decade, a large number of LCA studies have been performed to compare biofuels and fossil fuels from an environmental perspective [11], but they usually omitted ammonia. A recent study [12] investigated conventional resources-based ammonia generation routes through a comprehensive LCA to determine the most and least ecologically benign process. However, that study has not included conventional fuels, neither diesel oil nor gasoline. Last but not least, direct comparison of the results of LCAs conducted by different authors is not possible, because each involves too many individual assumptions, such as different input data, functional units, allocation methods or reference systems [11].

The aim of this study was to comparatively assess environmental impacts associated with ammonia, diesel oil and gasoline production, using LCA approach. In particular, the investigation was focused on present conventional fuel/chemical technology and adopted an European perspective.

2 Overview of fuel production technologies

Current work covers conventional technology of fuel and chemical production presently used in Europe. This means that diesel oil and gasoline come from the refining of crude oil extracted from oil fields around the world (according to the European mix of imported raw materials) and are intended for use in road transportation. Ammonia generation technology represents the main industrial production procedures of this chemical in Europe and, for obvious reasons, is originally not dedicated for use in road transportation. Haber-Bosch process for ammonia synthesis from atmospheric nitrogen and hydrogen is considered, with steam methane reforming (SMR) or partial oxidation of heavy oil (POX) as sources of hydrogen.

2.1 Diesel oil and gasoline production

Conventional, fossil fuels are derived from crude oil. In general, crude oil processing involves the following steps: separating hydrocarbons into fractions of similar properties, converting these fractions into more desirable products, purifying them and upgrading [12]. Each refinery is unique with its process configuration, depending on the quality of crude oil and desired end products. Separation of the hydrocarbons is usually carried out through distillation, according to the boiling point of the hydrocarbons. In basic case, gasoline is obtained from light fractions, typically light naphtha, while diesel oil from medium heavy distillate. In an advanced refinery, various intermediates can also be converted into certain fuels, depending on their shifting market price. Further technological processes commonly

used in modern refineries include: hydrotreating, (fluid) catalytic cracking or hydrocracking, catalytic reforming, isomerisation, alkylation, thermal cracking or visbreaking, and coking. This is not an exhaustive list and more detailed information on crude oil processing can be found in the literature, e.g. [13].

2.2 Ammonia production

The most commonly commercially available procedure for the production of ammonia today is Haber-Bosch process, in which nitrogen reacts with hydrogen in the presence of a metal catalyst under high temperature and pressure. The source of nitrogen is almost exclusively cryogenic air separation, while hydrogen can be generated via various methods, ranging from mostly used steam reforming of fossil fuels to electrolysis of water using energy form renewable sources such as solar power. It is clear that environmental effects of the whole ammonia production process depends strongly on the method of obtaining hydrogen [7]. In the case of European industry, two hydrogen production pathways dominate: steam reforming of methane (SMR) from natural gas and partial oxidation of heavy oils (POX).

2.2.1 Steam methane reforming

The SMR process consists in reaction of raw natural gas (methane) with superheated steam under high temperature pressure in the occurrence of a nickel-based catalyst to yield hydrogen and carbon monoxide (a minor quantity of carbon dioxide is also generated) [14]:

$$CH_4 + H_2O \rightleftharpoons CO + 3\ H_2 \tag{1}$$

Extra hydrogen is usually obtained in the reaction called a water-gas shift, where carbon monoxide undergoes a conversion to carbon dioxide in lower-temperature with the presence of a copper or iron catalyst [14]:

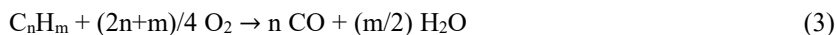$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{2}$$

Apart from natural gas, various alternative feedstocks for steam reforming are available, including naphtha, fuel oil and coal. However, natural gas is the most convenient from the technological point of view, therefore most of ammonia plants use it.

Conventional SMR currently in operation in Europe involves the following steps: desulphuration of methane, two-stage reaction of methane with steam (primary and secondary reformers are used in order to increase the conversion), water-gas shift reaction, removal of carbon dioxide, methanation, and compression [15].

2.2.2 Partial oxidation

The production of hydrogen from heavy feedstocks, such as residual oils and coal, can be achieved through partial oxidation. This non-catalytic, exothermic process takes place under high temperature and pressure, according to the reaction:

$$C_nH_m + (2n+m)/4\ O_2 \rightarrow n\ CO + (m/2)\ H_2O \tag{3}$$

In addition, some carbon dioxide, methane and soot can be formed. Like in SMR, water-gas shift reaction increases the hydrogen yield.

The most important stages of the POX process are: gasification – partial oil combustion with oxygen, removal of soot and sulphur, water-gas shift reaction, removal of carbon dioxide, purification of hydrogen by a liquid nitrogen wash, and final compression [15].

