

## SUSTAINABLE TRANSPORTATION FUELS FROM OFF-PEAK WIND ENERGY, CO<sub>2</sub>, AND WATER

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### ABSTRACT.

Doty Energy is developing advanced processes to permit the production of fully carbon-neutral gasoline, jet fuel, diesel, ethanol, and plastics from exhaust CO<sub>2</sub> and off-peak clean energy (wind and nuclear) at prices that can compete with fossil-derived products. Converting CO<sub>2</sub> into fuels will eliminate the need for CO<sub>2</sub> sequestration, reduce global CO<sub>2</sub> emissions by 40%, and provide a nearly insatiable market for off-peak wind.

It has long been known that it is theoretically possible to convert CO<sub>2</sub> and water into standard liquid hydrocarbon fuels at high efficiency. However, the early proposals for doing this conversion had efficiencies of only 25% to 35%. That is, the chemical energy in the liquid fuels produced (gasoline, ethanol, etc.) would be about the 30% of the input energy required. The combination of the eight major technical advances made over the past two years should permit this conversion to be done at up to 60% efficiency.

Off-peak grid energy averaged only \$16.4/MWhr in the Minnesota hub throughout all of 2009 (the cheapest 6 hours/day averaged only \$7.1/MWh). At such prices, the synthesized standard liquid fuels (dubbed "WindFuels") should compete even when petroleum is only \$45/bbl.

A more scalable alternative for transportation fuels is needed than biofuels. It is in our economic and security interests to produce transportation fuels domestically at the scale of hundreds of billions of gallons per year. WindFuels can scale to this level, and as they are fully carbon-neutral they will dramatically reduce global CO<sub>2</sub> emissions at the same time. Switching 70% of global transportation fuels from petroleum to WindFuels should be possible over the next 30 years. WindFuels will insure extremely strong growth in wind energy for many decades by generating an enormous market for off-peak wind energy.

WindFuels is based largely on the commercially proven technologies of wind energy, water electrolysis, and Fischer Tropsch (FT) chemistry. Off-peak low carbon energy is used to split water into hydrogen and oxygen. Some of the hydrogen is used to reduce CO<sub>2</sub> into carbon monoxide (CO) and water via the Reverse Water Gas Shift (RWGS) reaction. The CO and the balance of the hydrogen are fed into an FT reactor similar to those used to produce fuels and chemicals from coal or natural gas. The processes have been simulated, and key experiments are being carried out to help optimize process conditions and validate the simulations.

### 1. INTRODUCTION.

The planet urgently needs a transportation fuel that is sustainable, carbon-neutral, scalable to fit demand, and has little-to-no side effects on the environment or civilization. Fossil fuels fail both for their carbon intensity and in the limit of their supply and their eventual depletion. Renewable resources must be utilized to generate an alternative to fossil fuels. For the United States, wind energy is the most competitive renewable resource. Our proposed solution for transportation fuels – WindFuels – would use wind energy to recycle CO<sub>2</sub> into fuels. This would promote strong economic growth and stability, energy independence, and national security.

The WindFuels system uses a series of three sequential chemical reactions using off-peak low-carbon energy (mostly wind or nuclear) to convert CO<sub>2</sub> and H<sub>2</sub>O into stable liquid fuels – including gasoline, jet fuel, and diesel. Excess off-peak energy in high wind regions can be 95% carbon neutral energy. Simulations show it is possible to reduce CO<sub>2</sub> to CO at over 70% of theoretical efficiency limits (under 2 MJ/kg-CO). When combined with our other process advances and current catalysts, it will then be possible to synthesize liquid hydrocarbons and alcohols from off-peak wind energy and point-source CO<sub>2</sub> at system efficiencies in the range of 52-59%. There are sufficient amounts of domestic wind resources and point-source CO<sub>2</sub> to produce over twice our domestic current transportation fuel usage [1].

The limitations of biofuels are recently becoming more recognized: (1) Most biofuels are only 4% to 18% carbon-neutral when land-use change is considered [2-11]; and (2) Agrofuels compete with food for feedstock [8, 9, 12]; and (3) Contribute to all of the widely discussed issues associated with industrial agriculture [7, 9]. Water requirements for corn ethanol (mostly for irrigation) exceed water needs for oil extraction and refining by a factor of 25,000 [13]. A major issue facing cellulosic ethanol is most of the carbon content from the feedstock is released from the processing plant as CO<sub>2</sub> [14, 15]. Algal oils remain prohibitively expensive. After 3 decades of well funded development, the cheapest algal-derived fuel available today costs \$425/gal [16].

The advantage of an optimized chemical process rather than a biochemical process for fuels synthesis is most vividly brought into focus by a very simply rate calculation. Activation energies ( $E_A$ ) even with the best catalysts for desired new reactions are unlikely to be less than 100 kJ/mol. If  $E_A=110$  kJ/mol, the reaction rate would normally increase by a factor of *one billion* in going from 300 K to 590 K (Arrhenius equation). Therefore, some biological conversion processes that take many square miles can be put into a single building as a chemical process.

