REVIEW ARTICLE

Prospects for Gasoline and Petrochemical Production in the Context of the Energy Transition

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Abstract

Environmental commitments related to fuel production make it imperative that new forms of propulsion be developed in the future. This review discusses the most salient aspects related to recent alternative fuels, such as biofuels and electric fuels, considered low-carbon fuels, as well as zero-emission fuels, such as battery electric vehicles (BEVs), as part of the actions that are already foreseeable for the future replacement of fossil fuels. A section is related to the challenges that existing fossil fuels are facing during this energy transition. Petrochemical production is another important issue discussed in this document, addressing first the most relevant aspects related to the petrochemical industry, with special focus placed on the many chemical products that can be obtained, using route maps to describe their production paths and some of their applications. Finally, the review discusses the fundamental aspects that will prevail as the pillars for the development of the petrochemical industry in the future, which, among other things, considers C1 chemistry as the central axis of the long-term development of the petrochemical industry.

Keywords: low-carbon fuel, petrochemicals, C1-chemicals, e-fuels, syngas, bio-gasoline, bioethanol, biodiesel.

1 Introduction

Despite the reluctance of some world leaders, global warming is a scientifically proven fact that will affect all forms of life and will negatively reshape the earth's biosphere if the greenhouse gases that are provoking this climate change are eliminated from the atmosphere at a level that their effect is neglectable. By far, CO_2 is the most important GHG due to its high emissions to the atmosphere mainly from the human activities, and thus, this GHG is the focus of attention of the world climate organizations such as the IPCC [1]. To avoid its negative effects on the environment, scientists have predicted that as soon as 2030, a reduction of 43 to 45% to levels compared to those of the 2010-2019 decade, along with a net zero economy (one same amount of residual emission offset by same amount eliminated) by 2050 in order to maintain 1.5°C of global warming, which would avoid the effects on climate, it will be necessary to achieve this goal. To do so, a rapid energy transition must be deployed, considering renewable (low or zero carbon) energy sources as the predominant energy, thus, leaving behind fossil fuels such as oil and gas. In this context, fossil fuels must be transitioned to zero or low carbon fuels, and they must be gradually wiped

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out from the economy [2, 3].

By 2050, 80% of global energy production is expected to come from zero-emission renewable energies, i.e., from the use of gas and petroleum derivatives to clean and sustainable energy systems such as wind, solar, geothermal, tidal, and others. Despite this, in the case of transportation, gasoline will continue to play a key role for at least the next 25 years. However, the need to counteract the climate effects of CO_2 concentration in the atmosphere will make the use of emission-free propulsion technologies imperative, leading to an increase in the consumption of vehicles powered by zero-emission fuels, such as those powered by lithium-ion batteries (LIB), hydrogen, ammonia, or those that run on low-emission fuels such as bio-gasoline, biodiesel, and bio-alcohols, which together make up what are known as biofuels [4, 5].

On the other hand, the petrochemical industry is fed by the strong demand of products that adheres to the standard modern way of living, and that humans cannot leave them behind. Among others, the plastics industry moves a significant portion of the global economy while they are used almost in every aspect of life, such as in food packing and beverage, medicine, transportation, construction, electronics, textiles, etc [6].

As the global population grows, the increasing demand for these products will, over time, heighten the need for petrochemical raw materials to fulfill the demand of the chemical sector. This will also be affected by the creation of new needs, which will require new of these materials and the production of new ones, making the oil refinery operations turn into the chemical intermediates as a key priority. This way, petrochemicals will not be replaced like liquid fuels, and thus, new raw materials will need to be produced. It is here that C1 chemistry will play a key role as the mother raw material for the production of petrochemicals and fuels.

Although chemicals have an environmental impact, both in their production and after use, where many of them are not recycled and end up becoming part of terrestrial and marine ecosystems, they will hardly be replaced by other materials in the near future, although efforts are being made right now. When deposited in waterways, plastics, fertilizers, and other products cause damage to aquatic ecosystems. This review is dedicated to discussing the most salient aspects related to alternative sources to fossil fuels, their main characteristics, and advantages over petroleum sources. On the other hand, it details the most salient aspects of the petrochemical industry, including the most critical petrochemicals and their derivatives, as well as the prospects for this vital industry in the future, particularly its potential for sustainable development [7, 8]. Currently, to our knowledge, there is no text in the literature that reviews all possible alternative fuels, i.e., one that includes both low-carbon and zero-emission fuels and the challenges facing the fossil fuel industry, and also provides an assessment of the petrochemical industry in general terms (main products and their applications), as well as a forward-looking perspective on how this industry can tackle the production of petrochemicals without using oil derivatives.

2 Low-carbon fuels

Given the increasing energy demand of the modern world, especially in land transportation energy, which is coming along with the need for GHG emissions reduction, highly active and fruitful research is taking place on new propulsion systems such as electrification or low carbon fuels (LCF). In view of the dominant position of the internal combustion engines (ICEs) as the conventional propulsion systems, a replacement of these by electric vehicles in the short term will not be possible unless intermediate, non-fossil fuels are implemented in the existing ICEs, and the most studied approach are biofuels, which can re-incorporate the CO_2 emitted in the short term, thus they can achieve the carbon neutrality if the energy needed for the bio-refining of the raw material is acquired from renewable sources. The generation of electricity is another important application of biofuels, where their advantage lies in the low capital investment needed and simplified technological processes required, contributing also to the reduction of GHG emissions, but their exploitation is still in an early stage [9]. Biofuels or electric fuels (e-fuels) require sustainable production that complies with regulations to avoid damage to biodiversity and ensure GHG reduction. It is therefore essential to examine how LCFs can provide advantages in terms of fuel consumption and emissions reduction, considering the specific application of each fuel and its corresponding combustion processes, which may impact on the performance and scalability of each engine type [10, 11].

2.1 Biofuels

Given that oil takes millions of years to regenerate, it is considered a non-renewable resource, since the GHG emissions caused by the combustion of its derivatives would remain in the atmosphere for the same amount of time. However, if we consider that living organisms, which are composed of essential biomolecules (carbohydrates, lipids, proteins, and nucleic acids), as well as biopolymers such as cellulose, hemicellulose, lignin, etc. have much shorter life cycles, and that the carbon that can be expelled from the burning of the derivatives of these components can be absorbed by photosynthetic organisms, in a period where that mass of absorbed carbon can be easily re-incorporated in new biomass and, consequently, be used again as fuels, thus it can be considered that fuels derived from biomass (biofuels) as renewable fuels, although the carbon balance would hardly achieve neutrality, i.e., zero emissions. Thus, we can classify biofuels as low-carbon fuels. The following lines will delve into the classification, production, properties, and applications of biofuels [12–14].

Biofuels are essentially fuel sources derived from biomass (organic matter of plant or animal origin or from its transformation), organic waste, and plants. According to their source, they are classified into primary and secondary fuels. Primary fuels include, for example, firewood, charcoal, agricultural waste, or sugarcane bagasse, as well as whale oil, which was used for lighting in ancient times. Secondary fuels include those obtained from sources such as petroleum, natural gas, and coal through refining processes [5]. Biofuels are also classified into four generations according to the source of raw material used for their production. First-generation biofuels are produced from food crops such as sugarcane, corn, soybean, rapeseed, canola etc. These are used in the production of ethanol or butanol through alcoholic fermentation processes mediated by yeast and in the production of biodiesel through the transesterification process of the lipids present in vegetable oil, mostly triglycerides [15]. One of the main issues in first-generation biofuels is the direct competitive production of food and fuel. Life cycle assessment (LCA) of this type biofuels revealed negative energy profit of first generation biofuels [16] Second-generation biofuels are obtained from non-food sources, mostly forestry waste, agricultural residues such as sugarcane bagasse, or corn stover, and, more recently, waste cooking oil. Their LCA demonstrated to have an increase in net energy gain, offering a great advantage over first-generation biofuels [17, 18]. Third-generation biofuels are produced from macro and microalgae. Due to their high lipid content, CO_2 fixation capacity, and rapid growth rate, microalgae are an exceptional favorable source for biodiesel and biogas (methane) [19]. Third-generation biofuels include ethanol and butanol and hydrogen, all obtained from microalgae, and methane, ethanol, biocrude, and hydrogen from macroalgae. Several limitations and drawbacks of first- and second-generation biofuels can be overcome by algae, such as food supply, water supply or land use, although still some issues still should be addressed like the high costs, scalability, technical challenges, or environmental sensitivity related to the third generation biofuels [20, 21]. Further benefits of algae as fuel source are their high CO_2 sequestration capacity, large amounts of lipids content, high growth rate and wastewater bioremediation [22].

