Besides Petroleum

The promise of bio fuels to contribute to the solution of current challenges

Dr. Horst Walther (*horst.walther@pcfpp.com*)

Dr. Rainer Busch (*rainer.busch@pcfpp.com*)

Abstract:

Especially for the aviation industry there is a strong need to derive drop-in fuels from renewable feedstock. Jet fuel price once peaked at 180 USD / bbl. It is likely to approach this level over the next 5 years again. For airlines fuel expenses represent an ever growing fraction of their total operating expenses. IATA targets to reduce CO2 emissions by 50% of 2005 level during the next 40 years – mostly by bio fuels drop-in.

There is the general expectation, that only bio fuels from algae have the potential to deliver the required volumes. As of today, all algae production variants still come with severe challenges before they can be considered stable and competitive. However, while petro crude price increases over time, the price of algae crude and other biofeedstocks decreases due to improved efficiency, new methods etc. This development can be accelerated considerably provided adequate resources are made available to developers. Hence still considerable financial & intellectual investments are necessary.

The new Pacific Propellants bio refinery process promises to close the refining gap. Decentralized, inexpensive plants, e.g. near airports, could capitalize on the local potential of the region. For full value chain processing a joint venture of ppi a large scale algae feedstock producer is preferred.

The conference topic to which the paper is relevant:

- *The strategic orientations of industrial investment in the local economy.*

Challenges

Industry wide there is a strong need to derive drop-in replacement fuels from renewable feedstock. The reasons are well known and widely agreed upon. The challenges comprise of …

- Burning fossil fuels increases atmospheric levels of **carbon dioxide**. Due to the expected adverse effects (IPCC) on the global environment, replacement for burning fossil fuels is sought across industries.
- Although it is fiercely debated when global oil production will reach its peak (peak oil theory) and decline thereafter, it is not disputed that fossil fuels are a **finite resource**.
- Kerosene or jet fuel is a **volatile commodity**. Depending on changes in global demand on and additionally driven by speculative effects jet fuel price once peaked at 180 USD / bbl. It is likely to approach this level over the next 5 years again.
  This high price volatility puts enormous stress on air carriers, whose fuel expenses represent an ever growing fraction of their total operating expenses. According to the International Energy Agency (IEA) a contribution of up to 50% to the overall operating costs does not appear completely unlikely.
- For some industry sectors, however the choices seem to be limited more than for others. While electric cars are expected to become widespread within the next 5 years, airplanes, trucks, ships **cannot switch** to solar electricity easily.
- While the aviation industry currently accounts for just **2%** of greenhouse gas emissions due to human activity, it is expected that by 2050 aviation-related emissions will almost **equal** the amount from automobiles.
- For this reason the International Air Transport Association (IATA) has set the goal to make use of a 10% fraction of renewable fuels to reduce emissions per passenger by 25 % until 2020 and to reduce CO_2 emissions by 50% of 2005 level during the next 40 years – mostly by bio fuels drop-in. Since 2008 consortia of major airlines, aerospace manufactures and traditional oil business or at times new players in the renewable energies area started preparations for use of renewable fuels in civil and military aviation.
- Yet, only a few renewable feedstock types offer sustaining economic potential. Among those to mention are salicornia, jatropha, miscanthus and several strains of **algae**.
- Today refining renewable feedstock into renewable fuels requires huge capital **investments**. These high costs are caused by the nature of the employed processes, which usually require high temperatures and / or high pressures. Often they need rare or hazardous agents and catalysts, or produce likewise by-products.
- Among the major obstacles towards smooth phase-in of bio fuels into the existing processes and infrastructure is the fact, that processes in use today mostly do **not** deliver **hydrocarbons** but esters (most often FAME = **F**atty **A**cid **M**ethyl **E**ster) or ethanol, with limited compatibility to existing engines and infrastructure.

Solution

There is widespread consensus in the renewable fuels industry that fuels from algae are the most promising feedstock for the production of renewable fuels. A productivity comparison strengthens this picture:

Gallons of oil per acre per year (approximate)	
Corn	18
Soybeans	48
Safflower	83
Sunflower	102
Rapeseed	127
Oil Palm	635
Micro Algae	700 - 7000

Recently reported productivity figures from the CELLANA consortium on marine algae at its plant in Kona Pilot Facility, Hawaii are 2,800 gal / acre / year.

