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The Energy Penalty of Producing Hydrogen-Containing Fuels from Hydrogen

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Abstract:

Phasing out fossil carbon-based fuels as part of international climate change mitigation policies has put hydrogen on the agenda as an alternative transport fuel, but also as a chemical feedstock. Production, handling and transport of hydrogen are, however, energy intensive and complicated and therefore several approaches have been suggested for converting hydrogen into hydrogen-based energy carriers. Examples are so-called solar fuels or electro-fuels, producing methane or methanol, or ammonia. For the production of hydrogen the current routes using natural gas or other fossil carbon sources are being replaced by zero-carbon technologies based on renewable electricity. This paper will address the energy penalty resulting from the “degrading” of hydrogen to lower energy content fuels that are easier to handle. Exergy analysis is used, limited to the chemical exergies of the species considered. H₂ can be produced via bio-methane steam reforming or water electrolysis. It is here reported that production of ammonia from H₂ will give an exergy loss of 18-51%, production of synthetic methane 32-51% and production of methanol 18-40%, respectively. Producing ammonia from hydrogen obtained via steam reforming of methane gives a larger energy penalty than the widely used Haber-Bosch process. For methane and methanol the removal of CO₂ from flue gas for reaction with electrolysis H₂ gives a 4-7% lower exergy loss than when using CO₂ removed from air. Methanol production gives 11-14% smaller exergy losses than producing methane. The smallest exergy losses (~ 18%) may be obtained with methanol production via electrolysis of water and reaction with CO₂ from flue gas, or ammonia produced via electrolysis of water and a reversed fuel cell for ammonia production with nitrogen from an air separation process. When use as fuel is aimed at it can be argued that the chemicals produced cannot compete with the electricity spent (and battery technology).

Keywords:

Hydrogen; Hydrogen-containing fuels; Exergy

1. Introduction

The phase out of fossil carbon-based fuel as part of international climate change mitigation policies has put hydrogen on the agenda as an alternative especially for the transport sector, but also as a chemical feedstock. Production, handling and transport of hydrogen is, however, energy intensive and has complications and therefore several approaches have been suggested for converting hydrogen into hydrogen-based energy carriers. Examples are so-called solar fuels or electro-fuels, producing methane or methanol, or ammonia. For the production of hydrogen the current routes using natural gas or other fossil carbon-based sources are being replaced by zero-carbon technologies based on renewable electricity.

At the same time, process routes are developed that have fossil-derived (from a fossil fuel or a carbonaceous fossil material like limestone) carbon dioxide as a feedstock to produce, with hydrogen from a zero-emissions process like electrolysis of water, a synthetic natural gas, or methanol that is labelled “green”, or renewable. Obviously, this can be questioned since the production of a carbon-based fuel using a fossil carbon dioxide results in delayed rather than avoided emissions to the atmospheric, the delay of days, weeks or months largely irrelevant for the climate change mitigation human society must achieve. Thus, using fossil-derived CO₂ as a chemical that converts hydrogen into a fuel with more convenient properties when it comes to transport or storage needs to be considered with caution from a viewpoint of the later release of the CO₂ to the environment and possible claims of this being renewable fuel-derived emissions. If the objective is to use CO₂ for the purpose of producing synthetic natural gas / methane, or methanol then the CO₂ source for this has to be the atmosphere, not a process exit gas containing mainly or only fossil-derived CO₂.

This paper considers conversion of hydrogen into ammonia NH₃, synthetic methane CH₄ or (synthetic) methanol which have more attractive properties especially when it comes to transport or storage. The starting point is hydrogen produced via zero-emission routes, using electrolysis besides methane from a renewable (bio-based) resource. For the latter, steam reforming would produce hydrogen and CO₂ for which for example carbon capture, storage, CCS with underground storage of CO₂, can be an option. This “option” becomes a necessity if fossil carbon-based CO₂ is produced, which implies “blue hydrogen” rather than “gray hydrogen”.

This paper will address the energy penalty resulting from the “degrading” of hydrogen to lower energy content fuels that are easier to handle. Exergy analysis is used for this, limited to chemical exergy. The energy penalty of transporting hydrogen or chemicals produced from it is not addressed here, nor the reproduction of hydrogen from the chemicals after transport.

