

Comparative analysis of greenhouse emissions based on life cycle assessment of alternative fuels for transportation sector – A systematic literature review.

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Dedication

This thesis work is dedicated to my parents, Hugo and Luz Helena, who have always loved me unconditionally and whose good examples have taught me to work hard for the things that I aspire to achieve, and to my sisters Ana Maria and Maria Paula who have been a constant source of support and encouragement during the challenges of graduate school and life.

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ATJ

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ATR

Autothermal Reforming, 54

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BEV

Battery Electric Vehicle, 33

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ABSTRACT

The shift towards sustainable energy sources has become a primary subject of discussion when considering the future of energy. It is crucial to move from traditional to nonconventional and sustainable sources of energy, given the depletion of fossil fuels and growing environmental concerns about the rising concentration of GHG in the atmosphere. This phenomenon causes the Earth's average temperature to increase, which can result in significant climate changes.

Although Colombia only contributes to approximately 0.37% of global GHG emissions [1], it is largely affected by climate change, and is signatory of the Paris Agreement in 2015. Among the most outstanding and relevant goals proposed, is reduction carbon dioxide emissions by 51% and to achieve carbon neutrality by 2050.

In order to achieve carbon neutrality by 2050, decarbonization of the transport sector is imperative, given its strong dependence on fossil energy sources. Policies are needed to accelerate and promote the establishment of infrastructure to support zero-emissions vehicles and the incorporation of low carbon fuels that are critical to decarbonizing aviation, shipping, and heavy-duty road freight. The ultimate solution to decarbonize the transport sector is to replace fossil fuels with CO₂-lean energy sources. This requires identifying and supporting technologies that can deliver significant reductions in GHG emissions over the entire life cycle.

The National Energy Plan PEN 2020-2050 outlines a long-term vision for Colombia's energy sector and explores potential ways to achieve it. The plan acknowledges that the transportation sector will play a significant role in the energy transition, where GHG mitigation can be achieved through the adoption of improved technologies, vehicle electrification, and the use of hydrogen and other advanced biofuels. While alternative fuels are not expected to be the primary focus of the energy transition, it is becoming increasingly clear that they will need to be part of the strategy. Studies have shown that next-generation renewable fuels offer a transition path towards low carbon emissions for the transportation sector.

This study conducts a systematic literature review by collecting relevant studies related to the life cycle analysis of low carbon fuels intended for the transportation sector. The goal is to assess the potential of various alternative fuels for decarbonization. The study evaluates the life cycle GHG emissions and energy

consumption considering fuel characteristics such as: raw material, production pathways, utilization technologies, energy efficiency and environmental performance. Finally, a meta-analysis is conducted to compare the GHG abatement potential of all low carbon fuels and their pathways with fossil energy sources.

Key words: energy transition, life-cycle assessment, GHG emissions, Well-to-wheel, alternative fuels, low carbon fuels.

I. INTRODUCTION

Energy is a crucial driver of economic growth and is essential for sustaining modern economies. However, the world currently faces a crisis related to the depletion fossil fuels and concerns about global climate change caused by local pollution effects. The projected economic growth of countries depends heavily on the long-term availability of energy from sources that are affordable, accessible and environmentally friendly. Therefore, there is an urgent need to transition from conventional to nonconventional sustainable energy sources. This transition requires the exploration and exploitation of alternative fuels and means of transportation, particularly in the transportation sector, which is a major contributor to Colombia's GHG emissions. This sector consumes 40% of the country's energy, with 96% of that energy coming from fossil fuels. According to the Colombian national GHG inventory, the transportation sector is responsible for 12% of the country's emissions, equivalent to 28 million tons of carbon dioxide [2].

As transport activity continues to grow, it is essential for Colombia to implement targeted mitigation policies that are aligned with the country's objective of achieving carbon neutrality by 2050. The decarbonization of the transportation sector can be achieved through the substitution of fossil fuels with natural gas, bio-methane, biofuels, electricity, renewable hydrogen, and other low carbon fuels that meet specific criteria, including sustainability, pollutants emission, toxicity, effect on land use and damage, cost competitiveness, and infrastructure requirements.

The study aims to investigate a range of alternative fuels that have the potential to reduce GHG emissions. This study employs a systematic review based on the PRISMA 2020 methodology [38] to examine the life cycle GHG emissions of various alternative fuels and their production pathways. The primary focus is the GHG emissions generated throughout the full life cycle of fuel supply chain, encompassing each phase of its production and use, such as the feedstock's production and transport, land-use change, renewable fuel production, distribution and blending, and combustion process.

A meta-analysis based on literature results of the WTW CO₂ emissions of the LCA is performed. This enables a standardized approach to comparing different types of alternative fuels on a consistent basis, using a measure of grams of CO₂-eq per MJ of delivered energy.

II. OBJECTIVES

A. General objective

To perform a comprehensive literature review of a wide range of alternative or low-carbon fuels, including both neat fuel options and those blended with conventional fuels, intended for use in the transportation sector. The review will also examine their production pathways and analyze the potential benefits of these fuels in terms of reducing WTW GHG emissions, to consider additional transportation fuel options which can be incorporated into the ongoing energy transition in Colombia.

B. Specific objectives

- ✓ To compare quantitatively the WTW CO_2 emissions of the potential low carbon fuels intended for the transportation sector with the life cycle CO₂ emissions of petroleum baseline fuels, through systematic literature review and a meta-analysis, in order to evaluate the GHG abatement potential of selected low carbon fuels and its production pathways.
- ✓ To identify the drivetrain technologies and energy carrier production pathways that demonstrate the greatest potential to reduce WTW CO_2 emissions compared to the conventional ICE reference vehicle.

III. THEORETICAL FRAMEWORK

A. Global warming and environmental pollution

The industrial revolution and the progressive growth of the human population has resulted in the incremented use of fossil fuels. This has led to the accumulation of greenhouse gases at the atmosphere. The combustion of fossil fuels generates pollutant gases, such as carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxide (NO_X), un-burnt hydrocarbons (HC), with the transport sector being a significant contributor [4]. The accumulation of these gases, particularly CO₂, results in the trapping of solar heat and causes a rise in global surface and ocean temperatures. This process, over the long-term, causes the gradual melting of glaciers and polar ice caps, which poses a risk of inundation of the low-lying areas of earth; the drought in tropical countries, which affects their agriculture and water supply; the extinction of species and the acidification of oceans and therefore, which threatens marine life.

In 2012, Colombia partnered with the CCAC and is currently participating in the Supporting National Action and Planning, where it developed in 2018 the National Strategy for the Mitigation of SLCPs. The strategy aims to implement measures to reduce black carbon, methane, tropospheric ozone, and hydrofluorocarbons, while evaluating their impact on air quality.

Globally, the primary GHG emitted is CO₂, which results from the use of fossil fuels, deforestation, agriculture and soil degradation. Although other gases, such as methane (CH_4), nitrous oxide (N_2O) and fluorinated gases, are produced in smaller quantities, they contribute similarly to global warming. These gases are byproducts of agricultural activities, fossil fuels combustion and industrial processes. Figure 1 shows the contribution of each of these gases to global GHG emissions.



Fig. 1: Global Greenhouse Gas Emissions [3]

The transport sector is responsible for a large proportion of GHG emissions, accounting for 37% of CO_2 emissions from end-use sectors in 2021, as shown in Figure 2. This represents an increase of 8% (7.7 Gt CO_2) compared to the previous year, with the road transport sector being the largest contributor at 5.46 Gt CO_2 followed by rail (0.09 Gt CO_2), shipping (0.84 Gt CO_2), aviation (0.71 Gt CO_2) and pipeline transport (0.15 Gt CO_2) [4].



Fig. 2: Global CO₂ emissions from transport by sub-sector between 2000 and 2030 [4]

In Colombia in 2019, the transport sector emitted 34 Mt CO_2 as shown in Figure 3, which represents one third of the total CO_2 emissions (35-37%) emitted annually [5].



Fig. 3: Colombia's CO_2 emissions from the transport sector [5]

B. Energy security

Given the growth of the energy sector and increasing demand, it is crucial for the countries to ensure access to stable, affordable and sustainable energy, that can withstand challenges such as global warming, globalization and the depletion of fossil fuels. Energy security involves addressing both short and long-term challenges; the former dealing mainly with timely investments to meet economic and environmental needs; and the latter focusing on responding promptly to changes in the supply and demand.

To maintain energy supply in the transport sector, an analysis must be conducted of the current and future risks associated with petroleum-based fuels and their environmental impact, assess emerging gas security challenges, and consider the transition to renewable energy sources.

Currently, Colombia is seeking membership in the International Energy Agency, an organization that ensures that each country is sufficiently prepared to provide energy resources such as oil, gas, and coal in times of emergencies. To qualify for membership, countries must meet specific criteria, related to having a robust response system in the event of a national or global oil disruption, the reduction of oil consumption, and legislation and monitoring measures of oil companies. Colombia is currently working towards fulfilling these criteria.

C. Energy transition in Colombia

Between 1975 and 2019 there was a large industrialization of the country and therefore an increase in the energy consumption (from 738 PJ to 1.346 PJ) [6] especially by the manufacturing industry and the transport sector, this in addition to a change in the composition of the energy supply, replacing traditional low-efficiency fuels such as bagasse and firewood with liquid fuels (such as diesel), electricity and natural gas.

Currently, Colombia's energy supply is composed of oil and its derivatives (40%), followed by natural gas (21%) and finally by electricity (16%) [6]; most of which come from the internal resources of the country that in long term will be insufficient to meet the country's energy demand. The UPME shows that the supply of local gas, light and heavy crude, and LPG will be deficient by 2028, which generates the necessity of a change in the fuels used today and the implementation of new energies to the Colombian energy matrix.

On the other hand, the objective is to improve the country's energy efficiency by enhancing the technologies in the energy sector. Currently the sector with the greatest potential for energy efficiency is transport, which has a useful energy of 24% and equipment losses of 69% as shown in Figure 4. As an improvement, the propose is to replace the most inefficient diesel and gasoline vehicles with hybrid and electric vehicles that present efficiencies of 60% to 70% respectively, and that are also considered low and zero emissions.



Fig. 4: Final energy and useful energy of the transport sector [7]

In addition, energy transition aims to reduce GHG emissions from these fossil fuels and thus mitigate the effects of climate change. To achieve this, it is necessary to analyze the options of diversification of the energy matrix for the incorporation of non-conventional renewable energies such as solar, wind and geothermal, and the adoption of low- or zero-emission technologies such as nuclear and others like carbon capture and sequestration and even hydrogen, natural gas and LPG as transition fuels.

D. Colombia's energy matrix

The transport sector is responsible for 40% of the country's total energy consumption, primarily through the use of oil derivatives such as gasoline and diesel (which are the most widely used), as well as natural gas. The industrial sector comes in second, accounting for 22% of energy use, and relying on natural gas, coal, bagasse, and electricity. In third place is the residential sector, which uses firewood, electricity, natural gas, and LPG as energy sources and accounts for 20% of the final energy consumption. The tertiary sector demands only 5% of Colombia's energy and relies on electricity, natural gas, and LPG for energy [6].

According to Figure 6, the energy supply in Colombia follows a similar pattern to that of Latin America and the world. Oil and its derivatives are the most commonly used resource in all three, with Colombia using it for 40% of its supply, Latin America for 41%, and the world for 35%. Natural gas comes in second place, with Colombia using it for 21%, similar to Latin America's 18% and the world's 20%.

Electricity is in third place, with Colombia having a share of 16%, Latin America having 15%, and the world having 10%. Finally, coal represents 9% of Colombia's energy supply, which differs from the world's 20% and almost zero in Latin America [6].



Fig. 5: Energy supply for final consumption [6]

E. PEN (National Energetic Plan) 2020-2050

PEN 2020-2050 proposes a long-term vision for the Colombian energy sector and outlines possible paths to achieve an energy transformation that benefits present and future generations. The PEN takes into account the implications of each pathway and their contributions to the climate change. It seeks a diversification of the Colombian energy matrix, by reducing the use of fossil fuels and replacing them with renewable sources that are more efficient and have lower environmental impacts.

The transport sector will play a major role in this energy transformation and in mitigating climate change. This is due to the potential energy savings that can be achieved by adopting better technologies, progress in vehicle electrification, and the development of hydrogen and other advanced biofuels.

The PEN also aims to fulfill the sustainable development goals (SDGs), which seek to achieve a sustainable future through interventions in the different key areas, for the proper development of the society. The emphasis in this case is on the following objectives:

Objective 7: Affordable and clean energy.

Objective 9: Industry, innovation and infrastructure. Objective 11: Sustainable cities and communities. Objective 12: Responsible production and consumption. Objective 13: Climate action.

To achieve the set objectives, the following paths are proposed: evaluating the current supply possibilities of conventional energy sources used in Colombia and exploring non-conventional energy sources such as wind, solar, geothermal, biogas, nuclear, and other energy sources like hydrogen that can be added to the Colombian energy matrix. The focus will be on substituting high-emission fossil fuels with low or zero carbon footprint fuels, particularly in the transport and industrial sector.

F. Transportation sectors

Figure 6 shows that the transport sector comprises rail, shipping, aviation, and road, including light duty and heavy-duty vehicles. Light duty vehicles cover passenger vehicles such as cars, motorcycles, buses, and taxis, while heavy duty vehicles cover trucks and lorries. All these vehicles contribute to global CO_2 emissions, but in different proportions. Light and heavy-duty vehicles are the biggest emitters, producing 45.1% and 29.4% of CO_2 emissions, respectively. Aviation comes in third place, emitting 11.6% of CO_2 , followed by shipping with 10.6% and rail with 1%. Other emissions produced by the transport of oil, gas, water, steam, and other materials via pipelines are responsible for 2.2% of CO_2 emissions [8].



Fig. 6: Global CO2 emissions from transport [8]

G. Life Cycle Assessment (LCA)

As the world's economy and population continue to grow, it's become increasingly important to find ways to meet global needs while minimizing the negative impact of human production and consumption on the environment. To support this search for a more sustainable development, the LCA method has been developed as a standardized way to assess the potential environmental impacts of a product throughout its entire life cycle, from extraction to disposal or recycling as shown in Figure 7. By identifying hotspots that have a significant impact on human health, ecosystem health, and resources availability, we can compare options and make informed decisions to achieve sustainable development goals.



Fig. 7: Life Cycle Assessment [9]

The operational aspects of the LCA are covered by ISO 14044, who defines its principle and framework, as the compilation and evaluation of the inputs, outputs, and the potential environmental impacts of a product system throughout its life cycle [9]

The LCA with this systemic approach supports the country's SDGs shown in Figure 8 allowing for example: scenario analysis of eco-innovation (either technological innovations or behavioral changes); modeling different characteristics of product, production, transport, use, infrastructures, and citizen choices and behaviors; and the quantification of the potential benefit arising from each (or combination) of the innovations or options selected [9].



Fig. 8: LCA and the SDGs [9]

There are two main types of LCA studies: attributional (ALCA) and consequential (CLCA). These two types of studies have different objectives and methodologies, and their results can vary significantly. ALCA is primarily used as an accounting tool to estimate the environmental impacts of various activities in the supply chain, compare alternative systems, and identify environmental hotspots that can be targeted for improvements. It focuses on impacts directly related to the system of interest. On the other hand, CLCA not only examines the direct impacts of the system under study but also considers potential indirect consequences by analyzing various scenarios that could arise. For example, it can evaluate the potential impacts of biofuel feedstock cultivation on other land-using sectors and the effect this might have on the food production system and land use change (LUC) elsewhere in the global economy. However, CLCA is still under development, and most of the LCA studies found in the literature are attributional [10].

A number of different terms are frequently used in the context of assessing the "environmental impact", the most commonly used are (LCA) WTW (WTT and TTW), ecobalance, well to wake, cradle-to-grave and cradle to gate analysis.

The cradle to grave approach is a key component of the environmental life cycle assessment, aimed at reducing the impact of a product's entire life cycle on both the environment and human health. This approach specifically considers the sourcing of raw materials all the way through to the product's final disposal. By using this method, we can identify opportunities to substitute materials and energy with more environmentally friendly options, minimize waste generation, and create links to other products' life cycles to reduce the need for non-renewable materials and promote cascading reuse and recycling chains. However, it's important to note that this approach primarily focuses on environmental impact and may neglect social and economic aspects [11].

In addition to the cradle to grave approach, there are other models used in LCA, such as cradle to gate and cradle to cradle as shown in Figure 9. These two models differ from the cradle to grave method, the cradle to gate model assesses a product's environmental impact from raw material extraction until it leaves the factory gate. The cradle to cradle model also assesses a product's environmental impact from raw materials, but instead of a waste stage, it focuses on a recycling or upcycling process, effectively closing the loop and promoting a more sustainable approach.



Fig. 9: Life cycle of fuels and vehicles [12]

1) Well-to-wheel analysis:

The WTW method is a specialized approach within LCA that evaluates the production stages of various transport fuels, with a focus on their greenhouse gas (GHG) emissions, energy efficiency, and industrial cost. However, it does not consider the energy and emissions associated with constructing the facilities and vehicles used in the life cycle of fossil fuels.

The method is divided into two parts: Well to Tank (WTT) and Tank to Wheel (TTW) as shown in Figure 10. WTT focuses on the process from oil drilling or crop cultivation to the delivery of road fuel to a filling station, while TTW covers the process of the fuel getting into the tank of the vehicle and their consequently combustion.



Fig. 10: Steps of the Well-to-wheel [13]

When it comes to the WTW assessment of biofuels (such as bioethanol, biodiesel, methanol, HVO, DME, ethanol, and hydrogen), particular attention is given to their environmental impact. This is due to the need to evaluate the effects of the fuels in their production, as well as the resulting emissions throughout the growth of the feedstocks, which releases a substantial amount of carbon from soil and plant biomass. Another

crucial factor to consider in the WTW assessment of biofuels is Land Use Change (LUC), which is a significant source of GHG emissions resulting from the conversion of natural vegetation or forests to biofuel feedstocks.

