

ES2009-90182

SECURING OUR TRANSPORTATION FUTURE BY USING OFF-PEAK WIND ENERGY TO RECYCLE CO₂ INTO FUELS

F. David Doty, Laura Holte, and Siddarth Shevgoor

Doty Scientific, Inc., 700 Clemson Road, Columbia SC 29229 USA

ABSTRACT

Simulations have shown that it should be possible (within a relatively short time frame) to profitably synthesize high-purity carbon-neutral ethanol, gasoline, jet fuel, propylene, and many other hydrocarbons, in volumes that cannot be matched by any other renewable avenue, from captured CO₂, water, and cheap off-peak low-carbon energy, notably from wind farms. The process, dubbed *WindFuels*, requires no biomass, and it is expected to solve the grid stability and energy storage challenges of wind energy.

The process is based largely on the commercially proven technologies of wind energy, water electrolysis, and Fischer Tropsch Synthesis (FTS) chemistry. Wind energy is used to electrolyze water into hydrogen and oxygen. Some of the hydrogen is used in a process, the so-called reverse water gas shift (RWGS) reaction, that reduces CO₂ to carbon monoxide (CO) and water. The CO and the balance of the hydrogen are fed into an FT reactor, similar to that commonly used to produce fuels and chemicals from coal or natural gas. Improved sub-processes have been simulated in detail, and key experiments will soon be carried out to help optimize process conditions. Conversion efficiencies (from input electrical to output chemical) are expected to approach 60%.

Putting renewable hydrogen into liquid fuels solves the distribution and storage problems that have beset utilization of hydrogen in vehicles. Converting CO₂ into fuels can eliminate the need for CO₂ sequestration and reduce global CO₂ emissions by 40% by mid-century. The amount of water needed for the renewable FTS (RFTS) process is an order of magnitude less than needed for biofuels. The atmosphere will eventually provide an unlimited source for CO₂, though initially the CO₂ would come from ammonia plants, biofuel refineries, cement factories, fossil power plants, and ore refineries. When the input energy is from off-peak wind and reasonable monetary credit is included for climate benefit, *WindFuels* could compete when petroleum is as low as \$45/bbl.

1. INTRODUCTION

There is an urgent need for a renewable transportation fuel that is carbon-neutral, scalable to meet demand, and has little or no detrimental effect on the environment or civilization. The potential of advanced biofuels like cellulosic ethanol and microalgae has often been overstated (1-4). For example, it is not widely appreciated that under 29% of the carbon in the biomass feedstock ends up in the ethanol, with most of the rest released from the processing plant as CO₂ (5). The amount of carbon sequestered in soils and forest floors is estimated to be about 200 times the amount of fossil carbon currently being released annually. Cellulosic ethanol could worsen net carbon emissions by reducing the amount of sequestered bio-carbon (2). Many forms of cellulosic feedstocks today are 8 times more expensive than they were 8 years ago. Moreover, the price of wood products will likely begin to soar again within five years as the vast pine forests in North America that have been killed by the pine beetle over the past decade (over 500,000 km²) are mostly consumed by forest fires (6). If cellulosic feedstocks cost \$400/ton by 2015, ethanol produced from it would cost over \$5.50/gal. Recent studies indicate commercial-grade fuels from photosynthetic algae will likely cost over \$25/gal for many years [5].

Previous studies (1, 7) have shown that all the world's energy needs (140 PWhr/yr) – power grid, transportation, home heating, agriculture, and industrial can be met using global wind energy (630 PWhr/yr). The growth in the installed wind capacity has slowed recently, largely due to the grid stability challenge. Wind farms are often most productive when grid power demands are low – at night. Consequently, at off-peak times, grid energy often sells for less than 20% of the peak daytime rates, and its 'real-time market' price has at times even been negative (8).

Substantial resources have been directed over the past decade in efforts to enable the use of hydrogen in the transportation sector; but the cost challenges of storage, distribution, and end-use of elemental hydrogen have proved daunting. The best hydrogen storage option for automobiles

two decades from now seems still likely to be the 600-bar high-pressure tank, and fuel cells are still an order of magnitude more expensive than internal combustion engines [9]. The general optimism for market penetration by hydrogen vehicles seems to diminish annually. This experience underscores the importance of carbon-neutral fuels working seamlessly within the current fuel infrastructure. Hence, our focus has been toward efficient synthesis of ethanol, gasoline, and jet fuel from waste CO₂ and renewable hydrogen.

