



Techno-economic assessment of bio-oil aqueous phase-to-liquids via Fischer-Tropsch synthesis and based on supercritical water reforming



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ABSTRACT

High energy demand along with large capital costs have been the main drawbacks of Fischer-Tropsch plants, which may call into question the economic viability of the Fischer-Tropsch process. The second issue is the focus of this paper, which presents a techno-economic assessment of biofuels production by a low-temperature Fischer-Tropsch synthesis with electricity as a co-product from supercritical water reforming of the bio-oil aqueous phase. A plant size of 60 t/h was considered and a heat-integrated process was designed to be energy self-sufficient, which includes syngas production and upgrading, as well as liquid fuels production by Fischer-Tropsch synthesis and refining. The simulation and optimization was performed with the aid of Aspen Plus, and some case-studies were performed. Using a feeding concentration of 25 wt%, 2.74 t/h biofuels and 5.72 MWe were obtained. In this case, by performing a discounted cash flow analysis, with 10% rate of return and 100% equity financing, the minimum selling prices for the refined FT-gasoline, FT-diesel and FT-jet fuel were 1.20, 0.93 and 0.26 €/kg (0.84, 0.75 and 0.20 €/L), respectively, which are competitive prices with respect to the market values of the equivalent fossil fuels. Likewise, the decrease in the selling prices as the plant capacity increases was also analyzed.

1. Introduction

Although there are many renewable emerging technologies for large-scale electricity production, without or with low carbon emissions, the transport sector is entirely based on the use of fossil fuel. The rising price of crude oil until a few years ago and the potential fluctuations of oil market prices in future, along with global environmental problems, have promoted new efforts to find alternative processes to produce transportation fuels with improved energy and environmental efficiencies. This way, we have proposed a new process of Fischer-Tropsch (FT) fuels production from the syngas obtained by supercritical water reforming (SCWR) of the bio-oil aqueous phase. In the previous paper [1], Fischer-Tropsch synthesis was designed and analyzed, which provided a novel and efficient valorization for the waste-aqueous phase of bio-oil. This previous study has been completed by carrying out a techno-economic assessment of the overall process, once designed and revised some parts of the original process.

FT synthesis is a technology to produce a variety of liquid transportation fuels, such as diesel, gasoline and jet fuel from syngas, obtained by other technologies, such as gasification. FT-biofuels exhibit attractive advantages: they are well-suited to the existing market regarding technical specifications (for example, a high cetane number for

FT-diesel and the absence of sulfur or nitrogen) and compatible with available vehicle engine designs [2].

The interest in FT-liquids from gas-to-liquids (GTL), coal-to-liquids (CTL) and biomass-to-liquids (BTL) process has been increasing. Currently, there are several commercial plants around the world that produce FT-liquids from GTL [3] and CTL [4] process. However, FT-liquids production from biomass is still under development due to the great investment costs required, the high feedstocks prices and the low energy density of biomass, among other reasons. As an alternative, solid biomass might be converted into liquids bio-oils by a fast pyrolysis process, with a higher energy density as compared with solid biomass. However, this process generates a waste-aqueous stream (20–30 wt% organic compounds), named bio-oil aqueous phase, which may be valorized through supercritical water (SCW) reforming that is an emerging technology investigated by many authors and ourselves in the last years [5–7]. Supercritical water has properties very different from those of liquid water, which give advantages regarding other reforming technologies. Thus, the dielectric constant of SCW is much lower, the number of hydrogen bonds is much lower and their strength is much weaker. As a result, SCW behaves like many organic solvents, so organic compounds have a complete miscibility in SCW.

The aim of the paper is to estimate the total investment and

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production costs, obtaining the minimum selling price of the products (FT-gasoline, FT-diesel and FT-jet-fuel), by considering the selling of electricity and different scenarios, thus assessing the feasibility of the full process in a hypothetical plant size of 60 t/h of bio-oil aqueous-phase. The techno-economic analysis was performed in terms of net present value, payback period and break-even price, and a sensitivity study was carried out to investigate the effect of several factors, such as the uncertainty of the capital investment or the feedstock price, on the minimum selling price of the biofuels.

2. Methodology

In this section, a summary of the process design and simulation is given and the methods used for the process economics are described, for a SCWR-LTFT plant with a feeding of 60 t/h during 8000 h per annum.

2.1. Process design and simulation

The design and simulation of the process was extensively described in the previous paper [1], and only a summary is provided below. The process was designed to maximize the biofuels and electricity production for an industrial size of 60 t/h of bio-oil aqueous phase [8,9] under different feeding concentrations. The process is heat integrated and energy self-sufficient.

The SCWR reactor operates at 240 bar and 800 °C to increase the CO and H₂ yields [7]. The product gas leaving this unit is expanded to 15–40 bar by an expander (TURBINE) to generate electrical power. A fraction of syngas may enter a high-temperature water-gas shift (HWGS) reactor (operating at 350 °C) to increase the H₂ yield when the H₂/CO molar ratio at inlet Fischer-Tropsch reactor is lower than that specified. Then, the outlet gas is mixed with the by-pass stream and cooled down to 35 °C to condense the water. A fraction of syngas is sent to the furnace to achieve energy self-sufficiency (Fig. 1).

