

Review

Evaluation of thermochemical routes for hydrogen production from biomass: A review



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ARTICLE INFO

Keywords:

Biomass
Bio-oil
Gasification
Pyrolysis
Reforming
Hydrogen

ABSTRACT

H₂ is regarded as one of the cleanest future energy carrier that can be generated from renewable sources and will give rise to a reduction of CO₂ emissions and environmental problems related to the use of petroleum based feedstock. Thus, the thermochemical routes for sustainable H₂ production compared to other biomass treatment routes have a great potential for its industrial implementation. Gasification of biomass and reforming of the bio-oil produced by biomass pyrolysis are the most researched pathways, although some studies dealing with supercritical water gasification and bio-oil gasification can also be found in the literature. Nevertheless, pyrolysis and in-line catalytic steam reforming strategy is gaining great attention due to its advantages compared to gasification and bio-oil reforming, especially those related to the optimization of each step (pyrolysis and catalytic steps) and bio-oil feeding. This review deals with the different reactor configurations, operating conditions and catalysts used in each process and compares the different alternatives in terms of H₂ production, with emphasis placing on the advantages of the two-step strategy.

1. Introduction

The urgent need to reduce the current energy dependence on fossil fuels has promoted a large number of studies that focus on the development of existing and new processes that use biomass based materials as feedstock. Biomass derived fuels and chemicals can play a major role in reducing CO₂ emissions as well as become a strategic source in order to guarantee energy competitiveness and sustainability [1]. However, the establishment of a sustainable energy system should be based on biomass exploitation policies that take into account land usage in order to avoid competition with human and animal food and soil exhaustion [2]. Accordingly, lignocellulosic biomass wastes and crops are regarded as the most suitable alternative feedstocks [3].

Lignocellulosic biomass can be treated using several thermochemical or biochemical processes in order to produce energy, bio-fuels and bio-chemicals [4]. Thermochemical processes, such as gasification and pyrolysis, are characterized by their scalability to industrial units, where the syngas and bio-oil produced as intermediate products can be subsequently converted into valuable fuels and chemicals [5]. These processes have the advantage of being similar to the ones already implemented in oil refineries, although need further development in order to be cost effective compared to fossil fuels [6]. Fig. 1 displays the main processes involved in a lignocellulosic thermochemical bio-refinery for the production of valuable products such as automotive fuels, light

olefins and H₂.

The global hydrogen production accounts for approximately 7.7 EJ/year, which may rise to 10 EJ/year by 2050 [7]. The main applications are related to ammonia production (51%), oil refining (31%), methanol production (10%), and other uses (8%) [7] (Fig. 2). Furthermore, H₂ market is expected to increase in the near future in a 5–10% per year, basically due to its consumption in refineries for treating heavy oil fractions and because of the projected demand in the transportation sector or as energy vector [8].

The 96% of the H₂ production technologies are based on non-renewable sources, with the most used processes being natural gas (48%) and oil (30%) reforming, followed by coal gasification (18%) [9]. Only 4% of the H₂ produced is obtained by means of water electrolysis [9] (Fig. 3). Consequently, in order to meet the fossil fuel consumption and CO₂ release reduction targets, new sustainable processes derived from renewable sources must be developed, such as the thermochemical ones that use biomass as feedstock shown in Fig. 1.

Although each biomass conversion method has its own advantages and disadvantages, it has been reported that the H₂ production cost for gasification and pyrolysis is similar, around \$1.2–2.4/kg (slightly higher for the former), which is actually between two and three times higher than the cost for CH₄ steam reforming [10]. Therefore, the choice of the most adequate one needs a thorough assessment of the economic aspects in the area where it has to be implemented, as well as

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Nomenclature		LHSV	liquid hourly space velocity
BCC	brown coal char	RHC	rice husk char
BTX	benzene, toluene, xylene	S/B, S/C, S/CH ₄	steam to biomass ratio, steam to carbon ratio, steam to methane ratio
CFB	circulating fluidized bed	T, T _p , T _G , T _R	temperature, pyrolysis temperature, gasification temperature, reforming temperature
CNT	carbon nanotube	WGS	Water Gas Shift
DFB	dual fluidized bed	WHSV, W _B HVS	weight hourly space velocity and bio-oil weight hourly space velocity
DME	dimethyl ether		
GHSV, G _{C1} HVS	gas hourly space velocity and gas hourly space velocity in equivalent CH ₄ units		