Key attributes of micro algae as biofuel are …

- Reduced land footprint and indirect land use impacts (e.g. land needed for bio fuel to replacement of 50% of current petroleum Diesel using oil from corn would require nearly the total area of th US.),
- Can use non-fresh water to reduce demands on fresh water,
- High production potential for both whole biomass and neutral lipids,
- Potential source of high quality feedstock for advanced biofuels production,
- Need not compete with agricultural lands and water for food/feed production,
- Can potentially recycle CO_2, organic carbon, & nutrients from waste streams.

Algae are more productive than terrestrial energy crops. There is the general expectation, that only bio fuels from algae have the potential to deliver the required volumes.

However, affordable and productive commercial scale operations have not yet been demonstrated.

There are several strategies to the cultivation of micro algae and to some extend to macro algae as well – each has advantages:

- Open systems-typically outdoor open ponds
- Closed systems-enclosed clear plastic vessels (bags or tubes) known as photo bioreactors, or dark tanks (such as fermentation tanks)
- Offshore systems-growing algae in the open ocean-usually contained in some way (bags or ropes)

All established production types still offer several severe challenges before to be considered as stable and competitive.

Current market development shows, that as petro crude price increases – algae crude price decreases. This development of course can and must be boosted considerably provided adequate investments will be done.

Considering the regional characteristics of the gulf region, algae bio fuels offer a huge potential for development. This is especially true considering the different conditions within the UAE. There are countries without any oil like Ras Al-Khaimah, those which run out of oil soon like Bahrain and countries which still have plenty of

natural resources like Abu Dhabi but may wish to diversify its economy and prepare early for the inevitable decline of those resources.

Among the advantages of the Region as a preferred production site are:

- pre-requisite for fast growth: long daily sunshine duration,
- suitable temperatures: high growth rates expected,
- abundant (sea) water available,
- sufficient space (desert areas),
- financial & intellectual potential,
- the existence of traditional refinery infrastructure.

But to take advantage of these natural resources, considerable financial & intellectual investments are still necessary. Despite the advantage of algae being the fastest growing feedstock and having a lipid content of 5 – 50% depending on the selected strain, further processing still consumes a lot of its energy content. The good news is, that for harvesting, dewatering, drying & blending innovation is making progress fast.

However, to derive true hydrocarbons a cheap and efficient refinery process was still missing. Up until today, 8 biomass conversion techniques were known:

- Fermentation of Sugar/Starch Crops
- Fermentation of Lignocellulosic Biomass
- Transesterification of Triglycerides
- Gasification: Formation & Conversion of Syngas
- Fast Pyrolysis
- Fischer-Tropsch Synthesis
- Hydrogenation
- Anaerobic Digestion

A possible solution to this challenge can be seen in the novel refinery process developed by pacific propellants, Inc. (ppi), a young US start-up based in Reno / NV. This new ppi bio refinery process promises to close the refining gap.

Proposal

After pacific propellants, Inc. having developed a unique process to convert bio fuel feedstock into true jet fuel algae plus ppi could form a promising combination.

The ppi process offers advantages over established processes. It …

- delivers a fuel very similar to **traditional** fuel from fossil sources,
- requires **lower capital costs** than traditional refinery processes,
- is linearly **scalable** from mobile one-container-units to large plants,
- operates at **moderate** temperatures (~ 50 °C) and **normal** pressure,
- does not require expensive or low **availability materials** for input,

- does **not** produce any **hazardous** by-products.

Decentralized plants constructed to function according to the ppi technology, e.g. near airports, could capitalize on the local potential of the region. For full value chain processing a joint venture of ppi with a large scale (algae) feedstock producer is preferred: An existing large scale algae feedstock producer, who is well on the way to demonstrate a stable and profitable growing process is partnering with pacific propellants, Inc. and its unique bio refinery process.

Technical Background

Attempts have been made to connect the existing refinery and engine structure to the new, renewable feedstocks and outright create drop-in replacement fuels [3,4]. Even carbon dioxide itself has been proposed as feedstock to produce hydrocarbon energy carriers [8].

