

NEW PARADIGMS FOR STANDARD LIQUID FUELS FROM CO₂, H₂O, CH₄, AND OFF-PEAK ENERGY

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Introduction

There is an urgent need for transportation fuels that are renewable, carbon-neutral, and scalable to fit a rapidly growing global demand. The currently supported alternatives (algal oil, cellulosic ethanol, oil seed crops, high-temperature solar-driven thermochemical processes, batteries, etc.) have major shortcomings that will sharply limit their ability to grow to meet the need [1-7]. The *Windfuels* paradigm we have been developing [8-9], on the other hand, has the potential to supply several times the world's current usage of liquid fuels in a sustainable and competitive manner that is truly carbon neutral – and with an order-of-magnitude lower total carbon footprint than conventional biofuels. At the same time, it fully solves the grid-scale energy-storage challenge.

In the *Windfuels* paradigm, standard transport fuels are efficiently synthesized from just CO₂ and water using off-peak excess clean energy – usually wind, nuclear, or geothermal in the middle of the night, when it is very cheap (often under \$15/MWh) in regions that have seen high wind-energy penetration [10, 11]. Sufficient hydrogen must be stored to accommodate dynamic control issues during ramp-up and ramp-down cycles; but storage requirements are modest, as modern control technology allows the gas-loop processes to be adjusted quickly. The cost associated with storing energy in liquid hydrocarbons (HCs) is quite small.

The *Windfuels* concept, as illustrated in **Figure 1**, begins by electrolyzing water to get the needed renewable H₂. The second step is reducing CO₂ to CO via the Reverse Water Gas Shift (RWGS) reaction to get the CO needed in the subsequent Fischer Tropsch

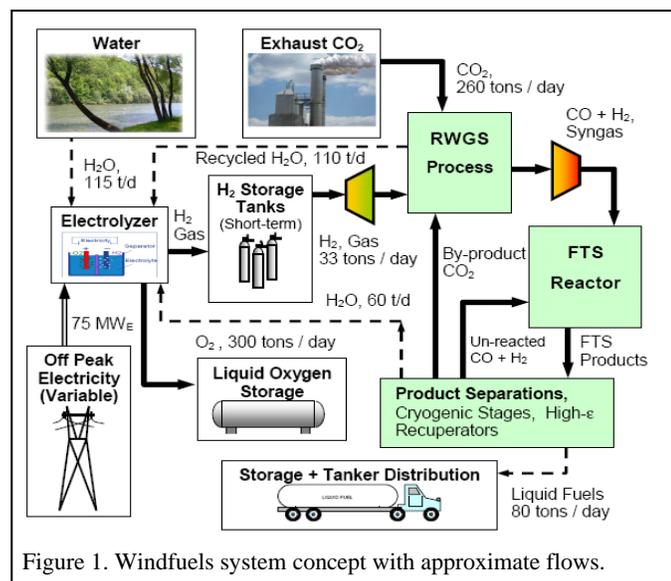


Figure 1. Windfuels system concept with approximate flows.

Synthesis (FTS) process. The third step is synthesizing HCs from the CO and renewable hydrogen in the FT reactor, and the fourth step is upgrading the straight-run FTS products (mostly linear alkanes and alkenes covering the full range, from C3 to C40) to on-spec fuels.

Higher-heating-value (HHV) stack efficiencies in hot-alkaline electrolyzers now reach 84% at full rated power and 94% at low

power [12-15], and the cost of high-performance electrolyzer stacks has dropped by 80% over the past decade [12]. Similar cost reduction from economies of scale appears likely in the coming decade if demand grows by an order of magnitude [12, 14] – and the *Windfuels* paradigm could drive an order of magnitude growth each decade for the next three decades.

Early simulations showed that an efficient multi-stage process could be developed using known catalysts for reduction of CO₂ to CO with total energy losses from this portion of the process of under 5% of the input energy [16, 17]. Advances in recuperator technology appeared necessary to reduce equipment costs [17], so a design toward that end was published [18]. However, recent experimental data from a novel RWGS catalyst in our laboratory, along with more detailed process simulations, show that a single-stage RWGS process should work even better – without requiring major advances in recuperator technology for acceptable equipment costs.

