Synthetic automotive fuels

The article explains the differences between synthetic fuels of first and second generation. The potential of e-fuels to reduce GHG emissions was indicated. The application requirements that synthetic fuels need to meet in order to be used for powering internal combustion engines have been described. The possibility of using synthetic fuels as "drop-in" fuels, in blends with conventional petroleum-derived fuels as well as by themselves was discussed. E-fuels developed and optimized to power compression ignition and spark ignition engines were characterized. The possibilities of synthetic fuels to reduce emissions of regulated and unregulated exhaust components and to improve the work and operational parameters of the engine were also analyzed using the research carried out so far as basis. At the end of the article, forecasts for synthetic fuels development and applications were presented in the form of a SWOT analysis.

Key words: synthetic fuels, combustion engines, synthetic fuel applications, exhaust emissions

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1. Introduction

The statutory requirements for climate protection result in an increasing need for a drastic reduction of greenhouse gases (GHG) generated by the transport sector. At the same time, the current and future limit values for exhaust emissions from regulated internal combustion engines must be met. Given the need to diversify future types of powertrains, several technological options are being considered. In particular, battery electric vehicles (BEV), fuel cell electric vehicles (FCEV), and advanced low-emission fuels, such as synthetic fuels and renewable biofuels [8, 11, 18, 23, 29, 30, 39, 40–43, 46], are mentioned as potential solutions to reduce greenhouse gas emissions in the transport sector. In order to minimize the total CO₂ emissions, it is necessary to rationally use various drive systems technologies, including internal combustion engines powered by synthetic fuels. It should not be forgotten that greenhouse gas emissions and climate change are inherently a global and complex problem that requires an integrated approach, one that encourages innovation and avoids dependence on a single technology. Meanwhile, the current EU legal regulations focus solely on e-mobility, leaving no room for other technologies or technological competition to achieve climate goals. This approach indicates a departure from the current practice of adopting a balance between different technologies. The significant potential to reduce CO₂ from the existing vehicle fleet is also being ignored. However, looking at the future development of the global vehicle fleet, even assuming a significant level of electrification of all newly registered vehicles in the coming years, a significant reduction in CO₂ emissions could still be achieved using even low levels of synthetic fuels admixture with classic fuels. The use of fully synthetic fuels to power internal combustion engines could bring even greater benefits, provided that the vehicles are properly adapted and optimized for the use of such fuels [11, 18, 23, 29, 30, 39, 40–43, 47]. Contrary to the complex influence of various factors on CO₂ emissions accompanying the rapid take-up of BEVs, where introducing large amounts of BEV too early may increase overall CO₂ emissions, the situation is almost linear for synthetic fuels. The sooner and more of them are introduced, the greater the benefits will be achieved in terms of reducing CO₂ emissions.

Synthetic fuels make it possible to integrate mobility into the sustainable energy systems of the future. They are assessed according to five criteria: I – CO₂ neutrality, II – sustainable availability, III – environmental impact, IV – cost effectiveness and V – functionality. Synthetic fuels appear in the literature under various names, such as: PtL (Power-to-Liquid), PtX (Power-to-X), Power-to-Gas (PtG), SynFuels, e-fuels.

Generally speaking, when synthetic fuels are used, the reduction in well-to-wheel CO₂ emissions depends on the production methods of these fuel components and can be as high as 100% when the CO₂ emitted by the synthetic fuel vehicle is fully neutralized by atmospheric CO₂ capture systems, given the electricity was also generated using renewable energy sources [18].

The sustainable production of Fischer-Tropsch diesel fuel using CO₂ and H₂ makes first-generation synthetic fuels, whose main components are isoalkanes and n-alkanes with a chain length of 11–22 [10]. However, these fuels are classified as harmful to human health and the environment. The ecological situation forces the introduction of fuels which are neutral in terms of CO₂ emissions, so having net zero emissions, but at the same time pose less of a threat to people and the environment. Since first-generation synthetic fuels (SynFuels) were classified as hazardous substances, they cannot achieve this goal. Therefore, it is necessary to introduce the second generation of fuels with further reduced ecological impact.

E-fuels are synthetic fuels, resulting from the combination (synthesis) of "green hydrogen" produced by water electrolysis (e.g. using sea water) powered with renewable electricity and CO₂ captured from a concentrated source (e.g. exhaust fumes from an industrial plant) or directly from the air by carbon capture. Thus, fuels that are synthesized using renewable electricity, often using inorganic raw materials, are classified as e-fuels. E-fuels include liquid and gaseous hydrocarbons such as methane and various...
gasoline-like fuels, diesel fuel, alcohols such as ethanol and methanol, and non-carbon fuels such as hydrogen and ammonia. Once refined, the produced e-fuels can be used as e-petrol, e-diesel, e-fuel oil and e-kerosene – and can completely replace conventional fuels in their roles. Due to their “drop-in” properties (can be used directly to power in-service internal combustion engines without the need for modification or tuning), e-fuels can be mixed with conventional fuels in any proportion for better effect.

They offer high energy parameters, are easy to transport and enable long-term storage without energy losses, and therefore have significant advantages over propulsion technologies based on either hydrogen or electric batteries [23, 29, 30, 39, 40–43, 48]. The analysis of the potential offered by synthetic fuels, in particular second-generation fuels (e-fuels) in automotive applications, became the motivation behind this article.

2. Requirements set for synthetic fuels

Synthetic fuels that are currently in production, including e-fuels, must meet the requirements of EN 228 or EN590 norms. In this case, they are referred to as “drop-in” fuels and therefore directly applicable for use in current internal combustion engines as single fuels or as admixtures to conventional hydrocarbon fuels.

Conventional petroleum fuels are complex mixtures of hundreds of individual components, separated through various stages of crude oil refining, the purpose of which is to achieve specific target fuel properties optimized for the requirements of internal combustion engines. Therefore, the baseline feature of each developed e-fuel should be its ability to as closely as possible resemble the properties of fuels (both physical and chemical) specified in the EN 228 or EN 590 norms [34]. This can be achieved through the proper selection and optimization of the most important fuel properties presented in Table 1, which are relevant to the efficiency, performance, handling characteristics and emissions of harmful engine exhaust components [22].