Important is the consideration whether or not hydrogen should be produced at a location where it will not be needed now or later because (renewable) electricity is an equally good or even better energy resource. Transport of electricity to where H₂ or a chemical produced from it is needed should always be preferred over destroying the exergy the electricity embodies while producing chemicals from hydrogen.

2. Conversion process routes from hydrogen to hydrogen carriers

Transport and storage of hydrogen may be less energy- or volume intensive if it is converted into another species rather than compression to very high pressures or cooling to extremely low temperatures. A drawback or risk is that this results in an energy-inefficient path towards a so-called hydrogen economy and exergy efficiency is used here to assess the potential losses. Perhaps the availability of cheap renewable electricity or special subsidies or tax reliefs can nonetheless motivate a significant energy inefficiency when converting hydrogen into another chemical species – this paper considers the destruction of exergy.

Three chemical species are most widely considered as a carrier for hydrogen, being 1) ammonia, NH₃, 2) synthetic methane, CH₄ or 3) methanol, CH₃OH. At ambient conditions the first two are gases while the latter is a liquid. Some properties of these, besides hydrogen and several other species relevant here are given in Table 1.

The standard chemical exergies of the species $b_{chem,species}^{\circ}$ are calculated from the Gibbs energy of formation $\Delta_f G^{\circ}$, the standard chemical exergies of the elements $b_{chem,element}^{\circ}$ and the number of atoms n of the elements in the species [1]:

$$b_{chem,species}^{\circ} = \Delta_f G^{\circ} + \sum_{elements} n_{element} \cdot b_{chem,element}^{\circ} \quad (1)$$

Values for $\Delta_f G^{\circ}$ are taken from database of the HSC10 (v. 10.0.8.5) software [2].

Table 1. Data including standard chemical exergies of the species considered in this paper

Species	Molar mass (g/mol)	Standard Gibbs energy of formation (kJ/mol)	Standard reference exergy b_{chem}° (kJ/mol)
H ₂ (g)	2	0	236.09
H ₂ O (l)	18	-237.14	0.93
H ₂ O (g)	18	-228.58	9.49
CH ₄ (g)	16	-50.53	831.9
CH ₃ OH (l)	30	-166.44	717.99
CO ₂ (g)	44	-394.36	19.87
NH ₃ (g)	17	-16.41	338.09
N ₂ (g)	28	0	0.72
O ₂ (g)	32	0	3.97

The chemical conversion routes with hydrogen as intermediate product resulting in NH₃, CH₄ or CH₃OH are given in Fig. 1.

Besides (liquid) water as a chemical feedstock for hydrogen production via electrolysis, air can be a source of oxygen O₂ or carbon dioxide, or an oxidiser for the traditional Haber-Bosch process route to NH₃ [3]. Methane is a feedstock for the Haber-Bosch process also, while via steam reforming it is a feedstock for hydrogen. Here, renewable / green methane from biogenic sources needs to be distinguished from fossil methane, i.e. (purified) natural gas where the latter would require a CCS or long-term carbon fixation CCU process in order to be CO₂-neutral.

Central in the scheme given in Fig. 1 is the production of hydrogen via electrolysis of water. This can be used for NH₃ production via electrolysis, with air as the source of nitrogen, N₂ (via conventional air separation). The electrolysis H₂ can also be used to produce synthetic methane (sometimes referred to as synthetic natural gas) or methanol.

The production of methanol follows the conventional route via hydrogen from methane, noting that is most cases this implies natural gas as mentioned above. Carbon for the production of synthetic methane or methanol can be CO₂ either removed from the air, which is becoming more and more economically viable, or CO₂ removed from a flue gas or other CO₂ containing process off-gas. Concentrations of CO₂ in air and typical process off gases or flue gases are around 0.04 %-vol and 10 – 100 %-vol, respectively.

