

HYDROGEN FROM BIOMASS GASIFICATION FOR UTILIZATION IN OIL REFINERIES

Alberto Alamia, Fredrik Lind, Henrik Thunman

Division of Energy Technology
Chalmers University of Technology
S-412 96, Gothenburg
Sweden

Introduction

Gasification of biomass is seen as one of the most suitable routes for production of fuels from renewable energy sources (RES). The process is known from almost one century, but its application on commercial scale has never been economically feasible, which is due to the low price of oil and natural gas. During the last decades, the interest in gasification technology has been raised, driven by the increasing price of the crude oil and the necessity to reduce CO₂ emissions. A number of research projects have been carried out during the last years and commercial pilot scale gasification units are in operation today. The technology for fuel production is on its way to be mature. However, if taxes fees and other restriction on fossil fuels are not considered the cost for the fuels produced from biomass will still be higher than that of oil-based fuels or natural gas for next decades.

Nevertheless, there is room for other application of the biomass gasification followed by gas upgrading rather than fuel production. The proposed idea is a gasification-upgrading process optimized for hydrogen production, intended for the integration in an oil refinery. Driving forces for the introduction of this process are; 1, the dependency of the crude oil price on the sulfur content, 2, making use of low temperature waste heat and 3, the possibility to utilize existing infrastructure to introduce RES in the refinery.

The hydrodesulfurization of the refined petroleum products requires pure hydrogen, which is usually obtained from the one contained in the oil itself. Crude oils with unfavorable sulfur to hydrogen ratio have a lower price on the market, but they require extra hydrogen for the desulfurization process. Hence, there is room for introducing an extra source of hydrogen from a RES as biomass. Despite the technological challenge introduction of a new process causes, a high marginal profit can be achieved from the purchase of low price crude oil with high sulfur content.

The process proposed in this work is suitable for integration, since it requires mainly low temperature heat (150 °C) which is abundant in an oil refinery and a small amount of electricity. The gasification process could then be seen as a perfect heat sink for low temperature waste heat, which otherwise usually is lost due to heat exchanging with the surrounding air.

Overlook of the proposed process

The proposed process where the final product is a high purity hydrogen stream (H₂>97 %vol) at a pressure of 25-30 bars, can be divided in eight main steps (Fig.1)

Drying: Lignocellulosic biomass is usually supplied as wood chips with dry content between 55% and 45%, or as wood pellets dry content of 90-93%. For wood chips literature [3] and preliminary results show that the drying is the most energy demanding step in the whole process. The energy demand for the drying of wood chips is around 15-20% energy content of the dried material. Therefore it becomes essential to use waste heat and low temperature heat available in the process as much as possible. The drying proposed includes two steps with an intermediate silos capacity; the first unit is an air dryer which uses heat available at 70-90 °C to increase the air

temperature. In this unit dry content is increased to about 80%. The second dryer is a steam dryer which uses steam from the refinery at 150 °C, to heat up the steam in the dryer which is blown through the biomass to evaporate the remaining moisture. Removal of the last moisture content requires temperatures higher than 100 °C and, hence, the low temperature dryer cannot be used for wood pellets. The outlet dry content is about 96-98% and the outlet temperature of the biomass is about 120 °C. Besides drying, steam is used to prevent the risk of auto-ignition of the biomass. Auto-ignition happens due to the electrostatic charge accumulated on the wood surface when air dryer are used, this problem is avoided when using steam.

Gasification of biomass: In this process, the biomass is gasified by indirect gasification in a dual fluidized bed gasifier. This unit consists in two reactors: a gasifier and a combustor. Biomass is introduced in the gasifier where it is devolatilized and part of the char is gasified with steam. The rest of the char is burnt in the combustor to provide the heat needed in the gasification step. The heat is transported to the gasifier by circulating an inert solid material between the two reactors. The main advantage of this technology is that a nitrogen-free gas is produced without the need of pure oxygen and consequently of an air separation unit. The temperatures in the units are around 900 °C in the combustor and 850 °C in the gasifier.