It has long been accepted that it should theoretically be possible to convert CO₂ and water into standard liquid hydrocarbon and alcohol fuels at high efficiency. The problem has been that prior proposals for doing this conversion have had efficiencies of only 25% to 35% [10]. That is, the chemical energy in the preferred liquid fuels produced (ethanol, gasoline, jet fuel, etc.) would be about 30% of the input energy. Efficiencies up to 44% have been thought practical for advanced methanol processes [11]; but pure methanol is not a preferred fuel for public transportation, owing to its toxicity, high vapor pressure, low energy density, low flash point, and corrosiveness.

Simulations of novel plant designs indicate it should become practical using available catalysts to synthesize preferred fuels including ethanol, jet fuel, and gasoline from CO₂ and H₂O at system efficiencies approaching 60% [12]. This would be about twice what was expected by most researchers just three years ago. The proposed process is based largely on the commercially proven technologies of wind energy, water electrolysis, and Fischer Tropsch Synthesis (FTS) chemistry [19]. Off-peak low-carbon energy is used to produce hydrogen. Some of the hydrogen is used in a reverse water gas shift (RWGS) reactor to reduce waste CO₂ to CO. The CO and the balance of the H₂ are fed into an FT reactor.

Detailed simulations show that major advances can be made in many of the key processes and components, including (A) separation of CO₂ from a complex synthesis gas, (B) cost-effectiveness of heat recuperators, (C) plant integration, and (D) thermodynamic cycles for conversion of waste heat to electricity. When the input energy is from off-peak wind and reasonable monetary credit is included for climate benefit, *WindFuels* should compete when petroleum is above \$45 to \$90/bbl. The major factors determining this competitive point more precisely are (1) the price of the off-peak low-carbon energy (which has recently ranged from \$12 to \$25/MWhr), (2) the market for the co-produced liquid oxygen, and the value of carbon credit available for climate benefit. At \$15/MWhr for the energy and 50% plant efficiency, the cost of the energy in a gallon of ethanol will be \$0.75. Hence, we expect *WindFuels* to be more competitive than advanced biofuels in future economies.

Our studies show that in good wind regions, *WindFuels* production per gross land area should exceed that of biofuels on good farm land by factors of 4 to 20. The amount of water needed for the *WindFuels* is an order of magnitude less than needed for biofuels.

In the following sections, we first present some additional relevant background material on the *Renewable FTS (RFTS)* process and brief discussions of a few of the important technical areas and developments. We then return with more general comments on sustainability.

2. ENERGY STORAGE for GRID STABILIZATION

Grid stability has become a pressing issue as more renewable power options penetrate the market. Off-peak wind energy periodically must be sold at negative prices just to protect the grid [8], and it is often available for less than \$20/MWhr. Storing this energy through electrolysis of hydrogen could completely stabilize the grid, since the hydrogen would be generated only when excess energy is available. However, the costs of storage and distribution of energy as pure H₂ are two orders of magnitude higher than for liquid hydrocarbons or alcohols.

Low-price and even negative-price wind energy will become increasingly available if it continues to be added faster than long-distance transmission capacity. The grid stability challenge will also be exacerbated by additional nuclear energy and clean-carbon, as they take many hours to turn down and have very small turn-down ratios. Electrolysis can be an important part of the solution, as excess grid energy can be utilized whenever it is available (in the middle of the night and on weekends) to produce hydrogen that can be stored temporarily in buffer tanks to keep an RFTS process going at a fairly steady rate around the clock.

Other energy storage mechanisms, such as compressed air and advanced batteries have been suggested for grid stabilization, but their capital costs range from \$150 to \$1000/kWhr [13]. The tank-component cost of energy storage in stable liquid fuels is only \$0.02/kWhr [14].

The electrolysis stage upstream of the proposed RFTS process could provide response to major changes in grid supply and demand in under 20 ms. Thus, *WindFuels* has the potential to allow complete stabilization of the grid, even if over 50% of the grid energy comes from wind.

Some may be concerned that commercially available electrolyzers currently achieve only 73% higher heating value (HHV) efficiency, they are still expensive, and progress has been slow over most of the past decade [15]. However, laboratory experiments have achieved over 87% HHV efficiency [16, 17], and we have shown that it should be possible to convert a much higher percentage of electrolyzer waste heat to electricity than hitherto [18]. Moreover, efficiency is immaterial if the energy is carbon-neutral and has a negative price. Our models, based on very recent data, suggest the amount of negative-priced energy available could steadily increase for about two decades, even with massive investments in the grid infrastructure and *WindFuels* – because new wind farms will be added at an even greater rate.