For more than three decades FTS has proven to be the most effective method of synthesizing the full range of HCs [19, 20], which are essential for modern societies. FTS has seen strong commercial growth over the past decade, and O&M costs excluding feedstocks but including cost of capital are only ~\$6/bbl of product in large plants [21]. When methane is the feedstock, the process is denoted Gas to Liquids (GTL), and plant efficiency has exceeded 65% [20]. Of course, plant optimization always involves tradeoffs, and plant efficiency above 75% would be possible if the cost of the feedstocks justified the increased capital costs [22].

In spite of the above reasoning, thus far enthusiasm for *Windfuels* has been limited – essentially for one valid reason: the current cost of electrolyzers. While analysis shows ROI (return on investment) should be attractive for *Windfuels* even at current electrolyzer and fuel prices in some regions, the capital outlay for the electrolyzers would be beyond what investors wish to consider in today's risk-averse world.

As it became clear that it could be some time before investors showed much interest in *Windfuels*, we began investigating avenues for substantial reductions in the carbon footprint of GTL that would be economically more attractive than *Windfuels* with today's electrolyzer prices. The outcome of this research is a process we have dubbed *CARMA-GTL*, for Carbon dioxide Advanced Reforming of Methane Adiabatically, with GTL.

As shown in **Figure 2**, *CARMA-GTL* is quite similar to *Windfuels* except that methane is used for about two-thirds of the input energy and carbon. The balance of the carbon comes from CO₂, and the balance of the energy comes from off-peak wind.

If the methane is of fossil origin, the fuels are about 40% cleaner (in carbon footprint) than conventional GTL fuels. This is better than expected for electric vehicles [2]. If the methane is from biogas or wood gas, the fuels are completely carbon neutral. When the inputs are off-peak wind and shale gas, the cost of the input energy at current typical U.S. prices is ~\$1/gal of fuels produced. The cost of capital and O&M expenses are expected to be similar, assuming 20-year financing. All told, with the combined expenses of the plant the fuels will cost less than \$2.20/gallon under a worst-case scenario.

CARMA-GTL is not the ultimate ultra-clean non-biological fuels solution that is offered by *Windfuels*, as biogas, wood gas, and even shale gas are very limited resources from a big-picture perspective. But *CARMA-GTL* is much more likely to be embraced by investors in the near term, as it requires less than a third the electrolyzer investment of *Windfuels* per gallon of product. *CARMA-GTL* is seen as a bridge technology that will drive the scale-up needed in the electrolyzer and wind industries to improve the competitiveness of *Windfuels*, which can ultimately provide all the ultra-clean hydrocarbons needed in the world of tomorrow. In

either case, a more highly optimized FTS process is justified for conversion of the syngas to ultraclean HCs, and our detailed simulations show that such will be straightforward and inexpensive.

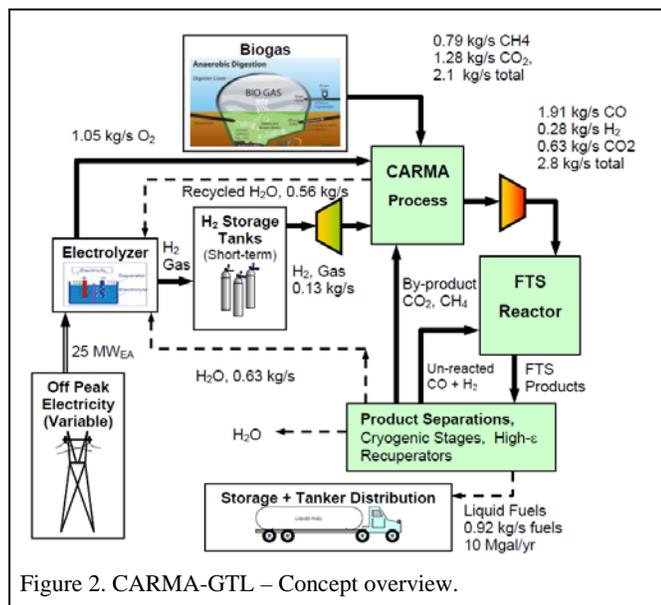


Figure 2. CARMA-GTL – Concept overview.

Highly Endothermic High-temp Processes are Very Expensive

“Dry reforming”, or CO_2 reforming of methane (see eq. 5), has often been proposed as a method of using concentrated solar heat at ~ 1300 K to produce syngas from the highly endothermic reaction of CO_2 with CH_4 [23, 24], but both coking [24] and heat transfer costs [16] have presented major challenges.