Last but not least are fourth-generation biofuels, which utilize raw materials for biofuel production obtained through the genetic modification of biomass, particularly microalgae and other microorganisms such as yeasts, fungi, and cyanobacteria [23]. Crops dedicated to CO_2 capture and urban waste are also included in this category. Fourth-generation biofuels represent a technological advance thanks to the

Table 1. Biomass sources, biofuel produced and yearly production volume.

Biomass source	Biofuel produced	Annual production (L/year)	Source
Lignocellulosic biomass	Bioethanol, biodiesel, SAF	130,000-150,000	[24]
Municipal solid waste	Biodiesel, synthetic fuel, SAF	5,000-15,000	[25]
Industrial residue	Bioethanol, bio-crude, advanced fuels	3,000-10,000	[24]
Sewage and animal residues	Biomethane, biodiesel	2,000-7,000	[26]
Agricultural and forestry residues	Bioethanol, biodiesel, SAF	720,000-740,000	[24]
Algae	Biodiesel, bio-oil	9,500-20,000	[27]

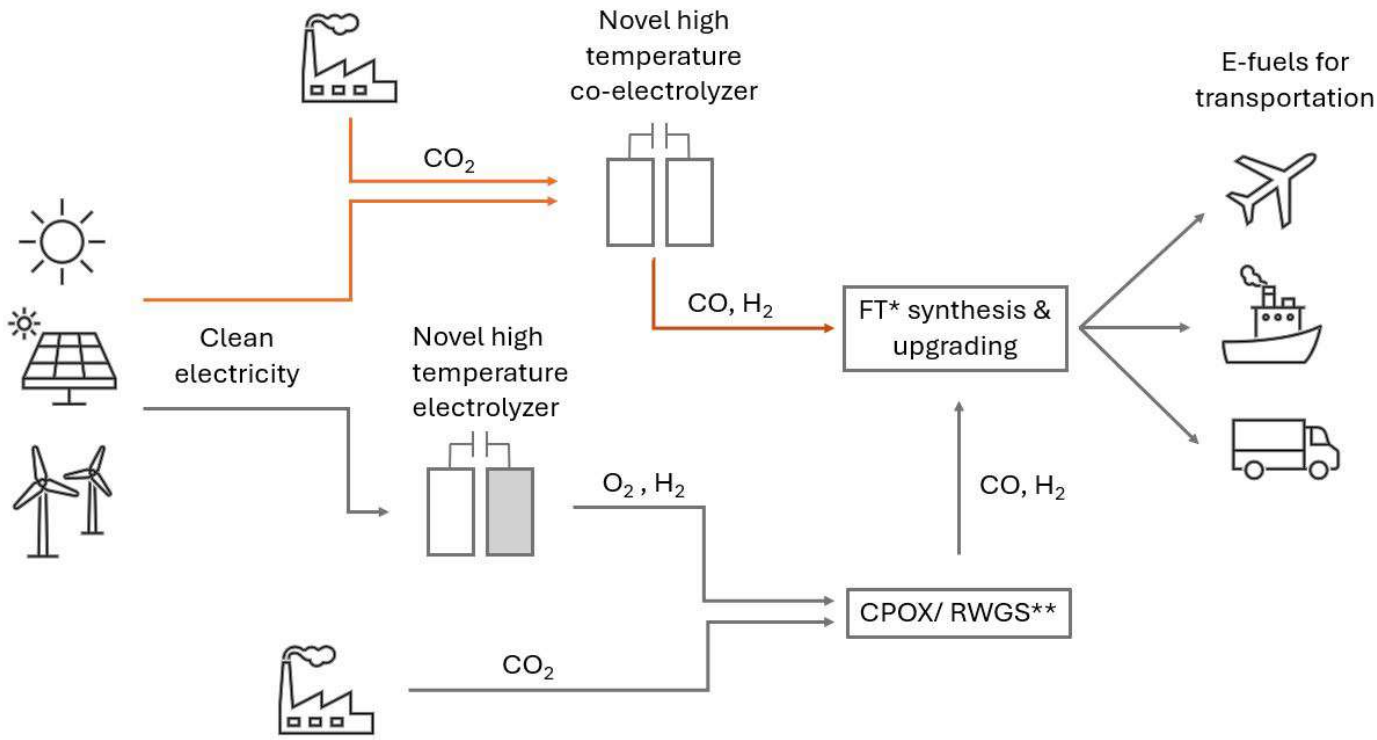

Figure 1. Production of electro-fuels for transport (CPOX: partial oxidation/RWGS: reverse water-gas exchange reaction). Modified from: https://www.e-fuel.fi/about/

ease of processing raw materials to produce liquid biofuels. The main innovation of this technology lies in the use of genetically modified biomass, which contains a reduced percentage of lignin and cellulose. This innovation enables the production of a greater amount of energy and the capture and storage of a substantially larger amount of CO_2. Although fourth-generation biofuels are still in a prolonged experimental development phase due to the complexity of the technologies involved and issues of scalability and economic viability, they also represent a promising path toward the future of sustainable energy with a lower environmental impact and great potential for application.

Other sources of biomass include municipal solid waste (MSW), which is composed of food waste, paper, plastics, garden clippings, rubber, textiles, wood, glass, and other materials, which vary according to local conditions, climate, and dietary habits. These have significant potential as raw materials for biofuel production, offering an innovative solution for both waste management and renewable energy challenges. The biodegradable portion of MSW may be turned into biofuels through biochemical and thermochemical processes. However, effective pre-treatment and separation of plastic waste is necessary before conversion. Technologies such as anaerobic digestion and fermentation enable the production of biogas and bioethanol, while processes such as gasification and pyrolysis transform waste into biofuels and synthetic fuels. The use of MSW for biofuel production not only reduces waste in landfills but also mitigates greenhouse gas emissions by preventing the decomposition of organic materials. Recent studies highlight advances in waste sorting and preprocessing techniques, which improve the efficiency and economic viability of recovering biofuels from municipal waste [4]. In addition, the integration of MSW into bioenergy systems promotes circular economy initiatives by reusing discarded materials to convert them into valuable energy sources. While challenges such as waste contamination and raw material variability persist, advances in waste-to-biofuel conversion technologies continue to improve the viability and sustainability of MSW as a key factor for the bioenergy sector. Table 1 presents the various biomass samples, the type of biofuel they produce, and their annual production.

2.2 Electric Fuels

Electro-fuels (e-fuels, power to X, or PtX), also known as synthetic fuels, refer to a wide range of low-carbon fuels synthesized from simple molecules such as hydrogen (H_2), carbon dioxide (CO_2) or carbon monoxide (CO) using renewable energy like wind, nuclear, or solar. E-fuels can take various forms, including gaseous options such as e-methane, also called synthetic natural gas, in a known as energy-to-gas conversion, and liquid synthetic fuels such as e-diesel, e-methanol or e-kerosene (energy-to-liquid conversion). Derived from clean energy sources, e-fuels can be considered as energy carriers, like hydrogen; therefore, they can also act as energy storage agents. While hydrogen is sometimes considered an e-fuel, existing technological options for combustion engines refer more to liquid synthetic fuels as substitutes for fossil fuels. Figure 1 illustrates a diagram of e-fuel production for transportation, where CO_2 serves as a carbon source. Hydrogen is preferably produced through water electrolysis. Alternatively, CO_2 can be reduced using an electrolyzer or by reacting with H_2 to produce CO, which, when combined with H_2 from water, generates synthesis gas (syngas), a mixture of H_2, CO and CO_2 [28]. This syngas can be reacted under the right proportions and under the promotion of a catalyst, in a reaction called the Fischer-Tropsch (F-T) process, hydrocarbons ranging from automotive gasoline to aviation fuel and specially diesel can be generated [29–32]. Under somewhat different conditions, methanol (CH_3OH) and dimethyl-ether (DME) are commercially produced from synthesis gas. These two liquid hydrocarbons have also been considered to as e-fuels, especially methanol, which has been added into the internal combustion engines [33] and is currently used as the raw material for the methanol to gasoline (MTG) process [34] currently commercialized by ExxonMobil.