Like biofuels, WindFuels uses carbon-neutral energy to recycle CO<sub>2</sub> into liquid fuels. However, unlike biofuels, WindFuels: (1) has no competition for feedstocks; (2) requires very little land or water; (3) has no externalities to consider (such as deforestation, competition with food, fertilizer run-off, etc) and (4) will be competitive in the global market.

The system uses variable off-peak grid energy to electrolyze H<sub>2</sub>O into H<sub>2</sub> and O<sub>2</sub>. The oxygen is liquefied and sold. CO<sub>2</sub> is reacted with some of the H<sub>2</sub> in an RWGS reactor to form CO and H<sub>2</sub>O. The water is recycled back through the electrolyzer. The CO and the balance of the H<sub>2</sub> are then combined in an FT reactor to form liquid fuels. This system should be extremely cost effective, in part due to the fact that it solves the off-peak energy challenge facing wind power – which merits some explanation.

## 2. OFF-PEAK GRID ENERGY FROM WIND.

Wind energy in good sites is often the least expensive new energy available – cheaper than new nuclear and even conventional coal in some cases. This has caused wind energy to see unprecedented growth rates over the last decade, as more interest in carbon-neutral energy has encouraged a flood of investment into what had seemed to be a perfect green technology. In 2009 there were a total of over 9800 MW of new wind turbines installed in the USA, bringing the total to over 35 GW – more than double the 16.8 GW total that had been installed at the end of 2007 [17]. .

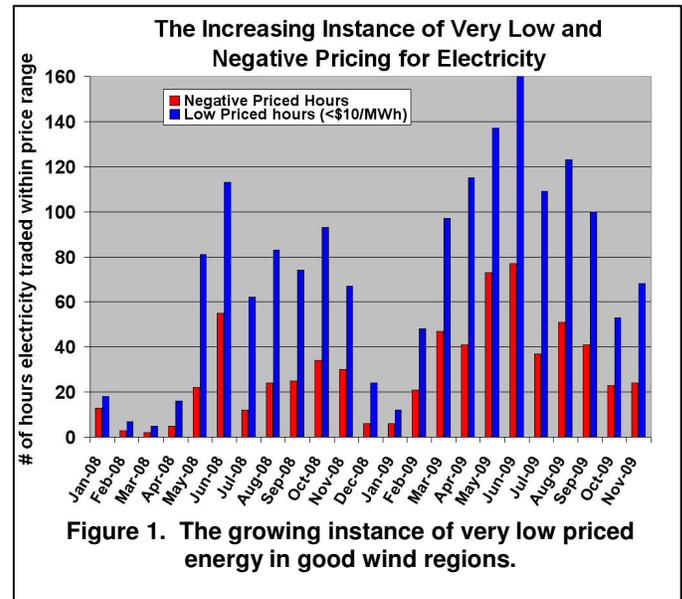
However, low production costs don't always mean high profit, and the rapid growth and continued interest in wind energy may become a liability for today's investors. Profitability and growth in the wind industry are constrained by transmission capacity, the utilization of off-peak excess energy, and size of the market. The winds are not always at their strongest when the demand is highest. In fact the opposite is often true. When the wind produces more energy than there is concurrent demand, the excess electricity must be dumped (sometimes at large expense) to maintain grid stability. Furthermore, usage of wind energy is restricted to local markets, as wind energy cannot be exported to foreign markets – without conversion first to a portable energy carrier such as WindFuels.

As illustrated in **Table 1**, in prime wind zones, the recent price for off-peak wind energy is generally less than half that seen in 2007 and earlier [18]. For example, in the Minnesota hub the average monthly price for off-peak grid energy in February of 2007 was \$62.5/MWhr, while in February of 2009 it was only \$22.10/MWhr. This off-peak energy is extremely clean (almost all nuclear and wind), as the fossil power plants are not eager to burn their fuels to produce electricity that has no value.

	2007	2008	2009
January	46.6	35.4	28.5
February	62.5	39.4	22.1
March	41.6	49.3	14.4
April	43.1	37.2	13.0
May	24.0	20.6	10.3
June	23.6	17.2	9.06
July	27.7	31.3	12.2
August	24.8	26.8	11.1
September	24.8	25.6	16.0
October	28.8	17.9	18.5
November	29.7	23.8	13.9
December	41.1	37.5	22.2

**Figure 1** shows the rapid increase in the availability of negative and very low priced energy in good wind regions [18].

Growth and profitability of wind (and nuclear) energy will be stunted without a means of utilizing the off-peak energy and idle capacity – and a means of collecting wind energy in a form that is easily stored, distributed, and sold on a massive scale [19].



