A Review on Gaseous Fuels for Dual-Fuel Diesel Engines

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Abstract. Dual-fuel diesel engines are praised for both being a more environmentally friendly alternative to conventional diesel engines and aiding in a smoother transition from fossil fuels to renewable sources. Depending on the type of dual-fuel engine, they can even be made by modifying an already existing diesel engine. The advantage of dual-fuel diesel engines, besides their ability to use diesel fuel in the case there's no gaseous fuel available, is their versatility regarding the gaseous fuels it can use. The most popular one currently is natural gas, although hydrogen-containing fuels such as biogas, ammonia, and syngas are also being explored as clean and renewable alternatives. Despite their praise, dual fuel engines have yet to be further studied to reduce some of their emissions, such as nitrogen oxides, unburned hydrocarbons, carbon monoxide, and particulate emissions, while at the same time maintaining higher levels of efficiency.

Keywords: Dual-fuel · Diesel engines · Renewable energy

1 Introduction

The state of our planet as we know it in present times is a result of humanity's careless actions, especially since the beginning of the Industrial Revolution. Because of our careless actions as a species, the prognosis of the Earth's future (and in direct consequence, ours too), actions in the form of stricter regulations and initiatives for alternative sources have been taken by most governments – at a greater or lesser extent – to reduce harmful emissions across sectors. The best solution to the ongoing climate change issue – one which most governments agree with – is renewable energy. Contrary to fossil fuels, these sources of energy never run out – like in the cases of solar energy and the kinetic energy of the wind and the ocean – or can be quickly regenerated, like in the case of biomass and energy crops. However, as all previously mentioned before, our huge reliance on fossil fuels doesn't necessarily make this transition an easy feat, and it's very difficult to achieve this on the short run. Moreover, given our reliance on fossil fuels, it's not at all recommendable: such a drastic transition from fossil fuels to renewable sources would truthfully bring upon modern civilization an economic and, ironically, an environmental catastrophe [1]. Before fully transitioning to a new technology, it must be ensured

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that this technology is sufficiently advanced to be replicated at an industrial level, and accessible enough pricewise.

When diesel engines came to existence in the second half of the 19th century, they revolutionized a wide array of industries across the world: they were much more efficient than steam engines and helped companies save huge sums of money since this meant that diesel fuel was much more energy efficient and dense compared to steam [2]. Nowadays, diesel engines are still very much relevant in our daily lives and are used in all sorts of applications, ranging from lawnmowers to motorcycles, and even to push cargo ships across the oceans. Besides transportation applications, diesel engines can also be used for electricity generation in off-grid locations such as small towns or remote islands [3]. Despite their wide array of applications and versatility, diesel engines are very much demonized by the public, because of "Dieselgate": a result of tampered TDI diesel engines that were sent directly for laboratorial control to make it seem like the engines met US standards when they emitted 40 times more nitrogen oxides than those detected in laboratorial conditions [4]. Since then, there have been stricter regulations regarding diesel engine manufacturing. Despite what the public might still think, diesel engines can play an important role in the transition from fossil fuels to alternate sources. Given the antiquity of this technology, diesel engines have had their efficiency improved upon countless times over its history, and improvements and explorations are still taking place: parameters such as an engines geometry are being explored and studied to help it increase its combustion efficiency – resulting in less fuel being consumed and consequently, less emissions. Treating exhaust emissions through the engine's tailpipe with the use of catalytic converters or diesel filters is another alternative. A third widely explored alternative is the use of alternative methods such as natural gas, hydrogen, biodiesel, fuel cells, ethanol, among others [5]. This paper's objective is to look at the different gaseous fuels and their advantages and disadvantages, alongside their emissions and different treatment methods that are available for them.

2 Dual-Fuel Diesel Engines

Dual-fuel (DF) diesel engines are often mixed up with other engine models that have similar yet different principles, such as "bi-fuel" and gas-diesel engines. The former uses two different fuels alternatively while it's ignited by an external source, whereas the latter employ different methods of introducing gaseous fuel, and don't undergo auto ignition by themselves [3]. In simple terms, dual-fuel engines use a combination of the compression ignition (CI) and spark ignition (SI) combustion processes [6]. Instead, a small amount of pilot fuel, usually diesel fuel, must be used to trigger an ignition within the engine.