The raw gas obtained from the gasifier contains mainly CO, H₂, CO₂, CH₄ and H₂O, but a significant part of the energy content is stored in hydrocarbons larger than C₂, including tars. From previous experiences in the Chalmers research gasifier and from the literature [4] the composition at the outlet of the gasifier is around: H₂ 25%, CO 40%, CO₂ 15%, CH₄ 15%, other hydrocarbons 5%, on dry basis.

This type of gasification is heat independent, since the heat demand from the gasifier is internally satisfied from the boiler. However, the air and the steam at the inlet of the two reactors should be pre-heated to as high temperature as possible and if heat is available by integration with the refinery, it should be used for this purpose.

Tar reforming through chemical looping reforming: Around 10% of the energy chemically stored in the gas is stored in the tar fraction; therefore, it needs to be reformed to hydrogen and carbon monoxide. It is not possible to crack the tar during the gasification because a temperature above 1100°C is needed, while it is technically impossible to operate fluidized bed gasifier at temperature higher than 900°C.

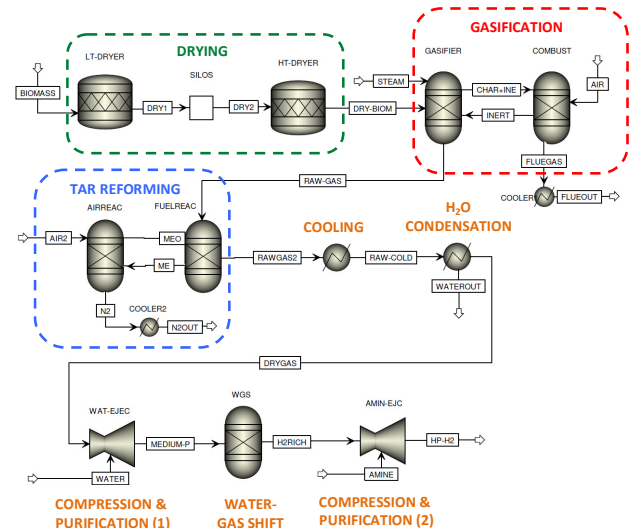


Figure 1: the proposed process for H₂ production

In the process proposed here tar is reformed in a chemical looping reformer (CLR) unit [1]. The CLR technology can to a large extent be compared with Fluid Catalytic Cracking (FCC), commonly used in oil refineries to increase the gasoline yield. Both systems consist of two interconnected fluidized bed reactors that have different gas atmospheres, but communicate in bed circulation. However, the main differences are that the CLR system is operated at higher temperatures and that the bed material in the CLR system allows for molecular transport in between the two reactors. In the CLR system an oxygen carrier material is circulated between the reactors. In the figure 1 the abbreviations Me and MeO are used to describe the reduced and oxidized form of the oxygen carrier material. The air reactor has a temperature of 900°C, here the oxygen carrier is oxidized with air, the reaction is strongly exothermic and part of the heat generated is transferred together with the oxygen carrier to the fuel reactor. In the fuel reactor the oxygen carrier is reduced while most of the fuel undergoes partial oxidation and steam reforming reaction. Furthermore, the oxygen carrier is also working as a catalyst for the water gas shift reaction, which increases the hydrogen yield. The temperature in the fuel reactor is about of 850°C. This technology has so far been demonstrated in lab scale [2]. Hydrocarbon longer than C₂, including tars are easily reformed in the CLR, while methane reforming can be harder to achieve. For hydrogen production it is appropriate to choose catalytic material which favors the methane reforming. Several different metal oxides are possible choices for this process e.g. nickel oxide (NiO), manganese oxide (Mn₃O₄) and Iron oxides (Fe₂O₃, FeO) The final composition depends on the material used as oxygen carrier and the amount of steam introduced in the fuel reactor. From equilibrium calculation using nickel oxide, the composition expected at the outlet of the CLR is: H₂ 50% , CO 27%, CO₂ 23% on dry basis, and a water content of 30-50%.

Gas cooling and drying: The gas from the CLR is cooled in a unit for production of saturated steam. Filters for fine particles will be placed at the outlet of this unit. As the gas has high water content the condensation heat is recovered. The heat obtained is suitable for utilization in the low temperature dryer.