Aside from increasing GHG emissions, LUC can also have other environmental impacts, such as soil erosion, nutrient depletion, water consumption, and loss of biodiversity. There are two types of LUC related to biofuels: direct (DLUC) and indirect (ILUC). DLUC involves the direct conversion of previously uncultivated areas, such as grasslands and forests, into croplands for biofuel feedstock production. On the other hand, ILUC occurs when the additional demand for biofuel feedstock leads to the displacement of food and feed crop production to new land areas that were not previously used for cultivation [10]. These environmental impacts, including direct and indirect LUC, will be discussed in more detail below.

Direct Land Use Change Emissions (DLUC): cultivating biomass on land previously used for other purposes can affect GHG emissions depending on the land's condition. When feedstock production occurs on a land with high carbon stocks, such as peat land or unmanaged forests, the DLUC effect can have a significant negative impact on the crops environmental performance. On the other hand, growing biofuel feedstocks on degraded soil can increase soil carbon content and contribute to a positive DLUC effect [14]. This can be measured by comparing carbon balances between the new and previous land uses and assessing changes in soil carbon stocks.

Indirect Land Use Change (ILUC): this occurs when biomass cultivation replaces food crops, which are then moved to new lands that may have high carbon stocks. The growing demand for biofuels worldwide has led to an increase in land use for both biofuel and food crop production, which can have significant impacts on greenhouse gas emissions, biodiversity, soil, and water quality. Unfortunately, it is often difficult to quantify these effects as ILUC can occur outside the country that fostered biofuel production.

Other environmental impact categories considered in biofuel LCA studies include acidification, eutrophication, photochemical smog, human toxicity and eco- toxicity.

Water Footprint: it is defined as the volume of freshwater used for its production; the major quantity of this water comes from the agricultural production stage. The WF consists of 3 components: the green WF, the blue WF, and the gray WF. The green WF refers to rainwater that evaporated during production, mainly during crop growth. The blue WF refers to surface and groundwater for irrigation evaporated during crop

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growth. The gray WF is the volume of water that becomes polluted during production, defined as the amount of water needed to dilute pollutants discharged into the natural water system to the extent that the quality of the ambient water remains above agreed water quality standards [15]

Soil Quality/Erosion: occurs when soil particles detach from the soil surface by rain or flowing water and are then transported by water or wind. Living vegetation or crop residues protect the soil surface from erosion, but when the soil surface is not covered by plant materials, water dislodges soil particles from aggregates. These detached particles bounce around on the soil surface and can plug large pores, which can lead to lower water infiltration, increased water runoff, and in turn, more soil erosion.

When farmers start growing crops for biofuel production, they should carefully consider strategies such as cover cropping and crop rotation to minimize soil erosion, especially if they are adopting new production practices that could increase the duration or area of bare soil [16].

Eutrophication and Acidification: intensive agriculture using fertilizers can cause eutrophication and acidification of the soil, an increased crop production for biofuels would tend to exacerbate this problem. The oceans have taken the 24-33% of the CO_2 emissions during the last five decades, which has resulted in changes in the seawater chemistry and the ocean acidification, putting at risk its organisms and their habitats. On the other side there is eutrophication, that consist of the process of nutrient over-enrichment of waters that can lead to hypoxia and harmful algal blooms, which among others can destroy aquatic life in affected areas [17].

H. Alternative Fuels

Currently, fossil fuels account for more than 80% of global energy consumption and over 95% of energy for the transport sector [18]. This heavy reliance on fossil fuels not only depletes global reserves but also causes environmental pollution that adversely affects human health. Harmful pollutants such as carbon monoxide (CO), unburned hydrocarbons (HC), oxides of nitrogen (NOx), suspended particulate matter (SPM), and aldehydes are present in engine exhaust. In addition to these harmful pollutants, CO_2 emissions contribute to long-term global issues such as the greenhouse effect and global warming. As such, exploring alternative fuels for the transport sector is crucial for improving energy supply security and reducing greenhouse gas emissions (GHG).

Alternative fuels refer to fuels derived from sources other than crude oil. Generally, alternative fuels include all fuels used in vehicles other than gasoline and diesel. There are several alternative fuels that can be used in current petrol or diesel internal combustion engines with little or no modification. These fuels have advantages such as cleaner burning than petroleum-derived fuels, lower emissions, and reduced dependence on non-renewable petroleum if derived from renewable biomass sources. However, alternative fuels do not necessarily have to come from renewable energy sources. Each fuel has its own advantages and disadvantages, such as cost, availability, environmental impact, vehicle/engine modification requirements, safety, customer acceptance, and legislation [19].

Alternative fuels are receiving attention because of the following reasons:

- Alternative fuels are mostly produced from domestic resources that reduce the energy dependence.
- Alternative fuels generally reduce the vehicle exhaust emission and hence improve the environmental air quality.
- Some alternative fuels have the potential to operate at a lower cost compared to petroleum products.

Currently, a variety of substances and their natural sources are being investigated as potential alternatives for fossil fuels, especially petroleum-derived fuels. The criteria for use depend largely on how the substance compares with standard fossil fuels with respect to the various desired fuel characteristics/properties [20]

The search for an alternative fuel has produced a long list of candidates and a series of arguments, which support and project their characteristics. The main alternative fuels for propulsion in transport are the following:

- Alcohols (methanol and ethanol): The primary alcohols (methanol, ethanol, propanol, and butanol) are preferred to be used as an IC engine fuels. This is because these alcohols possess characteristics as a higher-octane number, which permit them to be used as fuel in current generation IC engines.
- Vegetable oils and biodiesel: Biodiesel is methyl or ethyl esters of fatty acids derived from edible and nonedible type plant-derived oils, animal fats, and waste cooking oils or any other waste/residue triglycerides can be converted into diesel-like fuels through several routes. Vegetable oils in their raw form cannot be used in CI engines due to their inferior fuel properties; therefore, they have to be

chemically modified to produce biodiesel, which has improved physical and chemical properties for use as a fuel; this is done using transesterification process, in which the reaction of triglycerides present in the vegetable oils is done with primary alcohols in presence of a catalyst, which produces primary esters (biodiesel) and glycerol. The production of biofuels from both food and energy crops is limited by the availability of land, energy and co-product yields, and sustainability considerations.

- Gaseous fuels (natural gas, hydrogen, and liquefied petroleum gas):
 - Natural gas occurs as gas under pressure in rocks beneath the earth's surface or more often in solution with crude oil as the volatile fraction of petroleum, it is composed as a mixture of paraffinic hydrocarbons as ethane, propane, butane, with 80–98% methane, which is the main constituent. Natural gas commercially has been using as a fuel for centuries, however, for the past few decades natural gas has been receiving more attention due to the increase in price of petroleum products.
 - Liquefied petroleum gas (LPG) is a nonrenewable fossil fuel derived from lighter hydrocarbon fractions produced during refining of crude petroleum, that consist of a mixture of propane (C3H8) and butane (C4H10) gas, is a popular fuel for internal combustion engines. This popularity comes from many features of the fuel such as its high-octane number for spark ignited engines, comparable to gasoline heating value that ensures similar power output.
 - Hydrogen is one of the cleanest fuels in the world, as it does not contain carbon compounds. Hydrogen is a clean and efficient energy carrier with the potential to replace liquid and gaseous fossil fuels, as it can be combusted directly in the IC engines, via direct injection to cylinder (hydrogen IC engine), or it can be used in the fuel cell to produce electricity by manifold induction (hydrogen fuel-cell) and hydrogen-diesel dual fuel mode (hybrid electric vehicle). Hydrogen is manufactured from water using energy from either fossil or no fossil fuel sources. The methods to produce hydrogen include electrolysis, photolysis, thermochemical water splitting, and coal gasification.
- Ethers: Dimethyl ether is the commonly used blending component in gasoline fuel. Moreover, DME is a
 potential alternative fuel that can be used in engines as well as onboard hydrogen generation fuel cells.
 DME can be produced from organic feedstocks such as biomass, coal or natural gas, that are converted

into synthesis gas, which is a mixture of carbon monoxide, hydrogen and some other gases. Syngas is converted into methanol and finally into DME by dehydrogenation of methanol.

- Electricity and hydrogen: The study considered a wide range of options for electric and fuel cell vehicles, such as Battery Electric (BEV), Fuel Cell (FCV) and Hybrid Vehicles (Mild hybrid, Full hybrid, Plug-in hybrid) where the overall energy use and GHG emissions depend critically on the source of the electricity used, which can be generated from coal, natural, solar, fuel cell, on board diesel engine, gas, and nuclear energy; in general electricity and hydrogen are universal energy carriers and can be produced from all primary energy sources. Both can in principle be made CO_2 free, depending on the energy mix for production. Propulsion uses electric motors and energy can be supplied via three main pathways:
 - Battery-electric, with electricity from the grid stored in batteries. Application is limited to shortrange road transport.
 - Fuel cells powered by hydrogen, used for on-board electricity production. The development of costcompetitive fuel cells, on-board hydrogen storage, and strategic refueling infrastructure is the highest priority.
 - Overhead Line / Third Rail for tram, metro, trains, and trolley-buses, with electricity taken directly from the grid without the need of intermediate storage.

In general, the performance of the vehicle depends mainly on the performance, efficiency, durability and reliable operation of the battery or fuel cell.

Synthetic fuels: Synthetic fuels, substituting diesel and jet fuel, can be produced from different feedstock, converting biomass to liquid, coal to liquid or gas to liquid, this means it can be obtained from natural gas, coal, oil shale, and biomass sources through the Fischer–Tropsch synthesis process. Fischer–Tropsch (F–T) process is a process that produces variety of hydrocarbon fuels. The primary product is a diesel-like fuel from syngas (*H*₂) /CO), which can be produced by auto-thermal reforming of natural gas, biomass or coal.

Alternative fuels can be derived from various sources and production processes, but they share a common feature in that they are produced using sustainable and clean procedures, resulting in a clean

emission profile. Furthermore, they offer the potential for economic development and energy security by reducing dependence on fossil-based non-renewable fuel sources. Figure 11 illustrates the two main pathways for synthesizing alternative fuels: direct utilization of surplus electricity and thermochemical conversion of raw feedstock into useful gaseous or liquid fuels.



Fig. 11: Alternative fuels for transportation sector

Most alternative fuels have not yet reached commercial scale application due to limitations in their production and consumption processes and technologies. This is often due to a high energy penalty that these fuels undergo throughout their life cycle or to the lack of economic viability of the production process itself. Currently, biofuels are the only alternative fuel in commercial use, and its consumption is expected to increase further. Other alternative fuels, such as hydrogen, ammonia, methanol, biodiesel, biogas, and wastederived biofuels, have not yet reached commercial maturity, and their current consumption is negligible [21].

Finally, the main question would be: Which are the most opted options of alternative fuels for the different transport modes? The global prospective is:

- Road transport could be powered by electricity for short distances, hydrogen and methane up to medium distance, and biofuels/synthetic fuels, LNG and LPG up to long distance.
- Railways should be electrified wherever feasible, otherwise use biofuels.

- Aviation should be supplied from biomass derived kerosene.
- Waterborne transport could be supplied by biofuels (all vessels), hydrogen (inland waterways and small boats), LPG (short sea shipping), LNG and nuclear (maritime).

1) Alternative Diesel Fuels:

a) Synthetic Diesel Fuels:

Synthetic transportation fuels referred to a liquid fuel that can be produced from a wide range of feedstocks, including coal, natural gas, or biomass feedstocks trough Fischer-Tropsch synthesis process, into synthetic crude and/or synthetic liquid products. The Fischer-Tropsch process is the synthesis of long-chain hydrocarbons from CO and H_2 gas mixtures (Synthesis gas) produced from gasification of biomass and fossil fuels; where depending on the synthesis process, several types of fuels can be produced. Currently, the following three technologies are used to produce liquid synthetic fuels (CTL: coal to liquid, BTL: biomass to liquid and GTL: gas to liquid).

If the feedstock for the F-T process is natural gas, the production comes under the gas-to-liquid conversion process, likewise the F-T synthesis using coal is referred to as the indirect liquefaction of coal, which as can be seen, by being manufactured from fossil fuels brings no distinct greenhouse gas benefits in comparison with conventional fuels; on the other hand green diesel fuels or F-T fuels produced from lignocellulosic biomass, and more specifically from those parts of plants not used in food production, can achieve a significant greenhouse benefit, since CO_2 emissions are almost completely avoided when biomass is used to produce synfuel, this will be seen on the results section.


Fig. 12: F-T process [13]

A wide range of carbon containing feedstocks can be used for the F-T process, where the production of Fischer-Tropsch fuels requires that the feedstock is gasified, before syngas is send to the F-T reactors, CO_2 and sulfur compounds are removed, where CO_2 may be vented or captured and sequestered (with the CCS technology); finally the resulting synthesis gas is catalytically converted to hydrocarbons. These can be described in three steps as shown in Figure 12:

Synthesis gas generation: Conversion of the feedstock into synthesis gas, using commercially established technologies, for example gasification technologies for solid feedstocks such as coal and biomass.

Hydrocarbon synthesis: After the removal of impurities, the syngas is converted into a mixture of unbranched paraffinic and olefinic hydrocarbons.

Fuel upgrading: The syngas is upgraded through hydrocracking and isomerization, into fractionated middle distillate fuels (liquid fuels).

Syngas¹ can be burned directly to produce electricity or converted into hydrocarbons (such as gasoline and diesel), alcohols, ethers, or chemical products; where fuels derived from this process are cleaner than fossil fuel derived from crude oil, nontoxic, and less harmful to the environment due to its fuel properties, achieving this way an improvement on the air quality in cities without expensive and sophisticated technical modifications to vehicles and infrastructure.

b) DME (Dimethyl Ether) and OME Fuels:

Dimethyl ether is an LPG-like synthetic diesel fuel that is produced through gasification of a wide range of carbon containing feedstocks (coal, natural gas, or biomass), more specifically is produced from pure methanol by means of a process called catalytic dehydration, whereby the production of methanol and

¹ Syngas is a 1 : 1 mixture of carbon monoxide (CO) and hydrogen (H2)

DME is combined in one process, in which DME process possesses both methanol synthesis and methanol dehydration activity as shown in Figure 13. Since the production of DME and methanol are closely related, these processes can occur in separate reactors or in a common reactor, where methanol is formed first and the dehydration reaction to produce DME occurs thereafter in the same reactor.



Fig. 13: DME pathways [<u>140</u>]

Given that DME has been found to be an attractive fuel for combustion in a variety of applications as shown in Figure 14, and since there are several options for DME production, DME can be viewed as a multisource-multipurpose fuel, where this flexibility gives an advantage in terms of market introduction, as a variety of applications are possible for introducing DME into the commercial market.



Fig. 14: A schematic view of the flexibility of DME as a multisource-multipurpose fuel/chemical [19]

Since DME is a clean burning fuel due to the high cetane number and its simple chemical structure, with no carbon–carbon bond, it can limit the possibility of forming carbonaceous particulate emissions during combustion, and could reduce emissions compared with diesel fuel, however, the physical properties of DME are so different from those of conventional diesel fuel, that the entire fuel system must be redesigned, these means that fuel storage (pressurized fuel tank onboard the vehicle) and injection system needs to be replace in order to be able to use DME as an alternative to liquid diesel fuels. Therefore, the DME fuel is more likely to be used in certain niche applications, for example it can be blended with propane for the use in spark-ignited LPG engines, rather than provide a wide-scale alternative, due to not only the system redesigned required, but also to the additional requirements needed, related to the distribution infrastructure networks for storage and delivery. As with any new technology, the introduction of DME into the world markets faces obstacles, related with uncertainties, economics, and infrastructure concerns, specifically related to a no large-scale supply and distribution system for DME as a transport fuel.

Specifically, Oxymethylene Ether (OME) is a DME derivative, that is produced from methanol and formaldehyde as shown in Figure 15. It has an unlimited miscibility with conventional diesel fuel, is non-corrosive, non-toxic, and biodegradable; properties that allow the use of OME as a drop-in fuel with major advantages concerning pollutants and particles in the exhaust of diesel engine exhaust.

OMEs offer the possibility of partially or completely replace fossil-based fuels by renewable sources, such as biomass or CO_2 via the synthesis gas/methanol route, where in the first stage methanol is partially oxidized to formaldehyde.



Fig. 15: Process route to OME [13]

c) Biodiesel (FAME):

Biodiesel has gained much acceptance worldwide as an alternative to the fossil-based conventional diesel, because it is a renewable source of energy with favorable energy balance, biodegradable and

ecofriendly nature, excellent fuel properties, and nontoxic profile [22]. Alcohols, vegetable oils, and their derivatives are promising biomass sources for use in diesel vehicles; particularly ester based oxygenated fuels derived from biological sources, such as vegetable oils (e.g. rapeseed, soy bean, cottonseed, palm, peanut, sunflower, safflower, coconut), animal fats (typically tallow) and waste oils (frying and cooking oils) are gaining more importance currently as it does not require any engine hardware modification without affecting the engine performance, no sulfur emissions, and a reduction in greenhouse gas emissions. These types of fuels are defined as mono alkyl esters of long-chain fatty acids of lipids, and are produced by different conversion methodologies (microemulsion, pyrolysis, and transesterification). Among these various conversion methodologies, the transesterification of fatty acids is one and the most widespread method to reduce the viscosity of the acids – one major problem associated with the use of neat fatty acids/vegetable oils.

Although lack of sulfur, high ash point, and safe storage are considerable advantages of vegetable oils over petroleum diesel, their high viscosity, polyunsaturation character, low volatility, poor fuel atomization, incomplete combustion, insufficient mixture formation inside the combustion chamber, formation of carbon deposits, piston ring sticking, injector coking, long ignition delay, and reduced cold starting misfire are the main constraints for direct use of vegetable oils as an alternative to petroleum-based fossil fuels in diesel engine [22]. Where as previously mentioned, processes such as pyrolysis, microemulsification, and transesterification can be used to overcome the deficiencies associated with direct use of vegetable oil as a fuel in diesel engines, as follows:

<u>Microemulsification</u>: this technique demonstrates the feasibility of biodiesel fuel production through the vegetable oil extraction utilizing "diesel-based reverse micellar microemulsions" as extraction solvent. Although microemulsion of vegetable oil has been proved a means for lowering the viscosity of the vegetable oils, it has a series of disadvantages associated, such as heavy carbon deposits, uneven injector needle sticking, and incomplete combustion.

