

HIGH TEMPERATURE REACTOR: DRIVING FORCE TO CONVERT CO₂ TO FUEL

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ABSTRACT

The rapidly increasing cost of petroleum products and uncertainty of long-term supply have prompted the U.S. military to aggressively pursue production of alternative fuels (synfuels) such as coal-to-liquids (CTL). U.S. Air Force is particularly active in this effort while the entire military is involved in simultaneously developing fuel specifications for alternative fuels that enable a single fuel for the entire battle space; all ground vehicles, aircraft and fuel cells. By limiting its focus on coal, tar sands and oil shale resources, the military risks violating federal law which requires the use of synfuels that have lifecycle greenhouse gas emissions less than or equal to emissions from conventional petroleum fuels.

A climate-friendly option would use a high temperature nuclear reactor to split water. The hydrogen (H₂) would be used in the reverse water gas shift (RWGS) to react with carbon dioxide (CO₂) to produce carbon monoxide (CO) and water. The oxygen (O₂) would be fed into a supercritical (SC) coal furnace. The flue gas CO₂ emissions would be stripped of impurities before reacting with H₂ in a RWGS process. Resultant carbon monoxide (CO) is fed, with additional H₂, (extra H₂ needed to adjust the stoichiometry: 2 moles H₂ to one mole CO) into a conventional Fischer-Tropsch synthesis (FTS) to produce a heavy wax which is cracked and isomerized and refined to Jet Propulsion 8 (JP-8) and Jet Propulsion 5 (JP-5) fuels.

The entire process offers valuable carbon-offsets and multiple products that contribute to lower synfuel costs and to comply

with the federal limitation imposed on synfuel purchases. While the entire process is not commercially available, component parts are being researched; their physical and chemical properties understood and some are state-of-the-art technologies. An international consortium should complete physical, chemical and economic flow sheets to determine the feasibility of this concept that, if pursued, has broad applications to military and civilian aviation fleets and freight-hauling diesel engines.

I. INTRODUCTION

Transportation fuel availability and cost are currently dominating global energy concerns among oil-importing nations and sectors. Aviation and military fuel demands appear most vulnerable since the former has no alternative and the latter invokes national security prerogatives.

The U.S. Department of Defense (DOD) appears intent on encouraging private sector investment in production of synthetic fuels from coal and oil shale as secure, domestic sources of aviation fuel and possibly the single fuel it will use for the entire battle fleet. If national security were the only concern of the U.S. government, CTL and oil shale projects would seem prudent investments. However, international concern about increasing concentrations of climate-forcing atmospheric gases may soon impose severe economic penalties on CO₂ emissions if negotiated treaties requiring their reduction are enforced.

In a CO₂-regulated future compounded by diminishing oil reserves, those two dynamics will dictate decisions on where and how DOD and aviation fuel sources are acquired. This paper uses that future as a backdrop to propose a complex and advanced alternative to conventional petroleum that might appear impractical today but could transform pollution into profits, secure a future for coal in the electric power sector and satisfy domestic demand for diesel and aviation fuels.

By utilizing high temperature nuclear reactor exit gas to split H₂ and O₂ from water, the O₂ could be fed into a highly efficient coal-burning boiler and the H₂ used to react with the boiler's CO₂ to create a feedstock for a Fischer-Tropsch system (FTS) to produce synthetic fuels. This concept also presents a less complex mix of technologies but relies upon nuclear reactors to produce the H₂ and O₂. The coal-fired electric power plant is an added (not essential) feature that generates power for the grid and FTS plant as well as additional revenue to the entire synfuel project.

II. MILITARY INTEREST IN SYNFUELS INDUSTRY

A DOD OFFENSIVE ON FUEL SUPPLY/COST

The DOD has an abiding concern about increasing U.S. dependence on foreign oil and rising fuel costs for the military and how they relate to national security and defense capabilities. In 2006, the Pentagon charged the JASON, [1] an independent group of scientists advising the United States government on matters of science and technology, with assessing means to reduce the DOD's dependence on fossil fuels.