The synthetic fuels production technology allows for selectively influencing the final properties of the obtained fuel. In this way, within certain limits, it is possible to produce a fuel that reduces harmful exhaust components and/or allows to achieve higher engine efficiency. Examples include the C/H/O ratio and the aromatic content of the fuel. If the C/H/O ratio is shifted slightly in favor of a higher hydrogen content and a higher oxygen content, it will significantly reduce the amount of toxic components emitted by the engine they are fed to. Another example are diesel fuels in which a homogeneous, uniform combustible mixture is created [22]. The processes of homogeneous charge combustion require stable conditions of ignition, for which the fuel has a relatively large range of ignition delay times independent of the temperature. In addition, the fuel in question must have appropriate auto-ignition properties. This can be achieved by using to the optimal composition of carbon, hydrogen and oxygen, as well as by managing the chain lengths of alkanes and alkenes. In this respect, the composition of e-fuel may also be a starting point for the development and implementation of alternative combustion processes, optimized to reduce emissions of harmful ex-

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If e-fuels are only to be used as “drop-in” fuels, the first stage of their use should include the optimization of various aspects of gasoline and diesel combustion processes. The aim is to obtain higher knock resistance in SI engines or high oxygen content, as well as a low content of aromatic compounds in order to reduce the formation of soot in the combustion processes of both diesel and gasoline [45, 51]. This will save fuel by, among others, reducing the necessary frequency of the diesel particulate filter regeneration. The introduction of singular, standardized e-fuels could further change the direction of the development of fuels, but also engines, allowing them to be optimized both to the requirements of combustion processes and those related to the reduction of harmful exhaust emissions.

In the case of spark ignition (SI) engines, the research and motor octane number determines the resistance of a given fuel to unplanned detonation (engine knock), and thus the engine's ability to operate in the most effective conditions [34, 37]. While the specifications for octane numbers around the world vary slightly, e-fuels should have a Research Octane Number (RON) above 90–95 and a Motor Octane Number (MON) above 85–90. Density and boiling point are also important fuel properties ensuring the proper formation of a combustible mixture in the combus-
tion chamber in terms of its formation rate and mixing quality and thus preventing excessive amounts of leftover unburned hydrocarbons. These properties are usually determined by the molecular weight distribution of the fuel. The aromatics content of SI engine fuels is usually below 25% to avoid excessive particulate formation, and the alkene content is limited to 5% to maintain the required oxidation stability. Taking these limitations into account, an ideal e-fuel would be a suitable mixture of straight-chain and branched C2–C6 alkanes, C6–C8 cycloalkanes and/or C2–C8 aromatics [8]. The fraction of straight chain alkanes is usually restricted to the lower carbon chains as the octane number decreases with increasing chain length. Branched alkanes that have multiple methyl isomers are preferred, as this increases the octane number [4].

For compression ignition (CI) engines, the cetane number (CN) is an indicator of the ability of diesel fuels to ignite. Currently, typical CN values are in the range exceeding 50–55. A high CN allows achieving high combustion efficiency and high EGR (Exhaust Gas Recirculation) rates. Taking this into account, a CN of at least 55 is currently recommended [3, 57], and since the reduction of NOx emissions is influenced by a high EGR factor, it is desirable to increase the minimum CN up to even 70 if possible [57]. Density, viscosity and final boiling point are also important properties that regulate the combustion processes of the atomized fuel, engine performance and the formation of toxic components. The initial boiling point being above 150°C reduces the negative effects that the fuel has on the elements of the fuel injection system, such as wear of its components due to cavitation. For Category 5 diesel fuels, WWFC (Worldwide Fuel Charter) also recommends a final boiling point of 350°C. Eventually, efforts will be made to lower the final boiling point to 260°C in order to facilitate fuel vaporization and to better homogenize the combustible mixture formed in the combustion chambers, as well as to reduce dilution of the lubricating engine oil.

3. E-fuels for SI engines

So far, the only e-fuel for SI engines to meet the requirements of second-generation synthetic fuel in terms of complete combustion, without the formation of soot particles and without products that are harmful to the environment and human health, is a mixture of dimethyl carbonate (DMC) and methyl formate (MF), called DMC+. DMC+ has very good anti-knock properties (RON/MON >110). Its vapor pressure is within the range required by the EN 228 norm, as is the final boiling point of 90°C [3, 45, 47, 48]. The significant reduction of the final boiling point, from 210°C for EN 228 gasoline to 120°C, improves the homogenization of the mixture formation and combustion process. Pre-ignition resistance, and limited pre-ignition related to the so-called "hot-spots", is the result of the full (almost complete) combustion of the DMC+ fuel. Hence, impurities are not deposited in the fuel injectors and in the combustion chambers.

Potentially CO2 neutral fuels are most easily synthesized from carbon oxides, mainly CO2 and CO. Methanol is a fuel for SI engines with excellent combustion properties. It is always a basic product, whose direct use as a fuel for vehicles (SynFuel of the first generation) is limited in scope due to its toxicity. The conversion of methanol to non-toxic DMC using CO2 and to MF using CO significantly reduces the fuel’s harmful effects on the environment. In the case of DMC+ fuel with the composition of DMC 65/MF 35% (v/v), the so-called negative fuel sensitivity of > 3 should be noted. Negative fuel sensitivity (MON > RON) means that the anti-knock properties of the fuel increase with the thermal load present. The advantage of DMC+ when used in SI engines is the improvement of their efficiency. This is possible thanks to the very good anti-knock properties and the cooling effect of DMC+ fuel vapors injected directly into the combustion chamber of the engine, three times higher than that of petrol. Downsized engines powered by DMC+ were found to have the engine efficiency increase by 10%, and at full load by about 19% [13].

