International Journal of Hydrogen Energy 62 (2024) 959–968

Contents lists available at ScienceDirect

International Journal of Hydrogen Energy

journal homepage: www.elsevier.com/locate/he

Hydrogen production from wet biomass via a formic acid route under mild conditions

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ARTICLE INFO

Handling Editor: Jinlong Gong

Keywords:
Biomass oxidation
Technoeconomic analysis
Formic acid
Hydrogen
Decentral production

ABSTRACT

Renewable Hydrogen is a key building block for a sustainable energy economy. An attractive resource for its production is waste biomass. This contribution analyses a promising new Biomass-to-H_2 two-step approach, consisting of (1) biomass oxidation to formic acid and methyl formate in the so-called OxFA-Process and (2) hydrogen generation by dehydrogenation or decarbonylation of these intermediates. This contribution explains a novel hydrogen production concept and compares three distinct process routes for their efficient implementation. By using Aspen Plus® V12 the process was designed and optimized to achieve maximum hydrogen yield. An economic analysis allowed to compare the different characteristics of each process concept and to select the most promising option. The chosen concept was subject to a detailed cost and sensitivity analysis showing that this new route has high potential and competitiveness for hydrogen production from waste biomass.

1. Introduction

The need to lower greenhouse gas emissions and the exploitation of fossil resources drives the development and implementation of renewable energy technologies. The energy transition requires a multi-faceted approach, that includes a variety of sources, such as wind, solar, and hydropower [1]. To ensure a stable supply of electrical energy, these sources alone are not sufficient, as their availability fluctuates and depends on location and time. Hydrogen is a versatile energy carrier that has the potential to supplement and balance the energy provision and storage system. Currently, hydrogen is primarily produced from natural gas and coal [2]. In a sustainable scenario, water electrolysis is able to generate significant amounts of hydrogen, although it remains an expensive technology [3–5]. Gasification is regarded as a promising option for cheaper hydrogen production from biological resources. It offers a viable and sustainable method to harvest hydrogen from biomass wastes [6]. According to Ahmad et al., a few parameters (e.g. type of gasifier and the operations conditions) have the greatest effect on product quality and efficiency of the gasification process [7]. While there is considerable potential to mitigate greenhouse gas emissions by biomass gasification, this technology is associated with significant drawbacks [8,9]. Energy intensive crushing and drying of the biomass substrate is required [7,10,11] and the gasification process generates a multicomponent mixture from which high-quality hydrogen can only be obtained after intensive purification (tar and sulphur removal) [12]. An alternative thermochemical process for the decomposition of biomass is pyrolysis, however, the concentration of hydrogen in the gas phase is currently too low to make the process economically interesting [13]. One major disadvantage of gasification and pyrolysis lies in the demanding process conditions involving high temperatures and pressures of up to 1400 °C and 25 MPa [13]. Due to challenging conditions, the efficiency of these technologies decreases when moving from large, centralized facilities to smaller, decentralized plants that convert biomass wastes at the source. Establishing such decentralized plants can ease the transportation of wet biomass wastes, which typically have low energy density per unit volume. Zhang et al. [14] demonstrated a one-pot, two step reaction for generating hydrogen from various kinds of non-food-related biomass and daily waste. Initially, formic acid is acquired through a 1 vol-% dimethyl sulfoxide-promoted hydrolysis-oxidation of biomass. Subsequently, this formic acid is subjected to

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https://doi.org/10.1016/j.ijhydene.2024.03.163
Received 12 January 2024; Received in revised form 7 March 2024; Accepted 11 March 2024
Available online 16 March 2024

dehydrogenation using an iridium catalyst, yielding hydrogen with efficiencies reaching up to 95 %. The study demonstrated the versatility of the process by successfully working with various substrates such as wheat straw, reed, cardboard, and newspaper. Park et al. [15] investigated a comparable process employing dimethyl sulfoxide and hydrogen peroxide for hydrolysis-oxidation. They pre-treated biomass by mechanocatalytic depolymerization with citric acid using a blender. The resulting formic acid was then dehydrogenated with a Pd catalyst, showing high selectivity. Both studies highlight a genuine interest in a process for hydrogen production from biomass. However, it's important to note that neither study delved into the technical realization of their processes, e. g. stoichiometrically consuming H2O2 as an oxidant seems not feasible in a large scale process.

In this work, a novel process route is proposed to produce hydrogen in high yields from dry or aqueous/wet lignocellulosic biomass wastes, that takes place under mild process conditions, making it especially suitable for decentralized application. The proposed process scheme of the hydrogen production route is shown in Fig. 1. In a first step, the biomass is oxidized in the presence of water as a solvent by using oxygen or air (so-called OxFA-Process) [16–18]. Formic acid and carbon dioxide are the main products of this reaction. Recent studies have shown, that the usage or addition of methanol as a co-solvent almost completely suppresses total biomass oxidation to carbon dioxide, enabling an outstanding biogenic carbon efficiency [19]. The methanol containing system, however, leads to the formation of methyl formate through the esterification of methanol and biobased formic acid (so-called modified OxFA-Process) [20]. The ratio between the two products formic acid and methyl formate depends on the water/methanol solvent ratio, according to the thermodynamic equilibrium of the esterification reaction. However, their separation is facilitated by markedly different boiling points. For subsequent generation of hydrogen from these two intermediates, two different process routes are necessary. On the one hand, formic acid is dehydrogenated to hydrogen and carbon dioxide according to equation (1). On the other hand, the methyl formate part undergoes initial decomposition through decarbonylation to yield carbon monoxide and methanol (equation (2)). While methanol is recycled back into the

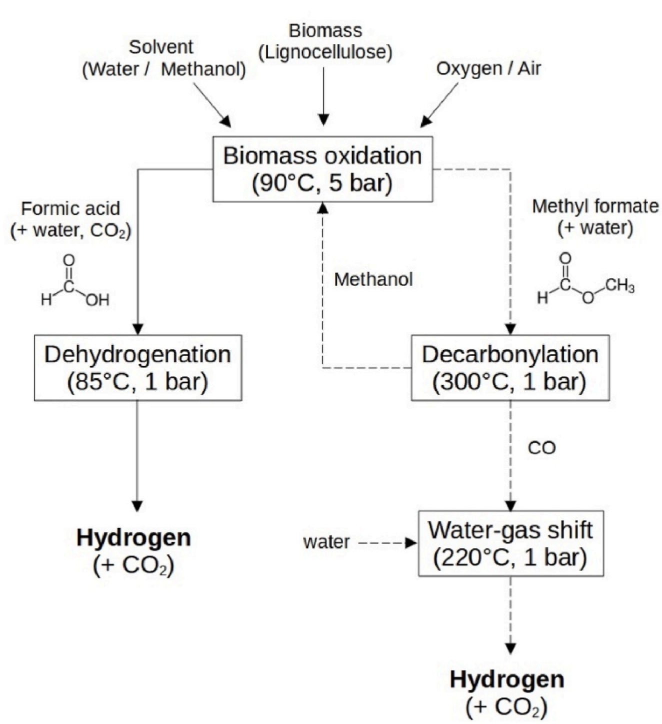


Fig. 1. Schematic representation of the production of hydrogen via methyl formate/formic acid starting from biomass oxidation.