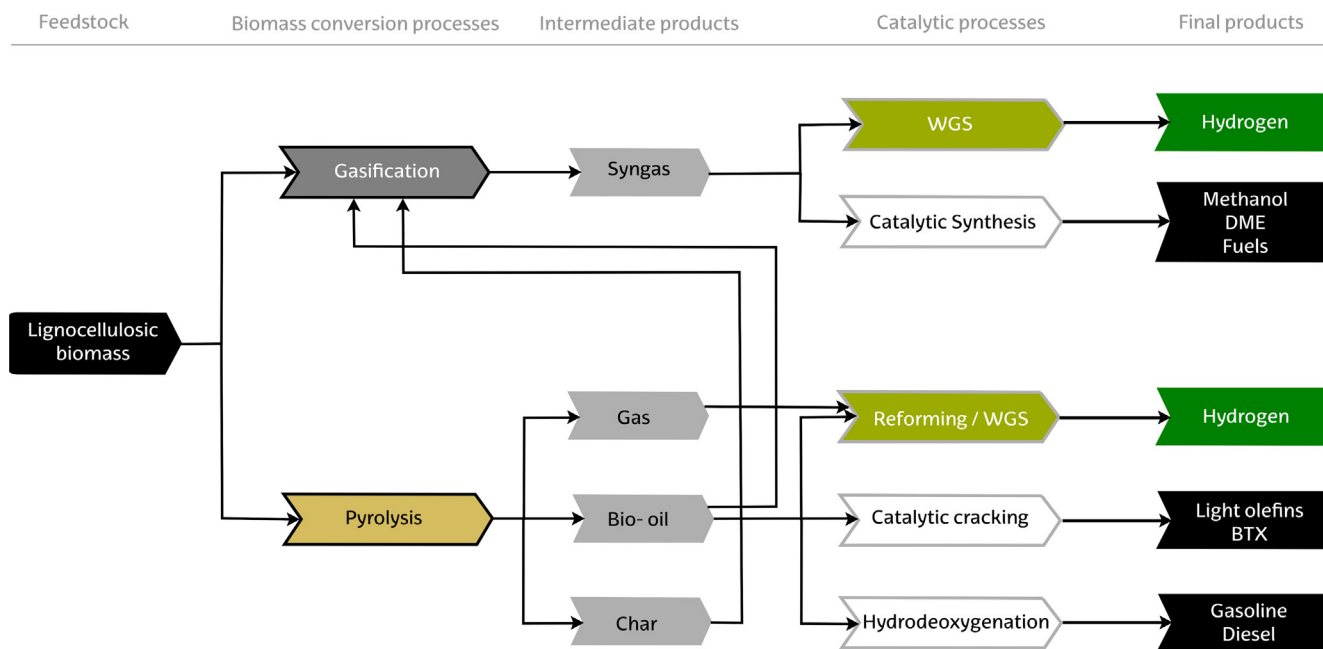


Fig. 1. Schematic representation of the main processes involved in a lignocellulosic thermochemical bio-refinery.

the availability of biomass resources, and the existence of large catalytic conversion units that can treat the intermediate products. These aspects allow making the choice between centralized processes, in which the final product is produced at the same unit where the biomass is primarily converted, or decentralized processes, in which the intermediate product (such as the bio-oil derived from flash pyrolysis) can be easily transported to catalytic conversion units.

The mostly studied and developed technologies for H₂ production are steam gasification [11–18] and the reforming of the bio-oil produced in biomass flash pyrolysis [19–25]; however, the biomass fast pyrolysis and in-line reforming of the volatiles has recently gained attention, with several studies published in the literature over the last years [26–31]. In this scenario, this one aims at reviewing the pyrolysis and in-line reforming strategy and comparing this technology with the

main thermochemical biomass conversion processes for H₂ production.

2. Biomass steam gasification

Biomass gasification has been widely studied during last decades, which is due to the fact the gaseous product can be directly used as fuel or as an intermediate product for the large scale production of fuels and chemicals [32–36]. The process characteristics entail establishing gasification plants in the regions where biomass is available, because the costs for the transportation of the raw material or the formed gaseous products would be excessive [37]. Fig. 4 shows a schematic

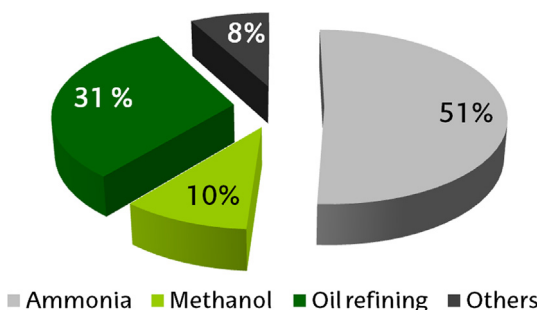


Fig. 2. Global consumption of hydrogen [7].

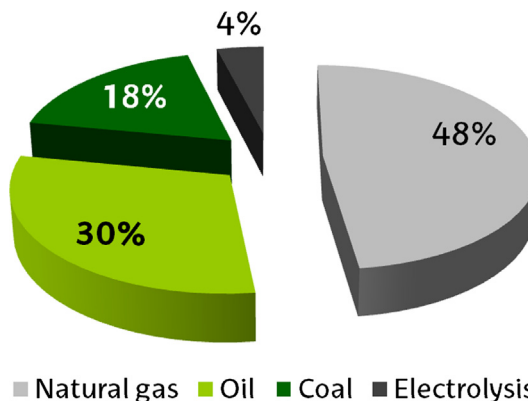


Fig. 3. Current sources of hydrogen [9].

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