The DMC admixture of 5–15% (v/v) to gasoline lowers HC emission [53]. DMC is a component that can be mixed with conventional gasoline. However, the negative properties of aromatic and olefin compounds (main high boiling point substances) present in gasoline that does meet the EN 228 requirements are further enhanced when mixed with oxygenates. This applies in particular to the soot particles number (PN) emission when 10% E10 or DMC is added to the mixture. In a comparative study, in which DIN EN 228 gasoline was replaced with an alkyl fuel (E DIN 51641), free from aromatics and olefins, the final boiling point was found at: 180°C along with a significant reduction in PN emission [24].

MF admixture in gasoline increases its octane number [12]. However, mixtures of MF with benzene undergo hydrolysis in the presence of water [12]. Research is currently being carried out on the behavior and properties of fuel mixtures containing MF.

In the case of gasoline used in blends with DMC and MF it is recommended to change the formula of the base fuel by eliminating aromatics and olefins and lowering the final boiling point from 210°C to 170–180°C. Knock resistance is guaranteed by the addition of MF and/or DMC. For fuel blends containing MF intended for use in SI engines, additives are developed to inhibit the undesirable hydrolysis of MF.

4. E-fuels for CI engines

As a result of many studies, oxytrimethylene ether (OME3, 3) was selected as a second-generation synthetic fuel for compression ignition engines [10]. A special molecular feature of OME is the alternating sequence of carbon and oxygen atoms. The absence of C–C bonds and the high oxygen content lead to almost complete elimination of soot formation during combustion. The boiling range of OME3, 3 is within the limits of 150–250°C which, combined with high volatility, promotes the formation of homogeneous flammable mixtures. The boost pressure requirements can be reduced without adversely affecting particulate emissions resulting from the delayed boost pressure build-up. In addition, the complexity of the fuel injection system can also be reduced by depressurizing the common rail and by using an appropriately configured split injection strategy. However, to counterbalance the lower energy density (when used as pure OME3, 3 fuel), the total fuel injection dose should be increased by 80% compared to diesel fuel.
by using larger diameter injector nozzle openings. Doubling the amount of fuel supplied into the cylinder also leads to a correspondingly increased cooling of the fuel dose in the cylinder through evaporation, and decreases the flame adiabatic temperature [32].

Standard OME₃.₅ has a flash point of 60°C, a cetane number CN ≥ 70, and a boiling point range between 150 and 260°C [54, 55]. The final boiling point of the fuel is approximately 100°C lower than that of conventional diesel fuels, which leads to OME₃.₅ evaporating easily. For further testing and possible market introduction of OME₃.₅ as a standalone fuel or blend component, the quality of the OME₃.₅ has to be standardized.

OME₃.₅ can be a component of a diesel fuel blend while being in accordance with the EN 590 norm. A 20% (v/v) admixture of OME₃.₅ into diesel fuel that meets the EN 590 B7 norm requirements results in a varied (throughout the engine operating range) reduction of the generated soot particulate mass, which can be found in the range of 50–80% of the original value [27]. This effect has been confirmed multiple times in the studies of mixtures containing 5–35% (v/v) OME₃.₅ [2, 9, 20, 25, 31, 35]. However, in order not to exceed the limits specified in EN 590, the maximum admixture of OME₃.₅ must not exceed 5–7% (v/v).

The highly polar OME has a limitedmiscibility with the less polar diesel fuel, especially at higher proportions of OME content in the mixture and at low temperatures [7, 31, 52, 54]. The hygroscopic properties of OME facilitate water penetration of the substance. This leads to a significant increase in the polarity of OME [38]. Therefore, it is necessary to investigate the stability of mixtures with OME in cold conditions in more detail. Effective dissociating agents must be found to prevent phase separation in the mixtures.

5. The potential of synthetic fuels in reducing exhaust emissions and improving engine operational parameters

So far, one of the most comprehensive studies on the impact of e-fuels on regulated as well as unregulated exhaust emissions (taking into account the future requirements of Euro 7 norm), and the GHG of SI engines, was carried out in 2021 by IFP Energies nouvelles (IFPEN) based in France, which was commissioned by T&E (Transport & Environment). The tests were performed both on the chassis dynamometer as well as in simulated and real driving conditions [21]. As no e-fuels were commercially available at the time of the tests, IFPEN developed custom fuel blends for testing, representing e-fuels that could be placed on the EU market in the future [21].

Three different e-fuel mixtures have been prepared:

- E-fuel 1: 100% paraffinic e-fuel, i.e. a mixture consisting of 100% hydrocarbon chains, which had no ring-shaped hydrocarbons with delocalized electrons such as benzene (i.e. aromatic hydrocarbons). It is a fuel that ensures efficient combustion and is representative of the basic e-fuels blend that could potentially be made available on the EU market [1, 21].
- E-fuel 2: 90% paraffinic e-fuel, 10% aromatic e-fuel. 10% of aromatic compounds were included in this mixture in order to check what influence this may have on the emission of harmful exhaust components [21].

E-fuel 3: 90% paraffinic e-fuel, 10% second-generation ethanol. However, the addition of ethanol to the paraffinic e-fuels blend caused significant miscibility problems. Looking for a solution to this problem, eventually it was found that adding 1% of fusel oil to the mixture would prevent ethanol separation [21].

The E10 homologation fuel mixture was used as the reference fuel, being representative for the current European fuel market, the fuel mixture was in accordance with the EN228 standard and the EU regulation 2008/692/EC [1, 5, 6, 21, 57]. The tests were carried out using a Mercedes A180 vehicle, which met the Euro 6d-temp exhaust emission norms. All tests measured both the raw engine exhaust emissions (upstream of the three-way catalytic converter) and the exhaust emissions after passing through the after-treatment system (tailpipe exhaust) [21].

The results obtained from NOₓ emission tests measured in the exhaust, carried out according to the WLTC (Worldwide Light Duty Test Cycle) procedure were, in the case of the above-described four fuels, all within the limits required by the Euro 6 norm and were very similar to each other in value. The average exhaust emission measured in WLTC was 24 mg/km for the E10 fuel, and 22–23 mg/km for e-fuels – Fig. 1 (variations in exhaust emissions were presented in percentage terms). The NOₓ emission results obtained in the RDE (Real Driving Emissions) road cycle test was 21 mg/km for E10, compared to 21–22 mg/km for e-fuels mixtures – Fig. 1 [14, 21].