OxFA-Process (as a solvent), the carbon monoxide is converted with water to hydrogen and CO_2 in a water-gas shift reaction (equation (6)).

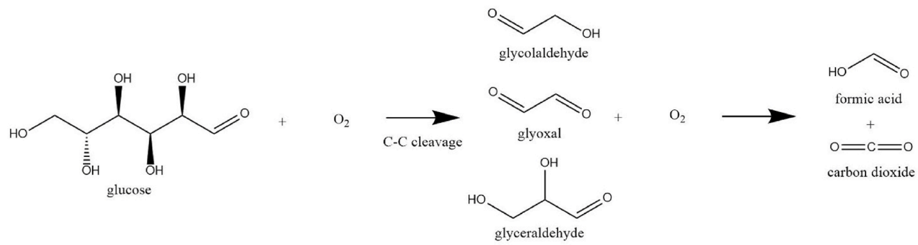
The objective of this study was to comprehensively examine the innovative hydrogen production process at a conceptual level, encompassing process design, various qualitative criteria (such as equipment requirements, biomass solubility, hazard potential, etc.), and its economic viability. A decisive aspect for the process design is the applied water/methanol solvent ratio. Starting from different compositions of solvents in the OxFA-Process (pure water, 10 wt-% methanol in water and 50 wt-% methanol in water) three process designs were devised and compared. A route in pure methanol was not considered since biomass itself contains water which is always diluting the system. First, the state-of-the-art of the individual process steps (OxFA-Process, dehydrogenation, decarbonylation and water-gas shift reaction) is described and analysed in detail.

1.1. Process step 1: biomass oxidation

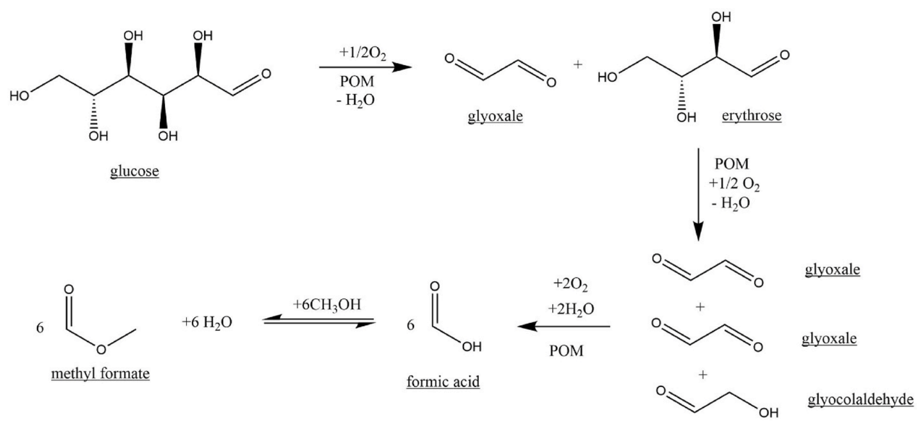
The OxFA-Process is a promising technology for the chemical valorisation of biomass. Its basic principle is the selective, catalytic oxidation of various biogenic substrates to produce formic acid (FA). The only two products that are formed at full conversion are FA and CO_2 [21]. This biomass oxidation process is mildly exothermic and operates under mild temperature conditions of typically below 100 °C using molecular oxygen or synthetic air as environmental benign oxidants. As water is applied as solvent, biomass of different origin, composition and humidity can be applied without drying [22]. The concept overcomes major problems of classical biomass gasification or reforming processes like necessary pre-drying of substrates or limited feedstock variety as well as lack of selectivity due to by-product formation [23,24]. By applying the OxFA-Process, a very broad range of biogenic raw materials can be converted into only two products that separate nicely into gas and liquid phase, its simplicity and robustness are clear advantages compared to other biomass valorisation technologies [25]. However, due to the thermodynamically favoured total oxidation to CO_2, only moderate FA yields up to 61 % from glucose using a polyoxometalate (POM) catalyst could be achieved (Scheme 1) [26].

In a modified version of the OxFA-Process reported in 2020, a simple change in the reaction medium of the POM-catalysed glucose oxidation leads to a step-change in performance (Scheme 2) [20]. In detail, the remarkable influence of methanol as a (co)-solvent lead to an overall formic acid/methyl formate selectivity of almost 100 % from glucose oxidation. Undesired side products that have been typically found in the traditional aqueous oxidation system, such as CO or CO_2, can be completely avoided in this way. A highly important finding is that glucose oxidation in methanol benefits from a faster re-oxidation of the HPA-5 catalyst. This enables effective re-oxidation at lower oxygen partial pressures and allows to work with air as oxidant at pressures as low as 5 bar.

Motivated by the intriguing effect of methanol on the catalytic system for its performance in selective glucose oxidation to FA, Wesinger et al. [27] analysed the role of the catalytic active species in greater detail using ^{51}V-NMR and EPR spectroscopy. It was found that a vanadate-methanol complex $[VO(OMe)_3]^n$ is responsible for the enhanced selectivity in methanolic solution compared to aqueous media. Both (aqueous and modified) OxFA processes are the subject of further research by various groups. Albert et al. [28] have investigated a potential utilization for the production of hydrocarbons by Fischer-Tropsch synthesis (FTS). By transforming biomass first into formic acid via the OxFA-Process followed by syngas formation by decomposition of FA and finally FTS using regenerative hydrogen (or if needed H_2 from the stored FA) to balance the C:H ratio allows an interesting pathway for green fuel production.



Scheme 1. POM-catalysed oxidation of glucose to formic acid in aqueous media [26].