The mechanisms for coke formation vary with different catalysts, but dehydrogenation of dienes and polymerization and condensation of polycyclic aromatic hydrocarbons (PAHs) usually play a dominant role [25, 26]. Gibbs energy minimization calculations [27] show that equilibrium concentrations of these precursors can be reduced by several orders of magnitude over the full temperature range (from 400 K to 1500 K) by adding sufficient H_2 and O_2 to the CO_2 and CH_4 primary reactants. However, a highly endothermic high-temperature gas-phase reaction (such as any of eqs. 4-7, or others that have been proposed) still requires a very large superalloy heat exchanger for the reactor.

If sufficient O_2 is added to make the net reaction enthalpy zero (autothermal), the reactor cost is reduced by one to two orders of magnitude, as the reactor becomes simply a stainless steel tank of catalyst rather than a large superalloy shell-and-tube heat exchanger [22, 28]. Moreover, the energy-providing reactants (CH_4 and H_2) required for an autothermal reaction are always less than the total that would be required to produce a similar amount of syngas from a highly endothermic reaction driven by external combustion because of practical losses associated with the latter.

The Beauty of Adiabatic Equilibrium-driven Hot Reactions

It is essential to use pure oxygen in the autothermal syngas reactions because of the high cost associated with separating N_2 from gas mixtures containing substantial fractions of H_2 , CO_2 , CH_4 , CO , and H_2O . (N_2 is detrimental in the FT reactor because it leads to parasitic NH_3 production.) If the needed oxygen is obtained by water electrolysis, twice as many moles of hydrogen are also produced. Both may be fed with the appropriate amount of CO_2 and CH_4 (and perhaps a little H_2O) to yield the desired syngas – usually 2:1 H_2/CO ,

with low CO_2 and CH_4 – from a single adiabatic reactor using a multi-functional catalyst.

Equilibrium yields are easily predictable from Gibbs energy minimization, and such calculations show that an advantageous syngas production process can be developed when hydrogen and oxygen are available in sufficient quantities to add to the feed mix (as they will be with wind-to-hydrogen).

The effective reactions present are listed below with reaction enthalpies ΔH given at 1100 K. Except for C, all species here are gas phase, 1 bar. They are listed below in order of decreasing equilibrium constant, K_p .



Results from a representative calculation using HSC7 [27] are shown in **Figure 3**, with the feeds as given in the figure caption. (Note that feeds are usually not near equilibrium at any temperature.) The equilibria products at 1150 K are 51 H_2 , 25 CO , 17 H_2O , 6.8 CO_2 , and 0.09 CH_4 . Calculated concentrations of direct coke precursors (dienes and aromatics) in the products were below 2E-15 – effectively zero. (Of course, for concentrations this small, the

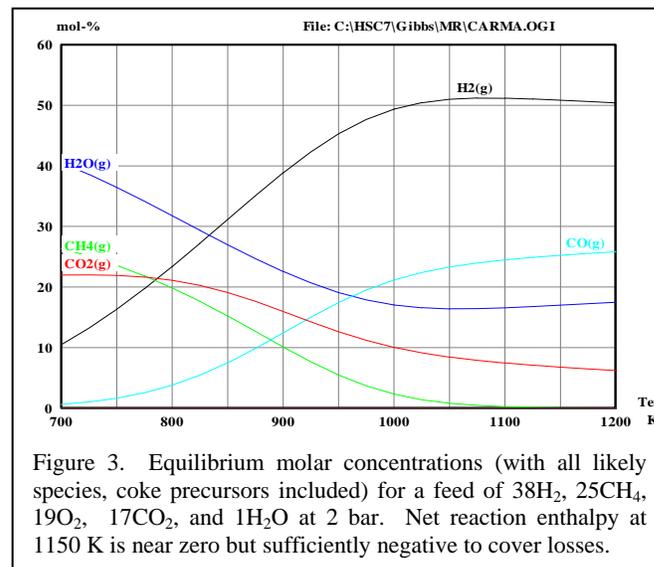


Figure 3. Equilibrium molar concentrations (with all likely species, coke precursors included) for a feed of 38 H_2 , 25 CH_4 , 19 O_2 , 17 CO_2 , and 1 H_2O at 2 bar. Net reaction enthalpy at 1150 K is near zero but sufficiently negative to cover losses.

uncertainty in the thermodynamics data on which these calculations are based could result in substantial errors.) Moreover, K_p for eq. (7) is 130 times that for eq. (9) at 1100 K. (However, the relative significance of the above listed equations is not that implied by their K_p 's.) Stoichiometric balancing suggests equations 2, 3, 5, and 8 are more significant and a substantial fraction of the feed H_2 and CO_2 doesn't participate in reactions before equilibria are well established.