<u>Pyrolysis</u>: this is a process by which thermal decomposition of the biomass is carried out in the absence of oxygen. Products resulting from pyrolysis of vegetable oils usually exhibit advantages like low viscosity; acceptable levels of sulfur and high cetane number; however, presents some disadvantages regarding ash contents and carbon residues. <u>Transesterification</u>: is a chemical process of transforming large, branched triglyceride molecules of the vegetable oils and fats into smaller, straight chain molecules as shown in Figure 16. This conversion process has gained much acceptance for the conversion of vegetable oils into products with technically more compatible fuel properties.



Fig. 16: Schematic biodiesel production pathway [32]

For the production of biodiesel, plant-derived oils are considered to be the most efficient feedstock/raw materials for biodiesel production due to their inexhaustible, biodegradable, nontoxic and renewable nature; where the choice of the feedstock is predominantly influenced by the geographical region and is one of the main factors to be considered for biodiesel production.

The potential feedstocks to produce biodiesel are classified into four categories: first-generation (edible oil crops), second-generation (non-edible crops and waste materials) and third generation (algae-based), as described in Figure 17.



Fig. 17: Feedstocks and production pathways of biofuels [10]

At present, more than 95% of biodiesel is produced by using first-generation feedstocks around the globe, where the production of biodiesel from first-generation feedstocks is more suitable and viable in those regions where agricultural land and water resources are abundantly available. However, the production of biodiesel from edible oil crops is not always favorable, as it increases land usage and can cause a shortage of food supply in the future. On the other side, the production of biodiesel from non-edible oil crops, such as waste cooking/frying oil, animal/plant fats, are considered as the most feasible feedstocks to synthesize biodiesel as they are abundantly available as a waste, these types of feedstocks do not affect the food chain supply, but land and water resources can be affected; specifically waste oil-based biodiesel is more feasible, environmentally safer, and cost-effective among all the available resources because it does not affect land usage, food chain supply, and water resources.

As can be seen in the Figure 18, refined vegetable oils, particularly soybean oil and canola oil, have been the most common biodiesel feedstock globally, where soybean oil accounted for about over the half of biodiesel feedstocks inputs between 2009 and 2017, on the other hand, advanced biodiesels from lignocellulosic feedstocks began to be produced at commercial production scales since 2016.



It can be observed from Figure 19, that developed countries are already focusing on synthesizing biodiesel to meet their energy needs.



Fig. 19: Global biodiesel production by country or region [25]

d) Hydrotreated Vegetable Oil (HVO):

HVOs are straight chain paraffinic hydrocarbons that are free from sulphur, oxygen and aromatic hydrocarbons, and has a high cetane number; also, the term HVO referred to renewable diesel fuels derived from hydrogenation and hydrocracking of different feedstocks such as tall oil, rapeseed oil, waste cooking oil, and animal fats.

Vegetable oils molecules are triglycerides with unbranched chains of different lengths and different degree of saturation. They have two broad classifications: edible oils (sunflower, soybean, palm oil, etc) and nonedible oils (jatropha, karanji, rubber seed oil, etc), which are derived mainly from four sources:

- Cultivated oil seeds (groundnut, rape-mustard, soybean, sesame, sunflower, safflower, castor, and linseed).
- Perennial oil-bearing materials (coconut and palm).
- Derived oil-bearing material (cottonseed and rice bran).
- Oil seeds of forest and tree origin (karanji and rubber seed oil).

Hydrotreating of vegetable oils, vegetable fats or animal fats offers an alternative to esterification for producing biobased diesel fuels, because it can overcome key detrimental effects of vegetable oils, in particular poor injection/atomization due to high kinematic viscosity. To comply with this, there are two competing reactions in the manufacturing by which this goal is achieved: hydrogenation and hydrocracking, where usually hydrotreatment is followed by hydrocracking/isomerization. Firstly as shown in Figure 20, in the hydrotreating process, oxygen is removed from the feedstocks consisting of triglycerides and/or fatty acids, then the fatty acids are converted to hydrocarbons by hydrodeoxygenation (removing oxygen as water) and/or decarboxylation (removing oxygen as carbon dioxide). The resulting products consist of straight-chained hydrocarbons with varying molecular size and properties, which depend on the feedstock characteristics and the process conditions.



Fig. 20: HVO production pathway [26]

In contrast to base-catalyzed transesterification process to produce FAME from vegetable oil feedstock, the HVO process is robust to high concentrations of FFAs, enabling other, lower-cost materials such as tallow oil and waste greases to be used as feedstocks.

2) Alternative Gasoline Fuels:

a) Ethanol:

Ethanol is an oxygenated fuel, produced from fermentation of biological renewable resources such as molasses, sugar cane, or starch. Because of benefits associated with ethanol, some countries started using ethanol as a substitute for gasoline, where its content covers a wide range from E5 to E85 (flex fuel). Although ethanol can be blended with gasoline, the unique chemical properties of ethanol must be accommodated in order to maintain engine performance, emissions, fuel economy, and drivability under all operating conditions. To support ethanol characteristics, engines must undergo certain modifications, these modifications included: compression ratio, amount of fuel injected, replacement of materials that would be corroded by contact with ethanol, among others.

Unmodified ethanol cannot be used as a fuel for conventional CI engines, and similarly unmodified CI engine cannot be used because the ethanol will not ignite by compression, due this, either the fuel or the engine must be modified. A desire to increase the use of ethanol fuel and a concern that high ethanol concentrations could cause material incompatibility, led to the development of a new type of vehicle, the flexible fuel vehicle (FFV), which is capable of burning any percentage of the resulting mixture of gasoline with ethanol (typically 85% of ethanol), where spark timing and fuel injection are adjusted according to the actual blend detected. Otherwise, in case of lower ethanol contents (typically up to 10%), no adjustments need to be undertaken.

Ethanol production process depends on the raw materials used, and it's commonly carried out into the major three steps: (1) to obtain the solution containing fermentable sugars, (2) conversion of sugars into ethanol by fermentation and (3) ethanol separation and purification, usually by distillation–rectification– dehydration [27].



Fig. 21: Schematic representation of production of ethanol from cane sugar, corn, and cellulosic biomass [27]

Based on Figure 21 one or more steps can be combined depending on the feedstock and the conversion technology, but commonly to obtained ethanol the first step in the manufacturing process is either a wet mill or dry mill process, which involves separating the grain kernel into its component parts (germ, fiber, protein, and starch) prior to fermentation; then, the liquefaction step takes place, by carrying out a partial hydrolysis of the starch, which breaks up the longer starch chains into smaller chains, the next step in producing the sugar molecules is called saccharification, that is another hydrolytic process, yielding glucose. The final step is the production of ethanol from glucose by enzymatic fermentation, followed by distillation, that separates ethanol from the remainder of the mash.

Bioethanol is commonly produced from agricultural raw materials containing sugar, starch, and cellulose. This material can be classified as first-generation raw materials (e.g., sugar and starch) and second-generation raw materials (e.g., lignocellulosic sugar). The preferred option is highly dependent on the region. Selecting a feedstock depends on many factors, such as how difficult it is to grow a specific crop (geographical climate, soils, water supply), and whether the crops are being set aside for other uses, such as livestock feed or human consumption. As examples, sugar cane is used in Brazil, cereals in the United States,

shrubs) form is a relatively new development, as it can be appreciated in Figure 22.



Fig. 22: Global ethanol production by feedstock [13]

The chart shown on Figure 23 shows the global ethanol production by country or region and its distribution among major ethanol producing countries in the world with their total production in billions of gallons, from 2007 to 2021. Overall, global production increased over time, where The United States is the world's largest producer of ethanol, having produced over 15 billion gallons in 2021. Together, the United States and Brazil produce 82% of the world's ethanol, where the vast majority of U.S. ethanol is produced from corn, while Brazil primarily uses sugarcane.



b) Methanol:

Methanol is the chemically simplest alcohol, it does not contain sulfur or any complex organic compounds. It is commonly known as "wood alcohol", it is produced as a liquid, where methanol is stored and handled like gasoline. In general, methanol is currently made from feedstocks like coal and natural gas using well-established thermochemical technology, but it can also be made from a wide range of biomass including municipal and industrial waste, so thereby it can serve as a low carbon emitting fuel and can be an important option for the replacement of gasoline.

Methanol finds increasingly more acceptance as a direct use blending component with gasoline to conventional gasoline, since it satisfies the requirements for the usage as motor fuel, in terms of cold-start behavior, drivability, higher octane number, which allows higher compression and following better effectiveness of the engine and reduction of emissions and as an indirect use fuel from the conversion of methanol to dimethyl ether, and also as one of the most promising sources of hydrogen for fuel cell systems.

Today most of methanol fuel produced is based on synthesis gas, which is generated either through steam reforming of natural gas or coal gasification. Apart from the use of fossil feedstocks for conventional processes, increasing amounts of renewable methanol are generated through sustainable production methods, such as biomass conversion or by hydrogenation of CO_2 with hydrogen obtained from wind-or solar-powered water electrolysis [13].

Conventional Methanol Production Processes: Methanol Production Via Synthesis Gas

All conventional routes to methanol start with the generation of synthesis gas, followed by the methanol synthesis itself and the methanol distillation/purification as presented in Figure 24. Methanol production via synthesis gas depends on the feedstock of choice, since synthesis gas may come from any number of different routes, including coal gasification, partial oxidation of heavy oils, steam reforming of natural gas.



Fig. 24: Methanol Production Via Synthesis Gas [29]

Renewable Methanol Production Processes:

The main principal options to produce methanol from renewable sources (urban wood wastes, primary mill residues, forest residues, agricultural residues and energy crops) are:

- Fermentation of biomass to methane ("biogas") with subsequent purification and reforming into synthesis gas for conversion into methanol.
- Gasification of biomass to generate synthesis gas, i.e., methanol.
- Hydrogenation of CO_2 captured from various sources with hydrogen which is produced by electrolysis using renewable power.

In general methanol production from biogas and solid biomass requires the same principal and established processes as used for fossil-based feedstocks despite differences in composition as well amount and type of feedstock impurities, as it can be seen in Figure 25 [13].



Fig. 25: Principal options to produce renewable methanol [13]

c) GTL Naptha:

New and expanding supplies of domestic natural gas due to the rapid development of shale gas have motivated renewed commercial interest in domestic gas-to-liquid (GTL) operations. Where Gas-To-Liquid (GTL) technology converts natural gas into high-quality liquid products, by using the Fischer-Tropsch process, which is a reductive oligomerization of carbon monoxide (CO) by hydrogen to form hydrocarbons.

Specifically, Gas-to-liquid (GTL) naphtha is formed as a co-product in the synthesis of GTL diesel fuel, where GTL naphtha it's a near-zero sulfur fuel that mainly contains hydrocarbons with a high proportion of straight chain paraffins; by which, it could mitigate some environmental concerns by displacing higher-sulfur fuels derived from petroleum.

3) Alternative Aviation Fuels:

SAF is a liquid biofuel currently used to power aircrafts (gas turbine engines), that has similar properties to conventional jet fuel but with a smaller carbon footprint, which reduces CO_2 emissions by up

to 80% [30]. This fuel is a "drop-in" fuel alternative and has the potential to serve as a direct replacement for conventional jet fuel, as it has similar molecular composition to conventional jet fuel, with the primary difference being a lack of aromatic compounds, requiring this way little or no modification to existing infrastructure or aircraft.

The use of SAF to replace or blend with conventional jet fuels, represents one of the opportunities examined by the aviation industry to achieve petroleum and GHG emissions reductions. Where the nature and properties of jet fuel produced from the different feedstock sources (waste oil and fats, green and municipal waste and nonfood crops) depends on the conversion process, that are presented on the Figure 26.



Fig. 26: SAF production pathways [31]

• Fischer-Tropsch synthetic paraffinic kerosene (F-T-SPK): F-T jet fuel can be produced from a variety of feedstock sources, including natural gas, coal and biomass, where syngas is produced from these feedstocks and then is converted to a range of drop-in hydrocarbons including synthetic kerosene and diesel.





• HEFA Jet Fuel: Hydro processed esters and fatty acid is a process that converts virgin vegetable oils or waste fats, oils, and greases into hydrocarbons through hydrotreating to deoxygenate the oil with subsequent hydro isomerization or hydrocracking to create a range of hydrocarbons that fill the distillation ranges of naphtha, jet, and diesel fuels.



• Pyrolysis-based Jet Fuel: The production of oil via fast pyrolysis, possibly including a hydrocracking step and the subsequent upgrading and refining of that oil produce a mixture of liquid fuels, such as gasoline, diesel, and jet fuels.



 Alcohol to Jet (ATJ): This process converts alcohols (ethanol, butanol) to hydrocarbons, this can be done by first producing alcohol through biochemical or thermochemical conversion and then upgrading that alcohol through a combination of dehydration, oligomerization, and finally hydrotreating to assemble drop- in hydrocarbons. This pathway can use conventional sugar and starch crops such as sugar cane and maize in addition to more challenging lignocellulosic feedstocks, such as energy crops or agricultural residues.



• Synthetic iso-paraffins (SIP): Instead of more-common alcohols processes, in the DSHC process, sugars are fermented to farnesene ($C_{15}H_{24}$), which has a longer carbon chain length and higher energy density than ethanol or isobutanol. Although farnesene is eligible for 10% blending with fossil jet fuel, process design includes additional hydrocracking and hydro isomerization, which produces an enhanced RJF with a higher blend level. This pathway primarily uses sugary feedstocks such as sugar cane or sugar beet, though it is possible to use cellulosic feedstocks if the cellulose is first hydrolyzed into sugar.



4) Alternative Maritime Fuels:

Shipping plays an indispensable role in the global economy, specifically for world trade; so, it's contribution to air pollution and climate change cannot be ignored. For this reason, alternative fuels for marine transport can play a crucial role in decarbonizing the shipping sector and ultimately contribute towards climate change goals.

Ships have been fueled by conventional marine fuels, such as HFO, MDO and MGO, for more than one hundred years. In the past two decades, some types of non-conventional marine fuels, such as LNG, LPG and methanol, have been used as alternative marine fuels owing to the maritime regulations on ship emissions. The alternative fuels that are most commonly considered today are electricity, biodiesel, and methanol; other fuels that are expected to be the main options for future low carbon or zero carbon shipping, include carbon-neutral biofuels and zero carbon synthetic fuels from all kinds of feedstock, such as Dimethyl Ether (DME), biomethane, synthetic fuels, hydrogen (particularly for use in fuel cells), Hydrogenation-Derived Renewable Diesel (HDRD) and pyrolysis oil.

The primary production processes include: thermochemical processes, such as refining, reforming, gasification, transesterification, hydrotreatment and the F-T process, with additional pre-treatment and after-treatment processes; biochemical processes, such as fermentation and anaerobic digestion; and electrolytic processes [33]. As it's seen in the Figure 32:



Fig. 32: Overview of alternative marine fuels production pathways [34]

5) Hydrogen:

Identification of low-emission alternative fuels is one of the feasible solutions to fossil fuel depletion and environmental degradation. Particularly hydrogen, among all the alternative fuels previously described, has a distinctive feature to provide an eventual freedom from energy-environment crises, as it is the least polluting fuel (as it does not contain carbon) that can be used in an internal combustion engine (ICE), and as a fuel cell in a FCEV.

Hydrogen has a variety of potential sources as shown in Figure 33. It can be produced from water and a number of fossil and non-fossil sources.; where currently hydrogen is being mainly produced from natural gas by steam methane reforming (SMR), partial oxidation (POx) and autothermal reforming (ATR); hydrogen can also be produced by gasification of coal or biomass, and by electrolysis splitting water with

electricity, which is more energy intensive but can be done using renewable energy, such as wind or solar, and avoiding the harmful emissions associated with other kinds of energy production.



Fig. 33: Hydrogen production pathways [35]

Although abundant on earth as an element, hydrogen is almost always found as part of another compound, such as water (H_2O) or methane (CH_4) , and it must be separated into pure hydrogen (H_2) for use in fuel cell electric vehicles. One challenge of using hydrogen as a fuel is efficiently extracting it from these compounds, for its use in fuel cells, where hydrogen fuel combines with oxygen from the air through a fuel cell, creating electricity and water through an electrochemical process.

There are five fundamental chemical and biological processes to produce hydrogen: (1) thermalchemical processes (reforming, gasification, and decomposition) of fossil fuels, biomass, and biofuels, (2) electrolysis, (3) thermal-water splitting, (4) photo-electrochemical process (photoelectrolysis or photolysis), and (5) biological processes (photolysis, fermentation, and electrolysis that happen in micro-organisms), as shown in the *Figure 34*.

a) Hydrogen Vehicles based on Internal Combustion Engine:

In the transportation industry, the development of hydrogen-powered cars aims to maximize fuel efficiency and significantly reduce exhaust gas emission and concentration in comparison to hydrocarbon fuels. Hydrogen possesses a wider flammability range, higher flame speed, and higher autoignition temperature than other fuels, it also has a higher stoichiometric fuel/air ratio and a much lower minimum

ignition energy than gasoline and other alternative fuels. Because of these differences in physicochemical properties, conventional engines can only operate on hydrogen with major modification of either hardware or in operating conditions, given the presence of undesirable combustion phenomena (Preignition and backfire), which negatively affects the engine performance and exhaust emission characteristics. As well significant changes in infrastructure are necessary in relation to possible utilization of hydrogen as an energy carrier.

b) Hydrogen in fuel cells:

Fuel cells work like batteries, but they do not run down or need recharging, so they are like continuously operating batteries producing electricity through an electrochemical reaction (hydrogen is combined with oxygen). A fuel cell as shown in Figure 34, consists of two electrodes, a negative electrode (or anode) and a positive electrode (or cathode), where hydrogen is fed to the anode and air is fed to the cathode. In a hydrogen fuel cell (commonly PEFC), a catalyst at the anode separates hydrogen molecules into protons and electrons, which take different paths to the cathode; the electrons go through an external circuit, creating a flow of electricity, and the protons migrate through the electrolyte to the cathode, where they unite with oxygen and the electrons to produce water and heat.