![Fig. 1. Changes in the mean NOₓ exhaust emissions for various synthetic fuels compared to conventional petroleum fuels as measured in the WLTC, WLTP and RDE tests [14, 21].](image)

Thus, the tested e-fuels did not have a large impact on NOₓ exhaust emissions from the tailpipe, which remained at the same level as for conventional fuel (E10) [21]. It is worth noting that the currently applicable Euro 6 norm sets the upper limit of nitrogen oxides (NOₓ) emission at 60 mg/km. CLOVE (a consortium working on behalf of the European Commission on the development of emission norms for new vehicles) proposed to lower this limit to at least 30 mg/km or even 20 mg/km for the upcoming Euro 7 norm [5, 14, 16, 21, 28].

Exhaust emissions of particulates from cars equipped with SI engines are governed by two different parallel restrictions, relating to:
- total particulate mass (PM) below the Euro 6 limit value of limited to 4.5 mg/km,
- total particulate number (PN) more than 23 nm in diameter, below the Euro 6 limit value of $6 \times 10^{11}$/km.

The measured PM emissions for the four tested fuel types were very low, at $< 0.1$ mg/km. Since the obtained result was lower than the measurement uncertainty it was not possible to assess the possible impact that the tested fuel (in particular e-fuels) could have had on the exhaust emissions. PN23 emissions, measured for all fuels, were below the Euro 6 limit value of $6 \times 10^{11}$/km. At the same time, three e-fuels showed a large reduction in PN emissions compared to the base E10 fuel throughout the test. In the WLTC tests, the mean exhaust emissions of PN23 for the three e-fuels were 97–98% lower than the corresponding emissions for E10 – Fig. 2 (changes in emissions were presented in percentage terms). In RDE tests, the reduction of PN23 when using e-fuels was less significant and amounted to 82–87% of the base fuel value – Fig. 2 [21, 38].

![Fig. 2. Changes in the mean level of PN emissions (> 23 nm) for various synthetic fuels compared to conventional petroleum fuels measured in the WLTC, WLTP and RDE tests [21, 38]](image)

It can be hypothesized that the reduction in particulate exhaust emissions observed for e-fuels was probably mostly the result of the low aromatics content in e-fuels. $< 0.1\%$ in the case of e-fuel 1 and 3 and $10\%$ in the case of e-fuel 2 compared to $26\%$ for E10. It is likely that future e-fuels will be low in aromatics. It has been shown that as the content of aromatic compounds in gasoline blends increases, the exhaust emission of particulate matter also increases [5, 16, 26, 28], and this effect was thorough to have been caused by the incomplete combustion of large (heavy) aromatic compounds [15, 16, 28, 33]. The aromatic have a lower hydrogen to carbon ratio compared to aliphatic hydrocarbons and require a higher excess air ratio to enable efficient combustion. Therefore, aromatic hydrocarbons are more likely to cause incomplete combustion and particulate/soot formation than aliphatic hydrocarbons.

During the IPFEN test program described in the article, the emission of solid particles with a size reduced to 10 nm (PN10) was also measured [21]. After taking into account the measured emission of PN10 particles, the total number of particles emitted in the WLTC test increased 1.7 times for E10 fuel and 2.1–2.3 times for e-fuels, with the largest proportional increase observed for e-fuel 3 [21]. For the RDE test the increase in PN emissions, after taking into account PN10, was similar for all fuels, i.e. about 2 times (in the case of e-fuels it was about 5% higher compared to E10). These results indicate that the SI engines emitted more of the currently unregulated particulates in the range 10–23 nm than the regulated particulates > 23 nm for all four fuels tested in the RDE test and all e-fuels tested in the WLTC. The proportion of particles with a size of 10–23 nm compared to PN23 is higher for e-fuels than for E10 fuels. In general, the total exhaust emissions of particulate matter were significantly lower for the three tested e-fuels than for the E10 in both test cycles [21]. In the future Euro 7 norm, CLOVE proposed to lower the limit of particulate matter emissions for cars powered by SI engines from the current $6 \times 10^{11}$/km to $1 \times 10^{11}$/km [5, 6, 16, 33], which is a very significant reduction.

During the tests [21], all three e-fuels resulted in a significant increase in CO emissions from the tailpipe measured in the WLTC. The increase measured was about a 2.5-fold more CO emissions compared to the values resulting from the combustion of E10 fuel. This increase in CO emissions was mainly in line with the expected significant increase in exhaust emissions during the cold engine start phase and in urban driving. In this engine phase, CO emissions from e-fuels exceeded the allowable CO emission limits, set by the Euro 6 norm, by as much as $23\%$ [40]. It is interesting that such a large increase was not observed when using the base fuel, only about 10% increase in CO emissions in the case of e-fuels compared to E10 – Fig. 3 (changes in exhaust emissions were presented as a percentage) [21, 38].

![Fig. 3. Changes in the mean CO exhaust emissions for various synthetic fuels compared to conventional petroleum fuels measured in the WLTC, WLTP and RDE tests [21, 38]](image)

This suggests that the large increase in CO emissions may have been caused by an exhaust aftertreatment system that was not optimized sufficiently for e-fuels to be used with an engine powered by such fuels. The increase in CO emissions from the exhaust pipe in the case of the tested e-fuels was lower in the RDE test, although in this case the overall CO exhaust emission when using the e-fuels was 20–50% higher than in the case of E10 – Fig. 3 [5, 21].
HC emission results obtained for e-fuels were favorable in both test cycles [5, 21, 33]. Switching to e-fuels reduced the mean HC emissions in the WLTC test by 23–40% compared to the E10 fuel – Fig. 4 (exhaust emission changes were shown as a percentage), with all emissions below the Euro 6 limit values. The most notable decrease was observed for high driving speeds in the case of the WLTC cycle – 54–77% [40]. Due to the very low HC emission measured in the RDE test for all tested fuels (<5 mg/km), the differences in exhaust emissions between the various fuels in this test could not be discerned – Fig. 4 [21, 38]. Overall, the obtained results indicate a possibility to reduce hydrocarbon emissions when using e-fuels for compression ignition engines.

