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Integration of high-temperature electrolysis in an HVO production process using waste vegetable oil

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Abstract

The production of substitutes for liquid fossil fuels is of utmost importance for the decarbonization of the transport sector. This paper assesses the economic feasibility of producing hydrotreated vegetable oil (HVO) using waste vegetable oils as feedstock. The supply of hydrogen for the upgrading of the oil is obtained through a high-temperature electrolysis process, fed by low-carbon electricity. The use of waste materials eliminates the competition with food crops (e.g. soybean or rapeseed) and promotes the recycle of substances that should be treated for disposal. The results of the study show that the production cost of HVO with the considered plant are around 33% higher than that of fossil diesel. Moreover, the variable that has the strongest impact on the production cost of HVO is the price of the waste vegetable oil, which affects the final results more than the electricity price and the cost of the electrolyser.

1. Introduction

The need for renewable fuels has become urgent in recent years due to the necessity to lower the emissions related to the transport sector [1]. In particular, diesel occupies a large share (71% in 2016 [2]) of the road transport

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final consumption in the European Union and it is almost completely of fossil origin. Some renewable alternatives are available and they are mainly: FAME (Fatty Acid Methyl Esters), obtained from the reaction of vegetable oils or animal fats with alcohols (transesterification); and HVO (Hydro-treated Vegetable Oil) resulting from the process of hydrotreatment of virgin or waste vegetable oils. Biofuels offer important advantages compared to fossil fuels, since they do not contain aromatics and their sulfur content is usually lower [3]. Besides, the advantages of hydro-treating over transesterification include the possibility of reaching higher blends in fossil fuels, and more flexibility in the raw material selection [4]. In fact, the chemical properties of HVO (also called "green-diesel" to be distinguished from the product of transesterification) are more similar to those of fossil diesel, especially for the absence of double bonds in the carbon chains. In the last 5 years, HVO production has developed rapidly, especially in Europe (3,870 kt/y of planned capacity by 2020) and in the US (1,155 kt/y of planned capacity by 2020) [5]. The production of HVO may also be integrated in diesel refining processes, by co-feeding the biologic and the fossil feedstock [6].

On the other hand, the hydrotreatment process requires a very large amount of hydrogen and, so far, the main source of hydrogen has been the steam reforming of hydrocarbons. A few studies have been published on HVO production from diverse raw materials [6]–[8], but none of them considered hydrogen coming from electrolysis processes. For this reason, the integration of a high-temperature electrolysis unit, i.e. composed of Solid Oxide Electrolysis Cells (SOECs), with the hydrotreatment of waste vegetable oils is investigated in this paper, both in terms of energy efficiency and in terms of economic viability. This concept is a way of promoting the decarbonization in the transport sector, where the promotion of renewable energy sources is slower. In addition to that, this process constitutes a valid alternative to Fischer-Tropsch synthesis and it has the advantage of using a waste material, without the need for a gasification process.

2. Feedstock and pre-treatment

The synthesis of HVO can be performed using virgin vegetable oils, waste oils or animal fats as feedstock. The conversion of waste materials, in particular waste vegetable oils (WVO), has been preferred because it is a feedstock that does not entail any crop competition with the food market. The main sources of WVO are food processing plants and food services (i.e. restaurants and fast foods). The used cooking oils should be collected in order to avoid occlusion problems in sewers. As these organic compounds favor the creation of fat deposits that obstruct the pipes, they should not reach the sewerage system. In addition to the environmental benefit, the price of used oils is much lower than that of virgin oils.

The pre-treatment process that vegetable oils usually undergo before hydrogenation, aims at abating phosphorous compounds, trace of metals and soaps that may negatively affect the quality of the final product and the life of the hydrogenation catalyst [9]. Catalyst deactivation can occur when phosphor- and sulphur-containing compounds reach the catalyst active sites and irreversibly adsorb onto them [10]. For the same reason, hydrogen sulphide or carbon monoxide should not be present in the hydrogen stream [10].