**Figure 1. The growing instance of very low priced energy in good wind regions.**

Electrolyzers could provide a completely flexible demand for such off-peak energy, as they can respond in milliseconds to load variation. There are widely held opinions within the renewables community that electrolyzers are extremely inefficient, but that is not true of large, next-generation electrolyzers. Stack efficiencies at low currents have exceeded 90% in hot alkaline electrolyzers and 94% in PEM electrolyzers [20]. System efficiencies in very large electrolyzers can come within 5% of stack efficiencies. Thus, the excess off-peak grid power can be used at very high efficiency to produce hydrogen.

A revolutionary Renewable Fisher Tropsch Synthesis (RFTS) system could use this hydrogen to efficiently recycle waste CO<sub>2</sub> into standard liquid fuels like gasoline, jet fuel, and ethanol [21]. Of course, the chemical processes should be designed for constant operation (both for cost effectiveness and longevity), but it is not difficult to store enough hydrogen during the cheap hours in the middle of the night to use throughout the day – to allow for constant RFTS operation.

These carbon-neutral synthetic fuels are fully sustainable. There will never be a shortage of CO<sub>2</sub> and H<sub>2</sub>O, and the global wind resource is at least five times the total global energy usage [1]. The RFTS approach presents an elegant, market-driven solution to three major challenges – oil depletion, CO<sub>2</sub> emissions, and grid stability.

The cost of Windfuels will depend mostly on the price of the off-peak energy, the market for the co-products (liquid oxygen and heat) and the credits available for climate benefit. Even before considering the incentives of a future cap-and-trade system for carbon emissions, if the mean input energy price were \$30/MWhr, Windfuels would usually compete when oil is above \$80/bbl. With off-peak energy at \$16/MWhr, Windfuels would often compete when oil is as low as \$50/bbl [22].

The profitability of WindFuels is extremely important for its potential impact. Any proposed off-peak demand solution that is not profitable on its own merit will never be able to scale up at the rate of wind power, resulting in at best a perpetual cycle of market saturation and threat to the wind industry. The fact that WindFuels will seamlessly compete in the global oil market promises decades of growth with little threat of market restrictions to their own growth.

The synergistic fit between the variable production rate of wind power and the variable demand capability of WindFuels would enable each to continue to scale up without restrictions for decades.

### 3. TECHNICAL ADVANCES ENABLING RENEWABLE FISCHER TROPSCH SYNTHESIS.

Simply piecing together current commercial technologies to synthesize gasoline from CO<sub>2</sub> and H<sub>2</sub>O – via electrolysis, RWGS, and RFTS – would achieve under 25% net system efficiency. However, this can be more than doubled by integrating novel technological advances. Recent progress should permit system efficiency to increase to 60%. As reviewed shortly, Doty Energy has shown a solution to dramatically reduce recycling losses (the biggest single efficiency loss in current technology), and has simulated a much more efficient process for reducing CO<sub>2</sub> to CO – using a new recuperator design that will dramatically reduce the associated costs of heat transfer and pressure drops. In addition, we have invented a more efficient thermodynamic cycle for improved conversion of the waste heat.

#### 3.1 Reduction in recycling losses.

In the FT production of products other than heavy oils and waxes, substantial production of H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, and C<sub>3</sub>H<sub>6</sub> is unavoidable, so the undesired output gases along with the un-reacted reactants (H<sub>2</sub> and CO) must be separated and processed or recycled. Achieving higher selectivity of the desired products requires accepting lower conversion per pass, which results in increased demands on separations. The theoretical minimum energy required for the needed separations is under 10 kJ/mol-CO<sub>2</sub>. Prior processes have seen this penalty above 150 kJ/mol [23, 24] – because of the separation complications associated with the combination of H<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, CO<sub>2</sub>, and H<sub>2</sub>O. Our simulations (using commercial process software) show that a novel combination of processes will reduce this penalty to less than 35 kJ/mol [25].

This process uses a novel high-pressure sequence of fractional condensations, eventually cooling the product mixture into the cryogenic range to separate out the CO<sub>2</sub> and very light HCs. The separated water is recycled back into the electrolyzer, the CO<sub>2</sub> is combined with the new CO<sub>2</sub> to be reduced into CO, and the rest of the syngas is recycled back through the FT reactor.

Depending on the FT catalyst selectivity and desired product emphasis, the gain in system efficiency can be 20-30% from this improvement. Traditional FT cannot easily use this much more efficient approach for a combination of reasons [25].

#### 3.2 Efficient reduction of CO<sub>2</sub> to CO.

The second most significant loss using current technology would be in the reduction of the CO<sub>2</sub> to CO. Dozens of solar-driven high-temperature (1200-1800 K) thermochemical routes (often including natural gas and a noble metal or metal-oxide catalyst) have been explored over the past decade [26-28]. Unfortunately, (1) efficiencies have usually been below 2%, (2) operational lifetime has often been only days, (3) conversion rates have been low, and (4) costs have been exorbitant [29]. As both oxidation resistance and rupture strength of receiver materials typically decrease by a factor of ~2.4 for every 100 K increase above 900 K, it is essential to use much less aggressive conditions to improve lifetime and cost effectiveness. The equilibrium constant  $K_p$  for the RWGS reaction at 900 K is 0.47, which is high enough to achieve the conversion needed for a practical process in three or possibly only two stages [29].