The production of e-fuels involves various technologies and consists of two main stages: (1) raw material production and (2) fuel production.

1. Raw material production: The chemical components of e-fuels (H_2, CO and CO_2) can be obtained with low carbon emissions from various sources. Methods for producing clean hydrogen can be found in the relevant literature [35–38]. Still, among them, green hydrogen —i.e., hydrogen produced from water electrolysis —can be mentioned as one of the most promising options for the future energy in terms of sustainability. CO_2 is, from all raw materials, the cheapest and more abundant gas that can be obtained elsewhere, i.e., from point sources such as the power generation plants, from the industrial waste gases or biogenic sources; it can be captured from every point source or taken from the air through direct air capture (DAC). Currently, CO is mainly produced by gasification of coal or steam reforming of methane, both of which produce large amounts of CO_2, so new processes such as the carbon neutral CO_2 splitting, are currently studied [39].

2. Fuel production: the synthesis gas is obtained by using catalyzed processes. It can be converted into hydrocarbons (fuels) using cobalt or molybdenum-based catalysts, in a process called Fischer-Tropsch [40], and also transformed into gases such as methane, methanol, dimethyl-ether, ethanol, which can be used as components of the gasoline blend. In the second part if this review, the C1-chemistry will be addressed, focusing on the huge potential of syngas and methanol to produced petrochemicals, which serve as commodities for the production of many everyday products and chemicals or fuels, thus contributing to the decarbonization of the chemical sector, provided that each process is run under zero emission energy sources [40, 41].

E-fuels are versatile and flexible fuel options that can help meet local and specific energy needs in the transport sector. E-fuels represent an excellent low-carbon replacement option for industries that are difficult to electrify, especially in sectors where the rapid adoption of low-emission modes of transport cannot be easily accomplished in the mid-term (like in the heavy transport sector). Policy makers and industrials highlight the crucial need for synthetic fuels as a key tool in the energy transition. Further advantages of e-fuels include simple transport and storage over long distances with no need of new infrastructure, contrasting with hydrogen, which offers significant infrastructure challenges for its transport, along with the energy losses related to electricity transmission, and costly battery storage technologies, that allows energy security benefits [29, 42, 43]. E-fuels can benefit the air quality of the area where they are consumed, because they do not contain sulfur compounds or aromatic hydrocarbons, present in petroleum-derived fuels. On the other hand, these types of fuels contribute to the market and revenue streams by valorizing CO_2 from carbon capture technologies. Additionally, they can utilize waste heat from nuclear energy centrals or from renewable sources, making the process completely zero-carbon.

Indeed, powering cars with synthetic fuels does not prevent greenhouse gas emissions, but they are significantly lower than those associated with the use of fossil-based gasoline and diesel. According to the German Automobile Association (ADAC), gas emissions (nitrous oxide and carbon dioxide) decreased by 39% with the use of synthetic fuels. This will enable internal combustion engines to continue operating, which will be crucial for the millions of owners of this type of vehicle. An ideal environmental scenario would be to use green energy directly in cars, thereby bypassing the internal combustion engine and eliminating the need for liquid or gaseous fuel. Therefore, the presence of photovoltaic cells in vehicles could be a viable and very environmentally friendly option [44, 45]. Figure 2 shows an example of Nissan's e-power technology® for low-emission vehicles [46].

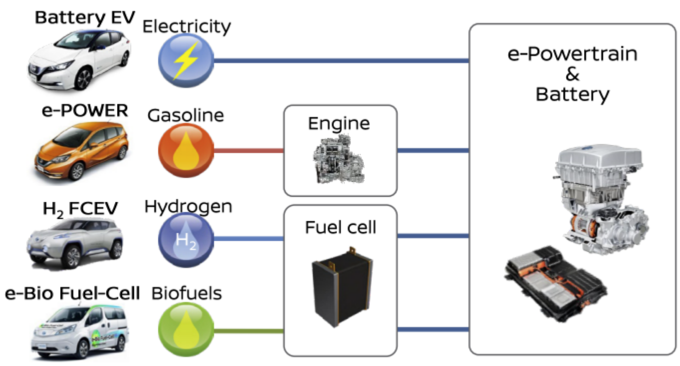

Figure 2. Nissan e-power technology for low-carbon vehicles.

Modified from: https://autobuzz.my/2024/08/28/a-hybrid-that-feels-more-like-an-ev-nissans-e-power-technology-explained/ [46].

3 Zero-emission Fuels

3.1 Electric vehicles

An electric vehicle is, as the name suggests, any vehicle that uses a source of electricity instead of a combustion engine to operate. These are powered by batteries that can be charged from an external source. The adoption of electric vehicles (EVs) is a significant step toward reducing environmental impact. Unlike vehicles powered by ICEs, battery electric vehicles (BEVs) do not produce GHG emissions or any air pollutant during operation. Though, the environmental impact of BEVs, as well as that of fuel cell vehicles (FCVs) and plug-in hybrid electric vehicles (PHEVs), can even be worse than that of modern fossil fuel-propelled vehicles because the production processes of such vehicles not only produce a significant amount of GHG emissions, but also solid and liquid wastes that turns to be highly pollutant for the soil and water sources [47]. The performance of EVs, FCVs and PHEVs also depends on the type and extent of driving, region, and the sources of electricity used. Despite these potential drawbacks, these zero-emission fuels, when combined with renewable electricity sources, become more sustainable in terms of the life cycle point of view [48]. To get a better understanding of the environmental impact of BEVs, life cycle databases should include data withdrawn during the production stage and from the energy sources applied. Recent studies show that the environmental impact of EVs can be strongly affected by the battery type and size and its energy requirements [48]. Alternative fuels, such as bioethanol, biodiesel, bio-methanol, biogas, and solar energy, could be viable options for the future in the transportation sector. One option that has become very popular is the hybrid vehicle, which is powered by both a gasoline engine and an electric motor and a battery, is considered a low-emission vehicle. These emissions would be virtually neutralized if the petroleum gasoline currently used were replaced by bio-gasoline or synthetic gasoline, further reducing the environmental impact of these units [49]. Therefore, it is crucial to include life cycle inventory databases in the future developments of the electricity sector to have a more complete understanding of the environmental impact of BEVs. In addition, the production phase and the energy sources used for their manufacture must also be considered, as BEVs are more sensitive to changes in the energy sector than traditional combustion vehicles. Figure 3 illustrates an image of a typical lithium-ion (Li) battery for a land vehicle.

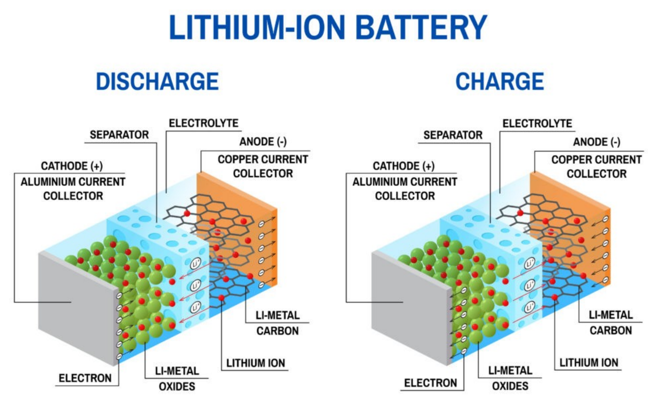

Figure 3. Representation of a lithium fuel cell.

Modified from: https://www.linkedin.com/pulse/working-principle-structure-lithium-ion-battery-davide-laverga/.