Detailed reaction kinetics studies show the above equations (which relate the stable species) actually summarize ~300 elementary reactions, with gas-phase reaction rates varying over 18 orders of magnitude [29]. (One of the fastest elementary reactions here at 1200 K is $\text{CH}_4 + \text{OH}$, yielding $\text{CH}_3 + \text{H}_2\text{O}$; and one of the slower ones is $\text{CH}_4 + \text{O}_2$, yielding $\text{HO}_2 + \text{CH}_3$ [30].) Combustion research is quite relevant here, though the CARMA process would take place at equivalence ratios (ratio of fuel to oxygen ratio to that ratio for complete combustion) about four times higher than in typical engines, for example [31].

Of course, one obtains identical equilibria results if steam is used to replace an equivalent amount of H_2 and O_2 in the feed – and one then has a mix of steam methane reforming (SMR, eq. 4) and dry reforming (eq. 5). While this, like pure SMR, does not present serious coking challenges, the reactors are extremely expensive. Hence, in practice, partial oxidation (POX, eq. 2) is generally used, with a little SMR to adjust the H_2/CO ratio as needed. The Gibbs calculations show higher coking tendency with POX than with CARMA, though an even greater benefit of the latter is that the fuels from this syngas process have substantially lower carbon intensity.

We have begun experimental evaluation of several novel mixed-oxide multifunctional composite catalysts. One of these catalysts for example, with BET surface area of $17 \text{ m}^2/\text{g}$ and particle size $\sim 1.0 \text{ mm}$, achieved the following RWGS activity at 926 K, 2.0 bar: $<0.1\% \text{ CH}_4$; $>99.8\% \text{ CO}$ selectivity; and $>90\%$ of equilibrium conversion for 2:1 H_2/CO_2 feed at $\text{GHSV}=53,000/\text{hr}$, which is two orders of magnitude above most previously reported RWGS experiments [32]. Other catalysts were evaluated with feed mixtures similar to that used in the calculations for Figure 3 and achieved conversions similar to equilibria expectations over the range of 1050-1200 K. More details on these catalysts and experiments will be reported in due course.

At high temperatures in cases where: (A) the net enthalpy is near zero, (B) the catalysts are inexpensive, and (C) the separations are simple, the pre-exponential (frequency) factors for the rates need not be high for the process to be quite inexpensive. When the goal is to achieve something close to thermodynamic equilibrium, the desired results can in principle (and often in practice at high temperatures) be achieved without a catalyst, or with any of a number of low-cost catalysts. Carbon deposition – leading to catalyst deactivation – has often been dominated by the Boudouard reaction (eq. 9). However, the K_p of the Boudouard reaction drops by seven orders of magnitude in going from 600 to 1100 K. Hence, it is not expected to be a problem in the CARMA process, and preliminary experiments confirm that expectation.

The equilibria calculations shown for the feed ratios presented in Figure 3 represent only the particular case where the feed H_2/O_2 ratio is 2.0 while the essential requirements are met: (1) the undesired products (CH_4 and CO_2) at equilibrium are acceptably low at a practical reactor temperature and pressure, (2) the reactor can be operated adiabatically, (3) the equilibria for coke precursors are extremely low, and (4) the H_2/CO ratio in the products is ~ 2 . Gibbs calculations show these four important requirements can be met for H_2/CH_4 supply ratios over the range of at least 0.9 to 5 with appropriate adjustments in the reactor operating conditions and in the other feed components (CO_2 , O_2 , and H_2O). For H_2/CH_4 supply molar ratios below 1.5, an additional source of pure O_2 is required, while the electrolysis process produces excess O_2 for higher H_2/CH_4 supply ratios. Thus, the process is extremely flexible in response to changing economics of renewable H_2 relative to CH_4 . It also works equally well with high levels of other light HCs in the feed gas.

Scaling Down GTL

GTL plants have recently been built at the scale of 30,000 to 150,000 bbl/d (4000-18,000 metric tons per day) [20]. This may be a hundred times larger than is likely to be considered for a CARMA-GTL plant in the foreseeable future for several reasons: (1) limited number of access points to off-peak clean power in excess of 75 MW, (2) the difficulty in financing projects larger than \$100M in today's world, and (3) the limited economic advantage of large plants compared to well optimized CARMA-GTL plants in the 10-30 Mgal/yr range.