The feedstock pre-treatment usually consists of three processes: neutralization, degumming and bleaching [11], [12]. The presence and the amount of impurities in the waste oil can vary depending on its type and it influences the pre-treatment process [13]. These contaminants include free fatty acids, which can be removed by means of a neutralization step that involves the use of alkaline solutions [13]. Other impurities, e.g. the calcium and magnesium salts of the phosphatidic acid are usually nonhydratable, therefore they are difficult to remove. Degumming is the process that eliminates all types of phosphatides, including the nonhydratable ones. If the phosphatide content is small (<20 ppm), as in palm oils, these impurities can be treated via a dry degumming process, with concentrated phosphoric acid [11]. Otherwise, different processes (e.g. acid or EDTA degumming) can be applied [11], [12]. Bleaching is the final step and it aims at diminishing the amount of non-converted phosphatides, trace metals and other contaminants present in the oil [10], [13]. Natural and activated earths can be used in this regard in a slurry configuration, to favor a good mixing between the oil and the adsorbents [10].

3. Plant Layout

The majority of the hydrogen is currently produced through steam-reforming of natural gas in oil refineries. Alternatively, hydrogen could be produced through electrolysis in case there is a large availability of cheap and low-

carbon electricity. In this study, high-temperature Solid Oxide Electrolysis Cells (SOECs) are used because of their high conversion efficiency and the abundant heat that they produce, which favors the thermal integration with the hydrotreatment, since the latter process requires considerable quantities of heat. The plant was considered to produce 40,000 t/year, working for 8,000 h/year. The simulations were performed in the process engineering software Aspen Plus using the RK-ASPEN thermodynamic model.

The model of the SOEC was adapted from Lorenzi et al. [14] and the water conversion has been set to 70% to avoid losses due to diffusion limitation. Then, part of the cathodic flow is recirculated to increase the hydrogen content (set to 10% in volume) at the inlet of the cathode, to avoid an excessively oxidizing environment, thus, limiting the risk of oxidation of the nickel catalyst of the cells.

The plant for hydro-treatment is modeled similarly to Letterio et al. [8] (Fig. 1), while the inlet waste vegetable oil is assumed to be completely composed of triolein as in Glisic et al. [7].
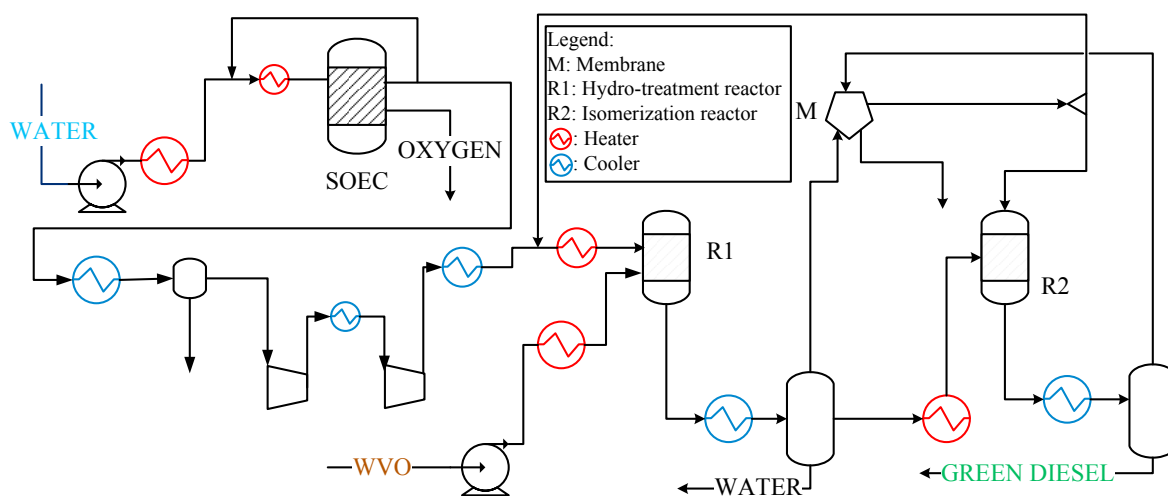

Fig. 1: Scheme of the integrated high-temperature electrolysis and hydrotreatment plant.