Ammonia emissions from cars are not regulated by the current Euro 6 norm, however CLOVE has proposed to place a limit on ammonia emissions at the level of 10 mg/km, which would be included in the future Euro 7 norm [5, 14, 21, 38].

The overall level of formaldehyde emissions was very low for each of the tested fuels and was below 0.3 mg/km in the WLTC test and 0.2 mg/km in the RDE test [21]. The highest exhaust emission of formaldehyde was observed during the engine cold start and in the initial phase of the WLTC and RDE tests, when it increased rapidly, even up to about 4 times the base value, most probably due to the catalyst temperature being too low, thus preventing optimal reduction of harmful exhaust components [1, 5, 21, 26].

Exhaust emissions of formaldehyde are also not regulated based on the Euro 6 emission norm, but an emission limit of 5 mg/km has been proposed to be included in the upcoming Euro 7 norm [14, 21, 33].

The presence of acetaldehyde when measured in the exhaust during the performed tests was below the detection limit for most of the test cycle run time for both the WLTC and RDE tests, with the exception of the engine cold start period [21]. Emissions measured in the so-called early phase (the first 3 km of the test) for the WLTC test was 3.0 mg/km in the case of fueling the engine with E10 fuel, and in the case of e-fuels it was lower by about 36–70%. In the case of the RDE test, the acetaldehyde emission for e-fuels was about 55–80% lower relative to the emissions from the E10 fuel.

Acetaldehyde emissions are also not regulated by the Euro 6 norm. So far, no proposal was made to introduce a direct acetaldehyde exhaust emission limit in the future Euro 7 norm. However, acetaldehyde emissions could be regulated under the Euro 7 as part of the CLOVE proposed non-methane organic gas emission limit (NMOG) of 25–45 mg/km [14, 21, 33].

The IPFEN research program included a portion measuring the exhaust emissions of three greenhouse gases, i.e. carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O). Currently, apart from the regulated emissions of carbon dioxide, emissions of other greenhouse gases are not regulated.

The test results showed that for all three of the e-fuels tested in the WLTC, carbon dioxide emissions were reduced by 3–4% compared to the emissions from the combustion of the regular E10 fuel. This is thought to have been caused by the higher ratio of hydrogen to carbon in the hydrocarbons making up the e-fuels compared to the E10 fuel, due to the lower content of aromatic compounds [16, 19, 33]. Furthermore, the higher energy content of e-fuels 1 and 2 (indicated by the increased lower calorific value) helped lower the fuel consumption and thus reduce the CO₂ emissions. The exhaust emission of methane (CH₄) in both tests (WLTC and RDE) were low and amounted to 1 mg/km for each of the fuels. During the cold engine start period, the exhaust emission values increased to about 10 mg/km, while after the exhaust aftertreatment system reached its operating temperature the emission dropped below the measurement uncertainty value [21]. Similar results were recorded for the emission of N₂O in the WLTP.
test, which was very low and similar for all the fuels tested (at around 1 mg/km). As with the other exhaust components, the highest N\textsubscript{2}O emission values were observed during the cold engine start. In the RDE test, nitrous oxide emissions were slightly higher (in the case of E10, e-fuel 2 and 3, the emission was measured at 2 mg/km, and in the case of e-fuel 1, at about 3 mg/km) [21].

Currently, the companies Mahle and Porsche are investigating the possibility of using DMC mixtures both in engine test benches as well as in vehicles, in road tests [5, 26, 33]. The results obtained so far on the engine test bench indicated a great potential of DMC mixtures, especially where the engine and its software was adapted to such a fuel, and determined all the effects the application of such a fuel could have on engine components [38]. On the other hand, the test results have shown that DMC should not be used as a standalone fuel, due to its melting point (−4°C) and a low calorific value of 15.8 MJ/kg, which would necessitate adapting the engine accessories, especially for the injection system as well as ECU reprogramming. The mixture of methyl formate (MF) and ethanol, as proposed in [17], solves the melting point problem, but not the low calorific value problem, so such a fuel would also require an adaptation of the engine hardware and injection system. To avoid this, an admixture of DMC to conventional fuel can be used. Tests were carried out to investigate this option, in which the base fuel was E5 SuperPlus98 gasoline (E5-SP98), to which DMC was added as an admixture of 5 to 20% (v/v) in the case of tests on an engine stand, or up to 50% (v/v) for laboratory tests [38]. While most of the relevant properties of the DMC20 blend were within the EN 228 norms, there still were slight variations in the density (slightly higher for the DMC20 fuel) as well as large variation in the oxygen content. When using a higher permitted oxygen content (for Super E10) in accordance with EN 51 626-1, an admixture of 5% (v/v) DMC to the E0 base would meet the requirements of EN 228. After introducing Super E20, it would be possible to add 10% DMC (v/v) to the E0 base. The DMC blend has advantages in terms of aromatic content.

One of the important technical aspects is the material compatibility of the components directly in contact with the fuel, especially the sealing and filtering materials. To test material compatibility with DMC20, the sealing materials widely used in combustion engines, such as hydrogenated acrylonitrile butadiene rubber (HNBR) and fluorinated rubber (FKM), were treated with E5-SP98 and DMC20 fuels for 500 hours at 60°C, and filter materials for 2000 hours at 60°C [38]. Before and after exposure to these fuels, the sealing materials were evaluated for changes in hardness, tensile strength, fracture strain, and volume changes. The obtained results showed that the addition of 20% (v/v) DMC to E5-SP98 adversely affected the hardness of the elastomers, but the effect was found to be small. As a consequence, the materials were concluded to meet the limit value requirements, so no reduction in functionality was to be expected. These materials show neutral or moderately better behavior when subject to tensile strength and strain at break for the DMC20 versus E5-SP98. On the other hand, the visible increase in volume in the case of HNBR and FKM materials subjected to DMC20 treatment may cause a problem from the functionality perspective. Similarly, the swelling tendency, which in the case of DMC20 may be even 80% greater than in the case of E5-SP98 [1, 38], should be noted. The test results prove that DMC20 cannot be assumed to be compatible with all the relevant materials (elastomers). Therefore, for each material exposed to DMC, its compatibility with DMC should be verified. Similarly to the sealing materials, tests were carried out on representational, single-layer filter papers used in fuel filters, both with natural and fully synthetic fibers [1, 38, 40]. All filter materials treated with the tested fuels passed the folding test.

