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# TOWARD EFFICIENT REDUCTION OF $CO_2$ TO CO FOR RENEWABLE FUELS

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## ABSTRACT.

Three major challenges – grid stability, domestic oil limitations, and climate change – could all be addressed simultaneously by using off-peak electrical energy to recycle $CO_2$ into liquid fuels (such as gasoline, jet fuel, and diesel).

Simulations have shown that recent innovations should make it practical to reduce $CO_2$ to CO at over 66% of theoretical efficiency limits. When combined with other process advances, it would then be possible to synthesize most hydrocarbons and alcohols from point-source $CO_2$ and clean off-peak grid energy (wind or nuclear) at system efficiencies in the range of 51-61%. Energy storage density in renewable, carbon-neutral kerosene is 44 MJ/kg, compared to ~0.4 MJ/kg for Li-ion batteries.

This process begins by electrolyzing water using clean energy to get the hydrogen required by the Reverse Water Gas Shift (RWGS) reactor and by a novel Renewable Fischer Tropsch Synthesis (RFTS) process. Off-peak grid energy averaged only $13/MWhr in the Minnesota hub in 2009. At such prices, the synthesized liquid fuels ("*WindFuels*") should compete even when petroleum is only $50/bbl.

Considerable effort over the past decade has been put into exploring high-temperature (HT) paths toward the production of renewable syngas ($H_2$ + CO) that could lead to sustainable synthesis of liquid fuels; but competitive fuel production from these HT thermo-chemical routes still appears to be decades away. An alternative path – the RWGS reaction – utilizes much less aggressive conditions and should be much more practical.

With low-cost hydrogen becoming available from off-peak wind and nuclear, efficient reduction of $CO_2$ to CO becomes viable at moderate temperatures (750-1000 K) via the RWGS reaction. Challenges arise because of equilibrium limits imposed by the reaction thermodynamics below 800 K and because of competing methanation and coking reactions above 800 K to 1000 K, depending on the catalysts. Several promising sets of conditions and catalysts are being evaluated. To drive the reaction to the right, a multi-stage process is required with efficient separation processes. This in turn depends on advances in cost-effective gas-to-gas recuperators for relatively low pressures to limit parasitic methanation reactions. Another challenge may be passivation of the recuperator surfaces to minimize hydrogenation of the CO during the heat recovery. Preliminary simulations indicate reduction of $CO_2$ to CO with about 2.2 MJ/kg-CO should be practical at commercial scale.

## 1. INTRODUCTION.

Considerable effort over the past decade has been put into research of paths toward renewable syngas production ($H_2$ + CO) that could lead to sustainable synthesis of liquid fuels. However, this effort has focused on high-temperature thermo-chemical reactions that continue to present enormous cost challenges. In this paper, we take a closer look at an alternative path – the reverse water gas shift (**RWGS**) reaction – which utilizes much less aggressive conditions and thus appears to have a much higher probability of success within the next few years.

Most of the research involving Solar-driven Thermo-Chemical Conversion (STCC) has focused on temperatures above 1200 K. The motivation for this has been driven at the fundamental level by the fact that no highly endothermic reactions (which can be used to absorb solar thermal energy) are thermodynamically and kinetically favored below about 1250 K. If the reactions are not highly favored, only low conversions are achieved. If the conversion is low, then separations and additional recycle are required, which can be complex and expensive – especially as the temperatures increase. The costs of the high-performance heat exchangers needed in efficient separation processes nearly double for every 100 K increase in temperature in the range from 850 K to 1350 K [*1*, *2*]. Hence, it has been assumed that the best path forward is to use highly endothermic processes that proceed sufficiently to completion at high temperatures (perhaps because of heterogeneous product phases) to eliminate the need for possibly complex separation processes.

As a point of clarification, we note that several recent articles in high-profile scientific magazines have mistakenly said that the maximum efficiency for reducing $CO_2$ to CO is established by Carnot limits, and that this motivates high-temperature conversion. Most readers probably appreciate that Carnot efficiency relates to heat engines and related processes operating between a source and sink, and it has no more relevance to reaction enthalpies than it does to the heat of fusion of ice, for example.

Many experiments have been carried out over the past five years on numerous receiver and reactor designs at temperatures above 1250 K [*3-13*]. However, all have suffered from a combination of serious practical deficiencies: (1) very short operating lifetime (usually a few hours to a few weeks) before efficiency drops over 30%; (2) low peak conversion efficiency (generally in the range of 0.1-0.3% for $Fe_3O_4$ routes and under 0.01% for ZnO routes); and (3) extremely high costs (over $\$30/W_T$, even above the 50 kW level). A thermochemical system that achieves 3% efficiency just to produce syngas, costs $\$30/W_T$, and operates at 10% capacity factor for just a month is *five orders of magnitude away from being practical*. (For comparison, thermonuclear fusion reactors were less than five orders of magnitude away from being practical two decades ago). These designs also all have limited prospects for scale-up due to one or several of the following challenges: (1) thermal or stress gradients that scale with size, (2) use of precious-metal catalysts, (3) batch mode operation, (4) solid reactants or solid products, (5) incompatibility with large receiver areas, or (6) impractically high optical precision.

The best prospects for a practical high-temperature (HT) commercial receiver (at the 100 $MW_T$ level with at least a decade of lifetime) appear to be based on a cylindrical arrangement of exposed metallic tubes, as proven in PowerTower plants at temperatures up to 840 K [*14*]. One example of this is Solar Tres. This plant achieves a peak solar thermal collection efficiency of 77% (product of heliostat and receiver efficiencies) and a mean annual collection efficiency of 41% [*14*]. It is clear from a recent study [*15*] that such designs could be extended to over 1200 K (possibly even to 1400 K) by using more expensive alloys of thicker sections. However, the receiver and reactor costs increase quickly beyond 1000 K. We show shortly that the collector plus receiver are likely to cost $\$30/W_T$ if used to drive a reaction at 1150 K. Clearly, an alternative approach is needed for practical success in $CO_2$ reduction.

Some effort has recently been put into the development of novel catalysts that may be effective for hydrogenation of $CO_2$ either *semi-directly* or *directly* into higher hydrocarbons (HHCs) and mid-alcohols using renewable $H_2$ [*16*]. However, conversion rates for desired liquid products with acceptable catalyst lifetime are only about 20%, which is too low to permit efficient recycling. The single-reactor experiments showing the better results all proceed through a two step process in which the $CO_2$ is first reduced to CO via the RWGS reaction, followed by FT reactions at other catalytic sites. The dramatically different pressures, temperatures, feed mixtures, and catalysts required for optimum RWGS compared to optimum Fischer-Tropsch (**FT**) reactions argue that near-term success is more likely if the RWGS and FT are handled in separate reactors.

