

# CO<sub>2</sub> derived e-fuels: research trends, misconceptions, and future directions

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## Abstract

CO<sub>2</sub> neutral fuels (e-fuels) are considered to be a pragmatic and practical way of decreasing overall CO<sub>2</sub> emissions derived from the transportation sector. However, for e-fuels to succeed and have a short-to-medium impact on climate mitigation, they should be fully compatible with existing fuel distribution infrastructure and vehicle technologies, such that they become literally drop-in replacements. In this short review, we first highlight the necessary properties that e-fuels should display to become a drop-in alternative to traditional petroleum derived fuels. With this information in hand, we revisit the current trends and limitations in the field of CO<sub>2</sub> conversion to fuels, highlighting the many misconceptions that the scientific literature has created over the last few years. Finally, we share our view on future research strategies that may help realize the widespread implementation of e-fuel technology.

**Keywords:** CO<sub>2</sub> conversion; Renewable Fuels; Methanol; Hydrocarbons

## **E-Fuels, why now?**

Liquid hydrocarbon fuels are widely used in road, air, and marine transportation, but the fossil feedstocks used to generate these fuels have significant environmental consequences [1]. The entire transport sector is responsible for nearly a quarter of total CO<sub>2</sub> emissions and consumes more than 50% of total liquid hydrocarbons produced, with more than 95% of the sector today continuing to rely on liquid hydrocarbons [2]. One way of decarbonizing mobility is to adopt battery electric vehicles (BEV) and/or hydrogen fuel cell vehicles (FCV) that do not rely on combustion of petroleum derived fuels. These technologies are rapidly increasing in commercialization and should be fully supported together with decarbonizing power generation and hydrogen production to lower life cycle emissions [3, 4]. However, even in the most ambitious scenarios for 2040, BEV and FCV only account for 30-50% of new car sales; nearly 75% of light duty vehicles on the road globally will still have internal combustion engines operating on liquid hydrocarbon fuels [5-7]. This is because plug-in hybrid vehicles will be sold in the marketplace for at least another two decades, and once on the road, they will remain in service for at least another 10 years. In addition, the widespread penetration of fully electric and fuel cell powertrains in heavy duty road vehicles and aviation is unlikely to be significant before 2050. Therefore, in order to meet global climate targets, there is an imminent need to commercialize low carbon or carbon-neutral liquid hydrocarbon fuels using renewable H<sub>2</sub> and CO<sub>2</sub> as the building blocks, the so-called **e-fuels** (see Glossary). E-fuels offer the only reliable approach for decarbonizing the large number of combustion engines that will remain in operation in the transport sector up to at least 2050. In this matter, the conversion of CO<sub>2</sub> to these carbon neutral fuels is a highly promising field that could tackle both our growing CO<sub>2</sub> emissions and the energy demand [5]. Not surprisingly, the number of publications in the field grows year after year [8-11].

However, there is a widespread misconception between typical CO<sub>2</sub> hydrogenation products and their usability and compatibility with existing power trains as e-fuels. To completely replace the use of petroleum hydrocarbons, it is important for e-fuels to be fully (or require very minor adaptations to be) compatible with existing fuel distribution infrastructure and vehicle technologies, such that they are literally drop-in replacements. E-fuels that are not drop-in replacements face significant hurdles to widespread adoption due to increased costs of vehicle modifications and infrastructure development. While alcohols, including methanol, ethanol, and

higher alcohols [12, 13] are suitable engine fuels, these, as well as other oxygenated fuels, face compatibility issues with existing fueling infrastructure when blended at very high concentrations. For example, compatibility studies have shown that alcohols [14, 15] have detrimental effects on various plastic and elastomer materials widely used in the fueling infrastructure. Therefore, the ideal drop-in e-fuels are non-oxygenated hydrocarbons with molecular structures not much different to those found in petroleum derived fuels.

Although excellent reviews exist on the CO<sub>2</sub> thermo-catalytic conversion field [16-23], very little emphasis has been put into highlighting the desired properties of CO<sub>2</sub> derived liquid e-fuels for a fast implementation. Nevertheless, and albeit being outside the scope of this review, the direct electrocatalytic reduction of CO<sub>2</sub> should also be taken into account, as highlighted in excellent recent reviews [24, 25]. Hence, in this short review, we first give some guidelines about fuel design and necessary properties to later critically assess the current trends and limitations in the field of CO<sub>2</sub> conversion to fuels. Finally, we outline a number of strategies that could fit the above requirements looking both at the catalytic results and techno-economic considerations.

### **Fuel requirements for a hydrocarbon mixture**

Conventional petroleum derived fuels are complex mixtures of hundreds to thousands of individual components resulting from various crude oil refining steps aimed at meeting specific target fuel properties. Therefore, the principal feature of a candidate e-fuel should be its ability to match the fuel properties (both physical and chemical). Gasoline, diesel, and aviation fuel properties are specified according to ASTM standards. Here, we focus on the most important fuel properties governing engine operation, while also ensuring compatibility with existing infrastructure.

In the case of **Spark Ignition (SI) engines**, research and motor octane numbers govern the fuel's ability to avoid knock (i.e., when the fuel/air mixture spontaneously ignites before the optimal time), and therefore the engine's ability to operate at its most efficient conditions [26]. While global octane number specifications vary slightly, a candidate e-fuel should have a **Research Octane Number (RON)** above 90-95 and **Motor Octane Number (MON)** above 85-90. Density, initial, and final boiling point are also important properties to ensure the right formation of a burnable mixture in the combustion chamber and to avoid too much unburned hydrocarbons. These properties are typically determined by the molecular weight distribution of the fuel. The aromatic content of SI engine fuels is typically less than 25% in order to avoid excess particulate matter

formation, while alkene content is limited to 5% to maintain adequate oxidative stability. Given these constraints, an ideal e-fuel would be an appropriate mixture of C<sub>5</sub>-C<sub>9</sub> linear and branched alkanes, C<sub>5</sub>-C<sub>6</sub> cycloalkanes, and/or C<sub>7</sub>-C<sub>9</sub> aromatics (see Table 1). The linear alkane fraction is typically limited to lower carbon chains because octane number decreases with increasing chain length. Branched alkanes preferably have multiple methyl substitutions, as this increases octane number [27].

