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Alternative thermochemical routes for aviation biofuels via alcohols synthesis: Process modeling, techno-economic assessment and comparison

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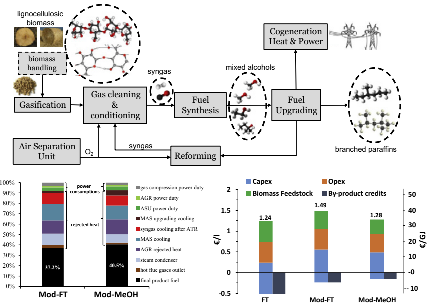
HIGHLIGHTS

- Novel thermochemical process for aviation fuels production from alcohols.
- Higher efficiency and carbon utilization than Fischer–Tropsch synthesis.
- High CAPEX for ATJ concepts makes them less competitive than FT.
- Biochemical pathways are economically more preferable.
- Promising and viable option to sell ATJ intermediates products (olefins–alcohols).

GRAPHICAL ABSTRACT



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ABSTRACT

This study presents the conceptual process design for the production of branched paraffins with high carbon number, based on the upgrading of alcohols synthesized from biomass-derived syngas and the economic evaluation and comparison with the Fischer–Tropsh (FT) process and biochemical pathways. Two routes, one based on n-butanol and another on isobutanol upgrading, are described and modeled in ASPENPlus™. The flow sheeting results reveal high performance for both process configurations, resulting in an aviation fuel yield 0.172 kg/kg$_{feedstock}$ and a thermal efficiency of 40.5% in the case of employing a modified Methanol catalyst for the mixed alcohols synthesis (MAS). Such alternative pathways offer higher efficiencies compared to FT synthesis because specific products such as C_{12+} branched paraffins for jet fuel applications are achieved with higher selectivity in the conversion processes. The water balance at the whole process reveals that the annual demands for fresh water from a 190 MW$_{th}$ biorefinery plant are 641,000 m^3, emerging the water management as an important issue with considerable environmental impacts. Simulations of the overall process show a rather high biomass carbon to product utilization ratio (up to 30%) leading to relative low CO_2 emissions. The economic evaluation reveals that the Minimum Jet Fuel Selling Price in a FT plant (1.24 €/l jet fuel) is lower than the corresponding price

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Abbreviations: AGR, acid gas removal; ASU, Air Separation Unit; ATJ, Alcohol-to-Jet fuel; ATR, Autothermal Reformer; CAPEX, capital expenditure; CCU, carbon capture and utilization; FTS, Fischer Tropsch Synthesis; GT, gas turbine; HA, higher alcohols; HC, hydrocarbons; LHV, lower heating value; MAS, mixed alcohols synthesis; MJFSP, Minimum Jet Fuel Selling Price; modFT, modified Fischer Tropsch synthesis catalyst; modMeOH, modified methanol synthesis catalyst; OPEX, operational expenditure; PSA, pressure swing adsorber; WGS, Water Gas Shift reaction.

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in a MAS plant (1.49 €/l and 1.28 €/l for cases with different catalysts). The biochemical route based on Acetone–Butanol–Ethanol fermentation is considered as the most economically desirable option (0.82 €/l). Moreover, the option of selling organic compounds, which are produced intermediately (i.e. light and heavy olefins, C4 alcohol isomers) via the alcohols' upgrading processes was proved promising enough for the feasibility of such biorefineries plants.

1. Introduction

In 2012, the worldwide flights produced 698 million tons of CO_2, making aviation fuels responsible for 12% of CO_2 emissions from all transport sources [1] with U.S. accounting for 40% of them [2]. In 2010, the world jet fuel consumption was calculated to nearly 5220 barrels per day [3]. Forecasts predict that by 2020 the global aviation emissions will be 70% higher than in 2005 and by 2050 they will further grow by 300–700% [4]. Apart from the significant increase in Greenhouse Gas emissions, other factors like high dependency of aviation fuels on fossil fuels and great uncertainty on oil prices have turned the attention on alternative sources of aviation fuels. Only 2% of global transportation fuels are based on biofuels derived from biomass [5], and these are commonly drop-in fuels i.e. that can be used in blends with existing fossil based fuels. It is reported [6] that in 2012, the most energy consumptive sector was the transportation sector, demanding 27 quadrillion BTU of energy. EIA's report forecasts, for 2040, a world production of liquid fuels from biomass up to 2.5 Mbpd (million barrels per day). In addition to this, by the year 2050, it is forecasted that biofuels will contribute to bringing down the dependency of the transportation sector on oil products to 29% [7]. Asia being the world's largest carbon dioxide emitter, has already turned its attention to the production and development of biofuels for both environmental and reducing fuel dependency reasons [8]. A worldwide research and development effort is underway to include more biofuels in the air transport [9].