The RWGS reaction is only mildly endothermic, and the equilibrium conversion of $CO_2$ to CO at 900 K is 65% for a 3:1 $H_2/CO_2$ feed. Thus, if low-cost renewable hydrogen is available, adequate $CO_2$ conversion to CO can be obtained at moderate temperatures (800-1000 K) when combined with efficient separation and multi-stage or recycle processes [*17*]. The price of off-peak wind energy plummeted in 2008-2009 in areas of high wind penetration [*18, 19*], and substantial strides have been made in efficiency of electrolysis of water [*20, 21*]. This combination permits an alternative path to renewable syngas that has been largely overlooked [*17*, *22*]. In the following sections, we first briefly review the basis for some of the technical challenges facing the HT STCC routes, and then present an overview of an alternative, promising path toward efficient, sustainable, syngas production.

## 2. Challenges of High-Temperature Solar Thermo-Chemical Conversion (STCC).

To better appreciate the challenges of high-temperature STCC, it is useful to briefly look at some of the prior related work. Perhaps the best reference point from a practical perspective is a recent study of an ultra-supercritical solar power plant at about 1000 K [*15*]. The receiver design used here is based on one that has been proven to have multi-decade lifetime potential at 840 K [*14*], and it can be extended to 1000 K with straightforward changes, primarily in the tubing alloy (from alloy 800 to alloy 617) and the heat transfer liquid (HTL) [*15*]. At the 140 $MW_T$ level, a receiver efficiency $\eta_R$ of 70% is expected at a solar flux of 200 $kW/m^2$ at 1000 K; and an $\eta_R$ of 85% is expected at 1 $MW/m^2$ [*15*]. Such a receiver, using Inconel 617 for the tubing and the bismuth-lead eutectic for the HTL was projected to cost about $\$1.8/W_T$ and permit a lifetime of ~20 years [*15*].

Superalloy 617 (22Cr, 12.5Co, 9Mo, 1Al, 0.3Ti, balance Ni) has over 4 times the 10,000-hour rupture strength and oxidation resistance of alloy 800 in the range of 800-1100 K – though alloy 617 costs over 3.5 times as much as alloy 800 (43Fe, 33Ni, 21Cr, 1Mn, 1Si, 0.3Al, 0.3Ti). The 10,000-hr rupture strength of alloy 617 decreases by a factor of ~2.4 for every 100 K increase between 900 and 1350 K [*23*], and attack on the tubing (internally from the HTL, and externally from the atmosphere) increases at a similar rate. The combination suggests receiver materials costs (for a 20-yr lifetime) could increase by a factor of 10 to 25 when going from 1000 K to 1250 K.

In addition to high rupture strength and outstanding oxidation and corrosion resistance, the tubing alloy needs good workability, weldability, elongation, and thermal conductivity. Alloy 230 (22Cr, 14W, 2Co, 2Mo, 1Fe, 0.5Mn, 0.3Al, bal Ni) has five times the oxidation resistance of alloy 617, which suggests better overall performance-to-cost ratio above 1200 K, though its 10,000-hr rupture strength in inert atmospheres is 30% lower [*24*].

Oxide dispersion strengthened (ODS) superalloys have much higher rupture strength above 1200 K and some have even better oxidation resistance [*23, 25*]. However, suitable tubing (~4 m long, ~0.05 m diameter) has not been available from ODS superalloys, as they require very expensive forging processes at very high temperatures, while much of the drawing and forming of the more ductile wrought superalloys (like 617 and 230) can be done near room temperature. It may be possible to produce tubing from novel ODS superalloys or from cast/wrought turbine-blade alloys (such as Udimet 710). Either approach might allow a 150 K increase in the temperature limit for the receiver, but at high cost.

The Pb-Bi eutectic is believed to be the best HTL option, particularly from a corrosion perspective, though data are sparse on corrosion rates from HTLs above 1000 K [*2, 15*]. At 1 $MW/m^2$ flux, even with a liquid-metal HTL, the peak tubing external surface temperatures will still exceed 1500 K. (The radial drop through the tube wall alone will exceed 100 K, and the thermal conductivity of the HTL is about one-fifth that of the tube-wall material.) An additional

50 K increase beyond this point would decrease oxidation resistance by a factor of three. Hence, higher fluxes or higher temperatures will not be practical with available wrought superalloys.

A commercial 1250-K 100-$MW_T$ receiver (meaning the HTL would exit at 1250 K) made from alloy 230 would be expected to cost about \$20/$W_T$ for a design lifetime of somewhere between 5 and 25 years. Extrapolating from 1000-K data (using the fourth-power temperature dependence for re-radiation), one expects this receiver could achieve $\eta_R$ of 70% at solar flux of 1 $MW/m^2$. This demonstrates a part of the challenge: ultra-high thermal flux is essential to get acceptable efficiency in a solar receiver at 1400 K surface temperature, as selective coatings are not expected to be possible. At 1 $MW/m^2$, a peak solar collection efficiency of 60% and a mean annual solar collection efficiency of 32% could be expected.

Efficiently heating an HTL to 1250 K would just be the first of a series of complex and expensive steps toward HT thermo-chemical conversion. Next, the heat would need to be transferred to the reactants, which are solid or gaseous. An additional temperature drop of 60-250 K would be expected there, even with a very expensive heat exchanger.

The above HTL path, following commercially proven technologies to the extent possible, appears to be the best general route toward STCC. Perhaps the outlined costs and temperature limitations explain why it apparently has not been pursued. However, the alternative approaches that have been explored appear to fall short of what is needed for competitive performance by four to six orders of magnitude when lifetime, system cost, and system efficiency are all considered.

For a gaseous reaction temperature of 1150 K, the above path may permit a 15-year lifetime with solar-to-chemical mean annual efficiency of ~25% at an initial cost below \$40/$W_T$ for the sum of the exchanger, reactor, receiver, and solar field (listed in expected order of cost, from most expensive to least). This temperature is sufficient for over 80% conversion of $CH_4$+$CO_2$ to syngas using expensive catalysts (Pt or Ru-based), but the separation of the remaining un-converted $CH_4$ from the syngas is expensive. Separation of $CH_4$ from syngas is an order of magnitude more energy intensive than separating $CO_2$ from syngas, and the $CH_4$ content needs be kept low if the syngas is going into a fully recycled FT process. Hence, even solar-driven dry reforming (as the above reaction is called) still appears to be more than an order of magnitude away from being competitive with the RWGS route discussed in the following sections.

