

Lignin-Based Advanced Biofuels: a Novel Route Towards Aviation Fuels

David Chiaramonti*^a, Marco Buffi^a, Pietro Palmisano^b, Silvia Redaelli^b

^aRE-CORD/CREAR, Department of Industrial Engineering, University of Florence, ITALY.

^bBiochemtex - Mossi & Ghisolfi, Tortona (AL)

david.chiaramonti@unifi.it

The need for sustainable alternatives in aviation stimulated significant R&D effort both in Academia and industry. Today, the Advanced Biofuel which is largely dominating the scene is represented by Hydrotreated Vegetable Oils (also called Hydrotreated Esters and Fatty Acids): however, the lipid feedstock necessary for this process still represent a considerable limitations in the EU both from the sustainability/environmental and economic point of view. Thus, identifying solutions based on lignocellulosic or non-conventional feedstock is today a major target. The use of lignin-rich stream, the co-product of the lignocellulosic ethanol chain, is among possible lignocellulosic routes to paraffinic fuels. This particular pathway would greatly benefit from the recent industrial development (at large demo industrial scale) of the lignocellulosic ethanol complexes, and would represent a very first and innovative integration of biochemical processes and thermochemical/chemical ones at the same site. The present work introduces this advanced biofuel route, and the related demonstration project EC FP7 BIOREFLY. Advantages and critical issues from the proposed biofuel chain are identified and discussed. Major process development steps and technical status are reported.

1. Introduction

The international aviation sector is the transport sector that continuously grew even in a period of economic crisis. As reported in the following figure, while all the other transport areas declined in terms of fuel demand, air transport for international use showed a rapid increase and a steady market also during the most difficult period 2008-2012.

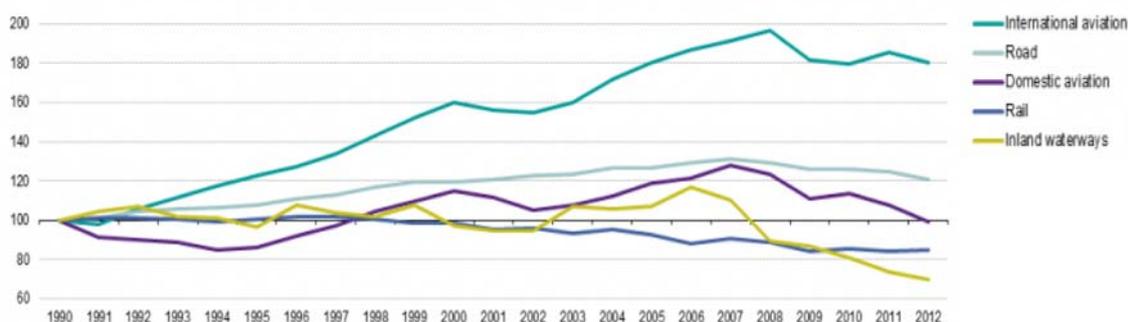


Figure 1: Transport fuel demand (source: Eurostat 2013).

The development of Advanced Biofuel technologies showed an impressive acceleration in Europe during the last years. A number of process routes were investigated, some of these suitable for producing paraffinic fuels for aviation (Chiaramonti et al, 2014). However, so far only lipid-based advanced biofuels achieved full commercial scale: Hydrotreatment of Vegetable Oils and lipids is today the major pathways towards biohydrocarbons for aviation. Nevertheless, the economic and environmental sustainability is largely

dependent on the feedstock origin and characteristics. In addition, the land use issue and the food versus fuel conflict makes this route highly debated in the UE and worldwide.

As regards Lignocellulosic Biofuels and demonstration activities, the thermochemical and the biochemical routes have been competing in recent years. From an industrial point of view, despite the large expectations on the development of commercial systems based on the various thermochemical pathways, the development of the lignocellulosic ethanol industry took the lead and spread worldwide. Today, major industries have completed the design and construction of large-scale industrial demonstration plants, and are moving towards full commercialization of the technology.