The expansion and contraction of the tested materials was negligible when exposed to both fuels. Visual inspection indicated no significant differences. The tear resistance of the filter materials has exceeded the threshold value of 0.1 N/mm², irrelevant of the type of fuel used [38].

Further studies of the impact of adding 20% (v/v) DMC to the E5-SP98 fuel showed that such an admixture of DMC reduces the calorific value of the fuel from 42.2 MJ/kg for the base fuel down to 37.1 MJ/kg for the DMC20 mixture [1, 38]. Therefore, the fuel injection duration should be extended for the same engine load when using the new fuel mixture. However, despite the lower calorific value of the DMC20 fuel and the need to inject more fuel, the engine rated power was not affected by this change. A more detailed analysis of the engine test results showed no influence of the DMC content, up to 20% (v/v), on the ignition timing, combustion duration, peak cylinder pressure or pressure gradient values. However, as the share of DMC was increased, the specific fuel consumption also increased due to the extension of the injection duration [1, 38]. Summarizing, it can be stated that from the thermodynamic point of view, it is possible to operate the engine on fuel containing up to 20% (v/v) DMC without the need for changes to the engine design or the control unit software. However, given the high knock resistance of the DMC20 fuel, a slight software modification of the engine control unit (ECU) could increase the engine performance.

In order to make an assessment of the DMC20 mixture’s averaged impact on exhaust emissions, measurements were carried out on a chassis dynamometer using a Porsche 911 Carrera GTS with a manual gearbox. No changes were made to the software of the engine control unit for the measurements. The exhaust emissions comparison was based on measurements performed as a part of the WLTP procedure [1, 5, 33, 38]. For emission measurements, reference fuel EU6 (EU6ref) was used, which met the requirements of the EN 228 norm, both as the base fuel and the fuel to which 20% (v/v) DMC was added [1, 5, 33, 38].

When assessing the obtained HC and CO emissions results, no significant difference between the tested fuels was found – Figs 3 and 4. However, in the case of NO\textsubscript{x}, the exhaust emission of that component for the DMC20 fuel was about 10% lower – Fig. 1. The emission of particulate matter (PN) was assessed based on the cumulative exhaust emission values in the WLTP test [38]. A significant increase in PN emission was observed for the DMC20 mixture during engine start and in the initial phase of its warm-up, up to about 100 seconds into the test. In that time peri-
od, the DMC20 produced around 70 percent more particulate matter than the reference fuel EU6ref. However, once the engine warm-up phase was complete, the changes in the exhaust emission of particulate matter in dynamic engine operating conditions, were clearly smaller in the case of the mixed fuel than in the case of the pure reference fuel. By the end of the study, the combined increase in particulate emissions from the DMC20 fueled engine dropped to around 15 percent — Fig. 2 [38]. When changing the fuel injection time during the tests it was found, that the PN exhaust emission value was characterized by a much greater sensitivity in the engine powered by DMC20 fuel (when compared to EU6ref). This increased response of PN emissions could result in increased particulate emissions during engine warm-up phase. Thus, the improvement of the particulate matter emissions result could be obtained through optimizing the fuel injection time control [38].

The research on the impact of using e-fuels to power compression ignition engines was carried out at several institutions, such as Ford [56]. The test vehicle was a Ford Mondeo equipped with a 1.5-liter diesel engine. It uses a Denso low-pressure fuel injection system optimized for DME fuel (max. injection pressure: 35 bar, max. fuel flow rate: 80 kg/h). Testing for changes in the measured mass of particulate matter (PM), NOx, and CO2 exhaust emissions from a test vehicle powered by standard commercial diesel fuel and DME fuel was conducted in accordance with the WLTC guidelines. It was found that by supplying the engine with DME fuel, it is possible to reduce the PM emission to a level close to zero, while at the same time significantly reducing the NOx emission (by about 30%). The exhaust emission of CO2 for an engine fueled by DME remained at close to the same level as for the diesel fueled engine [56].

A synthetic fuel with 33% organic content marked as R33 Blue Diesel has already been made available at some gas stations throughout Europe, and is approved for use in all compression ignition engines. Taking into account the methods used for the production of this fuel (in terms of the energy source used for the fuel production and the amount of atmospheric CO2 capture involved), it can help reduce CO2 emissions (measured as well-to-wheel) by 20% [11]. For synthetic diesel fuels, HVO (Hydrogenated Vegetable Oil) and Fischer-Tropsch middle distillates (GTL – Gas to Liquids) are already widely available. These fuels were standardized under the general label of paraffinic diesel oil (PD – Paraffinic diesel) in accordance with the EN 15490 norm. Due to its high purity, especially the low content of sulfur and aromatic compounds, PD fuel is an environmentally friendly alternative to conventional diesel oil for compression ignition engines.

6. Synthetic fuels prognosis – SWOT analysis

6.1. Strengths

- E-fuels can reach the market quickly through existing flexible distribution networks, making them easily accessible to consumers.
- A wide range of e-fuels can be produced, ranging from drop-in fuels to fuels optimized for engine efficiency increase or to minimize the regulated, unregulated and GHG emissions.
- E-fuels can be used both as admixtures to conventional fuels and as standalone fuels.
- E-fuels are suitable for use in all means of transport: cars, trucks, airplanes and ships. In addition, they can be used as a substitute for petroleum in the chemical industry.
- Renewable synthetic fuels (e-fuels) of the "drop-in" variety may in a very short time contribute to improving the CO2 exhaust emission balance of the existing vehicle fleet, since there is no need to introduce any modifications in the vehicles, thus avoiding incurring large investment costs in refueling infrastructure and operation. The reduction in CO2 emissions depends on the synthetic fuel production technology and can be as high as 100% when the CO2 emitted by a synthetic fuel vehicles is fully captured from the atmosphere while using only electricity from renewable sources to power fuel production.