Fig. 34: Operation principle of a PEFC [19]

Because of their high conversion efficiency, no emissions at the point of use and low noise, fuel cells can in the future play a major role in energy conversion and could partly substitute current power generation technologies. However, there are some issues regarding the implementation of FCEVs, due to the stack durability and lifetime, supply chain and the related infrastructures and safety concerns.

c) Fuel Cell Vehicle power train configurations:

Hydrogen powertrains, such as fuel cell-based powertrains installed in fuel cell electric vehicles (FCEVs) shown in Figure 35, are currently among the most feasible hydrogen technologies to use. However, in this field, when concentrating on onboard hydrogen use, the ability to store hydrogen efficiently emerges as a critical concern. That's how onboard storage of hydrogen is critical to the success of FCEVs to address the issues concerning driving ranges comparable to gasoline cars, low-storage volume, low weight, and low cost. Thereby without a widespread network of hydrogen stations, no large-scale introduction of fuel-cell cars is feasible.



Fig. 35: Hydrogen Fuel Cell Electric Vehicle [28]

Given the increasing trend in the FCEV market and the ongoing need to encourage a genuine transition to low-carbon fuels, and the widespread deployment of the necessary infrastructures to allow for a large-scale innovation, the present paper aims to present how hydrogen-fuel cell hybrid powertrains work in terms of conceptual layouts and operating strategies. A powertrain-oriented analysis on the main configurations of fuel cell-based vehicles is carried out, highlighting features and potentialities [35]

There are two primary FCEV configurations: a full FC-based powertrain as shown in Figure 37 and a hybridization of a powertrain with an FC-system as shown in Figure 36.



6) Electric vehicles: Hybrid and electrify power trains:

Electricity is an important tool for the industrial growth of the world, specifically in the transportation sector, electric mobility is emerging all around the world to minimize environmental impacts, reduce dependency on petroleum, and diversify energy sources for transportation. Originally, interest in EVs arose mainly from the concern over atmospheric pollution attributable to exhaust emissions from petroleum-powered cars, as these vehicles do not emit any tailpipe greenhouse gas emissions, and as the energy required to operate the vehicle (i.e., charging of battery) is produced from renewable energy sources.

All-electric vehicles (BEVs) and hybrid electric vehicles (PHEVs and HEVs), collectively referred to as electric vehicles (EVs)—store electricity in batteries to power one or more electric motors. The performance of these types of vehicles depends mainly on the performance, efficiency, and reliable operation of the battery, which is charged primarily by plugging into off-board sources of electrical power sources (generally the electricity grid) or recapturing energy during braking (regenerative braking).

Compared with oil-run vehicles, battery-powered work vehicles are more efficient and offer low maintenance costs as well as low running costs due to the lower cost of electricity and the use of off-peak power for recharging.

a) Electricity generation worldwide by energy source:

Electricity can be produced from a variety of energy sources, including natural gas, coal, nuclear energy, wind energy, hydropower, as well as solar energy. Globally in Figure 38, it's seen that coal, followed by gas, are the largest sources for electricity production. On the other side there are low-carbon sources, where hydropower and nuclear make the largest contribution, although wind and solar are growing quickly. Globally, 36.7% of the electricity produced in 2019 was low-carbon, the remaining two-thirds come from fossil fuels – mostly coal and gas; specifically of the 36.7% from low-carbon sources, renewables accounted for 26.3% and nuclear energy for 10.4% [36].



Note: 'Other renewables' includes waste, geothermal, wave and tidal.



In the charts presented in the Figure 39 and Figure 40, it can be seen the breakdown by source of the electricity mix of Colombia, which includes coal, gas, oil, nuclear, bioenergy, hydro, solar, wind and other renewables. It can be inferred from the figures presented, that Colombia despite of being a major coal producer, uses hydropower for most of its electricity needs, where in 2021 renewable sources accounted for nearly 70% [37] of the electricity production in Colombia, with hydropower accounting for the largest share.



Source: Our World in Data based on BP Statistical Review of World Energy (2022); Ember (2023) OurWorldInData.org/energy • CC BY Note: 'Other renewables' includes waste, geothermal, wave and tidal.



Fig. 39: Colombia electricity production by source [36]

Fig. 40: Colombia's electricity mix [36]

b) Battery Electric Vehicle (BEV):

The BEV consist as shown in Figure 41 of: a battery, motor, and controllers in addition to the normal components of the automobile, where electricity power stored in the battery drives the motor that runs the vehicle. The battery is charged by plugging the vehicle into an electric power source, where even though electricity production may contribute to air pollution, the U.S. Environmental Protection Agency categorizes all-electric vehicles as zero-emission vehicles because they produce no direct exhaust or tailpipe emissions [37]



Fig. 41: Battery Electric Vehicle [37]

c) Hybrid Electric Vehicle (HEV):

Hybrid electric vehicles as shown in Figure 42 are powered by an internal combustion engine in combination with one or more electric motors that use energy stored in batteries, where the extra power provided by the electric motor may allow for a smaller combustion engine.

An HEV cannot plug in to off-board sources of electricity to charge the battery. Instead, the vehicle uses regenerative braking by using the electric motor as a generator and storing the captured energy in the battery. This way HEVs combine the benefits of high fuel economy and low tailpipe emissions with the power and range of conventional vehicles.



Fig. 42: Hybrid Electric Vehicle [37]

d) Plug-in Hybrid Electric Vehicle (PHEV):

Plug-in hybrid electric vehicles (PHEVs) as shown in Figure 43 use batteries to power an electric motor, as well as another fuel, such as gasoline or diesel, to power an internal combustion engine or other propulsion source. PHEVs can charge their batteries by an outside electric power source, and by regenerative braking, where the electric motor acts as a generator, using the energy to charge the battery, thereby recapturing energy that would have been lost.

All-electric vehicles and PHEVs running only on electricity have zero tailpipe emissions, but electricity production, such as power plants, may generate emissions, and it will depend on the energy sources used for electricity generation.



Fig. 43: Plug-in Hybrid Electric Vehicle [37]

IV. METHODOLOGY

A. Systematic literature review

Undertaking a review of the related literature assessment is an important part of any discipline. It helps to maps and assesses the existing knowledge and gaps on specific issues by employing clear and methodical procedures to minimize the occurrence of bias during searching, identifying, evaluating, synthesizing, analyzing, and summarizing studies. Specifically, a systematic literature review is defined as a "systematic, explicit, and reproducible method for identifying, evaluating, and synthesizing the existing body of completed and recorded work made by researchers, scholars, and practitioners" [193].

The essential features of a systematic literature review and its accompanying method, meta-analysis, involve: (i) defining a clear research question that the study aims to address, (ii) establishing explicit and reproducible objectives with a transparent methodology, (iii) using comprehensive search criteria to identify all relevant studies that meet eligibility criteria, (iv) evaluating the quality and validity of the selected studies, (v) presenting and synthesizing extracted data from the chosen studies in a structured manner, and (vi) making

the findings accessible for scientific purposes and decision-making. As a result, most literature review works follow the Search, Appraisal, Synthesis, and Analysis framework (PSALSAR), as depicted in Figure 44.

	Steps	Outcomes	Methods
PSALSAR Framework	Protocol Search	Defined study scope Define the search strategy	Only the mountain ecosystem and its various ecosystem services Searching strings
		Search studies	Search databases
	Appraisal	Selecting studies	Defining inclusion and exclusion criteria
		Quality assessment of studies	Quality criteria
	Synthesis	Extract data	Extraction template
		Categorize the data	Categorize the data on the iterative definition and ready it for further analysis work
	Analysis	Data analysis	Quantitative categories, description, and narrative analysis of the organized data
		Result and discussion	Based on the analysis, show the trends, identify gap and result comparison
		Conclusion	Deriving conclusion and recommendation
	Report	Report writing	PRISMA methodology
	-	Journal article production	Summarizing the report result for the larger public

Fig. 44: Framework for systematic and meta-analysis studies [193]

In summary, a systematic literature review facilitates the gathering of all relevant publications and documents that meet predetermined inclusion criteria for addressing a specific research question. When executed correctly with minimal errors, systematic reviews fulfill various crucial functions and generate different types of knowledge for diverse users of reviews. They can offer syntheses of the current state of knowledge in a field, tackle questions that cannot be addressed by individual studies alone, and ultimately produce dependable findings and trustworthy conclusions that can aid scientific practitioners and decision-makers in making informed decisions.

B. PRISMA protocol

The Preferred Reporting Items for Systematic reviews and Meta-Analyses (PRISMA) statement, published in 2009, is a reporting guideline designed to help systematic reviewers transparently report why the review was done, what the authors did, and what they found.

Figure 45 presents the checklist of 27 recommended items in the PRISMA 2020 statement, which serves as a guide for reporting systematic reviews. These items cover reviews that use synthesis methods,

such as pairwise meta-analysis, as well as those that do not. The PRISMA 2020 items are also suitable for mixed-methods systematic reviews, which encompass both quantitative and qualitative studies.

Section and Topic	ltem #	Checklist item			
TITLE		*			
Title	1	Identify the report as a systematic review.			
ABSTRACT					
Abstract	2	See the PRISMA 2020 for Abstracts checklist.			
INTRODUCTION					
Rationale	3	Describe the rationale for the review in the context of existing knowledge.			
Objectives	4	Provide an explicit statement of the objective(s) or question(s) the review addresses.			
METHODS					
Eligibility criteria	5	Specify the inclusion and exclusion criteria for the review and how studies were grouped for the syntheses.			
Information sources	6	Specify all databases, registers, websites, organisations, reference lists and other sources searched or consulted to identify studies. Specify the date when each source was last searched or consulted.			
Search strategy	7	Present the full search strategies for all databases, registers and websites, including any filters and limits used.			
Selection process	8	Specify the methods used to decide whether a study met the inclusion criteria of the review, including how many reviewers screened each record and each report retrieved, whether they worked independently, and if applicable, details of automation tools used in the process.			
Data collection process	9	Specify the methods used to collect data from reports, including how many reviewers collected data from each report, whether they worked independently, any processes for obtaining or confirming data from study investigators, and if applicable, details of automation tools used in the process.			
Data items	10a	List and define all outcomes for which data were sought. Specify whether all results that were compatible with each outcome domain in each study were sought (e.g. for all measures, time points, analyses), and if not, the methods used to decide which results to collect.			
	10b	List and define all other variables for which data were sought (e.g. participant and intervention characteristics, funding sources). Describe any assumptions made about any missing or unclear information.			
Study risk of bias assessment	11	Specify the methods used to assess risk of bias in the included studies, including details of the tool(s) used, how many reviewers assessed each study and whether they worked independently, and if applicable, details of automation tools used in the process.			
Effect measures	12	Specify for each outcome the effect measure(s) (e.g. risk ratio, mean difference) used in the synthesis or presentation of results.			
Synthesis methods	13a	Describe the processes used to decide which studies were eligible for each synthesis (e.g. tabulating the study intervention characteristics and comparing against the planned groups for each synthesis (item #5)).			
	13b	Describe any methods required to prepare the data for presentation or synthesis, such as handling of missing summary statistics, or data conversions.			
	13c	Describe any methods used to tabulate or visually display results of individual studies and syntheses.			
	13d	Describe any methods used to synthesize results and provide a rationale for the choice(s). If meta-analysis was performed, describe the model(s), method(s) to identify the presence and extent of statistical heterogeneity, and software package(s) used.			
	13e	Describe any methods used to explore possible causes of heterogeneity among study results (e.g. subgroup analysis, meta-regression).			
	13f	Describe any sensitivity analyses conducted to assess robustness of the synthesized results.			
Reporting bias assessment	14	Describe any methods used to assess risk of bias due to missing results in a synthesis (arising from reporting biases).			
Certainty assessment	15	Describe any methods used to assess certainty (or confidence) in the body of evidence for an outcome.			

RESULTS					
Study selection	16a	Describe the results of the search and selection process, from the number of records identified in the search to the number of studies included in the review, ideally using a flow diagram.			
	16b	Cite studies that might appear to meet the inclusion criteria, but which were excluded, and explain why they were excluded.			
Study characteristics	17	Cite each included study and present its characteristics.			
Risk of bias in studies	18	Present assessments of risk of bias for each included study.			
Results of individual studies	19	For all outcomes, present, for each study: (a) summary statistics for each group (where appropriate) and (b) an effect estimate and its precision (e.g. confidence/credible interval), ideally using structured tables or plots.			
Results of syntheses	20a	For each synthesis, briefly summarise the characteristics and risk of bias among contributing studies.			
	20b	Present results of all statistical syntheses conducted. If meta-analysis was done, present for each the summary estimate and its precision (e.g. confidence/credible interval) and measures of statistical heterogeneity. If comparing groups, describe the direction of the effect.			
	20c	Present results of all investigations of possible causes of heterogeneity among study results.			
	20d	Present results of all sensitivity analyses conducted to assess the robustness of the synthesized results.			
Reporting biases	21	Present assessments of risk of bias due to missing results (arising from reporting biases) for each synthesis assessed.			
Certainty of evidence	22	Present assessments of certainty (or confidence) in the body of evidence for each outcome assessed.			
DISCUSSION					
Discussion	23a	Provide a general interpretation of the results in the context of other evidence.			
	23b	Discuss any limitations of the evidence included in the review.			
	23c	Discuss any limitations of the review processes used.			
	23d	Discuss implications of the results for practice, policy, and future research.			
OTHER INFORMATION					
Registration and protocol	24a	Provide registration information for the review, including register name and registration number, or state that the review was not registered.			
	24b	Indicate where the review protocol can be accessed, or state that a protocol was not prepared.			
	24c	Describe and explain any amendments to information provided at registration or in the protocol.			
Support	25	Describe sources of financial or non-financial support for the review, and the role of the funders or sponsors in the review.			
Competing interests	26	Declare any competing interests of review authors.			
Availability of data, code and other materials	27	Report which of the following are publicly available and where they can be found: template data collection forms; data extracted from included studies; data used for all analyses; analytic code; any other materials used in the review.			



C. Meta-analysis

Meta-analysis is a set of techniques used "to combine the results of a number of different reports into one report to create a single, more precise estimate of an effect". The aims of meta-analysis are "to increase statistical power; to deal with controversy when individual studies disagree; to improve estimates of size of effect, and to answer new questions not previously posed in component studies" [194].

Meta-analysis has the potential to produce accurate findings regarding the subject being studied. However, in order to achieve this, statistical methods must be utilized to analyze data from multiple studies. When conducted with care, meta-analysis can yield valuable insights. However, if studies of poor quality are included in the analysis, it can result in misleading statistics. One common mistake in meta-analysis is ignoring differences between studies and combining data that is not directly comparable. Fortunately, there are techniques available to address this issue. A meta-analysis sets itself apart from a systematic review by not only examining the existing knowledge on a particular topic, but also by measuring the statistical significance of the results and producing a comprehensive estimate.

D. Methodological approach

Despite the abundance of research articles on alternative liquid fuels none of them have conducted a systematic review of the literature. As a result, it is challenging to determine which alternative fuel has the greatest potential for reducing greenhouse gas emissions compared to its respective petroleum-derived fuel, due to variations in reported results caused by differences in scope, assumptions, and data sources. This study seeks to address this gap by conducting the first systematic review of scientific literature and gathering relevant data that meets pre-determined eligibility criteria to answer the research question posed.

To ensure that a systematic review is valuable to its intended audience, it is crucial to provide a clear, comprehensive, and precise explanation of the methodology used, including the process for identifying and selecting studies, as well as the outcomes, such as the results of the meta-analysis. To accomplish this, the review will utilize explicit and systematic techniques to identify, select, critically appraise, and summarize relevant research on life cycle analysis GHG emissions of alternative liquid fuels. To finally derive quantitative trends through meta-analysis using the harmonization approach, to evaluate the potential environmental impacts of these fuels compared to life cycle greenhouse gas emissions from fossil-based counterfactual fuels, EVs and FCEVs.

To compare the environmental performance of fossil fuels with alternative fuels and identify knowledge gaps, a systematic literature review with meta-analysis was conducted according to the following steps given by the PRISMA 2020 protocol, which are synthesized in 4 main steps, as it follows: (1) define the scope of the review, identify the databases and present the full research strategies for all databases, (2) specify the inclusion and exclusion criteria for the review, and the methods used to decide whether a study met the inclusion criteria; and how studies were grouped for the syntheses of the review, (3) specify the methods used to collect data from reports, and describe the results of the search and selection process from the number of records identified in the search to the number of studies included in the review, ideally using a flow diagram and (4) present results of the statistical (meta-analysis) synthesis conducted.

Step 1: In Step 1 of this systematic literature review, items #6 and #7 of the PRISMA 2020 checklist were followed by determining the information sources and search strategy. To conduct the search, different scientific databases were used, including Google Scholar, ScienceDirect, Scopus, WOS (Web of Science), and MDPI (Multidisciplinary Digital Publishing Institute). The search was conducted using specific keywords and inclusion/exclusion criteria. The selected scientific databases were first searched using different keywords in combination with the use of Boolean connectors; the first research formula used was 'Transportation sector' AND 'Alternative fuels' AND 'Life cycle analysis' AND 'Greenhouse gas emissions', where some amount of relevant publications to the topic of this review were being excluded, since many criteria of inclusion must be met at the same time. Therefore, additional refinement related to the research formula was applied with combination of the next keywords 'Transportation fuels' OR 'Alternative fuels' AND 'Life cycle analysis' AND 'Life cycle analysis' AND 'GHG emissions', defining this as the most appropriate research formula for the systematic review. The research was conducted on the 29th of August 2022, and yielded a total of 4022 papers.

