Is It Possible To Produce Sustainable Aviation Fuels From Lignocellulosic Biomass Waste?

Carolina M. Mendieta, Julia Kruyeniski, María E. Vallejos, and María C. Area *

Sustainable aviation fuels (SAF) are alternatives to fossil fuels produced from biological or non-fossil feedstocks to reduce greenhouse gas emissions. In the alcohol-to-jet (ATJ) route, alcohol (ethanol, isobutanol, or butanol) dehydration is the key conversion step to create long-chain hydrocarbons. In this context, this Editorial deals with the ethanol-to-ethylene-to-jet route (EEJ) technology and challenges for producing SAF from lignocellulosic biomass waste (LCBW).

DOI: 10.15376/biores.20.1.11-14

Keywords: Lignocellulosic biomass; Bioethanol dehydration; Catalyst; Bio-jet fuel

*Contact information: IMAM, UNaM, CONICET, FCEQYN, Programa de Celulosa y Papel (PROCYP), Félix de Azara 1552, Posadas, Argentina; *Corresponding author: cristinaarea@gmail.com*

Sustainable Aviation Fuel

All currently certified aircraft for passenger and cargo transport operate on aviation turbine fuel (ATF) that meets international standards, such as ASTM D1655 in the US, DEF STAN 91-91 in the UK, GOST 10227 in Russia, and GB6537 in China. In 2018, ethanol was approved as a feedstock for synthetic aviation fuel (ATJ) containing synthetic paraffinic kerosene (SPK) from alcohol (ASTM D7566, Appendix A5). ATJ-SPK can be used as a new fuel and additive, blended up to 50% with conventional aviation fuel. SPK comprises saturated hydrocarbons (single bonds) and open chains (acyclic).

The ASTM D7566 specifications for ATJ-SPK are: Freezing point lower than -40 °C, Flashpoint higher than 38 °C, Distillation temperature (10% to 90%) higher than 22 °C, Energy density higher than 42.8 MJ kg^{-1}, Density at 15 °C between 0.73 and 0.77 kg L^{-1}, Aromatic compound content less than 0.5%, Sulfur content less than 0.0015%, and Thermal oxidation stability (JFTOT) higher than 325 °C.

Bioethanol-to-bioethylene-to-jet (EEJ) Route Stages

LCBW derived from the forest industry represents an abundant, sustainable, and cost-effective source for bio-jet fuel production from dehydration of second-generation bioethanol, as shown in Fig 1. In second-generation bioethanol production, pretreatment is necessary to modify the structure of the lignocellulosic material for lignin removal. It is followed by an enzymatic saccharification process involving cellulose (and eventually hemicelluloses) depolymerization into simple sugars, then fermenting by yeasts to produce bioethanol. Bioethanol is then converted into bioethylene through a catalytic reaction, which undergoes oligomerization, forming long-chain oligomers, which can form branched alkanes after hydrogenation and isomerization, and finally, a further distillation of the mixture results in the jet fuel.

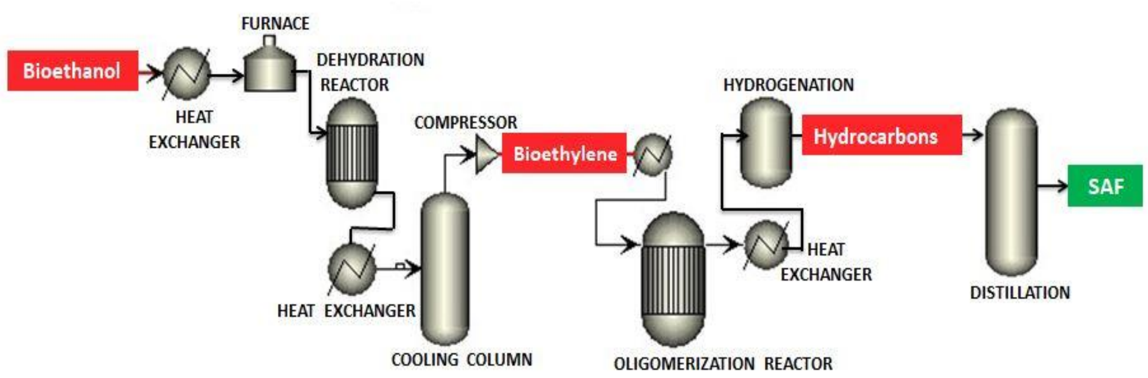

Fig. 1. Flow diagram of Sustainable Aviation Fuels (SAF) production from bioethanol

Pretreatment

Lignocellulosic biomass waste (LCBW) has a three-dimensional structure with cellulose as the backbone, surrounded by hemicelluloses and lignin, whose proportions vary by species. While cellulose and hemicelluloses are carbohydrate polymers, lignin is a phenolic polymer. This complex structure makes it difficult to separate the components. Therefore, specific pretreatments to remove lignin are required, increasing porosity and thus facilitating enzyme access to cellulose and hemicelluloses. An inadequate pretreatment can result in hard-to-saccharify materials or produce toxic byproducts that inhibit microbial growth.

The choice of method depends on the type of biomass, the desired product, cost, and environmental impact, with one of the main challenges being finding efficient and economical procedures. Alkali is one of the most effective agents for biomass swelling, opening the fiber pores to extract the maximum amount of lignin, thereby increasing enzyme accessibility and improving enzymatic conversion. Some organosolv pretreatments, e.*g.*, soda-ethanol, have shown a particular ability to facilitate biomass fractionation, improving hydrolysis performance.