In the case of **Compression Ignition (CI) engines**, the **Cetane Number (CN)** determines fuel reactivity in the engine [28], and values in excess of 45-55 are typical. Density, viscosity, and final boiling point are also important properties governing spray combustion, engine power, and pollutant formation. Specific molecular classes (e.g., aromatics and alkenes) are not constrained in diesel fuel specifications, but given the aforementioned properties, they are typically mixtures of C<sub>9</sub>-C<sub>20</sub> linear and branched alkanes, alkyl aromatics, and alkyl cycloalkanes (see Table 2). Aromatic and cycloalkane functionalities decrease cetane number, so these typically have long side chains (e.g., butylbenzene and butylcyclohexane) which increase cetane number. Linear alkanes have the highest cetane numbers, but solidify at room temperature above C<sub>17</sub>. High molecular weight lightly branched alkanes improve fuel volatility while also providing adequate cetane performance. The effects of skeletal branching to improve viscosity, cloud and pour points, cetane number, etc., have been explored in literature related to synthetic diesel fuel production. For example, hydrotreated vegetable oils (HVO) reaction conditions are typically optimized to obtain the desired ratio of iso-alkanes/n-alkanes [29]. The former are needed for their lower viscosity and cold flow properties, while the latter improve cetane performance [30]. Fuels derived from Fischer-Tropsch (FT) processes, such as gas-to-liquids fuels, have a high fraction of n-alkanes and poor cold flow properties [31]. Subsequent hydrocracking and hydroisomerization upgrading processes are designed to reach an optimal compromise between cold-flow properties and auto-ignition quality in the diesel fuel.

Finally, aviation fuels, or kerosene, are designed to operate in aero-propulsion engines (i.e., gas turbines) [32]. Aircrafts require high energy density fuels, so there is an imminent need to develop synthetic aviation fuels (SAFs) (e.g., e-fuels) with molecular compositions similar to current hydrocarbon fuels. Aviation fuels generally have less constraints on combustion properties (and hence composition) when compared to automotive fuels. This is largely because gas turbine

engines are designed to operate reliably on fuels that could vary significantly across international regions. Nevertheless, important jet fuel specifications around oxidative stability, cloud point, material compatibility, etc. do exist for safety concerns and to maintain engine operability limits. Large molecular weight hydrocarbons do not achieve the low freezing point requirements ( $\sim -40$  C), while smaller hydrocarbons lack the required energy density. Therefore, aviation fuels are typically C<sub>10</sub>-C<sub>16</sub> hydrocarbon comprising preferably normal and branched alkanes and cycloalkanes (see Table 3). Aromatics are less desirable due to their high sooting tendency, which results in smoky flames that produce less thermal energy available for propulsion. However, research has shown that a minimum level of aromatics (20-25%) is needed to prevent degradation of aged elastomers and subsequent fuel leakage. For this reason, most synthetic hydrocarbon aviation fuels (e.g., FT synthetic paraffinic kerosene, alcohol-to-jet, hydro-processed esters and fatty acids, etc.) must be blended with petroleum derived aromatics to achieve desired fuel specifications. It should be noted that prior use of oxygenates (e.g., fatty acid methyl esters from biologically derived oils) led to microbial growth and contamination of aviation fuel supply systems, such that these fuels are no longer permitted for safety reasons. Therefore, future aviation zero-carbon e-fuels should target composition similar to Table 3 to achieve drop-in compatibility.

### **Trends and limitations of the CO<sub>2</sub> conversion to fuels**

The main challenge in the conversion of CO<sub>2</sub> to fuels lies in the inertness of the CO<sub>2</sub> molecule and the associated substantial energy required for the carbon reduction. Additionally, controlling the selectivity of the desired product is not trivial due to the multiple competing reactions involved, like reverse water-gas shift (RWGS) or FT [33]. Therefore, developing active and highly selective catalysts is crucial to improve the process sustainability. This latter fact is of great importance because the above-mentioned inertness of CO<sub>2</sub> thus necessitates the use of expensive hydrogen as a co-reagent to activate CO<sub>2</sub> [34]. Therefore, any loss of selectivity implies the consumption of avoidable H<sub>2</sub> that hinders the final economical process viability. We will come back to this vital fact in the below techno-economical section of the review. Now, if we look at the current trends in CO<sub>2</sub> conversion to fuels, we can easily divide them into 4 subfields depending on the final product: i) CO<sub>2</sub> to Natural Gas (CH<sub>4</sub>); ii) CO<sub>2</sub> to methanol (MeOH); iii) CO<sub>2</sub> to higher alcohols; and iv) CO<sub>2</sub> to C<sub>2+</sub> hydrocarbons. From the above discussed fuel requirements, we can theorize that only the CO<sub>2</sub> to C<sub>2+</sub> hydrocarbons strategy could yield a drop-in liquid e-fuel compatible with

existing distribution infrastructure and vehicle technologies. We nevertheless need to remark the importance of MeOH produced from CO<sub>2</sub> as energy carrier and chemicals platform. MeOH is the simplest and safest to store and transport liquid oxygenated hydrocarbon and, although it cannot be used directly as drop in e-fuel in the actual vehicle engines, it can be efficiently used to generate electricity in fuel cells or as liquid energy storage [35]. Additionally, MeOH can also be used as chemical feedstock to produce olefins and aromatics as well as practically all hydrocarbons currently obtained from fossil fuels [36]. Moreover, MeOH is probably one of the easiest products to obtain from CO<sub>2</sub> with high selectivity and low undesired by-products [37], which makes it an indispensable partner to achieve the net zero CO<sub>2</sub> emissions target [38, 39].

Coming back to the CO<sub>2</sub> to C<sub>2+</sub> hydrocarbons strategy, there are two well-established routes to synthesize these C<sub>2+</sub> hydrocarbons from CO<sub>2</sub> depending on the reaction intermediate: i) the direct hydrogenation of CO<sub>2</sub> via FTS, or ii) the conversion of CO<sub>2</sub> into methanol on a metal oxide catalyst followed by subsequent transformation into hydrocarbons over a zeolite [23]. In case of the FTS pathway, the product distribution is limited by the well-known Anderson–Schulz–Flory (ASF) relationship [33], and, as consequence, the main challenge of this process is to control alkane selectivity while being able to optimize chain length. In this regard, Fe-K systems (either bulk [40, 41] or based on novel materials as Metal-Organic Frameworks (MOFs) [42]) have been recorded as the most promising catalysts, displaying CO<sub>2</sub> conversions close to 50% with reasonably high light-olefin (C<sub>2</sub>-C<sub>4</sub>) selectivities up to 40%. However, this route by itself cannot yield some essential components for the drop-in e-fuels (like cycloalkanes or alkylated aromatics, see Table 1 and Table 2).