## 3. BACKGROUND ON THE RWGS REACTION.

The water gas shift (**WGS**) reaction has been widely utilized, but there has not previously been a need for its reverse, the RWGS. Hence, prior research here has been limited.

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad (1)$$

$$\Delta H_{900K} = 36 \text{ kJ/mol, or } 1.30 \text{ MJ/kg-CO}$$

The RWGS reaction is only mildly endothermic, and it proceeds adequately at moderate temperatures with a number of catalysts. However, the equilibrium constant $K_P$ at the conditions that need to be used in a practical process (below ~1000 K at the reactor outlet) is rather low. Recall, $K_P$ for the RWGS would be defined as

$$K_P = \frac{p_{CO}\,p_{H2O}}{p_{CO2}\,p_{H2}} \qquad (2)$$

at equilibrium, where the *p*'s are the respective partial pressures. The value of $K_P$ is shown in **Figure 1** as a function of temperature [*26*]. It is nearly independent of total pressure for the relevant conditions (above 600 K and below 1 MPa) [*26*, *27*].

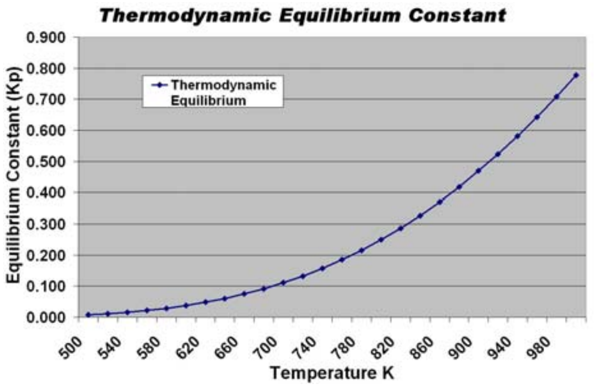

**Figure 1. The thermodynamic equilibrium constant for the RWGS reaction, shown here for 1 MPa, is nearly independent of total pressure.**

Optimization of an RWGS process is radically different from optimizing a WGS process. Somewhat higher $CO_2$ conversion can be obtained in the RWGS process by increasing the $H_2/CO_2$ ratio in the feed, but a much more powerful way to drive the reaction to the right (achieve higher $CO_2$ conversion) is to remove $H_2O$ and/or CO from the reaction as it progresses through a multi-stage or recycle process. Obviously, complete $CO_2$ conversion can, in principle, be obtained at any temperature if the $H_2O$ content is kept at zero.

No known separation processes could be competitive at high temperatures. Therefore, the best option is to simply cool the products, condense out most (~90%) of the water, and re-heat the remaining $H_2$-$CO_2$-CO-$H_2O$ mixture to the reaction temperature so $CO_2$ reduction can continue to the new equilibrium. In principle, cooling and re-heating an ideal gas would not require any energy if ideal recuperation were available. Highly effective heat recuperation between counterflowing liquids is not difficult to achieve or expensive, but that has not yet been the case for non-condensing gases – as is the case here (except for the condensation of a little water near the end of the cooling of the products). However, a novel solution with the potential for an order-of-magnitude improvement in high-effectiveness gas-to-gas recuperation for the relevant conditions has recently been reported [*2*, *28*]. This new *Compound Recuperator with Liquid Intermediary* (**CRLI**) is optimized for heat transfers below 1100 K involving clean, non-oxidizing gases at low pressures. The CRLI is conceptually similar to what was suggested four decades earlier and denoted the liquid-coupled exchanger. However, the thorough optimization of the CRLI dramatically changes how one now can approach low-conversion processes involving clean, non-oxidizing gases, even at low pressures, if needed.

There are a number of catalysts that are sufficiently active to RWGS, stable above 850 K, and appear to have very low selectivity to competing reactions. Most of the prior work on the RWGS has utilized copper catalysts, as they are much more active; but they are not stable above ~650 K, at which point $K_P$ is still too low. One of the challenges will be keeping methane production in high temperature reactors as low as desired, though it appears that keeping $p_{H2}$ low will permit a very low methanation rate. We will return later to discussing performance of several catalysts, but first we will walk through an explanation of an efficient RWGS stage in some detail – as highly recuperated multi-stage, equilibrium-limited processes are not common.

For the process presented in sections 4 and 5, we will assume the catalyst is sufficiently stable to 900-1000 K and that ultra-low-cost recuperators with high effectiveness $\varepsilon$ (over 90%) can be developed for these conditions – clean, reducing gases at pressures ~0.2 MPa.

## 4. THE NEEDED FTS REACTANTS.

For illustrative purposes, we choose to look at the case where an HT-FT reactor will produce 1 kg/s products with the following assumed distribution by product mass: 35% $C_{3+}$ alkanes, 9% oxygenates (mostly ethanol), 8% $CH_4$, 4% $C_2H_6$, and 45% olefins and other HCs. The alkanes and olefins are mostly in the gasoline, jet fuel, and diesel ranges, C4-C20. As shown approximately in **Appendix A: Mass Balance**, the input $H_2$ and CO required for the FT reactor would then be 0.28 kg/s and 1.9 kg/s respectively. (This assumes all the C comes from CO. The FT reactor may hydrogenate a small amount of $CO_2$ .) From eq. (1), the $H_2$ required for the RWGS reactor to produce 1.9 kg/s CO from $CO_2$ is 0.135 kg/s. An additional 0.01 kg/s is assumed desired for subsequent hydrogenation of the heavier olefins (to improve their value). Hence, the total $H_2$ required for 1 kg/s of products is 0.42 kg/s.

While only 0.135 kg/s $H_2$ will be converted to water in the process of producing 1.9 kg/s CO, excess $H_2$ and $CO_2$ are required – as $K_P$ is under 0.8 even at 1000 K. The greater the excess $H_2$ and $CO_2$, the less catalyst required to achieve the desired CO production, other things being equal. However, there are reasons to limit the amount of excess $H_2$ and $CO_2$. Increasing the former increases methane selectivity, and increasing the latter increases cost of the heat exchangers, turbomachinery, and separation processes.

The input $CO_2$ required to produce the desired amount of CO is 3 kg/s. The RWGS processes will not achieve complete conversion, so there will be $CO_2$ leaving the last stage. Preferably, the amount here will be low enough so it can just be sent through the FT reactor (along with the CO and $H_2$) to eliminate another separation operation. In this case, it just adds to that produced in the FT reactor from the WGS, which will ultimately be recycled through the RWGS reactor. Here, we assume the total $CO_2$ (new-source plus recycled) entering the first stage of the RWGS reactor will be 4.6 kg/s, which would leave ~1.6 kg/s excess coming out the last stage.