While DF diesel engines can be used with a wide array of gaseous fuels, the primary choice tends to be natural gas (NG). In DF diesel engines NG is a favorite go-to gas to use alongside diesel and this can be seen in the numerous studies that use NG alongside diesel fuel [7]. While other gases can be used in DF mode, NG has several attractive properties which include an energetic content higher than that of gasoline and diesel, a clean nature of combustion – nitrogen oxide (NO_x) emissions are greatly reduced when NG is added, and 20–30% less carbon dioxide is generated, alongside less particulate matter [7, 8] – and large proven reserves that are more evenly distributed compared to petroleum [8, 9]. These reserves are often located in the same place as petroleum reserves, but they can also be found in dry form or spaces not associated with oil gas fields, and it's possible to find significant NG reserves in more politically stable regions [10].

Because of the wide availability of information, NG is often used as a "standard": when other gaseous fuels are being combusted, they're oftentimes compared side-by-side with NG to determine their efficiency. An example is this study by Aytav et al., where a NG/mixture is compared to a biogas/diesel mixture in DF mode [11].

3 Alternative Fuels

Despite NG's favoritism, many researchers are studying the properties and potentials of other alternate fuels from renewable sources. The main purpose of alternative fuels is to reduce our dependency from fossil fuels and preferably to encourage the usage of local resources to rely less on outsides sources, all while reducing our carbon footprints. Gas energy, like liquid fuel, can be produced from energy crops, but can also be produced from municipal waste, non-food crops biomass, and even water and industrial wastes. Some of the most researched gaseous fuels include biogas, hydrogen, ammonia, and syngas.

3.1 Biogas

One of the main reasons for NG's attractive properties is tied to its methane content. NG is typically composed of around 90% methane, with trace amounts of heavier hydrocarbons (HC) like ethane, propane, butane, and diluent gases like nitrogen and carbon dioxide. Compared to other hydrocarbons – and even compared to gasoline and diesel fuel – methane has a very high lower heating value (LHV) of 50,01 MJ/kg, and its boiling point is drastically lower than that of other HC. Methane is also the responsible one for making NG have a cleaner nature of combustion: NG generally produces between 20–30% less carbon dioxide, 50–87% less HC that aren't methane, and can reduce carbon monoxide emissions up to 95% [9].

It's possible to produce methane in a renewable fashion – this process is known as biogas. This can be objectively achieved by collecting and treating methane from landfills and biomass decomposition, and consequently won't affect food production unlike other biofuels. In a study done by Aytav et al., a conventional DF engine was used to measure and compare the effectiveness of natural gas and biogas, where parameters such as engine vibration, emissions, and engine performance were measured [11]. Diesel fuel with no added gaseous fuel was also tested using the same engine for comparison purposes. In the case of engine vibrations, biogas has shown to lower the amplitude of these vibrations. It's hypothesized that the biogas's high CO2 and CH4 content is the cause since CO2 doesn't react during the combustion phase and reduces the volumetric efficiency of air to fuel (A/F) mixture in the combustion chamber. In the case of CH4, high concentrations of the gas increase antiknock properties. Regarding performance, the engine on DF mode using biogas/diesel (BG/diesel) mixture has shown a lower thermal efficiency in all loads, compared to NG/diesel, and diesel alone. Additionally, the BG/diesel mixture showed a higher specific energy consumption than that of NG/diesel and diesel alone. Just like the other two fuels, the specific energy consumption became gradually smaller the higher the loads, illustrating the engine's increased efficiency at higher loads because of the more efficient operating conditions being reached. Lastly, out of all three fuels, BG/diesel had the highest fuel equivalence ratio at all loads. An excessively large means a larger amount of air present which improves conditions for oxidation reactions to take place and may enhance the production of emissions such as NOx and CO2, while CO and hydrogen percentages decrease. The larger the fuel equivalence ratio number, more incomplete combustions will take place.

3.2 Hydrogen

Hydrogen is one of the most promising and researched fuels, because of its redeeming qualities, its high energetic content, and its clean production: hydrogen can be made from a wide array of fuels like fossil fuels, biomass, water, and even some industrial chemical waste [12]. However, many of hydrogen's redeeming characteristics also contribute to its instability, such as its high flame speed, wider flammability, and faster burning speeds. This higher instability is not ideal for IC engines since this can lead to a higher incidence of knocking. To not let this gas' potential go to waste – and because our current technology does not allow it – hydrogen is mostly used as an additive for other gaseous fuels, which will be discussed further ahead. There have been, nevertheless, advancements in the development of hydrogen-fueled internal combustion engines over the last two decades, but the same issues that hinder hydrogen's commercialization persist: storage, portability, transport, and purity of the fuel. This has led to exploring other hydrogen-rich fuels such as brown gas, oxyhydrogen, and especially ammonia [13].