3 Materials and methods

For the environmental evaluation of the selected fuels, LCA was performed. This method is defined as "a systematic set of procedures for compiling and examining the inputs and outputs of materials and energy and the associated environmental impacts directly attributable to the functioning of a product or service system throughout its life cycle" [16]. In general, life cycle of a transportation fuel can be divided into: acquiring of raw materials, transportation of raw materials, generation and supply of energy, manufacturing of a fuel, storage and distribution of a fuel, burning of a fuel in vehicle's combustion engine. The scope of the current LCA study includes all the steps mentioned above up to a fuel storage. The knowledge on ammonia distribution (as a fuel) and combustion in engines is limited, and therefore would distort the results of the comparison of ammonia with conventional fuels. Quantitative data on the fuel technology was retrieved from Ecoinvent database [15, 17].

Comparison of different systems in the LCA is allowed provided that the results are expressed in a common functional unit, to which the inputs and outputs of a system can be assigned [16]. In this investigation the functional unit is 1 GJ of the energy content of fuel. The consequence of this assumption is that more than twice as much ammonia (with lower heating value of 18.6 MJ/kg) is needed to produce the same energy compared to gasoline (44.0 MJ/kg) and diesel oil (42.4 MJ/kg).

The measures chosen as quantitative indicators of environmental load of fuel production technology include: total emission of selected pollutants, i.e. particulate matter (PM_{10}, $PM_{2.5}$), non-methane volatile organic compounds (NMVOCs), methane (CH_4), nitrogen oxides (NO_x), sulphur oxides (SO_x), and carbon oxide (CO), as well as total water use. Additionally, three indicators based on impact assessment methods, i.e. Eco-indicator 99 (EI99), Cumulative Energy Demand (CED) and IPCC 2007, commonly employed in the LCA studies, were calculated. EI99 evaluates overall environmental effect, dividing it into three broad categories: human health (damage due to climate change, ozone layer depletion, carcinogenic effects, respiratory effects and ionising radiation), ecosystem quality (damage due to ecotoxicity, acidification, eutrophication and land use), and resources (damage due to the depletion of mineral resources and fossil fuels) [18]. CED and IPCC 2007 are single-issue methods, covering only one aspect: primary energy consumption and greenhouse gas emissions, respectively. Sima Pro 7 software was used for the calculations.

4 Results and discussion

In Figure 1 results regarding pollutant emissions from the production of gasoline, diesel oil and ammonia, obtained in SMR and POX are presented. Generally, in each case the technology of conventional fuels has an advantage over the technology of ammonia. Diesel oil production is the least harmful to the environment in terms of pollutant emissions into the air. Gasoline production has only slightly higher rates. POX is particularly unfavourable for the environment, with pollutant emissions significantly higher (e.g. 15–19 times for PM and 7–9 times for SO_x) than those for the production of conventional fuels. One of the reasons for this is the assumption that in POX process both the feedstock and the fuel are heavy fuel oil. Therefore environmental impact of both was added, resulting in large values of pollutant emissions. As expected, SMR is characterized by high methane emission. Only

NMVOC emission has close values for all fuels. It should be noted, however, that this study did not take into account fuel consumption in the engine. This would significantly increase emissions from conventional fuels, namely NMVOC and CO emissions in the case of gasoline and PM emissions in the case of diesel oil.
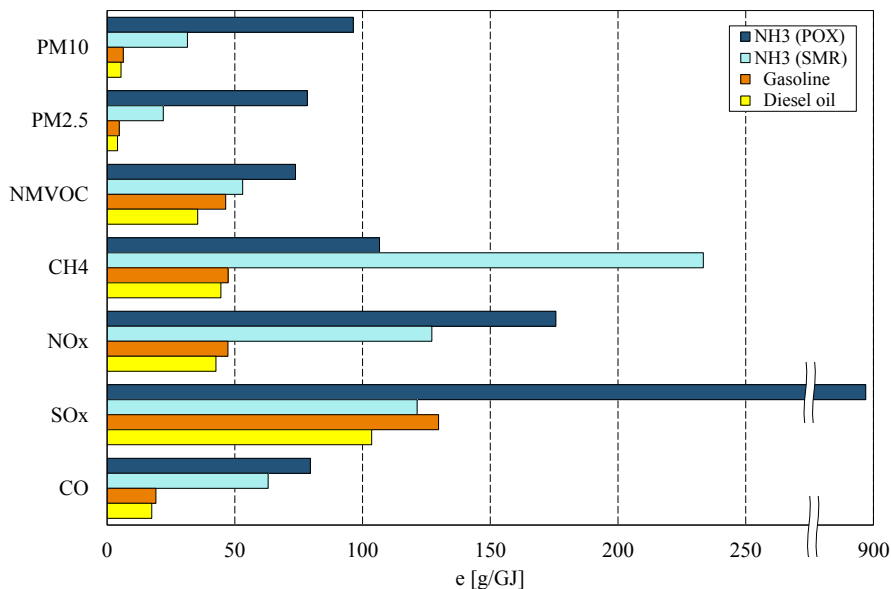

Fig. 1. Pollutant emissions from the production of ammonia and conventional fuels (POX – partial oxidation of heavy oils, SMR – steam methane reforming).