More than 250.000 t/y lignocellulosic ethanol capacity is already installed in the EU and abroad, with several hundreds million euro invested (Chiaramonti, 2014). The deployment of this sustainable advanced biofuel chain will thus make available on site and in a continuous mode a lignin-rich stream flow. This feedstock is today burnt for combined heat and power, but it is also available for further processing into high added value products, in a wider and integrated Biorefinery concept.

The combination of biochemical processing (the lignocellulosic ethanol chain) with thermochemical routes (the lignin-to-biofuels/bioproducts pathway) is thus the logical development of these new industrial complexes.

2. The FP7 BIOREFLY project

The BIOREFLY project, supported by the European Commission through the 7th Framework Programme, addresses the conversion of lignin-rich stream, the co-product of lignocellulosic ethanol production, into aviation biofuels, at a scale of 2000 t/y production, through a chemical-catalytic process. The project merges a group of complementary partners, coordinated by Bichemtex (Mossi & Ghisolfi group): ETH-Zürich, RE-CORD, WIP, KLM and SkyNRG. BIOREFLY will investigate the production of lignin-based paraffinic fuels for air transports, its test in gas turbines and under real flight conditions (test flight).

The feedstock is obtained from the pre-treatment, hydrolysis and fermentation of biomass: C5 and C6 sugars are converted from the hemicellulose and cellulose fraction into alcohol (or other possible products, in a sugar platform concept (E4TECH et al, 2015), while the lignin-rich stream – today burnt to generate heat and power for the plant - goes through the process and is collected for downstream treatment into biokerosene, i.e. a paraffinic biofuel suitable for aviation. As shown in the following paragraphs, the technology adopted to process this stream is the result of several years of development at Biochemtex, from very small-scale batch and continuous reactors to pilot unit. The project workprogramme includes pilot and test demonstration activities in micro and commercial scale gas turbines, as well as a LCA analysis of the whole chain.

3. Lignin-rich stream to biokerosene

Converting the lignin-rich coproduct in a lignocellulosic ethanol complex offers a number of advantages, in terms of industrial system configuration:

- The feedstock is continuously produced and made available at the industrial site. The entire logistic is already developed for the “upstream-existing” lignocellulosic ethanol plant, thus the lignin-to-biofuels/bioproducts section entirely benefits from a collection, storage and feeding point of view.
- The physical and chemical characteristics of the feedstock, which derives from the upstream steps of pretreatment, hydrolysis and fermentation of lignocellulosic biomass, are rather constant, as well as the mass flow. It is therefore possible to design an optimized industrial system to process this stream.
- The integration in a biorefinery complex will offer opportunities for energy integration and system optimization, thus improving performances and reducing operational costs.

However, the amount of lignin-rich stream actually available for bioproducts/biofuel production will have to be carefully assessed based on GHG reduction considerations, as the main biofuel generated in the biorefinery, i.e. the lignocellulosic ethanol, as well as the “secondary” biofuel, the biokerosene, will have to meet the EU sustainability criteria, that requires a minimum GHG saving (European Commission, 2009; European Commission, 2012). Thus, a well designed energy integration (cogeneration) is necessary, and only part of the feedstock could be sent to biofuel/bioproduct conversion. In addition, particular attention will have to be given to operational flexibility, as higher process integration generally corresponds to a more “rigid” industrial systems due to increased interdependencies and linkages between process steps.

Based on the Biochemtex lignocellulosic ethanol PROESA[®] technology, the following scheme shows the main process steps. The MOGHI[®] process is the step producing the phenolic oil from lignin that is then further converted to biokerosene/biohydrocarbons, or BTX for downstream conversion into biobased products. In fact, once the bio-reformate from lignin is obtained, it can be transformed into biohydrocarbons, aromatic chemicals, nylon intermediates, resins and other products through available petrochemical technologies (Giordano, 2013).