3. RFTS SYSTEM OVERVIEW

FTS technology has matured over the past seven decades for the production of gasoline, diesel, and waxes from fossil-derived CO and H₂ [18, 19]. Reported efficiencies have exceeded 62% for synthesis of Higher Hydrocarbons (HHCs) from methane and about 50% for HHCs from coal [19]. FTS processes for synthesis of mid-alcohols (ethanol, propanol, and butanol) from CO and H₂, have also been well optimized though with much less commercial success. Despite having a higher theoretical efficiency limit, the actual efficiencies for

mid-alcohols from methane have been between 25% and 45% [20].

An indication of the potential for higher efficiency during ethanol synthesis may be observed by noting that its synthesis from H_2+CO_2 results in 1.5 molecules of water per carbon atom in the fuel, whereas the synthesis of alkanes or alkenes results in 2 molecules of water by-product per carbon atom.

A theoretical efficiency limit may be calculated based on the fuel energy of the output compared to input. Using the HHVs, one readily calculates that the theoretical maximum chemical efficiency of ethanol synthesis (1366 kJ/mol) from H_2 (286 kJ/mol) and CO_2 is 80% when the exothermic reaction heat is not utilized [12]. If this heat (typically available at ~600 K) is also converted in an ideal heat engine, the theoretical combined-cycle efficiency limit is ~90%. This simple calculation motivated the development of *WindFuels*.

Catalysts have recently been investigated for hydrogenation of CO_2 either *semi-directly* or *directly* into higher hydrocarbons (HHCs, C_{2+}) and mid-alcohols using renewable H_2 [21, 22]. However, these catalysts appear to be many years away from commercialization. Our focus, on the other hand has been to look at what can be done to improve the system efficiency of indirect production of fuels and chemicals from CO_2 and renewable H_2 with well characterized catalysts and novel process optimizations. This implies the reduction of CO_2 to CO followed by hydrogenation of CO to HHCs and mid-alcohols using available FT catalysts [12, 23]. Catalysts never change the thermodynamics of a reaction – they only impact the kinetics and selectivity. Thus, in a fully recycled process, progress in catalysts tends to have only minor influence on the system efficiency. However, catalysts may have more influence on costs and operations.

The general concept design is easily summarized with reference to **Figure 1**: First, water and renewable electrical power are fed into an electrolyzer, which produces the

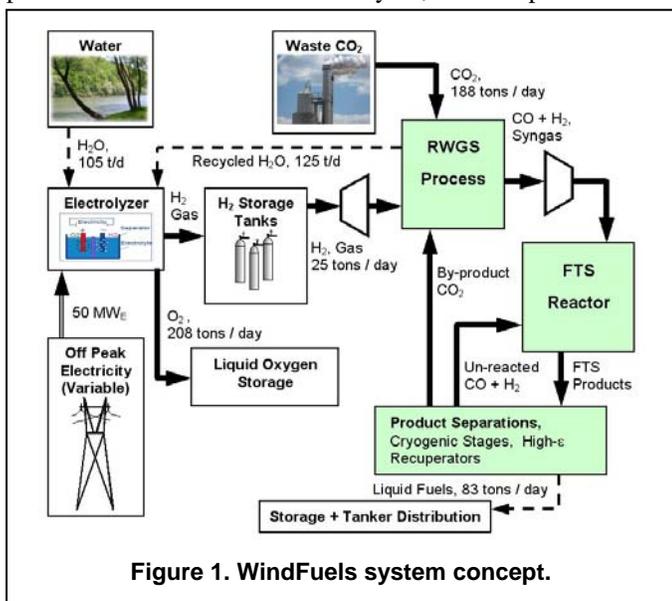


Figure 1. WindFuels system concept.

required hydrogen during times that excess electricity is locally available. Then waste CO_2 and renewable hydrogen are reduced to the needed CO in an optimized RWGS process, at efficiencies approaching theoretical limits (ultimately, over 94%). The CO and H_2 are then fed into a fully recycled FTS

process. The FTS reactor converts a fraction of the CO and H_2 into the desired products while the balance is efficiently separated and recycled. The desired liquid fuels and chemicals may be stored and distributed by conventional means. The electrolyzer also produces pressurized oxygen in large quantities, which may be sold if market conditions warrant, or it may be utilized in novel processes to improve the plant efficiency.

