

Renewable Pathways to Fuels Such as Kerosene and Diesel

Here are some key renewable fuel plants in Europe:

0) Ensus, UK. (<http://www.ensusgroup.com/>). Corn-based bioethanol.

I believe this will never amount to much because:

- a) it is constrained by the Biomass Limit, which depends upon land with sufficient annual insolation, water and nutrients, and for most developed countries is only about 10 to 30% of the transport fuel demand.
- b) it uses a 'food' feedstock, so is further constrained by the 'food-fuel' conflict.
- c) it uses a fermentation process, so is constrained to a temperature range of 0 to 100 C and roughly atmospheric pressure. Thus compared with gasification plants, the residence time is longer and the plant size is much larger.
- d) the energy return on energy invested (EROI) – for US conditions - is only 0.64 to 1.18.

(<http://netenergy.theoil Drum.com/node/6761>).

1) Inbicon, Denmark. (<http://www.inbicon.com>). Straw-based bioethanol.

Because it uses cellulosic feedstocks such as wheat-straw, it is less constrained by the 'food-fuel' conflict, but is still constrained by the Biomass Limit. However the yield of alcohol could be increased by using the CO₂ from the fermentation process, together with electrolytic hydrogen produced with wind electricity, to make methanol. Charles Nielsen, then of Elsam - a predecessor of DONG Energy - outlined this as their 'VENzin Vision'.

(http://130.226.56.153/rispubl/SYS/syspdf/energconf05/session2_cnielsen_pre.pdf Slide 25, 26).

Richard Pearson and I visited Charles Nielsen of DONG Energy at their Research Centre near Fredericia on 2008-06-30. We were shown around the Inbicon pilot plant. Their main concerns were further developing this process and building the demonstration plant at Kalundborg. This has since been completed.

(<http://www.greencarcongress.com/2009/11/inbicon-20091120.html> and

<http://www.greencarcongress.com/2010/08/inbicon-20100830.html#more>). The annual production target of 5.4 million liters of ethanol, at an HHV of 23.4 MJ/l, implies an average output of 126 TJ/y = 4 MW_{fuel}.

2) Choren, Germany. (<http://www.choren.com/en/>).

Woody feedstock is gasified to produce 'designer fuel', otherwise known as F-T Diesel, which is sulphur-free.

However, all biofuels are subject to the 'Biomass Limit', and Choren plan to import much of the woody feedstock. They have built Alpha and Beta (size) plants, and are planning Gamma plants.

(<http://www.purdue.edu/discoverypark/energy/pdfs/cctr/presentations/CHOREN-Purdue-May2008.pdf> Slide 10).

However, the 'Alpha' pilot plant is of about 1 MW_{fuel} output. (Slide 25).

Interestingly, the founder - Bodo Wolf, a chemist - proposed producing methanol. Only when VW, Daimler and Shell became involved did they switch to F-T fuels, using the Shell Middle Distillate Synthesis Process, a variant of F-T as used in their Gas-to-Liquid plant in Bintulu. (Slide 10). Shell have since dropped out, presumably leaving access to their MDS process.

3) BioMCN, Netherlands. (<http://www.biomcn.eu/>) This uses glycerine – a by-product of bio-diesel production - to produce methanol. This is attractive because the 4-stream plant - using methane as feedstock - already existed, and they have added a stage for gasifying the glycerine. However, this can only ever be a limited resource, and will decline as biodiesel – a first generation biofuel - is phased out. They realise this very well, and are interested in air capture and wind-electricity to produce hydrogen, which could be added as a 'front-end'. The plant is located on the coast - ideally placed for electricity supplied from offshore wind farms.

4) Varmlands Metanol, Sweden. (<http://www.varmlandsmetanol.se>).

Woody feedstock is gasified to produce syngas then methanol, as Choren planned originally. Their approach is to use existing technology. Having failed to get even partial government support, they simply scaled up their plans and went to investors, who are backing them. However, unlike most developed countries, ample woody feedstock is available in Sweden, which has a low population density and is already managing it's forests sustainably for the pulp and paper industry.