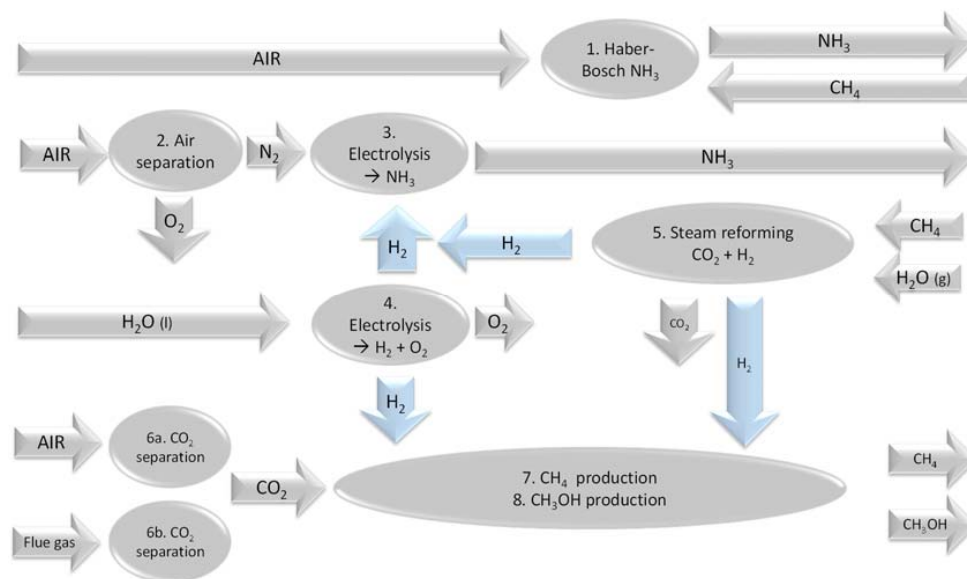


Fig. 1. Schematic of hydrogen conversion processes and hydrogen-based products.

For the CO₂ used it is of great importance if this is from a renewable, biogenic source or fossil carbon based. Using a fossil carbon CO₂ source for production of synthetic methane or methanol gives hardly a CO₂ emissions mitigation effect – the analysis given below gives the exergy destruction.

3. Assessment of exergy losses resulting from hydrogen conversion

3.1. Production of hydrogen, H₂

The standard chemical exergy of hydrogen is 236.09 kJ/mol [1], which corresponds to 118 MJ/kg. Production of hydrogen using electrolysis gives for an ideal reversible process the Gibbs energy difference 237.14 kJ/mol (at 25°C) [2], a minor difference from 236.09 that results from slight differences in how reference surroundings are defined and described. Using the data in Table 1, $\Delta b^{\circ}_{\text{chem}} = \Delta b^{\circ}_{\text{chem products}} - \Delta b^{\circ}_{\text{chem reactants}} = 238.08 - 0.93 = 237.14$ kJ/mol

The efficiency of H₂ production from water via electrolysis was recently reported to vary from 65 to 85% [5]: these two values are used here for calculating the actual exergy one mole of H₂ produced via electrolysis embodies.

Likewise, for the steam reforming of methane (route 5 in Fig. 1) to obtain hydrogen an exergy difference $b^{\circ}_{\text{chem, products}} = 241.06$ kJ/mol H₂ for CO₂ + 4H₂ – $b^{\circ}_{\text{chem, reactants}} = 208.44$ kJ/mol H₂ for reactants CH₄ + 2H₂O gives $\Delta b^{\circ}_{\text{chem}} = 32.61$ kJ/mol H₂ produce. With an exergy efficiency of 66.6% as reported by de Oliveira [4] this effectively becomes $\Delta b^{\circ}_{\text{chem}} = 48.92$ kJ/mol H₂ produced.

3.2. Production of ammonia, NH₃

The production of ammonia is for more than 90% of the world production of 235 Mt (in 2019) via the Haber-Bosch process route [3,6], route 1 in Fig. 1. Nitrogen from air is combined with hydrogen from methane (primarily from natural gas) which can be summarised as two sequential chemical reactions as given in Table 2.

Using the data in Table 1, chemical exergy of methane equals $813.91 \times \frac{1}{2} = 415.96$ kJ/mol H₂ while the chemical exergy of ammonia = $338.09 \times \frac{2}{3} = 225.39$ kJ/mol H₂ in NH₃. This means a loss of 45.81% of the chemically bound hydrogen exergy when converting H₂ into NH₃; this can be compared with the exergy efficiency of 56.11% of the Haber-Bosch process as reported by Szargut et al. [1]. The difference of 45.81% vs. 43.89% (100-56.11)% losses is the exergy in some steam produced in the process considered in [1].