Water plays a vital role in the production of fuels. Its total demand is shown in Figure 2, ranging from 106.6 m^3/GJ for ammonia obtained through POX to 16.3 m^3/GJ for diesel oil. Again, technological processes of ammonia are more water-intensive than those of conventional fuels. Water is the third, after air and hydrocarbon source (natural gas/heavy oil), most relevant raw material for ammonia production. Apart from steam generation, it is also used in other processes, such as water-gas shift, water scrubbing and cooling of process equipment.
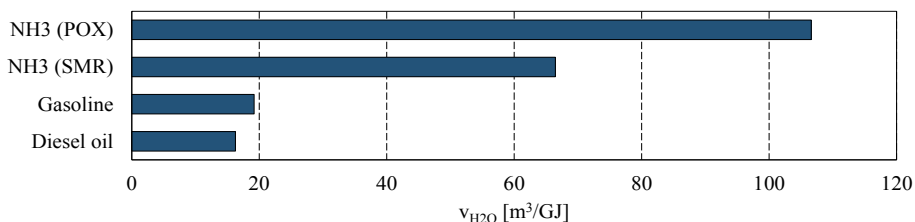

Fig. 2. Total water consumption in the production of ammonia and conventional fuels (POX – partial oxidation of heavy oils, SMR – steam methane reforming).

Comprehensive environmental impact of fuel production according to EI99 is illustrated in Figure 3. Of all the inputs and outputs from different fuel technological processes, the damage they cause to human health, ecosystem quality and resources is calculated, and then these three categories are combined into a single score. Generally it can be observed that EI99 scores show similar tendency to pollutant emissions and water use. More analytically,

EI99 reveals that resources is the category with the highest impact, followed by human health, while ecosystem quality is of the least importance. Regarding total scores, ammonia obtained in POX gained 16.7 Pt/GJ, ammonia from SMR has 8.8 Pt/GJ, gasoline presents 4.7 Pt/GJ and diesel oil only 4.6 Pt/GJ. Thus, ammonia contributes to higher environmental impact than conventional fuels for the reasons that were previously explained. In addition, there are differences in the importance of individual categories for a given fuel technology. Conventional fuels are, for obvious reasons, related to the consumption of resources, therefore this category has the largest share in the total environmental load (87% for gasoline and 88% for diesel). For ammonia, the impact on human health is more significant, which implies a reduction in the share of resources in the total value of EI99 (77% in the case of ammonia from SMR and 59% for POX).
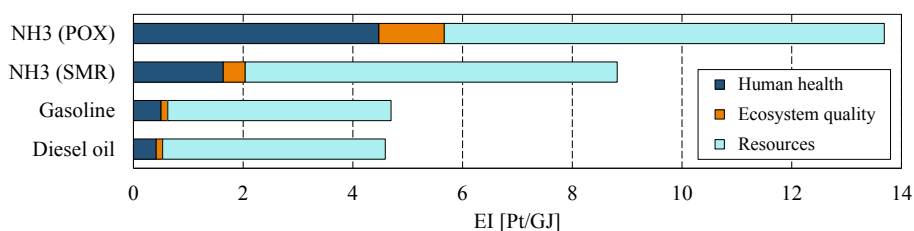

Fig. 3. Environmental impact of fuel production according to Eco-indicator 99 (POX – partial oxidation of heavy oils, SMR – steam methane reforming).

The most important environmental effect due to ammonia production is a large energy consumption, mainly from the combustion of fossil fuels, and the emission of carbon dioxide as a consequence. Within this research, the energy demand of fuel technology was investigated using CED approach. Results can be seen in Figure 4. Regardless of the type of fuel and technology, energy obtained in fuel was lower than energy needed to produce fuel. Conventional fuels require little surplus energy of 30% (1.3 GJ/GJ for gasoline and diesel oil), whereas ammonia, depending on the hydrogen production technology, even 170–120% (2.7 GJ/GJ for POX and 2.2 GJ/GJ for SMR). In addition, it is the energy from non-renewable sources that dominates. The main reason for large differences between the results for conventional fuels and ammonia is that the theoretical thermodynamic minimum energy consumption of ammonia process is practically unattainable in the industry. According to [15], over a half of the excess energy consumption is due to compression losses.
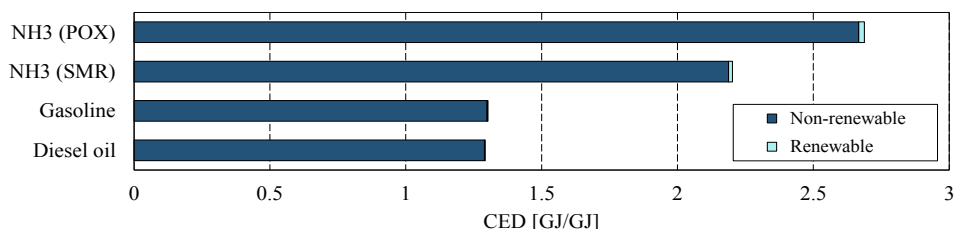