Based on proven reserves, estimated resources, and the rate of discovery of new resources, no extended worldwide shortage of fossil-fuel production was reasonably expected over the next 25 years. While long term availability of aviation fuel was not a priority concern, the JASON report relied upon U.S. Energy Information Agency (EIA) oil price projections of \$40-\$50/barrel within the next few years based, in part, upon a forecast that increased production and refining capacity will match global demand. The International Energy Agency (IEA) does not share that optimism.

The IEA projected a supply deficit of 12.5 million barrels per day by 2015 [2] above current planned production. This is a decisive shift from earlier, more positive supply estimates and indicative of a recent and repeated global impression that major oil fields in leading oil-producing nations may soon, or have already reached their production plateau without new fields of comparable reserves coming on line. The May 2008 benchmark crude broke a record by closing at \$136/bbl on the New York Mercantile Exchange doubling the price of the previous May. Now, it is generally accepted that oil could one day exceed \$150-\$200 per barrel and likely not return to a

price below \$100. For the U.S. Air Force, the cost of jet fuel has become of paramount concern. In fiscal year 2007, DOD consumed almost 4.8 billion gallons of mobility fuel and the Air Force share was 2.6 billion [3] gallons. For the Air Force, the fuel bill last year was nearly \$6 billion; triple its 2003 \$2 billion fuel cost.

Air Force estimates a \$10/bbl rise in the price of oil costs add an additional \$600 million to the fuel bill. Operating a fleet of 6,000 aircraft (a B-52 bomber can burn 47,000 gallons of JP8 in a single mission) around the globe has become a serious challenge and DOD is in battle-mode searching for alternative means to assure adequate supply and cost control.

DOD ALTERNATIVE FUELS PROGRAM

The Air Force purchased gas-to-liquid synfuels from domestic producers and Shell's Malaysia operation for aircraft engine tests and performance. Thus far, a 50-50 blend of synthetic and petroleum-based fuels has been successfully tested in the B-52, C-17 and the B-1 bomber. The Air Force intends to certify the use of the synfuel in every plane-type by 2011. This synfuel certification program is the first step in the long-term plan to fuel half of the North American fleet with a synfuel blend of 50-50 by 2016. That would require 400 million gallons of coal-based synfuels. [4]

In addition to pursuing alternative fuel for the Air Force fleet of aircraft, DOD initiated a program to develop a Joint Battlespace-Use Fuel of the Future (JBUFF); a single fuel for all the military's gas turbine and tactical diesel engine applications. This fuel must comply with JP-8 or JP-5 specifications. JP-8 is virtually identical to Jet A-1 commercial aviation turbine fuel. JP-5 meets requirements of aviation fuel used on aircraft carriers where its higher flashpoint provides an additional degree of safety in fuels handling.

The JBUFF program may, by virtue of its single fuel objective, limit technologies to those producing high energy density fuels. Ethanol has only 60% the energy content of Jet-A and would require much larger plane engines and wings to store the fuel thus add weight to the plane and reducing its fuel efficiency. Consequently, DOD is giving a priority focus to alternative fuels derived from the FTS method of processing coal, natural gas, and biomass-coal blend feed stocks.

As evidence, the Pentagon's Defense Logistics Agency issued, in 2006, an RFI to identify potential sources of synthetic fuels for aviation purposes that meet FTS fuels specification for delivery to Air Force and Navy installations for multiple weapons systems testing and subsequent use. Air Force requested 100 MMgal. of JP-8 and the Navy requested 100 MMgal. of JP-5. [5]

Of the 28 firms responding, 20 of 22 intending to manufacture the synfuel proposed to use domestic coal in a FTS coal-to-liquid process. The JBUFF objective is being advanced by the promise of coal liquefaction.