An alternative route to ammonia starts with hydrogen produced via electrolysis of water and reacting that in an electrolysis process with nitrogen from air separation (route 2+4+3). As described above, H₂ (with $b^{\circ}_{\text{chem}} = 237.14$ kJ/mol) can be produced with 65 to 85 % exergy efficiency. For the air separation unit, based on cryogenic distillation of air, exergy efficiencies of 30 to 47% have been reported [7,8,9]: here an efficiency of 45% is assumed for that step.

For the reversed fuel cell that converts H₂ with N₂ into NH₃ an (exergetic) efficiency of 70% was recently reported [10,11]. Note that the first step of the reversed fuel cell for NH₃ production involves production of hydrogen; for the reaction between H₂ and N₂ the Gibbs energy difference ΔG taken from the HSC10 software databases is used for the exergy difference, giving $\Delta G = -16.41$ kJ/mol NH₃ = -10.94 kJ/mol H₂ in NH₃.

As shown in Table 2, this gives an over loss of chemical exergy of 18 or 38% when converting H₂ into ammonia using electrolysis of water with 85 or 65 % efficiency for the production of hydrogen. The rather low efficiency of the air separation process is much less problematic than the other inefficiencies.

A second alternative for NH₃ production from hydrogen and N₂ from air is based on using steam reforming of methane for the production of H₂. As noted, in order to obtain a CO₂-neutral NH₃ product it is important to use a renewable (most probably bioprocess-derived) methane as the feedstock for this. Here, the input chemical exergy of methane again needs to be considered, as for the Haber-Bosch process, besides the exergy effect of the steam reforming process. For the latter, de Oliveira [4] reported an exergy efficiency of 66.6% as mentioned above. Combining this again with the reversed fuel cell for production of NH₃, gives as the result given in Table 2 an overall loss of chemical exergy of 51.1%. This is less good than what is obtained with the Haber-Bosch process: clearly the methane steam reforming process leaves room for improvement as part of this concept.

It can be concluded that production of ammonia via route 2+4+3 is clearly the superior of the three routes. Surprisingly, the Haber-Bosch process route is more efficient than a combination of steam reforming, air separation and a reversely operated ammonia fuel cell.

Table 2. Chemical exergy losses from hydrogen (carrier) conversion to ammonia, NH₃.

Process Figure 1	Chemistry	Exergy input kJ/mol H ₂ in NH ₃	Efficiency, % [reference]	Exergy input kJ/mol H ₂ in NH ₃	Exergy output kJ/mol H ₂ in NH ₃	Loss of chemical exergy %
1	CH ₄ + O ₂ → CO ₂ + 2 H ₂ 3 H ₂ + N ₂ → 2 NH ₃ overall: 3CH ₄ + 3O ₂ + 2N ₂ → 3 CO ₂ + 4NH ₃	415.96 (CH ₄)	see text	415.96	225.39	45.81
2	Air → 0.79 N ₂ + 0.21 O ₂	2.25 *	45 [7,8,9]	3.33		37.94
4	H ₂ O → H ₂ + ½O ₂	237.14	65 - 85 [5]	364.83 - 278.99	225.39	- 17.94
3	N ₂ + 3H ₂ → 2NH ₃	-10.94	70 [10,11]	-7.66		
2	Air → 0.79 N ₂ + 0.21 O ₂	2.25 *	45 [7,8,9]	5.85		
5	CH ₄ + 2 H ₂ O → CO ₂ + 4 H ₂	415.96 (CH ₄) + 32.61 (R5)	66.6 (R5) [4]	464.88	225.39	51.06
3	N ₂ + 3H ₂ → 2NH ₃	-10.94	70 [10,11]	-7.66		

* $\Delta b^{\circ}_{\text{chem air separation}} = 1.77$ kJ/mol air \times (1/0.79) mol N₂/mol air = 2.25 kJ/mol N₂

3.2. Production of synthetic methane, CH₄

The production of synthetic methane from hydrogen and a carbon-neutral CO₂ stream is a widely studied field, also Finland where a significant bio-refinery sector is blooming and expanding. Yet again, fixing a CO₂ from a fossil carbon fuel or mineral source with hydrogen in a synthetic methane yields delayed fossil CO₂ emissions rather than a CO₂ emissions mitigation effect. The reaction deployed here is the Sabatier reaction of methanation of CO₂ [3], reaction 7 in Figure 1.

