



Promising catalytic synthesis pathways towards higher alcohols as suitable transport fuels based on H₂ and CO₂



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ABSTRACT

To address the pressing challenges of energy security and global warming, the coupling of the energy generation and transport sectors using *Power-to-Fuel* (PtF) technologies is an attractive strategy. PtF means the synthesis of transport fuels based on CO₂ from industrial exhaust gases and H₂ produced from renewable electricity via electrolysis.

This paper provides a comprehensive overview of the synthesis possibilities and potentials of H₂ and CO₂-based methanol and higher alcohols (C₁–C₈; from methanol up to octanol) as alternative transport fuels by adapting established and novel alcohol synthesis pathways to the PtF concept and assessing their technical maturity using the Technology Readiness Level (TRL) method. A literature review reveals that among the alcohols, methanol, ethanol, 1-/2-/iso-butanol and 1-octanol have the highest relevance for fuel blending. With the aim to give a first impression, we roughly estimated and discussed the production costs depending on the H₂ costs. We estimated the TRL of promising synthesis pathways towards alcohols at 8 for methanol and at 4 for ethanol, 1-butanol and iso-octanol. For 1-octanol, no suitable synthetic pathway is currently known.

1. Introduction

In the process of transitioning towards a sustainable energy system (in German: the *Energiewende*), the replacement of conventional energy sources with renewable ones, as well as the reduction of CO₂ emissions across all sectors, are fundamental objectives. Since renewable energy sources are subject to natural fluctuations and thus may not always match with demand, suitable energy storage technologies must be developed to ensure the security of supply. A promising storage option to harness the energy that cannot be used directly in the system is the production of H₂ by means of electrolysis. The secondary energy carrier H₂ can then be used in the currently fossil fuel-based transport sector, for instance in fuel cell vehicles. Aside from use in fuel cell cars, an attractive strategy to surmount the challenges arising from the *Energiewende* is coupling the energy generation, industrial and transportation sectors using *Power-to-Fuel* (PtF) technologies: the synthesis of transport fuels based on CO₂ and H₂ produced from renewable electricity by electrolysis [1–8]. In the literature, these fuels are

increasingly referred to as electrofuels [9–12] or e-fuels [7,9,13,14].

In a sustainable system, CO₂ can for instance be sequestered from biogas or industrial exhaust gases, e.g. from cement, steel and chemical industry. Also CO₂ sequestration from air can be considered. In cement plants for instance, 70% of the emitted CO₂ is chemical reaction [15] related. According to Harp et al. [16], for an integrated steelwork, the only economically feasible way to de-carbonize in the short term is to use the CO₂ emissions as a feedstock, e.g. for a *Power-to-Methanol* process. In an integrated steelworks, the use of coke oven gas can also be a source for the required H₂ [16]. In Germany, around 19Mt CO₂ were emitted by the cement industry in 2016 [15]. This amount of CO₂ is more than 8 times higher than the CO₂ demand which *Power-to-Fuel* processes would have been required to cover Germany's fuel ethanol consumption in 2016 of 1485 million liters [17].

Beside the catalytic conversion based on H₂ and CO₂, the conversions via biocatalytic systems [18,19], bioelectrocatalytic systems [20] and electro-reduction [21] towards fuels and chemicals are emerging fields.

Abbreviations: BuOH, butanol; CI, compression-ignition; EtOH, ethanol; EC, European Commission; DME, dimethyl ether; FT, Fischer-Tropsch; MAS, mixed-alcohol-synthesis; MeOH, methanol; MON, motor octane number; MTD, methanol-to-DME; OME, polyoxymethylen dimethyl ether; PrOH, propanol; PtF, *Power-to-Fuel*; RFS, renewable fuel standard; RON, researched octane number; rWGS, reverse water-gas shift; SI, spark-ignition; SoA, *state-of-the-art*; TRL > 9; STD, synthesis gas-to-DME; TRL, technology readiness level

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The use of non-food based feedstocks (lignocellulosic, algal biomass and CO₂, CO/H₂ from industrial flue gases or from waste or biomass gasification) is an emerging field [22]. Potential advantages of biocatalysis and bioelectrocatalysis are moderate temperatures and pressures, toleration regarding trace amounts of contaminants in feed gas, decreased sensitivity to syngas component ratio, higher conversion due to irreversibility of biological reactions and high yield due to high enzymatic specificity [20,23]. Especially bioelectrocatalytic processes show high economic potential [20]. Syngas fermentation is still a relatively immature technology but may play a role in future energy systems [23,24]. Main challenges of biocatalytic processes are the up-scale from laboratory-scale, the unclear sustainability and the many examples of slow and resource intensive development [18].

According to Qiao et al. [21], beside low catalyst activity, low product selectivity, insufficient fundamental understanding, and non-optimized electrode/reactor and system design for practical application, insufficient catalyst stability/durability is probably the biggest challenge of electro-reduction processes. The CO₂ reduction product strongly depends on the electro catalyst material [25]. Mixtures of low hydrocarbons and oxygenates can be produced with Cu catalyst. Using Cu catalyst, direct electro-reduction of CO₂ to ethene seems to be a competent pathway [26].