Scheme 2. Reaction mechanism for the modified OxFA-Process (exemplified for glucose oxidation to methyl formate in aqueous-methanolic solution).[18]

1.2. Process step 2a: dehydrogenation of formic acid

The dehydrogenation of the biogenic formic acid to produce hydrogen and carbon dioxide proceeds according to equation (1).

$$HCOOH \rightleftharpoons CO_2 + H_2 \tag{1}$$

In the past, various catalysts, both homogeneous and heterogeneous, were investigated for this reaction. Graseman and Laurenczy [29] have compiled an overview of different catalysts and their performance. The homogeneous systems often consist of ruthenium complexes [29]. A promising concept is to use a $RuBr_3 \bullet xH_2O$ catalyst in a $5HCOOH/2NEt_3$ reaction mixture with triphenylphosphine (PPh_3) at temperatures of 40 °C [30]. An alternative approach uses $RuCl_3 \bullet xH_2O$ with meta-trisulfonated triphenylphsophine (*m*TPPTS) and HCOONa as additive for the aqueous formic acid [29]. Here, full conversion of formic acid at 90 °C is possible and no carbon monoxide is formed as a by-product. Fink and Laurenczy [31] carried out dehydrogenation with a rhodium complex ($[Cp^*Rh(dpm)Cl]Cl_2$) and found catalytic activity starting at 55 °C. Maximum activity was observed at 105 °C (TOF = 1085 h^{-1}) and the catalyst showed no loss of activity over four cycles. Note, that the biomass oxidation via the OxFA-Process produces an aqueous formic acid solution. During dehydrogenation with a homogeneous catalyst, the gaseous products are removed, and the catalyst remains behind in the solvent (water). In a continuous reactor, the catalyst is thus washed out or must be continuously concentrated (e.g. by water evaporation), leading to a high energy demand and additional equipment. Bulushev, D.A. [32] showed the promising activity of immobilized homogeneous catalysts (Ru, Ir, and Fe) for formic acid-based hydrogen. With heterogeneous or immobilized catalysts, no further separation is necessary, making them particularly attractive in dilute aqueous environments. Most groups have studied formic acid dehydrogenation with solid catalysts in liquid phase in batch experiments. Only a few groups [33–36] have used a continuous experimental setup so far. For heterogeneously catalysed reactions, gold is a promising metal. Gazsi et al. [37] have investigated this on various supports in a continuous fixed-bed reactor. As an example, a H_2-yield of 99.5 % was obtained with 1 % Au/SiO_2 at 523 K. It was also found that water has a positive influence on the yield and selectivity of H_2 production, as it suppressed CO-formation. This confirms observations by Solymosi et al. [38], who achieved H_2-yields of 98.3 % at 473 K with iridium on carbon. Kosider et al. [39] have shown that commercial palladium catalysts (Pd/C and Pd/Al_2O_3) exhibit high activity as well as selectivity to H_2 and CO_2 even at room temperature, but a strong deactivation of the catalyst occurs due to CO-poisoning of Pd. Nevertheless, pseudo-continuous operation can be realized by regeneration of the catalysts with hydrogen peroxide. In this respect, it is important to note that the long-term stability of heterogeneous catalysts in particular has been a major challenge to date [39]. Jia et al. [40] promoted Pd/C catalysts with various alkali metals (K, Cs, Na, and Li) and observed that the addition of potassium (10 wt-%) significantly increased the turnover frequency by up to 65 times. The researchers also proposed a reaction mechanism that involves the decomposition of formate ions, which is accelerated by a liquid phase within the pores - potentially facilitated by the condensation of formic acid or the presence of water. So far, dehydrogenation of aqueous formic acid remained restricted to a laboratory and pilot scale. However, the findings indicate that formic acid can be fully converted at ambient pressure and temperatures of 85 °C [31]. These mild conditions make the formic acid dehydrogenation attractive for decentralized hydrogen production by combination with the OxFA-Process. However, for heterogeneous concepts mainly the catalyst robustness and for homogeneous concepts its separation need to be addressed in further development to enable stable dehydrogenation in the proposed scenario.

1.3. Process step 2b: decarbonylation of methyl formate

In the production of methyl formate through the modified OxFA-Process, it should be noted that only the formyl group of the molecule is derived from the decomposed biomass. The methyl part, on the other hand, originates from the methanol previously used as a co-solvent. Therefore, a first decarbonylation step is required to isolate the biobased carbon.

Two routes are known in literature for the decomposition of methyl formate, either by decarbonylation into methanol and CO (equation (2)) or by decarboxylation into methane and carbon dioxide (equation (3)). Note that the latter is thermodynamically favoured [41].

$$C_2H_4O_2 \rightleftharpoons CH_3OH + CO \tag{2}$$

$$C_2H_4O_2 \rightleftharpoons CH_4 + CO_2 \tag{3}$$

For the purpose of the discussed scenario, (2) is desired to liberate CO for further conversion. In this regard, it is noteworthy that methanol can undergo further decomposition to produce hydrogen and carbon monoxide (equation (4)), or it can react to form dimethyl ether and water (equation (5)).

$$CH_3OH \rightleftharpoons CO + 2\, H_2 \tag{4}$$

$$2\, CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \tag{5}$$

The formation of methane and dimethyl ether are undesired side reactions, as these products cannot be used further in the process routes considered. The decomposition of methanol forms hydrogen and CO that can be shifted in a subsequent process, however, these products do not originate from (renewable) biomass. Furthermore, the decomposed methanol cannot be reused for the biomass oxidation process and must be replaced by a methanol make up stream, leading to increased material expenses.

Most of the published work on methyl formate decarbonylation was performed in lab scale batch experiments. Thereby, heterogeneous and homogeneous catalysts found application. Homogeneous decarbonylation of formate esters is commonly carried out at temperatures ranging from 180 to 230 °C using transition metal complexes based on copper or ruthenium, while the latter shows higher turnover rates [42]. Interestingly, small amounts of water contained in the inlet stream, just as expected for our scenario, enhance turnover rates of Ru-based catalysts by several factors [41].

The heterogeneous materials often base on alkali metals, especially supported KCl. As one of the first, Sano et al. [43] used KCl on activated carbon and reached a CO-yield of 99.5 % and a methanol yield of 96.2 % at 270 °C. Lee et al. [44] also used KCl/MgO as a catalyst and achieved 92.8 % conversion and 91.8 % methanol selectivity in a continuous experimental setup at 300 °C and atmospheric pressure. The only observed side reaction was methanol decomposition. One of the most recent articles is authored by Li et al. [45] who used a continuous-flow fixed-bed reactor and a ZnO catalyst on activated carbon. They achieved full conversion with 94.1 % selectivity to methanol at a liquid hourly space velocity (LHSV) of 0.7 h^{-1} and a temperature of 230 °C. Currently, to the author's knowledge, there is no publication that has investigated the decarbonylation of methyl formate on a larger scale. However, since methanol and CO yields exceeding 95 % have been demonstrated and product separation (methanol/CO) is facile, upscaling of the process may be easily achievable.

