

Diesel fuel from biomass: today and tomorrow

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Biomass is an abundant and carbon-neutral renewable energy resource for the production of biofuels. Climate change mitigation, energy security, rising oil prices and economic objectives are stimulating strong interest in the development of efficient processes for the production of energy vectors and biofuels. Road transport alone accounts for about 20% of global anthropogenic carbon dioxide emissions. Therefore a great contribution to the sustainability will come from transport biofuels more clean, economic and renewable. [1]

Accordingly the production of renewable fuels is continuing to expand worldwide as a result of increasing petroleum prices, government regulations, and commitments to greenhouse gas reduction. First generation biofuels (i.e. bioethanol and biodiesel) are currently produced from conventional food crops so competing with their use for food and animal feed, and in some parts of the world we are already seeing the economic consequences of such competition. Many of these problems could be addressed by the production of the second generation biofuels, manufactured from agricultural and forest residues and from ligno-cellulosic non-food energy crops. Second generation biofuels are expected to be superior to many of the first generation biofuels in terms of energy balances, greenhouse gas emission reduction, land requirement and competition for land, food, fiber and water.

This communication will present some examples of process for the production of biofuels, focusing the attention on the diesel fuel which is presently the most appealing on the European fuel market. In fact, the EU-27 road fuel demand is characterized by a steadily shifting from gasoline to diesel and by a steadily grow of heavy duty diesel demand. [2]

Greendiesel

Existing technology for producing diesel fuel from vegetable oil has largely centred on production of FAME biodiesel. While FAME has many desirable qualities, such as high cetane, there are other issues associated with its use such as poor stability and high solvency leading to filter plugging problems.

A more radical innovation in bio-based diesel fuels considers the complete hydrogenation of the triglyceride feedstocks to hydrocarbon mixture, avoiding the side-production of glycerol and allowing a better integration of the process and the product in the existing refinery infrastructure and fuel distribution system.

Several companies have been developing such a kind of triglycerides hydroprocessing (e.g., Neste Oil, BP, Conoco-Phillips, Petrobras, Dynamic Fuels, Haldor Topsoe, Axens and UOP-Eni). [3]

The UOP/Eni Ecofining™ process is based on catalytic hydrodeoxygenation, decarboxylation and isomerization reactions to produce a diesel fuel rich in isoparaffins. [4] This alternative product is called green diesel. As this kind of process is very flexible to the feedstocks, it can be considered also for inedible (e.g. jatropha and camelina) and unconventional (e.g. used and cooking oils, animal fats) triglycerides. In this concern green diesel can be considered as a bridge between first and second generation biodiesel.

The main improvement of the Ecofining technology compared to the conventional FAME biodiesel, is that it allows refiners to obtain a synthetic fuel that has a similar chemical composition and similar chemical-physical properties compared to petroleum diesel. For this reason the product can be easily blended with conventional refinery streams. In addition, all of the Ecofining by-products are already present during normal refinery operation and do not require any special handling.

A range of vegetable oils are suitable for Ecofining process, including soybean, rapeseed, palm and jatropha oil, tallow and greases derived from animals[4].

Second and Third generation Lipids

Lipids can also be obtained from biomasses different from the usual edible oleaginous crops. A alternative route is based on the utilization of particular microorganisms (e.g. yeasts, bacteria, fungi). These organisms are grown on mixed sugars, which in turn are obtained from lignocellulosic biomasses through hydrolyses. If these are waste biomasses (e.g. agricultural or domestic wastes) or energetic crops grown on marginal fields, the derived lipids can be considered of second generation.

Selected yeasts are able to accumulate up to 70% w/w of lipids, under proper fermentation conditions [5]. The recovered lipids are suitably processed by Ecofining process so obtaining second generation green diesel.

Microalgae can provide third generation lipids. Microalgae reproduce themselves using photosynthesis to convert sun energy into chemical energy, completing an entire growth cycle every few days. Moreover they can grow on both sea water or waste domestic or industrial water, requiring sunlight, CO₂ and some other simple nutrients (N, P) [6]. They have much higher growth rates and productivity when compared to conventional forestry, agricultural crops, requiring much less land area than other vegetable oils feedstock of agricultural origin, such as rapeseed or soybean crops. eni R&M division have built a pilot unit, with a one hectare pond field, in a Sicily refinery. The microalgae are cultivated on waste waters, by feeding a CO₂ stream coming from the refinery. The lipids withdrawn from the algae are suitable for green diesel production [7].

Bio-oils

The direct conversion of whole biomass in order to produce biofuels could be achieved using thermochemical processes, such as pyrolysis, liquefaction and gasification. Apart gasification, the other processes produce a liquid hydrocarbon fraction generically called bio-oil. Pyrolysis oils are hydrocarbon complex mixture, typically water soluble and have an higher oxygen content than liquefaction oils. The pyrolysis bio-oils are non-thermodynamically controlled products and are not stable. Liquefaction oils are normally water insoluble and have a lower oxygen content and, therefore, higher energy content than

pyrolysis oils. Bio-oils are used as fuel directly in designed engine motors. So far, four main tracks have been studied with respect to the upgrading of bio-oil with improved quality: cracking (e.g. FCC), decarboxylation, hydrodeoxygenation and hydrotreating [8]. The liquefaction process is particularly suitable for processing domestic organic wastes and sewage sludges [9].

Biomass to Liquid (BtL)

Another catalytic process to transform biomass to liquid fuels, in particular to middle distillates including diesel cuts, is the so called BTL. [10] The main steps of this technology include thermal gasification of biomass, followed by syngas clean up and Fisher-Tropsch synthesis of synthetic fuels. Similar processes are currently widely used to produce synthetic fuels from coal or natural gas (i.e. CTL and GTL).

An example of a running BTL plant is the Choren-Shell process, [11] in Germany. The Beta plant produces 300 barrel/day of sundiesel. The yields are around 20%, compared to the biomass.

Other companies who have been developing commercial FT technologies, mainly devoted to GTL applications (e.g. Sasol, Shell, BP, COP, eni-IFP/Axens, ExxonMobil, Statoil, Rentech, Syntroleum), are in a favourable position for BTL projects [12].

References

1. G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.* 106 (2006) 4044.
2. A. Heilbrunn, World Refining & Fuels Conference, Brussels – May 2007.
3. J.R.G. Bray “Advances in Biodiesel and Renewable Diesel Production” PEP Report 214A, SRI Consulting, December 2007.
4. F. Baldiraghi, M. Di Stanislao, G. Faraci, C. Perego, T. Marker, C. Gosling, P. Kokayeff, T. Kalnes, R. Marinangeli, in *Sustainable Industrial Process*, G. Centi, F. Trifirò, S. Perathoner, F. Cavani Ed's, 2009, Wiley-VCH, Weinheim, pp 427-438.
5. D. Bianchi, G. Franzosi A. Romano, WO 2010/046051 to ENI S.p.A
6. P. McKendry, *Bioresource Technology* 83 (2002) 47.
7. E. N. D'Addario, F. Capuano, E. D'Angeli, R. Medici, WO 2010/000416 to ENI S.p.A
8. Stocker M. *Angew Chem Int. Ed.*, 47 (2008) 9200.
9. A. Bosetti, D. Bianchi, G. Franzosi, M. Ricci, WO 2011/030196 to ENI S.p.A
10. P. McKendry, *Bioresource Technology* 83 (2002) 47.
11. C. Kiener “Start up of the first commercial BTL production facility”, Valencia, June 3 2008
12. J-L. Duplan, Biofuel2G International Congress, Pamplona, 23-24 January 2008