3.2 Challenges of Fossil Fuels During the Transition to Low-carbon Fuels

Until now, transportation in virtually all sectors has been powered almost entirely (>98%) by combustion engines, mostly running on liquid fossil fuels. Both the private sector and governments are continually pushing for the use of biomass-derived fuels and changes in land transport propulsion towards gasoline/electric hybrid vehicles, fully electric vehicles, or fuel cell systems (utilizing renewable hydrogen) [32, 50]. Meanwhile, the current challenges for vehicles powered by internal combustion engines can be categorized as follows:

a) How to customize fuels for engines with advanced combustion cycle systems that increase the total conversion of chemical energy from fuel into mechanical energy. These advances in engine engineering would result in a reduction in total fuel consumption per mile, resulting in lower GHG emissions into the atmosphere. An immediate case is shown by the gasoline compression ignition (GCI) engine, which can use low-octane gasoline ignited by compression to achieve efficiencies like those of diesel engines.

b) Matching renewable fuels to gasoline equivalents that can be compatible in existing combustion engines. Matching fuels and engines are essential to ensure their suitability for end-user purposes and maximize engine efficiency, so additional joint revamping of engines and fuels may be required.

c) Use of fuels that optimize and improves the complex interactions of their physical-chemical properties. Power generation in the combustion chamber involves a process of physical and chemical interactions, such as the evaporation of fuel multicomponent, charge turbulence, ignition, piston movement, and pollutant production. All of these depend on specific operating conditions, which, in turn, depend on time and are interwoven in physicochemical couplings. As a result, some properties are preferred under operating and environmental conditions. A fuel conditioned to these environments would be preferred over other fuels, so combustion systems that include both an engine and a fuel optimized to operate under one or two conditions could have advantages over others.

d) Obtaining aviation fuels that meets stricter requirements and specific properties that helps to maximize combustion efficiency. Modifications in engine design and even components is critical to keep the condition of the aircraft to be in flight. Progress in gas cycle turbine engines may require an upper cetane number limit to avoid pre-ignition in tilted injection designs, and possibly a lower limit to avoid premature explosive events. For example, regarding the concentration of aromatic compounds, their concentrations must fall between 8 and 25% to ensure the seal swelling. If the aromatic limit is lowered and the H/C ratio is increased, this would result in lower particulate matter (PM) emissions, smog, and increased heat release. In addition, the thermal stability of the fuel would improve the ability to recover more energy from it, as well as cycle efficiency, reducing maintenance and operating costs.

e) In case of current processes for the production of gasoline from oil, the use of energy efficient processes, considering renewable energy, application of circular economy principles and optimization of catalytic processes [51], deserves special attention to get low-carbon gasolines with lower CO_2 emissions.

4 Overview of the Petrochemical Industry

A simple oil refinery are usually limited to certain processes such as atmospheric and vacuum distillation; on the other hand, more complex refineries incorporate additional energy-demanding processes like fractionation, cracking, hydrotreatment, and incorporation of fuels into gasolines, lubricants, heavy fuels, and residue processing for asphalt production; most complete refineries incorporate the production of petrochemicals. In this last case, additionally to distillation, the gases produced in various thermal cracking processes are also available for further processing. Both catalytic and thermal cracking processes result in the formation of unsaturated hydrocarbons, particularly ethylene (C_2H_4) and propylene (propene, C_3H_6) or butenes with their different isomers (C_4H_8), as well as diolefins such as butadiene (C_4H_6), and small amounts of saturated hydrocarbons such as ethane (C_2H_6), propane (C_3H_8), butanes (C_4H_{10}), and methane (CH_4). On the other hand, hydrogen (H_2) is another important by-product in some refining processes. Not all paraffins and olefins are obtained in the same process. For example, paraffins such as ethane, propane, and butane are obtained from the cracking of naphtha, whereas their olefin counterparts (except butadiene) are produced through dehydrogenation processes of these compounds [52, 53].

On the other hand, another important group of petrochemicals is the so-called BTX (benzene,

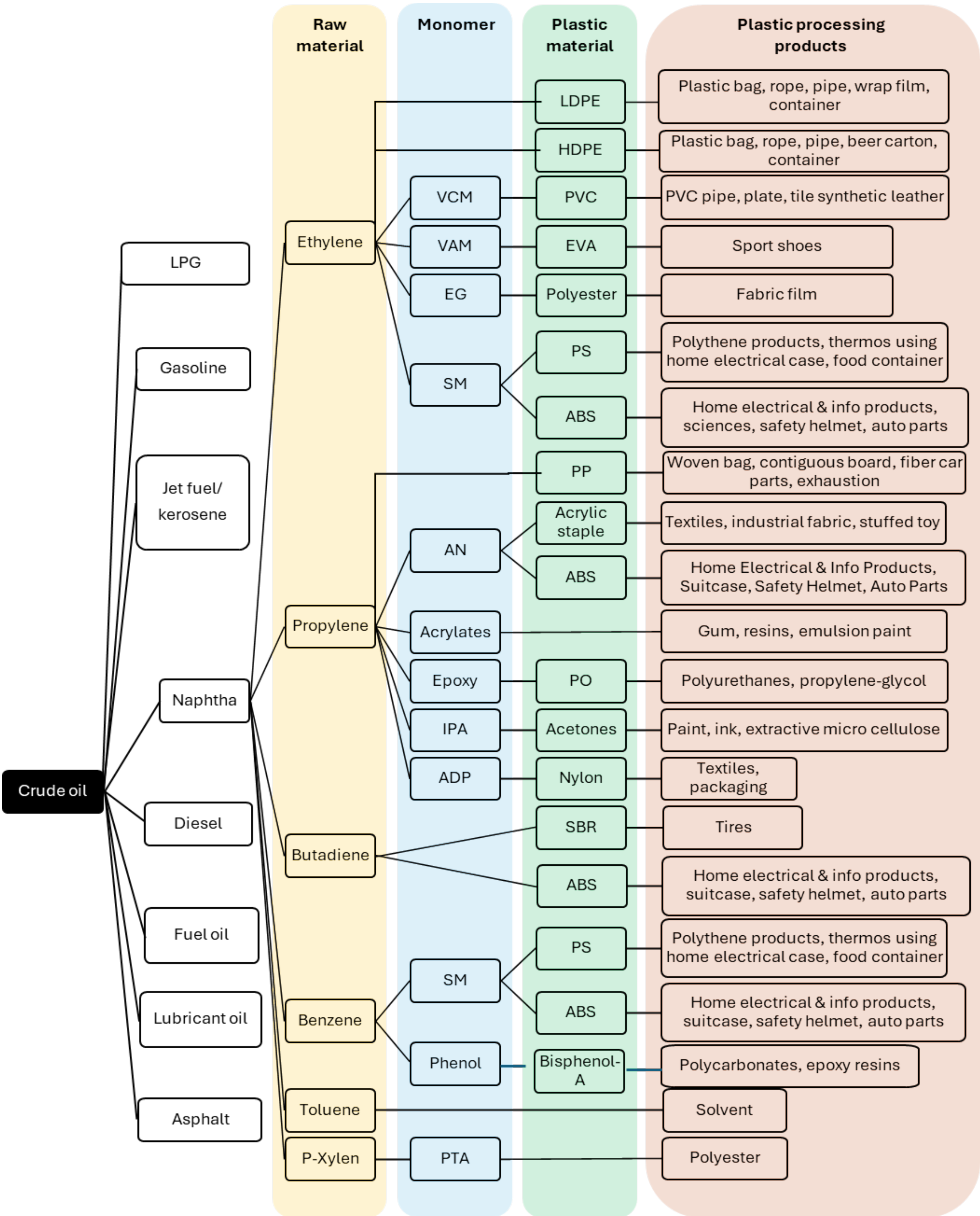

Figure 4. Selected petrochemical products and their applications.

toluene, and xylene), which, along with butadiene, are normally obtained as products of naphtha cracking [53]. For analysis purposes, petrochemicals are usually divided into two subcategories: primary petrochemicals, intermediates, and derivatives. Primary petrochemicals include all the compounds mentioned above, as well as methanol, while intermediate compounds and derivatives can be produced through different processes, for example, either directly from primary petrochemicals or through intermediates containing heteroatoms (oxygen, chlorine, or nitrogen) or through intermediates that do not include them. In any case, these products can be considered finished products. Figure 4 provides an overview of some of the applications of the various petrochemicals derived from naphtha, which are obtained through different oil refining processes.

4.1 Olefins, Paraffins, and Their Derivatives

Olefins (C_2H_{2n}) are basic components in many chemical syntheses. These unsaturated materials are incorporated into polymers and rubbers, where they react with other reagents to form a wide variety of useful compounds, including epoxides, alcohols, amines, halides, etc.

Possibly the most important petrochemical product is ethylene, which is derived from ethane extracted from natural gas, as the predominant raw material for ethylene cracking units. Ethylene has numerous applications as a raw material, for example, in the production of polymers through its polymerization or copolymerization with other monomers, or as a reagent for the synthesis of various chemicals, including solvents, reactive intermediates, fuels, and plastics. To mention just a few of the applications, products made from ethylene include items such as plastics, soaps and detergents, solvents, medicines, fertilizers, pesticides, explosives, synthetic fibers and rubbers, paints, epoxy resins, and flooring and insulation materials. Petrochemicals are found in products as diverse as aspirin, luggage, boats, automobiles, aircraft, polyester clothing, and recording discs and tapes (Figure 5) [54, 55].