Congress is encouraging the JBUFF initiative while trying to balance its concern regarding U.S. carbon dioxide (CO₂) emissions contributing to global warming. The Energy Independence and Security Act of 2007 included Section 526 prohibiting federal agencies from buying alternative or synthetic fuels unless their lifecycle greenhouse gas emissions associated with production and combustion are less than or equal to such emissions from the fuels produced from conventional petroleum sources. [6]

In the case of FTS CTL plants, CO₂ emissions are 1.8 times that of crude oil production and refinement. Sponsors of CTL plants will have to guarantee CO₂ will be captured and permanently disposed to qualify under Section 526. Carbon Capture and Sequestration (CCS) is used on a small-scale where CO₂ is piped to oil and gas fields to enhance recovery. Proven commercial-scale CCS of the hundreds of millions of tons of CO₂ emitted by a mature CTL industry is not likely before 2025 according to US government estimates. Alberta's CO₂-intensive oil sands industry sees Section 526 barring its synthetic crude oil from sale to DOD and has launched an aggressive effort to reverse that constraint. ⁽¹⁾

Banking on the promise of CCS technology, the Air Force has issued tentative plans to lease property at Malmstrom Air Force Base in Montana for private sector design, construction and operation of a CTL facility. It has the enthusiastic support of coal-state legislators and President Bush who share the commitment to reduce oil imports by relying upon America's vast coal resources. That goal has obvious merit as does the Pentagon's single fuel endeavor but they share a fundamental weakness; namely, reliance upon coal-based technologies to accomplish both goals without the certainty of CCS technologies. Meanwhile, the U.S. Congress, European Union and United Nations Framework Convention on Climate Change have mutual interests that may soon conflict with interests being pursued by the Pentagon.

The U.S. political attitude toward global agreement on climate change mitigation is anticipating a sweeping change following the Presidential election and European efforts to jumpstart the international compliance with carbon mitigation schemes are well underway and EU leaders intend to make CO₂ reduction measures apply to American companies as well. For the global aviation industry, it is just a matter of time before passengers begin paying for the CO₂ their travel emits.

⁽¹⁾ The pending fiscal year 2009 Defense Appropriation Act includes an amendment designed to weaken restrictions imposed by Section 526. At this writing, it is unclear the Congress will complete action on this legislation.

Currently, the EU maintains an Emission Trading Scheme (ETS) that is the cornerstone of its regulatory approach to curbing global warming. In July, the European Parliament voted to include airlines in the scheme requiring a 3% CO₂ emission cut by 2012 and 5% thereafter. While military flights will be exempt, international flights regardless of origin will be included and required to purchase CO₂ E.U allocation credits. [7] EU allocations for delivery in December 2008 traded at \$US eq. of \$36.81/ton CO₂. The Republic of Germany issued about 4 million tons of CO₂ allowances in April at an average cost of US\$35 equiv/ton.

How the ETS credit cost will affect international air travel is illustrated by the following example: A Boeing 747 carrying 500 passengers averages 5 gpm of fuel [8]. Round trip distance is 9440 miles. Total fuel consumed is 47,200 gallons and at 21.095 lb. CO₂/gal JA-1, CO₂ emissions would total 498 tons. At \$35 allocation credit, the entire flight would cost an additional \$17,424 or a ticket increase of \$34. While that fare increase may not appear prohibitive, add the additional cost of higher priced fuel and cross-oceanic flight begins to take on individual budget considerations that may cause a reduction in passenger numbers and airlines.

The Air Force and civilian aviation are joined in a two front battle to survive diminishing oil supplies driving up per barrel price and the economic impact of regulating global CO₂ emissions. What are the options the military can employ and how can they benefit the civilian aircraft fleet?

III. CHARACTERISTICS OF AVIATION FUEL

DOD faces challenges beyond its priority tasks to plan, prepare for and deploy to more than one theater of action anytime, anywhere in the world. Its resources, manpower and planning capabilities are constrained by a massive deployment of troops and material to the Middle East, severe federal fiscal constraints, global oil supply and price tensions and certainty that there will be limits imposed on emissions of global warming gases. Within the confines of any one of these boundaries, DOD must focus on technologies with commercial application and production capacities sufficient to serve the largest fuel consumer in America. It has two fundamental questions regarding the search for that appropriate fuel: How big is it? How much does it weigh?

Based on the volumetric energy density of fuels in Table 1 FTS is the likely candidate technology on which the private sector- encouraged by DOD- will concentrate in the near term.