5) TBM (Technology Platform Bioenergy and Methane), Germany. (No dedicated web site). The AER gasification process developed by Dr Michael Specht et al is mentioned in the ZSW Annual Report for 2009. (http://www.zsw.e-technik.uni-stuttgart.de/fileadmin/ZSW_files/Infoportal/Informationsmaterial/Jahresberichte_docs/JB_2009/JB09_ZSW.pdf). Page 28: 'The BtG platform is closely linked to the AER gasification plant owned by the operating company TBM (Technology Platform Bioenergy and Methane) in Geislingen-Türkheim (Federal State of Baden-Württemberg), Germany, which is expected to be commissioned in 2011'.

A search found this: <http://www.igu.org/html/wgc2009/papers/docs/wgcFinal00802.pdf>
Page 4: 'The feasibility of new concepts adapted to the peculiarities of biomass gasification was shown e. g. by a 18 MW plant for wood chip gasification in Värnamo (Sweden) [9] and by a 8 MW wood gasification in Güssing (Austria) [10], the latter operating successfully since 2001. In the last few years sidestream experiments for methanation/SNG synthesis and for Fischer-Tropsch synthesis were added to the Güssing plant with promising results [11] which promoted further research projects throughout the EU.

For the time being, a 10 MW plant for biomass gasification is going to be realised in Geislingen (Germany) by the TBM corporation (Technology platform Bioenergy and Methane [12]) founded by local utility companies and Universität Karlsruhe. Production in that plant will start in the end of 2010. The TBM complex will also include a biomass and waste fermentation plant [and a gasification plant], see Figure 5, for the production of bio SNG. In a first step all the gases will serve to produce electric energy directly on place. Parallel, the plant will offer the possibility to try new concepts for methanation in pilot scale under real operation conditions'.

6) Carbon Recycling Inc., Iceland. (<http://www.carbonrecycling.is>). They are using hydro and geothermal electricity - the cheapest in the world - to make electrolytic hydrogen and - with geothermal CO₂ - produce fully synthetic methanol. Founded in 2007, they are through the pilot plant stage and are completing their 'Industrial Scale Plant', with 2 streams - one due at the end of 2010 and the second due in mid-2011. This plant uses current technology. While they involved Professor George Olah as a consultant, I judge that this was mainly for their (partly) American investors. When investing in a renewable fuel plant, an association with a Nobel Laureate in Chemistry probably adds credibility.

I attach a draft document with my analysis of this plant - with all data taken from the web - and the prospects for meeting the Icelandic 'gasoline' demand and for exports. In brief, the renewable electricity resource - even without wind turbines - would suffice for nearly 5 times the Icelandic 'gasoline' demand. This draft document is for your use only, since I have sent it to their Chief Technical Officer - Oddur Ingolfsson - as the basis of a possible co-authored published paper.

In my analysis, I assumed that because H₂S must be removed from the geothermal water/steam before use, the CO₂ was captured and concentrated at the same time, so I did not deduce the CO₂ capture energy.

The CO₂ capture energy is a function of the logarithm of the partial pressure. (<http://people.ucalgary.ca/~keith/papers/116.Cherry.Heidel.CapCO2FromAtmosp.p.pdf> Page 4). As for the partial pressure of geothermal CO₂, this is the nearest I could find: (<http://www.landsvirkjun.is/media/rannsoknir/0250-CO2-Emissions-from-the-Krafla-Geothermal-Area-Iceland.pdf> Fig. 4). This shows CO₂ concentrations of 6 to 0.2%, but it varies widely in time and presumably with the borehole.

7) Solar-Fuel GmbH, Germany. (<http://www.solar-fuel.com>) This uses renewable electricity from wind and solar, with CO₂ captured from air, to synthesise methane. The technology was developed over many years by Dr Michael Specht et al, at ZSW, Stuttgart, and the methane will be used as in the recent thesis by Dr Michael Sterner at Fraunhofer IWES, Kassel. (<http://www.upress.uni-kassel.de/publi/abstract.php?978-3-89958-798-2>). An 'Alpha' pilot plant in a container has been built at ZSW for Solar-Fuel. This has an input power of 25 kWe and an energy efficiency of about 40%. (<http://www.solar-fuel.net/loesung/alpha-anlage-laeuft/>). A 'Beta' plant of 6.3 MWe is expected to have an efficiency of 54% and 'Gamma' plants of 20 MWe an efficiency of over 60%. Solar Fuel was established in November 2007 and is now headquartered in Stuttgart. The founder and managing director is Gregor Waldstein, Dipl.-Ing. ETH, MBA.