To solve this issue, zeolites can also be combined with Fe-based catalysts forming a bifunctional system that can directly transform CO<sub>2</sub> to a great variety of chemicals with selectivities that break the ASF distribution [23]. Wei and coworkers designed a multifunctional catalyst by coupling a Na–Fe<sub>3</sub>O<sub>4</sub> catalyst with different zeolites in order to obtain gasoline range hydrocarbons [43]. In particular, with the Na–Fe<sub>3</sub>O<sub>4</sub>/ZSM-5 bifunctional combination they reached C<sub>5</sub>–C<sub>11</sub> hydrocarbon selectivity up to 78% at a CO<sub>2</sub> conversion of 25% (see Figure 1). The driving force of this bifunctional system was attributed to the oligomerization and aromatization of the light olefins (produced in the Na–Fe<sub>3</sub>O<sub>4</sub> component) on the ZSM-5 zeolite. The same authors also observed that the selectivity could be shifted to mostly branched alkanes if ZSM-5 were replaced by

HMC-22 [44]. Similarly, a recent study by Liu and coworkers demonstrated a strategy to achieve above 90% selectivity to aromatics in the liquid fraction over a bifunctional Na-Fe/ZSM-5 catalyst [45]. Additionally, they were able to shift the p-xylene in total xylenes from 24–26% to 70% when ZSM-5 was coated with SiO<sub>2</sub>. This coating on the external surface of the zeolite suppressed the external acid sites and avoided the further transformation of the as formed p-xylene. Similar results were also recently reported by Cui and colleagues [46] with a ZnFeO<sub>x</sub>/ZSM-5 system. Nevertheless, despite some of the above works claiming the direct production of fuels from CO<sub>2</sub>, none of them characterized the produced liquid hydrocarbons (via RON/MON/CN measurements) to determine their suitability as a drop-in e-fuel.

Considering now the methanol-mediated route, several bifunctional catalysts have been studied based typically either on SAPO-34 (targeting olefins) or ZSM-5 (targeting aromatics) [23]. For example, Li and coworkers reported a ZnZrO/SAPO-34 bifunctional catalyst that displayed 80% light olefins selectivity among hydrocarbons [47]. Similar results with high selectivity to light olefins in the hydrocarbon fraction were reported over other SAPO-34 based systems like In-Zr/SAPO-34 [48] or ZnGa<sub>2</sub>O<sub>4</sub>/SAPO-34 [49]. Nevertheless, despite the promising results, this product range is not suitable for its use directly as e-fuel. Apart from SAPO-34, ZSM-5 zeolite has also been widely studied looking for selective production of aromatics [50-53]. As we observed from the above work of Wei and colleagues [43], this metal-zeolite combination could be much more promising in the synthesis of e-fuels with the target composition mentioned above. In this frame, Gao and colleagues [52] reported the direct conversion of CO<sub>2</sub> into liquid fuels with high selectivity over a bifunctional catalyst based on the combination of Indium Oxides and ZSM-5. In particular, they achieved high selectivity to gasoline-range products (C<sub>5+</sub>, >75%) with a very low methane selectivity (1%) among hydrocarbons. Moreover, they also performed industry-relevant tests with pellet catalysts and a tail-gas recycling reactor that improved further the catalytic performance. It goes without saying that similar this experimental approach is of vital importance for industrial applications of bifunctional CO<sub>2</sub> conversion systems. In a more recent work, Wang and colleagues reported a bifunctional catalyst composed of Cr<sub>2</sub>O<sub>3</sub> and ZSM-5 zeolite that displayed aromatics selectivity up to 75% in the hydrocarbon fraction with CO<sub>2</sub> conversion of 35% [50], one of the highest aromatic yields reported to date. Special emphasis was given towards the modification of the zeolite with the already discussed encapsulating with silica to suppress the undesired alkylation and isomerization of xylenes.

None of the above MeOH-mediated works characterized the fuel compatibility of the produced liquid hydrocarbon mixtures. We also need to remark that usually the main product of the MeOH route is undesired CO due to the usually high temperatures needed for the zeolite to be active (i.e., 350 °C), often above the comfort zone of the MeOH producing catalyst (~250 °C) [23]. To camouflage this drawback, several groups report CO free hydrocarbon selectivities instead of total selectivities, painting an unrealistic picture of the catalyst performance. New lines of research claim lower CO selectivity when additional CO is co-fed to the system [53] due to equilibrium displacement but, still, development of low CO selectivity MeOH catalysts at high temperature operation is a must for the future of this methanol bifunctional route.

Additionally, we also need to remark on the common practice of absolute lack of deep characterization of the zeolite component after reaction. Since multiple reactions are involved in the zeolite component (e.g., oligomerization, cracking, dehydrogenation, cyclization, alkylation, and isomerization), a deep understanding of the chemistry that takes place here is essential to advance the field forward. Instead, the general accepted trend lies on focusing on SAPO-34 or ZSM-5 and combining them with all possible mixed oxides of the periodic table to achieve higher selectivities/yields to these so-called fuels (that are also not characterized in terms of octane/cetane number). To try to unravel these complex reaction mechanisms, several groups have recently started to perform in-depth characterization via solid-state magic angle spinning Nuclear Magnetic Resonance (NMR) spectroscopy on the spent zeolites [54, 55], as they are key components of the bifunctional systems. We have found that CO plays a key role in these bifunctional systems via formation of surface-carbonylated species on the zeolite framework (Figure 2). Hence, further studies on this direction are needed to unravel the complicated reaction network and achieve the final goal of high selectivities to the desired e-fuel fraction.

### **Thermodynamic and Techno-economic considerations**

From the above sections we can conclude that, despite abundant misconceptions, there are already some promising bifunctional catalytic systems (especially based on ZSM-5) that could eventually yield drop-in e-fuels. However, little effort has been dedicated to assess how these results will fit into a real industrial process. The first hurdle to arrive to good assessments is the lack of kinetic studies on new catalytic systems. Indeed, for instance, most kinetic studies on the MeOH-mediated route focus on the commercial CuZn catalyst [20, 56-60].

From a thermodynamic point of view, the Fischer-Tropsch route seems more convenient considering that in this case only the first (RWGS) is equilibrium limited. To surpass equilibrium limitations, membrane reactors [61] with *in-situ* water removal have been applied [62, 63]. Recently, Li and colleagues [61] demonstrated that water conduction nanochannels could be created by assembling NaA zeolite crystals into a continuous, defect-free membrane (Figure 3). Water separation with high H<sub>2</sub>O/CO<sub>2</sub> selectivity (~ 550) was the result of a gating effect of the Na<sup>+</sup> ions located in the 8-oxygen ring apertures that regulated their effective size. This highly efficient *in situ* water removal through water-conduction nanochannels led to a substantial increase in CO<sub>2</sub> conversion (up to 61.4%, above the equilibrium conversion), resulting in a methanol space-time yield (STY) of 809 mg·g<sub>cat</sub><sup>-1</sup>hour<sup>-1</sup> at GHSV of 10500 ml·g<sub>cat</sub><sup>-1</sup>hour<sup>-1</sup>, 250 °C and 35 bar, the highest value ever reported under similar conditions. However, this promising concept has only been experimentally applied to (again) the methanol synthesis pathway. We envision that applying this kind of water removal reactor concepts to the bifunctional catalyst family targeting e-fuel will undoubtedly help to reach better and better fuel yields. In particular, applying this water removal process could help to increase the conversion of CO<sub>2</sub> above the thermodynamic limitations and, at the same time, help to prolong the lifetime of the zeolite component by preventing dealumination by steam [64, 65].