1.4. Process step 3: water-gas shift reaction

The production of hydrogen by the water-gas shift (WGS) reaction is a well-known industrial process and is described by the following reaction equation.

$$H_2O + CO \rightleftharpoons CO_2 + H_2 \tag{6}$$

It is a reversible, exothermic reaction, resulting in higher equilibrium conversions at lower temperatures [46]. One can distinguish between two types of WGS reactions: The high temperature shift (HTS) and the low temperature shift (LTS) reaction. The HTS reaction is carried out at temperatures of 310–450 °C and mostly uses iron oxide/chromium oxide catalysts that experience strong activation losses at lower temperatures [47]. Under these conditions an outlet gas containing 2–4 % of residual CO is generated. In order to achieve higher H_2 yields, the LTS process applies catalysts that have high activity at temperatures of 200–250 °C. For this purpose, a mixture of CuO, ZnO and Al_2O_3 is used to achieve a CO concentration <0.1 % [47,48]. In the last two decades, scientists have investigated new materials and combinations of catalyst and support for the WGS. A main focus is to further increase hydrogen yields and lower CO residues by reducing the required reaction temperature (<200 °C) [49–51]. From such technologies particularly a decentral WGS application would benefit. LeValley et al. and Pal et al. have summarized these developments of the last years and expect further improvements in terms of activity, deactivation and reaction conditions [52,53]. For the here envisaged scenario of decentralized hydrogen production from biomass a one-step low-temperature WGS is most suitable to reduce invest costs. Such smaller scale WGS technologies are already successfully in operation [54].

2. Material and methods

2.1. Simulation

The three different process routes with varying solvent composition (pure water, 10 wt-% methanol in water and 50 wt-% methanol in water) were simulated using Aspen Plus® V12 and optimized for maximum hydrogen yield, based on an input flow of 1 kmol/h glucose. The thermodynamic method UNIQUAC was employed. The energy and carbon efficiencies are calculated using the following equations:

$$\eta_{Energy} = \frac{\dot{M}_{H2} \bullet LHV_{H2}}{\dot{E}_{In}} \tag{7}$$

$$\eta_{C,Gluc} = \frac{\dot{N}_{H2\ from\ Glucose}}{6 \bullet \dot{N}_{Glucose,0}} \tag{8}$$

$\dot{M}_{H2}$ is the mass flow rate of hydrogen produced, LHV_{H2} is the lower heat value of hydrogen and $\dot{E}_{In}$ represents the energy input required to drive the processes [55]. For the calculation of the required heating and cooling power of the routes, the individual energy demand of the units (energy required to reach reaction temperature and reaction enthalpy) is summed up. The determination of power values was executed using the Aspen Energy Analyzer® V12, and wherever feasible, heat integration was implemented. As this contribution aims to introduce a novel hydrogen production concept, the subsequent economic analysis primarily incorporated operational costs. Expenses associated with pumping, product purification (e.g., through adsorption or absorption technologies for hydrogen purification) and recycling were not considered on this stage. Furthermore, any unreacted and discharged methanol was deemed recyclable. Uniform pricing for heating and cooling, independent of energy quality, employing a single price for all energy levels, was used as the basis. Specific pricing details (as of Sept. 2022) can be found in Table 1. Hydrogen production costs were determined by dividing the operational costs by the quantity of hydrogen generated.

2.2. Description of the simulated processes

The goal of the process analysis and simulation was to understand

Table 1
Cost inputs for economic analysis.

	Price	Source
Methanol	540 €/t	[56]
Glucose	300 €/t	[57]
Oxygen	140 €/t	[58]
Water	1 €/t	[59]
Heating	80 €/MWh	[60]
Cooling	5 €/MWh	[61]
Electricity	260 €/MWh	[62]

how process operation (e.g., methanol content in OxFA-Process) and design (combination of reaction units) affect hydrogen production costs and practicability of the new approach. A quantitative goal was to reach maximum hydrogen yield at the lowest possible production costs. Glucose was used as a model biomass substrate for the comparison and a feed rate of 1 kmol/h was assumed for all routes. Experimental data for the classic and the modified OxFA-Process are available in literature [17, 20].

Route 1 uses an aqueous solution of glucose as a feed, without the addition of methanol. A schematic representation of the entire route is given in Fig. 2.

The glucose is concentrated to its solubility limit in water (47.8 wt-%), and the stoichiometric addition of oxygen produces formic acid as the only desired product, as previously described [63]. For the first reaction (biomass oxidation), a temperature of 90 °C and an oxygen (pure) pressure of 5 bar were assumed. Carbon dioxide is produced as an undesired by-product and is removed from the product by phase separation. The liquid product stream, consisting of a mixture of formic acid and water, is then fed into the dehydrogenation reactor. At a temperature of 85 °C and atmospheric pressure, formic acid is completely decomposed into carbon dioxide and hydrogen. The liquid outlet stream consists of pure water, while the gaseous stream is composed of a mixture of carbon dioxide, hydrogen, and water. The water is subsequently separated from the gaseous stream using a flash at 25 °C and atmospheric pressure. The main flowsheet from Aspen Plus® V12 can be found in Fig. S1 and the mole flows in Table S1 in the ESI.

In **Route 2** some methanol is added to the OxFA reactor to minimize the formation of carbon dioxide. This route is shown schematically in Fig. 3.

Previous studies have shown that 10 wt-% of methanol as a co-solvent can be sufficient to effectively reduce the formation of carbon dioxide in the modified OxFA-Process [20]. Methanol in these amounts is assumed not to affect the solubility of glucose in solution, in comparison to pure water [64]. The process conditions for the biomass oxidation are identical to those in Route 1. Here, formic acid is the primary product, but methyl formate is also generated as a second product by consecutive esterification of formic acid with methanol, that is assumed to be in equilibrium. A small amount of carbon dioxide (0.18 kmol/h) is produced, which is removed from the reactor via the gas phase. The resulting liquid product stream is then fed into a column where methanol and methyl formate are separated as light-boilers from the residual components and recycled for the OxFA-Process. By recycling the methanol, only a small amount of methanol fill up (<1 wt-%) is required in the feed. The column separates 99 % of methanol and methyl formate, with the bottom product of the column consisting of a formic acid/water mixture that is fed into a dehydrogenation reactor, as in Route 1 (same process conditions). As previously described, formic acid is converted into hydrogen and carbon dioxide, and then excess water is separated in a flash. The main flowsheet from Aspen Plus® V12 can be found in Fig. S2 and the exact mole flows in Table S2 in the ESI.

In **Route 3**, the effect of increasing the methanol content in the feed stream further to 50 wt-% was investigated. The goal was to increase the production of methyl formate and further reduce the formation of carbon dioxide. The various steps in the process are shown in Fig. 4.