Step 2: For Step 2 of this systematic literature review, item #8 of the PRISMA 2020 checklist was followed by outlining the selection process. This involved establishing the methods used to determine whether a study satisfied the review's inclusion criteria, where Well-to-wheel analysis typically requires a well-defined scope that includes the following elements: functional unit, system boundaries, reference system, impact categories, and allocation. The literature was eligible for inclusion in the review based on the following eligibility criteria:

Life cycle approach: Defining the goal and scope is a crucial initial step in reviewing Life Cycle Assessment (LCA) studies, as the specific methodological approaches used heavily rely on the stated objectives and scope of the study. The defined goal and scope of the study determine the system boundary and the life cycle phases that will be evaluated. This review will consider papers with a system boundary from wells to wheels (WTW), which encompasses both the well-to-pump (WTP) stage, covering the production and transportation of feedstock and the production, transportation, and distribution of fuel, as well as the pump-to-wheel (PTW) stage, covering vehicle operational activities.

<u>Functional unit</u>: In LCA, the term 'functional unit' describes the function of the system under study and represents the unit of analysis on which the study is based. The selection of the functional unit should align with the study's objective and should accurately reflect the system(s) being investigated and their main purpose. For this review, the functional units used are associated with the production and use of MJ of the end-use energy, or per km basis where the TTW denotes the energy consumed per kilometer (MJ/km) and the WTT denotes the total amount of GHG emissions per unit of energy ($g_{CO_2 eq}/MJ$ electricity generation).

Step 3: For Step 3 of this systematic literature review, item #16a of the PRISMA 2020 checklist was followed by describing the results of the search and selection process using a flow diagram as shown in Figure 46. Initially, we identified 2996 papers with no duplicates. After screening the papers by title, abstract, and full text, we selected 327 papers that met the criteria for investigation in this review, and excluded 2669 papers that did not comply with the eligibility criteria defined in Step 2. Ultimately, we included 165 papers in the quantitative synthesis (meta-analysis) to analyze the retrieved data using inferential statistics. Thus, the initial 4022 papers were reduced to 327 for detailed screening, and finally to 165 for inclusion in the meta-analysis.



Fig. 46: PRISMA Flow Diagram for new systematic reviews which included searches of databases and registers only [38]

Of these 165 papers, Figure 47 and Figure 48 provide a statistical overview of the meta-analysis data reviewed, in terms of transportation sector and by the type of fuel. Among them, 20.9% assessed for SAF, 15.8% for ethanol, 13.7% for electricity, 13.3% for hydrogen, 8.8% for biodiesel, 8.7% for synthetic fuels, 7.0% for HVO, 3.5% for DME and 1.9% for methanol; which are evaluated for different transportation sectors, being road transportation the most evaluated, followed by aviation and maritime.


Distribution of reviewed studies by type of fuel

Fig. 47: Distribution of reviewed studies by type of fuel

Distribution of reviewed studies by transportation sector



Fig. 48: Distribution of reviewed studies by transportation sector

Step 4: In Step 4 of this systematic literature review, the results of syntheses are presented by following items #20a, 20b,20c and 20d of the PRISMA 2020 checklist, which includes an evaluation of heterogeneity. Despite selecting studies with similar characteristics, different reviews may yield significantly varying outcomes. Therefore, it is essential to investigate the root causes of this heterogeneity by employing meta-analysis, which uses statistical methods to quantitatively combine and synthesize results obtained from the systematic literature review. This approach helps identify or rule out heterogeneity and publication bias across all the studies gathered, enabling to draw reliable conclusions about the potential GHG abatement (measured in terms of WTW CO₂ total emissions) of the low-carbon fuels studied.

V. RESULTS AND DISCUSSION

This section presents the WTW analysis results for all researched and proposed alternative fuels and their pathways in terms of GHG CO_2 emissions per MJ and per km basis. The purpose is to facilitate a comparison between the LCA results of the different alternative fuel studies that were gathered and the baseline fossil fuels.

Due to the multiple production routes available for each alternative fuel and the broad range of feedstocks that can be utilized for their production, we offer a summary in Figure 49 of all the alternative fuels evaluated and the feedstocks used to produce them.



Note: the feedstocks used for alternative fuel production, are categorized as follows: Fossil-based feedstocks, including coal, crude oil, natural gas, and CO_2 ; First-generation biofuels, such as vegetable oils (canola oil, camelina oil, jatropha oil, palm oil, pongamia oil, rapeseed oil, salicornia oil, soybean oil, sunflower oil), sugar-based feedstocks (sugar beet, sugar cane, bagasse), corn (corn stover, corn starch, corncob), and cassava; Second-generation biofuels, such as animal fat (tallow, poultry fat, beef tallow), waste/residues (forestry residues, agricultural residues, municipal solid waste (MSW), sewage sludges, swine manure, used cooking oil (UCO), unmanaged hardwood residues, yellow grease, citrus waste, black liquor, husk), woody forage (eucalyptus, farmed wood, poplar, spruce, willow), perennial forage (miscanthus, pennycress, switchgrass), biogas, wheat straw, rice straw, sorghum straw; and third-generation biofuel, namely algae.



Effective communication of statistical findings requires the use of data visualization. By utilizing graphical displays, complex statistical information can be presented in a comprehensible manner and facilitate comparisons between data sets. Therefore, data visualization techniques play a crucial role in the exploration and communication of meta-analytic data and results.

The purpose of this results section is to gather all pertinent studies and subject them to meta-analysis, a technique that generates high-quality evidence by reconciling potentially divergent results from individual articles. To process standard meta-analytic outputs, there are various software applications available, including open-source options. This study utilizes the powerful capabilities of Python and its extensive collection of libraries that offer a wide range of estimators, statistical tests, and visualizations in order to conduct the meta-analysis.

Boxplots are utilized to exhibit the distribution of WTW CO₂ total emissions, providing a visual representation of the spread of values in the dataset. This method allows for the assessment and comparison of data distributions using a five-number summary (i.e., "minimum," first quartile [Q1], median, third quartile [Q3], and "maximum"). Such a summary can reveal whether the data is symmetrical, how tightly grouped it is, and whether it is skewed, thereby aiding in the identification of outliers and the visualization of distribution spread.



A. WTW CO₂ net emissions for road transport diesel alternative fuels

Fig. 50: WTW CO_2 emissions in $g CO_{2 eq}/MJ$ of alternative diesel fuels

In Figure 50, a comparison is shown between the life cycle WTW CO_2 emissions of fossil diesel fuel, alternative diesel fuels, and other viable low-emission alternative fuels, such as hydrogen (not intended for internal combustion engines) and electric vehicles. The comparison is made relative to their respective petroleum-derived fuel, which in this case is diesel, having a well-to-wheel GHG emission intensity ranging from 83.34-98 g $CO_{2 eq}/MJ$. The aim of this comparison is to assess which alternative fuels have the potential to achieve greater GHG abatement.

	CTL FISCHER-TROPSCH DIESELWTW CO_2 EMISSIONS											
Reference	Year	Fuel	Transportation sector	Feedstock	Production pathway	System boundary	Country	WTW CO2 net emissions	Functional unit			
[63]	2011	CTL	ICEV	Coal	Fischer-Tropsch	Well to wheel	US	238.45	g CO2 eq/ MJ			
[63]	2011	CTL	ICEV	Coal	Fischer-Tropsch	Well to wheel	US	129.77	g CO2 eq/ MJ			

TABLE I

Figure 50 illustrates that using coal-to-liquids (CTL) technology may not result in reduced GHG emissions. For Fischer-Tropsch diesel derived from coal, insufficient data is available, so an individual value plot is used to display each value separately. The plot reveals that the life cycle WTW CO_2 emissions, which are higher than those of petroleum diesel, increase regardless of CCS is utilized. This increase in WTW CO_2 emissions is primarily due to the mining process, as well as the higher energy inputs and the high C/H ratio of coal. In the case of CTL (See Table I) without CCS, WTW CO_2 emissions (238.45 $g CO_{2 eq}/MJ$) would increase by 58.82% over those from fossil diesel chains. Even with CCS, emissions from CTL chains are still 25% higher (129.77 $g CO_{2 eq}/MJ$). Therefore, CCS offers an opportunity for substantial reductions of CO_2 emissions.

Reference	Year	Fuel	Transportati on sector	Feedstock	Production pathway	System boundary	Country	WTW CO2 net emissions	Functional unit
[169]	2009	BTL	ICEV	Woody forage	Fischer- Tropsch	Well to wheel	Netherlands	31.00	g CO2 eq/ MJ
[171]	2013	BTL	ICEV	Rapeseed oil	Fischer- Tropsch	Well to wheel	Spain	56.89	g CO2 eq/ MJ
[171]	2013	BTL	ICEV	Soybean oil	Fischer- Tropsch	Well to wheel	Spain	23.55	g CO2 eq/ MJ
[171]	2013	BTL	ICEV	Biogas	Fischer- Tropsch	Well to wheel	Spain	21.29	g CO2 eq/ MJ
[192]	2014	BTL	ICEV	Camelina oil	Fischer- Tropsch	Well to wheel	Canada	24.72	g CO2 eq/ MJ
[39]	2010	BTL	ICEV	Waste/Residu es	Fischer- Tropsch	Well to wheel	UK	50.00	g CO2 eq/ MJ
[39]	2010	BTL	ICEV	Soybean oil	Fischer- Tropsch	Well to wheel	UK	49.00	g CO2 eq/ MJ
[61]	2010	BTL	ICEV	Rapeseed oil	Fischer- Tropsch	Well to wheel	China	25.00	g CO2 eq/ MJ
[61]	2010	BTL	ICEV	Soybean oil	Fischer- Tropsch	Well to wheel	China	30.00	g CO2 eq/ MJ
[63]	2011	BTL	ICEV	Waste/Residu es	Fischer- Tropsch	Well to wheel	US	77.02	g CO2 eq/ MJ
[65]	2016	BTL	ICEV	Waste/Residu es	Fischer- Tropsch	Well to wheel	US	62.51	g CO2 eq/ MJ
[65]	2016	BTL	ICEV	Waste/Residu es	Fischer- Tropsch	Well to wheel	US	32.89	g CO2 eq/ MJ

 TABLE II

 BTL FISCHER-TROPSCH DIESELWTW CO2 EMISSIONS

The BTL boxplot provides an indication of the spread of values in the data. In this particular boxplot, the data is skewed towards the high end of the graph, resulting in an asymmetric boxplot where the median divides the box into two unequal portions that are closer to the bottom. The majority of the CO_2 WTW emissions data for BTL is located on the high side of the graph, indicating that the CO_2 WTW emissions from BTL using different feedstocks are consistently above 30 $g CO_{2 eq}/MJ$.

In general, the CO_2 WTW emissions from BTL chains are significantly lower than those of fossil diesel, ranging from between $21.29 - 77.02 g CO_{2 eq}/MJ$ (as shown in Table II). These emissions are primarily associated with biomass cultivation, harvesting, pretreatment, and transportation. However, the cultivation and harvesting of biomass can have a negative impact on the environment, such as the use of synthetic fertilizers to increase crop yields and the release of carbon dioxide due to biomass cultivation. Furthermore, land use changes resulting from biomass cultivation can lead to increased GHG emissions, land degradation, water resource depletion, forest degradation, and higher food prices. Overall, the sustainability of biofuels depends mainly on the sustainability of the initial biomass, with second-generation biofuels having greater potential to reduce GHG emissions than first-generation biofuels, as they are more sustainable.

Reference	Year	Fuel	Transportation	Feedstock	Production	System	Country	WTW CO2 net	Functional
			sector		pathway	Doundary		emissions	umi
[47]	2018	DME	ICEV	NG	Catalytic dehydration	Well to wheel	Australia	120.00	g CO2 eq/ MJ
[47]	2018	DME	ICEV	NG	Catalytic dehydration	Well to wheel	Australia	80.00	g CO2 eq/ MJ
[54]	2021	DME	ICEV	Rapeseed oil	Catalytic dehydration	Well to wheel	Australia	71.00	g CO2 eq/ MJ
[54]	2021	DME	ICEV	Soybean oil	Catalytic dehydration	Well to wheel	Brazil	78.00	g CO2 eq/ MJ
[54]	2021	DME	ICEV	Palm oil	Catalytic dehydration	Well to wheel	SE Asia	45.00	g CO2 eq/ MJ
[54]	2021	DME	ICEV	Waste/Residues	Catalytic dehydration	Well to wheel	UK	13.00	g CO2 eq/ MJ
[82]	2019	DME	ICEV	CO2	Catalytic dehydration	Well to wheel	Netherlands	80.00	g CO2 eq/ MJ
[85]	2018	DME	ICEV	Biogas	Catalytic dehydration	Well to wheel	Germany	18.20	g CO2 eq/ MJ
[88]	2012	DME	ICEV	Coal	Catalytic dehydration	Well to wheel	China	264.59	g CO2 eq/ MJ
[105]	2013	DME	ICEV	Rice straw	Catalytic dehydration	Well to wheel	SE Asia	72.00	g CO2 eq/ MJ
[105]	2013	DME	ICEV	Rice straw	Catalytic dehydration	Well to wheel	SE Asia	25.00	g CO2 eq/ MJ
[140]	2016	DME	ICEV	NG	Catalytic dehydration	Well to wheel	US	99.00	g CO2 eq/ MJ
[140]	2016	DME	ICEV	Waste/Residues	Catalytic dehydration	Well to wheel	US	11.00	g CO2 eq/ MJ
[140]	2016	DME	ICEV	NG	Catalytic dehydration	Well to wheel	US	97.00	g CO2 eq/ MJ
[140]	2016	DME	ICEV	Biogas	Catalytic dehydration	Well to wheel	US	2.00	g CO2 eq/ MJ
[140]	2016	DME	ICEV	Biogas	Catalytic dehydration	Well to wheel	US	0.00	g CO2 eq/ MJ

TABLE IIIDME WTW CO2 EMISSIONS

Note: Direct synthesis of DME passes in two reaction steps: methanol synthesis followed by methanol dehydration (Catalytic dehydration).

The boxplot in Figure 50 illustrates the spread of values in the data for DME, which is synthesized from syngas and can therefore be produced from a range of different feedstocks. The data in this boxplot is skewed towards the bottom, indicating a lopsided distribution where the median divides the box unevenly, with the majority of the CO_2 WTW emissions data located on the lower end. This suggests that DME produced from different feedstocks such as natural gas, coal, biogas, vegetable oils, rice straw, and waste or residues (UCO and Black liquor) generates less than 72 $g CO_{2 eq}/MJ$, where the total CO_2 WTW emission reduction from the use of bio-DME can differ, depending on the feedstock:

When DME is produced from biogas, the electricity used in the production process is generated by burning biogas instead of the regional electricity mix. This results in WTW CO_2 emissions ranging from

 $0 - 18.20 \ g \ CO_{2 \ eq}/MJ$ for DME made from biogas derived from manure. These emissions are 100% and 81.63% lower than those generated from diesel fuel. For DME produced from black liquor gasification, a significant amount of incremental electricity is required, making the source of electricity important. If electricity is generated from biomass, CO_2 emissions can be reduced to around 11 $g \ CO_{2 \ eq}/MJ$, achieving an 88.7% reduction on a MJ basis. Both the energy consumed for DME from biogas or black liquor is mostly renewable, which could significantly reduce fossil fuel consumption and WTW CO_2 emissions, as demonstrated in Figure 50 or Table III.

Life cycle WTW CO_2 emissions of using rice straw bio-DME for transport compared to diesel fuel are shown in Figure 50. The findings reveal that the WTW emissions from using bio-DME are $72 g CO_{2 eq}/MJ$ when considering the GHG burdens of rice straw cultivation, which is the primary source of LCA CO_2 emissions. However, when these burdens are excluded, the WTW CO_2 emissions are reduced to $25 g CO_{2 eq}/MJ$.

When it comes to WTW CO_2 emissions, most DME options produced from renewable sources demonstrate a reduction compared to their fossil fuel counterpart. However, this reduction is dependent on the type of feedstock used, as first-generation biofuels can have land use change effects. Conversely, WTW analysis shows that using fossil feedstocks such as natural gas and coal results in life cycle WTW CO_2 emissions comparable to diesel fuels. On an MJ basis, WTW CO_2 emissions are 18.3% and 60.2% higher than diesel fuel, respectively.



Fig. 51: WTW CO_2 emissions in g $CO_{2 eq}/MJ$ of biodiesel according to the type of feedstock

The two most critical stages in biodiesel supply chains are feedstock production and biodiesel conversion. In feedstock production, the primary components contributing to GHG emissions are N_2O emissions resulting from fertilizer application, fertilizer manufacturing, and on-farm energy use. The primary components contributing to biodiesel conversion are fossil carbon from conventional methanol used.

Figure 51 illustrates that life cycle WTW CO_2 emissions are dependent on the feedstock or crop used for biodiesel production, as crop production or farming is the most carbon-intensive stage. For firstgeneration biodiesel, WTW CO_2 emissions show a wide variation across LCA studies, with CO_2 WTW emissions ranging from 2.77 to 343.06 $g CO_{2 eq}/MJ$. Second-generation biodiesel ranges from -33.3 to 283 $g CO_{2 eq}/MJ$, and third-generation biodiesel ranges from 62.2 to 523 $g CO_{2 eq}/MJ$. In most cases, the average WTW CO_2 emissions of biodiesel from all the considered feedstocks are lower than those of fossil diesel. Lignocellulosic biofuels produced from agricultural and forest residues, which belong to the second generation of biofuels, exhibit lower CO_2 WTW emissions compared to biodiesel from energy crops (first generation biofuels). This is because waste and residues are considered to have no environmental burdens, as these are allocated to the original crop from which the waste is derived, and therefore do not share the emissions of upstream activities. This implies that waste greases, such as used cooking oil (UCO) and inedible tallow, unlike edible vegetable oils, could potentially promote the circular economy and reduce WTW emissions. In contrast, the life cycle WTW CO_2 emissions for biodiesel derived from third generation biofuels vary greatly among studies. Microalgae diesel, in particular, can either significantly reduce or increase GHG emissions. However, the majority of studies suggest that, at the current level of development, algal biodiesel has higher life cycle GHG emissions than fossil diesel fuel. This is mainly due to the lower algal yield and high energy use in the cultivation, harvesting, and drying stages, which result in higher emissions.