Fig. 4. Cumulative energy demand of the production of ammonia and conventional fuels (POX – partial oxidation of heavy oils, SMR – steam methane reforming).

Greenhouse gas emissions, expressed as an equivalent emission of carbon dioxide, from the production of ammonia and conventional fuels are presented in Figure 5. It is clear that in this category conventional fuels again outperform ammonia. Diesel oil contributes do the emission of 12.3 g_{CO2eq}/GJ, gasoline 16.0 g_{CO2eq}/GJ, while ammonia 158.9 g_{CO2eq}/GJ (POX)

and 105.8 g_{CO2eq}/GJ (SMR). Total emission of greenhouse gases is between 6 and 12 times larger for ammonia, depending on the origin of hydrogen. Since the emission of carbon dioxide is closely related with the use of fossil fuels, POX is particularly unfavourable due to heavy oils, which are the feedstock rich in carbon. Utilizing low-carbon feedstocks, such as natural gas in SMR, reduces the emissions of greenhouse gases significantly. Another solution easily implemented in ammonia technology is the recovery of carbon dioxide for its further use. However, this applies if there is a demand for this gas by the downstream facilities.
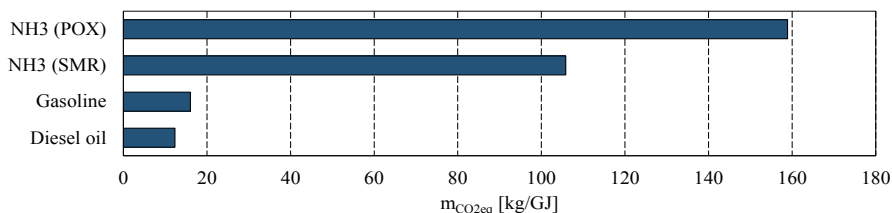

Fig. 5. Greenhouse gas emissions from the production of ammonia and conventional fuels according to IPCC 2007 (POX – partial oxidation of heavy oils, SMR – steam methane reforming).

Like all LCA studies, the current one should be approached with some reserve, as there are many specific assumptions and inevitable sources of uncertainties that affect its results. First of all, in the present study, ammonia and conventional fuels were compared as if they were both fuels used in transportation. This assumption is more advantageous for gasoline and diesel oil, the production of which is larger and therefore more efficient. Secondly, only the two most commonly used industrial methods for obtaining hydrogen were considered in the study. There are a number of other methods that have lower environmental impact [7, 10]. A lot depends on the feedstock used, e.g. POX can be conducted with viscous hydrocarbons and plastics, offering an environmentally-oriented alternative for future utilisation of wastes. Finally, results depend on a calorific value of fuels. If referred to the mass of fuel, a completely different trend can be observed in some results, e.g. EI 99 single score equals 0.21 Pt/kg for gasoline, 0.19 Pt/kg for diesel oil, but only 0.16 Pt/kg for ammonia obtained in SMR. However, transportation fuels should be compared on the basis of their energy content.

5 Conclusions

In this study, the LCA of two ammonia generation pathways was performed with fossil gasoline and diesel oil used as the reference scenario. Based on the obtained results, the following conclusions can be drawn:
– Current commonly used industrial methods for producing ammonia, compared to fossil fuel technologies on an energy basis, have a more negative impact on the environment, as they contribute to higher emission of pollutants (including greenhouse gases), higher consumption of primary energy and water, and higher overall score according to EI99.
– Considering the mass of fuel produced, and not its energy content, ammonia production is characterized by a lower overall environmental burden according to EI99, lower primary energy consumption, but higher water consumption and generally higher pollutant emissions than the production of conventional fuels.
– The environmental load from the ammonia production process depends directly on the method of obtaining hydrogen – among those currently used in European industry, SMR has lower negative impact on the environment than POX.

– In order for ammonia to be considered as a potential transportation fuel from an environmental perspective, the use of hydrogen generation pathways that are less burdensome to the environment should be promoted, e.g. nuclear electrolysis or underground coal gasification with carbon capture storage.

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