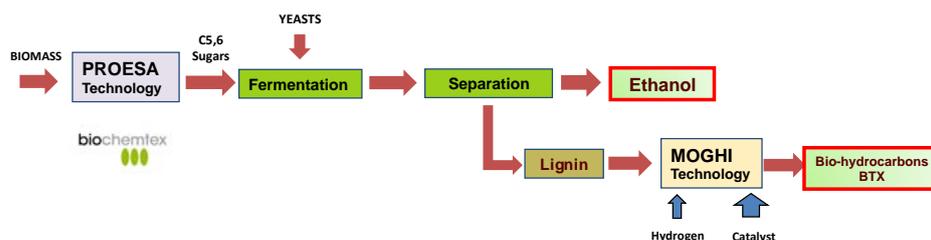


Figure 2: The route to biohydrocarbons and BTX from lignin-rich stream in the lignocellulosic ethanol chain.

3.1 Conversion to biofuels: process development

The study and development of the process converting lignin-rich stream to biofuels and bioproducts started in 2009 at Biochemtex at lab scale (Giordano, 2013) in 50 cc-8 liters and 12 liters batch (CSTR and Tubular catalytic Parr downer) reactors, and then in 500 cc continuous reactors. The process first converts lignin to phenol oil, and then phenol oil into a bioreformate. This first lab-scale step aimed at analytical characterization and providing essential information for process definition. Based on these first positive results, a 2.5 kg/h (feed) lignin-to-jet pilot plant was designed, built and operated, which allowed to move forwards to process validation and preliminary estimation of process data as energy consumption, water demand, water recyclability, H₂ consumption, and catalyst lifetime. Preliminary cut samples showed distillation temperatures in the range of 145-180°C, starting to match the typical chromatogram of a JET fuel, in particularly with reference to the heavy compounds (long alkane chains C11-C16), as reported in the following paragraphs.

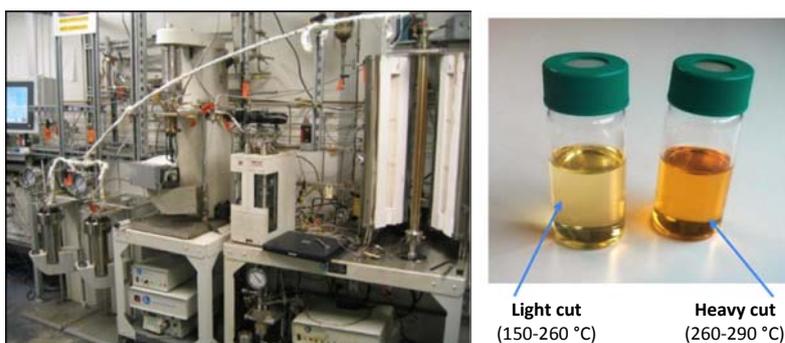


Figure 3: Earlier lab unit (left), and light/heavy cuts.

Finally, the design of the 2000 t/y BIOREFLY demo project started. A process scheme is shown in figure 4, where major conversion steps are indicated.

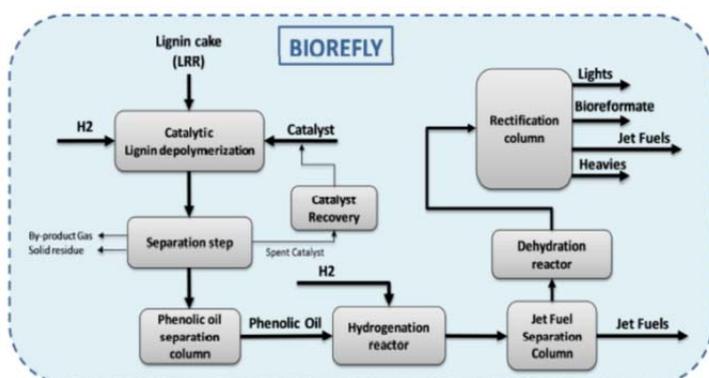


Figure 4: Lignin-to-bioerosene process route used in the Biorefly project.

