Full Length Article

Process modeling of hydrodeoxygenation to produce renewable jet fuel and other hydrocarbon fuels

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HIGHLIGHTS

- Composition of feedstock oils affects product distribution and hydrogen demand.
- Feedstock affects thermal and electrical energy requirements.
- Oil content of the oilseed is a key parameter.
- Strategic heat integration reduces thermal energy demand.

ARTICLE INFO

ABSTRACT

The focus of this work is to model the hydrodeoxygenation process to produce renewable jet fuel and co-products from low-input oilseeds, specifically camelina, carinata (non-edible oil) and used cooking oil (UCO), taking into account the fatty acid compositions by incorporating the stoichiometric hydrodeoxygenation reactions. This methodology provides insight into the effect of feedstock composition and hydrodeoxygenation reactions upon product yields, product distribution, hydrogen consumption and process utilities. The resulting product slates, hydrogen gas and utility demands are specific to each of the camelina, carinata and UCO feedstocks.

The yield of kerosene-range alkanes ranged from 53 to 54% of the incoming oil, with 13–14% diesel range alkanes, 13–15% naphtha, and 7–9% liquefied petroleum gas, depending upon the fatty acid composition. The hydrogen consumption rate ranged from 26 to 30 kg per tonne of incoming oil, depending upon the degree of bond unsaturation. Thermal energy demand is 2.8 GJ/tonne oil when processing used cooking oil, versus 5.2 and 5.7 GJ/tonne of oil for carinata and camelina, respectively, owing to the additional energy required for oil extraction. Electricity demand was 73 kWh/tonne oil for UCO, versus 170 and 227 kWh/tonne oil for carinata and camelina.

1. Introduction

The aviation industry relies on petroleum-based fuels, but potential adverse environmental impacts from these fuels have been identified. The combustion of fossil fuels is of particular concern due to the impact of greenhouse gas (GHG) emissions on climate change. Development of low GHG intensity fuels is an emerging frontier to address growing climate change concerns in the aviation industry.

The International Air Transport Association (IATA) has responded by creating an emission reduction roadmap, which aims to lessen the environmental impact of air travel by improving fuel efficiency by 1.5% annually until 2020; achieve carbon neutral growth beyond 2020; and halve overall aviation emissions from 2005 levels by 2050 [1–3]. The EU Emission Trading Scheme (ETS) based on a "cap and trade" system also aims to reduce emissions [4]. As of 2012, airlines operating or providing services within the European Economic Area (EEA) are subject to the ETS, although the aviation industry was temporarily exempted from the ETS while the EU negotiates an agreement with the International Civil Aviation Organization (ICAO). The ETS is currently only applicable to flights within the EEA; a global market-based mechanism is being developed by ICAO to cover international aviation emissions, to be implemented by 2020 [5].

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Biojet produced from the hydrodeoxygenation (HDO) process is currently one of the biofuels used in demonstration and commercial flights. It is also a technology that has been commercialized to produce renewable diesel. Due to its technological maturity, it is expected that this pathway will play a major role in producing low carbon intensity jet fuels. The HDO process to produce hydroprocessed renewable jet (HRJ) from triacylglycerides (TAG) includes hydrogenation, deoxygenation, isomerization and hydrocracking stages. Hydrogenation is the first reaction, saturating all TAG bonds. Deoxygenation follows hydrogenation, and consists of three parallel reactions, including decarboxylation, decarbonylation and hydrodeoxygenation, as illustrated in Fig. 1 (adapted from Veriansyah et al. [6]). The alkanes produced are referred to as synthetic paraffinic kerosene (SPK) or HRJ, and are commonly known as hydroprocessed esters and fatty acids (HEFA) SPK. HDO fuel products are molecularly similar to their petroleum counterparts, with the notable difference being a lack of aromatic content. The TAG can be from diverse virgin and used oil feedstocks. Based on the fatty acid composition of the feedstock, the product yields, product distribution, hydrogen consumption and process utilities of the HDO process might vary, perhaps considerably. This issue, however, has not previously been investigated, and a key objective of this work is to rigorously evaluate the impact of fatty acid composition upon these key operating parameters.

UOP is a leading technology provider for the HDO process and has partnered with several biofuel producers, such as Altair and Ensyn, to convert vegetable oils and pyrolysis oil into liquid fuels, respectively. UOP has also developed their Green Jet Fuel™ Process (Fig. 2) using proprietary multifunctional catalysts [7] to target the production of HRJ. The catalysts selectively hydrocrack the deoxygenated fatty acids, to maximize production of jet fuel range alkanes while reducing the co-production of lower value lighter hydrocarbons. Since the process is patented, the specific reaction conditions, including its product slate, are not publicly available. The UOP process has produced fuels for most of the biojet test flights using vegetable oils.