The feed composition introduced into the OxFA-Process, compromising two recycled streams and the incoming biomass stream, is characterized by a solvent mixture of 50:50 (water/methanol), while the solubility limit (13.7 wt-%) of glucose in the biomass stream is maintained [64,65]. This heightened methanol content within the solution not only leads to increased methyl formate production but also effectively suppresses the formation of carbon dioxide as a by-product [20]. A liquid product stream consisting of methanol, water, methyl formate and formic acid is produced by biomass oxidation at 5 bar and 90 °C and subsequently separated in a distillation column. The head of the column removes 99 % of methyl formate and feeds it into a decarbonylation process decomposing methyl formate into methanol and carbon monoxide, while some methanol is further decomposed to carbon monoxide and hydrogen in a subsequent reaction (8.2 %). Decarbonylation takes place at a temperature of 300 °C under atmospheric pressure. Subsequently, the stream is cooled down to 25 °C, and flash separation is employed to isolate methanol and any unreacted methyl formate, which are then recycled back into the OxFA-Process. Carbon monoxide undergoes a water-gas shift reaction at 220 °C, reacting with water to produce carbon dioxide and hydrogen. At the outlet, the carbon monoxide content is less than 0.02 %. Finally, any excess water is separated through a flash at 25 °C. In the lower section of the column, water, methanol, and formic acid are extracted, with 80 % of these components being directed back into the OxFA-Process, while the remaining portion is purged from the system to prevent the accumulation of excess water. To avoid the loss of formic acid, a dehydrogenation step is incorporated into this route, similar to Routes 1 and 2. This results in the production of two H_2/CO_2 mixtures via distinct routes. Fig. S3 in the ESI contains the main flowsheet from Aspen Plus® V12, while Table S3 provides the exact mole flows.

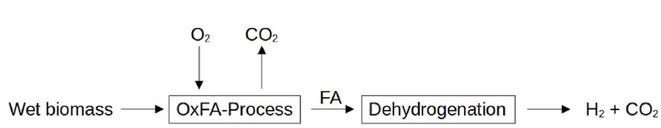


Fig. 2. Flowsheet of Route 1 (no methanol in biomass oxidation); FA = wet Formic acid.

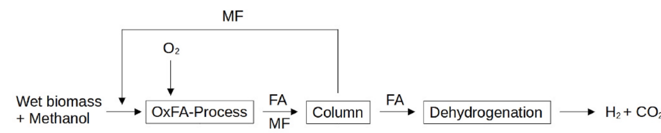


Fig. 3. Flowsheet of Route 2 (10 wt-% methanol in biomass oxidation); FA = wet Formic acid; MF = Methyl formate.

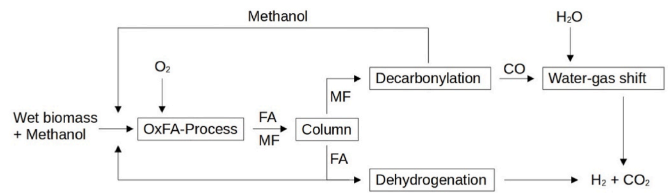


Fig. 4. Flowsheet of Route 3 (50 wt-% methanol in biomass oxidation); FA = wet Formic acid; MF = Methyl formate.

3. Results and discussion

3.1. Evaluation of the simulation data

3.1.1. Qualitative evaluation aspects

The three described scenarios can first be evaluated and compared on the basis of qualitative criteria (see Table 2). As the proposed hydrogen production concepts are in an early stage of development and

Table 2
Qualitative criteria to evaluate and compare the three routes for bio-based hydrogen production.

Criterion	Route 1	Route 2	Route 3
Equipment needs	++	+	–
Biomass solubility	++	++	–
Required volume flows in biomass oxidation	++	++	–
Hazard potential	++	+	–
Carbon loss by CO_2 formation	–	+	++

as the process equipment so far only exists on a demonstration level, an estimate for equipment costs is afflicted with high errors. For this reason, investment costs were not considered in this comparison of the scenarios. However, a qualitative evaluation provides insight into the relative CAPEX of the scenarios. The influence of the investment costs is estimated qualitatively via the number of large-scale units required. Route 1 can be realized by only two reactors, due to a direct coupling of the biomass oxidation process with the dehydrogenation of formic acid. In contrast, Route 2 requires an additional intermediate column to separate the methanol/MF mixture from the FA-stream in between. Route 3 follows two parallel paths to extract hydrogen once from the intermediate formic acid and once from the MF part, making equipment for both pathways necessary. In total four reactors, one column and two heat exchangers are required, resulting in highest investment and maintenance cost for Route 3.

The three concepts differ in the applied water/methanol solvent ratio in the biomass oxidation step. By that, the physical properties of the reaction mixtures are different. An important aspect is the solubility of the biomass building blocks. For our model substrate glucose, the solubility in water at a temperature of 20 °C is 47.8 g_{Gluc}/g_{Sol}. However, when mixed in a 50/50 ratio with methanol (as in Route 3), the solubility drastically decreases to only 13.7 g_{Gluc}/g_{Sol}, necessitating a larger quantity of solvent [63]. Route 1 & 2 have similar feed streams (375 kg/h & 446 kg/h) into the OxFA-Process, with that of Route 2 being slightly higher due to the addition of the recycling stream. In contrast, Route 3 experiences a reduction in the solubility of the biomass stream, leading to significantly larger recycle streams and resulting in a substantial feed stream of 8382 kg/h. Due to this higher mass flow rate, more energy for liquid pumping and for product separation in a consecutive column is required. The higher solvent steam due to poor substrate solubility adversely impacts the CAPEX side, by necessitating larger reactors and pipelines, leading to significantly increased expenses compared to Routes 1 and 2.

The hazard potential of these processes is another qualitative aspect that must be taken into account. If methanol is introduced to the biomass oxidation process as a co-solvent (like in scenarios 2 and 3) MF is formed in certain amounts. Both substances, methanol and MF are light boiling compounds with a vapour pressure at reaction temperature (90 °C) of 2.55 bar and 5.99 bar, respectively. In a gas mixture with air or oxygen, both compounds can form explosive mixtures within their explosion limits (approx. 5–40 vol-% for methanol and 5–25 vol-% for MF) [66,67]. Our initial estimate suggests that explosive mixtures can occur, particularly in Route 3.

Taking together the aspects compared in Table 2, Route 3 in particular scores poorly overall, while Routes 1 and 2 can be positively rated. However, for the comparison of the proposed routes, the following quantitative evaluation will particularly focus on how the suppression of CO_2 formation by the addition of methanol in the biomass oxidation affects the economic efficiency of hydrogen production via the process routes.