The RWGS-RFTS process is outlined in the simplified process diagram shown in **Figure 2** for the process we simulated for the production of mostly ethanol and light HCs from CO_2 . (The bold numerals in braces refer to component labels in Figure 2.) Pressurized H_2 and O_2 are assumed produced in alkaline electrolyzers {123} at about 80% efficiency. Captured CO_2 is reduced to CO in the multi-stage RWGS process {128} using a portion of the H_2 . The remainder of the renewable H_2 and the CO (and minor amounts of other gases) form the new syngas {134}, which, along with the unreacted syngas {147}, is sent to the FT reactor {140} for partial conversion to the desired fuels and chemicals.

Initial separations of the heavier condensable gases exiting the reactor are achieved in a series of condensers {141} at the full reactor pressure. This is an important part of maximizing plant efficiency and is a major departure from current practice [19, 20]. Lighter gases are condensed out {143} after compression to a pressure high enough to permit sufficient removal of the CO_2 (generally below 15 molar %) from the syngas. Expansion {146} back to the pressure desired in the FT reactor provides the cooling capacity needed. The remaining light HCs may be separated by absorption in cold oils (and other processes) prior to reheating {147} of the recycled H_2 , CO, and CO_2 back to the reactor temperature.

FTS demonstrations of mid-alcohols (from methane or coal) have previously seen the losses associated with recycling equal to about half of the energy content of these components [19]. A recent demonstration required over 6 MJ/kg for CO_2 separation from a syngas [24]. The high-pressure (10 to 20 MPa) refrigeration process presented here requires adding a boost compressor into the recycle loop {142} with its attendant costs and power demand, but most of the compression power is subsequently recovered in the expansion {146}, which also provides the refrigeration needed for the separations (and for liquefaction of the LOX byproduct). Simulations indicated the energy required for adequate CO_2 separation from syngas can be under 0.8 MJ/kg.

The pressure, temperature, and H_2/CO ratio chosen for the simulations were near the mean of: (A) that used in the recent highly promising results on a K_2CO_3 -promoted $\beta-Mo_2C$ catalyst [25], (B) those preferred for high selectivity of mid-alcohols from Cu/ZrO₂ catalysts [19], and (C) that which has been shown to give best selectivity toward mid-alcohols with K/C/Co-promoted MoS_2 catalysts [26].

The catalytic selectivities on the basis of C-atom-% were assumed to be similar to those demonstrated recently with a K_2CO_3 -promoted $\beta-Mo_2C$ catalyst: 24% ethanol, 17% methanol, 8.5% propanols, 6% C_5-C_7 olefins, 6% propylene, 6% methane, 4% C_8-C_{12} olefins, 4% butenes, 3.5% $C_{13}-C_{19}$ olefins, 3% butanols, 2% ethylene, 2% C_{20+} , 2% acetone, 1.5% C_4-C_7 alkanes, and lesser amounts of others. The assumed

total CO conversion per pass was 28%, with 10% water gas shift.

We call the process “full recycle” because all the unreacted H₂ and CO are recycled without expansion to a pressure far below the FT reactor pressure (such expansion and recompression would lead to large energy losses). To our knowledge, no such full recycle in FTS has been done before. One of the important reasons it has not been implemented with fossil- or biomass-based FTS is that there is insufficient flexibility in controlling the H₂/CO ratio in the syngas coming from a reforming process to compensate for the variability that will be seen from changes in the water-gas-shift (WGS) reaction in the FT reactor. Maintaining the desired H₂/CO ratio in an RWGS-RFTS process, on the other hand, is not an issue, as one has complete and independent control over both the H₂ and the CO feed rates in the new syngas.