Enzymatic Saccharification, Fermentation, and Purification

Enzymatic saccharification of cellulose is a process catalyzed by cellulases, enzymes from the glycoside hydrolase (GH) family. Cellulases depolymerize cellulose into glucose through an enzymatic process involving several stages. First, endoglucanases (EG) break cellulose chains into shorter fragments within the amorphous regions. Then, exoglucanases or cellobiohydrolases (CBH I and CBH II) act on the ends of the chains, producing cellobiose. Finally, β-glucosidases hydrolyze cellobiose into glucose, completing the conversion. Generally, this stage is carried out at relatively high temperatures (40 to 50 °C) and at a pH between 4.5 and 5.0.

In fermentation, glucose monomers from the previous stage are turned into bioethanol by *Saccharomyces cerevisiae* yeasts, a yeast considered GRAS (Generally Recognized as Safe). It is highly effective due to its high productivity, tolerance to ethanol, appropriate acidic pH range, and temperature range of 25 to 35 °C. The simultaneous saccharification and fermentation (SSF) strategy is adequate for bioethanol production. It combines both reactions in one reactor, preventing enzyme inhibition from sugar buildup, minimizing bacterial contamination, and reducing processing costs. Bioethanol purification involves removing substances from the fermentation broth using steam stripping to separate solids and non-volatile substances.

The separated liquid is evaporated into syrup and then mixed with the solid fraction for combustion. Then, the aqueous solution is distilled to obtain approximately 95% bioethanol in purity. This step is highly energy-intensive and significantly impacts overall energy consumption. Through distillation with desiccants, pervaporation, or membrane techniques, the reached purity can be 99%.

Bioethanol Dehydration

Bioethanol dehydration at high temperatures involves a water molecule removal, generating bioethylene. Using acidic catalysts favors the formation of bioethylene and diethyl ether, while basic catalysts tend to produce acetaldehyde. At low temperatures, acidic catalysts primarily promote diethyl ether, whereas at high temperatures, bioethylene is the main product. The HZSM-5 zeolite, with its microporous structure and Brønsted and Lewis acidic sites, is particularly effective in this process, as these sites facilitate the protonation of bioethanol and the formation of the carbocation intermediate necessary for water removal and bioethylene production. The Si/Al ratio in HZSM-5 zeolite significantly impacts bioethanol dehydration to bioethylene, affecting acidity, stability, selectivity, and accessibility of the catalyst’s active sites. A lower Si/Al ratio (higher Al content) increases acidity, facilitating carbocation formation and water removal to produce bioethylene. However, it may reduce thermal stability and increase susceptibility to poisoning and deactivation due to coke formation. Conversely, a higher Si/Al ratio improves stability and selectivity towards bioethylene by reducing acidity and allowing better bioethanol diffusion. The optimal Si/Al ratio for a balance between acidity and thermal stability is between 20 and 30, providing high catalytic activity and good selectivity for bioethylene.

Bioethylene Oligomerization and Hydrogenation

Ethylene conversion into various liquid hydrocarbons through chemical synthesis in dual-tube catalytic reactors is a process used since the 1960s. Direct oligomerization in stirred liquid-phase reactors uses catalysts, preferably of heterogeneous type, such as zeolites and acid mesoporous materials, since homogeneous catalysts are costly and difficult to separate. Transition metal catalysts (mainly Ni, but also Cr and Fe) at low temperatures (80 to 160 °C for ethylene) produce linear α-olefins, while solid acid catalysts create a mix of branched hydrocarbons.

After oligomerization, alpha-olefin hydrogenation proceeds at high hydrogen partial pressures. This process, usual in the petrochemical industry, converts olefins to paraffins using low amounts of hydrogen and controlled pressure and temperature conditions. In the hydrogenation reactor, hydrogen is added to the double bonds of the unsaturated hydrocarbons, converting them into saturated hydrocarbons. The hydrogenation is performed gently to remove small amounts of branched carbon chains in jet fuel, using palladium catalysts at pressures above 20 bar and temperatures between 200 and 350ºC.

Fuel Distillation

The product of oligomerization and hydrogenation is a mixture of hydrocarbons of various sizes, including both light and heavy compounds suitable for aviation fuel. Then, the mixture must be separated and purified through fractional distillation in a column with multiple trays to meet the quality requirements. The process involves heating the mixture, causing the components to evaporate at different temperatures; lighter components rise and condense in the upper stages, while heavier ones accumulate at the bottom. Fractional distillation may require multiple heating and cooling stages to obtain final products such as kerosene, diesel, and aviation gasoline, which are tested to ensure their quality and purity.

Final Remarks

Producing second-generation bioethylene from bioethanol presents several challenges, primarily due to the feedstock nature, availability, and quality. Processing challenges involve the yield and efficiency of bioethanol production, the conversion rates and selectivity towards bioethylene, the catalyst efficiency, and regeneration possibilities. The competition of bioethylene with fossil-based ethylene and first-generation bioethylene, among others, is an economic issue to resolve. Besides, there are environmental factors to consider, such as ensuring that the entire process is carbon-neutral or has a low carbon footprint. A Life Cycle Analysis and a Technical-Economic Evaluation are essential to solve the above.

The direct process from bioethylene to fuels is feasible, as demonstrated at a laboratory scale. However, its selectivity needs improvement and optimization to be economically competitive with other production methods. Consequently, the development and deployment of SAF highly depend on supportive policies and government incentives.