The two main types of aviation fuels are gasoline (avgas) and jet fuel (kerosene) (C8—C16) [10]. They are composed mainly of paraffins and cycloparaffins and smaller amounts of aromatics and olefins along with some additives specified by each category of aviation fuel [11].

Due to the special conditions during flight there are strict guidelines for the aviation fuel properties concerning its melting point, viscosity, non freezing or cloudiness phenomena at low temperatures, etc. [12]. At atmospheric conditions both gasoline and kerosene are in liquid form. Owed to the lower carbon chain number in gasoline mixtures, it is more volatile than jet fuel (boiling points: 40–200 °C and 150–300 °C respectively). The characteristics of each aviation fuel type are strictly specified due to the extreme conditions under which combustion takes place. Avgas is used in internal combustion engines that can operate up to a limited altitude ceiling (<6000 m) and therefore is used in reciprocating engines like small aircrafts and light helicopters. This constraint has led to the predominance of jet engines in the air transport sector (more than 98% of the total aviation fuel consumed is jet fuel [13]). Concerning jet fuels, there is a greater variety in categories which are separated based on the military (e.g. JP4 and JP8) and commercial (e.g., Jet A1 and Jet B) use, since each service has its own operational requirements.

The main conventional method for aviation fuels production is through refining of crude oil. The main processes of upgrading crude oil to fuels are fractional distillation, hydrotreating and hydrocracking. Refining may include one or a mix of these processes depending on the specifications needed for the aviation fuel. Another method is through Fischer Tropsch Synthesis (FTS) where the feedstock (coal, natural gas or biomass) is firstly converted into a H_2/CO gas mixture (syngas) via gasification, following by the hydrocarbons synthesis mainly of long chain paraffins, olefins, alcohols and aldehydes. Depending on the catalyst used, the operating temperature and pressure of the FTS reaction and the H_2/CO ratio of syngas, the carbon number of the fuel product can be oriented, thus meeting the requirements for aviation fuels [14]. However, FTS process using as feedstock coal or gas (Coal-to-Liquids, Gas-to Liquids concepts) has some drawbacks: Apart from the high cost of the process and the uncertainty on gas prices, there is an issue about CO_2 emissions as they are higher than refining crude oil [15]. Biomass, being a renewable source, offers the potential production of alternative fuels that have a smaller CO_2 emissions footprint compared with the fossil based fuels. This is the main drive that attracts policies and correspondingly industries to do business in this sector [16]. Yet, not only need the biomass derived fuels for the aviation sector to have the same specification with the conventional jet fuel types, but they also should be compatible with the typical jet fuel engines because of the aircrafts long lifetime [14]. Chuck and Donnelly [17] have examined the compatibility of several bio-derived fuels with Jet fuel and their potential for blending with the conventional aviation fuel.

Currently, there are companies that have adopted the FT process. Sasol, a South African company, produces and distributes aviation fuel, made from coal via Fischer Tropsch [18]. Another company, Syntroleum, produce jet fuel from FT process using natural gas as feedstock [19]. Both companies have turned their attention to producing jet fuel derived from biomass. U.S. Air Force (USAF), which is the leading user of aviation fuels worldwide, has embraced these methods and started co-operating with these companies by using a 50:50 blend of synthetic fuel and conventional kerosene [15,20].

Along with the biomass derived fuels trend, another method for producing aviation fuels is conducted by Gevo [21]. During that process, biomass feedstock is firstly fermented to iso-butanol followed by dehydration to olefins, oligomerization and hydrogenation, resulting to iso-paraffinic kerosene, a blendstock for jet fuel with C12—C16 hydrocarbons. This final product can be blended up to 50:50 ratio with petroleum-derived jet fuel and has a low freezing point (−80 °C) suitable for aviation use. Last but not least, Byogy Renewables Inc. [22] currently produces jet fuel from biochemically-derived ethanol. Ethanol after being dehydrated, it is converted into long chain hydrocarbons via catalytic synthesis that are continuously fractionated into jet fuel and gasoline. Apart from ethanol, Byogy's technology can effectively process either propanol or butanol. The produced jet fuel can be used even as a fully substitute for oil-derived jet fuel or used at any blend ratio with conventional jet fuel [23].

In this study, the techno-economic evaluation of various thermochemical pathways for branched paraffins production from biomass that are aimed at aviation fuel substitution is performed. Unlike the majority of similar assessments, this study pays attention to the fuel upgrading section, resulting to the desired final product (here, the long chain hydrocarbons as aviation fuel substitution). Among the under investigation cases, the conventional FTS