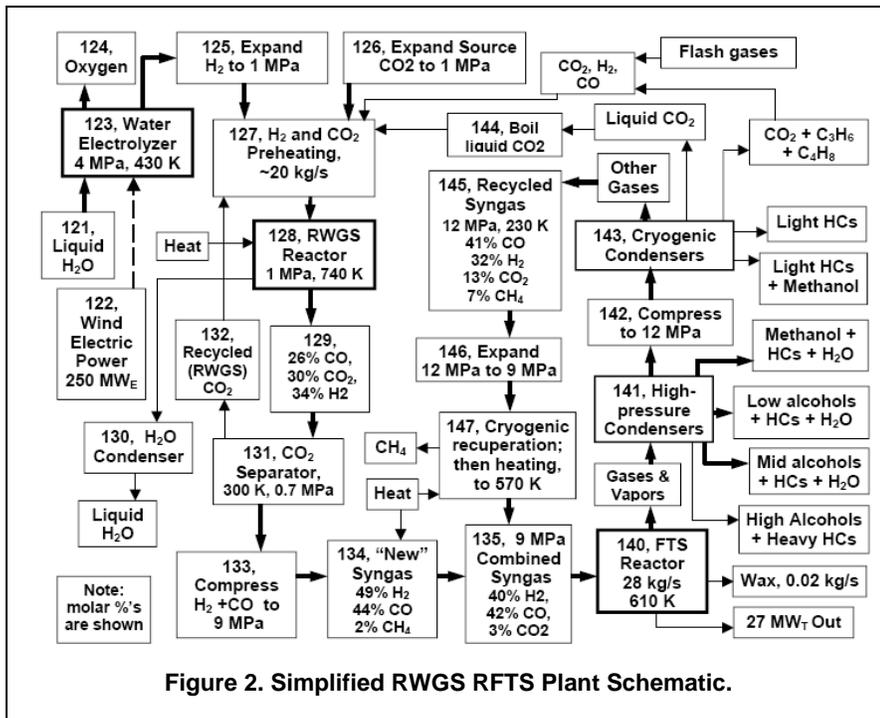


Figure 2. Simplified RWGS RFTS Plant Schematic.

The next challenge with full recycle is keeping the CO₂ in the syngas low enough with very low energy penalty. Some FT demonstrations have shown little loss in catalyst lifetime or activity with mean CO₂ content in the syngas above 25% [19], though 10-15% seems to be a better limit, partly because the costs of the turbomachinery and other components increases with increasing “inert” fraction in the product stream, and partly because there is some (conflicting) evidence of more rapid loss in catalyst activity, especially for mid-alcohols, with CO₂ contents of even 5% [27]. As noted above, the high-pressure refrigeration process was seen to have order-of-magnitude advantages over alternative processes for FT reactor pressures at 9 MPa with large WGS activity when CO₂ below ~12% was adequate. It is not yet clear whether the same would be true for much lower FT pressures and much lower WGS activity, as would be expected in a plant optimized for mid-weight alkanes for production of jet fuel. This is a question we expect to investigate in the near future.

More detailed analyses and simulation results of all of the primary and the crucial secondary sub-processes have been presented elsewhere [12]. Even with low conversion per pass,

we expect the chemical energy of the products to approach 72% of that in the source H₂ [12], or 58% of that in the electrical energy going into the electrolyzer.

4. A HIGH-EFFICIENCY RWGS PROCESS

A key to any indirect RFTS process will be efficiently reducing CO₂ to the CO that is needed in the FT reactor. Simulations and experiments indicate the multi-stage RWGS process should work well [12],



though advanced recuperators [28] are needed to achieve high efficiency. Sufficient success in reducing CO₂ has been reported to establish that it can deliver the robustness needed [29, 30], though efficiency seen thus far is well below what will be desired.

The equilibrium (K_P) limits imposed by the reaction thermodynamics below 700 K and competing methanation and coking reactions above 800 K give rise to challenges.

The most effective near-term solution to driving the RWGS reaction to the right (towards products) would include only H₂O separation by condensation in a multi-stage process. Separating the dilute gas products from the RWGS partial-reaction mixture with very high efficiency is challenging, as current high-effectiveness gas-to-gas recuperators for these conditions are very expensive.

Several sets of conditions appear very promising: (1) five stages at ~740 K, ~1 MPa, with Cu/alumina catalysts [29]; (2) three stages at ~820 K, ~0.6 MPa, with Fe₃O₄/Cr₂O₃ catalysts [31]; or (3) two stages at ~900 K, ~0.25 MPa, with ZnAl₂O₄ catalysts [30]. The equilibrium constant K_P will still be in the range of 0.14 to 0.5, which means the product of the CO and H₂O fractions will be quite low. Therefore, high conversion of the CO₂ requires a multi-stage or recycle process that works well with a low fraction of products in the RWGS output stream.

Most prior RWGS experiments have been with syngas flow rates below ~0.03 g/s. Very limited data are available from the one known experiment at ~1 g/s [30], but perhaps it achieved ~50% efficiency. More details on proposed processes that should permit over 90% efficiency (meaning under 1.55 MJ/kg-CO) have been published [12].