3.3 Ammonia

Ammonia has been proposed as an alternative fuel given its hydrogen content and how easy it is to store and transport. Additionally, this carbon-free fuel is lighter than air and is highly soluble in water, which diminishes the risks of any fires or explosions since this property ensure the control of any spillage. Ammonia's high-octane content (<111) equates to less knocking and is an attractive choice for engines with high compression ratios. Ammonia as a single combustion fuel is more plausible, having been studied in the past. However parameters such as its narrow flammability limit, high minimum ignition energy, and high auto-ignition temperatures still complicate its single usage [12, 13]. Even though using ammonia as a single fuel is not quite yet feasible, adding a secondary fuel (such as diesel, kerosene, methanol, ethanol, or gases such as hydrogen and methane) in DF mode can be very beneficial since this secondary fuel can enhance ammonia's properties.

Despite its advantages, ammonia also presents some technical challenges of its own: ammonia is a very difficult fuel to burn given its high latent heat of vaporization (1369.5 kJ/kg, compared to 350 kJ/kg for gasoline and 230 kJ/kg for diesel). It's initially presented in liquid form, and before it burns it must first vaporize and mix with air. Ammonia is also less dense than gasoline or diesel with a density of only 0, 63 kg/liter, and it also has a relatively low energy density per liter: ammonia's LHV is of around 18,8 MJ/kg. For comparison purposes, gasoline's LHV is between 42, 5 and 43, 5 MJ/kg, and diesel's LHV is between 42,6 and 44 MJ/kg. Some of these challenges can be theoretically alleviated if certain measures are taken: blending ammonia with traditional fuels such as diesel can help lower the ignition temperature and helps reduce the requirements for engine modifications. Not only that but adding traditional fuels – alongside other methods like preheating and higher compression ratios – help reduce flame velocity. More studies should be done to determine the optimum amount of premixed and diffusion combustion and the diesel substitution of the total fuel energy [13]. Another challenging characteristic ammonia has is related to its nitrogen content. Ammonia's evidently high nitrogen content inevitably leads to high NO_x content and unburned ammonia gas when partial combustion takes place. Even though a partial combustion is not ideal, the presence of ammonia combined with the exhaust steam could be beneficial for selective catalytic reduction systems that could subsequently help reduce the NO_x into N_2.

3.4 Syngas

Also known as synthetic gas or producer gas, syngas is the resulting byproduct of gasification. Despite using mostly coal and other materials with significant CO2 emissions, what makes gasification such an attractive technology is its versatility: any material can be used so long as there's carbon molecules in its composition [17].

Syngas is composed of methane, carbon monoxide, hydrogen, and small amounts of heavier hydrocarbons, making it considered as a "transition between carbon-based fuels and hydrogen-based fuels". These fractions can be each larger or smaller depending on factors like raw material, gasifier type, the heat exchange process, and its operating conditions [16, 17]. Syngas composition can change ever so slightly from one process to the next, just like its heating value. For example, if water vapor or oxygen were used as a gasifying agent, the produced syngas would have a heating value between 10–28 MJ/Nm3, whereas the use of air would result in a lower heating value: 4–7 MJ/Nm3. Despite this, a syngas's heating value is not as important as it seems, because in stoichiometric scenarios its energetic density is nearly the same to that of fossil fuels. This is due to its low air-fuel ratio between the syngas and air mixture.

Some characteristics that differentiate syngas from fossil fuels include its high flame propagation speed and its wide flammability limits. Defined as the propagation rate of the normal flame front relative to the unburned mixture, laminar flame speed is an important property for a premixed flame as it gives fundamental information on characteristics such as diffusivity, reactivity, and the exothermicity of the combustible hydrocarbon mixture. [18]. In practice, its flame propagation speed is a characteristic that significantly impacts a motor's efficiency and is calculated based on the ratio of hydrogen and carbon monoxide that's presented in the syngas. Out of all the gases present in syngas, hydrogen demonstrates to have a more significant impact in the flame propagation speed: the more hydrogen present, the faster its speed. A more significant presence of methane is equal to a slower flame propagation speed [19].

Its second characteristic is its wide flammability limits. Also known as explosive range, it can be defined as the limiting values of chemical composition or pressures beyond which ignition cannot be achieved and is bounded by the upper and lower flammability limits (UFL and LFL) which are respectively the maximum and minimum concentrations of fuel in fuel-air mixture that would still allow for ignition-initiated flame to propagate and sustain itself. The presence of this helps the motor use syngas even when it's not in stoichiometric conditions. This parameter is influenced by the composition of the gaseous fuel - particularly by the presence of hydrogen in it – the direction of propagation, size and shape of the combustion chamber, temperature, and pressure [20]. Compared to gasoline and natural gas, syngas is more flammable [19].

