

## PP01: COST-EFFECTIVE AND SUSTAINABLE DECARBONIZATION OF AVIATION FUELS

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**Abstract.** Jet biofuels are becoming a prominent source of aviation energy, especially since their production process ensures sustainability and economic growth. An alternative approach for enabling an extended increase of biomass utilization for the production of greener aviation fuels is co-hydroprocessing of bio-based feedstocks with fossil counter parts as well as hydroprocessing upgrading of intermediates. This approach allows utilization of existing refinery technology and equipment, rendering it a more economically attractive solution. The co-processing of waste cooking oil (WCO) with petroleum feedstock was thoroughly investigated for hybrid jet fuel production, while the stabilization of wood derived bio-oil in two-stage hydrotreatment was also evaluated for drop in jet biofuel production. The results have shown that co-processing of petroleum fraction with biobased feedstocks is a well promising technology for transportation as well as aviation sector, while, the stabilization of wood derived bio-oil via hydrotreatment leads to the production of very light hydrocarbons in the jet and diesel range that can be used as drop in jet biofuels.

**Keywords:** hydrotreatment, waste cooking oil, pyrolysis oil, jet fuels, hybrid fuels

### INTRODUCTION

Aviation currently accounts for ~10% of global transport energy consumption, with a forecast increase in revenue-tonne-kilometres of ~5.1% per year to 2030 and rise by 225% of the Green House Gas (GHG) emissions. For this reason, the aviation industry is putting a lot of effort towards GHG emissions reduction, which can be partially achieved by improving fleet rollover, aircraft infrastructure, as well as engine performance. Nevertheless, the use of renewable aviation fuels is expected to activate the largest reduction of CO<sub>2</sub> emissions, which could reach up to 1.4 billion tons per year by 2050.

The lower fuel quality of conventional biofuels (ex. FAME, bioethanol) and high investment and production costs associated with advanced biofuels (ex. HEFA, BtL), as well as the dependence of drop-in production technologies on energy crops, limit the sustainable growth of these markets. On that basis, co-processing of 2G and 3G bio-based feedstocks (ex. waste lipids, fats, microalgal oils) and intermediates (ex. pyrolysis bio-oils, hydrothermal liquefaction oils, FT-waxes) with fossil-based fractions for the production of partially decarbonized fuels render a promising alternative technology.

The hydroprocessing group of the Centre for Research & Technology Hellas (CERTH) at the Chemical Process and Energy Resources Institute (CPERI) is dynamically involved in co-hydroprocessing liquid biomass and bio-based intermediates with petroleum fractions for the production of partially decarbonized fuels (Bezergianni et al. 2011, Bezergianni et al. 2014a). Technical and environmental assessment confirms the superiority of integrating biomass in refineries vs. stand-alone technologies producing drop in biofuels that are blended with fossil fuels at 10-50% with their fossil counterpart.

The benefits of co-processing include low investment and production costs as existing conversion capacity in underlying refinery units is employed, as well as product quality stabilization which is ensured from the optimal petroleum conversion pathways and final blending systems. Furthermore, the co-processing pathway enables the controlled decarbonization of transportation fuels and gradual crude-oil consumption mitigation, promoting a sustainable and future for aviation and all other transportation fuels.

The aim of this study is firstly to examine co-processing of WCO with petroleum feedstock for hybrid jet fuel production and secondly the stabilization of wood derived pyrolysis oil for drop in jet biofuel production. The experiments took place in the CPERI/CERTH. A hydrotreating continuous flow pilot plant with capacity 60ml/hr was utilised for the experiments, more details about the pilot plant could be found in an author's previous work (Bezergianni et al. 2014a).

## RESULTS

Hydrotreating of petroleum fractions with lipids feedstocks offers a unique opportunity to produce a sustainable hybrid diesel fuel completely compatible with existing fuel infrastructure and engine technology. Co-processing of petroleum fractions (i.e. gas-oil) with WCO (from restaurants and households) was examined for hybrid jet fuel production. A commercial NiMo/ $\gamma$ Al<sub>2</sub> catalyst was utilised according to the results of an author's previous work (Bezergianni et al. 2014b). The results were evaluated in terms of distillation curve, product yields as well as conversion rate. Five blends of gas oil with WCO were investigated (95/5, 90/10, 85/15, 80/20 and 70/30 Gas Oil/WCO). The resulting product known as hybrid fuel has a density ranges from 0.78 to 0.85 g/ml, significantly high cetane number (50–101) and also high net heating value (43.3–47 MJ/kg) (Bezergianni S and Dimitriadis A. 2013). The cold flow properties are also quite diverse based on the catalyst and operating parameters employed, for example pour point is between -20 and 26°C, while the cloud point ranges between -23 and 20°C (Simacek P, Kubicka D 2010). Furthermore, the hybrid fuels are also low sulphur (3–13 ppmwt) and aromatics free (0.1–1.2%wt) fuels, thus they can be considered "clean fuels".