3.1. SOEC model

The electrolyser is fed with pure water available at 20 °C and 1 atm. The water-electrolysis reaction is considered to take place at 850 °C. Part of the oxygen produced at the anode is recirculated and it acts as a sweep gas, avoiding the use of air that could compromise the quality of the outlet oxygen, which, in this case could be collected and used for other applications. After the electrolyzer, the cathodic flow is cooled down to 80°C and it enters a flash separator in order to obtain a hydrogen stream with 99% purity, that constitutes one of the reactants for the hydro-treatment process. The active area of the SOEC is calculated according to [14], considering that the operation occurs in thermo-neutral conditions and that the Area Specific Resistance (ASR) is equal to 0.5 Ω cm^2. The flow of hydrogen enters an intercooled compression reaching 70 bar, which is the pressure at which the catalytic hydrotreatment takes place.

3.2. Hydro-treatment section

The conversion of vegetable oils into green diesel occurs in a fixed bed reactor at 290°C (R1), using a commercial Co/Mo catalyst dispersed on an alumina support [6]. The production of HVO is mainly based on the reactions of hydro-deoxygenation, hydro-decarboxylation and decarbonylation, in which vegetable oils are converted into chains of n-paraffins in the range C_{15}-C_{20} [3]. These three processes remove oxygen from the oil molecules, producing liquid hydrocarbons, propane, CO_2, CO and water in different proportions. These three processes are summarized in equation (1), that occurs in R1. Only heptadecane and octadecane are considered as

products as in [15]. The flow of hydrogen directed towards R1 is double compared to the stoichiometry of the reaction.

$$C_{57}H_{104}O_6 + 10H_2 \rightarrow CO_2 + 3H_2O + CO + C_3H_8 + 2C_{17}H_{36} + C_{18}H_{38} \tag{1}$$
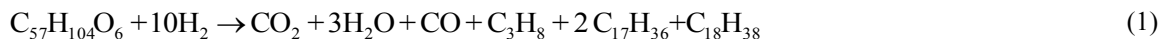
The outlet stream of the reactor firstly goes through a flash tank, operating at 70°C, which is used to separate the oil from water and syngas. The vapor stream from the first flash tanks enters a ceramic membrane (M) with a hydrogen selectivity of roughly 100% and the resulting stream is split: a part is recirculated to R1, while the remaining part is sent to the isomerization reactor (R2). The liquid stream reaches 355°C and 50 bar and it is directed towards R2 with the function of partially isomerizing the n-alkanes to improve the cold properties [16]. In the simulation we assumed that 10% of both $C_{17}H_{36}$ and $C_{18}H_{38}$ are isomerized into 6-pentyldodecane and 8-propylpentadecane respectively. At the same time a small fraction of heptadecane (6.6% wt) is cracked into propane (equation (2)) [8].

$$14H_2 + 3C_{17}H_{36} \rightarrow 17C_3H_8 \tag{2}$$

The products of the isomerization are cooled down to 50°C and a flash tank separates the HVO from the gaseous components that are recirculated.

Due to high H_2 flows required for both reactors, the hydrogen-rich streams are recirculated. Finally, a flash tank is used to separate the product oil from gases and water. The results of the simulations are summarized in section 5.

