

Fischer-Tropsch biofuels production from syngas obtained by supercritical water reforming of the bio-oil aqueous phase



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ABSTRACT

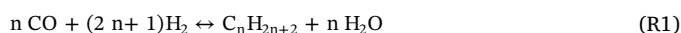
A new process to produce low-temperature Fischer-Tropsch products from the syngas obtained by supercritical water reforming technology of the bio-oil aqueous phase is developed and analyzed. The process includes four sections: syngas production from supercritical water reforming, syngas upgrading by water-gas-shift and dry reforming reactors as well as pressure swing adsorption systems, Fischer-Tropsch synthesis and products refining and upgrading through a distillation columns train and hydrocracking reactor. The aim is to produce maximum biofuels and electrical power, achieving the overall energy self-sufficiency. The energy scheme also involves cogeneration (e.g., hot water for district heating) and removal of CO₂ for sequestration. Process simulations were carried out by Aspen Plus. The effect of the main operating parameters (feed concentration and composition, as well as operating conditions of Fischer-Tropsch reactor) on the process performance (carbon efficiency with or without refining, biofuel and electricity production) was studied by a sensitivity analysis. This way, the optimal conditions were found, so for a feeding of 60 t/h with a total organic concentration of 35 wt%, carbon efficiency with refining is 38.5% (4.6 t/h biofuel) and 5.3 MWe is generated. The CO₂ for sequestration is 0.50 kg/kg of organic feeding.

1. Introduction

A few main routes make it possible to produce gas and liquid biofuels, such as extraction of vegetable oils, fermentation of sugars to alcohol, or gasification and chemical synthesis. Some recent studies indicate that the use of Fischer-Tropsch (FT) technology for biomass conversion to synthetic hydrocarbons may offer a promising alternative to conventional diesel and gasoline [1–3]. This synthesis was developed in the 1920s as a chemical process to produce hydrocarbons of different length (i.e. light gases, gasoline, jet fuel, diesel and wax fractions) from a mixture of CO and H₂ called syngas.

Hydrocarbon formation in the FT synthesis is comparable to a polymerization mechanism in which the chain initiation involves the adsorption and dissociation of CO reactant on the catalyst surface. This is followed by hydrogenation of surface carbon atoms to form methylene groups that act as monomer units (–CH₂–) in the polymerization. Thus, free radical species methylene (·CH₂) react with hydrogen to form a methyl group, which is the chain initiator. Chain propagates by sequential integration of methylene to alkyl groups thus leading to long-chain hydrocarbons. The termination step occurs by reduction or β-hydride abstraction to produce n-paraffins or α-olefins, respectively [4]. The highly exothermic reactions describing the formation of paraffins

and olefins from syngas in FT synthesis are represented by reactions (R1) and (R2) [5]:



Hydrocarbon production in FT synthesis depends on temperature, thus distinguishing high-temperature FT (HTFT) synthesis (300–350 °C), and low-temperature FT (LTFT) synthesis (180–250 °C) [2]. HTFT process produces mainly light hydrocarbons (LPG and gasoline) and LTFT produces heavier hydrocarbons (mainly, diesel and wax). The cobalt-based catalyst is used on an industrial scale in either fixed-bed reactors (Shell) or slurry reactors (Sasol), but only for low temperature Fischer-Tropsch (LTFT) process, while iron-based catalyst is used for both HTFT and LTFT synthesis processes [4].

Liquid synthetic fuels (with high volumetric energy density) can be transported by the same means as oil and are free of sulfur, nitrogen and aromatics, which are typically found in normal gasoline and diesel. Thus, emissions from internal combustion engines are reduced. Liquid synthetic fuels are receiving much attention as a real alternative to reduce the petroleum dependence of the transportation sector and can be easily obtained from natural gas, coal and biomass gasification. The resulting processes are known as gas to liquid (GTL), carbon solid to