One important feature here is that of the H₂ produced as feedstock for this, 50% of will end up in the synthetic methane and the other 50% in water by-product.

The production of H₂ via steam reforming of methane is of course not considered here. The production of H₂ via electrolysis of water was described above. For the Sabatier reaction an exergetic efficiency of 80% has been reported [12], see also [13].

For the exergy input requirements for CO₂ removal from air (with CO₂ concentration of 0.04 vol-%) is given as 0.9 – 1.29 kJ/kg electricity + 4.19 kJ/kg heat per kg CO₂ removed from air [14]. Assuming an amine-based CO₂ scrubber/stripper process (see, e.g. [15]) where reboiler heat of 120°C is needed this corresponds to an exergy requirement equal to 2.16 MJ/kg CO₂ = 95.04 kJ/mol CO₂. Since 1 mole methane-bound H₂ corresponds to ½ mole CH₄, ½ mole of CO₂ is required for 1 mole methane-bound H₂. Thus, the exergy losses of producing synthetic methane from air-captured CO₂ and electrolysis water hydrogen range from 39 to 52% depending on the efficiency of H₂ production.

As an alternative for the above, a CO₂ capture from a flue gas can be considered. For CO₂ concentrations ranging from 10 to (near) 100 %-vol, [14] gives 0.03 – 0.11 kJ/kg electricity + 1.3 – 3.3 kJ/kg heat per kg CO₂ requirements. Similar to the previous analysis this gives an average exergy requirement equal to 0.66 MJ/kg CO₂ = 29.04 kJ/mol CO₂, which gives 14.52 kJ/mol per mole of methane-bound H₂. Thus, the exergy losses of producing synthetic methane from air-captured CO₂ and electrolysis water hydrogen range from 32 to 47% depending on the efficiency of H₂ production.

It can be concluded from the resulting values in Table 3 that an as pure as possible CO₂ source is preferable for synthetic methane production, but from a climate change mitigation and phase-out of fossil carbon fuels point of view the CO₂ should not derive from a fossil carbon source unless integrated with CCS. See [16] for a recent discussion on “blue” versus “green” hydrogen. The state-of-the-art water electrolysis and Sabatier process chemistry cannot bring the losses below 30%.

Table 3. Chemical exergy losses from hydrogen (carrier) conversion to synthetic, CH₄.

Process Figure 1	Chemistry	Exergy input kJ/mol	Efficiency, % [reference]	Exergy input kJ/mol	Exergy output kJ/mol	Loss of chemical exergy %
		H ₂ in CH ₄		H ₂ in CH ₄	H ₂ in CH ₄	
4	H ₂ O → H ₂ + ½O ₂	237.14 ×2 **	65	364.83 ×2		
			-	-	415.96	51.56
			85 [5]	278.99 ×2		-
6b	CO ₂ from air → pure CO ₂	47.52	see text	47.52		39.45
7	4 H ₂ + CO ₂ → CH ₄ + 2 H ₂ O(l) **	65.22	80 [12]	81.53		
4	H ₂ O → H ₂ + ½O ₂	237.14 ×2 **	65	364.83		47.01
			-	-	415.96	-
			85 [5]	278.99		32.17
6a	CO ₂ from flue gas → pure CO ₂	14.52	see text	14.52		
7	4 H ₂ + CO ₂ → CH ₄ + 2 H ₂ O(l)	65.22	80 [12]	81.53		

** As noted in the text: 50% of H₂ to H₂O, 50% to CH₄.

3.3. Production of synthetic methanol, CH₃OH

As an alternative for the production of synthetic methane from hydrogen and (assumed here) a carbon-neutral CO₂ stream the production of methanol, CH₃OH, or MeOH can be considered. This has the benefit of being a liquid at ambient conditions, with an atmospheric boiling point of 64.7°C and a density of 792 kg/m³.

The reaction deployed here is reaction 8 in Figure 1. One important feature here is that of the H₂ produced as feedstock for this, ⅔ will end up in the synthetic methanol and the other ⅓ in water by-product.

The production of H₂ via steam reforming is of course not considered here; the production of H₂ via electrolysis of water is described above. For the methanol production reaction an exergetic efficiency of 72% has been reported [17].