One stage of an effective process – irrespective of the catalyst chosen – is shown in **Figure 2**. The entering reactants – mostly $H_2$ and $CO_2$, plus 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.

Here, we assume about three-fourths of the total available hydrogen is fed into the first RWGS reactor – 0.3 kg/s, to be precise in the first case. We also assume the feed mixture contains 0.09 kg/s $H_2O$ (from drying the source $H_2$ and $CO_2$ only to 302 K dew point), 0.02 kg/s $CH_4$, and 0.01 kg/s $C_2H_6$. These latter two are from incomplete separation from $CO_2$ recycled from the FT reactor. Thus the total feed into the first stage is 5.02 kg/s. In the following discussion, we adopt the convention of listing mass fractions or volume fractions in the following order: $CO_2$, $H_2$, CO, $H_2O$, $CH_4$, and $C_2H_6$, as also listed in Table 1. The $C_2H_6$ component is assumed constant at 0.01 kg/s throughout the process. The mass fractions going into the first reactor are 0.919, 0.06, 0, 0.016 0.004, and 0.002; and the total flow rate is 5.02 kg/s at component **1** in Figure 2 for the first stage. The respective molar feed fractions are 0.404, 0.577, 0, 0.0162, 0.005, and 0.0013; and the mean molecular mass is 19.4. A simple model for real partial pressures of the constituents was fitted to RefProp real-gas data within about 0.3% [*29*].

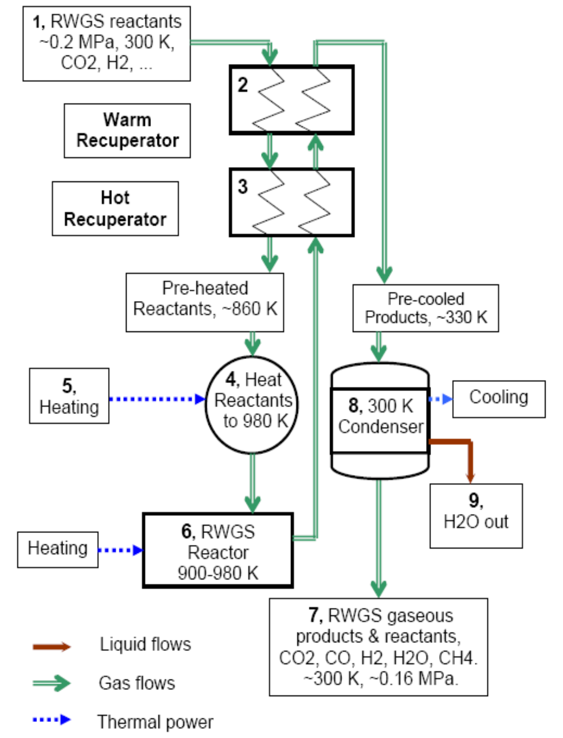

**Figure 2. One stage of a multi-stage RWGS process.**

Steady-state conditions will normally prevail, even though the renewable hydrogen will be generated only when cheap off-peak energy is available – usually in the middle of the night. However, it is a simple matter to store 18 hours worth of hydrogen to keep the RWGS and the FTS processes running at a steady rate around the clock. More cheap clean energy will also be available on the weekends, so perhaps up to 36 hours worth of hydrogen would be stored for gradual draw-down over the week. However, the RWGS and FTS processes could also easily adjust to weekly and seasonal variability with little loss in efficiency. We return later with a few more comments on the effects of operating above and below design flow rates.

## 5. DRIVING RWGS TO THE RIGHT.

Results on several catalysts (as discussed in the next section) have shown: (1) CO selectivity above 98%, (2) conversion exceeding 80% of equilibrium $CO_2$ conversion limits at space velocities above 3000/hr, and (3) excellent catalyst lifetime at temperatures above 870 K. However, even with a 2:1 $H_2/CO_2$ feed ratio and with an entry dew point of 300 K (in a production process it may not be practical to aim for a lower water content in the feed), the CO molar fraction in the products then would only be ~0.14 – implying substantial separation penalties downstream. Thus, it will be beneficial to use a multi-stage process with inter-stage removal of the water so higher total conversion can be achieved.

For the entry mixture indicated in the preceding section, the mean $C_P$ (specific heat) of the reactant-mixture from 300 to 900 K (at 0.28 MPa) is 1.82 kJ/kg-K and that of the products is 1% to 4% less (depending on how much $H_2$ is converted). If the recuperator's ε (effectiveness) is only 0.75, the additional preheating required is 295 kJ/kg for a mixture that may produce only ~0.2 kg-CO per kg of feed in the first stage, and less in subsequent stages. Hence, the preheating would require more energy than the reaction itself requires in the first stage, and it gets much worse in subsequent stages. The extra preheating would end up as low-grade heat in the products going to separations and have little recovery value. Using conventional recuperator technology to preheat the reactants to the reactor temperature with ε>0.8 would be extremely expensive, and the viscous losses through such recuperators would add an even greater penalty.

In the process shown in Figure 2 for the case at hand, recuperation is assumed to provide 93-96% of the preheating needed from 300 K to the reactor outlet temperature. This heat gets the reactants to 860 K for a reactor outlet temperature of 900 K. The reactants are then further heated to 950 K (requires ~0.9 MW, as $C_P$=2.03 kJ/kg-K) by an external source, perhaps methane combustion, before being fed into the RWGS reactor, where additional heat may be needed.

For the feed mixture here, the relative partial pressures (approximately equal to the molar fractions) for equilibrium at 900 K would be 0.2186, 0.3871, 0.1877, 0.2117, and 0.0073 (assuming just under 1% of the $CO_2$ and $H_2$ go into $CH_4$). (At 900 K, $K_P$=0.469, and 0.1877*0.2117/ 0.2186/0.3871=0.469.) However, the RWGS reaction rate is zero at equilibrium. As conversion approaches the equilibrium limits, the local specific productivity of the catalyst ($kg_{CO}/kg_{cat}$/hr) will be approximately proportional to the local kinetic factor $K_2$, defined as:

$$K_2 = 1 - \frac{p_{CO}\, p_{H2O}}{K_P\, p_{CO2}\, p_{H2}} \qquad (3)$$

At 80% of conversion limits, $K_2$ =0.49 for these conditions. Thus, 80% of the equilibrium CO limit may be a reasonable target – to limit the size of the reactor. At this level, the CO mass flow rate in the product stream is 1.07 kg/s, so the reaction enthalpy required in the reactor is 1.39 MW/kg. If the reactants entered at 950 K and the mixture leaves at 900 K, its temperature drop provides 510 kW (2.02 kJ/kg-K * 50 K * 5.02 kg/s), so an additional 880 kW of heating of the reactor bed is required, and 100 kW of that is assumed to come from viscous heating. An alternative which may be less expensive than a single heated reactor would be to have two or even three adiabatic reactors in series for the first stage, with the reactants/products re-heated to ~950 K between them.