Phase 1: Lignin to Phenolic Oil - The first phase of the process focuses on the continuous conversion of the lignin-rich feedstock by means of a hydro-cracking reaction in presence of hydrogen gas and heterogeneous

metal catalyst. This process phase aims at liquefying and depolymerizing the feedstock into a dense and quite viscous oil. The reaction usually occurs in a temperature range between 250°C to 370°C and in a pressure range between 120 to 200 bar. The produced oil is a rich aromatic-oxyphenolic mixtures that can be classified as 20% w/w of monomers (mainly guaiacol, syringol, and other substituted oxyphenols), 20-40% of dimers and trimers and the remaining part as heavies (long aliphatic chains, as well as oligomeric lignin fragment). Due to its chemical characterization it has been decided to name this product as "phenolic oil". The starting lignin derived from the Biochemtex PROESA® technology is characterized by having ~60% moisture content. The characterization of lignin cakes derived from two different biomass (table 1) is reported below, as well as the elemental analysis of a lignin cake derived from Wheat straw.

Table 1: Compositional characterisation of Wheat Straw and Arundo Donax lignin cakes

Lignin cake		Wheat Straw	Arundo Donax
Soluble compounds	%wt dry basis	4,23	0,83
Glucans	%wt dry basis	26,08	28,71
Xylans	%wt dry basis	4,00	2,92
Arabinan	%wt dry basis	0,41	0,00
Insoluble acetyls	%wt dry basis	0,91	0,57
Klason lignin	%wt dry basis	45,26	52,56
Ashes	%wt dry basis	13,40	14,4
other insolubles	%wt dry basis	5,72	0,00
Moisture content	%	60,30	60,95

Table 2: Elemental analysis of Wheat Straw lignin cake (O by difference)

%wt dry basis	C	H	N	S	O	Ash
Lignin cake from Wheat Straw	46,9	5,2	0,85	0,7	31,95	14,4

The feedstock is particularly low in sulphur and halogens (S < 1% w/w), as chemicals are not used in the PROESA™ process during the pre-treatment step, differently from other processes such as pulp&paper. Phenolic oil is particularly stable compared to pyrolysis oil due to its lower oxygen content (less than 20% w/w, ~50% the oxygen content in the feedstock) and acid free: the reaction is adjusted in order to gasify the residual sugars present in the feedstock avoiding any sugar/carbohydrates degradation towards formic, acetic, propionic acid, as well as furfural and 5-HMF. The presence of hydrogen and a proper catalyst during the reaction is needed in order to avoid the presence of radical free compounds in the phenolic oil, that usually lead to the re-polymerization reactions. As regards the phenolic oil stability, the molecular weight distribution of the oil does not change even after long-term storage (1-6 months) at environmental temperature.

Table 3: Phenolic oil elemental analysis (O by difference)

%wt	C	H	N	S	O	Ash
Phenolic oil	73,1	9,2	0,4	0,3	16,8	0,2

Finally, major chemical and physical characteristics can be summarized as follows:

- Gross calorific value: 38,16 kJ/kg
- Water content: less than 1% w/w
- Acidic Content: 27 mg_{KOH}/g
- Density at 15°C: 1030 kg/m³
- Viscosity at 40°C = 200cp; at 80°C= 50cp.
- Average molecular weight distribution: Mn=300; Mw=700; Pd=2,3

Phase 2: Lignin to Phenolic Oil - The produced phenolic oil is converted to a less viscous and dense oil, rich in long chain alkanes, cyclic aliphatics (naphthenics) and small amount of cycloalcohols with a negligible amount of oxygen (~1%) and a lower molecular weight distribution. The goal is achieved through a second catalytic hydrogenation/hydrodeoxygenation reaction.