Although the water-gas shift (WGS) reaction has been widely used for the past century, the RWGS has not had a prior commercial application and has seen relatively little study. Most prior RWGS experiments have focused on conditions below 680 K and have had

mass flow rates below 0.05 g/s. Efficiencies (never reported) were probably a few percent. Limited data are available from the largest known experiment, that operated in the range of 720-1000 K at ~1 g/s [30]. Analysis of the available data suggests it may have achieved ~30% thermal efficiency and up to 60% CO<sub>2</sub> reduction. Our simulations of novel, scalable, low-cost processes show 70% thermal efficiency and 65% conversion should be quite practical for the three-stage process [29], and that level of conversion would be sufficient to allow the RWGS products to be sent directly into the FTS process without additional CO<sub>2</sub> separation processes.

Synthesis of low-value products is seldom competitive unless gas hourly space velocity (GHSV) (volume of gas feed/hr per volume of catalyst, normalized to STP) above 1000/hr can be achieved, and more often GHSV above 3000/hr is needed. Hence, most of the prior published RWGS experiments, where GHSVs were usually below 400/hr, are of limited value, even though selectivities were often above 98%. It is also important to achieve high conversion per stage to limit the number of stages, and this will require operating at higher temperatures than copper catalysts allow, as they are not sufficiently resistant to sintering above ~650 K.

Although Fe<sub>3</sub>O<sub>4</sub>/Cr<sub>2</sub>O<sub>3</sub> catalysts are much less active than copper, they are stable in syngas (H<sub>2</sub>+ CO) to ~700 K. They have been used to catalyze the WGS reaction at ~620 K [31], where an activation energy of 122 kJ/mol has been reported, so the exponential term in the rate constant increases by a factor of 10 when going from 620 K to 700 K. Hence, the Fe<sub>3</sub>O<sub>4</sub>/Cr<sub>2</sub>O<sub>3</sub> catalyst (70 m<sup>2</sup>/g) may permit RWGS GHSV above 2000/hr at 700 K with CO<sub>2</sub> conversion up to 85% of equilibrium (i.e., 32% conversion at 700 K for an H<sub>2</sub>/CO<sub>2</sub> feed ratio of 2) – but probably not for long. The Fe<sub>3</sub>O<sub>4</sub> would gradually be reduced to Fe<sub>2</sub>O<sub>3</sub> and metal, leading to unacceptable yield of CH<sub>4</sub> and higher HCs. Moreover, with 68% of the CO<sub>2</sub> not converted per stage, it would still be necessary to have at least four stages in series (with inter-stage H<sub>2</sub>O removal) to achieve sufficient total conversion. Hence, it is important to look at other options that could permit higher temperatures – and fewer stages. ZnAl<sub>2</sub>O<sub>4</sub> catalysts have shown good stability to at least 970 K, where they have achieved over 90% of equilibrium limits at GHSV above 15,000/hr [30]. That said, the unknowns here (selectivity, lifetime, surface area, optimal preparation methods...) are even greater.

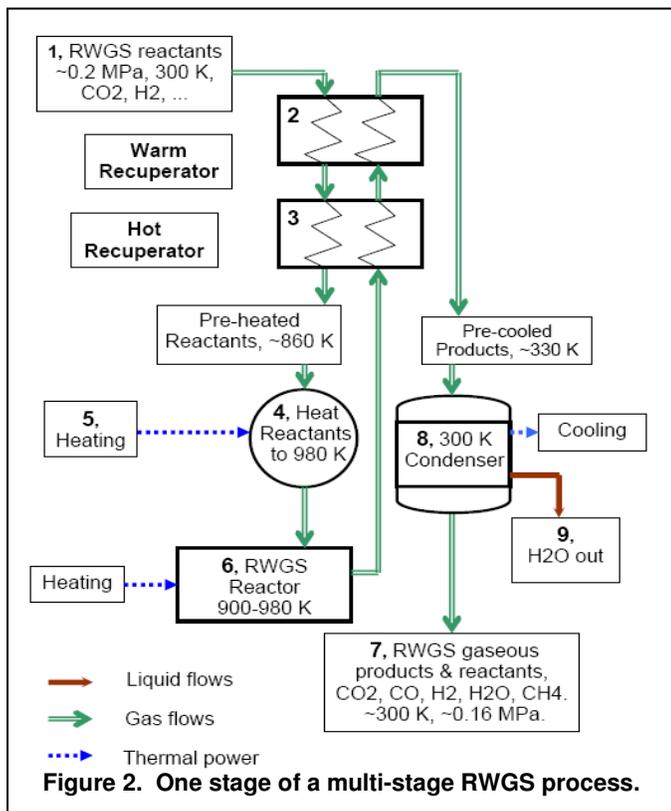
Other metal oxides are also known to have WGS activity and outstanding stability in highly reducing environments, but data are limited. One of the more promising appears to be MoO<sub>3</sub>/ZnO. For a catalyst with BET surface area of 35 m<sup>2</sup>/g, particle size ~1.5 mm, the following were reported [32] at 873 K, ~1 bar, with GHSV=3000/hr: 0% CH<sub>4</sub>; 99.9% CO selectivity; and 73% of equilibrium conversion for ~1:1 H<sub>2</sub>/CO<sub>2</sub> feed. Even after 700 hr of operation at 903 K with ~2:1:1 H<sub>2</sub>/CO/CO<sub>2</sub> feed gas, the CH<sub>4</sub> selectivity was only 0.2%, and CO<sub>2</sub> conversion in this experiment was just a few percent below equilibrium limits. Evaluations of a number of promising RWGS catalysts (including those mentioned above) are beginning, with publication of results expected in the near future.