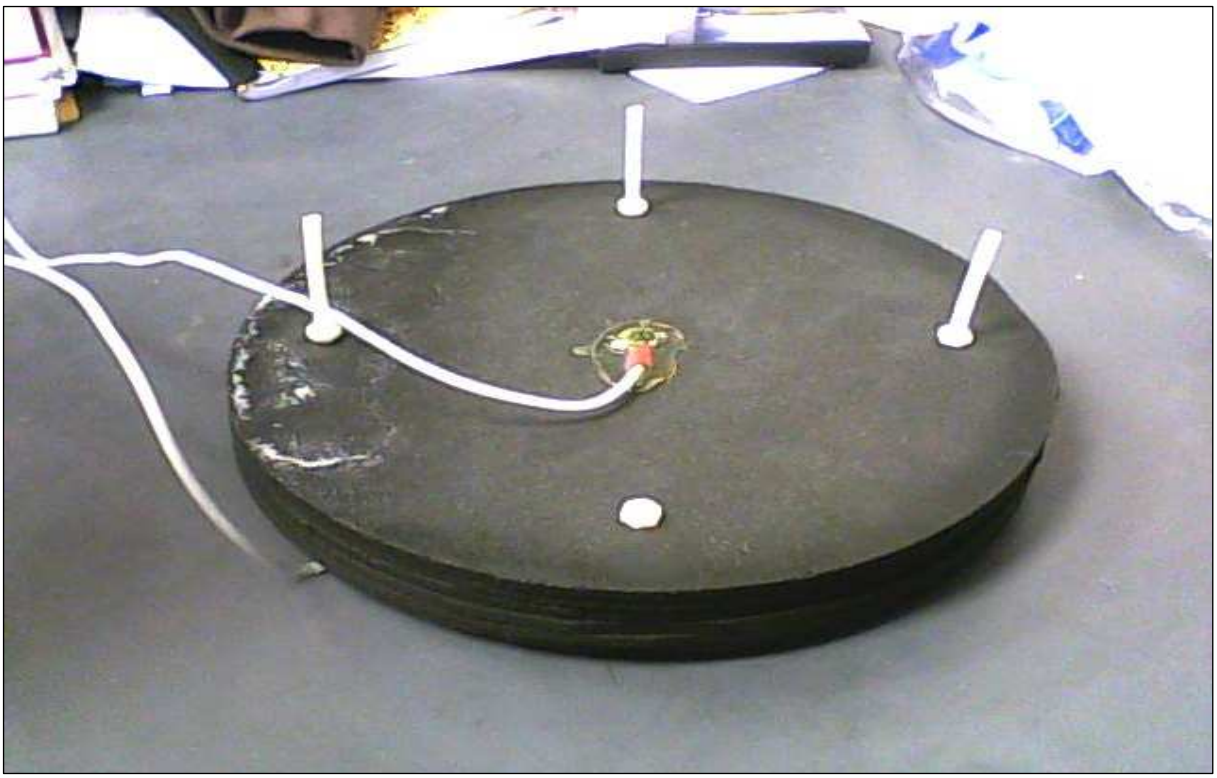
However, while Fischer-Tropsch and related technology has been operated successfully in South Africa and elsewhere for decades, it doesn't adapt well to the widely distributed nature of ligno-cellulosic feedstocks with low energy-density. Choren, a german company pioneering in the field of renewable hydrocarbon fuels, claims wooden feedstock more than approx. 50 km away from the plant can no longer be converted to fuels economically due to transportation overhead [5].

Lipid-based feedstock has been converted to 1st generation biofuels (aka biodiesel) with increasing efficiency, however, its compatibility with existing diesel engines is limited, and, due to its inadequate low-temperature performance it doesn't lend itself well to even more demanding applications such as jetfuel.

Electrochemistry is a field which has great potential for biofuel production. Low capex allows for rapid and wide deployment as well as return on investment.