On the other hand, propylene, another essential petrochemical product, is produced by the thermal and catalytic cracking of gas oils and naphtha and, as well as propane dehydrogenation. Propylene and butylene are mainly by-products of the catalytic cracking units, particularly from cracking of naphtha or light gas oil, which also produce a many other olefins. Virtually all propene or propylene is manufactured from propane, which is obtained from natural gas extraction plants or refinery gases. Butenes (1- and 2-butene) are of great industrial importance, for example, in the manufacture of car tires and, in general, for the synthesis of rubbers and plastics (polybutadiene). These are mainly derived from refinery gases or from the cracking of other crude oil fractions. Butadiene can also be recovered from the same gases; however, it is primarily produced through catalytic dehydrogenation processes of the two precursor butenes [53, 56, 57].

Polymerization processes are crucial in the petrochemical industry, as they are used to producing a vast array of everyday products from materials derived from crude oil refining processes. Polyethylene, for example, is produced from ethylene at moderate temperatures (100-120°C) and high pressures (10 to 20 atm) in the presence of a free radical initiator. Low pressures can also be used with catalysts based on alkyl aluminum salts, for example, or nickel (NiO), chromium (CrO_3), and cobalt (CoO) oxides supported on carbon or alumina. Polypropylene, a polymer derived from propylene, is synthesized in a manner like ethylene and can be polymerized alone or in the presence of ethylene or other monomers to produce specialty copolymers, resulting in products with diverse mechanical and chemical properties for a wide range of applications. Polybutadiene, obtained from the polymerization of butadiene, is essential in the tire, plastics, latex, synthetic rubber, rope, and, in general, all rubber-based products industries. Like ethylene or propylene, butadiene is copolymerized with styrene or acrylonitrile to prepare polymers with specific properties [53, 58–61]. Figure 6 shows some of the products that can be obtained from propylene and butylenes. It should be noted that the wide range of polymers that can be obtained from these olefins is not included in this discussion.

4.2 Aromatic Compounds in the Petrochemical Industry

Aromatic compounds refer to a class of organic substances whose molecules contain at least one benzene ring (C_6H_6). Compounds of this type are found in abundance in some fractions of crude oil. In refinery streams, separation processes give rise to three main types of aromatic compounds: benzene (C_2H_6), toluene ($C_6H_5CH_3$), and xylene ($C_6H_4(CH_3)_2$). These compounds are part of a family known in the petroleum industry as the BTX family. However, naphthalene, an aromatic compound with two rings ($C_{10}H_9$), is also found in crude oil refining products [62–65]. Among the most important applications of aromatic compounds is the preparation

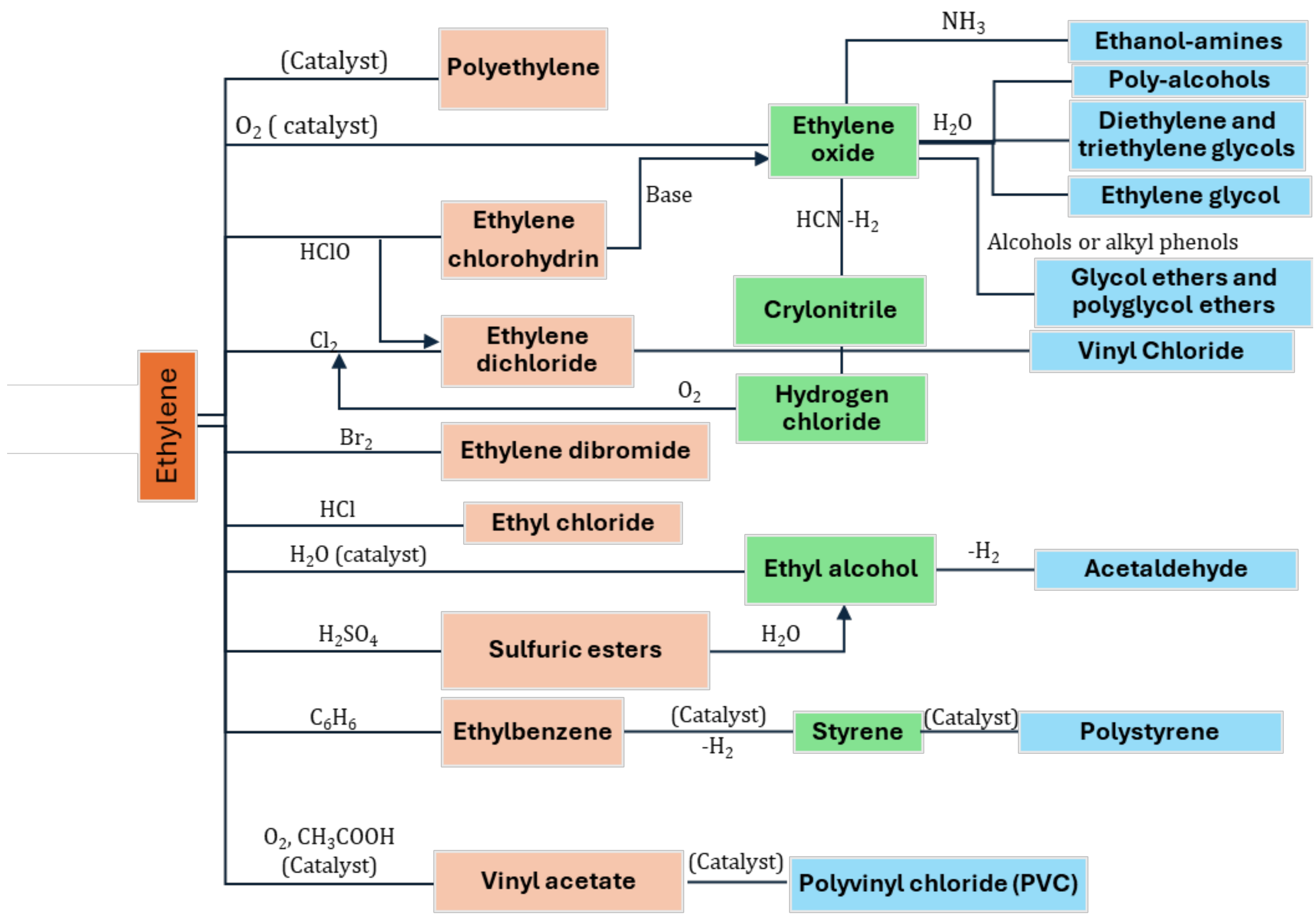

Figure 5. Ethylene petrochemicals.

of polymers such as polystyrene, produced from the alkylation of benzene with ethane, and its subsequent dehydrogenation to obtain styrene, which is polymerized by free radicals. Polystyrene is used for various purposes, including packaging, insulation materials, construction, medical equipment, and other applications. One of the important applications of BTX is in the preparation of terephthalic acid (TFA) from xylene, which is used in the manufacture of beverage bottles, among many other applications [53, 66]. It is worth mentioning that polyethylene terephthalate, also known as PET, has raised concerns about the toxicity of TFA, sparking debate about its use in the food industry [67]. Figure 7 presents a more comprehensive overview of the products derived from the BTX family of compounds.

4.3 Natural Gas Petrochemicals

The processing of natural gas, whether associated with crude oil production processes or not, results in methane, which is the simplest hydrocarbon that exists in nature and which, due to its high H/C ratio, has a very high calorific value per unit mass among hydrocarbons [68]. However, despite its widespread use as an energy source, methane is also widely utilized in the petrochemical industry, primarily as a source of heavier hydrocarbons or in the production of hydrogen, whose use in refining processes is crucial [69, 70]. Other products derived from methane include acetylene, hydrogen cyanide, carbon, CO, and chlorinated products, all of which, in turn, are intermediate in a significant number of chemical products [53]. Figure 8 provides a summary of the most important chemicals produced from methane.