**Figure 2** shows one stage of a multi-stage RWGS process. The entering reactants, mostly H<sub>2</sub> and CO<sub>2</sub> (plus some moisture and the CO produced in the preceding stage(s) if this is not the first stage), are preheated to the extent practical using the enthalpy of the reactor products. Then the additional heat needed for the endothermic reaction is added and the reaction proceeds until near equilibrium.

The products are then cooled to condense out most of the water so a subsequent reaction could further convert more CO<sub>2</sub> to re-establish equilibrium. In order to accomplish this, however, heat recuperators of very high effectiveness  $\epsilon$  are needed to transfer the heat of the RWGS products to the next stage's RWGS reactants; else the efficiency drop will render this process non-viable.

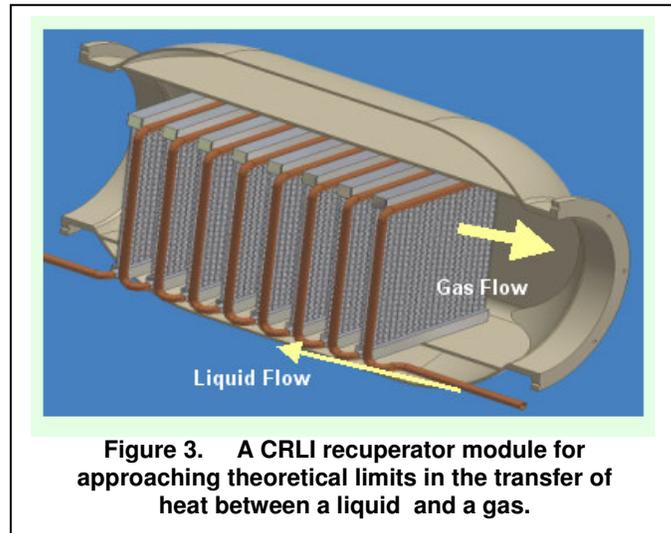
We recently published detailed analysis and simulation results of a novel compound recuperator with liquid intermediary

(CRLI) that promises order of magnitude improvement in both pressure drops and cost effectiveness for heat recuperation at very high  $\epsilon$  (up to 98%) between non-oxidizing gases for exchanges above  $\sim 200$  kW at temperatures up to at least 850 K [33]. Without an advance of this magnitude, the cost of the recuperators needed for efficient inter-stage removal of water in the multi-stage RWGS process could be discouraging.



The CRLI as shown in **Figure 3** is remarkable for its conceptual simplicity, and yet it represents a dramatic departure from standard practice. Each recuperator module resembles an arrangement of thermally isolated, serially connected, adjacent, cross-flow, finned-tube cores, such as used in air-conditioning condensers. They are arranged so as to effectively achieve counterflow exchange between the tube-side heat transfer liquid (HTL) and the shell-side gas stream. With a sufficient number of cross-flow cores in series, up to 99% of the exergy (available energy) from the gas can be transferred to the HTL. A second similar recuperator module then transfers up to 99% of the exergy from the HTL to the second gas stream. The pressure drops in the gas streams can be two orders of magnitude below what is often seen for conventional shell-and-tube recuperator designs. This is quite important to RWGS performance, as gas pressures will probably need to be under 0.3 MPa to limit parasitic methane production to an acceptable level, and pressure drops in compact recuperators (where the flow *necessarily* is in the laminar regime) are inversely proportional to the square of the pressure. The cost reductions in the CRLI come partly from the reduction in material usage, owing to the small fin spacing that is possible when the flow path is short and the flow velocity low.

The analysis is unequivocal, but a sizable demonstration is still essential, particularly to strengthen the cost projections. Numerous other major applications for the CRLI have also been identified. Detailed plans for the CRLI development and demonstration are being made.