3.1.2. Quantitative evaluation aspects

The quantitative evaluation aims to study the economic feasibility of the proposed green hydrogen processes. The simulation of the three scenarios for a biomass input stream of 1 kmol/h allows for the calculation of required oxygen, of the produced hydrogen and thermal energy demand as well as for the energy/carbon efficiency and hydrogen costs. The calculated values are shown in Table 3.

The energy efficiencies, as determined by equation (7), range from 29 % to 48 %, slightly below the efficiencies calculated in gasification, which typically fall between 50 % and 65 % [55,68,69]. It is noteworthy that these gasification figures exclusively consider biomass as the energy input. In contrast, Wang et al. [70] factored in steam and electricity in their calculations, yielding an energy efficiency of 38 % for gasification. Under these considerations, the efficiencies for the considered routes are 25.19 % (Route 1), 32.16 % (Route 2), and 26.38 % (Route 3).

Table 3
Quantitative comparison of Route 1 (biomass oxidation in water), 2 (10 wt-% methanol in biomass oxidation) and 3 (50 wt-% methanol in biomass oxidation) for an inlet flow of 1 $kmol_{Gluc}/h$.

	Route 1	Route 2	Route 3
η_{Energy}	29.14 %	47.81 %	45.55 %
$\eta_{C,\ Gluc}$	56.67 %	92.33 %	96.58 %
O_2 Feed	137 kg/h	96 kg/h	96 kg/h
Heating	117 kW	362 kW	818 kW
Cooling	618 kW	484 kW	877 kW
H_2 from Glucose	6.81 kg/h	11.17 kg/h	11.68 kg/h
H_2 costs per kWh	0.38 €/kWh_{H2}	0.27 €/kWh_{H2}	0.40 €/kWh_{H2}
H_2 costs per kg	12.82 €/kg_{H2}	9.11 €/kg_{H2}	13.50 €/kg_{H2}

Stoichiometrically, a maximum of six molecules of hydrogen can be formed from one molecule of glucose. Routes 2 and 3 utilize over 90 % of this potential, as the high carbon efficiency values show (92.33 % & 96.58 %). The higher methanol content in Route 3 compared to Route 2 (50 wt-% instead of 10 wt-%) only results in a very limited benefit in carbon efficiency. In Route 1, a significant portion of glucose is converted into CO_2 and H_2O through the OxFA-Process explaining the low hydrogen yield of only 56.67 %. The total oxidation reaction consumes the double oxygen amount compared to the partial oxidation to formic acid. Consequently, Route 1 necessitates approximately 43 % more oxygen than the other two routes to convert the same quantity of glucose.

The energy demands for individual units encompass two key components: the reaction enthalpy and the energy required to heat or cool the feed stream to the desired reaction temperature. In Route 1, the sole source of heat demand is the endothermic dehydrogenation, which necessitates 117 kW (118 kW for dehydrogenation minus 1 kW provided by cooling the feed from 90 to 85 °C). Route 2 entails a dehydrogenation process that uses 144 kW, with 11 kW supplied by the hot stream from the column. Thus, the total heat demand for the dehydrogenation step in Route 2 is 133 kW. Additionally, the evaporator in Route 2 demands 229 kW of heating power, making the overall heating requirement three times higher compared to Route 1. For Route 3, which utilizes methyl formate, the higher mass flow of reactants lead to increasing heat demands. The evaporator in Route 3 requires 305 kW of heating power, significantly more than in Route 2. The dehydrogenation step in Route 3 totals 426 kW (151 kW for the reaction and 275 kW for feed heating). Furthermore, the endothermic decarbonylation necessitates 84 kW (67 kW for the reaction and 17 kW to heat the feed), and the exothermic WGS requires 2 kW (14 kW to heat the stream, of which 12 kW are provided by the exothermic WGS itself). As a result, Route 3 has the highest heating demand of 818 kW in total.

In all three scenarios, process cooling plays a vital role in removing the heat generated, e.g. by biomass oxidation. In Route 1, this cooling requirement amounts to 498 kW (with a total of 522 kW for the reaction and 24 kW dedicated to the heating of the feed). Additionally, there is a need for 120 kW of cooling power to facilitate the flash separation of water at the end of the route. For Route 2, a cooling power of 55 kW is essential in the condenser of the column to enable methanol/methyl formate separation. The OxFA-Process in this route requires a total cooling power of only 304 kW, significantly less than in Route 1. The reason is that the total oxidation occurs at lower rate, resulting in only 332 kW of energy being released by the reaction, while the feed stream to be heated is slightly larger, requiring 28 kW. The flash separation process in Route 2 necessitates a cooling capacity of 125 kW. In Route 3, the condenser in the column has to cool a large mass flow with 391 kW. The OxFA-Process requires 178 kW, although 346 kW are released from the reaction, as 168 kW are directly utilized for heating the feed stream. Additionally, cooling is needed for phase separation at three flashes: In flash 1 following the decarbonylation and in flash 2 following the WGS reaction only minimal cooling of 6 kW each needs to be considered. However, Flash 3, subsequent to the dehydrogenation, demands 296 kW. The cooling power differs significantly between Flash 3 and Flashes

1 & 2. This is mainly because Flashes 1 and 2 have two heat exchangers in front of them, which is described in more detail below.

Note, that a pinch analysis was carried out for all three routes. Due to the different temperature levels of the individual units heat integration according to the Aspen Energy Analyzer® V12 is only rewarding within Route 3 (Fig. S4 in ESI). Here, by placing two heat exchangers (upstream of the decarbonylation and upstream of the water-gas shift reactor), saving approx. 700 kW by heat integration is achieved. This integration is already considered in the calculation of the values in Table 3.

Taking the operational material and power requirements into account, Route 2 results in the cheapest hydrogen production price of 0.27 €/kWh$_{H2}$. The largest cost drivers of the other routes are the loss of carbon via total oxidation when no methanol is present in the OxFA-Process (Route 1) and the poor solubility of the substrate glucose in methanol (Route 3). Due to the high mass flow rates of methanol in Route 3, the column can no longer separate methyl formate with reasonable effort, and more hydrogen would be produced by the undesired decomposition of methanol to H_2 and CO in the decarbonylation reactor than from the biomass itself. Consequently, the sustainable character of this novel hydrogen production process would no longer be guaranteed.

The favoured Route 2 is examined in more detail below. Fig. 5 shows the composition of the cost shares for this route.