It is worth pausing to discuss hydrogen, which is a material that, although not organic in nature, is extremely important in the oil industry because processes such as aromatic reforming would not be possible without it. On the other hand, hydrogen has become essential as an energy source, or as a reactive intermediate for the synthesis of higher hydrocarbons, such as e-fuels, alcohols, or ammonia, a crucial product in the manufacture of fertilizers. To date, there is no other source of hydrogen more abundant than that

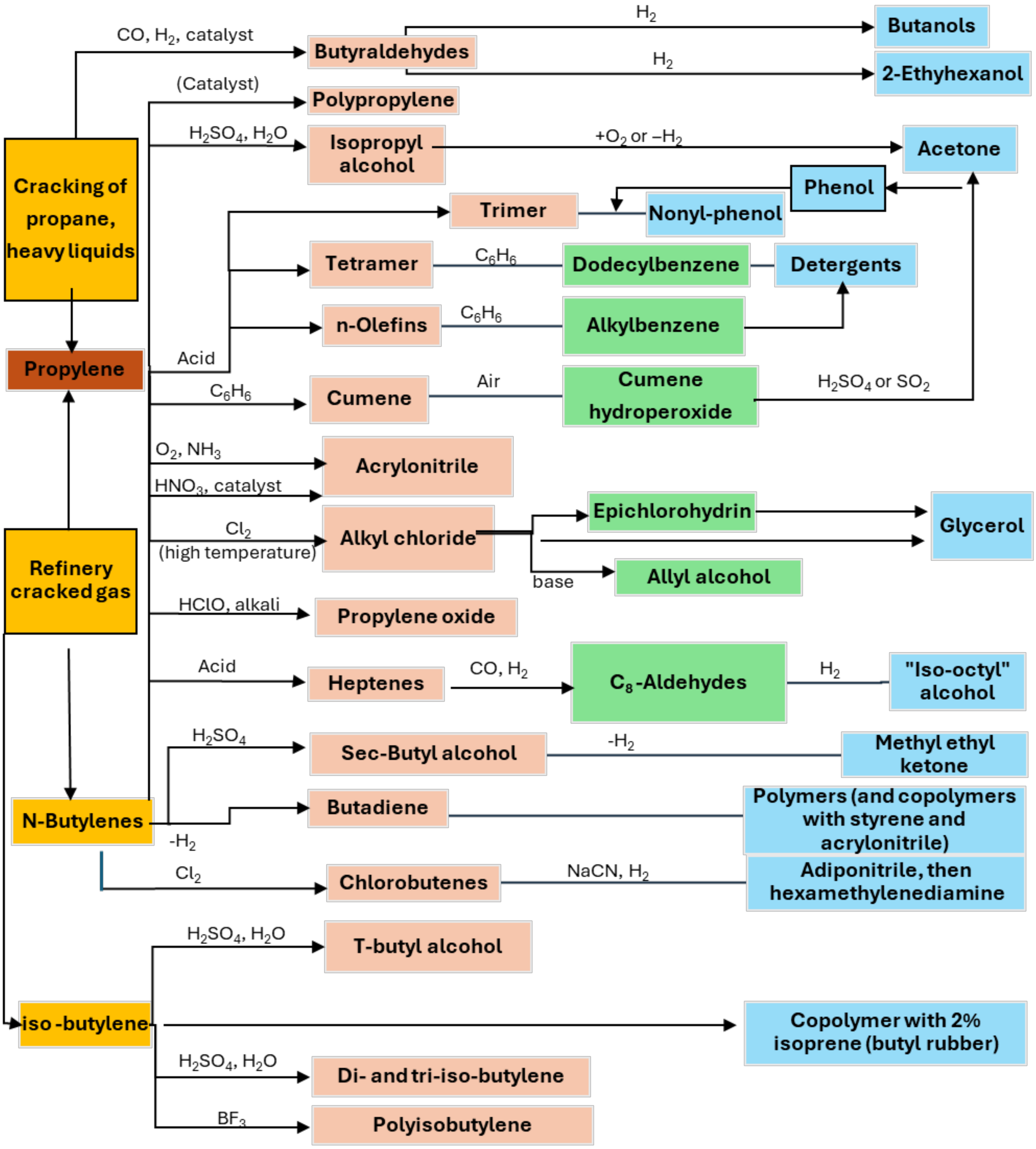

Figure 6. Selected petrochemical products from propylene and N-butylene.

derived from the methane reforming process, which produces large emissions of CO_2 into the atmosphere. This is why research related to obtaining H_2 from renewable sources is essential to reduce the enormous amounts of GHG associated with this product.

4.4 Synthesis Gas

Although synthesis gas (a mixture of CO and H_2) is not a direct product of refining processes, this component is of great importance in the petrochemical industry. Synthesis gas is mainly obtained from the reforming of natural gas (methane), but also from other hydrocarbons in thermal processes (pyrolysis) [71]. One of the most important products derived from synthesis gas is methanol, which serves as an intermediate for many different chemical compounds, including formaldehyde. However, with the invention of the F-T process, the use of synthesis gas has

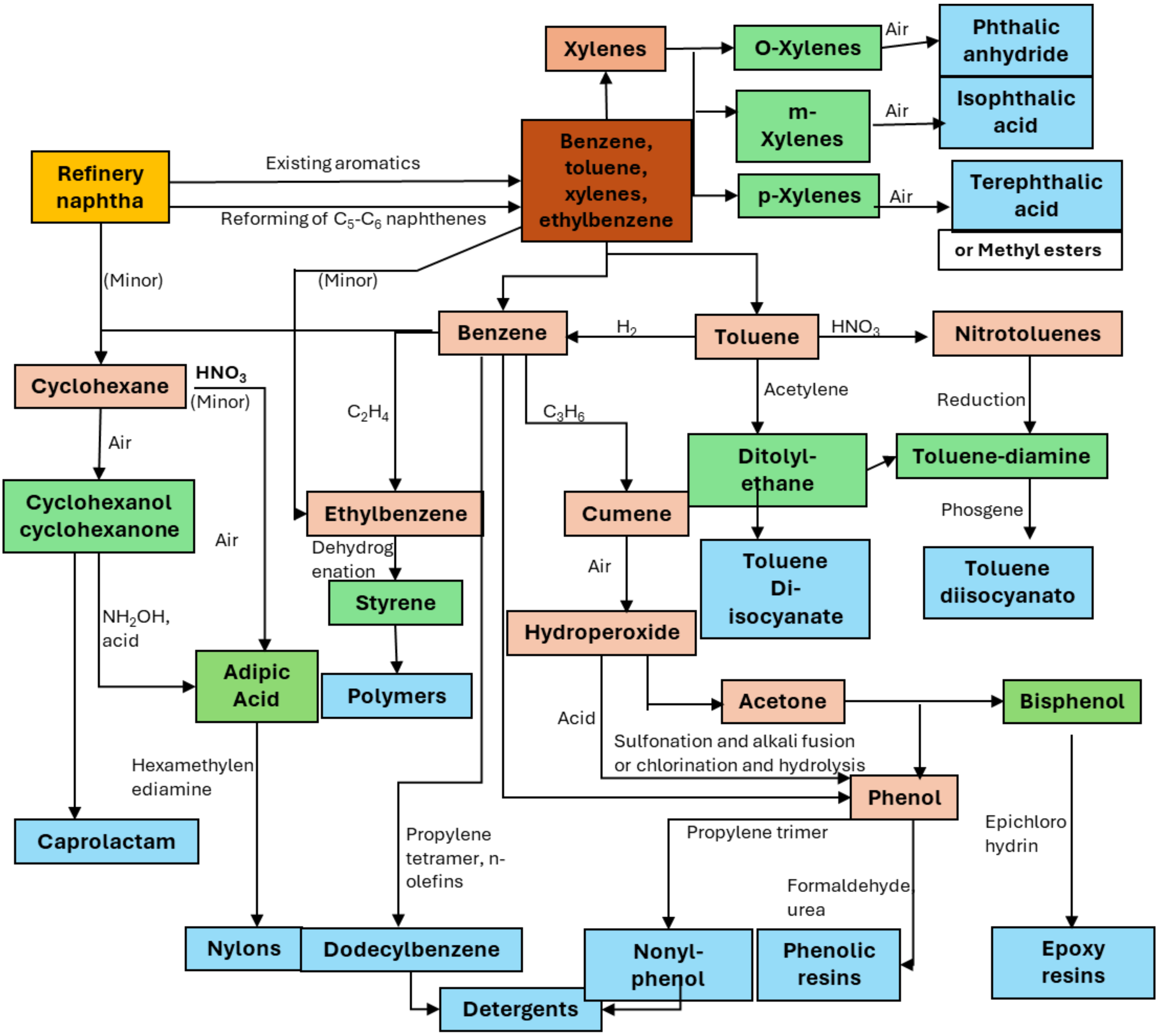

Figure 7. Petrochemical products are produced from BTX (benzene, toluene, xylene).

become particularly interesting for producing higher hydrocarbons, such as synthetic gasoline, synthetic diesel, or aviation fuel, which, when produced from green hydrogen, become e-fuels [72–75]. This versatility, particularly when coupled with green hydrogen to produce e-fuels, makes syngas an especially critical intermediate for a sustainable future. Figure 9 details the most important chemicals that originate from syngas.