The principles of sector coupling are described in detail by Robinus et al. [27]. The roles of the transport sector and alternative fuels in the context of the Energiewende for a carbon-neutral economy are also outlined in detail in the literature [4,11,27,28]. Since electrofuels offer a convenient storage option for renewables from all sources and can at the same time be added to the existing infrastructure and used in conventional vehicles, these fuels have great potential to harness renewable energy for the transport sector in the near future. Furthermore, as outlined in the literature, especially for heavy duty vehicles, there is a long-term need for liquid fuels [4]. The main conceivable electrofuels can be subdivided into three groups [4]:

1. Hydrocarbons
2. Alcohols (methanol, ethanol, ...)
3. Ethers (DME, OME_n)

In their recent review regarding the production costs of electrofuels, Brynolf et al. [9] consider hydrocarbons, methanol and DME. This can be accounted for by the gap in the literature concerning the production of higher alcohols via the PtF concept. However, the suitability of alcohols as fuels is discussed in detail in the literature [29–34]. Apart from methanol, synthesis processes for the selective production of C₁–C₈ alcohols are biomass or petrochemistry-based. Based on the interest in PtF on the one hand and alcohols as transport fuels on the other, the aims of this contribution are to:

- Deliver a comprehensive overview regarding the suitability of methanol and higher alcohols (C₁–C₈; up to octanol) as transport fuels and corresponding possible synthesis pathways based on H₂ and CO₂.
- Develop synthesis pathways by adapting known and novel processes to the PtF concept.
- Estimate the technical maturities of the adapted processes.
- Make a first selection regarding the most promising synthesis pathways.
- Identify further research gaps for further investigation.

It is worthwhile to note, that the discussed synthesis pathways also offer promising syntheses for chemicals. This is especially the case for methanol, since it is the one of the most important industrial bulk chemicals. However, this paper is focusing on fuels since the transport sector offers a big market volume.

According to Otto et al. [35], the potential of CO₂ consumption for fine chemicals in the EU corresponds to ~0.029% of EU greenhouse gas

emissions. It thus can be concluded, that fine chemicals do not offer an avoidance option for large amounts of CO₂ [35]. Bulk chemicals other than urea, which already uses CO₂ as a feedstock, have a CO₂ avoidance potential of ~20 million tons CO₂, which corresponds to ~0.43% of the EU's greenhouse gas emissions [35]. In contrast to that, the transport sector accounts for ~23% of the global anthropogenic CO₂ emissions [36].

In order to give a first impression, the production costs are roughly estimated and compared with the current resale price of bioethanol, methanol from natural gas and the refinery wholesale price of fossil gasoline.

2. Methods

A future fuel produced with PtF technologies will need to fulfill two key criteria: suitability as a fuel with easy integration into the existing fuel systems and an economically-viable synthesis [3,4]. The focus of this contribution is the development of synthesis pathways by adapting known and novel processes to the PtF concept. At the same time, in this step the technological maturities of the pathways are estimated to make a closer selection in favor of the most promising synthesis pathways.

In this contribution, the technical maturity of the process steps and synthesis pathways is evaluated via the technology readiness level (TRL) method which ranks the maturity of a technology on a scale from 1 to 9. This method was developed by the United States Department of Defense [37] and adopted by the European Commission in the Horizon2020 program [38]. Since the adaption of the original TRL method to other research fields lacks in clear definition, the European Commission developed a guidance which is consistent among energy related research fields [39]. This guidance does not replace existing definitions, but rather clarifies the definitions to be consistent all energy related research fields.

The adapted TRL steps from 1 to 9 referring to the guidance principles for renewable energy technologies of the European Commission [39] are listed in Table 1. Commercial industrial processes are defined as state-of-the-art (SoA) in this work.

3. Suitability of alcohols as transport fuels

This section provides an overview of investigations regarding the suitability of alcohols as blend partners for conventional gasoline and diesel fuels. Due to their oxygen content, alcohols are in general not suitable for usage as aviation fuels. One reason for this is the lower calorific value compared to hydrocarbons [40]. This would reduce the vehicle's range and the fleet's efficiency. According to the standard for synthetic jet turbine fuels, ASTM D7566, oxygen-containing components must be hydro-processed to remove essentially all of the oxygen [41]. Besides the thermal stability, another reason for this is that oxygenated species can impact ground handling equipment by attacking the materials [42].

Their physical properties limit or qualify alcohols as blending admixtures for conventional gasoline and diesel fuels. For European countries, the requirements to be met by automotive diesel and gasoline are described in the standards EN 590 [43] and EN 228 [44], respectively. Leitner et al. [45] state that the impact of each property relates to their various technical and environmental impacts, as well as to the tendencies of the desired values of each property to enable a clean and efficient combustion.

The basic physical properties of gasoline [46,47] and diesel [4,47,48] fuels are extensively discussed in the literature. The fundamentals of compression-ignition (CI) and spark-ignition (SI) engines, including their respective combustion processes, are for instance described in detail by Bergthorson and Thomas [49] and Leitner et al. [45].

Alcohols from methanol (C₁) through to octanol (C₈) are also extensively discussed. The most frequently discussed alcohols are

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