There are a number of reactions (primarily yielding methane and coke) that may compete with the RWGS reaction, but all are higher order than the RWGS reaction in at least one of their reactants and thus their rates may be reduced relative to the desired reaction by reducing the partial pressure of an offending reactant. For example, the most significant competition is usually the highly exothermic CO₂-methanation reaction,



which is roughly fourth-order in hydrogen partial pressure p_{H_2} . By keeping p_{H_2} below 0.35 MPa and p_{CO} below 0.25 MPa, it is

hydrogen just began to surface in 2006, and partly because a major advance was needed in recuperators. However, the RWGS approach we have proposed (in more detail elsewhere [12]) appears now to have low technology risk and much more promise than the alternatives that have been proposed for reduction of CO₂ to CO [10, 34, 35]. Key experiments will soon be carried out to help optimize process conditions.

6. SUSTAINABILITY and the BIG PICTURE

The enormous challenges of using pure hydrogen as a transportation fuel have become abundantly clear over the past five years, and nowhere are these challenges better analyzed and evaluated than in a recent paper by Pearson et al [36]. Moreover, advanced internal combustion engines may achieve well-to-wheel efficiencies equal to or better than that of fuel cells [37]. Thus carbon-neutral liquid fuels should have a major role in future transportation.

The CO₂ for *WindFuels* would come initially from current commercial sources, including mostly ammonia production. The current cost of CO₂, delivered by pipeline at about 150 bar, 97% purity, is about \$65/ton. An extensive CO₂ pipeline network is beginning to be developed for enhanced oil recovery (EOR). A study by the DOE estimates there will be a demand for over 12 B tons of CO₂ for EOR over the next 20 years – twice the demand from the current CO₂ market, which is dominated by the beverage industry.

Of course, coal power plants are the current largest CO₂ emitters and will remain so for several decades, but their CO₂ will not be required to meet the demands from EOR and *WindFuels*. Other enormous point sources of CO₂ that are more economical than coal power plants include bio-ethanol refineries (both corn-based and cellulosic), low-grade natural gas sources, cement factories, and ore refining. These sources will be growing throughout this century and will be more than sufficient for EOR and *WindFuels* for at least the next two decades.

Eventually, “air capture” of CO₂ may become practical [34], though our estimates indicate the cost of CO₂ from the atmosphere is not likely to drop below \$400/ton for at least another decade. The CO₂ concentration in the exhaust from point sources is two to three orders of magnitude greater (depending on the type) than in the atmosphere. The theoretical limits on energy for gas separations scale only logarithmically with partial pressure in the source stream [38], which would imply CO₂ separation from air might be only 7 times more expensive than from point sources. However, a large portion of the cost of separations always scales inversely with the concentration of the component of interest in the input stream, and this implies an enormous cost disadvantage for CO₂ from air relative to point sources.

The biggest initial climate benefit of *WindFuels* comes from using carbon-neutral fuels in place of high-carbon fossil fuels, such as tar sands, coal-to-liquids, shale oil, and deep-water oil. One way to think about the climate benefit of *WindFuels* is that since almost all of the carbon in the RFTS fuels is captured from point sources, there is very little *new* carbon that is added to the atmosphere for each gallon burned (essentially only the reduced efficiency caused by the carbon capture). Thus, about 1700 gallons of wind-ethanol may need

to be burned to add one ton of additional carbon to the atmosphere. Conversely, because of the carbon-intensive upstream processing of tar sands, about one ton of fossil CO₂ is added to the atmosphere for each 80 gallons of fuels from tar sands that are burned. So, assuming the expensive tar-sands fuels will be most quickly displaced by market competition of RFTS fuels, every 100-120 gallons of *WindFuels* produced and consumed would reduce net atmospheric CO₂ by one ton.

The oil industry globally requires at least 3 million bbl/day annually of new production just to keep up with the decline from depletion of mature wells. Meeting this global need completely with *WindFuels* would require building about 1000 250-MW plants each year. Of course, it will take at least two decades to build a nascent industry to such a massive scale, but it is doable – because *WindFuels* will be more competitive than biofuels within a decade. There is enough available CO₂, water, and wind to maintain this build rate throughout this century – though at the rate of 1000 plants per year it would take only 30 years to replace all petroleum usage with *WindFuels*. Moreover, over 99.9% of the gross area required for wind energy (~0.1 km²/MW) is available for dual use (1), which could include grazing, farming, natural habitat, fishing, and solar energy use. Clearly, there is no fear of growth constraints from resource limitations.

Solar PV has seldom been available in substantial amounts at times when grid power is less than \$160/MWhr – an order of magnitude beyond what is currently desired for RFTS. Barring major breakthroughs in photocatalytic conversion [17], which currently seem remote, solar energy seems unlikely to be a competitive contributor to fuels synthesis. The solar energy will almost always be worth more as a source of heat or peaking electricity than for RFTS.