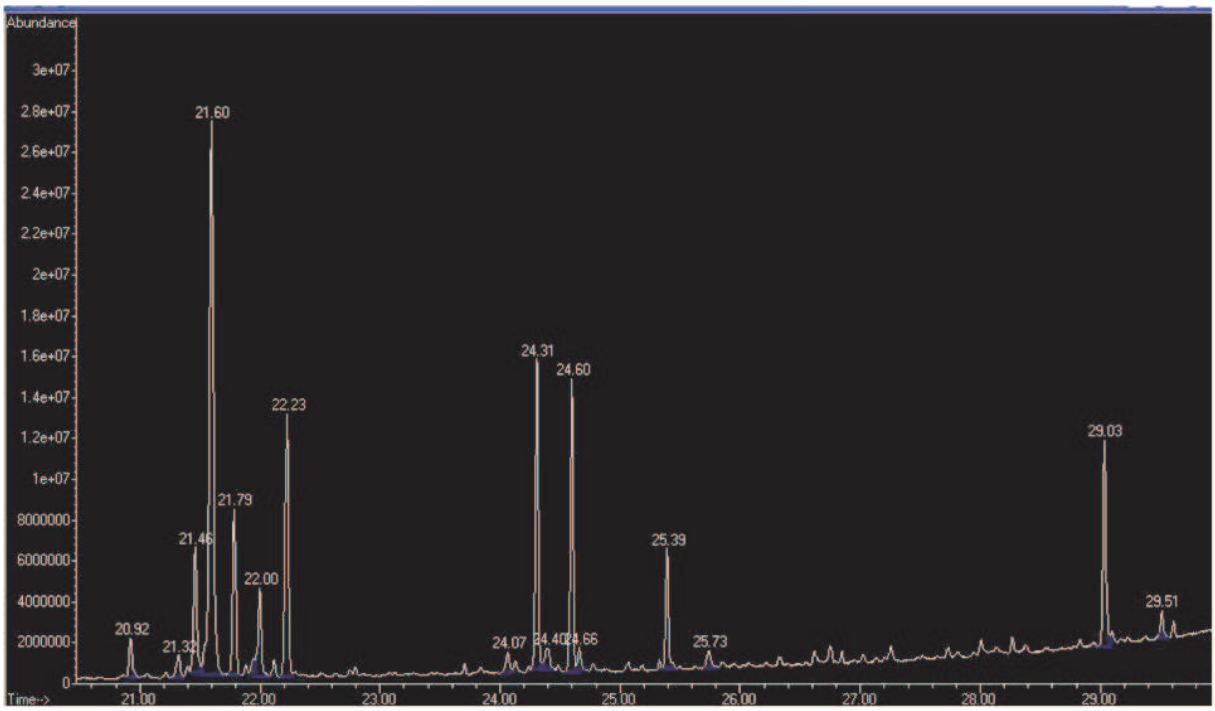
There are two general categories of electrochemical processes of importance: processes in which voltage is created by a chemical reaction, such as a battery, and processes in which external electrical energy is used to drive a reaction, such as electrolysis. The latter category of electrochemistry is what is instrumental in our research. Electrolysis involves a solution which conducts electricity, known as an electrolyte; a direct electric current (DC current) which drives the flow of electrons and causes chemical reactions to happen; and two electrodes, known as the anode and cathode, where oxidation and reduction (using electrons as agents instead of chemicals) occur, respectively. Depending on the specific desired reaction, there are many important variables to consider in electrolysis, such as the composition of the electrolyte, the material and configuration of the electrodes, and the required voltage to drive the reaction.

Shown below is an experimental electrode pack, which – fully scaled up – can produce up to 10 gal/hr.



This also presents the potential of directly using renewable electricity derived from solar panels (DC current) with very high efficiency, instead of AC current derived from fossil fuels via the public power grid and converted to DC with a loss.

We are especially interested in electrolysis which leads to the decarboxylation of carboxylic acids [6]. Two important categories which can perform decarboxylation of fatty acids are Kolbe and non-Kolbe (or Hofer-Moest [1]) electrolysis. During Kolbe electrolysis, the carboxyl group (COOH) on the end a fatty acid molecule is knocked off in an oxidative step and forms carbon dioxide, with the left over hydrocarbon chain from the fatty acid forming a radical with a free electron. This radical then bonds with another radical fatty acid in a step called dimerizing, to form a hydrocarbon molecule that is twice the length of the original hydrocarbon chain from the fatty acid molecule. In the Hofer-Moest decarboxylation, the carboxyl group is again oxidized into carbon dioxide, but instead of dimerizing, the free electron combines with another electron provided by the electrical current to form a double bond between last two carbon atoms in the chain, removing a hydrogen atom from the next-to-last carbon [7]. Our goal in this project is to selectively drive the non-Kolbe or Hofer-Moest process for medium- and long-chained carboxylic fatty acids to create a middle distillate liquid hydrocarbon product similar to diesel fuel. Pacific Propellants, Inc. has developed a unique process to convert bio fuel feedstock into true hydrocarbons. JV's with algae producers, which are being negotiated, could form very promising fuel producers.