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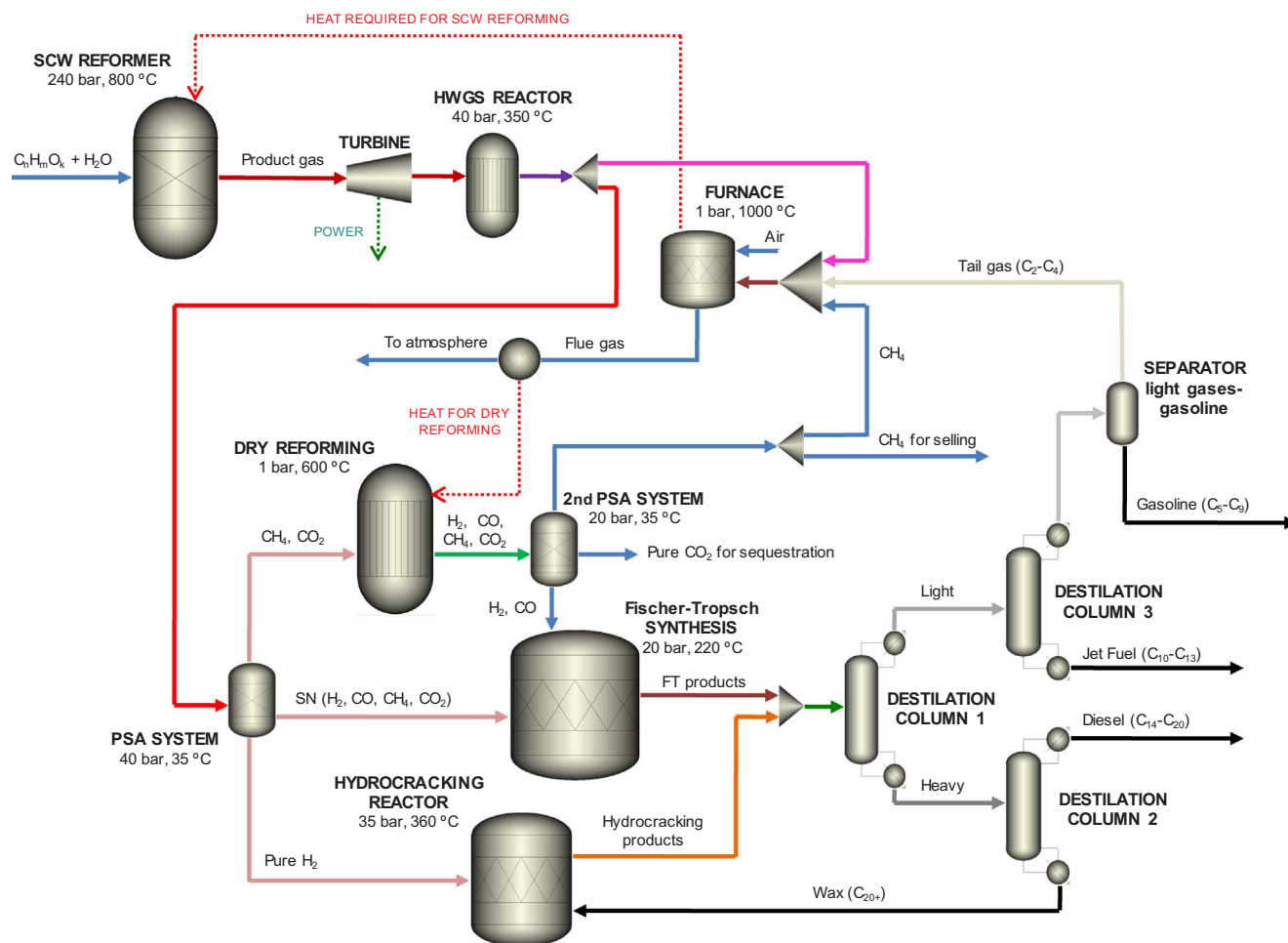


Fig. 1. Block flow diagram of the process.

liquid (CTL) and biomass to liquid (BTL), respectively [3]. CTL may involve considerable emissions of CO_2 , SO_x and NO_x and particulate matter, so gas cleaning systems are necessary. Likewise, availability, transportation, handling, storage and low energy density of biomass are obstacles in the development of large scale biomass processing. For these reasons, biomass can be converted into more transportable forms such as liquid bio-oils through fast pyrolysis, which involves thermal decomposition reactions that occur in a few seconds in the absence of oxygen. Liquid bio-oil has a higher energy density as compared with solid biomass, so those storage space and transportation problems associated with biomass are reduced [6].

By adding water, bio-oil can be separated in a valuable oil phase and in a waste- aqueous phase, which contains organics compounds (20–30 wt%) and may be reutilized and valorized. In this case, supercritical water (SCW) reforming is a suitable process because water does not need to be vaporized. Besides, SCW has additional advantages such as a high capability to solubilize gaseous organic molecules. Indeed, SCW reforming is an emerging technology that has been investigated the last years, as shown in our previous works about the valorization of glycerol from biodiesel production [7–11].

2. Aims and scope

High energy demand along with large capital costs have been the main drawbacks of FT plants, which may call into question the economic viability of the FT process. The first issue is dealt with in this manuscript, and the second one will be treated in a future to optimize the price of biofuels. Thus, in this paper, a new process of synthetic

fuels production from the combination of supercritical water reforming (SCWR) of aqueous phase of bio-oil and Fischer-Tropsch synthesis is designed and analyzed, achieving a novel and efficient via of valorization for the waste-aqueous phase of bio-oil. Therefore, liquid carbon from waste to liquid (WTL) is the process considered in this study.

Fig. 1 depicts the concept in a simple way using a block flow diagram. Aqueous phase of bio-oil is reformed under supercritical conditions and converted into syngas. Syngas from SCWR process is expanded in a turbine to generate electrical power and upgraded through water-gas shift and dry reforming reactors as well as by two pressure swing adsorption (PSA) systems. This way, the molar flow rate of H_2 and CO in syngas are increased and a desired H_2/CO ratio is achieved at the inlet of the FT reactor, which includes a loop to recirculate the unreacted syngas, thus increasing the overall conversion of CO into biofuels. A fraction of recycle gas is purged to avoid inert gases accumulation, and FT liquid is separated in different cuts by a distillation train. In addition, high conversion of the LTFT wax can be obtained under mild hydrocracking conditions thanks to the high chemical reactivity of heavy paraffin and the absence of catalysts contaminants like sulfur or nitrogen compounds [12]. Industrially, the operation of LTFT followed by hydrocracking is industrially applied, as in the Shell Middle Distillate Synthesis Process [13]. An external fuel is not needed as a heat source, because the process is designed to be energy self-sufficient by burning the off-gas from different sections. The proposed process is designed to maximize its performance in terms of (1) biofuels production and (2) net electrical power generation, as well as (3) cogeneration water and (4) pure CO_2 for sequestration.

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