Most studies assume that the production of biojet from lipids is independent of the feedstock oil and fatty acid profiles, and that the conversion of fatty acids produces only alkanes, carbon dioxide and water [9–13]. These assumptions do not account for the different degree of saturation of fatty acids, which would affect the H_2 needed for the hydrogenation reaction that converts TAG into fatty acids and propane. Stratton's LCA work to screen biojet production pathways examined the cracking reaction based solely on *n*-octadecane, a representative C18 molecule, which may not accurately represent the co-production of naphtha or other shorter alkanes when a diverse alkane pool is present [9]. Subsequent publications using data from Stratton [9] have incorporated this simplified view of the conversion process. While helpful for an initial evaluation, these simplifying assumptions do not reflect actual conversion reactions. This was later addressed by Pearlson [14,15]; using product yields from the literature for diesel products from soybean oil and jet fuel yields from jatropha oil, he calculated product yields including co-products such as propane, LPG and naphtha. However, Pearlson [14] has generalized the yield and conversion based upon soybean oil. Han et al. [13] pointed out the need to tailor the hydrogen (H_2) requirements based on the oil feedstock composition, but assumed the complete conversion of diesel into biojet [13], which is unlikely based upon typical cracking reactions and process technology.

The aim of this work is to model the HDO process from *Camelina sativa* (camelina), *Brassica carinata* (carinata), and used cooking oil (UCO), quantifying the H_2 demand, energy, electricity requirements and product slate from each set of triglycerides. Due to the scarcity of technology specific data such as for the UOP process, the modeling work is based on published studies describing the HDO conversion of fatty acids into paraffins. The methodology developed in this study will provide insight into the impact of feedstock composition upon product yield and hydrogen gas consumption. These parameters are crucial when modeling the HDO process, to quantify the total thermal energy and electricity demands and corresponding GHG emissions for the jet fuel product, when coupled with information on the thermal energy source and electricity grid. Results of the study also serve as a benchmark for comparison against literature data that used simpler modeling approaches, with soy oil and jatropha oil as feedstocks.
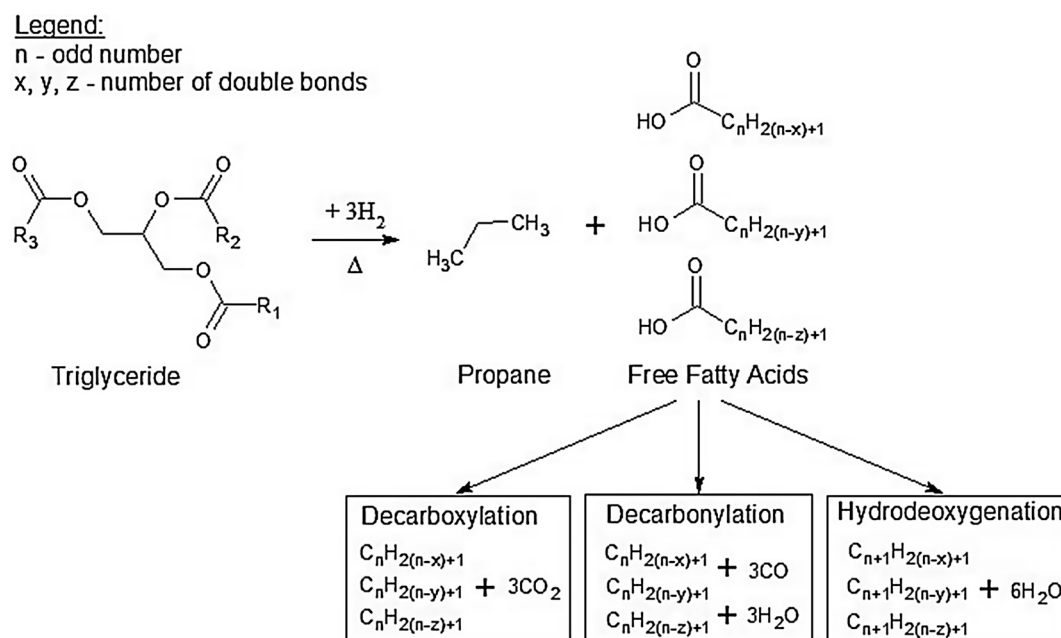

Fig. 1. The chemistry of hydrocracking of a TAG molecule that produces carboxylic acids and propane. The carboxylic acids subsequently undergo oxygen removal reactions. Adapted from Veriansyah et al. [6].