The gas mixture (with reactor exit flow rates and molar fractions as listed in Table 1) leaving the first-stage reactor proceeds through the recuperators, where it is cooled to near the point that water begins condensing. The product stream here contains 0.8 kg/s $H_2O$; and ~90% of that will be condensed out upon cooling to 300 K, releasing ~1.7 MW from the condensation plus ~300 kW from the gas cooling.

The mixture at 300 K (saturated with $H_2O$ vapor) then proceeds to the second stage, essentially identical to the first stage, except the numbers are a little different. For the same reactor outlet temperature, the maximum CO production would now be only half that seen in the first stage because of the additional starting CO, but some additional $H_2$ could be injected to increase equilibrium conversion. Here, we assume 0.05 kg/s $H_2$ is added to the input stream. Still, both reactant concentrations are lower, so $K_2$ decreases more quickly as equilibrium is approached. We assume CO production in the second stage is 75% of the limit, or 0.53 kg/s, which gives an exit $K_2$ of 0.41. The story is similar in the next stage, where we again assume 0.05 kg/s $H_2$ is injected with the input mixture. Here, we assume CO production is 66% of the thermodynamic limit, or 0.3 kg/s. In this case, exit $K_2$ would be 0.45.

The viscous losses in the recuperator will depend heavily on the technology. Initial estimates indicate total pressure drop with a first-stage entry pressure of 0.28 MPa will be ~0.15 MPa through all the reactors and recuperators if fully optimized. (Only about 20% of that drop is in the CRLI recuperators. Pressure drops could be nearly two orders of magnitude higher in conventional high-ε recuperators.) Compressing the initial feed gas (flow rate of 5.02 kg/s, 300 K, $C_P/C_V$=1.36, $C_P$=1.8 kJ/kg-K, ρ=0.93 kg/m$^3$) from an assumed starting pressure of 0.13 MPa to 0.28 MPa with polytropic efficiency of 86% gives a compressor outlet temperature of 380 K and requires 760 kW, but most of this reappears as viscous heating in the reactors.

The key results from the 3-stage model are summarized in **Table 1**. The columns "r.p.p." show relative partial pressure (approximately molar fraction) at the reactor outlet. In the last line, values in the "Recup" columns are the total heat recovered through the recuperators. The "React" columns show the additional heating needed in the reactors (the last two stages are adiabatic), and the "Net columns" are the total net heating needed in that stage (losses plus final pre-heating of reactants plus any heat added directly into the reactor). The small effects of viscous heating (~2%, mostly in the reactors) and external heat losses (~1.5%) are also included. The total net input heating power for the three stages – for production of 1.9 kg/s of CO – is seen to be ~3.5 MW, and ~760 kW is required for the compressor. The theoretical minimum for the reaction enthalpy is ~2.8 MW [*30*], so the total losses in this RWGS process are ~1.46 MW. If the recuperators were assumed to have 98% rather than 95% effectiveness (defined relative to heat transfer from the weaker stream, the products), the net heating required would drop by 400 kW, but the recuperator cost may triple and the compressor power increases. At ε=0.75, the total net heating input increases to 6.4 MW.

The 1 kg/s of HCs and alcohols that will be produced from the FT reactor from the 1.9 kg/s of CO and 0.284 kg/s $H_2$ will have mean HHV of about 42 MJ/kg, giving a chemical output power of 42 MW. From this perspective, the 1.46 MW of losses in the 3-stage RWGS process with ε=0.95 is quite minor. Of course, about 3 MW of low grade heat (~320 K mean) is rejected from the three condensers, but that is not likely to be of value.

There is still considerable uncertainty in activities of the catalysts that would be selected. However, based on the more relevant published data, it appears a normalized gas hourly space velocity (GHSV) of at least 6000/hr (maybe twice that) will be achieved for the conditions assumed here. Recall,

$$\text{GHSV} = V_1'/V_\text{C} \qquad (4)$$

where $V_1$' is the volumetric flow rate per hour at STP and $V_\text{C}$ is the gross volume of the catalyst. For the second reactor, the mass flow rate is 4.35 kg/s and the density of the feed mixture at STP is 0.87 kg/m$^3$, giving a normalized volumetric flow rate $V_1$' = 1.78E4 m$^3$/hr. That would imply a catalyst bulk volume of under 3 m$^3$. Somewhat more would be required for the last reactor if one of the measures mentioned above for increasing its exit $K_2$ is not included. In Table 1, the reactants to the last stage have been dried to a 285 K dew point, as seen from the low input $H_2O$.

There is promise for strong progress in cost-effectiveness of recuperators for these conditions. However, the cost of high-temperature recuperators of 95% effectiveness may still exceed the sum of all the other RWGS components – the reactors, catalysts, compressor, condensers, fans, and ducts. At large scale, the recuperator cost will be roughly proportional to the product of $(0.99\text{-}\varepsilon)^{-1}$ and the total amount of heat transferred. The latter increases with the number of stages, the mass flow rate, and the reactor outlet temperature $T_\text{R}$. A preliminary estimate is that the CRLI recuperators can be produced in large volume at a cost of ~\$0.2/W for a mean temperature difference of 30 K, as is the case here at ε=0.95. Clearly, there is an incentive to reduce the number of stages.

Production per stage can be increased by increasing either feed $CO_2$ or $H_2$. However, sending additional $CO_2$ into the RWGS reactors is not desired, as it is beneficial to keep the $CO_2$ low enough to avoid the need for a $CO_2$ separation process on the mixture leaving the last RWGS reactor – so it can simply be dried and then sent directly into the FT reactor.

Sending all the available $H_2$ (0.42 kg/s) into the first reactor could permit a 2-stage solution. Simply increasing the $H_2$ fraction may lead to excessive methane production, as its rate increases at least as the third power of $p_{\text{H2}}$. However, the $H_2$ molar fraction can be increased without increased methanation if the total pressure is reduced. With only two reactors, this is possible.

**Table 2** shows calculated results for a two-stage RWGS process in which $T_\text{R}$ =940 K, the inlet pressure to the first stage is reduced from 0.28 MPa to 0.21 MPa, ε=0.95, and all the available $H_2$ is fed into the first reactor. This puts the inlet $H_2/CO_2$ molar ratio at 2.0, compared to 1.42 for the previous 3-stage example. The $H_2$ partial pressure in the first reactor has decreased from 0.15 MPa to 0.13 MPa, and the compressor power has decreased from 780 kW to 440 kW.

