SUSTAINABLE HEFAS FOR AVIATION

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Abstract. There are several technological pathways for the production of alternative and high sustainable aviation fuels, aspiring to mitigate GHG emissions. Hydrogenated Esters and Fatty Acids (HEFAs) are ASTM-certified aviation biofuels with no technical or safety consideration during the numerous demonstration applications, with only limitation their production cost. In this work, the sustainability potential of HEFAs for aviation applications is examined, considering the cultivation/transportation and hydroconversion of different lipid sources/feedstocks (plant oils and microalgae). The hydroconversion of each lipid source is evaluated with respect to the individual quality characteristics (fatty acids content type, chain length, saturation degree) providing a theoretical evaluation protocol for different potential feedstocks. The results indicate that lipid sources consisting of saturated fatty acids of close-to-jet carbon-chain length (C12-C14) are the most promising feedstocks for aviation HEFAs production.

Keywords: HEFA, hydroconversion, lipids, microalgae, LCA

INTRODUCTION

Aviation transport has specific climate impacts compared to other transport modes mainly because most air-transport emissions occur at a high altitude. Air transport currently accounts for a small share (10%) of global energy consumption but its growth rate is one of the largest ones (5% annually according to IATA), rendering an expected 1.5-3% growth in aviation fuels consumption, and subsequent increase of GHG emissions. In order to mitigate the corresponding climate change effects attributed to the aviation sector, a 1.8 billion tons reduction of the equivalent CO_2 emissions is required by 2050. This target can be partially achieved by improving fleet rollover, aircraft infrastructure as well as engine performance, while a 25-50% CO2 emission reduction is expected by the use of renewable aviation fuels. Thus, the technology development of new alternative and high sustainable aviation fuels that can mitigate GHG emissions is of outmost importance.

At present there are several technological pathways leading to aviation biofuels, based on thermochemical and/or enzymatic conversion of biomass (ex. lipids, sugars, and lingo-celulosic material. The available technological pathways and produced aviation biofuels offer different advantages and disadvantages with regards to the production costs, quality characteristics, and feedstock flexibility/availability. Hydrogenated Esters and Fatty Acids (HEFAs) are ASTM-certified (D7566) biofuels that have demonstrated no technical or safety problem in flights, while their production is already supported by several plants in operation. Nevertheless, the dependence on plant oil contained lipids and high production costs (1700-2400$/t) limit HEFAs market growth and sustainability potential. A simplified process diagram of HEFAs production is given in Figure 1.

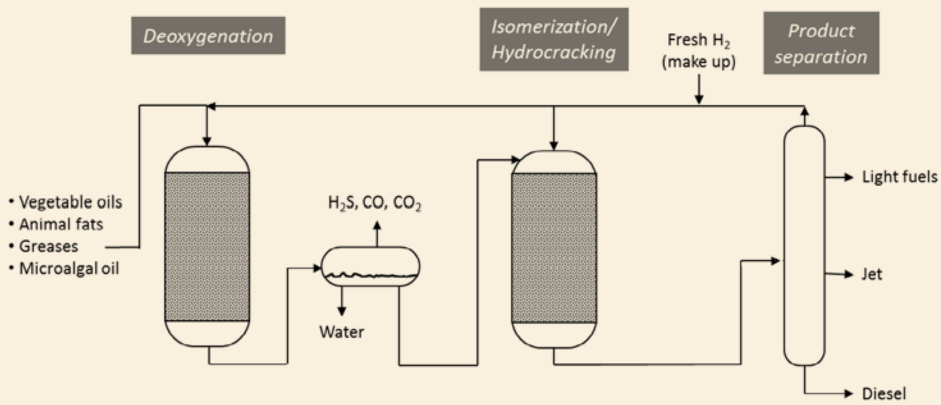

Figure 1. HEFA biofuels production simplified schematic

In this paper, HEFAs sustainability optimization potential is evaluated with respected to the lipids feedstock type, taking into consideration the cultivation/harvesting costs and the hydrogen consumption associated with the underlying conversion reactions.

AVIATION HEFAS SUSTAINABILITY

HEFAs sustainable production is strongly related with the lipid sources cost and the downstream catalytic hydroconversion process operating cost. Regarding the later, over 77% is attributed on the H_2 utilized according to Lehmus (2011), as H_2 consumption affects both the operating cost and the final fuel carbon footprint.