Primary compression and bulk CO₂ removal: In this step the aim is to provide a final product with high hydrogen purity and at a high pressure, the compression and separations steps are the one which could drop the efficiency most as well as raise the investment cost. To make the proposed feasible a water jet ejector is proposed to compress the gas from atmospheric conditions to 6 bars. Besides the pressure increase, a water jet ejector also works as a gas cleaning device. The driving media, water, is used to absorb the CO₂, H₂S and HCl in the gas. An ejector does not include any rotating part, it is reliable and represents a much lower investment cost than a turbo compressor. The drawback is of course an increase of the energy consumption, which is about 65% higher than a traditional compressor. Figure 2 shows the circuit for a water jet ejector. In the separator unit the solution of water and the absorbed gases is heated close to the water boiling point to release the off gas. The off gas will be a mixture of CO₂, H₂S, HCl, CH₄ and other hydrocarbons.

Water gas shift (WGS): To increase the hydrogen content and to convert most of the remaining carbon monoxide a low temperature water gas shift reactor is used. Since, some H₂S still can be present at this stage the catalyst used must be sulfur resistant.

Final compression and H₂ purification: In this step the pressure is increased to a level sufficient for the downstream operations (28 bar). Compression and final CO₂, and H₂S removal is performed with ejector similar to the primary compression, but in this case amine is used instead of water as driving medium.

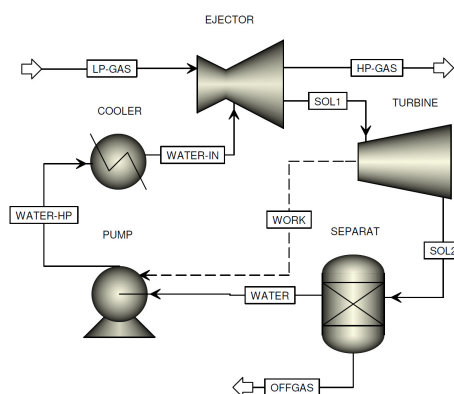


Figure 2: Water ejector for compression and CO₂ removal

This will remove all the CO₂ and H₂S left from the previous separation and the CO₂ generated in the WGS reaction. Purity higher than 97% vol is possible.

For evaluation of the input parameters and the feasibility of the proposed processes, data and experience from Chalmers University indirect gasification and downstream gas cleaning technologies that have been developed during several years are used. Chalmers gasifier is a 4 MW biomass input research gasifier that has been operated for more than 500 hours per year since 2007. The chemical looping combustion and reforming have been widely investigated in lab scale units of the sizes of a few W to 100 kW during nearly a decade. This experience is converging towards different new processes, like the process proposed above. The process is investigated by the use of Aspen Plus for a 100 MW biomass input process. At the time of the writing only partial results are available.

Final remarks and comments

The investigated process is expected to have a production capacity between 0.042 and 0.075 kg of H₂ per kg dry biomass, which correspond to 0.8-1.6 ton/h of H₂ for a production plant of 100 MW biomass input. The purity of the hydrogen produce is higher than 97% vol and it is delivered at 28 bar. The direct advantage of the process is the possibility to produce hydrogen, suitable for desulfurization, from a RES. The secondary advantage is the increased economic margin deriving from the possibility to purchase lower quality oil. The process itself is easy to integrate within a refinery plant as most of the heat demanded needed can be provided at low temperature (in the drying steps), while the heat released from the coolers and the WGS reactor is at higher temperature. This could potentially lead to a raise in the overall efficiency. The gasification technology is fuel flexible compared to other renewable fuel processes e.g. fermentation processes and forest residuals and sorted waste materials can thereby be used as main fuel.

References

1. Rydén M., Lyngfel A. *Hydrogen and power production with integrated carbon capture by chemical looping reforming*. 2005
2. Lind F., Seemann M., Thunman H. *Continuous Catalytic Tar Reforming of Biomass Derived Raw Gas with Simultaneous Catalyst Regeneration*.
3. Phil E., Heyne S., Thunman H., Jhonsson F. *Highly efficient electricity generation from biomass by integration and hybridization with combined cycle gas turbine (CCGT) plants for natural gas*. 2010
4. Neves D., Thunman H. *Characterization and prediction of biomass pyrolysis products* 2011