4.5 Future Expectations for the Petrochemical Industry

As with fossil fuels, the reduction in raw materials derived from petroleum will be one of the premises for the future of the oil industry. This will be achieved through greater investment in C-1 chemistry technologies, i.e., the chemistry of compounds with one carbon atom. As is well known, methane can be obtained directly from associated gas in oil fields, as well as from biogenic sources such as natural gas, or as components of methane hydrates in the subsoil or deep seas [70]. The development of more efficient technologies for producing chemical compounds from methane will minimize future dependence on raw materials from refining processes, since virtually all chemical precursors that currently come from petroleum derivatives (paraffins, olefins, aromatics, CO, and hydrogen) can also be obtained from methane [69]. Initiatives in the development of technologies for dry reforming methane, partial

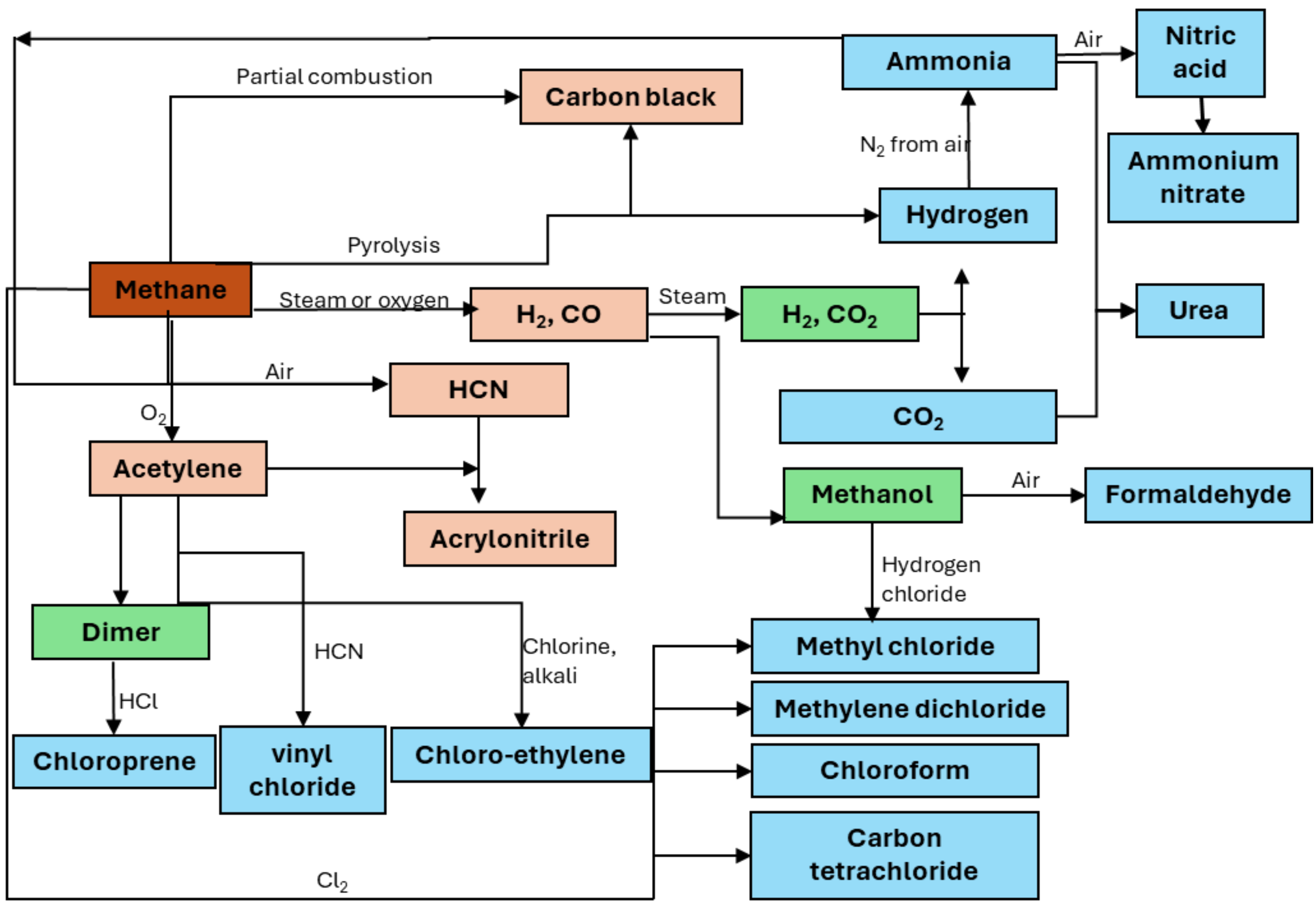

Figure 8. Chemicals obtained from methane.

oxidation, etc., which yield synthesis gas ($CO + H_2$), would lead to transformation processes in which petrochemical processes could be simplified using C1 chemistry as the primary raw material. Another important challenge is obtaining hydrogen, as the current process for producing it is highly polluting (gray hydrogen). Although methane is an important source of hydrogen, investments in obtaining this valuable gas by electrochemical methods from water represent a much more sustainable alternative for the future. As shown in Figure 9, methanol, a high-demand chemical product on the market, is currently produced from synthesis gas. Therefore, in the coming years, processes such as methanol-to-olefins (MTO), methanol to propylene (MTP), and the F-T process, which convert synthesis gas into hydrocarbons, are expected to achieve production levels that will cover more than 50% of market demand. For this reason, sustainable hydrogen production must be completed in the near future, which is closely related to the more efficient use of renewable energies, such as solar, wind, or nuclear, to obtain the energy needed to break down water molecules. Figure 10 effectively illustrates the material and energy fundamentals necessary for the sustainable development of the oil industry in the coming decades.

4.6 Process Simplification

The implementation of the Net Zero objective, which aims to eliminate all CO_2 emissions across the economy, will soon make the procurement of raw materials and renewable energy sources a critical necessity. While changes cannot happen overnight, the reconstruction of petrochemical processes will need to be restructured in different stages, depending on the evolution of the maturity of current petrochemical processes, the level of equipment utilization, and the availability of renewable energy, which will evolve in the short, medium, and long term. This is clearly illustrated in Figure 11, which displays the short-, medium-, and long-term simplification routes.

In the short to medium term, green hydrogen and electricity technology will gradually reach maturity and scalability. Therefore, CO_2 emissions from C1 chemical technology will be significantly reduced