In the biodiesel boxplot chart, it can be found some outliers, which are data values that are far away from other data values; these values correspond specifically to the WTW CO_2 emissions of biodiesel from animal manure (-33.3 $g CO_{2 eq}/MJ$) [153] in which the avoided emissions from waste management often lead to considerable GHG credit, and specifically biofuels produced from manure usually have negative life-cycle GHG emissions by avoiding the CH_4 emissions from traditional manure management [153]. In the opposite case there are outliers which represent higher WTW CO_2 emissions compared to fossil diesel fuel, these are algae-based biodiesel (523 $g CO_{2 eq}/MJ$) [77] and pongamia biodiesel (343.06 $g CO_{2 eq}/MJ$) [52]; in the case of pongamia the cultivation phase is the biggest contributor for CO_2 emission in the system, and the majority of these emissions are due to burning of fuel wood, and for algae the GHG emissions depends on the electricity demand for cultivation and the recycling rate for nutrients.



Fig. 52: WTW CO_2 emissions in $g CO_{2 eq}/MJ$ of HVO according to the type of feedstock

The HVO production involves several different activities, such as production of hydrogen, hydrogenation of the triglycerides, isomerization of the obtained paraffinic chains and combustion of the diesel, where the main source of GHG emissions in hydrotreating of vegetable oil is the CO_2 released from oil extraction processes and hydrogen production in hydrotreatment processes.

As seen in Figure 52 the WTW CO_2 emissions of HVO vary according to the type of feedstock, and at the same time the WTW CO_2 emissions of the feedstock may vary according to the geographical location of the production plant and soil type in the cultivation area, where feedstock cultivation can be done in certain locations with minimal GHG emissions from the cultivation processes by using minimal amounts of fertilizer nutrients. Generally renewable diesel production has relatively low GHG emissions, where GHG emissions for first-generation HVO shows a large variation across the LCA studies, with the CO_2 WTW emissions ranging between -10.0 and $412 g CO_{2 eq}/MJ$, second generation HVO raging between 1.9 and $167.22 g CO_{2 eq}/MJ$, and third generation HVO raging between 32.71 and 198.87 $g CO_{2 eq}/MJ$; where the results show that vegetable oil-based renewable diesel produces higher GHG emissions than fossil fuels if cultivation is done by converting forest into cultivation areas, and that the GHG emissions from production of HVO depends on the productivity per hectare of the biofuel.

After LUC, cultivation processes represent the highest emission source in the total carbon footprint of HVO, where the main factors contributing to GHG emissions from cultivation are nitrogen fertilizer and the N_2O emissions connected with nitrogen fertilizers, so then attention should be focused on land use change and cultivation processes.

In the HVO boxplot chart, it can be found some outliers, which are data values that are far away from other data values; these values correspond specifically to the WTW CO_2 emissions of HVO from palm oil, in which one of the central carbon footprint-related issues in palm oil production is methane collection from palm oil mill effluent, where if POME is not treated by methane collection it can be a significant GHG emission source (228 $g CO_{2 eq}/MJ$) [133], and if there is methane collection, emissions of palm oil HVO production are very low (-10.0 $g CO_{2 eq}/MJ$) [133]. For HVO from canola oil, the CO_2 sequestration of the cultivation process, lead to a considerable GHG credit (0.037 – 0.063 $g CO_{2 eq}/MJ$) [119]. In the opposite, using algae feedstock resulted in much higher GHG emissions relative to the petroleum-derived fuels, being the major contributor to the GHG emissions algae cultivation, due to the high electricity consumption during the algae cultivation process (225.63 $g CO_{2 eq}/MJ$) [129].





Fig. 53: WTW CO_2 emissions in $g CO_{2 eq}/MJ$ of alternative gasoline fuels

Figure 53 displays a comparison of the life cycle WTW CO2 emissions for various fuels, including fossil gasoline, alternative gasoline fuels, and low-emission alternative fuels like hydrogen (which is not meant for internal combustion engines) and electric vehicles. The emergence of these alternative fuels worldwide is due to their ability to minimize environmental impact, decrease reliance on petroleum, and diversify energy sources for transportation. The reference baseline for this comparison is conventional gasoline, which has a WTW GHG emission intensity ranging from 81-104.48 $g CO_{2 eq}/MJ$. The purpose of this comparison is to determine which alternative fuels have the greatest potential for reducing GHG emissions.

For GTL pathway the results in Table IV shows that GTL can lead to GHG emissions reductions (3.59 – 90.60 $g CO_{2 eq}/MJ$) relative to a petroleum gasoline baseline, since the energy involved is less carbon intensive. Actually, the GTL process could be viewed as a carbon concentration process, where a large

fraction of the expended energy is in form of hydrogen, which is free of aromatic and sulfur compounds. So, it can clearly be seen that the combustion CO_2 emissions of synthetic diesel fuels are lower than those for fossil fuels, because the C/H ratio is lower for the former.

Reference	Year	Fuel	Transportation sector	Feedstock	Production pathway	System boundary	Country	WTW CO2 net emissions	Functional unit
[166]	2010	GTL	ICEV	NG	Fischer-Tropsch	Well to wheel	China	13.54	g CO2 eq/ MJ
[169]	2009	GTL	ICEV	NG	Fischer-Tropsch	Well to wheel	Netherlands	3.59	g CO2 eq/ MJ
[57]	2013	GTL	ICEV	NG	Fischer-Tropsch	Well to wheel	US	90.60	g CO2 eq/ MJ
[57]	2013	GTL	ICEV	NG	Fischer-Tropsch	Well to wheel	US	85.30	g CO2 eq/ MJ
[57]	2013	GTL	ICEV	NG	Fischer-Tropsch	Well to wheel	US	89.40	g CO2 eq/ MJ
[57]	2013	GTL	ICEV	NG	Fischer-Tropsch	Well to wheel	US	77.00	g CO2 eq/ MJ
[83]	2011	GTL	ICEV	NG	Fischer-Tropsch	Well to wheel	Qatar	88.70	g CO2 eq/ MJ
[83]	2011	GTL	ICEV	NG	Fischer-Tropsch	Well to wheel	Qatar	86.20	g CO2 eq/ MJ
[113]	2013	GTL	ICEV	CO2	Fischer-Tropsch	Well to wheel	China	62.00	g CO2 eq/ MJ

TABLE IV GTL FISCHER-TROPSCH GASOLINE WTW \mathcal{CO}_2 EMISSIONS

Even when included LUC GHG emissions, the use of ethanol as a fuel in general may result in GHG emission reductions mainly because the carbon in fuel ethanol is taken up from the air during biological plant growth via photosynthesis. Thus, use of ethanol to displace gasoline result in reductions from 8% - 130%, when compared with gasoline. Figure 54 shows that corn ethanol in general has moderately lower GHG emissions, but cellulosic ethanol (switchgrass, miscanthus, wheat straw, forestry residues, woody forage, etc) has much lower GHG emissions than gasoline does.



Fig. 54: WTW CO_2 emissions in $g CO_{2 eq}/MJ$ of ethanol according to the type of feedstock

Specifically, for corn as a feedstock for ethanol production, fertilizer production and associated N_2O emissions, are the largest GHG emissions source, where the impact of fertilizer-related parameters on WTW GHG emissions results depends on the fertilizer intensity of feedstock farming. Briefly the stages that contribute to corn ethanol GHG emissions are: ethanol production, nitrogen fertilizer production and use, corn farming, production and use of other chemicals such as pesticides and herbicides, leading to a considerable GHG credit that range between $-8.3 - 200.24 g CO_{2 eg}/MJ$.

Another notable aspect of Figure 54 is that perennial forage offers the greatest WTW CO_2 emissions reduction (-6.7 - 82 $g CO_{2 eq}/MJ$) among the other feedstocks evaluated, because of the high yield of miscanthus and switchgrass, which result in a significant increase in SOC. This implies that any cellulosic feedstock with a high yield, such as miscanthus, could sequester significant amounts of GHGs.

The WTW CO_2 emissions are also dependent on the source of energy for powering the production plant, for the case of sugarcane and advanced cellulosic ethanol pathways, they use much less fossil energy

and thus represent greater GHG emissions reduction, because a significant part of the energy can be generated by making use of co-products. This is the case of sugarcane $(10.0 - 73.40 \ g \ CO_{2 \ eq}/MJ)$, which use bagasse for generation of electricity, and the case of non-fermentable materials from pathways starting from straw or wood.

For the case of wood-based pathways, as previously mentioned, exhibit favorable WTW CO_2 emissions balance $(-14.0 - 46.0 g CO_{2 eq}/MJ)$ as less fossil energy is involved in the process, because the energy needed is generated from the non-fermentable part of the feedstock. The straw option on the other hand is less favorable, because increased farming input is also needed in order to grow this part of the plant (not only the grain), leading to WTW CO_2 emissions between $39.20 - 108 g CO_{2 eq}/MJ$ for wheat straw, and WTW CO_2 emissions between $26.30 - 145.39 g CO_{2 eq}/MJ$ for sorghum straw.

In the ethanol boxplot chart, it can be found some outliers (See Figure 54), which are data values that are far away from other data values; these values correspond specifically to the WTW CO_2 emissions of algae ethanol (804 $g CO_{2 eq}/MJ$) [77] in which WTW CO_2 emissions are exceeding the WTW CO_2 emissions of gasoline, due to the low energy yield, in which a high amount of algae biomass has to be cultivated and harvested, leading this way to high WTW emissions. In the opposite case there are outliers which represent lower WTW CO_2 emissions compared to gasoline, these are ethanol produced from cellulosic residues, such as citrus waste ($-32.10 g CO_{2 eq}/MJ$) [156] and forestry residues ($-10.34 g CO_{2 eq}/MJ$) [115]; which can alleviate competition for land conventionally used for food and feed production, and can displace fossil reference products, significantly reducing life cycle GHG emissions.

For biogasoline, this is produced from a hydropyrolysis and hydroconversion process, in which H_2 production is the main source of emissions, due to the anthropogenic CO_2 emissions from the reforming of natural gas to produce the hydrogen. Results presented in Table V shows that forestry residues result in much lower GHG emissions (12.75 – 47.75 $g CO_{2 eq}/MJ$) relative to petroleum-derived gasoline (81-104.48 $g CO_{2 eq}/MJ$), likewise renewable gasoline fuel produced from woody biomass show considerable GHG savings (39.0 $g CO_{2 eq}/MJ$) compared to their fossil fuel counterpart. In general, the production of biogasoline shows the importance of the interplay between feedstock production emissions and H_2 production emissions.

Reference	Year	Fuel	Transportation sector	Feedstock	Production pathway	System boundary	Country	WTW CO2 net emissions	Functional unit
[171]	2013	Biogasoline	ICEV	Biogas	Hydropyrolysis and Hydroconversion	Well to wheel	Spain	87.92	g CO2 eq/ MJ
[173]	2014	Biogasoline	ICEV	Woody forage	Hydropyrolysis and Hydroconversion	Well to wheel	US	39.00	g CO2 eq/ MJ
[174]	2011	Biogasoline	ICEV	Corn	Hydropyrolysis and Hydroconversion	Well to wheel	US	14.68	g CO2 eq/ MJ
[174]	2011	Biogasoline	ICEV	Corn	Hydropyrolysis and Hydroconversion	Well to wheel	US	33.67	g CO2 eq/ MJ
[174]	2011	Biogasoline	ICEV	Corn	Hydropyrolysis and Hydroconversion	Well to wheel	US	36.49	g CO2 eq/ MJ
[174]	2011	Biogasoline	ICEV	Waste/Residues	Hydropyrolysis and Hydroconversion	Well to wheel	US	39.80	g CO2 eq/ MJ
[174]	2011	Biogasoline	ICEV	Waste/Residues	Hydropyrolysis and Hydroconversion	Well to wheel	US	47.75	g CO2 eq/ MJ
[175]	2015	Biogasoline	ICEV	Woody forage	Hydropyrolysis and Hydroconversion	Well to wheel	Spain	39.41	g CO2 eq/ MJ
[79]	2016	Biogasoline	ICEV	Corn	Hydropyrolysis and Hydroconversion	Well to wheel	US	29.50	g CO2 eq/ MJ
[79]	2016	Biogasoline	ICEV	Waste/Residues	Hydropyrolysis and Hydroconversion	Well to wheel	US	12.75	g CO2 eq/ MJ

TABLE V BIOGASOLINE WTW CO_2 EMISSIONS

Note: Cellulosic and woody biomass can be directly converted to hydrocarbon gasoline through the use of IH^2 (Integrated Hydropyrolysis and Hydroconversion) technology, which is a continuous catalytic thermochemical process estimated to provide a cost-effective route, from a broad spectrum of organic wastes to fungible liquid hydrocarbon transportation fuels.

Methanol can be produced from any carbon-containing feedstock, where conventional methanol is produced from NG and coal, and renewable methanol is mainly produced from second generation biomass, such as wood, forest residues, agriculture residues and municipal solid waste. As shown in Table VI, in the scenario where methanol is manufactured from coal, the WTW CO_2 emissions are around 252.60 g $CO_{2 eq}/MJ$, for methanol from biogas the WTW CO_2 emissions are around 16.70 g $CO_{2 eq}/MJ$, and for methanol synthesized using CO_2 as feedstock for fuel production, it shows a reduction potential of 94% (6.0 g $CO_{2 eq}/MJ$).

TABLE VI METHANOL WTW *CO*2 EMISSIONS

Reference	Year	Fuel	Transportation	Feedstock	Production	System	Country	WTW CO2 net	Functional
Reference	Ital	I uci	sector	recustock	pathway	boundary	Country	emissions	unit
[82]	2019	Methanol	ICEV	CO2	Hydrogenation	Well to wheel	Netherlands	6.00	g CO2 eq/ MJ
[85]	2018	Methanol	ICEV	Biogas	Biogas upgrading	Well to wheel	Germany	16.70	g CO2 eq/ MJ
[88]	2012	Methanol	ICEV	Coal	Gasification	Well to wheel	China	252.60	g CO2 eq/ MJ

Note: Thermocatalytic CO_2 hydrogenation to methanol via heterogeneous catalysis is a promising environmental-friendly route for combatting CO_2 emissions.



C. WTW CO₂ net emissions for conventional vehicles and alternative vehicles technologies

Fig. 55: WTW CO_2 emissions in $g CO_{2 eq}/km$ of alternative diesel fuels



Fig. 56: WTW CO_2 emissions in $g CO_{2 eq}/km$ of alternative gasoline fuels

The WTW CO_2 emissions of FCVs and BEVs, for various hydrogen and electricity production pathways are compared with the conventional derived petroleum fossil fuels as seen in Figure 55 and Figure 56. In general, most of the alternative powertrain types (BEVs, HEVs, PHEVs, FCEVs and FCHEVs) are less emission intensive than conventional powertrains fueled by fossil-based gasoline and diesel; however, lifecycle WTW emissions of alternative powertrain vehicles can exceed conventional vehicle emissions in certain situations, as is the case when using a fossil-based electricity mix for charging and H_2 production. This way using electricity generated by coal or oil had higher emissions than their corresponding gasoline and diesel based ICEVs, due to the relatively high energy demand and GHG emission intensity of coal compared to petroleum derived fuels. Therefore, it should not be assumed assume that EVs and FCVs are more environmentally friendly (in terms of GHG emissions) than ICEVs without considering the electricity generation mix. On the other hand, if the electricity is generated by natural gas, lignocellulosic biomass or renewable energy sources, EVs and FCVs have less negative impacts on the environment than ICEVs.

It is important to note that ICEVs have significant GHG emissions in the vehicle operation stage, where tail-pipe exhaust GHG emissions account for the largest portion; and in contrast, both EVs and FCVs

have zero emissions during the vehicle operation, but account for the majority of GHG emissions during the fuel production, therefore the conversion process and the feedstock used for hydrogen and electricity production are decisive when it comes to achieving significant emissions reductions in these alternative vehicles technologies.

In general, FCVs are unable to compete with EVs WTW GHG emissions reduction via electricity pathways due to the lower overall energy conversion efficiency chain, however thermo chemical conversion routes for hydrogen production offer efficiency gains which can reduce or eliminate the gap between EVs and FCVs operational WTW performance. In comparison to the fossil fuels, FCVs could reduce the total WTW CO_2 emissions using thermo chemical conversion routes and electrolysis but only when using renewable electricity sources.

In the case of battery-electric vehicles, they demonstrate some of the lowest WTW GHG emissions amongst all drivetrains due to high energy conversion chain efficiencies, where the WTW emissions performance strongly depends on the electricity generation method, or the electricity mix used. This meaning that renewable energy- based electricity generation results in lower WTW GHG emissions, while fossil fuel-based electricity can lend itself to higher emissions than the petroleum ICEVs. Specifically, in the vast majority of the cases the superiority of BEVs is further confirmed as BEVs have lower WTW *CO*₂ emissions than PHEVs and HEVs; however, consideration should be given to the electricity mix used, since high EI electricity shows lowest GHG emissions for PHEVs and HEVs due to the efficiency of using gasoline or diesel and lower GHG emissions during vehicle manufacturing; while considerable reductions in GHG emissions with BEVs in this case are unlikely.





Fig. 57: WTW CO_2 emissions in $g CO_{2 eq}/MJ$ of alternative aviation fuels

Figure 57 displays various fuel options that have the potential to replace traditional jet fuel and the potential reductions in terms of WTW CO_2 emissions that each bio-jet fuel can offer. These bio-jet fuels are produced from different feedstock sources and through various fuel pathways, resulting in variable WTW CO_2 emission reductions. However, most studies show that alternative bio-jet fuel pathways generally have superior life cycle GHG emissions performance compared to petroleum jet fuel. Depending on the feedstock source and fuel conversion technology, alternative bio-jet fuel pathways can lower life cycle GHG emissions

by 8% in the worst-case scenario and up to 120% in the best-case scenario, compared to petroleum jet fuel $(82 - 141 g CO_{2 eq}/MJ)$.