So why have recent GTL plants been so much larger? A larger plant does permit significant economies when the goal is to make hundreds of different chemicals, fuel blending stocks, lubricants, and on-spec fuels.

The products that come directly from the FT reactor are mostly n-alkanes and 1-alkenes. Fractionation alone does not lead to on-spec fuels – the gasoline would have very low octane, and the diesel and jet fuel would freeze in cold weather. A substantial fraction of branched HCs is required to meet motor-grade fuel requirements [33, 34]. These may be obtained by alkylating the light olefins with the linear alkanes or by isomerization reactions [22, 26, 33-35]. The challenge here is that achieving high conversions of many of the HCs requires catalysts optimized for a specific (or very narrow range of) input species [33-35]. Hence, scores of distillation columns and associated equipment might be needed to utilize the full range of FTS HCs in motor-grade fuels without blending limits.

A complete set of simulation flowsheets for a multi-billion-dollar GTL plant will contain thousands of pieces of equipment – scores of columns (towers) of all types (distillation, absorption, stripping), scores of flash drums and tanks, hundreds of heat exchangers of all types, hundreds of mass flow controllers and valves, and dozens of compressors, expanders, pumps, mixers, and reactors. The small plant can be dramatically simplified by limiting the number of finished products produced. It would be sufficient for the small sustainable synfuels plant to produce only a few fuel blending stocks (for local blending at up to 20% in gasoline, jet fuel, and diesel) and half a dozen straight-run products (LPG, naphtha, oxygenates, light oil, heavy oil, and wax) that can easily be transported to regional refineries that will pay a premium price for these high-purity low-carbon feedstocks.

After reducing the number of pieces of equipment on the system flowsheets by an order of magnitude (and that may be a realistic limit), most of the flowsheet components can be scaled down by up to three orders of magnitude with a surprisingly small increase in their cost per product rate.

Much of the needed equipment for very small scale is available commercially, and the simulation tools are generally good for flows from under 0.01 g/s to hundreds of kg/s. Two important exceptions are the phase separators and the columns – fractionators, absorbers, and strippers. The reason is that trayed columns are seldom practical at flow rates below $\sim 0.03\text{-}1 \text{ kg/s}$ (depending mostly on the pressure), and most commercial columns in the petrochemical industry operate at flow rates in the range of 0.2-200 kg/s using trayed columns [28].

Packed columns can be used at flow rates under 0.2 mg/s, and they can be very efficient at flow rates from 20 mg/s to 2 kg/s. However, good methods for analyzing packed columns were not well developed until the mid-1990s [36, 37], and there has been limited motivation to improve the versatility, accuracy, and robustness of the packed-column models in the process software we have evaluated [27, 38]. Most of the data for packed columns (using Raschig rings, Pall rings, or similar) in the classic compilation by Billet and Schultes [36] are for column diameters of 0.5-1 m and packing ring diameters of 20-70 mm, with extrapolations to smaller sizes. Better data are

needed for packed columns with diameters and packings an order of magnitude smaller. We are beginning some appropriate experiments that will be the subject of future reports.

The potential savings are easy to appreciate. The cost of the smallest stainless steel trayed distillation column normally seen in a commercial-scale petrochemical plant (1-m diameter, 20 trays, 10-m height) is ~\$300K [28], and such a column could be suitable for a feed flow rate of ~1 kg/s of mid-weight HCs. Unfortunately, the total production in the C8-C10 range from a 10 Mgal/yr plant would be less than half that, and divided amongst at least six primary species.

Clearly, most of the separations in the 1-30 Mgal/yr CARMA-GTL plant would be better handled by packed columns with diameters in the range of 0.03 to 0.7 m and heights of 1.2 to 5 m – corresponding to 8-25 theoretical plates using 6-mm to 8-mm Raschig rings. The cost (in small quantity production) would range from \$2-40K per stainless-steel column [28]. For either trayed or packed columns, the pumps, reboiler, condenser, sensors, controls, and connections must be added. After their development – which may be the largest single R&D cost area – their cost would likely range from \$8-120K per separation.

A large portion of the cost of pilot plants arises from the fact that broad-use adiabatic phase separators (flash drums) and columns (towers) with robust controls are simply not available as off-the-shelf items. They are always custom designed for specified conditions. However, it is straightforward to show (using standard process simulation software) that with the right controls a given column could achieve the desired split at near optimum efficiency for flow rates varying over an order of magnitude in range. Adiabatic phase separators could operate over a range of many orders of magnitude (actually, from zero to an upper design limit).