The hydrogen consumption during the catalytic hydroconversion of lipids into aviation biofuels (biojet) involves a reaction network series including saturation, oxygen removal, isomerization and cracking, which is described in Figure 2. In particular the first reaction involves the hydrogenolysis of the triglyceride molecules into fatty acids and propane. For plant oil lipids, consisting mainly of triglycerides, this reaction has to take place before any other reaction and is associated with a large amount of hydrogen consumption. In the case of microalgae lipids, however, this reaction is does not occur, as free fatty acids are mainly constituting microalgae-based feedstocks. Saturation is the second type of reaction that takes place (Eq.2), but for this reaction step, the hydrogen consumption depends on the type of fatty acids contained in the feedstock, i.e. plant oils with a large percentage of unsaturated fatty acids such as sunflower consume larger amounts of hydrogen for saturation. For this reason the hydrogen consumption during the saturation step varies significantly for different plant oils. The third group of reactions is deoxygenation, which leads to the removal of oxygen from the fatty acid molecules. There are three different possible routes including hydrogenation (Eq. 3a), decarbonylation (Eq. 3b) and decarbonxylation (Eq. 3c). The last two routes are definitely the most desired ones as they only consume 1 mol of hydrogen per mol of fatty acid. However, the current commercial hydrotreating catalysts are not as selective towards the last two routes and they are mostly activating the hydrogenation step which consumes a lot of hydrogen. The fourth reaction step is isomerization, which is required in order to convert n-paraffins to iso- and cyclo-paraffins, improving the cold flow properties, and is not associated with significant hydrogen consumption. Finally, hydrocracking is the reaction that is required in order to crack C-C paraffin bonds to produce smaller carbon-chain length molecules, which are within the desired C9-C13 range.

Reaction type	Reaction mechanism	H2/oil (mol/100mol)
Triglyceride hydrogenolysis	$CH_2\text{-O-C(=O)-R} \mid CH\text{-O-CO-R} \mid CH_2\text{-O-C(=O)-R} + 2 \cdot H_2 \longrightarrow 3 \cdot R\text{-}CH_2COOH + CH_3\text{-}CH_2\text{-}CH_3$ (1)	2·100
Saturation	$R\text{-}(CH{=}CH)_n\text{-}COOH + n \cdot H_2 \longrightarrow R\text{-}CH_2\text{-}CH_2\text{-}COOH$ (2)	3·n n=50-225*
Deoxygenation	$R\text{-}CH_2COOH + 3 \cdot H_2 \longrightarrow R\text{-}CH_2CH_3 + 2 \cdot H_2O$ (3-a) $R\text{-}CH_2COOH + H_2 \longrightarrow R\text{-}CH_3 + CO + H_2O$ (3-b) $R\text{-}CH_2COOH + H_2 \longrightarrow R\text{-}CH_3 + CO_2$ (3-c)	3·100
Isomerization	$R\text{-}CH_2\text{-}CH_2\text{-}CH_3 \longrightarrow R\text{-}CH(CH_3)\text{-}CH_3$ (4)	0
Hydrocracking	$R\text{-}CH_2\text{-}CH_2\text{-}CH_3 + H_2 \longrightarrow R\text{-}H + CH_3\text{-}CH_2\text{-}CH_3$ (5)	3·(78-95)**

*Based on range of content of unsaturated fatty acids of each vegetable oil
**Based on range of content of large-carbon chain fatty acids of each of each vegetable oil

Figure 2. Main catalytic hydroconversion reaction mechanisms of lipid feedstocks

Based on the detailed examination of the aforementioned reaction network for HEFAs production, the fraction of long-chain fatty acids, degree of saturation and the free fatty acids (that require no hydrogenolysis) varies with the type of lipid source as it was presented in Winayanuwattikun ***et al.*** (2008), rendering some lipids more demanding than others in terms of the hydrogen consumption associated with the different reactions. In fact, based on the aforementioned analysis, hydrogen consumption and thus the overall production cost would significantly decrease if the lipid source consisted of saturated fatty acids of close-to-jet carbon-chain length (C12-C14).