6.2. Weaknesses

- If only drop-in admixture e-fuels that meet the requirements of EN228 and EN590 are used to power vehicles, only a slight decrease in the regulated emissions and harmful exhaust components such as HC, CO and NOx will be achieved, compared to the emissions of petroleum-powered piston combustion engines.
- The current e-fuel production technology is still in the demonstrative phase. Solving some of the more serious challenges to the development of large-scale commercial installations will require an installation scaling of up to 100,000 times what has been demonstrated so far, or 100 times the scale of the project recently announced in Norway. Currently, there are only a few full-scale pilot or production plants, operating or planned in Europe and worldwide, to produce e-fuels for road transport. However, in order to fully decarbonize the new cars from the existing vehicle fleet a huge amount of e-fuels would be needed.
- Renewable electricity is a prerequisite for the development of low-carbon e-fuels production to the extent necessary to have a measurable effect on reducing the greenhouse gas emissions. Therefore, the plan requires a significant increase in the production of electricity from renewable sources.
- The low efficiency of e-fuels means that they are a very costly technology to use in decarbonizing road transport. In 2030, the cost of energy needed to power a car with an SI engine and e-fuel will be nearly four times higher than in the case of an electric vehicle (BEV).

6.3. Opportunities

- Despite the plans made by many governments to ban the sale of cars with internal combustion and hybrid en-
gines, some experts believe that the transition to electric vehicles will not happen soon enough to meet the environmental targets. The provision of carbon-neutral synthetic fuel for passenger cars, trucks and airplanes with internal combustion engines would therefore be a welcome step along the way towards the goal of being carbon-neutral.

- Combustion of synthetic fuel releases CO₂ back into the atmosphere, but because it can be recovered (through carbon capture) and reused to make e-fuels once again, the process forms a closed loop that can help reduce 10 billion tons of carbon added to the atmosphere per year. E-fuels have also been shown to reduce particulate emissions and are sulfur-free, helping to reduce the local air pollution.

- Siemens Energy and Porsche have already started their production of synthetic fuel, setting up a pilot plant in Chile. The factory will produce e-fuels that are almost completely CO₂ neutral. At the same time, the German government has created a special program to reduce CO₂ emissions by 10 million tons per year starting from 2030 and based on the production and use of e-fuels. The German government will allocate 1.54 billion euros for this purpose until 2024.

- Currently, there are no alternatives to synthetic fuels in aviation and maritime transport, while in the automotive industry a huge advantage is the fact that synthetic fuel can be used for both vehicles already in use (drop-in fuel) as well as new vehicles, optimized to run on synthetic fuels with a special formulation, in order to further reduce the exhaust emissions.

- E-fuels will be critical for transportation applications, for which there are currently no electric propulsion systems commercially available. Therefore, it is now up to policymakers and industry to create a framework that would make e-fuels economically attractive enough for the market.

- Without developing and employing e-fuels, meeting the ambitious goals of climate neutrality by 2045 might not be achievable, and the milestones set will not be met. The reason is the huge number of vehicles with internal combustion engines in operation. Internal combustion engines, especially when combined with e-fuels, still offer great development potential and can therefore make a significant contribution to the global reduction of CO₂ emissions.

- All the studies carried out so far and the forecasts developed have shown that in the future, even in markets with a very high share of electrified vehicles, e-fuels would still be needed to cover energy demand in transport. This is mainly related to aviation and shipping, but also to the supply of e-fuels for commercial vehicles and passenger cars (ICE, PHEV, REEV, FCEV).

6.4. Threats

- The current EU regulation of CO₂ emission only considers the CO₂ reduction achieved by the engine itself, not the fuel or energy that is used to propel it. This is not in line with the principle of technological neutrality pursued by the EU. It is not the internal combustion engine itself that causes the vehicle exhaust emissions, but the fuel used to propel it. With the upcoming revision of CO₂ emission norms, the European Commission indicated that it would investigate the possibility of including new mechanisms in the regulation, which would allow for the emissions reduction achieved by clean fuels, such as synthetic fuels. It should be considered a good step forward. It should not be forgotten that greenhouse gas emissions and climate change are inherently a global and complex problem that requires an integrated approach that encourages innovation while avoiding over-dependence on a single technology.

- From a technical point of view, in addition to renewable H₂, also other renewable liquid energy sources such as synthetic fuels (e-fuels) – should be considered as an integral part of the program enabling the use of renewable energy sources on a large scale. However, the political reality is different – quite often e-fuels are seen as an ineffective option aimed only at extending the lifetime of internal combustion engines.

- Greenhouse gas (GHG) emissions from synthetic fuels depends to a large extent on the type of electricity used to produce the fuel. CO₂-based synthetic fuels produced from coal-based electricity are likely to increase the overall greenhouse gas emissions compared to those produced from crude oil. In contrast, CO₂-based synthetic fuels (e-fuels) produced using excess renewable electricity – for example, off-peak night-time wind power that has no other use aside from storage – could have a much lower carbon footprint compared to the fuels produced from crude oil [44].

- Some sources indicate that advanced biofuels and liquid fuels will not make a significant contribution to reducing GHG emissions by 2030, and will be limited in the medium term by land availability and insufficient renewable energy sources to produce sufficient amounts of synthetic fuels [49].

- Presently, any forecast of future e-fuel production is burdened with high uncertainty – these are assumptions rather than factual forecasts. In addition to legal uncertainty and political perception, the enormous investment costs and the expected decline in the number of passenger cars with internal combustion engines over the next decades are also significant obstacles to the development of e-fuels production.