Figure 1 presents the distillation curve A) as well as the jet fuel yields and conversion B) of the products from co-processing of variable blends of petroleum fractions with lipid-containing feedstocks (gas-oil/WCO). The jet fuel yield was estimated as the vol% of the total liquid product that has a boiling range between 193°C and 277°C (see Figure 1). The results have shown that 6 to 9% of liquid product is in the range of jet fuel while the conversion varies from 6 to 7%. The other product is heavier hydrocarbons in the range of diesel. It is obvious that co-processing of petroleum feedstock with biomass based feedstock can render a small percent of jet fuel hydrocarbons which can be further increased by optimising the operating parameters of the hydrotreating process (reaction temperature, reaction pressure, LHSV and H<sub>2</sub>/Oil).

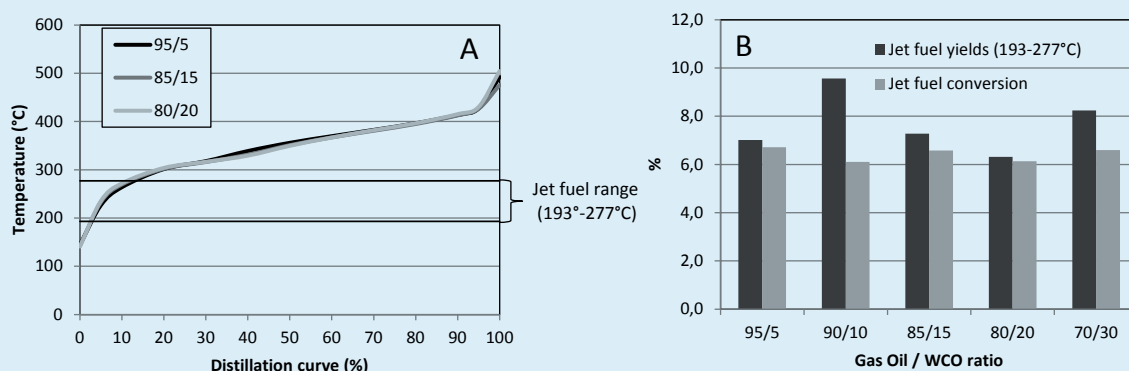


Figure 1. Distillation curve A) and Jet fuel yields and conversion yields B) from co-processing of Gas oil / WCO blends (95/5, 85/15 and 80/20).

Furthermore, the stabilization of wood derived pyrolysis oil was also examined for jet drop in biofuel production in terms of jet fuel yields, conversion and distillation. In general, pyrolysis is a simple way to produce oil from biomass by thermal decomposition at moderate temperatures, ambient pressure and very short reaction time. This process can convert solid biomass and wastes such as wood to higher added-value liquid products (pyrolysis oil). The advantage of this process is that it can be used to the whole biomass without any pretreatment (Bridgwater A. V. 2004). However, pyrolysis oil has disadvantages as an aviation fuel. Pyrolysis oil is a dark brown, free-flowing liquid with about 20-30% water, high acidity and low oxidation stability (Torri et al. 2010). For the above reasons, pyrolysis oil needs further upgrade. Wood-derived pyrolysis oil can be stabilized and converted to a conventional hydrocarbon fuel by converting oxygenates.