The key to versatility is having the needed flow, temperature, pressure, and liquid-level sensors, with suitable pumps, regulators, and controllers. We are beginning development of small packed columns that will be compatible with operation as an absorber, stripper, or fractionator over a wide range of temperatures, pressures, and flow rates. We see this as essential for low-cost development of process plants of all sizes – for Windfuels, CARMA-GTL, and for most other advanced fuels, including direct solar fuels.

Process Optimization for Future Energy Value

Most current petrochemical plants were designed at a time when oil had been in the range of \$2.5-\$3.5/bbl for most of the preceding three decades, and many design traditions established during those days have had remarkable staying power. Yet, some recent analyses expect oil will reach 100 times those prices by 2015 [39].

As noted in the introduction, current GTL plants typically achieve about 65% energy efficiency in conversion of methane to jet fuel and diesel. More than a third of these losses are associated with getting the needed ultra-clean syngas from natural gas. Detailed simulations indicate that the CARMA-GTL process should make it straightforward to reduce losses in getting the syngas by a factor of three – partially because the hydrogen addition reduces the thermodynamic coking affinity (i.e., equilibria concentrations of dienes and aromatics, or Gibbs energy driving force) by three orders of magnitude compared to POX.

All prior published and patented FTS processes – other than our developments – share a remarkably inefficient process for handling primary gas-loop separations [17]. Carbon conversion per pass in commercial FT reactors is generally in the range of 40-55%, as attempting to achieve higher per-pass conversion leads to poor control over selectivity and lower mean catalyst productivity. Hence, it is essential to recycle the un-reacted reactants – H₂ and CO – and deal with a very wide range of separations, some of which are not

straightforward. In addition to the feed gases, the products from the FT reactor also include substantial amounts of CO₂, H₂O, CH₄, and most linear alkenes and alkanes from C₂ to at least C₄₀ along with some oxygenates and – for high-temperature FT – aromatics. Lab-scale demonstrations never consider doing these separations efficiently (because it's not easy), and the same has been true of pilot plants – because the simulations are complex and the design and custom fabrications are expensive. And then the pilot plant usually dictates the design of the commercial plant. For example, prior separations of CO₂ from recycle syngas have required about 140 kJ/mol [20, 40, 41]. Yet, the theoretical limit here can be shown to be less than 10 kJ/mol. Our recent detailed simulations show that there would actually be no capital-cost penalty at commercial scale associated with reducing these losses by at least a factor of four compared to standard approaches, though that is not true at pilot scale and certainly not true at lab scale. There are many additional opportunities for substantial improvements in process efficiency, especially via thorough heat integration and improved efficiency in conversion of the heat rejected by the highly exothermic FT reactor [9, 16-18, 22, 42]. Detailed flowsheet simulations provide extremely accurate predictions of system performance and equipment requirements in processes such as these (no solid phase) [22], but pilot-plant demonstrations are still essential for improved cost estimates of commercial-scale plants [28].

Discussion

It is very important to look at big-picture economic issues when possible new paradigms are being considered. The major economic issues were briefly mentioned earlier, but it is worth summarizing them here and mentioning some additional issues that have often been relevant for sustainable fuels.

Input Energy Cost. Off-peak clean energy prices have dropped dramatically in areas of high wind-energy penetration over the past three years, even in the face of increasing wind curtailment and transmission grid expansion [1, 11, 43]. This glut in curtailed and ultra-cheap excess clean energy will continue to increase, as it is driven by legislated Renewable Electricity Standards (RES's, previously called RPS's) [44]. If the cost of the input energy is \$20/MWh and the Windfuels plant efficiency is 55% (as predicted by detailed simulations), the cost of the input energy in synthesized diesel (37.7 kWh/gal) would be ~\$1.40/gal if no value is attributed to oxygen production, and only \$0.90/gal when the oxygen co-product (at \$44/t) is properly included.

Most integration technologies (grid-scale battery storage, hydro-storage, CAES, etc...) assume *zero-cost* energy input, and yet are still embraced by the power industries and the DOE due to the critical need for grid stabilization. Hence, there should be no difficulty initially getting some energy contracts for \$10/MWh or even less.