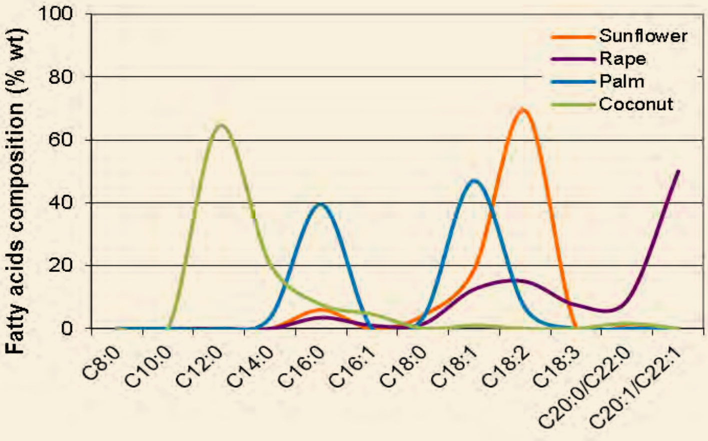

Figure 3. Fatty acid composition of four plant lipids examined

Nevertheless, nature renders great variability with respect to the consistency of various lipids sources (see Figure 3), which is reflected in the theoretical H_2 consumption during their hydroconversion to jet fuel, as shown in Table 1. Sunflower oil contains triglycerides consisting of C18 fatty acids which are mostly (89%) unsaturated, therefore its conversion to jet molecules would require significant H_2 for both saturation and hydrocracking reactions. While the other two widely used plant oils (rape and palm) do not render significant savings on H_2 consumption, coconut oil exhibits significant improvement as 92% of each contained fatty acids are saturated and 85% are within the desired C12-C14 range. Microalgae based lipids have the advantage of containing free fatty acids, therefore not requiring hydrogenolysis, which are mostly saturated. However, with the exception of *Strichodesmium erythraeum sp.* which consists of C10-C14 molecules, all other well established species render C14-C16 hydrocarbons, thus requiring hydrocracking.

It is significant to note that plant lipids containing triglycerides demand H_2 during hydrogenolysis (Figure 2-Eq.1) but render triple volume yields on the produced jet molecules (1 mole plant-oil contained triglycerides renders around 3 moles of jet), while microalgae lipids consisting of free fatty acids may not require hydrogenolysis but have no volume increase (1 mole microalgae-oil fatty acids renders 1 mole jet). For this reason H_2 consumption difference is less significant when it is presented in mol H_2 per mol of jet produced (see Table 1).

When the sustainability of different lipid sources is compared, one has to take into account the energy and other inputs demand during all the steps prior to the biofuels conversion plant, i.e. cultivation and transportation costs. Based on a recent study by Edwards *et al.* (2014), the GHG emissions of the four plant lipid sources examined range between 16.4-26.7g CO_2-eq/MJ_{oil} which according to the expected volume yield increase discussed above corresponds to 185.1 – 301.3 g CO_2-eq/lit jet produced, while microalgae lipid sources render a 50-80% reduction of the GHG emissions per lit of jet fuel produced, based on Patil *et al.* (2007) and Benemann (2012) data.

Table 1. Theoretical H_2 consumption and GHG emissions for aviation HEFAs production from different lipid sources

	Plant oils				Microalgae oils			
	Sunflower	Rape	Palm	Coconut	*Dunaliella sp.*	*Chlorella sp.*	*Nannochloropsis Oceanica*	*Strichodesmium erythreeum sp.*
1. Hydrogenolysis	2.0	2.0	2.0	2.0	0.0	0.0	0.0	0.0
2. Saturation	6.3	1.4	0.6	0.1	0.0	0.0	0.0	0.5
3. Deoxygenation	6.0	6.0	6.0	6.0	2.0	2.0	2.0	2.0
4. Isomerization	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5. Hydrocracking	2.6	2.6	2.5	0.5	0.9	0.8	0.7	0.4
Total (mol H_2/mol oil)	16.9	12.0	11.1	8.5	2.9	2.8	2.7	2.4
Total (mol H_2/mol jet)	**5.6**	**4.0**	**3.7**	**2.8**	**2.9**	**2.8**	**2.7**	**2.4**
GHG (g CO_2-eq/l jet)	**6.0**	**4.3**	**3.9**	**3.0**	**3.1**	**3.0**	**2.9**	**2.6**

CONCLUSIONS

The sustainability potential of aviation HEFAs was evaluated in terms of the cultivation/transportation and hydroconversion requirements of different lipid sources/feedstocks (plant oils and microalgae). Based on this study, the microalgae originating lipids had favourable carbon footprint vs. the plant lipids. Particularly for the plant lipids, it was shown that their cultivation/transportation steps were the main contributors to the overall jet production carbon footprint, due to the excessive input demands of their cultivation steps. The microalgae lipids had a significantly lower demanding cultivation steps, favouring the overall footprint. The hydroconversion energy requirements (H_2 consumption) were much lower as compared to those of the cultivation steps for all types of lipid sources. In fact the hydroconversion energy inputs of some plant oil contained lipids (palm and coconut) where comparable with the microalgae ones per unit volume of the jet produced.

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