Seasonal storage of renewable energy – from spring to summer, and from fall to winter – is desired from both security and economic perspectives [39]. Energy storage on such a scale is feasible only in the form of chemical bonds in stable liquids. The cost of the tanks for storing three months supply of U.S. transportation fuel usage in jet fuel, ethanol, and diesel would be under \$50B. (The cost is somewhat higher for gasoline, because of the increased risk.) The cost of storing that much energy in batteries, pumped-hydro, or CAES would be several thousand times greater.

7. CONCLUSIONS

Converting CO₂ into fuels will dramatically reduce global CO₂ emissions and hence the need for CO₂ sequestration. Fuel synthesis from captured CO₂ and electrolytic hydrogen from off-peak wind energy could provide the carbon-neutral liquid fuels needed in the transportation sector along with providing the rapid-response energy storage needed to stabilize the grid. The development, deployment, and rapid scale-up of CO₂-recycle fuels synthesis could finally eliminate our reliance on conventional oil and stabilize fuel supply and hence fuel prices – as these “wells” will never go dry once they are built.

ACKNOWLEDGEMENTS

We greatly appreciate the valuable inputs and comments provided by S.R.G. Taylor. Our work and its presentation have immensely benefited from his contributions.

REFERENCES

- [1] Mark Z Jacobson, "Review of Solutions to Global Warming, Air Pollution, and Energy Security", *Energy Environ. Sci.*, 2009, 2, 148-173, <http://www.rsc.org/delivery/ArticleLinking/DisplayArticleForFree.cfm?doi=b809990c&JournalCode=EE>.
- [2] T Searchinger et al, "Use of U.S. Croplands for Biofuels...", *Sci.* 319, 1238-1240, Feb 29, 2008.
- [3] JF Kreider and PS Curtiss, "Comprehensive Evaluation of Impacts from Potential Future Automotive Fuel Replacements", *Proc. Energy Sustainability 2007*, ES2007-36234.
- [4] The National Academies Summit on "America's Energy Future", National Research Council, www.nap.edu, 2008.
- [5] Doty Energy website, <http://dotyenergy.com/Markets/Biofuels.htm>, 2009.
- [6] SW Running, "Ecosystem Disturbance, Carbon, and Climate", *Science* 321, 652-3, 1 Aug, 2008.
- [7] JF Decarolis, DW Keith, "The economics of large-scale wind power...", *Policy*, pp395-410, 2006. <http://www.ucalgary.ca/~keith/Other%20Energy.html>.
- [8] Uclia Wang, "Texas Wind Farms Paying People to Take Power", *Greentechmedia*, Dec 10, 2008.
- [9] K Chandler and L Eudy, "Fuel Cell Transit Buses: Evaluation Results", NREL/TP-560-40615, <http://www.nrel.gov/hydrogen/pdfs/40615.pdf>, 2006.
- [10] C Delacourt, PL Ridgway, JB Kerr, and J Newman, "Design of an Electrochemical Cell Making Syngas (CO+H₂) from CO₂ and H₂O Reduction at Room Temperature", *J Electrochem. Soc.*, Vol 155, Issue 1, pp B42-B49, 2008.
- [11] G Olah and A Molar, *Hydrocarbon Chemistry*, 2nd ed., Wiley, 2003.
- [12] FD Doty, "Hydrocarbon and Alcohol Fuels from Variable, Renewable Energy...", PCT WO 2008/115933, <http://windfuels.com/PDFs/WO2008115933.pdf>.
- [13] Dan Rastler, "New Demand for Energy Storage", *Electric Perspectives*, Sept 2008, 30-47, <http://disgentest.epri.com/downloads/2008-09-01-EPEnergyStorage.pdf>.
- [14] A 600,000 gallon tank was quoted by Brown Minneapolis Tank Company as costing about \$420K, or under \$0.02/kWhr for jet fuel.
- [15] J Ivy, "Summary of Electrolytic Hydrogen Production", NREL/MP-560-36734, 2004.
- [16] SPS Badwal, S Giddey, and ET Ciacchi, "Hydrogen and oxygen generation with polymer electrolyte membrane (PEM)-based electrolytic technology", *Ionics* 12:7-14, 2006.
- [17] MW Kanan and DG Nocera, "In Situ Formation of an Oxygen-Evolving Catalyst in Neutral Water Containing Phosphate and Co²⁺", *Science*, 321, 1072-1075, 14 Sept., 2008.
- [18] FD Doty, "High-Temperature Dual-source Organic Rankine Cycle with Gas Separations", PCT to be published in early 2009.
- [19] AP Steynberg and ME Dry, eds. *Studies in Surface Science and Catalysis 152, Fischer-Tropsch Technology*, Elsevier, 2004.
- [20] PL Spath and DC Dayton, NREL/TP-510-34929, 2003.
- [21] H Wang, M Kim, K Wadumesthrige et al, "Synthesis of Higher Hydrocarbons from CO₂ Hydrogenation" presented at AIChE annual meeting, Philadelphia, 2008.
- [22] PSS Prasad, JW Bae, KW Jun, KW Lee, "Fischer-Tropsch Synthesis by Carbon Dioxide Hydrogenation on Fe-based Catalysts", *Catal Surv Asia*, 12:170-183, 2008.
- [23] FD Doty et al, "WindFuels – Competitive Fuels from Wind Energy and Waste CO₂", presented at AIChE annual meeting, Philadelphia, 2008 http://windfuels.com/PDFs/WindFuels_Sci_Engr_Basics_doc_1.pdf.
- [24] S Phillips, A Aden, J Jechura, and D Dayton, "Thermochemical Ethanol via Indirect Gasification and Mixed Alcohol Synthesis of Lignocellulosic Biomass", NREL/TP-510-41168, 2007.
- [25] M Xiang, D Li, H Qi, W Li, B Zhong, Y Sun, "Mixed alcohols synthesis from CO hydrogenation over K-promoted β -Mo₂C catalysts", *Fuel* 86, 1298-1303, 2007.
- [26] X Li, L Feng, Z Liu, B Zhong, DB Dadyburjor, and DL Kugler, "Higher Alcohols from Synthesis Gas Using Carbon-Supported Doped Molybdenum-Based Catalysts", *Ind. Engr. Chem. Res.* 37, 3853-3863, 1998.
- [27] V Subramani and SK Gangwal, "A Review of Recent Literature to Search for an Efficient Catalytic Process for the Conversion of Syngas to Ethanol", *Energy & Fuels* 22, 814-839, 2008.
- [28] FD Doty and S Shevgoor, "Compact, High-Effectiveness, Gas-to-gas Compound Recuperator with Liquid Intermediary (CRLI)", HT2009-88372, ASME Joint Conferences, San Francisco, 2009.
- [29] JE Whitlow and C Parrish, "Operation, Modeling and Analysis of the Reverse Water Gas Shift Process", 2001 NASA/ASEE summer program, JFK Space Center.
- [30] SE Park, JS Chang, KW Lee editors, *Carbon Dioxide Utilization for Global Sustainability, Studies in Surface Science and Catalysis 153*"; OS Joo, KD Jung and J Yonsoo, "CAMERE Process for methanol synthesis from CO₂ hydrogenation", pp 67-72, Elsevier, 2004.
- [31] CH Bartholomew and RJ Farrauto, *Industrial Catalytic Processes*, Wiley, 2006.