### 3.3 Efficient conversion of waste heat.

The third largest loss using conventional technology would stem from inefficient utilization of the waste heat from the FT reactor and the electrolyzer. The FT reaction is highly exothermic, and FT reaction enthalpies for mid-weight hydrocarbons (HCs, mostly alkenes and alkanes) are typically about 22% of the higher heating value (HHV) of the products produced. Conversion of the reaction heat (at 510-600 K) has usually been at  $\sim 40\%$  of Carnot limits. The low-grade waste heat (at  $\sim 420$  K) generated by a hot-alkaline electrolyzer (where current technology achieves 80% HHV stack efficiency [20]) could be converted at  $\sim 25\%$  of Carnot limits using current cycles.

Detailed simulations have shown that when both a low-grade and a mid-grade waste-heat source are simultaneously available, a novel Dual-source Organic Rankine Cycle (DORC) can convert both the low- and mid-grade waste heats to electrical energy at over 60% of Carnot limits [34]. The latent heat of vaporization of the working fluid and the differences in specific heats between the liquid and vapor phases make full optimization (approaching second-law limits) impossible with a single heat source. When two heat sources are utilized, this problem may be solved by essentially eliminating a major pinch point.

The T-S diagram for the Dual-source Organic Rankin Cycle (DORC) is shown in **Figure 4**. Thermodynamic and systems analyses show that over 65% of Carnot limits for each of the sources should be practical when using this cycle with high- $\epsilon$  gas-to-gas recuperation.

The easiest way to understand the fundamental advantage of the DORC is to see that the maximum temperature drop from each heat source is a small fraction of that in standard cycles, and this allows a substantial reduction in irreversibilities. Experiments are currently underway to validate these simulations and address key feasibility issues.

We note that this thermodynamic cycle (though impressive sounding) is actually much less significant than the other advances mentioned. The amount of waste heat from the FT reactor remaining for conversion after other efficient uses are satisfied will only be about 10% of the RFTS plant input energy. The difference between whether this is utilized at 30% or at 60% of Carnot limits is less than 1.5% of the input energy.

preliminary 2-D model indicates that it will be possible to have a factor of 4 to 15 increase in specific productivity, along with reduced CH<sub>4</sub> and CO<sub>2</sub> selectivity.

## 5. SCALABILITY AND ECONOMICS.

Discussions of our developments thus far have led us to anticipate that certain questions about the economics and scalability of the RFTS process will likely arise. These questions concern: (1) the future availability of clean off-peak energy; (2) the market for the co-produced LOX; (3) the capital cost of an RFTS plant; and (4) the compatibility of the produced liquids as fuels and feedstocks to meet current petrochemical demand. The short answers are:

- 1) Trends of the past five years suggest the availability by 2020 of 100 TWh/yr (360 PJ/yr) of excess domestic wind energy in off-peak hours [1, 15]. At 52% RFTS plant efficiency, this would be sufficient to produce 1.4 billion gallons (Bgal) per year of carbon-neutral fuels (mostly gasoline and jet fuel, >44 MJ/kg). A 25%/yr growth rate beyond that is quite realistic because the Windfuels products would be market driven. There is sufficient wind resource to be developed economically in the U.S. and sufficient point-source CO<sub>2</sub> to synthesize over twice the domestic fuel demand and meet all other domestic energy needs [38].
- 2) The capital cost of an RFTS plant at commercial scale can be estimated with fairly high confidence because most of the major components (or similar components) are already in large-scale production for other purposes. The largest uncertainty in RFTS costs involves the electrolyzers, but DOE studies project their costs will drop 6-fold from economy of scale within a decade [20]. Projections indicate the second 250-MW RFTS plant 8 years from now, producing 40 Mgal/yr of gasoline and jet fuel from CO<sub>2</sub> and off-peak grid energy, would cost \$350M [22].
- 3) The LOX market is not essential for profitability of RFTS in future economies, though it would certainly help. One rapidly growing oxygen market is waste-water (sewage) treatment, and another enormous future market will be oxy-combustion.
- 4) The liquids directly produced would be mostly straight-run gasoline (C<sub>5</sub>-C<sub>11</sub> linear alkanes and alkenes) and kerosene (C<sub>8</sub>-C<sub>18</sub> HCs). Smaller streams of LPG, mixed alcohols, and a light oil would also be produced. All would have sub-ppm levels of sulfur, metals, and other impurities, and would be essentially aromatic-free. Some further processing on the products (isomerization and alkylation) will be needed to meet octane and pour-point requirements for use as major components in standard motor fuels; but that is not difficult on ultra-clean products, and only a little low-grade heat is needed. Plant emissions would be essentially zero.

## 6. SYSTEM EFFICIENCY PROJECTIONS.

We have presented, in excruciating detail, the results of simulations of a complete 250 MW RFTS plant [25] in our pending patents, which have recently been published. The simulations were carried out with DESIGN II by WinSim (a package with capabilities and validation history similar to that of Aspen Plus), as well as some supplementary models. Many details of the plant designs and simulation results can also be found in other recent publications [21, 29, 33, 34].