For the CARMA-GTL process, up to about two-thirds of the input energy comes from methane, which recently has been ~\$4/GJ (\$14.4/MWh) in many areas in the U.S. for industrial customers. Recent forecasts see these prices increasing at ~11%/yr for the next decade, to ~\$10/GJ by 2020. Well before then, Windfuels would often be more attractive than CARMA-GTL; but with liquid transport fuels then likely over \$50/GJ (~\$7/gal) [39], either source of input energy would be extremely competitive.

The CO₂. Biogas, wood gas, and often raw shale gas contain some percentage of CO₂ needed for the CARMA-GTL process. Rather than expending energy to separate that CO₂, both the methane and CO₂ can be effectively utilized in a CARMA-GTL reactor, allowing significant reductions in total efficiency losses for GTL. Of course the Windfuels process requires CO₂; and some sources of natural gas may have insufficient concentrations of CO₂ for

CARMA-GTL, requiring that additional CO₂ be purchased. There is sufficient point-source CO₂ potential in the U.S. (over 4 gigatons per year, Gt/yr) and sufficient wind energy potential (~60 PWh/yr) to synthesize over twice the current U.S. liquid fuel usage (~0.7 Gt/yr) via the Windfuels process *and* supply twice its other energy needs (~20 TWh/yr).

A CO₂ pipeline network is rapidly expanding for enhanced oil recovery (EOR), and it is expected to grow by an order of magnitude over the next decade. (The CO₂ flow rate in an EOR pipe 1 m in diameter could be sufficient to feed more than 1000 Windfuels plants each producing 10 Mgal/yr.) The price of EOR-grade CO₂ (97%, 80-150 bar) is currently ~\$30/ton. It will need some further cleaning, but that is cheap – about \$15/ton to go from EOR grade to beverage grade, and another \$5/ton to go to FT-reactor grade. The CO₂ may initially contribute about \$0.50/gal to the cost of Windfuels though that cost will drop as CO₂ emissions regulations become stringent. In our analysis we do not include the energy required for separating the CO₂ from power plant exhausts and then piping it because we assume the CO₂ is being purchased from an available supply that is steadily increasing due to mandates.

Equipment Costs. As the required chemical processes do not involve any solid-phase processes, they are all amenable to accurate simulations by mature, well validated, commercial software. All but two of the processes (electrolysis and CARMA or RWGS) have been implemented at the scale appropriate for plants producing fuels at rates over 100 times what has been demonstrated for cellulosic ethanol, over 10,000 times what has been demonstrated for algal oil and direct solar fuels, and over a million times that likely from microbial fuel cells in the foreseeable future. The equipment costs are easily predictable from industrial trends that have been followed for decades and have been quite predictable for the past three years. The amortized cost of the FT reactors and catalysts, for example, should contribute about \$0.10/gal of product. This is undoubtedly surprising to many accustomed to thinking of costs of biological reactors, but non-biological processes can operate at intensities of 1-6 MW/m³, 1000-5000 times that of typical fermenters and microbial fuel cells respectively. Fixed-bed FT reactors are readily scalable, as 2-D FT reactor models developed at large laboratory scale are essentially sufficient for commercial scale design [20].

Water. Water usage for Windfuels (~1.2 gal-H₂O per gallon of fuel produced) is two to four orders of magnitude below that for biofuels. The cost of the water needed for Windfuels will be under 0.4% of total operating costs. (A windfuels plant producing 10 Mgal/yr would use about as much water as a small rural town with a few hundred residents.) Since thermal power sources (such as coal) require ~500 gallons of water per MWh, every 1 MWh of additional wind energy that is brought onto the grid will reduce total water consumption of the region by 500 gallons. As Windfuels will allow unhindered growth of wind energy, it would allow considerable savings in water usage even beyond that associated with reduced irrigation for energy crops.

Scalability. There is sufficient global wind-energy resource (700-1200 PWh/yr) to provide over five times the world's total energy needs (~150 PWh/yr, 150 petawatt-hours/year) [45]. Nuclear energy will grow more quickly in some countries and may have similar long-range potential. Both are clean from a climate perspective. Of course, solar energy can also be used when it becomes competitive with off-peak wind or nuclear.

Grid Stability and Climate Benefit. An objection sometimes raised is that, like electric cars, coal energy from the grid would be used. But this objection fails to consider two important distinctions: (1) WindFuels production can be sited in areas of high wind penetration, rather than being restricted to the region where the

consumer lives; and (2) electrolyzers allow millisecond response to changes in grid supply and demand to easily and efficiently utilize only the low-cost energy when the local grid is mostly from renewable sources.