The total recuperator duty for the 2-stage process (12 MW) is 84% of that for the 3-stage process. The net heating required is only 0.1 MW lower, but the compressor power is reduced over 0.3 MW. The primary question is whether or not catalysts will have sufficient lifetime and selectivity at the higher temperatures. The answer to that question is not yet known. If fact, it is not yet completely clear if reported catalysts will be adequate with a 900 K reactor outlet temperature, though that appears highly likely. The reactor outlet temperatures for the 3-stage process could be reduced to 800 K and still achieve the needed CO production by increasing the $H_2/CO_2$ feed ratio to 2.0 and accepting a lower specific productivity (exit $K_2$ =0.3) – and thus larger reactors.

The next logical question is: "What temperature would be required to achieve the needed conversion in a single stage?" There is more uncertainty in $K_\text{P}$ above 1000 K, but it appears that a single stage with a 2.0 feed ratio could produce the needed amount of CO with $T_\text{R}$=1150 K, at 93% of the conversion limit and $K_2$=0.29. However,

**Table 1.** 3-stage RWGS Reactor, 900 K outlet, $K_\text{P}$ = 0.47

| | First stage | | | | | Second stage | | | Third stage | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | in1 kg/s | in1 mass f | in1 mol. f | out1 kg/s | out1 r.p.p. | In2 mol f | out2 kg/s | out2 r.p.p. | In3 mol f | out3 kg/s | out3 r.p.p. |
| $CO_2$ | 4.6000 | 0.9180 | 0.4047 | 2.8911 | 0.2548 | 0.2687 | 2.0279 | 0.1906 | 0.1861 | 1.5275 | 0.1418 |
| $H_2$ | 0.3000 | 0.0599 | 0.5761 | 0.2186 | 0.4197 | 0.5453 | 0.2257 | 0.4622 | 0.5511 | 0.2493 | 0.5042 |
| CO | 0.0000 | 0.0000 | 0.0000 | 1.0700 | 0.1480 | 0.1561 | 1.6000 | 0.2360 | 0.2305 | 1.9000 | 0.2769 |
| $H_2O$ | 0.0812 | 0.0162 | 0.0150 | 0.7915 | 0.1697 | 0.0190 | 0.4453 | 0.1018 | 0.0230 | 0.2969 | 0.0671 |
| $CH_4$ | 0.0200 | 0.0040 | 0.0048 | 0.0300 | 0.0072 | 0.0077 | 0.0400 | 0.0102 | 0.0101 | 0.0500 | 0.0126 |
| $C_2H_6$ | 0.0100 | 0.0020 | 0.0013 | 0.0100 | 0.0013 | 0.0014 | 0.0100 | 0.0014 | 0.0013 | 0.0100 | 0.0014 |
| Total | 5.0112 | 1.0000 | 1.0019 | 5.0112 | 1.0006 | 0.9981 | 4.3489 | 1.0022 | 1.0022 | 4.0337 | 1.0040 |
| $K_2$ | | | | | 0.49 | | | 0.41 | | | 0.45 |
| | | | | | | | | | | | |
| Heat Requirements | | | | | | | | | | | |
| | | Recup. | React. | Net | | Recup. | React. | Net | Recup. | React. | Net |
| kW | | 5230 | 780 | 1910 | | 4700 | 0 | 960 | 4650 | 0 | 580 |

manufacturing processes for CRLI recuperators are not yet proven – at any temperature. The probability that they will be able to be made at low cost for use up to 800 K appears very high, and the probability appears reasonably high up to 900 K. At this point, however, the manufacturing challenges appear very high for temperatures above 1000 K. Using conventional recuperators above 950 K would make the RWGS process quite expensive, even with $\varepsilon$=0.75. With $\varepsilon$=0.75, the net heating required is 5.1 MW for the single-stage case (assuming the catalysts can be developed). With $\varepsilon$=0.95, the heat required is only 5% below what is needed for the 2-stage process, so the motivation to try to go from two stages to one stage is rather low.

The CRLI recuperators operate in the laminar flow regime. Moreover, the sum of the effects of flow inhomogeneity, axial conduction (from hot to cool end), and viscous losses on effectiveness is only about 1%. Such a recuperator with $\varepsilon$=0.95 at design flow rate would see $\varepsilon$ increase to 0.97 at half design flow rate, or drop to 0.91 at twice design flow rate. Hence, the RWGS process could be expected to operate over a range of a factor of 4 in flow rates with acceptable performance. The rest of the RFTS system could also be made to operate over a similar range with little affect on performance, as discussed elsewhere [*17*].

## 6. RWGS CATALYSTS.

Copper is probably the most active WGS/RWGS catalyst at low temperatures, and a common choice for WGS is $Cu/ZnO/Al_2O_3$ in the 500-600 K range. Experiments at 673 K using Cu/alumina have achieved ~80% of $K_p$ limits for RWGS – with $CH_4$ below 0.5%, but at GHSV of only ~150/hr [*31*]. Higher temperatures than what copper will handle are needed, both for increased $K_P$ and for higher activity.

Although $Fe_3O_4/Cr_2O_3$ catalysts are much less active than copper at low temperatures, they are stable in syngas to ~750 K. They are commonly used to catalyze the WGS reaction at ~620 K, where an activation energy of 122 kJ/mol has been reported [*26*]. A careful reduction process of the $Fe_2O_3$ starting catalyst to the active magnetite phase, $Fe_3O_4$, is required to avoid reduction of some of the oxide to the metal. (Iron metal is very active toward production of methane, and it can easily be carbided by CO to the Hagg carbide, $Fe_5C_2$, which is active to other hydrocarbons.) This reduction process is not difficult to control adequately for the WGS reaction, as it proceeds well at temperatures below 650 K. At a typical WGS pressure of 3 MPa, the catalyst effectiveness factor is ~0.5 for particle sizes of 6 mm; and methane selectivity is a few percent or less. The high activation energy means the rate constant increases by a factor of 60 when going from 620 K to 750 K. Hence, a standard, commercial, WGS $Fe_3O_4/Cr_2O_3$ catalyst (BET surface area of 70 $m^2$/g) may permit RWGS GHSV ~2000/hr at 750 K. However, 750 K is still not high enough to achieve the desired conversion in three stages, and it is likely methane production would increase more rapidly than desired as the catalyst ages.