Table 1. Volumetric (NET) Energy Density of Fuels

Fuel	MJ/L	MJ/kg
Fischer-Tropsch Synfuel	33.6	44.2
Jet A/Jet A-1	34.9	43.2
Liquid Hydrogen	8.4	120
Liquid Methane	21.2	50
Methanol	15.9	19.9
Ethanol	21.6	27.2
Premium Gasoline *	32.9	43.85
Biodiesel	33.9	38.9
Aviation Gasoline	33.5	46.8

* New Zealand Energy Data File, June 2008 [9]

The DOD pursuit of a single fuel for all the military’s gas turbine and tactical diesel engine applications creates a very narrow field of fuel choices since that fuel must comply with JP-8 or JP-5 specifications. There will be only one jet fuel specification since there is only one supply chain. Therefore, a change in property limits will apply to all jet fuels for military and commercial aviation fleets. Table 2 illustrates that narrow band of technology choices relative to conventional jet fuel

TABLE 2. ALTERNATIVE FUEL SPECIFIC CHARACTERISTICS

FUEL COMPARISONS			
	CONVENTIONAL	FTS FUEL	SASOL C-T-L
	JET FUEL		
SPEC ENERGY	43.26 MJ/kg	44.19 Mj/KG	43.7 Mj/KG
	18,600 Btu/lb	19,000 Btu/lb	18,788 Btu/lb
SPEC GRAVITY	798 kg/m3	754 kg/m3	781 kg/m3

Source: [10]

III. FTS, CONVENTIONAL OIL AND CO₂

FTS was discovered 88 years ago by German chemists Franz Fischer and Hans Tropsch as a process to convert the synthesis gas derived from carbon sources such as coal, peat and natural gas into hydrocarbons and oxygenates. During World War II the German military powered its vehicles and fueled its Luftwaffe with synthetic fuels processed from 25 plants making 6.4 million tons of product in 1944.

Currently FTS technology is utilized by Sasol Synfuels (pty) Limited, which South Africa founded in 1950 to produce liquid petroleum fuels from its vast coal deposits. When the U.N. sanctioned an international oil embargo against South Africa, one-third of the nation’s oil demand was met using FTS. In 2007, Sasol’s S.A. complex produced 51x10⁶ bbl/YR of petroleum products and earned the distinction of being the largest CO₂ emitting source in the world. Table 3 identifies CO₂ emissions by plant and equipment sources

TABLE 3. CO₂ EMISSIONS FROM SASOL SOUTH AFRICAN PLANTS

PLANT	CO ₂ SOURCE	CO ₂	CO ₂
		MMTPY	CONCEN
Sasol 1	Boilers& Heaters	7	10-15%
Sasolburg	Downstream Gasifiers	4	90-98%
Sasol 2	Boilers& Heaters	9	10-15%
Secunda	Downstream Gasifiers	14	90-98%
Sasol 3	Boilers& Heaters	9	10-15%
Secunda	Downstream Gasifiers	14	90-98%
TOTAL		57	

Source: [11]

Carbon dioxide is not a regulated “criteria pollutant” under the U.S. Clean Air Act. However, the U. S. Supreme Court, in April 2007, found that: “Because greenhouse gases fit well within the (Clean Air) Act’s capacious definition of “air pollutant”, EPA has statutory authority to regulate emissions of such gases from new motor vehicles”. [12]

While estimates vary on CO₂ emissions from production of conventional oil versus several current synthetic oil production processes, Table 4 is an approximation for the purpose of comparing alternative fuel options the DOD has with respect to the requirements under Section 526.

TABLE 4. CO₂ FROM CONVENTIONAL AND UNCONVENTIONAL PROCESSES

UPSTREAM EMISSIONS (KG CO ₂ /BBL)		
FUEL OR FUEL PROCESS	LOW	HIGH
	EMISSIONS	EMISSIONS
Gasoline	137	
Diesel	108	
Oil Sands	228	387
Expanded Oil Recovery	149	233
Oil Shale	318	1224
Gas to Liquids	174	233
Coal To Liquids (FTS)	507	700

Source: [13]

IV. COAL: FROM NECESSITY TO INVENTION

As the DOD progresses to develop specifications and complete testing of alternative fuels to select a single fuel for the entire battle space (the JBUFF Program) capitalization, construction and operation of the facilities will not fall upon the Department. Instead, it intends to catalyze the private sector to produce the fuels and provide all incentives needed

to accomplish that objective by taking down impediments that hinder investment and production.