[32] FD Doty, “Compact, High-Effectiveness, Gas-to-gas Compound Recuperator with Liquid Intermediary”, PCT to be published in early 2009.

[33] FD Doty and S Shevgoor, “A Dual-source Organic Rankine Cycle (DORC) for Improved Efficiency in Conversion of Low- and Mid-grade Heat Sources”, ES2009-90220, ASME Joint Conferences, San Francisco, 2009.

[34] See http://en.wikipedia.org/wiki/Carbon_capture_and_storage .

[35] See http://dotyenergy.com/Investors/Others_Patents.htm , 2009.

[36] RJ Pearson, JW Turner, and AJ Peck, “Gasoline-ethanol-methanol tri-fuel vehicle development and its role in expediting sustainable organic fuels for transport”, to be published, Low Carbon Vehicles Conference, Institution Mechanical Engineers Conference, London UK, May 20-21, 2009.

[37] See a comparative study of high efficiency vehicles by Toyota, http://www.toyota.co.jp/en/tech/environment/ths2/SpecialReports_12.pdf , 2004.

[38] KZ House, CF Harvey, MJ Aziz, and DP Schrag, “The energy penalty of post-combustion CO₂ capture & storage and its implications for retrofitting the US installed base”, Energy & Envir. Sci., 2, 193-205, 2009.

[39] GN Doty, FD Doty, LL Holte, D McCree, S Shevgoor, “Securing Our Energy Future by Efficiently Recycling CO₂ into Transportation Fuels – Driving the Off-peak Wind Market”, Proceed. WindPower 2009, paper 175, Chicago, 2009.