Numerous compressions and expansions are required for optimum performance. To illustrate a few examples: the electrolyzer may need to operate at ~2MPa; the RWGS may need to operate at

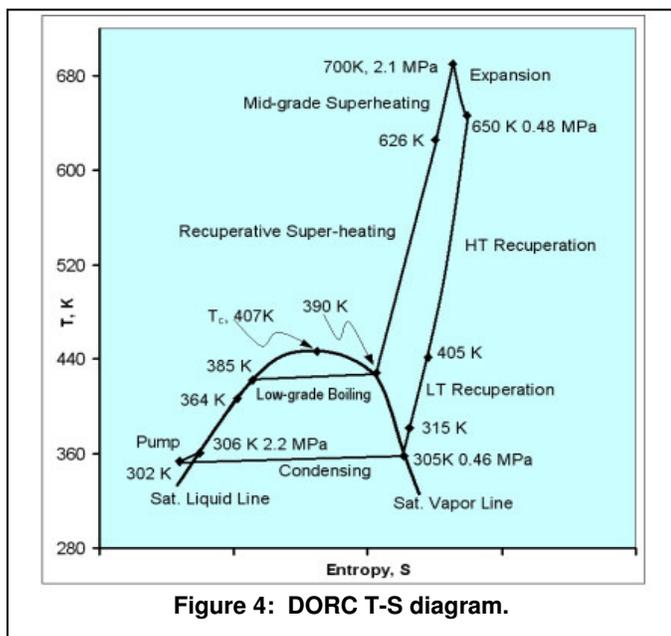


Figure 4: DORC T-S diagram.

## 4. The FT Reactor.

Development of a compact, scalable, 2-phase FT reactor is necessary. High temperature (HT) reactors (540-610 K) are needed to center the product distribution nearer the center of the gasoline (C<sub>8</sub>) or jet fuel (C<sub>13</sub>) ranges. The best current HT-FT technology for middle HCs (the latest Sasol SAS design) uses K-promoted fused-iron catalyst (mostly Fe<sub>5</sub>C<sub>2</sub>) in 2-phase fluidized beds (dry particles) at 550-600 K, 1.5-3 MPa, with H<sub>2</sub>/CO ratio close to 2 [23]. The fused-iron Fe<sub>5</sub>C<sub>2</sub> catalyst (mean particle size ~40 μm) has excellent lifetime in HT-FT reactors, and it is not expensive. The maximum mid-weight fraction in the products per pass is about 40%. The biggest problem with either the fluidized-bed or the bubble-column reactor is that neither is scalable to the smaller sizes needed for RFTS—especially the pilot-scale needed for the early development phases.

Fixed-bed reactors are readily scalable over a very wide range, but they have had unacceptable heat transfer limitations for FT unless liquid is present in the reactor (trickle flow) and the temperature is below ~540 K [23]. In this case, (1) the product yield is shifted toward heavy oils and waxes, (2) pore diffusion resistance is increased by two orders of magnitude (because the particles are wet), and (3) particle size cannot be too small (>2 mm) – to limit pressure drops (and perhaps to limit reaction rates for heat transfer reasons). Attempts with trickle beds to produce mid-weight HCs using iron catalysts have seen specific productivity below 0.07 g<sub>HC</sub>/g<sub>cat</sub>/hr [35] – more than an order of magnitude below that achieved in the SAS reactor. Moreover, both CH<sub>4</sub> and CO<sub>2</sub> selectivities have been unacceptably high. Low selectivities to CH<sub>4</sub> and CO<sub>2</sub> are readily obtained with cobalt catalysts at lower temperatures; but the catalysts are expensive and the products are still mostly heavy oils and waxes, which require further processing to be of high value.

Impressive progress has been made in the past few years by several groups working on micro-channel reactors (which should scale from 0.1-8000 bbl/d) that demonstrate better selectivity and activity [36, 37], but the published designs have serious cost challenges.

The novel design we are pursuing promises substantial cost reductions while retaining most of the heat transfer, selectivity, and activity advantages of the best current micro-channel reactors. Our

low as 0.2 MPa; the FT reactor may require between 1 and 5 MPa, and the separations loop will require as high as 20 MPa. The polytropic efficiencies assumed for these compressions and expansions were all consistent with turbomachinery technology that has been available for at least the past five years. (Major advances in CFD codes a decade ago allowed for considerable improvements in standard turbomachinery.)

The efficiencies seen in our plant simulations – 68% to 72% conversion efficiency from input H<sub>2</sub> to products – may appear less surprising in light of the fact that recent GTL plants achieve 64% efficiency in conversion of the chemical energy in the input CH<sub>4</sub> into the liquid products. Both conversions require a series of complex processes. The steam methane reforming (SMR) required in conventional syngas processes is over five times more endothermic than the RWGS reaction, and it is less favored (its  $K_p$  is lower) below 870 K. SMR does have the advantage that it becomes highly favored at high temperatures ( $K_p = 250$  at 1100 K), which means complete conversion can be obtained without subsequent separations. However, it is not difficult to condense water from syngas to make the multi-stage RWGS process just as practical.