The private sector has a very narrow choice of technologies and feedstock from which to choose as it enters the one-fuel-fits-all competition. This paper will assume the off-the-shelf technology of choice for industry suppliers of alternative fuels will be the FTS process. Currently viable feedstocks for FTS are coal, natural gas, biomass and a coal-biomass mixture.

When the DOD chooses the appropriate single fuel there be a tedious transition while the synfuel industry gradually develops to meet a 100 million gallon annual demand by 2012 [14]. If the entire synfuel demand was derived from a single feedstock, the following is an estimate of total resource demand for the FTS process based on feedstock design:

Coal (IL #6)	875 thousand tons	⁽²⁾
Biomass	875 thousand tons	
Natural Gas	.017 bcf	[15]

Resource availability and cost of delivery will weigh heavily on feedstock options but a yet to be determined additional cost burden might have greater impact (i.e. eventual penalty cost per ton of CO₂ emitted).

On a per barrel basis, FTS CO₂ emissions ⁽³⁾ for each of the feedstock choices accentuate the challenge facing DOD to balance single-fuel costs with environmental requirements (assuming a penalty of \$5-\$15/ton CO₂ emitted without allocated or purchased credit).

Coal (IL #6)	2.1 MMTPY CO ₂ = \$ 10.2 - \$ 31 million
Biomass	88 MMTPY CO ₂ = \$.440 - \$ 1.320 billion
Natural Gas	15 MMTPY/ CO ₂ = \$ 75 - \$ 225 million

Fuel costs for coal and natural gas are affected by world oil prices. According the U.S. EIA July 18 price for Illinois basin coal (11,800 Btu/lb) was \$70/ton and Henry Hub natural gas price was \$11.15/mcf.

In a CO₂ regulated environment, the DOD might be faced with the prospect that its single-fuel objective will prove expensive and fall back upon conventional petroleum products despite the longer term risks. Or, its focus on encouraging C-T-L will motivate government R&D of technologies designed to reduce CO₂ emissions and reduce product costs and possibly generate CO₂ offsets as an ancillary benefit. In fact, a possible answer for DOD and commercial aviation fuel requirements, in the long term, could very likely be built around converting coal's CO₂ emissions to a feedstock for synthetic fuels production.

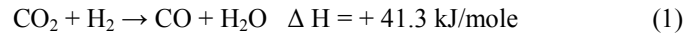
⁽²⁾ Estimates derived from "Life-Cycle Greenhouse Gas Emissions Inventory For Fischer-Tropsch Fuels"; see [15]

⁽³⁾ See footnote 1, @ pg. 33.

V. CARBON DIOXIDE AS A FUEL RESOURCE

The reverse water gas shift (RWGS) reaction is a common industrial process that has been widely used in chemical plants for many years where the adjustment of the relative amounts of CO₂, CO and H₂ is important.

The RWGS reaction is:



It could become the backbone of a unique synthetic fuel production strategy that melds high temperature nuclear reactors to coal-burning electric generation plants for the purpose of providing a conventional FTS plant with its CO feedstock and reduced CO₂ emissions.

A configuration of the several technologies involved -and in sequence of their performance- is as follows and proposed in scale sufficient to supply H₂ to the RWGS and O₂ to a 400 MW supercritical coal-fired electric generation power plant burning Illinois #6 coal and operating at 85% on-line factor:

- a.) High temperature nuclear reactor drives a high temperature electrolysis or thermo-chemical Sulfur-Iodine water-splitting process.
- b.) Product oxygen is piped to an adjacent supercritical coal-fired electric boiler to replace combustion air.
- c.) The coal furnace flue gas - primarily CO₂ and H₂O - is cooled, stripped of H₂O and impurities and piped to the RWGS where it is reacted with H₂ derived from the water splitting process
- d.) From the RWGS reaction, the CO is fed into an FTS process and the product heavy wax is refined to JP-8 specifications or specifications set by the DOD's single fuel requirements.
- e.) Any additional O₂ produced from the various water-splitting processes can be marketed for commercial use but this may have limited potential if no ready markets exit in the vicinity of the FTS plant (piping O₂ over a distance imposes safety risks).