The exergy input requirements for CO₂ removal from air or flue gas have been quantified in the previous section. Similar to CH₄, ½ mole of CO₂ is required for 1 mole MeOH-bound H₂. Thus, the exergy losses of producing synthetic methane from air-captured CO₂ and electrolysis water hydrogen range from 23 to 40% depending on the efficiency of H₂ production.

As an alternative for the above, CO₂ capture from a flue gas can be considered. This shows that the exergy losses of producing synthetic methane from air-captured CO₂ and electrolysis water hydrogen range from 18 to 37% depending on the efficiency of H₂ production.

This results, see Table 4, suggest that besides ammonia production via a reverse-operation fuel cell, methanol production has the smallest exergy penalty from a hydrogen conversion point of view. Indeed, as a marine fuel its potential has already been recognised [18]. For road transport the future looks bleak for hydrogen, at least in Europe [19] and methanol fuel use by a large general public is ill advised because of the health risk it carries.

Table 4. Chemical exergy losses from hydrogen (carrier) conversion to synthetic methanol, CH₃OH.

Process Figure 1	Chemistry	Exergy input kJ/mol H ₂ in CH ₃ OH	Efficiency, % [reference]	Exergy input kJ/mol H ₂ in CH ₃ OH	Exergy output kJ/mol H ₂ in CH ₃ OH	Loss of chemical exergy %
4	H ₂ O → H ₂ + ½O ₂	237.14 ×1½ **	65 - 85 [5]	364.83 ×1½ - 278.99 ×1½	- 359.0	40.07 - 23.66
6b	CO ₂ from air → pure CO ₂	47.52	see text	47.52		
7	3 H ₂ + CO ₂ → CH ₃ OH + H ₂ O(l) **	3.07	72 [17]	4.26		
4	H ₂ O → H ₂ + ½O ₂	237.14 ×1½ **	65 - 85 [5]	364.83 - 278.99	359.0	36.58 - 17.90
6a	CO ₂ from flue gas → pure CO ₂	14.52	see text	14.52		
7	3 H ₂ + CO ₂ → CH ₃ OH + H ₂ O(l) **	3.07	72 [17]	4.26		

** As noted in the text: ½ of H₂ to H₂O, ⅔ to CH₃OH

4. Conclusions

Producing ammonia, methane or methanol from hydrogen gives significant energy penalties in the form of exergy losses. Preferably, starting with hydrogen obtained via electrolysis of water, 1) ammonia is produced with nitrogen from an air separation process using a reverse ammonia fuel cell, or 2) methanol is produced from electrolysis-produced hydrogen and CO₂ obtained from a flue gas. Exergy losses may be limited to 18%. For the latter case is it important that the CO₂ derives from a biogenic source: fossil CO₂ + H₂ does not give a renewable chemical or fuel but merely delays fossil CO₂ emissions. Such “greenwashing” is causing concern and needs to be avoided.

The production of synthetic methane gives a significantly larger penalty than the production of methanol. An alternative to the Haber-Bosch route to ammonia is presented by integrating an air separation unit with hydrogen production via electrolysis and a reversed ammonia fuel cell: it can bring the exergy penalty down to 18%, from 44% for the Haber-Bosch process. To finalise: the transport of electricity is less complicated than the production of hydrogen by electrolysis followed by conversion to ammonia, methane or methanol. Storage of hydrogen in the form of another “energy carrier” chemical can only be motivated by very cheap (renewable) electricity, cheaply obtained CO₂ from biogenic, CO₂-neutral sources and improved conversion technology efficiencies (while battery technology development would have to stay behind).

Acknowledgments

The author acknowledges the various people who during the last few years reached out for discussion on the benefits and pitfalls of converting hydrogen into ammonia or carbon-containing fuels. The use of renewable electricity for hydrogen production followed by conversion into other chemicals may not be beneficial in a society where the energy infrastructure is electrified. More dramatically, using a fossil carbon CO₂ resource for producing synthetic methane or methanol is recognised as delayed fossil CO₂ emissions, “greenwashing”, and a trend against “de-fuelling” energy systems. This may harm rather than support proper development of a so-called hydrogen economy and climate change mitigation that may offer. I dedicate this paper to those who keep the discussion alive.

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