In the above chromatogram, the peaks between 20.92 minutes and 29.03 minutes are of particular interest. By looking at the fragmentation patterns from mass spectroscopy, it can be concluded that the group of peaks between 20.92 and 22.23 all have molecular weight 236 and are likely variations (possibly isomers) of the expected C17H32 hydrocarbon product, 1,8-Heptadecadiene. The peaks between 24.31 and 25.39 are likely variations of the hydrocarbon product. The peak at 29.03 is a small amount of the methyl ester of oleic acid, which is an undesirable product. Using crude analysis, it is estimated that about 91% of the product is some form of hydrocarbon and 9% is methyl ester. Analysis and optimization of this experiment are still ongoing.

With the results of the experiment that has been run, we are optimistic that this process can provide an economical method to convert medium- and long-chained carboxylic fatty acids into a hydrocarbon fuel source. To calculate approximate electrical costs, our current flow can be converted directly into production of hydrocarbons by assuming that every 2 electrons of electrical flow produces one molecule of hydrocarbon per electrochemical cell in the reactor. Using this assumption, it is possible to produce 1120 g hydrocarbon/kW-hr using 5 cells and 20 volts. From the Department of Energy website, the average price of 1 kW-hr commercially in Nevada is 10.23 cents in 2010 [2], which means it would be possible to produce each gallon of hydrocarbons for about $0.27 (plus the cost of the feedstock fatty acids). This is the theoretical minimum cost. In practice, we hope to achieve a cost of $0.35-$0.40 per gallon of hydrocarbons.

In the context of energy yield, this means an eroi (energy return on investment) of about 10000%, i.e. 100 times of the electrical energy put into such a system would be returned in the form of a liquid transportation fuel.

Outlook

Pacific Propellants is engaged in developing new, inexpensive and distributed refining techniques to enable manufacturing large amounts of renewable fuels from various renewable feedstocks, one of which is already in the beginning scale-up phase [6].

As mentioned before, we believe electrochemistry has great potential for biofuel production. Hence we are working on a number of other paths to produce biofuels from renewable feedstock, including both lipids (fats and oils) and lignocellulosic feedstock (wood and other structural plant materials)

1. Electrochemical n-propanol and propene synthesis (in progress)

This project intends to utilize a related electrochemical process at the cathode to produce an oxygenate capable of being blended with gasoline using glycerol (~10% byproduct of biodiesel manufacturing from lipids) as inexpensive feedstock. Polymer-grade propylen, LPG and other C3 compounds can possibly also be derived from this route.

With some sophisticated additional development in the future this and related processes can also be tuned to “reuse” the electrons consumed in the middle distillate synthesis described above and share the same equipment, real estate and contribute to minimizing opex cost of this technology and create value-added products at both electrodes.

Preliminary experimentation has commenced.

2. Electrochemical jet fuel synthesis (in progress)

We are evaluating another electrochemical pathway to directly and very economically produce very targeted, branched, saturated hydrocarbon compounds with excellent low-temperature performance using cellulose derivatives and related renewable feedstock. These compounds can directly replace jet fuel (and other middle distillate applications, such as diesel/heating oil etc.)

Any low-cost biomaterials such as harvest residues, fast-growing bioenergy plants, carbohydrates derived from algae etc. can be utilized as primary feedstock for this pathway.

Preliminary experimentation has commenced.

Conclusion

Picking up the challenge to provide a considerable fraction of fuels consumed in the future via renewable fuels we selected and propose a probable pathway to success.

For several reasons discussed here we suggest that renewable fuels produced by industrial algae farming as the most promising way to be taken towards a future of renewable fuels. In order to overcome challenges still remaining over a mid-term horizon, considerable financial and intellectual investments are necessary next to a proper selection of fitting technology. This development is considered to be following a continuous improvement process.

For the subsequent refinement of algae crude into true hydrocarbons the breakthrough technology currently under development by pacific propellants, Inc. offers a competitive advantage.

In the combination of industrial algae farming, refining according to the ppi process and the special conditions within the Gulf region we recognize the potential for a highly competitive set-up which offers a unique development chance for the whole region.

Literature

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