From the process point of view, process simulations in the CO<sub>2</sub> conversion field have primarily focused on the CO<sub>2</sub> to methanol reaction [66-68]. In fact, most of the process flowsheets in these studies share the same blocks and unit operations, only the hydrogen or CO<sub>2</sub> sources vary. In short, the process (Figure 4) consists of: (i) several feed compression steps; (ii) a fixed bed reactor (always filled with the commercial CuZn catalyst due to the lack of kinetics for other systems); (iii) a first flash separation where the liquid fraction is removed and the water-free gases are recycled to the reactor; (iv) a purge to avoid the accumulation of inerts; and (v) a final distillation column to obtain the high purity methanol. The recycle of the water-free gaseous stream is fundamental here as overall CO<sub>2</sub> conversions higher than 90% can be achieved [49]. Hence, single pass conversion is not as critical as the selectivity for a real process due to the recycle stream. . Finally, yet importantly, all the discussed ASPEN process simulations share one vital fact: with the current green hydrogen prices [16, 34, 69] the CO<sub>2</sub> conversion to MeOH is not financially viable and H<sub>2</sub> prices below 2\$ per Kg are needed to reach breakeven [66-68]. This fact is of special importance as, with the current electrolyzers, a price of around 2.5\$ per Kg is only foreseen for

the next decade [34]. Therefore, either a severe taxation to CO<sub>2</sub> emissions or a drastic increase of MeOH prices (>2 fold increase) is currently needed [68]. Moreover, most of the process simulations are carried out assuming that the H<sub>2</sub> will be delivered at 30 bars from the electrolyzer which is not realistic and, therefore, H<sub>2</sub> compression costs should also be included. This will undoubtedly hinder even more the viability of the process as H<sub>2</sub> compression is one of the most expensive processes in industry and, even with the 30 bars feed assumption, these compression steps are already the most expensive units in the above discussed simulations followed by the heat exchangers network [66-68]. Hence, economic considerations also need to be taken in consideration and the process must be kept as simple as possible to overcome the drawback of the high hydrogen price while always looking towards highly selective catalysts to minimize hydrogen consumption. Summing up, here we envision that the forthcoming process for the direct production of liquid e-fuels from CO<sub>2</sub> will be very simple and close to the one depicted in Figure 4 with minor changes required, like replacing the CuZn catalyst in the reactor to a highly selective e-fuel bifunctional catalyst (that needs to be kinetically modelled) or adapting the final distillation step to separate water and the e-fuel instead of methanol.

### **Concluding remarks**

In conclusion, we believe that more focus should be brought to the field of e-fuels for them to become a practical (and pragmatic) solution to the issue of CO<sub>2</sub> emissions derived from mobility. Considering that the existing infrastructure, both in terms of distribution and power trains, will remain nearly unchanged for the years to come along with the more than urgent need to move our society towards carbon neutrality, one can easily identify the great opportunity for e-fuels. However, it is of the highest importance for those working in the field to realize that the chances for these CO<sub>2</sub> derived fuels to succeed will strongly depend on their compatibility with existing technology and infrastructure. In spite of the challenge, from a fundamental point of view, the design of e-fuels opens great opportunities for catalysis experts and process engineers. Indeed, most of the boundary conditions (fuel composition, price, feedstock) for near- and medium-term deployment are clear, now it is a matter of finding the most economical route towards the synthesis of these fuels from CO<sub>2</sub> and green hydrogen. To reach this objective: (i) fundamental mechanistic understanding; (ii) the development of efficient multifunctional catalysts; (iii) the rigorous testing and characterization of the obtained fuels; and (iv) the design of the most adequate process layout, have to go hand by hand. We specially believe that the lack of ex situ characterization of the spent

zeolite catalyst component needs to be addressed by the scientific community in order to achieve a fundamental mechanistic understanding, essential requisite for catalyst development. We also call for a ban of the misleading practice of reporting CO free selectivities masked as total selectivities, as this will only cause confusion to the potential readers and give an unrealistic view of the catalyst performance. Last but not least, improvements in harvesting of renewable energy and its utilization for the manufacture of green hydrogen and CO<sub>2</sub> capture, along with the development of appropriate policy for CO<sub>2</sub> neutral fuels will define the economic viability of these processes. In the long term, synergizing the design of novel fuel and vehicle engine technologies can pave the way for a wider range of e-fuel candidates to be commercialized. It goes without saying that, in doing so, the benefits of CO<sub>2</sub> neutral fuels for the environment and for the future of our society must play a decisive role in their widespread implementation.

## **Glossary**

**Cetane number (CN):** quantitative metric of a fuel's ignition quality under non-premixed combustion conditions found in CI engines. Higher cetane number fuels display better ignition quality and fuel burn within the engine of a vehicle. The cetane number is similar to the octane rating in that it is a rating assigned to a fuel to rate the quality of its combustion.

**Compression Ignition (CI) engine:** internal combustion engine in which ignition of the fuel is caused by the elevated temperature of the air in the cylinder due to the mechanical compression (adiabatic compression).

**e-fuels:** fuels, such as hydrogen, methane, synthetic petrol, diesel, or kerosene that have been generated from renewable electricity.

**Research Octane Number (RON) and Motor Octane Number (MON):** quantitative metrics of a fuel mixture's resistance to "knocking" under premixed combustion conditions found in SI engine. The octane number of a particular sample is measured against a standard blend of n-heptane, which has zero octane, and iso-octane, which has 100 octane. The RON simulates an SI engine operating under low severity conditions (at 600 rpm and 49 °C air temperature), whereas the MON reflects more severe conditions (at 900 rpm and 149 °C air temperature).

**Spark Ignition (SI) engine:** internal combustion engine where the combustion process of the air-fuel mixture is ignited by a spark from a spark plug.