## 6. CLIMATE BENEFIT.

Most grid energy today comes from fossil fuels, but the RFTS plant will draw power only during extreme off-peak hours, when essentially all the regional grid power is coming from wind, and nuclear generation. So the local grid energy that would be consumed by the WindFuels process is over 90% carbon neutral. The strongest climate-benefit arguments are: (1) Windfuels will initially displace tar sands – which means that every ~90 gallons of WindFuels sold will offset one tonne of CO<sub>2</sub> emissions [39], and (2) Windfuels will create an insatiable market for off-peak energy in high-wind areas and thus drive strong growth in wind energy [15, 19, 21]. This in turn will quickly halt the construction of new coal plants, cause many existing coal plants to be nearly shut down at night, and accelerate the decommissioning of old coal plants.

Unlike traditional sequestration concepts, the WindFuels process offers a large profit in the global market, even without subsidies or carbon offsets, which will allow it to grow as quickly as a highly profitable industry can scale-up. This will offer growth, rather than burden, to all countries that have sufficient wind and nuclear resources to use this technology – the U.S., the U.K., northern China, Russia, northern Europe, northwestern Africa, Canada, Peru, Somalia, Brazil, and many other countries.

The CO<sub>2</sub> needed for the Windfuels would initially come from point sources (power plants, cement factories, CO<sub>2</sub>-rich natural gas, etc.) for a simple economic reason – it will always be much cheaper to get CO<sub>2</sub> from a point source than from the atmosphere [40]. The Windfuels plants will purchase CO<sub>2</sub>, usually delivered via the pipeline network that is rapidly expanding for Enhanced Oil Recovery (EOR), the beverage industry, and other purposes. The separation of CO<sub>2</sub> will be handled initially by current commercial technology. Today, the most efficient, proven method is pressure-swing absorption (PSA) using solutions of amines, and state-of-the-art processes require 3 MJ/kg-CO<sub>2</sub> for separation from point sources, though the theoretical limit is ~1 MJ/kg-CO<sub>2</sub> [40], or about 7% of the energy in the fuels that can be synthesized from that CO<sub>2</sub>.

By the time coal usage drops to under one-third the current levels and the CO<sub>2</sub>-rich natural gas resources are largely depleted (if not sooner), some CO<sub>2</sub> will need to be separated from the atmosphere to provide sufficient carbon for Windfuels to meet the global need for liquid-transport fuels. Simulations have shown that a novel process will eventually allow separation of pure CO<sub>2</sub> from the dilute atmosphere with nearly an order of magnitude less energy consumption than has previously been thought likely.

While perhaps not as exciting as the potential impact on carbon emissions, a third climate benefit will come from the drastic reduction of contaminate emissions – both from transportation fuels and from point sources. The produced WindFuels will have several orders of magnitude lower contaminate levels (SO<sub>x</sub>, NO<sub>x</sub>, salts, halides, heavy metals, etc...) than typical fuels, and will be offsetting the use of tar-sands fuels, which have far higher than average contaminate levels [39]. Windfuels will be synthesized from captured CO<sub>2</sub> emissions, which must be scrubbed to sub-ppm contaminate levels. So the production of WindFuels could result in an even more rapid reduction in global contaminate emissions than in global CO<sub>2</sub> emissions reduction.

## 7. SUMMARY.

By using Windfuels (synthesized from CO<sub>2</sub> and wind or nuclear energy) for transport fuels, other options such as tar sands, oil shale, and coal that would be exploited to produce similar products for the global market could remain in their current state. Abating the production of these high-carbon fuel alternatives would result in a much larger reduction in GHGs than could be achieved by a program that is not market driven – such as direct sequestration of carbon. The sale of Windfuels will provide the needed market driver to eliminate the exploitation of tar sands, heavy oils, and eventually coal.

The next major step will be to build the first RFTS pilot-plant. This will improve confidence in the simulations. The key features of larger subsequent plants should be present, though their efficiencies will not be as high as could be achieved in commercial scale. This first pilot plant should produce straight-run gasoline and kerosene at the rate of at least 10 gal/day and serve as a platform for model refinement, catalyst characterization, and optimization of process conditions.

Windfuels in good wind regions will be able to produce liquid fuels at 5 to 20 times the rate per area as biofuels in fertile farming areas. The available global wind resource exceeds the current total global energy usage by at least a factor of five, and its mean levelized cost is less than a quarter that of solar where there is adequate market during off-peak hours. The US may be better positioned than any other country to establish leadership in WindFuels. The development, deployment, and rapid scale-up of CO<sub>2</sub>-derived fuels could eventually eliminate our reliance on unstable regimes for transportation fuels and stabilize fuel supply and (hence) fuel prices – since once the WindFuels plants are built, these “wells” need never go dry.

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