Syngas's flammable properties make it an ideal fuel for boilers and DF diesel engines, suggesting that it could even be used as a primary fuel. In a study done by Jatinderpal Singh et al. [21], two syngases from different raw materials were used in DF mode. Although syngas derived from raw cotton stalks outperformed syngas derived from wheat straw, both overall showed significant NOx emissions decrease yet have also shown increases in HC and CO emissions. This is possibly due to the large amounts of hydrogen and CO present in syngas, alongside being a result of the incomplete combustion that takes place in gasification since this process uses little oxygen.

4 Emissions

Emissions from DF diesel engines are mostly made of diverse NO_x, carbon monoxide, carbon dioxide, hydrocarbons, and particulates. The composition of emissions is influenced by several factors such as fuel composition and properties, the pilot fuel employed, the engine type, size, and geometry, among others. Although NG has a clean nature of combustion and can significantly reduce emissions by up to 95% (for example, with carbon monoxide) and produce nearly no particulate matter and smoke, the same cannot be said for other fuels. Their polluting properties can be reduced or even "taken advantage of" with the help of additives or exhaust gas recirculation (EGR).

4.1 Additives

The purpose of additives is to enhance the properties of the gaseous fuels, ideally to have a higher energy efficiency and to reduce pollutants. The most popular additives used in DF diesel engines are oxygen and hydrogen. Current technologies do not allow us to use these gases as single fuels, so using them as additives is ideal to not let their properties go to waste.

Oxygen. Oxygen has proven to be very beneficial during the combustion process and for reducing certain emissions. Unlike some additives, oxygen is beneficial in both low and high loads: In lower loads, oxygen improves the stability of combustion, accelerates partial oxidation, and a more complete combustion process takes place. In higher load conditions, oxygen decreases ignition delay and shortens combustion durations, leading to a lower tendency to knock. This is especially useful with NG-diesel dual-fuel engines since at high loads too much NG can lead to prolonged ignition delay, allowing time to transfer heat to the end gas resulting in potential knocking. Oxygen counteracts this. Oxygen enrichment is also a viable technique for DF biogas-diesel engines a high loads due to improvements in several characteristics like thermal efficiency, decreases in the ignition delay, high burning rates, and lower methane emissions [14]. Oxygen also helps reducing CO and HC emissions, and it has been shown to reduce substantially soot emissions and diesel pilot smoke levels. However, it also increases NOx emissions. This is due to the increase in temperature that takes places during a more efficient combustion process. Another challenge that presents itself is the uncertainty regarding the optimum ratio of oxygen that must be added to the mixture: in high loads, for example, too much oxygen can have the opposite desired effect and encourage knocking [10]. More studies must be done regarding the use of oxygen as an additive to eradicate these uncertainties.

Hydrogen as an Additive. Despite hydrogen being a promising fuel because of its clean and easy production and its qualities which include its fast combustion rate, wide flammability limit, and short quenching distance [15], its instability still makes it unsuitable for its usage as a single fuel. To not waste hydrogen's properties and benefits, researchers have compromised with the prospect of using hydrogen as an additive while more research is done for its use as fuel. As an additive to natural gas, hydrogen has several benefits such as enhancing the gaseous fuel's ignition, increasing its flame velocity, better combustion efficiency, and a more stable combustion. The last characteristic applies in the presence of methane, so this is true for both natural gas and methane when used alone as a fuel. As a result the mixture of natural gas and hydrogen have a lower C/H ratio and therefore emit fewer emissions compared to fossil fuels [16].

Besides the properties mentioned prior, there are several characteristics that make hydrogen more appealing than other fuels and explain why it's such a good additive. Compared to diesel and NG, hydrogen has a higher-octane number of approximately 130, and a high Lower Heating Value (LHV) content of 119, 93 MJ/kg, higher than that of NG and diesel. This means an increased engine efficiency and control of the auto-ignition point, in the case of HCCI engines [17]. Hydrogen's flammability limits are much wider than those of natural gas, and its flammable mixtures can go from an air-to-fuel ratio of as lean as 10 and as rich as 0, 14. Its density is much lower than that of diesel and natural gas, and the same applies to its molecular weight. Additionally, hydrogen's flame velocity is on average nearly ten times faster than that of diesel, and 6, 5 times faster than that of natural gas.