Here is a short article:

(<http://www.engineeringnews.co.za/article/storing-green-electricity-as-natural-gas-2010-08-06>).

Their web site includes links to three videos. While they contain no more numbers than are in the text documents, moving pictures of the 'container-sized' pilot plant are very convincing.

a) http://www.youtube.com/watch?v=w_-aaIpCTCA

The 'talking heads' are: Dr Michael Sterner of Fraunhofer IWES, Dipl.-Ing. Gregor Waldstein of SolarFuel, Dr Michael Specht of ZSW, and Dr Martin Egginger of JKU (Johannes Kepler U., Linz, Austria). This last seemed to be involved with the use of the fuel. He must have mentioned methane, but I also heard methanol, benzene (gasoline) and diesel.

b) <http://www.youtube.com/watch?v=jnzDORcz4ds>

c) (<http://www.zdf.de/ZDFmediathek/beitrag/video/1018744/Aus-Strom-mach-Gas---Oekostrom-speichern>)
Dr Michael Sterner is talking in front of large displays showing the changing amounts of electricity from wind, PV and biogas. This is a notable result of the 'Kombikraftwerk' project, run by ISET (now IWES) at UniKassel. (<http://www.kombikraftwerk.de>). This showed how to achieve 100% renewable electricity with no need for any new way of storing electricity. Michael Sterner has since shown that electricity could be stored as renewable methane on a huge scale, so enabling 100% renewable energy for electricity, transport fuels and heat. The other 'talking head' is Gregor Waldstein, CEO of Solar Fuel.

I believe that in practice some - even much - of the product should be methanol (as 6) CRI), since this can be used in 'gasoline' (Spark Ignition) vehicles, whereas methane requires Compressed Natural Gas vehicles, which must be either dedicated or 'Bi-Fuel' (Gasoline/CNG). Like methane, methanol can also be transported and stored for use in 'peaking' gas turbine generators. However the proportions of methane and methanol is mainly an engineering optimisation issue rather than a difference in philosophy.

Here are some key synthetic renewable fuel activities in the USA:

8) NAU Northern Arizona University, Steve Atkins. (<http://ses.nau.edu/AZSynFuels/>)
Steve Atkins attended the recent AFS meeting in the UK. He has followed the approach of Specht and Bandi of using CO₂ and hydrogen to produce methanol. (<http://www.methanol.org/pdf/ZSWMethanolCycle.pdf>). The energy efficiency has been estimated as 62%. (http://ses.nau.edu/AZSynFuels/literature-refs/Methanol_Energy_Balance.pdf Page 5). He has also built a small pilot plant which uses concentrated CO₂, supplied by a local brewery, and hydrogen produced notionally from wind electricity.

The web site has links to two YouTube videos. (<http://ses.nau.edu/AZSynFuels/literature-refs.html> and <http://ses.nau.edu/AZSynFuels/press.html>). These mention the US demand for gasoline as 140 billion gallons a year and the potential supply using such clean concentrated CO₂ streams as 8 billion gallons of methanol a year. However, on an energy basis, this would be only $8/(140 \times 2) = 2.8\%$ of the gasoline demand.

9) PARC Palo Alto Research Center, Karl Littau.
Karl Littau gave a presentation at Google in their TechTalk series on 2008-08-28. (<http://www.bestechvideos.com/2008/09/16/carbon-neutral-synthetic-hydrocarbon-fuels>). It runs for an hour, and is very well worth watching, including the discussion. He reviews the options for capturing CO₂ from the air, with ranges of values for the capture energy. I noted them as 'electrochemical' as potentially 45-70 kJ/mol CO₂ and 'electrodialysis' as potentially 30-50 kJ/mol CO₂. He concludes in favour of an absorption process with electro-dialytic regeneration and has built a small bench-scale plant. For the rest, he proposes to follow Specht and Bandi and produce methanol. You could request a copy of the presentation from Karl.Littau@parc.com

Following several exchanges by email, Richard Pearson visited him and they have since co-authored a couple of papers.