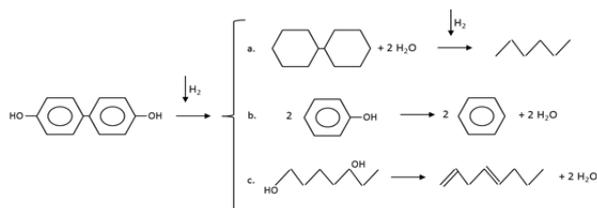


Figure 5: Scheme of hydrogenation/hydrodeoxygenation reaction pathways for dimers in the phenolic oil.

The deoxygenated oil is then distilled, in order to obtain two or more distillation cuts characterized by different chemicals/physical properties falling in the Jet-fuels cut as (i) kerosene type jet-fuels (C8-C16) and (ii) wide cut or naphtha type jet-fuels (C5-C15). A comparison among the jet fuel cuts and Jet-A1 is reported in the following figure.

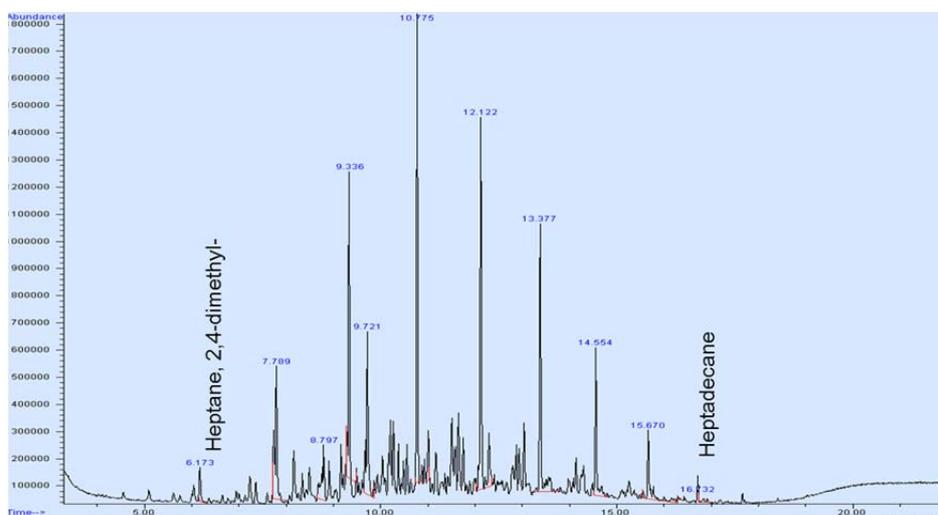


Figure 6: Comparison of jet fuel cuts from lignin (black line) and Jet-A1 (red line) chromatograms.

3.2 Use of biokerosene: pilot tests and demonstration activities

The fuel will be first tested in micro gas turbines, available at RE-CORD experimental area, to carry out preliminary evaluations of fuel behavior in gas turbines under real operational conditions. A Garret GPU/APU 25 kWe and a Capstone C30 gas turbines are available for the scope. The first one, Garret, is a military-derived gas turbine, with a silo-type combustion chamber, thus suitable for investigation and testing of unconventional fuels. This microgas turbine was modified by RE-CORD/CREAR to run with diesel, kerosene, biodiesel, pure vegetable oil, alcohol and pyrolysis oil (under investigation nowadays). The Garret GT origin dates back to the 1960's, as APU (Auxiliary Power Unit) and GPU (Ground Power Unit). The turbine configuration comprises both radial 1-stage turbine and compressor, no bearings in the hot section, a single can type silo combustor, a single pressure swirl injector. The turbomachine directly couple turbine-generator, constant rot speed, ≈ 53000 rpm, with a reduction gearbox - output shaft ≈ 8000 rpm. The primary Output is 25 kVA, 0.8 pF, 400 Hz, 120/208 V.