At least since Benbellil et al.'s article [16] publication in November 2021, there has been and there is a lot of publications available about the use of NG enriched with hydrogen used for diesel engines, however the contrary is to be said about articles relating to the use of this same fuel in dual fuel diesel engines. Nevertheless, existing results suggest that adding hydrogen to NG not only improves its brake thermal efficiency, but it also enhances the combustion process by increasing the heat release rate HRR and cylinder peak pressures, and reduces combustion velocity because of hydrogen's higher lower heating value [18, 19].

4.2 Exhaust Gas Recirculation

Exhaust Gas Recirculation (EGR) is an NOx technique used where part of the emitted NOx is recirculated back into the combustion chamber with the objective of potentially reburning in the next cycle, and to dilute the oxygen present from the air stream, resulting in a more complete combustion leading to more heat absorption, reducing in-cylinder temperatures and NOx emissions. Reduction of temperature is essential for less NOx formations, since NOx forms in peak temperatures, therefore the decrease in temperature equals to less NOx formations. Besides NOx emissions, EGR reduces CO and HC emissions, especially in low to intermediate loads [10, 20]. However, the usage of EGR can be more counterproductive than beneficial in high loads: if large amounts of NG are introduced into the engine, the amount of oxygen available in proportion to the gaseous fuel is subpar and there's not enough oxygen for combustion. This would instead aggravate the problem and create more CO and HC emissions [20].

Despite the amount of research done already regarding this subject, some uncertainties remain yet to be sorted out, such as those related to stationary applications where EGR temperatures could be controlled, and finding an optimum EGR percentage where NOX reduction in large quantities can still be achieved without having to compromise things such as thermal efficiency [10]. In the case of finding the optimum EGR percentage, this issue arises from the fact that the ratio of optimum EGR percentage changes depending on the operating conditions. High levels of NG involve more air being consumed and used, and EGR becomes unviable even though NOx levels increase drastically because of the high temperatures that are being worked with. In the case of stationary applications, more studies must be done regarding the ideal amounts of cooled EGR and hot EGR to find the best balance between NOx reduction and optimal thermal efficiency.

EGR and H2 as an Additive. EGR may help reduce NOx emissions, but when levels are too high this can deteriorate the combustion process and increase the levels of other emissions such as CO, HC, and PM. A solution that has been proposed for this issue is adding hydrogen to help stabilize combustion, since it has been widely studied within the use of NG. Hydrogen helps increase the reactivity of the gaseous fuel and counterbalance the slow mixing and combustion rates caused by high EGR amounts, thus making the combustion process more efficient. Additionally, adding hydrogen helps reduce greenhouse gas emissions such as those of CO_2 and CH_4, due to the lowered carbon-to-hydrogen ratio of the blended gaseous fuels and the improved combustion. It has been shown that on average, for every 10% of H_2 concentration increased, HC and CO emissions were reduced by 15–20%, and PM emissions were reduced by 10%. With enough concentrations of hydrogen, black-carbon emissions could be eliminated [10].

Despite all these benefits, there's also a catch: increasing hydrogen concentration also increases NOx emissions, which could be due to the higher temperatures found within the cylinder, or the increased prompt-NO formation due to increased OH radical concentrations. Overall, more research must be done regarding this topic to find a proper compromise and the optimum ratios and conditions for its best work.

5 Conclusion and Future Direction of Research

DF technology is a promising step in the right direction, and a great technology that aids in the transition from fossil fuels to renewable sources. Like any other technology, DF engines are in a constant process of improvement and exploration. Besides the well-known NG, alternative fuels of cleaner origins such as biogas, hydrogen, ammonia, and syngas are being researched. Most of these fuels have a great potential mostly because of their hydrogen content, and some have the added advantage of being carbon neutral. Despite the wide amount of research available on DF diesel engines, most researchers suggest for future and more comprehensive research to take place. The composition of gaseous fuels is a topic that remains having a lot of research potential. For example, NG has several shortcomings that include limited replacement ration, efficiency deterioration, low combustion efficiency due to the incomplete combustion nature of methane, lower gas energy density compared to that of other HC, and unburned methane emissions, which are an issue because of their high global warming potential. Other fuels present their own issues, like hydrogen and their instability, and ammonia with its high nitrogen content and corrosive properties. The current technology allows for these setbacks to be mitigated with the help of additives as seen before, yet further research is encouraged to develop new technologies compatible with these fuels.

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