The cost breakdown reveals that more than half of the total costs is attributed to providing the substrate glucose at its market price of 300 €/t, owing to its value as a product and its use in other processes. Note, that glucose was used as a model substrate here, to have defined physical properties and a broad set of published experimental data available. Heat is the second largest expense, with one-third of the cost associated to the dehydrogenation and two-thirds linked to the evaporator of the separation column. The evaporator requires a temperature of 122 °C, for which medium-pressure steam can be used, while the dehydrogenation proceeds at 85 °C making low-pressure steam sufficient [71]. Oxygen for biomass oxidation, is the third largest cost driver, whereas other cost shares are negligible in the considered scenario. Electricity is needed for compression of the oxygen gas stream and contributes only marginally to the total hydrogen costs and methanol can be recycled to a major extend (2.29 kg/h loss). The cost share for cooling is relatively low, as it was assumed that the evaporator, the OxFA reactor, and the flash separator are cooled with inexpensive river water.

3.2. Sensitivity analysis

A sensitivity analysis, varying the three largest cost drivers (glucose, heating and oxygen) was carried out in order to illustrate the influence of price developments (Fig. 6). The costs were reduced from the assumed standard price (100 %) down to 0 % (replacement of the feedstock by a free alternative) and increased up to 160 % (increase in the price of raw materials, e.g. due to market fluctuations).

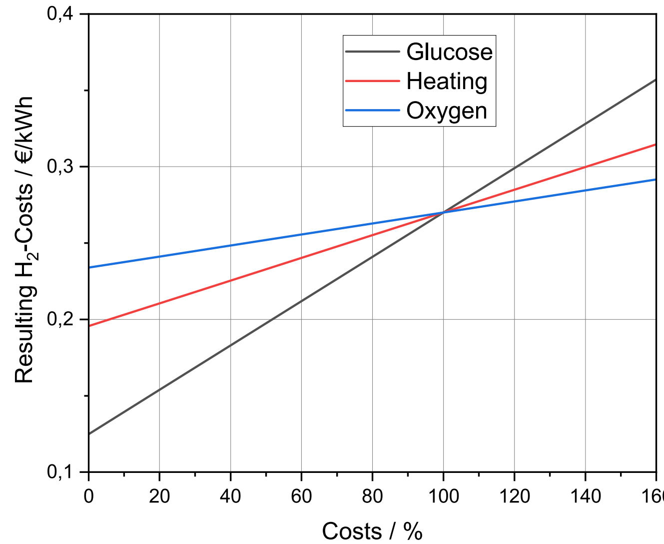


Fig. 6. Sensitivity analysis of the three largest cost contributors for Route 2 (10 wt-% methanol in biomass oxidation).

The greatest effect can be achieved by reducing the cost for the biomass feedstock. A reduction by 50 %, from 300 €/kg to 150 €/kg leads to a hydrogen price of 0.20 €/kWh$_{H2}$. Glucose was selected as the model substrate for this study, due to the aforementioned reasons. However, a real application of the novel hydrogen production concept is only feasible when waste biomass materials are used, that are usually much cheaper to purchase, compared to glucose. As shown by the sensitivity analysis, the substitution of glucose with a more affordable alternative would highly increase the economic competitiveness of the process. Albert et al. [28] and Niu et al. [72] have shown that biomass oxidation using the conventional OxFA-Process (no methanol addition) can be performed with various complex biomasses, such as beech wood, straw and even effluent sludge (Formic acid yield between 15.7 and 75.2 %), why it can be assumed, that these substrates are also applicable in the methanol-modified OxFA-Process. Another attractive low-cost substrate are hemicellulose-rich hydrolysates. A substitution could potentially reduce the costs of the feedstock by 50–70 %.

The price of these biomass substrates is subject to a strong volatility. Fig. 7 illustrates the price developments of selected biomasses (glucose, wood, and straw) over the past three years. The data for glucose and

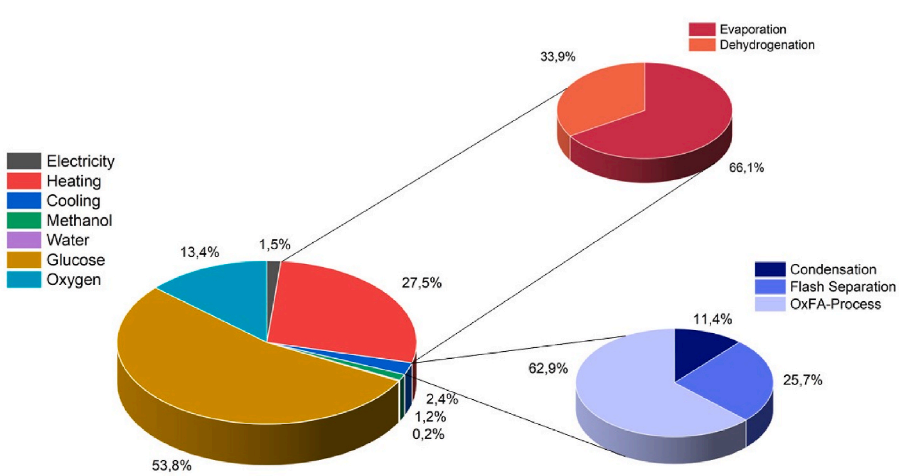


Fig. 5. Distribution of cost shares for hydrogen production via Route 2 (10 wt-% methanol in biomass oxidation).