This configuration of technologies and processes has never been assembled on a bench-scale or demonstration level.

The chemical reactions are initially driven by temperatures exceeding 850°C and limit the heat source to a nuclear reactor or solar collector apparatus.

In the realm of nuclear reactors, it is the exit heat temperature that will determine the reactor choice. Since H₂ is a reacting agent for initiating the conversion of CO₂ to the CO feedstock for a FTS process, high temperature heat delivery to the several electrolysis and thermo chemical water-splitting processes available to produce H₂ is paramount.

CANDIDATE NUCLEAR HEAT SOURCES:

- Advanced light water reactors
 - Supercritical Water-Cooled Reactor (SWCR)
 - Advanced Pressurized Water Reactor (APWR)
 - Simplified Boiling Water Reactor (SBWR)
- Advanced liquid-metal-cooled reactors
 - Sodium-cooled Fast Reactor (SFR)
 - Pb/Pb-Bi Cooled Fast Reactor (LFR)
- Advanced high temperature reactors
 - Pebble bed/Modular Helium Reactor (PBMR)
 - Advanced Gas Reactor (AGR)
 - Gas Fast Reactor (GFR)
 - Advanced High Temp. Reactor (AHTR)
 - High-Temperature Fuel, Molten Salt Coolant
 - General Atomics Modular Helium Reactor [16]

The high temperature H₂ production technologies considered chemically understood but not yet feasible at scales envisioned in this concept are high temperature steam electrolysis (HTSE) and Sulfur-Iodine Thermo chemical Process (SI). [17]

Figure 1 provides a graphic value given to high temperature exit heat by plotting the energy efficiencies (η_{H}) of the HTSE and SI against the exit temperature. In the figure, the AGR-SCO₂ HTSE is an advanced gas-cooled reactor supercritical CO₂ power cycle to produce H₂ using high temperature steam electrolysis. Considerable research and development are required before either process can be considered ready for commercial deployment

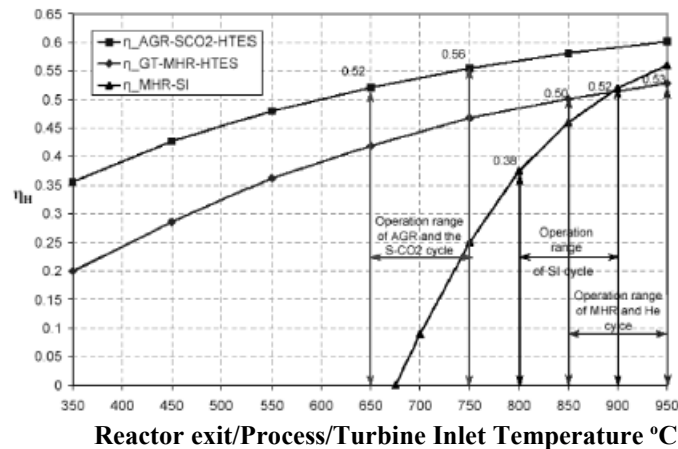
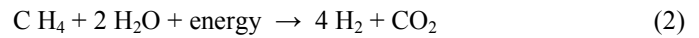


Figure 1. Comparison of thermal-to-hydrogen efficiencies of High Temperature Electrolysis and SI thermochemical processes. [18]

VI. Water Splitting And ASU Process for H₂ AND O₂

(A) STEAM METHANE REFORMATION

H₂ production in the U.S. is 11 million TPY and 95% is derived from the process of steam reforming of methane (SMR) involving endothermic reaction of methane with high temperature steam according to the reaction:



Each gram of H₂ requires 2.0 g of methane and 4.5 g steam and has a CO₂ intensity of 5.5 kg per kg of H₂ produced. Based on U.S. H₂ production by SMR, \approx 60 MM TPY CO₂ is emitted while using \approx 6 % of U.S. natural gas consumption.