Even though F-T jet fuel produced from fossil feedstock sources such as natural gas (GTL) and coal (CTL) significantly reduces petroleum energy use, these fossil sources result in greater WTW CO_2 emissions (91 – 225 $g CO_{2 eq}/MJ$) for CTL (See Table VII) and (100.40 – 130 $g CO_{2 eq}/MJ$) for GTL (See Table VII), compared with petroleum jet fuel (82 – 141 $g CO_{2 eq}/MJ$). For CTL even with CCS (91 – 130 $g CO_{2 eq}/MJ$), CTL fuel has life cycle GHG emissions over 36.9% of conventional jet fuel; and without carbon capture, CTL has 63.6% higher WTW GHG emissions compared with petroleum jet fuel of the emissions of conventional jet fuel. Since the goal is to reduce GHG emissions, then coal and natural gas alone appears to be a poor choice.

Reference	Year	Fuel	Transportation sector	Feedstock	Production pathway	System boundary	Country	WTW CO2 net emissions	Functional unit
[181]	2008	CTL	Aviation	Coal	Fischer-Tropsch	Well to wake	US	208.00	g CO2 eq/ MJ
[183]	2012	CTL	Aviation	Coal	Fischer-Tropsch	Well to wake	US	225.00	g CO2 eq/ MJ
[183]	2012	CTL	Aviation	Coal	Fischer-Tropsch	Well to wake	US	102.00	g CO2 eq/ MJ
[183]	2012	CTL	Aviation	Coal	Fischer-Tropsch	Well to wake	US	148.00	g CO2 eq/ MJ
[96]	2012	CTL	Aviation	Coal	Fischer-Tropsch	Well to wake	Germany	210.00	g CO2 eq/ MJ
[96]	2012	CTL	Aviation	Coal	Fischer-Tropsch	Well to wake	Germany	130.00	g CO2 eq/ MJ
[123]	2021	CTL	Aviation	Coal	Fischer-Tropsch	Well to wake	US	184.40	g CO2 eq/ MJ
[147]	2009	CTL	Aviation	Coal	Fischer-Tropsch	Well to wake	US	194.80	g CO2 eq/ MJ
[147]	2009	CTL	Aviation	Coal	Fischer-Tropsch	Well to wake	US	91.00	g CO2 eq/ MJ

TABLE VII CTL FISCHER-TROPSCH WTW \mathcal{CO}_2 EMISSIONS FOR AVIATION SECTOR

	GIL FISCHER-TROPSCH WIW \mathcal{LO}_2 EMISSIONS FOR AVIATION SECTOR										
Reference	Year	Fuel	Transportation sector	Feedstock	Production pathway	System boundary	Country	WTW CO2 net emissions	Functional unit		
[181]	2008	GTL	Aviation	NG	Fischer-Tropsch	Well to wake	US	102.40	g CO2 eq/ MJ		
[96]	2012	GTL	Aviation	NG	Fischer-Tropsch	Well to wake	Nigeria	130.00	g CO2 eq/ MJ		
[96]	2012	GTL	Aviation	NG	Fischer-Tropsch	Well to wake	Nigeria	110.00	g CO2 eq/ MJ		
[96]	2012	GTL	Aviation	NG	Fischer-Tropsch	Well to wake	Russia	110.00	g CO2 eq/ MJ		
[98]	2011	GTL	Aviation	NG	Fischer-Tropsch	Well to wake	EU	126.56	g CO2 eq/ MJ		
[147]	2009	GTL	Aviation	NG	Fischer-Tropsch	Well to wake	US	100.40	g CO2 eq/ MJ		

ED TRADECH WTW CO EMICCIONS FOR AVIATION SECTOR

TABLE VIII

In terms of feedstock, in Figure 58 it is shown that waste/residues, such as agricultural residues, forestry residues, municipal solid wastes, used cooking oil and yellow grease, delivers some of the highest GHG reductions $(-127.16 - 73.40 g CO_{2 eq}/MJ)$ of any feedstock assessed; and on the opposite, the food and oil crops are characterized by higher feedstock cultivation emissions, since the amount of CO_2 sequestered during the biomass growth is mitigated by the emissions associated with the farming and collection process, high fertilizer use and hydrogen needed for fuel upgrading.



Fig. 58: WTW CO_2 emissions in $g CO_{2 eq}/MJ$ of SAF according to the type of feedstock

In the SAF boxplot chart (See Figure 58), it can be found some outliers, which are data values that are far away from other data values; these values correspond specifically to the WTW CO_2 emissions of sustainable aviation fuels from municipal solid waste (-127.16 $g CO_{2eq}/MJ$) [84] in which the avoided emissions are due to not only the fact that this is a high carbon saving feedstock, but to the amount of CO_2 captured from the syngas of the F-T process; likewise for SAF from jatropha oil (-53.20 $g CO_{2eq}/MJ$) [164] generates lower GHG emissions because the jatropha cake/husk was considered as fertilizer to displace synthetic fertilizer, mitigating this way the emissions related to fertilizer use. In the opposite, using soybean oil as a feedstock resulted in much higher GHG emissions (289 $g CO_{2eq}/MJ$) [147], because as discussed earlier, the use of food crops in the production of renewable oils for fuels production may lead to emissions from land use change, where the magnitude of land use change emissions can depend on the type of land being converted to cropland, the type of crops being grown, etc.



Fig. 59: WTW CO_2 emissions in $g CO_{2eq}/MJ$ of SAF according to the production pathway

In the Figure 59 can be seen the technologies which are expected to become commercially available in the near- term, for the production of bio-jet fuels, these are Hydroprocessed Esters and Fatty Acids (HEFA), Fischer–Tropsch (F-T), Hydrothermal Liquefaction (HTL), Hydrodeoxygenation (HDCJ), Alcoholto-Jet (ATJ), Direct Sugars to Hydrocarbons (DSHC) and Advance Fermentation (AF); where most of these pathways yield to significant GHG emissions reductions compared to fossil jet fuel.

In general, the production and use of hydrogen plays an important role in current and future of renewable jet fuels production, as it is required in almost all pathways (except for Fischer-Tropsch); where hydrogen is produced through steam methane reforming (SMR) of natural gas, which corresponds to the current production practice of hydrogen, thus being an important contributor to the overall WTW GHG emissions. Hence, sustainable hydrogen production technologies can have an important contribution towards reducing the emission intensity of RJF, especially when produced through electrolysis using renewable electricity from wind and solar, and through gasification of biomass.

The F-T pathway shows the highest GHG emission savings $(-127.16 - 163 g CO_{2 eq}/MJ)$ of the pathways considered, due to mainly the self-sufficiency of the process and excess electricity production; followed by AF $(-4.9 - 65.6 g CO_{2 eq}/MJ)$, DSHC $(32.4 - 56 g CO_{2 eq}/MJ)$, ATJ $(11 - 87 g CO_{2 eq}/MJ)$, HEFA $(-53.20 - 289 g CO_{2 eq}/MJ)$, HTL $(20.0 - 131.9 g CO_{2 eq}/MJ)$ and HDCJ $(25.78 - 104.5 g CO_{2 eq}/MJ)$, which are processes with low conversion yield and high hydrogen consumption, that are the main contributors to higher WTW CO_2 emissions. Therefore, improving the conversion efficiency of jet fuel and decreasing energy consumption will lead to emissions reductions in all pathways.

E. WTW CO_2 net emissions for alternative maritime fuels

Figure 60 demonstrates that alternative fuels are crucial for reducing greenhouse gas emissions in the shipping industry, and there is not a single route solution for achieving this goal. The potential of liquid alternative fuels and their respective production pathways are evaluated to determine how various feedstocks can be converted into fuels capable of replacing distillate fuel in shipping. The fuels options range from traditional fuel oils (MGO) to alternative fuels, including fossil-based fuels (GTL, ammonia, and methanol), biomass-based fuels (HVO, biodiesel, methanol, ethanol, BTL, and DME), and non-bio renewable energy (hydrogen). In general, the extent of emissions reductions varies greatly depending on the fuel's production pathway and feedstock, with the latter being more critical than the conversion technology in determining the fuel pathway's WTW CO_2 emission reductions.



Fig. 60: WTW CO_2 emissions in $g CO_{2 eq}/MJ$ of alternative maritime fuels

In Figure 60 it can be seen that alternative fuels utilizing a carbon-intensive production pathway, will not provide decarbonization, instead these pathways shift emissions elsewhere in the supply chain. This is the case of GTL where the life cycle GHG emissions is reported to be $102 g CO_{2 eq}/MJ$, and thus will no generate GHG reductions relative to MGO fuel (90 $g CO_{2 eq}/MJ$), since it is produced from a fossil-based source.

Likewise, life cycle CO_2 emissions of ammonia will depend on the energy sources for its production, where as it is synthesized from nitrogen and hydrogen; therefore, green ammonia production, similar to hydrogen production, depends on utilization of renewable electricity. When ammonia its produced by HaberBosch pathway using renewable electricity for the production of hydrogen, the life cycle GHG emissions is reported to be 83 $g CO_{2 eq}/MJ$.

DME production is carried out by the catalytic dehydration of methanol, thus the feedstocks are similar to the methanol ones, which include NG, coal, oil, biomass and wastes. Where for DME produced from NG the life cycle GHG emissions is reported to be $100 \ g \ CO_{2 \ eq}/MJ$, for first generation biomass is $5.0 \ g \ CO_{2 \ eq}/MJ$ and for second generation biomass is $0.0 \ g \ CO_{2 \ eq}/MJ$ for miscanthus and $7.0 \ g \ CO_{2 \ eq}/MJ$ for forestry residues. Therefore, only DME produced from lignocellulosic feedstocks would generate notable reduction in life cycle GHG emissions relative to MGO.

Ethanol can be produced through hydration of ethylene or fermentation of sugars. Nowadays, almost all ethanol is derived from biomass; by sugar feedstock (42 $g CO_{2 eq}/MJ$), cellulosic feedstock such as agricultural residues (16 $g CO_{2 eq}/MJ$).

Biodiesel WTW CO_2 emissions varied depending on the feedstock, as shown in Table IX, secondgeneration biofuels made from wastes and lignocellulosic biomass ($-18.41 - 41.54 g CO_{2 eq}/MJ$) offer the deepest GHG reductions: 53% to 120% well-to-wake GHG emission savings compared with MGO, due to their small impact on land use and the modest use of fossil fuel energy for feedstock conversion. In contrast, first-generation biofuels produced from vegetable oils generate high GHG impact ($-14.91 - 126.67 g CO_{2 eq}/MJ$), because it induces additional land conversion to maintain food supply and demand balance.

-									
Deference	Voor	Fuel	Transportation	Foodstock	Production	System	Country	WTW CO2 net	Functional
Kelefence	Ital	Fuel	sector	recustock	pathway	boundary	Country	emissions	unit
[49]	2019	Biodiesel	Maritime	Rice straw	HTL	Well to wake	Brazil	41.54	g CO2 eq/ MJ
[49]	2019	Biodiesel	Maritime	Wheat straw	HTL	Well to wake	Sweden	10.83	g CO2 eq/ MJ
[49]	2019	Biodiesel	Maritime	Corn	HTL	Well to wake	Brazil	33.27	g CO2 eq/ MJ
[49]	2019	Biodiesel	Maritime	Woody forage	HTL	Well to wake	Brazil	-18.41	g CO2 eq/ MJ
[49]	2019	Biodiesel	Maritime	Woody forage	HTL	Well to wake	Brazil	5.13	g CO2 eq/ MJ
[49]	2019	Biodiesel	Maritime	Wheat straw	HTL	Well to wake	Brazil	-12.56	g CO2 eq/ MJ
[49]	2019	Biodiesel	Maritime	Sugar	HTL	Well to wake	Brazil	-14.91	g CO2 eq/ MJ
[49]	2019	Biodiesel	Maritime	Sorghum straw	HTL	Well to wake	Brazil	-8.37	g CO2 eq/ MJ
[49]	2019	Biodiesel	Maritime	Wheat straw	HTL	Well to wake	Sweden	2.75	g CO2 eq/ MJ
[49]	2019	Biodiesel	Maritime	Woody forage	HTL	Well to wake	Sweden	6.81	g CO2 eq/ MJ
[50]	2020	Biodiesel	Maritime	Waste/Residues	Transesterification	Well to wake	US	28.00	g CO2 eq/ MJ
[50]	2020	Biodiesel	Maritime	Animal fat	Transesterification	Well to wake	US	30.00	g CO2 eq/ MJ
[50]	2020	Biodiesel	Maritime	Soybean oil	Transesterification	Well to wake	US	96.00	g CO2 eq/ MJ
[50]	2020	Biodiesel	Maritime	Palm oil	Transesterification	Well to wake	US	98.00	g CO2 eq/ MJ
[73]	2021	Biodiesel	Maritime	Rapeseed oil	Transesterification	Well to wake	China	51.00	g CO2 eq/ MJ
[74]	2020	Biodiesel	Maritime	Canola oil	HTL	Well to wake	SE Asia	28.06	g CO2 eq/ MJ
[74]	2020	Biodiesel	Maritime	Soybean oil	HTL	Well to wake	SE Asia	55.00	g CO2 eq/ MJ
[74]	2020	Biodiesel	Maritime	Palm oil	HTL	Well to wake	SE Asia	126.67	g CO2 eq/ MJ
[74]	2020	Biodiesel	Maritime	Algae	HTL	Well to wake	SE Asia	-1.39	g CO2 eq/ MJ
[74]	2020	Biodiesel	Maritime	Waste/Residues	HTL	Well to wake	SE Asia	28.33	g CO2 eq/ MJ
[75]	2016	Biodiesel	Maritime	Rapeseed oil	HTL	Well to wake	EU	69.00	g CO2 eq/ MJ

 TABLE IX

 BIODIESEL WTW CO2 EMISSIONS FOR MARITIME SECTOR

Note: Hydrothermal liquefaction (HTL), also refers to as hydrous pyrolysis, is a thermochemical depolymerization process in an enclosed reactor to convert wet biomass into biocrude oil.

HVO such as FAME, can be produced from the same feedstocks, e.g., vegetable oils, animal fats and lignocellulosic biomass, through a hydrotreating process; as shown in Table X. Generally renewable diesel production has relatively low GHG emissions, with the CO_2 WTW emissions ranging between 3.28 and 94 $g CO_{2 eq}/MJ$; where the results show that vegetable oil-based renewable diesel produces higher GHG emissions than MGO if cultivation is done by converting forest into cultivation areas.

	HVO WTW CO_2 EMISSIONS FOR MARITIME SECTOR										
Reference	Year	Fuel	Transportation sector	Feedstock	Production pathway	System boundary	Country	WTW CO2 net emissions	Functional unit		
[49]	2019	HVO	Maritime	Rice straw	FPH	Well to wake	Brazil	39.69	g CO2 eq/ MJ		
[49]	2019	HVO	Maritime	Wheat straw	FPH	Well to wake	Sweden	16.92	g CO2 eq/ MJ		
[49]	2019	HVO	Maritime	Corn	FPH	Well to wake	Brazil	10.04	g CO2 eq/ MJ		
[49]	2019	HVO	Maritime	Woody forage	FPH	Well to wake	Brazil	5.88	g CO2 eq/ MJ		
[49]	2019	HVO	Maritime	Woody forage	FPH	Well to wake	Brazil	13.14	g CO2 eq/ MJ		
[49]	2019	HVO	Maritime	Wheat straw	FPH	Well to wake	Brazil	16.59	g CO2 eq/ MJ		
[49]	2019	HVO	Maritime	Sugar	FPH	Well to wake	Brazil	3.28	g CO2 eq/ MJ		
[49]	2019	HVO	Maritime	Sorghum straw	FPH	Well to wake	Brazil	9.04	g CO2 eq/ MJ		
[49]	2019	HVO	Maritime	Wheat straw	FPH	Well to wake	Sweden	7.66	g CO2 eq/ MJ		
[49]	2019	HVO	Maritime	Woody forage	FPH	Well to wake	Sweden	5.22	g CO2 eq/ MJ		
[50]	2020	HVO	Maritime	Waste/Residues	Hydrotreating	Well to wake	US	22.00	g CO2 eq/ MJ		
[50]	2020	HVO	Maritime	Soybean oil	Hydrotreating	Well to wake	US	83.00	g CO2 eq/ MJ		
[50]	2020	HVO	Maritime	Palm oil	Hydrotreating	Well to wake	US	94.00	g CO2 eq/ MJ		
[73]	2021	HVO	Maritime	Rapeseed oil	Hydrotreating	Well to wake	China	48.00	g CO2 eq/ MJ		

TABLE X IVO WTW *CO*2 EMISSIONS FOR MARITIME SECTOR

Note: Fast pyrolysis bio-oil upgrading by catalytic hydrogenating (FPH).

Methanol is traditionally produced in three steps, i.e., syngas production, methanol synthesis and processing of crude methanol, and can be produced from any carbon-containing feedstock; where conventional methanol is produced from NG and coal, and renewable methanol is mainly produced from second generation biomass, such as wood, forest residues, agriculture residues and municipal solid waste. By far, the majority of methanol is currently produced from natural gas (90% of methanol produced worldwide) and the rest is from coal [74]. As shown in Table XI, in the scenario where methanol is manufactured from coal, the WTW CO_2 emissions are between 190 – 305 $g CO_{2 eq}/MJ$, for methanol from NG the WTW CO_2 emissions are between 90 – 234 $g CO_{2 eq}/MJ$, and for renewable methanol emissions are between $4.0 - 25 g CO_{2 eq}/MJ$.

METHANOL WTW CO_2 EMISSIONS FOR MARITIME SECTOR												
Reference	Year	Fuel	Transportation sector	Feedstock	Production pathway	System boundary	Country	WTW CO2 net emissions	Functional unit			
[50]	2020	Methanol	Maritime	Perennial forage	Gasification	Well to wake	US	18.00	g CO2 eq/ MJ			
[50]	2020	Methanol	Maritime	Corn	Gasification	Well to wake	US	25.00	g CO2 eq/ MJ			
[50]	2020	Methanol	Maritime	NG	Catalytic synthesis	Well to wake	US	99.00	g CO2 eq/ MJ			
[73]	2021	Methanol	Maritime	NG	Catalytic synthesis	Well to wake	China	90.00	g CO2 eq/ MJ			
[73]	2021	Methanol	Maritime	Coal	Gasification	Well to wake	China	190.00	g CO2 eq/ MJ			
[73]	2021	Methanol	Maritime	Waste/Residues	Gasification	Well to wake	China	4.00	g CO2 eq/ MJ			
[74]	2020	Methanol	Maritime	NG	Catalytic synthesis	Well to wake	SE Asia	234.72	g CO2 eq/ MJ			
[74]	2020	Methanol	Maritime	Coal	Gasification	Well to wake	SE Asia	305.56	g CO2 eq/ MJ			
[75]	2016	Methanol	Maritime	NG	Catalytic synthesis	Well to wake	EU	92.00	g CO2 eq/ MJ			
[75]	2016	Methanol	Maritime	Waste/Residues	Gasification	Well to wake	EU	8.00	g CO2 eq/ MJ			

TABLE XI METHANOL WTW CO_2 EMISSIONS FOR MARITIME SECTOR

Note: Methanol catalytic synthesis is the formation of methanol from carbon oxides and hydrogen, these meaning is a CO hydrogenation reaction.