**Zeolite:** microporous aluminosilicate minerals commonly used as commercial adsorbents and catalysts.

## References

1. WMO Statement on the State of the Global Climate. (2019) World Meteorological Organization (WMO).
2. International Energy Outlook 2019. (2019) U.S. Energy Information Administration.
3. Bauer, C. et al. (2015) The environmental performance of current and future passenger vehicles: Life cycle assessment based on a novel scenario analysis framework. *Appl. Energy*. 157, 871–883.
4. Wang, D. et al. (2013) Life cycle analysis of internal combustion engine, electric and fuel cell vehicles for China. *Energy*. 59, 402-412.
5. BP Energy Outlook 2019. (2019) BP p.l.c.
6. B. Kilbey, 2020 Long Term Electric Vehicle Outlook
7. Kapustin, N.O. et al. (2020) Long-term electric vehicles outlook and their potential impact on electric grid. *Energy Policy*. 137, 111103.
8. Shih, C.F. et al. (2018) Powering the Future with Liquid Sunshine. *Joule*. 2, 1925-1949.
9. Dittmeyer, R. et al. (2019) Crowd oil not crude oil. *Nat. Commun*. 10, 1818.
10. Fennell, S. et al. (2017) The role of CO<sub>2</sub> capture and utilization in mitigating climate change. *Nat. Clim. Change*. 7, 243–249.
11. Centi, G. et al. (2013) Catalysis for CO<sub>2</sub> conversion: a key technology for rapid introduction of renewable energy in the value chain of chemical industries. *Energy Environ. Sci*. 6, 1711-1731.
12. Sarathy, S.M. et al. (2014) Alcohol combustion chemistry. *Prog. Energy Combust. Sci*. 40-102.
13. Sarathy, S.M. (2016) Fuel Class Higher Alcohols, in *Biofuels from Lignocellulosic Biomass*. Wiley-VCH, Germany.
14. Kass, M. et al. (2012) Compatibility Study for Plastic, Elastomeric, and Metallic Fueling Infrastructure Materials Exposed to Aggressive Formulations of Ethanol-blended Gasoline. Oak Ridge National Laboratory. Report ORNL/TM-2012/88.
15. Durbin, T.D. et al. (2016) Compatibility Study of Alternative Fuels with Existing Infrastructure. California Energy Commission. CEC-500-2016-042.
16. Hepburn, C. et al. (2019) The technological and economic prospects for CO<sub>2</sub> utilization and removal. *Nature*. 575, 87-97.

17. Saeidi, S. et al. (2014) Hydrogenation of CO<sub>2</sub> to value-added products-A review and potential future developments. *J. CO<sub>2</sub> Util.* 5, 66-81.
18. Álvarez, A. et al. (2017) Challenges in the Greener Production of Formates/Formic Acid, Methanol, and DME by Heterogeneously Catalyzed CO<sub>2</sub> Hydrogenation Processes. *Chem. Rev.* 117, 9804-9838.
19. Wang, W. et al. (2011) Recent advances in catalytic hydrogenation of carbon dioxide. *Chem. Soc. Rev.* 40, 3703–3727.
20. Saeidi, S. et al. (2017) Mechanisms and kinetics of CO<sub>2</sub> hydrogenation to value-added products; A detailed review on current status and future trends. *Renew. Sust. Energ. Rev.* 80, 1292-1311.
21. Li, W. et al. (2018) A short review of recent advances in CO<sub>2</sub> hydrogenation to hydrocarbons over heterogeneous catalysts. *RSC Adv.* 8, 7651–7669.
22. Yang, H. et al. (2017) A review of the catalytic hydrogenation of carbon dioxide into value-added hydrocarbons. *Catal. Sci. Technol.* 7, 4580-4598.
23. Dokania, A. et al. (2019) Heterogeneous Catalysis for the Valorization of CO<sub>2</sub>: Role of Bifunctional Processes in the Production of Chemicals. *ACS Energy Lett.* 4, 167-176.
24. De Luna, P. et al. (2019) What would it take for renewably powered electrosynthesis to displace petrochemical processes? *Science.* 364, eaav3506.
25. Jhong, H.M. et al. (2013) Electrochemical conversion of CO<sub>2</sub> to useful chemicals: current status, remaining challenges, and future opportunities. *Curr. Opini. Chem. Eng.* 2, 191-199.
26. Sarathy, S.M. et al. (2018) Recent progress in gasoline surrogate fuels. *Prog. Energy Combust. Sci.* 65.
27. Boot, M.D. et al. (2017) Impact of fuel molecular structure on auto-ignition behavior – Design rules for future high performance gasolines. *Prog. Energy Combust. Sci.* 60, 1-25.
28. Pitz, W.J. and Mueller, C.J. (2011) Recent progress in the development of diesel surrogate fuels. *Prog. Energy Combust. Sci.* 37, 330-350.
29. Simacek, P. et al. (2011) Premium quality renewable diesel by hydroprocessed sunflower oil. *Fuel.* 90, 2473– 2479.
30. Lapuerta, M. et al. (2016) Effects of methyl substitution on the auto-ignition of C<sub>16</sub> alkanes. *Combust. Flame.* 164, 259–269.
31. Dry, M.E. (2002) The Fischer–Tropsch process: 1950–2000. *Catal. Today.* 71, 227– 241.