Figure 7: Garret microgas turbine: main scheme (left), view of the system (center) and silo-type combustion chamber (right).

The Capstone C30 GT is instead a regenerated micro gas turbine with an annular combustion chamber, with high efficiency and performances even if at very small scale. Both systems allows for testing the biofuel without requiring large biofuel volumes. In addition to this, a spray test bench is under design and will be set up to perform injection/spray studies. Afterwards, more in-depth testing will be developed at dedicated aviation gas turbine test facilities. Finally, a test flight will be carried out.

3.3 Sustainability and fuel qualification

A detailed LCA analysis to estimate the GHG savings from the process towards conventional fossil fuels will be carried out. As said, the additional biofuel production from the lignin-rich stream in a lignocellulosic ethanol complex as to be evaluated through a comprehensive and integrated approach with the main biofuel production. The first phase of the work was the definition of Goal and Scope, which - according to ISO 14044 standard – means to identify (a) the product system to be studied, (b) the functions of the product system or, in the case of comparative studies, the systems, (c) the functional unit, (d) the system boundary, (e) the allocation procedures, (f) the impact categories selected and the methodology of impact assessment, and subsequent interpretation to be used, (f) the data requirements, (g) the assumptions, (h) the limitations, (i) the initial data quality requirements, (j) the type of critical review, if any, and (k) the type and format of the report required for the study. Currently, system boundaries and reference case are being agreed among the partnership. Finally, given the complexity of the certification step for aviation biofuels, as well as the need to achieve detailed accounting of fuel sustainability, the project will initially investigate the steps necessary to qualify the fuel according to ASTM standard.

4. Conclusions

Sustainable production of paraffinic fuels from lignocellulosic feedstock represents a major target for the advanced biofuel industry, as the options for greening the aviation sector are very limited and shifting to biofuels is the main possibility. The challenge of converting lignin-rich streams from lignocellulosic ethanol chain offers a significant number of advantages, but also incorporates several critical industrial elements. The development of the technology requires the implementation of demonstration activities, such as the BIOREFLY project here reported. This approach will determine the full exploitation of the biomass feedstock into a number of products, in a real large scale integrated bio-thermochemical scheme.

Acknowledgments

Authors wish to acknowledge the European Commission, DG Energy, for the support given to the BIOREFLY project through the Grant Agreement n. ENER/FP7/612747.

Reference

- Chiaromonti D., Martelli F., Balan V., Kumar S., 2014, Industrial initiatives towards lignocellulosic biofuel deployment: an assessment in US and EU, *Chemical Engineering Transactions*, 37, 313-318, DOI:10.3303/CET1437053.
- Chiaromonti D., 2015, Conversion of lignocellulosic and algal biomass into fuels and products, EU-CANADA Workshop: Renewable Carbon Sources processing to fuels and chemicals <<https://ec.europa.eu/energy/en/events/renewable-carbon-sources-processing-fuels-and-chemicals-workshop>> accessed 31.12.2015.
- European Commission. Directive 2009/28/EC. On the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC.2009.04.23. Official J Eur Union 2009.L 140: 16-62.
- European Commission, 2012, Proposal for a Directive of the European Parliament and of the Council amending Directive 98/70/EC relating to the quality of petrol and diesel fuels and amending Directive 2009/28/EC on the promotion of the use of energy from renewable sources [COM(2012) 595 final, 2012/0288 (COD)] <http://ec.europa.eu/clima/policies/transport/fuel/docs/com_2012_595_en.pdf> accessed 31.12.2015.
- E4TECH, RE-CORD, WUR, 2015, From the sugar platform to Biofuels and Biochemicals <<https://ec.europa.eu/energy/sites/ener/files/documents/EC%20Sugar%20Platform%20final%20report.pdf>> accessed 31.12.2015.
- Giordano D., 2013, Green chemistry and biobased products: PROESA and Chemtex approach based on PROESA, Third International Conference on Lignocellulosic Ethanol.