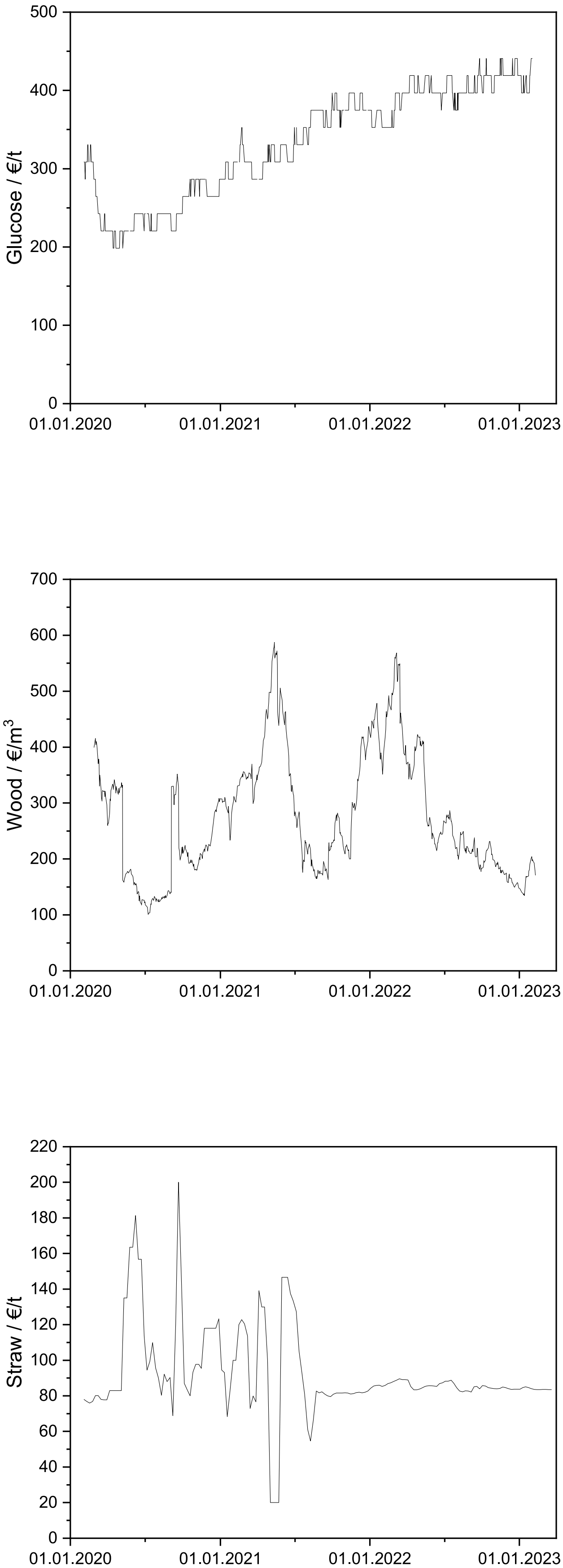


Fig. 7. Price development of glucose, wood and straw from 02.2020 to 02.2023 [73–75].

wood was sourced from international trade markets, while the price for straw was derived from the cost of a round bale in Germany [57,73–75]. Over the past two years, the price of glucose has exhibited a nearly continuous upward trend, while the expenses associated with wood and straw have demonstrated significant fluctuations around a consistent baseline. This factor should be taken into careful consideration when evaluating additional biomass substrates. As a result, our primary focus turns towards waste biomass, as it presents a highly cost-effective option, and in some instances, disposal costs are actually offset. This strategic shift has the potential to substantially diminish the overall expenses associated with hydrogen production.

The second largest cost driver is process heating, where a reduction of 50 % from 80 €/MWh to 40 €/MWh leads to a hydrogen price of 0.23 €/kWh$_{H2}$. This can be accomplished by integrating the plant into a surrounding where low and medium pressure steam is available. Reducing the cost of oxygen by 50 % from 140 €/t to 70 €/t would result in a hydrogen cost reduction by 0.02 €/kWh$_{H2}$ to 0.25 €/kWh$_{H2}$. One potential method to achieve this is by producing oxygen directly on site using a pressure swing adsorption coupled to the process [76]. Li et al. [77] has shown that the OxFA-Process also works with air, instead of pure oxygen. However, this would require the air to be compressed onto a higher level in order to achieve the same oxygen partial pressure. If we now assume a scenario in which all three factors, biomass substrate, heat and oxygen cost are reduced by 50 %, the hydrogen price reaches a level of 0.16 €/kWh$_{H2}$. It is important to note at this point that the assumptions made in Table 1 are a current estimate and local prices can fluctuate greatly due to various factors (e.g., political and economic situation, location, etc.).

For comparative analysis, let's consider biomass gasification as a method for producing green hydrogen. In this process, the biomass undergoes initial steps of crushing and drying to eliminate moisture content [78]. Subsequently, it is subjected to gasification at high temperatures and pressures in the presence of an oxidant, such as oxygen or air. This process generates a product gas comprising predominantly of CO_2, CO, H_2, and CH_4 [78]. To refine this product, two reactors are employed to eliminate tar and sulphur, facilitating hydrogen production via a two-stage water-gas shift reaction involving both high and low temperatures. In the final phase, hydrogen is separated from the remaining gas stream using pressure swing adsorption to achieve a high level of purity [79].

The cost associated with producing hydrogen from biomass via biomass gasification has been estimated to range from 0.10 to 0.15 €/kWh$_{H2}$, encompassing all investment expenditures and ongoing operational costs, such as maintenance [69,79,80]. However, the high operating temperatures and the high reactor costs make this application more interesting for large, centralised plants, whereas the concept presented here would also be possible in smaller, decentralized plants. It is worth noting that while the production of hydrogen from biomass using the OxFA-Process, particularly with glucose, remains comparatively more expensive, there is significantly potential for cost reduction by substituting the feedstock. The above-mentioned studies on biomass gasification have assumed significantly lower prices for biomass, which is also more realistic for a commercial application of this process. It is important to acknowledge that this study did not incorporate investment costs due to a lack of reliable data at this time. Ongoing research and improvements in operational efficiency hold the promise of substantially lowering various expenses and bolstering the competitiveness of this approach. With further advancements, especially in optimizing feedstock selection, the production of hydrogen from biomass via the OxFA-Process stands poised to become more economically feasible and gain a competitive advantage.

4. Conclusion

In summary, this study has explored a promising novel process for hydrogen production from biomass. The process consists of a first biomass oxidation step, producing formic acid and/or methyl formate in the so-called OxFA process, followed by hydrogen release from these intermediates. Depending on the water/methanol solvent ratio in the biomass oxidation step, the process design for hydrogen generation differs strongly. Three different process designs were carefully evaluated and compared with regard to qualitative and quantitative economic criteria. The incorporation of methanol as a co-solvent during the OxFA-Process, along with the recycling of methyl formate, suggests that carbon loss can be minimized and resource utilization optimized. The new process route is characterized by its consistently mild reaction conditions and a low hazard potential, which makes the application particularly attractive for decentralized hydrogen production from biomass residues. In a sensitivity analysis, various cost reduction measures could be identified to further enhance the economic feasibility of the novel route. While our analysis used glucose as a model biomass, the application of various biomass wastes like straw or effluent sludge has the potential to produce hydrogen to competitive costs of 0.16 €/kWh_{H2}. In conclusion, this study proposes a novel hydrogen production route that offers a sustainable and cost-effective solution in line with the evolving landscape of renewable energy and environmental sustainability. Further studies and advancements in this direction hold promise for a greener and more economically viable future in hydrogen generation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors gratefully acknowledge the funding of the Bavarian Ministry of Economic Affairs, Regional Development and Energy (Grant number: 84-6665a2/164/4). The authors further gratefully acknowledge the Federal Ministry of Education and Research for funding of the BMBF Junior Research Group FAIR-H2 (Grant number (FKZ): 03SF0730).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2024.03.163.

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