A more promising option appears to be $MoO_3/ZnO$ [*32*]. For a catalyst with BET surface area of 35 $m^2$/g and particle size ~1.5 mm, the following were reported at 873 K, ~1 bar, with GHSV=3000/hr: 0% $CH_4$; 99.9% CO selectivity; and 73% of equilibrium conversion for ~1:1 $H_2/CO_2$ feed. Even after 700 hr of operation at 903 K with ~2:1:1:0.02 $H_2/CO/CO_2/H_2O$ feed gas, the $CH_4$ selectivity was only 0.2%, and $CO_2$ conversion in this experiment was reported to be just a few percent below equilibrium limits, which would be 0.337:0.139:0.264:0.084. The output $K_2$ would have been ~0.05, so GHSV could have been at least doubled with an increased flow rate with little loss in conversion.

$ZnAl_2O_4$ catalysts have shown good stability in syngas to at least 980 K, where they have achieved 90% of RWGS equilibrium limits at GHSV above 15,000/hr [*33*]. However, there is still considerable uncertainty with respect to activity, $CH_4$ selectivity, coking, and lifetime. Many other oxides are expected to have good RWGS activity, and tests are underway to evaluate some that are known to be exceptionally stable in highly reducing environments.

The benefit of higher temperature operation was shown clearly in experiments with $ZnAl_2O_4$, as the productivity increased by more than a factor of 5 in going from 800 to 900 K, although the recuperators become more expensive and methane production increases. Low methanation is very important if the syngas is going into a fully recycled RFTS process, as separation of $CH_4$ from syngas is an order of magnitude more energy intensive than the other separations required.

**Table 2.** 2-stage RWGS Reactor, 940 K outlet, $K_P$ = 0.58

| | First stage | | | | | Second stage | | | |
|---|---|---|---|---|---|---|---|---|---|
| | in1 kg/s | in1 mass f | in1 mol. f | out1 kg/s | out1 r.p.p. | In2 mol f | out2 kg/s | out2 mass f | out2 r.p.p. |
| $CO_2$ | 4.6000 | 0.8964 | 0.3280 | 2.4511 | 0.1756 | 0.2065 | 1.5557 | 0.3668 | 0.1323 |
| $H_2$ | 0.4200 | 0.0818 | 0.6535 | 0.3186 | 0.4972 | 0.5867 | 0.2743 | 0.0647 | 0.5083 |
| CO | 0.0000 | 0.0000 | 0.0000 | 1.3500 | 0.1518 | 0.1787 | 1.9000 | 0.4479 | 0.2537 |
| $H_2O$ | 0.0819 | 0.0160 | 0.0160 | 0.9723 | 0.1695 | 0.0220 | 0.4615 | 0.1088 | 0.0955 |
| $CH_4$ | 0.0200 | 0.0039 | 0.0039 | 0.0300 | 0.0058 | 0.0069 | 0.0400 | 0.0094 | 0.0093 |
| $C_2H_6$ | 0.0100 | 0.0019 | 0.0010 | 0.0100 | 0.0010 | 0.0012 | 0.0100 | 0.0024 | 0.0012 |
| Total | 5.1319 | 1.0000 | 1.0024 | 5.1319 | 1.0009 | 1.0022 | 4.2416 | 1.0000 | 1.0003 |
| $K_2$ | | | 1.00 | | 0.49 | 0.96 | | 0.38 | |

Heat Requirements

| | | Recup. | React. | Net | | Recup. | React. | Net | |
|---|---|---|---|---|---|---|---|---|---|
| kW | | 6610 | 900 | 2370 | | 5390 | 0 | 1020 | |

Another issue may be re-conversion of the CO in the recuperator while the reactor products are being cooled – either via the WGS, hydrogenation, or the Boudouard reaction. Large areas of copper, steel, or nickel alloys cannot be exposed to the RWGS products before they are cooled sufficiently that the reaction rates are too low to be of concern. (The RWGS equilibrium moves in the opposite direction to what is needed for high $CO_2$ conversion as the products are cooled, so the WGS reaction must be kinetically limited.) We expect it will be straightforward to adequately passivate the recuperator surfaces with silver or carbon films (~1 μm may be sufficient) to keep the unwanted reactions from being catalyzed there.

Thermal (uncatalyzed) reactions could still be significant during the initial cooling of the RWGS products, so it is also important to minimize the residence time in the high-ε recuperator. Studies are currently underway to measure the primary thermal reaction rates and to better quantify the extent of surface passivation required.

## 7. Capital Cost Estimates.

Rough cost estimates are always of interest when new processes are being proposed. The biggest item will clearly be the electrolyzers. Producing 0.42 kg/s of $H_2$ at 80% HHV efficiency requires 74 MW. The largest commercial electrolyzers currently available are about 2 MW and cost about \$0.7/W. However, DOE-supported studies project the cost should drop to \$0.15/W as production volumes increase over the next decade [*20*]. (While such cost reductions may sound optimistic, they are actually less than what is usually seen when production volumes scale up by two orders of magnitude.)

If the electrolyzer operates only one-third of the time to take advantage of cheap off-peak wind energy, the cost of the electrolyzers (220 $MW_P$) would be \$33M. The tanks (and ancillary compressors, expanders, and recuperators) needed to store the extra 24 tons of hydrogen (950 MWhr) produced during off-peak hours to keep the RWGS process running steadily around the clock might cost about \$9M. The cost of liquefying the co-produced oxygen and providing sufficient storage for bi-weekly pickup (~1000 tonnes LOX) might be an additional \$5M.

If the CRLI recuperators can ultimately (at high volume production) be produced for \$0.2/W, their cost in an RWGS process producing 1.9 kg/s CO would be ~\$2.5 M, though such costs may be more than a decade away. The adiabatic RWGS reactors would probably cost only \$50K each, but the first-stage shell-&-tube reactor (with 900 kW of heating) might cost \$1M. A high efficiency 1000-hp compressor might cost \$800K, and the water condensers (3 MW total) might cost ~\$150 K. Four tons of RWGS catalyst might cost ~\$150 K.

The capital cost estimates for generating syngas at the rate needed to produce 10 Mgal/yr from off-peak wind energy are summarized in Table 3. Clearly, cost reduction R&D should focus on electrolyzers, large hydrogen gas storage systems, oxygen liquefaction systems, and recuperators for reducing gases at low pressures.

As shown, the RWGS system presented in this paper has an estimated capital cost of \$1 per watt of mean chemical output power in the syngas. When an appropriate amount of the cost of the wind turbines is added, the total capital cost might be \$1.5/W, as it is assumed that most of the cost of the wind turbines is paid for by grid demand during peak hours.

For comparison, if an STCC system costs \$40 per watt of peak receiver power, achieves a mean annual thermal capacity factor of 25%, and achieves 60% receiver-to-syngas conversion efficiency (two to four orders of magnitude beyond most demonstrated technology), the capital cost of an STCC system would be \$270 per watt of mean chemical output power in the syngas.