32. Maurice, L.Q. et al. (2001) Advanced aviation fuels: a look ahead via a historical perspective. *Fuel*. 80, 747-756.
33. Riedel, T. et al. (2003) Fischer-Tropsch on iron with H<sub>2</sub>/CO and H<sub>2</sub>/CO<sub>2</sub> as synthesis gases: The episodes of formation of the Fischer-Tropsch regime and construction of the catalyst. *Top. Catal.* 26, 41–54.
34. Glenk, G. et al. (2019) Economics of converting renewable power to hydrogen. *Nat. Energy*. 4, 216–222.
35. Olah, G.A. et al. (2009) *Beyond Oil and Gas: The Methanol Economy*. Wiley-VCH Verlag GmbH & Co. KGaA
36. Yarulina, I. et al. (2018) Recent trends and fundamental insights in the methanol-to-hydrocarbons process. *Nat Catal.* 1, 398–411.
37. Alvarez, A. et al. (2017) Challenges in the Greener Production of Formates/Formic Acid, Methanol, and DME by Heterogeneously Catalyzed CO<sub>2</sub> Hydrogenation Processes. *Chem. Rev.* 117, 9804–9838.
38. Pontze, F. et al. (2011) CO<sub>2</sub>-based methanol and DME – Efficient technologies for industrial scale production. *Catal. Today*. 171, 242-250.
39. Daggash, H.A. et al. (2018) Closing the carbon cycle to maximise climate change mitigation: power-to-methanol vs. power-to-direct air capture. *Sustain. Energ. Fuels*. 2, 1153-1169
40. Russkikh, A. et al. (2020), Turning Waste into Value: Potassium-Promoted Red Mud as an Effective Catalyst for the Hydrogenation of CO<sub>2</sub>. *ChemSusChem*. DOI: 10.1002/cssc.202000242
41. Visconti, C. G. et al (2017). CO<sub>2</sub> hydrogenation to lower olefins on a high surface area K-promoted bulk Fe-catalyst. *Appl. Catal. B Environ.* 200, 530-542.
42. Ramirez, A. et al. (2018) Metal Organic Framework-Derived Iron Catalysts for the Direct Hydrogenation of CO<sub>2</sub> to Short Chain Olefins. *ACS Catal.* 8, 9174-9182.
43. Wei, J. et al. (2017) Directly Converting CO<sub>2</sub> into a Gasoline Fuel. *Nat. Commun.* 8, 15174.
44. Wei, J. et al. (2018) Catalytic Hydrogenation of CO<sub>2</sub> to Isoparaffins over Fe-Based Multifunctional Catalysts. *ACS Catal.* 8, 9958-9967.
45. Xu, Y. et al. Selective production of aromatics from CO<sub>2</sub>. *Catal. Sci. Technol.* 9 , 593-610.
46. Cui, X. et al. (2019) Selective Production of Aromatics Directly from Carbon Dioxide Hydrogenation. *ACS Catal.* 9, 3866-3876.

47. Li, Z. et al. (2017) Highly Selective Conversion of Carbon Dioxide to Lower Olefins. *ACS Catal.* 7, 8544-8548.
48. Dang, S. (2018) Role of Zirconium in Direct CO<sub>2</sub> Hydrogenation to Lower Olefins on Oxide/Zeolite Bifunctional Catalysts. *J. Catal.* 364, 382-393.
49. Liu, X. et al. (2018) Selective Transformation of Carbon Dioxide into Lower Olefins with a Bifunctional Catalyst Composed of ZnGa<sub>2</sub>O<sub>4</sub> and SAPO-34. *Chem. Commun.* 54, 140-143.
50. Wang, Y. et al. (2019) Rationally Designing Bifunctional Catalysts as an Efficient Strategy To Boost CO<sub>2</sub> Hydrogenation Producing Value-Added Aromatics. *ACS Catal.* 9, 895-901.
51. Ni, Y. et al. (2018) Selective Conversion of CO<sub>2</sub> and H<sub>2</sub> into Aromatics. *Nat. Commun.* 9, 3457.
52. Gao, P. et al. (2017) Direct Conversion of CO<sub>2</sub> into Liquid Fuels with High Selectivity over a Bifunctional Catalyst. *Nat. Chem.* 9, 1019.
53. Li, T. et al. (2019) Direct CO<sub>2</sub> hydrogenation to light olefins by suppressing CO by-product formation. *Fuel Process. Technol.* 196, 106174.
54. Ramirez, A. et al. (2019) Effect of Zeolite Topology and Reactor Configuration on the Direct Conversion of CO<sub>2</sub> to Light Olefins and Aromatics. *ACS Catal.* 9, 6320-6334.
55. Dokania, A. et al. (2020) Acidity modification of ZSM-5 for enhanced production of light olefins from CO<sub>2</sub>. *J. Catal.* 381, 347-354.
56. Villa, P. et al. (1985) Synthesis of alcohols from carbon oxides and hydrogen. 1. Kinetics of the low-pressure methanolsynthesis, *Ind. Eng. Chem. Process Des. Develop.* 24, 12-19.
57. Vanden Bussche, K.M and Fromen, G.F. (1996) A steady-state kinetic model for methanol synthesis and the water gas shift reaction on a commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst, *J. Catal.* 161, 1-10.
58. Seidel, C. et al. (2018) Kinetic modeling of methanol synthesis from renewable resources, *Chem. Eng. Sci.* 175, 130-138.
59. Riedel, T. et al. Kinetics of CO<sub>2</sub> Hydrogenation on a K-Promoted Fe Catalyst. *Ind. Eng. Chem. Res.* 40, 1355-1363.
60. Willauer, H.D. et al. (2013) Modeling and kinetic analysis of CO<sub>2</sub> hydrogenation using a Mn and K-promoted Fe catalyst in a fixed-bed reactor. *J. CO<sub>2</sub> Util.* 3-4, 56-64.
61. Coronas, J. and Santamaría, J. (1999) Catalytic reactors based on porous ceramic membranes. *Catal. Today.* 51, 377-389.

62. Li, H. et al. (2020) Na<sup>+</sup>-gated water-conducting nanochannels for boosting CO<sub>2</sub> conversion to liquid fuels. *Science*. 367, 667.
63. Gallucci, F. et al. (2004) An experimental study of CO<sub>2</sub> hydrogenation into methanol involving a zeolite membrane reactor. *Chem. Eng. Process*. 43, 1029-1036.
64. Li, C. and Fujimoto, K. (2015) Efficient conversion of carbon dioxide to non-methane light hydrocarbons - Two stage process with intercooler. *Fuel Process. Technol.* 136, 50-55.
65. Lucas, A. et al. (1997) Dealumination of HZSM-5 zeolites: Effect of steaming on acidity and aromatization activity. *Appl. Catal. A: Gen.* 154, 221-240.
66. Van-Dal, E.S. and Bouallou, C. (2013) Design and simulation of a methanol production plant from CO<sub>2</sub> hydrogenation. *J. Clean. Prod.* 57, 38-45.
67. Milani, D. et al. (2015) A model-based analysis of CO<sub>2</sub> utilization in methanol synthesis plant. *J. CO<sub>2</sub> Util.* 10, 12-22.
68. Pérez-Fortes, M. (2016) Methanol synthesis using captured CO<sub>2</sub> as raw material: Techno-economic and environmental assessment. *Appl. Energy*. 161, 718-732.
69. González-Garay, A. et al. (2019) Plant-to-planet analysis of CO<sub>2</sub>-based methanol processes. *Energy Environ. Sci.* 12, 3425-3436.