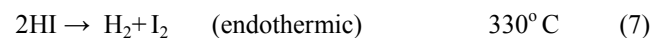
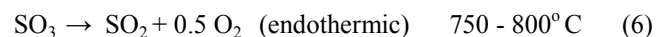
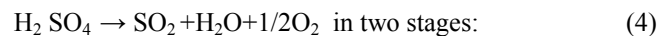
(B) WATER ELECTROLYSIS

Conventional water electrolysis has an efficiency of about 80% converting electric energy into hydrogen energy (requiring \sim 54 kWh/kg H₂). However, the modest conversion efficiency rating of a low temperature reactor or fossil fired electric generation unit, on the order of 32-35% reduces the overall electrolysis efficiency and increases capital and O&M costs for masses of H₂ and O₂ required in this proposed concept of recycling CO₂. For a 400 MW SC coal-fired oxy-combustion unit about a 2MMTPY O₂ is required. Using conventional water electrolysis would require 1,650 MW generating capacity and emit 9 MMTPY CO₂.

(C) THERMOCHEMICAL WATER-SPLITTING

Hydrogen production by direct thermal decomposition of water requires high temperature heat of several thousand Kelvin. By combining high temperature endothermic chemical reactions and low-temperature exothermic chemical reactions, it is possible to decompose water at lower temperatures. [19]

One of the most promising cycles is the Sulfur-Iodine Thermo-Chemical Process (SI). It consists of three chemical reactions using heat with temperatures lower than 1000° C:



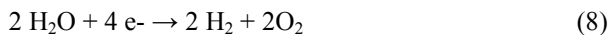
While the SI appears to be a potential water-splitting process, on a conversion efficiency basis, it is a highly complex and corrosive technology reliant upon Iodine, which is relatively

scarce and expensive. Any cyclic process is sensitive to material loss that must be replaced and treated as a possible environmental contaminant. A SI hydrogen production plant coupled to a 600 MW high temperature reactor requires \approx 3000 tons of recycling Iodine. [20] Contract Iodine prices range from \$14 to \$15/kg. The Iodine cost would exceed \$38 million. Chile is the largest Iodine-producing country and, in 2002, exported roughly 10,000 metric tons (51 percent of the global market). [21]

(D) HIGH TEMPERATURE STEAM ELECTROLYSIS

High-temperature steam electrolysis uses electricity to produce H_2 from steam. High-temperature electrolysis is more efficient than conventional room-temperature electrolysis because some of the energy is supplied as heat that is cheaper than electricity. Electrolysis reaction is more efficient at higher temperatures.

The electrolytic cell consists of a solid oxide electrolyte with conducting electrodes deposited on each side of an electrolyte. A mixture of steam and H_2 at 750-950°C is supplied to the cathode. At the cathode-electrolyte interface, it comes to the reaction:



Upper bound of efficiency of high temperature electrolysis has been estimated to 51% [22].

(E) AIR SEPARATION UNIT

Assuming an air separation unit (ASU) is used to produce O_2 , a 2002 National Energy Technology Laboratory comparison of advanced fossil power systems provides an estimate of the energy demand. The ASU produced 7570 tpd O_2 and consumed 64 MW and 34 MW to compress the CO_2 -rich stream. The 98 MW demand (parasitic power) equates to 730×10^6 kWh and at 0.7 kg CO_2 /kWh would emit 562,000TPY CO_2 . [23]

VII. COMBINING THE COMPONENTS

We propose a technology option that replaces the ASU and its energy demand and CO_2 emissions. Its total assemblage is chemically and physically complex, not commercially available even on a small scale and its economic viability has yet to be evaluated. Nonetheless, it is made up of a sequence of processes that are being vigorously researched (high temperature electrolysis, high temperature nuclear reactors, RWGS reaction and SI thermochemical water splitting) and commercially deployed (e.g., SASOL's FTS plants and oxy-combustion coal boilers). It culminates in hydrogenation of the CO_2 captured from a coal-fired power plant, thus turning that looming environmental problem into a resource and

finally a vital and domestic fuel. Figure 2 provides the complete block diagram for this option.