10) Doty Energy (Windfuels), David Doty. (<http://www.windfuels.com>)

The extensive web site compares many energy options and proposes using wind electricity to produce – via F-T synthesis – ethanol, gasoline, jet fuel and diesel. The processes have been simulated in considerable detail and they claim that an energy efficiency of 58% is a reasonable near-term goal.

(http://windfuels.com/PDFs/WindFuels_Sci_Engr_ppt.pdf Slide 17). David Doty and colleagues have also authored many papers documenting the special features of their processes. I have had extensive email exchanges with him, including commenting on drafts of some of the papers. They focus on the special features to attract government funding and on developing IPR to attract private investments.

A near 5 minute video was produced for broadcast. (<http://www.youtube.com/watch?v=TIRavcMZpX4&NR=1>). However, unlike Solar Fuel, there is no hardware to show. Also, David Doty seems not to know of them and that they - following Stucki et al of PSI and Specht et al of ZSW - invalidate his claim to be the only company or group proposing fuels produced from wind energy.

Discussion

The current status of biofuels in the USA is summarized in the Regulatory Impact Analysis from the EPA: (<http://www.epa.gov/oms/renewablefuels/420r10006.pdf> P 115). Table 1.4-1 lists the processes, products and (mostly US) companies associated with them. Almost all are producing first generation biofuels, with only two – Range Fuel and Cello – producing second generation biofuels, of which Range Fuel is currently producing methanol. (<http://www.greencarcongress.com/2010/08/rangemeoh-20100818.html>). However, I believe that in most developed countries, biofuels could meet only 10 to 30% of the transport fuel demand. Thus to meet the challenges of climate change and resource depletion, synthetic renewable fuels would be required to meet the remaining 70 to 90%. Yet I know of no fully synthetic renewable fuel plants above bench scale in the USA and even 8), 9) and 10) are more or less self-funded. That said, they are very valuable as confirming the synthetic renewable fuel proposition and describing possible process routes.

Gasoline is most compatible with existing Light Duty Vehicles and kerosene and diesel are essential for aircraft, trains, trucks and ships. The latter are especially critical because they carry people and goods, including food and raw materials, both within and across national borders. When producing gasoline, kerosene and diesel, I believe that the synthesis of methanol-MtGasoline or MtSynfuel pathway is preferable to F-T synthesis, because the former processes have higher selectivities, so avoiding the need to upgrade co-product naphtha and waxes. Thus while methanol etc is two-stage and F-T seems at first to be single stage, such upgrading makes it also two-stage. Moreover, I believe that the co-production of waxes must mean that the risk of blockage is high with conventional reactors and would be even higher with microchannel reactors.

Companies and Groups	Ethanol	Methane	Methanol	Fischer-Tropsch Diesel Etc
First Generation Biofuel	0)			
Second Generation Biofuel	1)	5)	3), 4)	2)
Synthetic Renewable Fuels		7)	6), 8), 9)	10)

Taking the synthesis of methane as very similar to that of methanol, this pathway is favoured by seven companies and groups and F-T synthesis by only two. Where the 7) Solar Fuels 'Alpha' pilot plant for methane has a nominal output of 10 kW_{fuel}, the 2) Choren 'Alpha' pilot plant – latterly producing F-T Diesel – has an output of 1 MW (i.e. 100 x), while 10) Doty Energy (Windfuels) - proposing F-T - has so far been limited to desk studies. While Doty Energy claim their F-T pathway should have a near-term energy efficiency of 58%, Solar Fuel claim their 'Gamma' commercial-scale plant for methane synthesis should have an efficiency of over 60%.

Of the demonstration plants, the 1) Inbicon Kalundborg plant for cellulosic ethanol, the 2) Choren Beta plant for F-T Diesel, the 5) TBM plant for bio SNG, the 6) CRI ISP for synthetic methanol and the 7) Solar Fuel Beta plant for synthetic methane are all roughly comparable in size. The first two are up and running, the third and fourth should be complete by the end of 2010, and the Solar-Fuel Beta plant may be ready about three years later.