4. Cost estimation

The economic performance of the plant is measured through the Levelized Cost of Product (LCOP). An accurate description of this methodology can be found in [16], while the coefficient used for its determination are reported in [17]. In order to estimate the volume of the reactors the Liquid Hour Space Velocity (LHSV) was established. In R1 the LHSV is 1.0 h^{-1} [6], therefore, the volume flow rate entering the reactor is equivalent to the volume of the reactor itself and the vessel is considered to be vertical. The isomerization reactor has a LHSV of 2.1 h^{-1} [7]. The plant is able to supply all the thermal energy that is needed for the chemical processes using no external source of heat. Thermal integration using the Pinch Analysis methodology [18] has been applied in order to calculate the minimum external thermal energy requirement and to obtain the corresponding surface of the heat exchangers. The considered heat-exchange coefficients are 200 W/(m^{2}K) for liquid-liquid heat exchange and 100 W/(m^{2}K) for gas-gas. The sizing of the flash tanks was done according to the methods described in [19].

For all the aforementioned components, as well as for the pressure changers, the bare erected costs were determined according to the formulations in Turton et al. [8] and expressed in \$$_{2001}$. The SOEC cost for unit of active area is 4400 \$$_{2007}$/m^2 [20] and the stack is assumed to be replaced every 10 years, which is half of the plant life. All the costs have been harmonized in \$$_{2014}$ using the CEPCI index ($C_{I,2014}$=576.1, $C_{I,2007}$=525.4, $C_{I,2001}$=397).

Few studies investigate the vegetable oil pre-treatment costs. However, an estimate can be derived from the work of Zhang et al. [21], where an economic feasibility study is made on different processes that produce biodiesel via transesterification. The pre-treatment cost is assumed to be 0.76·M\$, referred to a biodiesel production of 8000 t/year. Considering a yield for the transesterification process of 90% [22], the value of the pre-treatment cost over the annual waste cooking oil inlet is equal to 85.5 \$ for every ton of waste cooking oil fed to the plant. Therefore, it is assumed that the pre-treatment cost for a HVO plant is comparable with that of a biodiesel production plant.

5. Results

5.1. Energy efficiency

The efficiency of the plant described in section 3 is expressed by equation (3):

$$\eta = \frac{LHV_{HVO}*\dot{m}_{HVO}}{W_{el}+LHV_{WVO}*\dot{m}_{WVO}} \tag{3}$$

The energy inputs are the electric power (W_{el}) required by pumps, compressors and electrolyzer, as well as the energy content of the feedstock expressed as lower heating value (LHV_{WVO}) multiplied by the mass flow rate. The obtained values are reported in Table 1. The flow rate of HVO determines the power consumption of the other components of the plant. The thermal integration of the plant allowed the external thermal need to be eliminated, with a saving equal to 2.6 MW. Without this optimization the resulting efficiency would have been equal to 83.6%.

Table 1: I/O streams and plant efficiency

Quantity	Unit	Value	Quantity	Unit	Value
WVO inlet flow	t/h	5.84	Water inlet flow	t/h	1.83
HVO outlet flow	t/h	4.97	Electrical consumption (W_{el})	MW	5.9
Lower Heating Value WVO	MJ/kg	39.5	Plant efficiency (η)	%	86.7%
Lower Heating Value HVO	MJ/kg	44			

5.2. Economic Results

The economic performance of the plant is estimated through the calculation of the levelized cost of product (LCOP), which is the revenue received by the plant operator per liter of produced HVO assuming that this cost is constant throughout the entire plant lifetime. Table 2 reports the total plant cost (TPC), indicating the share for each group of components, the costs for the feedstock (FC), for electricity and for the replacement of the disposables (e.g. catalyst). The TPC is multiplied by the factor 1.2 to obtain the Total Overnight Cost (TOC) which includes land, legal fees and permission costs, preliminary feasibility analyses, capital inventory and cost of securing financing [16]. The LCOP was then estimated by using equation (4):