In neither of the above cases is the cost of conversion of syngas to liquid fuels included, but that is minor. In large plants it has been about \$0.20/W [*34*], though it may be \$0.40/W for the plant size considered here.

## 8. Conclusions.

Preliminary results from several catalysts indicate that using three RWGS stages can eliminate the need for expensive $CO_2$ separation, as sufficiently high $CO_2$ conversion can be achieved that the products can be sent directly into an FT reactor. With the promise of dramatically improved recuperator technology, the process should be able to achieve efficiency above 65% of theoretical limits at low cost. The ultra-low pressure drops in advanced recuperators are as important to RWGS performance as their high effectiveness and expected low cost.

Table 3. Capital Cost Estimate – Syngas for 1 kg/s fuels

| Description | Details | Cost, \$M |
|---|---|---|
| Electrolyzer | 220 $MW_P$ | 33 |
| Hydrogen storage tanks | 25 tonnes $H_2$ | 9 |
| $O_2$ liquefaction system | 1000 t storage | 5 |
| Recuperators | 12 MW, $T_\delta$=30 K | 3 |
| Shell & tube reactor | 900 kW, 950 K | 1 |
| Final reactant preheaters | 2.5 MW | 1 |
| Compressor | 1000 hp | 0.8 |
| RWGS catalyst | 4 tons | 0.2 |
| Condensers | 3 MW | 0.2 |
| Adiabatic reactors | 2 $m^3$ | 0.1 |
| Controls, fans, ducts... | misc | 0.7 |
| Total | | 54 |

Two stages may also achieve sufficient $CO_2$ conversion with known catalysts. Using two stages would require higher temperatures and would reduce the amount of heat recuperation required, but it still may increase system cost. Using three stages would make it easier to achieve high $CO_2$ conversion with low methanation and longer catalyst lifetime. The effect of the number of stages on efficiency is minor.

The largest unknown at this point is the cost of the high-ε recuperators as a function of temperature. The long-term stability of the recuperator surface coating needed for passivation, presumably carbon or silver, is also unknown.

The detailed analysis and simulations of multi-stage RWGS processes promise a dramatic improvement in both efficiency and cost effectiveness in the reduction of $CO_2$ to CO compared to the more widely explored routes using high-temperature solar-driven thermo-chemical conversion.

## APPENDIX A. RFTS MASS BALANCE.

For the production of alkenes in the FT reaction subsequent to the RWGS, precisely half of the $H_2$ goes into the HCs and half goes into water (assuming no parasitic WGS). For alkanes, the water consumes a little less than half. For example, for decane (the desired center of the distribution for gasoline and jet fuel),

$$10CO + 21H_2 \rightarrow C_{10}H_{22} + 10H_2O \qquad \text{(A1)}$$
$$\Delta H_{600K} = -1634 \text{ kJ/mol.}$$

In the FT-HT reactor with fused iron catalysts at the expected conditions, most of the product yield will be alkanes and alkenes – both mostly in the C3-C20 range. There will also be some (~8%) CO-methanation,

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad \text{(A2)}$$
$$\Delta H_{600K} = -218 \text{ kJ/mol,}$$

in which two-thirds of the $H_2$ goes into (low-value) methane and one-third into water. As the HT-FT reactor may produce ~4% $C_2H_6$, a separate accounting for it can be worthwhile:

$$2CO + 3H_2 \rightarrow C_2H_6 + 2H_2O \qquad \text{(A3)}$$
$$\Delta H_{600K} = -366 \text{ kJ/mol.}$$

At the high operating pressures we anticipate, about 10% of the yield will be alcohols and other oxygenates. For ethanol, 75% of the $H_2$ goes into the product,

$$2CO + 4H_2 \rightarrow C_2H_5OH + H_2O \qquad \text{(A4)}$$
$$\Delta H = -272 \text{ kJ/mol.}$$

Of course, there will be WGS in the FT reactor converting some of the water and CO into $H_2$ and $CO_2$. However, this has no net effect on the total amount of new-source $H_2$ needed (in a system with full recycle), as each molecule of $H_2$ produced from WGS in the FT reactor requires another molecule of $H_2$ in the RWGS reactor to produce the CO the FT-WGS consumes. Likewise, the WGS has no effect on carbon balance, so the FT-WGS can be ignored for purposes of estimating total (source) $H_2$ and carbon requirements.

Minor amounts of other HCs and oxygenates will also be produced, but it is sufficient here to assume their $H_2$ and CO reactant requirements are similar to those of alkenes or ethanol respectively and include them there. Hence, the required amounts of $H_2$ and C for the FT reactions with HCs centered at C10 are approximately

$$m_H = 21/71 * m_A + 2/7 * m_B + 3/8 * m_M + 4/23 * m_O \qquad \text{(A5)}$$

$$m_C = 60/71 * m_A + 6/7 * m_B + 3/4 * m_M + 12/23 * m_O \qquad \text{(A6)}$$

where $m_A$, $m_B$, $m_M$, and $m_O$ are the amounts of alkanes, alkenes, methane, and oxygenates respectively.

The accuracy of the above expressions can be improved by listing more of the products separately, starting with ethane, as noted earlier. The $H_2$ needed for the CO required from the RWGS reactor is simply 1/6 of the carbon requirement. The oxygen (chemically) in the fuel is ~35% of the oxygenates.

For illustration purposes, we have chosen to look at total production of 1 kg/s with the following yield assumptions: 35% $C_{3+}$ alkanes, 9% oxygenates (mostly ethanol), 8% $CH_4$, 4% $C_2H_6$, and 45% olefins and other HCs, mostly in the gasoline and jet fuel ranges. In this case, using the above equations, the $H_2$ and C required for the FT reactor are 0.284 kg/s and 0.812 kg/s respectively. (The sum here is 1.096 kg/s, even though the fuel produced also includes 0.03 kg/s oxygen, because 0.131 kg/s of the $H_2$ leaves the reactor in the 1.18 kg/s water it produces. Most of the $C_2H_6$ actually begins as $C_2H_4$, but gets hydrogenated to $C_2H_6$ before leaving the system.) The additional $H_2$ required for the RWGS reactor to reduce 2.98 kg-$CO_2$/s to CO is 0.135 kg/s. Hence, the total $H_2$ required is 0.42 kg/s. Almost all of the oxygen in the source $CO_2$ ends up in water, either from the RWGS or the FT reactors.

A more detailed accounting than above was carried out for the complete expected yield distribution, and it came up with slightly different numbers for the needed inputs for 1 kg/s FTS products: 0.412 kg/s $H_2$, and 0.78 kg/s C.

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