The rest goes into two pressure swing adsorption (PSA) units, to obtain pure H₂, pure CO and a CO₂ + CH₄-rich stream [10]. A fraction of H₂ along with the CO stream are conveyed to the FT synthesis loop. The CO₂ + CH₄-rich stream enters a dry-reforming (DR) reactor to increase the amount of CO and H₂ fed to the low-temperature Fischer-Tropsch (LTFT) reactor; besides, CO₂ emissions are reduced (environmental advantage). DR operating conditions are 600 °C and 1 bar to boost the CO and H₂ production, as verified by simulation [11]. The gas

leaving the DR is cooled to remove the water, and then it is compressed before entering the second PSA system to further increase the flow of H₂ and CO fed to the FT reactor (Fig. 2).

Reactions in LTFT reactor, which operates at 220 °C, 20 bar and 2.0 inlet molar ratio H₂/CO, are highly exothermic (about 150 kJ per mole of CO converted [12]). The heat is released by an evaporator, and saturated steam is formed (212 °C, 20 bar). A fraction of this stream is sent to preheat the inlet stream of the FT reactor, and the rest of the steam is expanded to 1 bar in a turbine (TURB2) to produce additional electricity. The statistical distribution model by Anderson-Schulz-Flory (ASF) was used to obtain hydrocarbon molar fractions [13]. An α -value (probability of chain growth) of 0.90 was obtained using the equation by Song et al. [14] for cobalt-based catalysts used in LTFT. CO conversion per pass was assumed to be 50% [15], and the overall CO conversion in the loop was close to 90%. The stream leaving the FT reactor is cooled, and liquid phase is separated from the gas. The former is sent to a decanter to separate water from hydrocarbons, while the gas phase splits in a recycle stream and a purge to avoid the build-up of inert gases (Fig. 3).

The purge stream of the FT loop and the gas leaving the hydrocracking reactor are mixed, compressed and cooled before entering a flash separator to remove most of the gases from liquid. This latter and the liquid phase of the FT loop are mixed and sent to three distillation columns to separate the different biofuels (gasoline, jet-fuel and diesel). The lightest fraction is re-used in the process, and the heaviest fraction is sent to the hydrocracking. Hydrogen required by the hydrocracking is that non-converted in the FT reactor (separated by the PSA4 unit) plus a fraction of H₂ leaving the PSA1 unit. The hydrocracking reactor operates at 360 °C, 35 bar, and 0.06 kg-H₂/kg-wax using a platinum-based catalyst (Fig. 4).

Finally, and regarding the heat integration, several heat exchangers were suitably located in the process. The strategy followed is based on minimizing the exergy losses, so small temperature-driving forces must be achieved by using countercurrent flows and small temperature differences at the ends of the exchangers. In this approach, the high-temperature hot streams heat up the high-temperature cold streams, and the low-temperature hot streams warm up the low-temperature cold streams, by taking the reformer along with the furnace as a central point, where maximum temperature is required.

All the simulations were performed by Aspen Plus, and more details of the process and units are given in Section 3.2 and elsewhere [1].

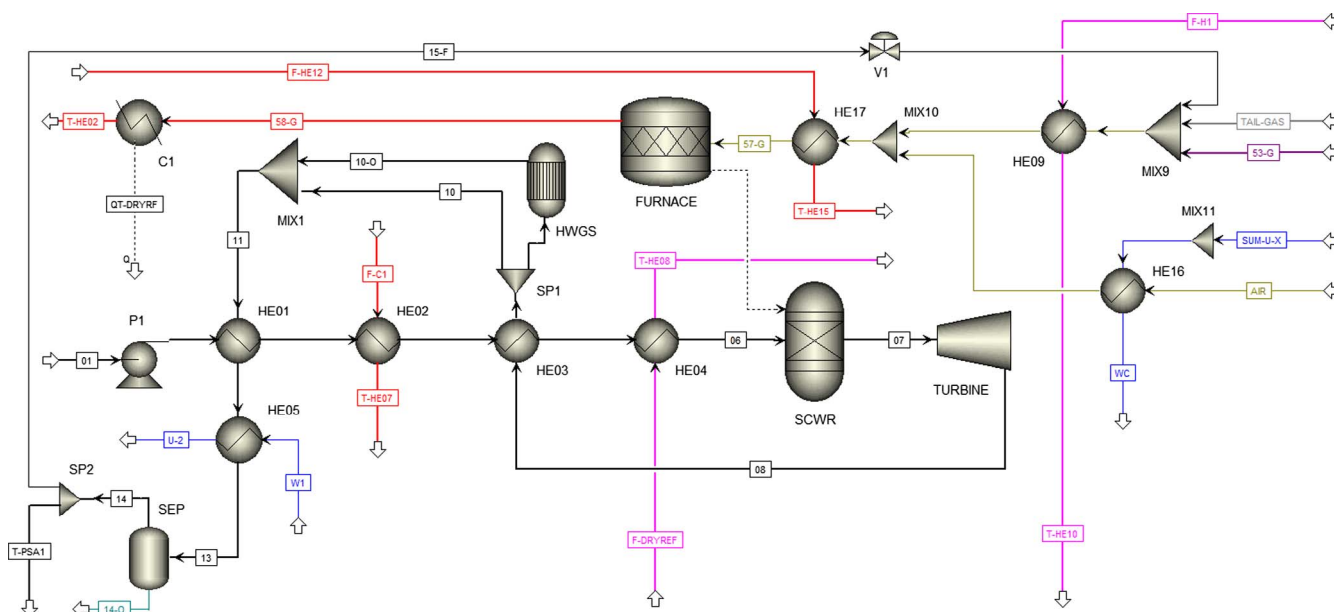


Fig. 1. SCWR and HWGS section.

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