- The assumption that e-fuels will contribute to the automotive exhaust emissions decarbonization in the next 10 years bears a high risk as there are currently no widely available e-fuels on the market for either spark ignition or compression ignition engines.

- The current EU legal regulations focus on e-mobility, leaving no room for other potential technologies or technological competition in achieving the set climate goals. However, this approach means a departure from the current practice and the adoption of a balance between different technologies. Worse, the issue will not be discussed again in the EU until 2023. Moreover, the potential for CO₂ reduction in the existing vehicle fleet has been so far largely ignored, and the major contribution of CO₂ exhaust emissions from transport has hardly
been taken into account. Looking at the future development of the road vehicle fleet, even assuming a significant level of electrification of newly registered vehicles in the coming years, significant reductions in CO₂ emissions could be achieved even at low levels of e-fuels blending with classic fuels. Especially considering the huge worldwide population of vehicles with conventional drive systems, not to mention the benefits of using clean e-fuels to power internal combustion engines as long as they are adapted and optimized for the use of such fuels.

- The production and distribution of e-fuels will not be possible without political support. All scenarios indicate that significant amounts of e-fuels can only be produced and sold with a subsidy level of 1.0–1.5 EUR per liter or greater. This corresponds approximately to a cost of 300–500 EUR for every ton of CO₂ savings, which is more than most, if not all, of the current biofuel subsidies. Thus, a significant support of the e-fuels production technology development would require an unprecedented level of political support to reduce the EU’s CO₂ emissions by less than 0.2%. It seems possible that reductions in greenhouse gas emissions in the transport and industrial sectors could be achieved at a lower cost with other measures. Therefore, policymakers are considering the legitimacy and possibilities of supporting the development of production and distribution of synthetic fuels.

7. Conclusions

1) The current ecological situation forces the introduction of CO₂-neutral fuels with a reduced potential harm to human health and the environment. First generation synthetic fuels, classified as hazardous substances, cannot meet these requirements. Therefore, it is necessary to introduce the second generation of fuels (e-fuels), which will be less harmful to the human health and the environment. In order to achieve this, as a result of an extensive selection process, C1 OME₃,₅ fuels and DMC/MF (DMC+) have been proven to be particularly suitable for CI and SI engines respectively.

2) Synthetic fuels are technically feasible and commercially viable, especially provided the availability of renewable energy. Synthetic fuels will support the production of H₂ and the circular CO₂ economy.

3) Synthetic fuels produced with electricity obtained from renewable energy sources can significantly reduce the carbon footprint of combustion engine vehicles that are already in operation.

4) E-fuels make it possible to optimize the use of the global potential of solar and wind energy around the world.

5) E-fuels can be easily stored and safely transported over long distances without any waste of energy. They solve one of the main problems related to the energy transformation: the inability to continuously supply the grid with renewable energy, and thus its continuous availability.

6) The use of e-fuels in cars with internal combustion engines (ICEs) will not solve the air pollution problems to the extent set by the EU. Tests of three different e-fuels, in a Euro 6d-temp compliant car on a chassis dynamometer in WLTC and RDE cycles, described in detail in [21], have shown that e-fuels are not clean combustion fuels and, apart from particulate emissions, they will not significantly contribute to reducing the exhaust emission of both regulated and unregulated toxic pollutants, relative to E10 fuel. However, other studies show significant benefits in terms of reducing CO₂ emissions in the life cycle of an e-fuel vehicle [38]. Some studies point to the great potential of e-fuels to improve engine efficiency [13].

7) The conducted tests have shown that e-fuels do not have a large impact on the amount of NOₓ emissions released, and therefore one of the most harmful components of exhaust emitted by internal combustion engines of vehicles remains mostly unaffected. No significant effect of e-fuels use on hydrocarbon emissions was observed in RDE tests. On the other hand, the emission of toxic carbon monoxide increased significantly, as well as the emission of ammonia, which contributes to the increase in the emission of particulate matter [21]. However, other studies emphasize that even the admixture of e-fuels to conventional gasoline is enough to reduce PM, NOₓ, and HC emissions from an SI engine [38].

8) The results of the greenhouse gas emissions measurements carried out in the performed WLTC and RDE tests indicated that the use of e-fuels in road transport is unlikely to be entirely climate neutral. While it is widely assumed that CO₂ emissions from burning e-fuels produced through the use of direct atmospheric CO₂ capture are carbon neutral, the production of the two more potent greenhouse gases – methane and nitrous oxide – in the engine and the exhaust emission control system is not taken into account. At the same time, the research described in [6] proves that the cumulative GHG emissions of e-fuels powered vehicles are fully competitive to the corresponding emissions generated in the BEV or FCEV in their whole life cycle.

9) The results of the research that has been carried out on the impact of e-fuels on the exhaust emissions of regulated and unregulated exhaust components and GHG from internal combustion engines often present inconsistent results. These conflicting assessments are caused by testing e-fuels of different origins, composition, use of different test methods, different engine generations and different adaptation (optimization) of the engines themselves and their exhaust aftertreatment systems to be powered by e-fuels.

10) Second-generation synthetic fuels (e-fuels) can provide a significant reduction in the exhaust emission of harmful components and greenhouse gases from internal combustion engines, making them potentially useful even after 2050.

Acknowledgements

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### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Term</th>
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<tbody>
<tr>
<td>BEV</td>
<td>battery electric vehicles</td>
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<tr>
<td>CH₄</td>
<td>methane</td>
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<td>CI</td>
<td>compression ignition</td>
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<td>CN</td>
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<td>dimethyl carbonate</td>
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<td>FCEV</td>
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<td>FKM</td>
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<td>GHG</td>
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<td>HC</td>
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<td>HNBR</td>
<td>hydrogenated acrylonitrile butadiene rubber</td>
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<td>HVO</td>
<td>hydrogenated vegetable oil</td>
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<td>NH₃</td>
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<td>worldwide light duty test cycle</td>
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<td>worldwide harmonized light vehicles test procedure</td>
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<td>worldwide fuel charter</td>
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