The big limitations of electrolysis have been the cost of storage and distribution of hydrogen and a lack of hydrogen demand. WindFuels solves these problems, as hydrogen would only need to be stored locally in sufficient quantities to meet dynamic and controls requirements within the synfuels plants. Modern control technology allows all of the gas-loop processes to be adjusted surprisingly quickly, as significant temperature changes are not needed to go from 3% to 100% (or the reverse) of maximum syngas and/or FT production rates. Fast response in most of the controls is required anyway, as without it the temperature of the fixed-bed FT reactor could climb 100 K in two minutes under some failure modes, leading to down time for replacement of the catalyst.

A Renewable Fischer Tropsch Synthesis (RF_{TS}) process has the potential to permit unconditional stability of the grid, even if over 50% of its energy comes from wind. The tank-component cost of energy storage in stable liquid fuels is only \$0.02/kWh, which is orders of magnitude less than for compressed air, batteries, flywheels, or ultra-capacitors [11].

By generating strong demand for clean energy whenever it can be produced, CARMA-GTL and Windfuels would stimulate strong growth in the wind, electrolyzer, and process equipment industries. The growth in the wind industry sans its storied grid-stability challenges will effectively end the building of new coal power plants in regions with strong wind resources and will accelerate the decommissioning of older coal plants. To put this into perspective, consider that every MW of electrolyzers operating at 40% capacity factor (cf) would enable ~3 MW of additional wind energy (33% cf) to be integrated into a currently saturated grid – with current average grid capabilities. This means that for every 1 MWh that gets consumed by the electrolyzers, as much as 1.5 MWh of additional carbon-neutral energy could be integrated into a grid, allowing 1.5 MWh of fossil energy to be removed from the grid. This means that the production of 1 gallon of diesel from WindFuels would indirectly result in a reduction of grid-based CO₂ emissions by 30-90 kg (and as pointed out before, ~32 gallons of water consumption would likewise be reduced), and 1 gallon of diesel produced from a CARMA-GTL process would indirectly reduce grid emissions by 10-30 kg-CO₂ (and ~13 gallons of water). Obviously, it would be the increased penetration of wind energy that would get credited for these emissions reductions, but that cannot happen without a viable integration platform, which both WindFuels and CARMA-GTL provide.

But on the direct side, if it is assumed that future tar-sands fuels are offset by the production of fuel from a WindFuels or CARMA-GTL process; then every gallon of diesel from CARMA-GTL using biogas, woodgas, or landfill methane would directly offset 15 kg-CO₂, every gallon of diesel produced from WindFuels would directly offset 13.6 kg-CO₂, and every gallon of diesel produced from CARMA-GTL using shale gas would directly offset 6.2 kg-CO₂.

Because CARMA-GTL can almost immediately be competitive with tar sands and deep-water oil, it can be market driven. Hence, these processes have the potential to cut use of coal and oil in half in many countries – including the U.S., Canada, and China – over the next three to four decades. No other known competitive fuel alternative appears to have similar potential for reduction of greenhouse gases (GHGs) over the next few decades.

Domestic Economic Benefits. The competitiveness of the proposed processes and the absence of any resource constraints means that the U.S. could end oil imports within three decades and at

the same time begin building a clean-fuels export industry of even greater magnitude, which will have enormous security and economic benefits.

The U.S. is in a unique position of being able to competitively turn CO₂ into fuels at the scale needed to affect the global fuels markets. No other country is similarly blessed with excess clean-energy resources, point-sources of CO₂, and the requisite industrial infrastructure. The net positive effect on foreign-trade balance of a market-driven industry of this magnitude could exceed one trillion dollars annually by 2040. Such a positive effect on trade balance would lead to the net creation of 10,000,000 jobs.

The U.S. eventually will not compete successfully with Asia in solar panels, batteries, or EVs, but the United States can supply most of the world with carbon-neutral liquid fuels forever.

Conclusions

We reported results from Gibbs energy minimization calculations for a novel non-biological process we have called CARMA that shows strong promise for efficient syngas production with exceptionally low coking tendency in low-cost adiabatic reactors using a combination of biogas or shale gas and electrolysis hydrogen from off-peak clean energy. We reported preliminary experimental data on a novel catalyst with exceptional RWGS activity, selectivity, and lifetime. We summarized results from complete system simulations of two CO₂-to-fuels processes that show substantially more promise than other putative sustainable alternatives with respect to competitiveness, scalability, total GHG reductions, and U.S. domestic energy security and economic issues.

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