**Table 1.** Hydrocarbon composition for a Spark Ignition (SI) engine e-fuel.

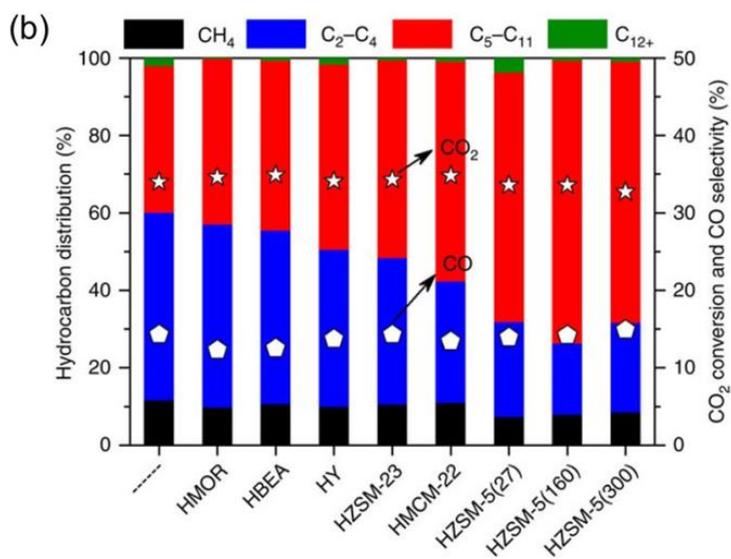
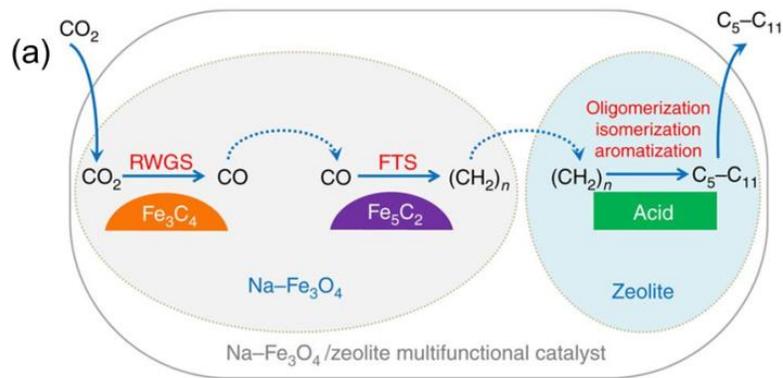
<b>Hydrocarbon Family</b>	<b>Composition range (volume %)</b>
C <sub>5</sub> -C <sub>9</sub> linear alkanes	10-20
C <sub>5</sub> -C <sub>9</sub> branched alkanes	40-50
C <sub>5</sub> -C <sub>6</sub> cycloalkanes	10-20
C <sub>7</sub> -C <sub>9</sub> aromatics	20-25

**Table 2.** Hydrocarbon composition for a Compression Ignition (CI) engine e-fuel.

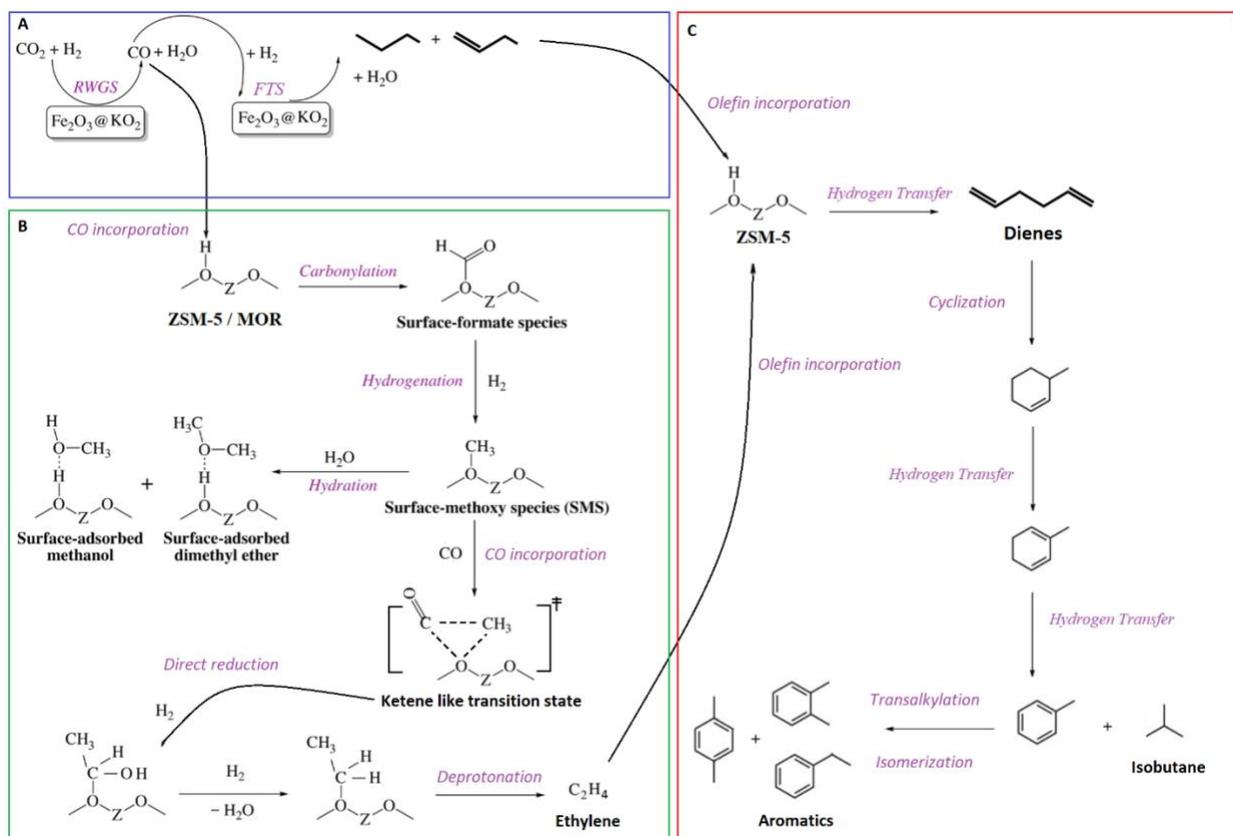
<b>Hydrocarbon Family</b>	<b>Composition range (volume %)</b>
C <sub>9</sub> -C <sub>16</sub> linear alkanes	35-50
C <sub>9</sub> -C <sub>20</sub> branched alkanes	10-20
Alkyl aromatics	20-30
Alkyl cycloalkanes	20-25