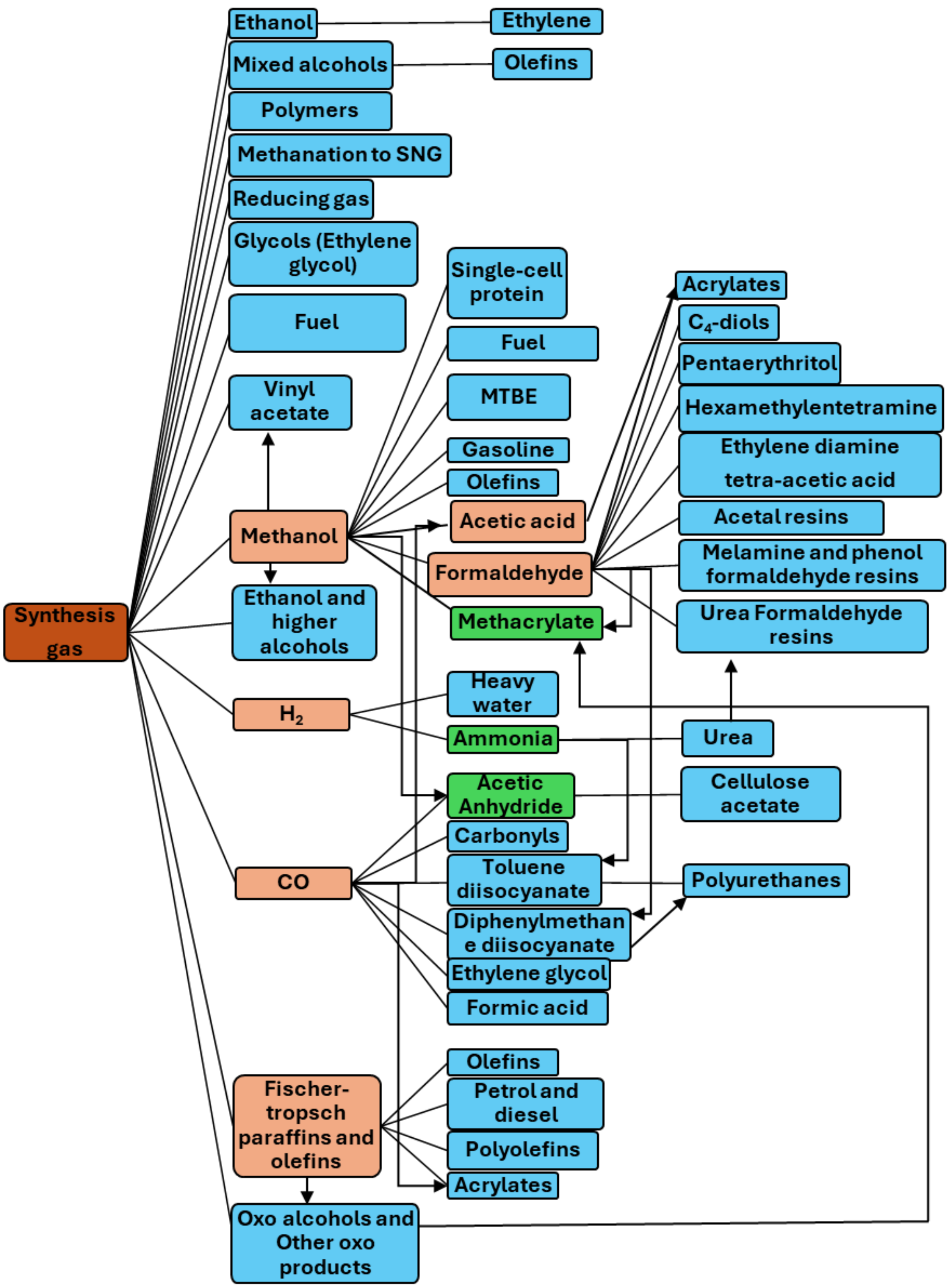

Figure 9. Syngas-derived chemicals.

thanks to the advent of green hydrogen production and renewable energy, which will replace gray hydrogen and fossil fuel electricity production. The forecast for olefins and aromatics produced using C1 chemistry is that they will be highly profitable, provided renewable energy as the process energy input. At this stage, based on current petroleum processes, simplified procedures could be implemented for heavy fractions (e.g., heavy and residual oils). In the long term, C1 chemical technology is expected to be fully developed, coupling

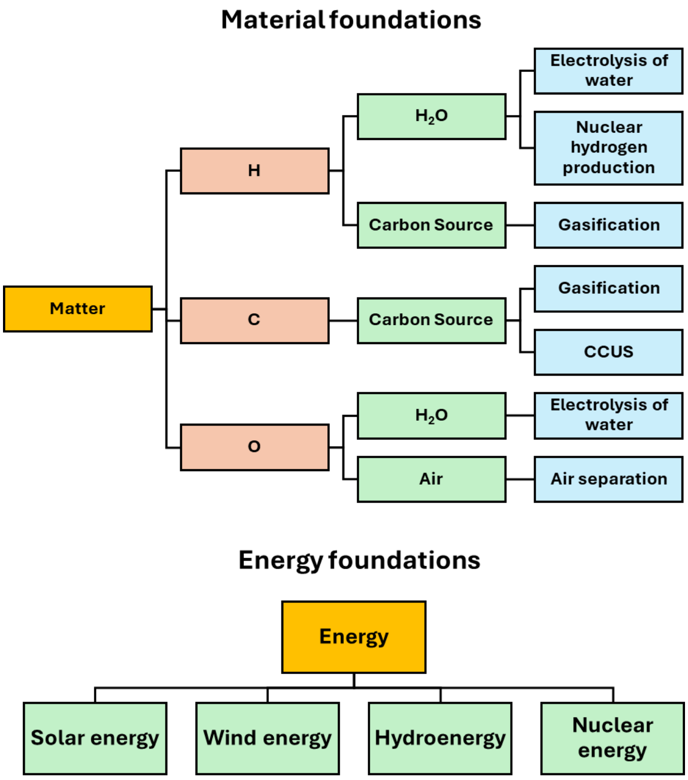

Figure 10. Material and Energy Bases for the Sustainable Development of the Petrochemical Industry.

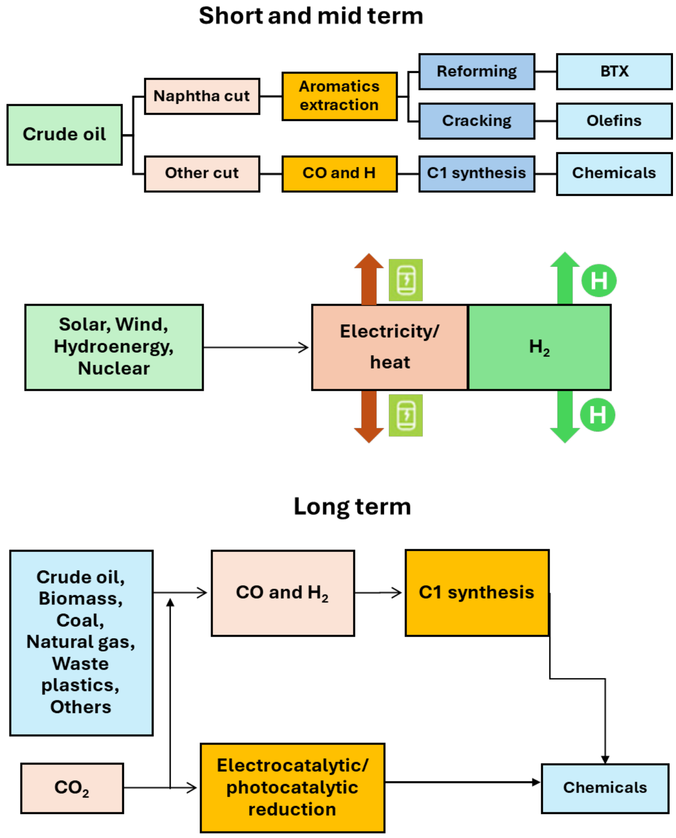

Figure 11. Short-term, medium-term, and long-term process simplification routes in petrochemical processes.

chemical transformation processes from synthesis gas with green hydrogen production and the use of renewable energy in a unified method for producing chemicals from natural gas, crude oil, biomass, coal, and plastic waste, as well as CO_2 as an additional carbon source. Such transformation processes must be sufficiently energy efficient and highly selective to prove highly economically viable [7, 76]. In the medium to the long term, once transportation fuels are replaced by electric batteries, global crude oil consumption is estimated to be significantly declined. At that point, there will be a total modification of the balance between oil supply and demand, most probably, the price of carbon from crude oil and that from coal will be equalized, and the cost of gasification from both sources will be unified.

5 Conclusions

With current advances in sustainable energy technologies, humanity has the tools it needs to meet the current emission reduction targets agreed upon for 2050. It is essential to recognize that current advances and future developments share a primary objective in research and development processes: to achieve the long-awaited goal of sustainable development. It is worth noting that the automotive industry has one of the largest commitments of any sector, second only to the construction and steel industries. Additionally, the oil industry, as we know it, is expected to decline significantly over the next few decades. The adoption of hydrocarbon-free technologies, such as fuel cells, the use of alternative fuels like hydrogen, ammonia, and formic acid, as well as the application of rapid renewable biofuels, will enable the transportation industry to finally break free from fossil fuels. On the other hand, the petrochemical industry is moving away from petroleum derivatives by seeking innovations in the field of C1 chemistry, i.e., derivatives of synthesis gas, which may one day result in the production of petrochemicals without the need for petroleum, i.e., they will only bear the name. On the other hand, the recycling industry must be able to grow rapidly to capitalize on petrochemical waste, primarily plastics, from which synthesis gas can be obtained, allowing the cycle to begin again. There are still significant challenges, but with increased investment in science and technology, they can be overcome in an optimistic scenario.

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