Pyrolysis oil of the current study was produced via catalytic pyrolysis of lignocellulosic biomass (wood from tree beech), which was characterized by 21wt% oxygen content, high density (1.051kg/lit) and high acidity. A dual stage hydrotreatment was examined with a commercial NiMo/ $\gamma$ Al<sub>2</sub> catalyst, incorporating a mild hydrotreatment stage that is aimed in stabilization and pre-conditioning, followed by a more severe hydrotreatment stage allowing further upgrading and production of fuel-like products. A single stage hydrotreatment of biomass (wood) pyrolysis oil renders a heavy (density:1.056 kg/lit), high sulfur (657 wppm), high O<sub>2</sub> (18 wt%), tar-like product with a boiling point range from 100°-670°C, as a result an additional 2<sup>nd</sup> stage HDT is required. The product from 2<sup>nd</sup> stage is characterized by lighter hydrocarbons with density 0.8471 kg/

lit, 1% O<sub>2</sub> content, in the range of 78°-580°C boiling point and calorific value 44.7 Mj/kg. Figure 2 presents the distillation curve A) and the product yields B) of the two stage hydrotreatment. The results have shown that after a first stage mild hydrotreating of pyrolysis oil, almost 30% of the products is in the range of jet fuel, while 27% is lighter hydrocarbons and 43% is heavier hydrocarbons in the range of diesel. However, after a second more severe hydrotreatment stage, lighter products could be achieved, the results of two stage hydrotreatment have shown that almost 47% of the liquid products is in the range of lighter hydrocarbons (<193°C boiling point), 24% is in the range of jet fuel (193°-277°C) while almost 30% is in the range of diesel fuel (>277°C). It is clear that high added-value liquid fuels can be produced via hydrotreatment stabilization of wood derived pyrolysis oil.

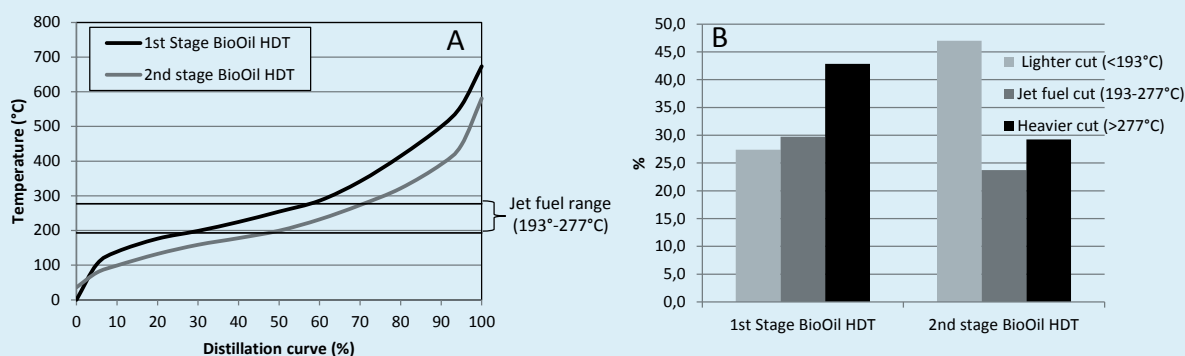


Figure 2. Distillation curve A) and product yields B) from 1<sup>st</sup> and 2<sup>nd</sup> stage bio oil hydrotreated

## CONCLUSIONS

WCO is considered as an alternative feedstock blend for catalytic hydroprocessing of gas oil. Catalytic hydroprocessing of gas oil/WCO mixtures was evaluated as an alternative approach for integrating residual biomass in the aviation sector by utilising the existing infrastructure of a refinery. The effect of increasing WCO content in the hydroprocessing feed was assessed in terms of jet fuel yields and conversion. The results have shown that the addition of WCO (5% to 30%) in HAGO not only does not affect negative the quality of the final product but rather improves some of its properties without lowering the yield (Bezergianni et al 2014b). Co-processing 5–30% WCO with Gas Oil would render up to 10% jet biofuels.

Moreover, a dual stage hydrotreating upgrade of wood derived pyrolysis oil was also examined in order to produce high quality jet biofuels. Pyrolysis oil in general is not appropriate for aviation sector without upgrading. However a dual stage hydrotreatment technology proved to be very advantageous. The results have shown that a first mild hydrotreating upgrade renders better quality products with lighter hydrocarbons and low oxygen and water content. After a first stage hydrotreating of pyrolysis oils up to 30% of the products are in the range of jet fuel hydrocarbons, while after a second stage hydrotreatment, the final products are even lighter with zero oxygen and water content and high calorific value.

As aviation currently accounts for ~10% of global transport energy consumption, a 10% to 30% jet fuel yields of the described technologies is very promising. It is obvious that, co-processing of lipid feedstock with petroleum fractions as well as hydroprocessing upgrading of pyrolysis oil render a promising alternative technology for aviation sector.

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