**Table 3.** Hydrocarbon composition for an aviation engine e-fuel.

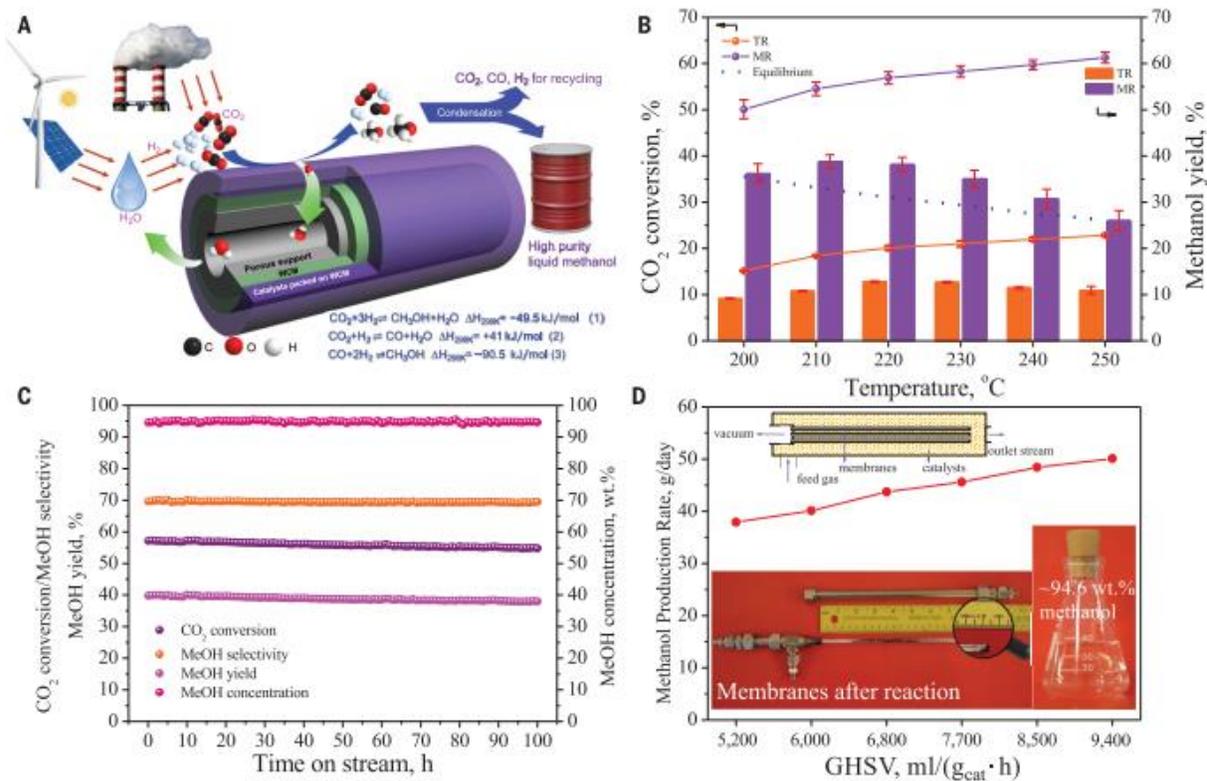
<b>Hydrocarbon Family</b>	<b>Composition range (volume %)</b>
C <sub>10</sub> -C <sub>12</sub> linear alkanes	10-30
C <sub>10</sub> -C <sub>14</sub> branched alkanes	20-40
Alkyl aromatics	20-25
Alkyl cycloalkanes	20-40



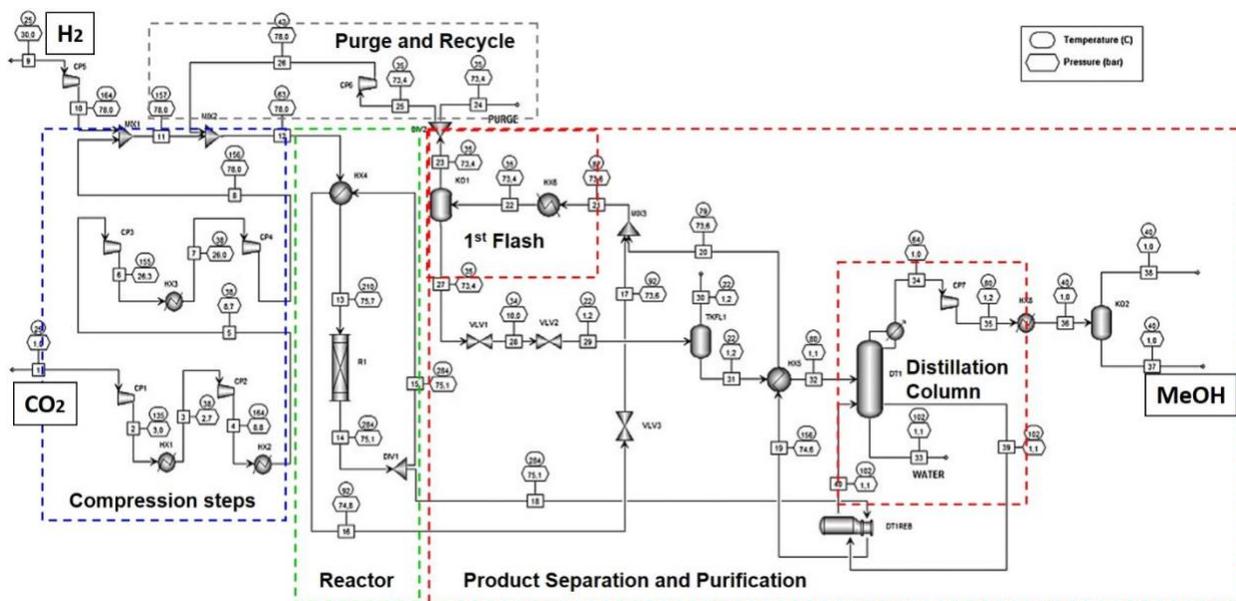
**Figure 1.** (A) Role of different active sites of a multifunctional catalyst in CO<sub>2</sub> hydrogenation to make gasoline-range hydrocarbons. (B) Product selectivity over different Na-Fe<sub>3</sub>O<sub>4</sub>/zeolite catalysts. Reproduced with permission from ref 43.



**Figure 2.** Proposed reaction pathways of the  $\text{Fe}_2\text{O}_3 @ \text{KO}_2$ /zeolite-catalyzed hydrogenation of  $\text{CO}_2$  to light olefins and aromatics. (A)  $\text{CO}_2$  hydrogenation pathway on the stand-alone  $\text{Fe}_2\text{O}_3 @ \text{KO}_2$  catalyst, (B) CO incorporation pathway on MOR and ZSM-5, (C) Aromatization pathway on ZSM-5. Reproduced with permission from ref 54.



**Figure 3.** (A) Schematics of the membrane reactor (MR) concept and (B, C, D) catalytic performance of the MR. Reproduced with permission from ref 62.



**Figure 4.** Flowsheet of the  $\text{CO}_2$  to methanol process plant. Adapted with permission from ref 66.