$$LCOP = LF*\frac{CCF*TOC+FC+VOM+FOM}{AP}\left[\frac{\$}{l}\right] \tag{4}$$

Table 2: Total plant cost, fixed and variable operation and maintenance costs

Item	Unit	Value	Item	Unit	Value	Item	Unit	Value
Pre-treatment	M$	5.84	WVO	$/t	260	Operating labor (10 people)	k$/y	750
Pressure Changers	M$	13.55	Demineralized water	$/t	2.1	Administrative labor (30% op. lab.)	k$/y	225
Reactors and separators	M$	24.24	Electricity	$/kWh	0.04	Maintenance (2%TPC)	M$/y	2.35
Heat exch. and coolers	M$	1.82	Catalyst hydrotreatment	M$/y	1.40	Insurance (1%TPC)	k$/y	782
SOEC stack	M$	5.93	Catalyst isomerization	M$/y	1.37			
Total plant cost (TPC)	M$	51.39	Var. O&M cost (VOM)	M$/y	2.77	Fixed O&M cost (FOM)	M$/y	4.10

Where LF is the levelization factor (LF=1.268) CCF is the capital charge factor (CCF=0.111) [15] and AP is the annual production expressed in liters per year and equal to 50 Ml/y (density: 0.8 kg/l). Therefore, the value of LCOP is 0.68 $/l. Finally, considering a final diesel price of 1.5 $/l and assuming that 35% is attributable to crude oil and refinery costs, the corresponding fossil diesel production cost is 0.53 $/l, which is 22% lower than the LCOP for HVO.

6. Discussion and Conclusion

The value of LCOP depends on some optimistic assumptions on the cost of electricity and on the lifetime of the SOEC, therefore, a sensitivity analysis on these two variables have been performed (Fig. 2 a) and b)). The results show that these variables have a limited influence on the LCOP and the highest cost share is represented by the hydrotreatment plant. Moreover, the price of the oil feedstock has a large impact on the production cost of HVO as pictured in Fig. 2 c). In conclusion, the economic convenience of the analyzed process is substantially dependent on the availability of waste vegetable oil at a low price, which influences the LCOP to a larger extent than the availability of cheap electricity for hydrogen production. The availability of WVO is, thus, an important variable to be verified for the economic viability of the plant.
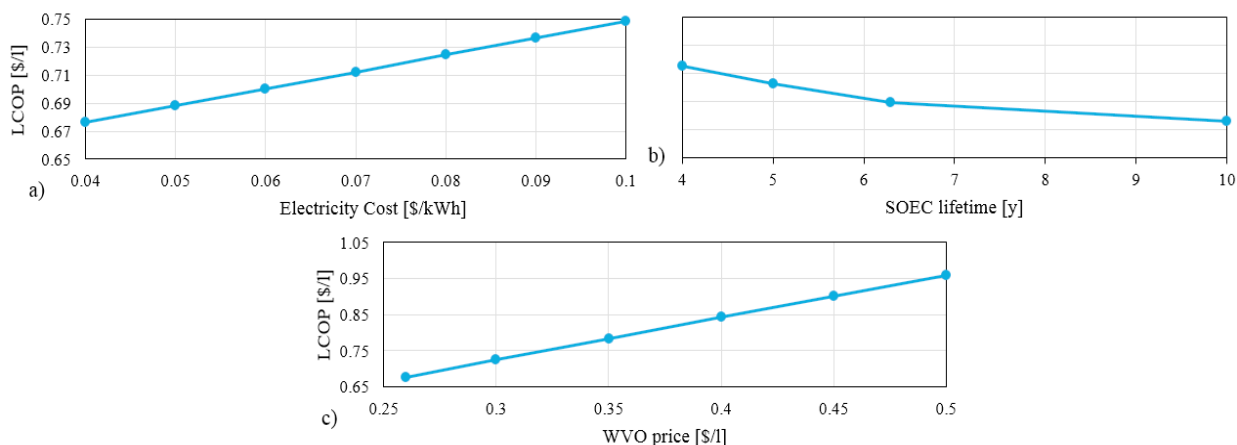

Fig. 2: Sensitivity analysis for the LCOP of HVO for varying electricity cost (a), SOEC lifetime (b) and WVO price (c)

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