Hydrogen can be produced from a wide range of energy sources, including fossil fuels (coal, oil and natural gas either with or without zero emissions using carbon capture technology), biomass, as well as nonbio renewable electricity (e.g., wind, solar, nuclear and hydro energy). With the mentioned energy sources, hydrogen can be produced via several production pathways, such as NG reforming, coal gasification with CCS and water electrolysis.

Although hydrogen production from fossil fuels is relatively inexpensive, the process relies on the separation of hydrogen from fossil fuels and emits large amounts of CO_2 , ending with CO_2 WTW emissions ranging between 27.78 - 61.39 $g CO_{2 eq}/MJ$ with CCS, and CO_2 WTW emissions ranging between 100.0 - 165.56 $g CO_{2 eq}/MJ$ without CCS. On the other side, non-bio renewable energy, such as wind, solar and nuclear energy can lead to a sustainable hydrogen production, with significant WTW CO_2 emissions reduction $(3.0 - 38.33 g CO_{2 eq}/MJ)$.

	$\frac{1}{10000000000000000000000000000000000$										
Reference	Year	Fuel	Transportation sector	Feedstock	Production pathway	System boundary	Country	WTW CO2 net emissions	Functional unit		
[73]	2021	Hydrogen	Maritime	NG	SMR	Well to wake	China	100.00	g CO2 eq/ MJ		
[73]	2021	Hydrogen	Maritime	Renewable electricity	Electrolysis	Well to wake	China	9.00	g CO2 eq/ MJ		
[74]	2020	Hydrogen	Maritime	NG	SMR	Well to wake	SE Asia	114.44	g CO2 eq/ MJ		
[74]	2020	Hydrogen	Maritime	NG	SMR	Well to wake	SE Asia	61.39	g CO2 eq/ MJ		
[74]	2020	Hydrogen	Maritime	Coal	Gasification	Well to wake	SE Asia	165.56	g CO2 eq/ MJ		
[74]	2020	Hydrogen	Maritime	Coal	Gasification	Well to wake	SE Asia	27.78	g CO2 eq/ MJ		
[74]	2020	Hydrogen	Maritime	Renewable electricity	Electrolysis	Well to wake	SE Asia	12.78	g CO2 eq/ MJ		
[74]	2020	Hydrogen	Maritime	Renewable electricity	Electrolysis	Well to wake	SE Asia	38.33	g CO2 eq/ MJ		
[74]	2020	Hydrogen	Maritime	Renewable electricity	Nuclear Power Plant	Well to wake	SE Asia	3.33	g CO2 eq/ MJ		
[75]	2016	Hydrogen	Maritime	Renewable electricity	Nuclear Power Plant	Well to wake	EU	3.00	g CO2 eq/ MJ		

TABLE XII HYDROGEN WTW \mathcal{CO}_2 EMISSIONS FOR MARITIME SECTOR

Note: Natural gas contains methane (CH_4) that can be used to produce hydrogen with thermal processes, such as steam-methane reformation (SMR), that is a process by which natural gas or methane containing streams, such as biogas or landfill gas, is reacted with steam in the presence of a catalyst to produce hydrogen and carbon dioxide.

F-T diesel can be synthesized from fossil fuels, such as coal and natural gas, or from lignocellulosic biomass such as forestry residues, woody forage, wheat straw, rice straw and corn and sugary feedstocks, where depending on the feedstocks used for F-T synthesis, the final products are derived from coal-to-liquid, gas-to-liquid, or biomass-to-liquid. Specifically renewable F-T diesel WTW CO_2 emissions are between $-29.85 - 21.78 \ g CO_{2 \ eq}/MJ$.

-				2					
Reference	Year	Fuel	Transportation	Feedstock	Production	System	Country	WTW CO2 net	Functional
			sector		pathway	boundary		emissions	unit
[49]	2019	BTL	Maritime	Rice straw	Fischer-Tropsch	Well to wake	Brazil	21.78	g CO2 eq/ MJ
[49]	2019	BTL	Maritime	Wheat straw	Fischer-Tropsch	Well to wake	Sweden	13.85	g CO2 eq/ MJ
[49]	2019	BTL	Maritime	Corn	Fischer-Tropsch	Well to wake	Brazil	4.22	g CO2 eq/ MJ
[49]	2019	BTL	Maritime	Woody forage	Fischer-Tropsch	Well to wake	Brazil	-29.85	g CO2 eq/ MJ
[49]	2019	BTL	Maritime	Woody forage	Fischer-Tropsch	Well to wake	Brazil	-27.54	g CO2 eq/ MJ
[49]	2019	BTL	Maritime	Wheat straw	Fischer-Tropsch	Well to wake	Brazil	-27.58	g CO2 eq/ MJ
[49]	2019	BTL	Maritime	Sugar	Fischer-Tropsch	Well to wake	Brazil	-11.14	g CO2 eq/ MJ
[49]	2019	BTL	Maritime	Sorghum straw	Fischer-Tropsch	Well to wake	Brazil	4.46	g CO2 eq/ MJ
[49]	2019	BTL	Maritime	Wheat straw	Fischer-Tropsch	Well to wake	Sweden	1.66	g CO2 eq/ MJ
[49]	2019	BTL	Maritime	Woody forage	Fischer-Tropsch	Well to wake	Sweden	8.64	g CO2 eq/ MJ
[49]	2019	BTL	Maritime	Woody forage	Fischer-Tropsch	Well to wake	Sweden	4.54	g CO2 eq/ MJ
[50]	2020	BTL	Maritime	Perennial forage	Fischer-Tropsch	Well to wake	US	0.00	g CO2 eq/ MJ
[50]	2020	BTL	Maritime	Corn	Fischer-Tropsch	Well to wake	US	8.00	g CO2 eq/ MJ
[73]	2021	BTL	Maritime	Waste/Residues	Fischer-Tropsch	Well to wake	China	5.00	g CO2 eq/ MJ

TABLE XIII

BTL FISCHER-TROPSCH WTW CO_2 EMISSIONS FOR MARITIME SECTOR

F. WTW CO_2 net emissions of fuel cell vehicles



Fig. 61: WTW CO_2 emissions in $g CO_{2 eq}/km$ of hydrogen fuel cell vehicles energy sources

Concentrating on the fuel cell option, Figure 61 reviews the WTW CO_2 emissions of a range of primary energy sources for hydrogen production, where in general terms very large differences arise on the WTW emissions data ($0.31 - 523.73 \ g \ CO_{2 \ eq}/km$). Therefore, several potential hydrogen options using renewable and non-renewable energy sources are discussed, including steam reforming of natural gas, water electrolysis using grid electricity and renewable electricity, coal gasification with and without carbon sequestration, and biomass gasification of wood and lignocellulosic residues. Since there are many potential hydrogen production routes, and the results are critically dependent on the pathway and the feedstock selected as seen in Figure 61, each one of them will be discussed below:

In general, renewable energy-based hydrogen production processes exhibit relatively low GHG emissions, however, the primary energy demand for these processes varies significantly depending on the process; as may be appreciated in Figure 61, electrolysis using electricity from waste incineration $(1.0 \ g \ CO_{2 \ eq}/km \ and 18.00 \ g \ CO_{2 \ eq}/km)$, biogas CHP (92.0 $g \ CO_{2 \ eq}/km)$, renewable electricity (hydropower, wind power, nuclear, and photovoltaic power) (2.0 – 120.0 $g \ CO_{2 \ eq}/km)$, and biomass gasification of wood (12.0 $g \ CO_{2 \ eq}/km \ and 51.00 \ g \ CO_{2 \ eq}/km)$, represent the pathways with the lowest WTW CO_2 emissions.

For hydrogen production from lignocellulosic waste feedstocks, they offer low overall WTW CO_2 emissions essentially since the majority of the GHG emissions demand have been accounted in the upstream process; on the other hand, hydrogen from biomass gasification has the potential to save substantially GHG emissions as well, but issues such as land and biomass resources, efficiency and costs, may limit the application of these pathway. Lastly, electrolysis hydrogen from renewable electricity shows a greatest capability for minimizing environmental impacts; however, these resources have a limited potential for the foreseeable future, and are at present expensive, retarding this way its commercial viability.

Hydrogen from NG-based SMR is likely to be the primary mode of production for the initial introduction of FCVs, since natural gas is the only viable and cheapest source of large-scale hydrogen; where despite of being produced from a primary source of fossil fuel energy, steam methane reforming using natural gas demonstrate the lowest WTW CO_2 emissions (55.0 – 671.22 $g CO_{2 eq}/km$) amongst the other fossil fuel resources, like coal (53.0 – 520.0 $g CO_{2 eq}/km$) and crude oil (356.0 $g CO_{2 eq}/km$), which exhibit the highest GHG emissions. Clearly, hydrogen from carbon-intensive fossil fuels such as coal would only make sense if coupled with CO_2 capture, achieving WTW emissions around 53.0 $g CO_{2 eq}/km$ and 68.37 $g CO_{2 eq}/km$.

As well, hydrogen produced from electrolysis using electricity from the grid exhibit high GHG emissions for FCEVs (98.0 – 523.73 $g CO_{2 eq}/km$), because it depends on the coal dependency in the electricity generation mix of each country.


G. WTW CO₂ net emissions of battery electric vehicles

Fig. 62: WTW CO_2 emissions in $g CO_{2 eq}/km$ of battery electric vehicles energy sources

In the transport sector, electric vehicles are widely accepted as the next technology paradigm, capable of solving the environmental problems associated with internal combustion engine vehicles (ICEVs). However, WTW CO_2 emissions for EVs are strongly related to the electricity generation mix of the country (See Figure 63), where in countries without an environmentally friendly electricity generation mix, EVs may not be effective in lowering greenhouse gas emissions. In countries with high coal dependency in their electricity generation mix, WTW CO_2 emissions are higher, which is the case of China where the electricity mix relies 72% on coal, getting this way WTW emissions between $158.0 - 244.0 \ g CO_{2 \ eq}/km$; therefore, the ratio of coal in the electricity generation mix should be lowered for the EVs to be effective in alleviating GHG emission problems. On the opposite, pathways that are powered by a low-carbon electricity grid offers a greatest emission reduction potential; this is the case of countries like Austria where the electricity mix is

76% from renewable energy (21.94 $g CO_{2eq}/km$) and Sweden where the electricity mix is 60% from renewable energy (3.48 $g CO_{2eq}/km$), represent lower WTW CO_2 emissions.

Country	Total Net Electricity Generation (Billion kW h)	Coal (%)	Natural Gas (%)	Oil (%)	Nuclear (%)	Hydro (%)	Wind (%)	Biomass (%)	Solar (%)
China	4768	72	2	0	3	20	1	3	0
United States	4048	38	30	1	19	6	4	2	0
India	1052	72	8	1	3	12	3	0	1
Russia	1012	14	49	3	17	17	0	0	0
Japan	966	30	43	12	0	8	1	4	2
Germany	585	45	10	2	16	3	10	8	6
Korea, South	500	42	23	4	29	1	0	0	0
Iran	239	0	65	27	2	6	0	0	0
Saudi Arabia	255	0	62	38	0	0	0	0	0
Canada	616	12	10	1	16	58	2	1	0
Brazil	538	3	9	4	3	69	1	11	0
United	336	32	30	1	19	2	8	7	1
Kingdom									
South Africa	239	92	0	1	6	0	0	0	0
Indonesia	185	49	20	23	0	7	0	0	0
Mexico	279	11	49	19	3	14	2	1	0
Australia	235	67	20	1	0	6	4	1	1
France	533	3	3	1	76	11	3	1	1
Ukraine	187	35	10	0	51	4	0	0	0
Egypt	155	0	73	17	0	9	1	0	0
Norway	145	0	2	0	0	94	2	1	1

Fig. 63: Electricity generation mix in each country [89]

EVs look promising as a pathway for reducing in some cases GHG emissions even if coal is used, getting WTW CO_2 emissions between $49.0 - 560.0 g CO_{2 eq}/km$; however, if the goal is to substitute petroleum with coal, then the associated increases in GHG emissions due to use of a higher carbon content fuel, must be carefully comprehended.

These high WTW emissions, can be reduced even lower if the electricity portfolio includes other generation technologies, such as electricity pathways with non-fossil energy as the main raw material (such as nuclear, biomass and hydropower). In general, renewable energy-based electricity production processes exhibit relatively low GHG emissions, as may be appreciated in Figure 62, electricity from renewable energy sources (hydropower, nuclear, wind power, photovoltaic, geothermal) have WTW CO_2 emissions between $0.7 - 250.0 \ g \ CO_{2 \ eq}/km$, from lignocellulosic waste its reported net zero WTW emissions, from wood emissions of $11.0 \ g \ CO_{2 \ eq}/km$ and $23.0 \ g \ CO_{2 \ eq}/km$, and from biogas emissions $32.0 \ g \ CO_{2 \ eq}/km$ and $34.0 \ g \ CO_{2 \ eq}/km$.

VI. CONCLUSIONS

Assessing the environmental impact of low carbon fuels in the transportation sector requires a thorough life-cycle analysis that considers their greenhouse gas emissions throughout the entire production process, using the Well-to-Wheel methodology. Since there are multiple alternative fuels and production pathways available, LCA serves as a decision-making tool to identify the options that provide the greatest reduction in terms of environmental emissions for each transportation sector. Technical feasibility and commercial viability should also be taken into account, alongside environmental impacts, to determine which alternative fuel is best suited for specific conditions and needs in the transportation sector.

The adoption of alternative fuels across all transportation sectors is now a reality due to their significant reduction in GHG emissions, some even reaching net-zero or sub-zero levels when evaluated over the entire well to wheel life cycle. However, this adoption must be a gradual and long-term process as a sustainable transportation system requires careful consideration of numerous factors. Therefore, selecting the most promising pathways and technologies is crucial before embarking on a new era of alternative transportation fuels.

Due to various uncertainties associated with methodology, scope, and other factors such as feedstock type, process configuration, and operating conditions, it can be challenging to draw meaningful comparisons in terms of life cycle emissions between low carbon fuels and their fossil fuels counterparts. However, by following the methodology developed by PRISMA for a proper systematic review, the WTW CO_2 emissions data in the meta-analysis can be considered comparable. Other factors such as the inclusion of LUC emissions, local requirements, technology, and co-product allocation may also impact the results.

Biofuels show great potential as next-generation fuels because they are capable of reducing life cycle emissions and can be used with existing engine technologies and infrastructure. However, the large-scale application of biofuels is still challenged by their reliance on food crops and vegetable oils, which raises the debate of "food versus fuel". This debate is further complicated by population growth and the increasing fuel demand for transport applications, which may compete with food production for land resources. To address this issue, land areas for fuel and food production must be used as efficiently as possible, with a focus on utilizing marginal land that does not compete with food production for biofuel feedstock production. The primary source of emissions in the life cycle production of biofuels has been identified as crop production, farming, and the resulting direct and indirect LUC. To make biofuels a more attractive option for mitigating climate change, it is necessary to improve agricultural practices and combine production pathways with carbon capture and storage, in order to achieve net-zero or carbon-negative WTW CO_2 emissions. By addressing the emissions associated with crop production and LUC, it is possible to enhance the GHG life cycle emission performance of biofuels.

When considering the use of first-generation feedstocks for biofuel production, a range of factors must be taken into account, including the risk of deforestation, land use demands, and the use of fertilizers, pesticides, and freshwater, all of which can have negative environmental impacts. Second-generation and third-generation feedstocks offer a potential solution to these issues by avoiding food competition and reducing land use demands. Second-generation biofuels are assumed to have no environmental burdens as they use waste materials, and third-generation biofuels can be produced from microalgae grown on nonarable land and wastewater. However, both second and third-generation biofuel processes are more complex than producing first-generation biofuels, presenting challenges during production and harvesting phases. Therefore, the future of biofuels may involve a combination of all three generations to meet the increasing demand resulting from depletion in the world's oil resources.

The use of hydrogen fuel cells and electrification of vehicles through various technologies, such as HEV, PHEV, and BEV, presents a promising opportunity to progressively reduce GHG emissions. Alternative powertrain vehicles, in general, have lower emissions than conventional powertrains fueled by fossil-based petroleum (ICEV). However, the lifecycle GHG emissions of alternative powertrain vehicles can exceed conventional vehicle emissions in certain situations, particularly when using fossil-fuel based electricity and natural gas-based hydrogen. To ensure GHG abatement through alternative powertrains, it is crucial to use electricity generated from zero- or low-carbon sources. Therefore, the implementation of CCS technologies for both electricity generation and fossil-based hydrogen production is necessary to achieve significant GHG emissions reductions.

Full battery-electric vehicles show some of the lowest WTW CO_2 emissions amongst all drivetrains when renewable or non-fossil-based electricity is used as source, due to relatively high energy conversion chain efficiencies; however, due of the relatively short driving range per charge and the relatively high cost of the vehicles, BEVs may be conditioned primarily for specific applications like urban driving. We discussed various hydrogen options utilizing renewable and non-renewable energy sources, and it was determined that FCVs fueled with electrolysis hydrogen generated from renewable electrification have the highest potential for reducing well-to-wheel CO_2 emissions. However, there are significant obstacles to overcome, such as the high cost of constructing hydrogen delivery infrastructure and the expensive production costs of electrolysis based FCVs given the current level of technological development.

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APPENDIX