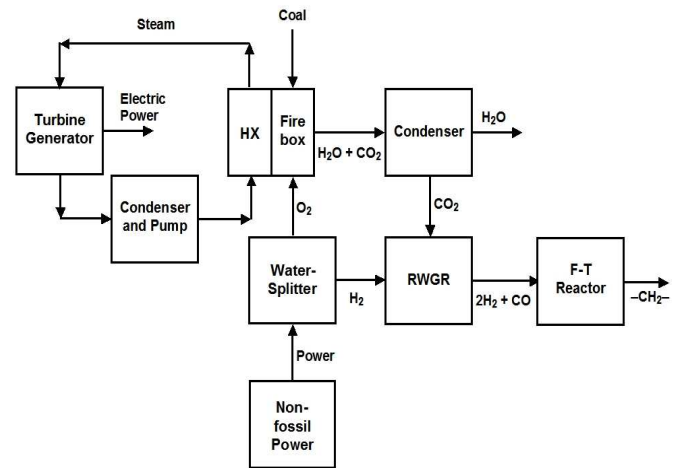


Figure 2. An Oxy-fuel Coal Plant and FTS with H_2 and O_2 supplied from HTR-driven Water Splitting [24]

(A) COAL-FIRED OXY-COMBUSTION

As fuel is burned in air, CO_2 concentration is only about 15% of the flue gas and poses a high-energy penalty if its capture and removal are required. By feeding O_2 (95% purity or higher) into a SC coal-fired boiler the overall efficiency of the boiler increase from 33-35% to 44-48% and the CO_2 flue gas concentration increases to $\geq 90\%$. Typical temperatures with air combustion are about 3,000°F (1649°C), whereas temperatures with conventional oxygen-enriched systems can rise to 5,000°F (2760°C). Temperatures above a certain level (about 2,000°F (1093°C) create extra wear on the furnace refractory and cause increased NO_x emissions. To control furnace temperature about 70-80% of the CO_2 exhaust gas is recycled back to the boiler to control the combustion temperature. The remainder of the fuel gas comprised mainly of CO_2 and H_2O , SO_2 , N_2 , NO_x other constituents from air leakage and elements in the fuel are stripped and cleaned.

Fuel costs are lower and the monoethanolamine CO_2 separation process with its energy penalty of $\approx 29\%$ or chilled ammonia separation process with its 10% parasitic energy demand are avoided.

(B) CO_2 HYDROGENATION (RWGS)

The reduction of CO_2 by H_2 , which constitutes the reverse water-gas shift reaction, is an active area of research because of its connection with the production of methanol and other fuels.

The reaction temperature range required could only be provided by the utilization of high temperature nuclear reactors such as identified in Section V.

Figure 3 illustrates the equilibrium CO₂ as a function of higher temperatures for 1:1, 3:1 and 4:1 H₂:CO gas compositions.

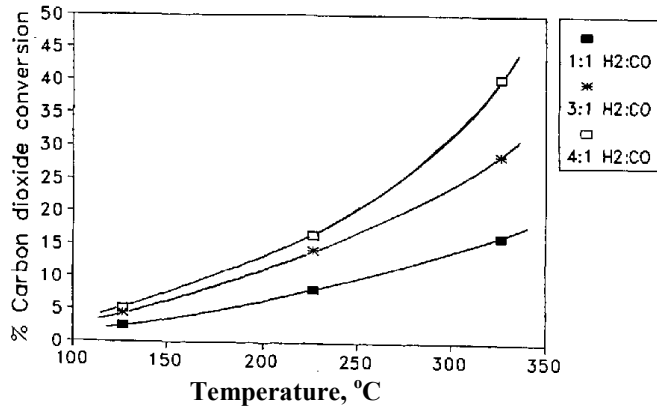


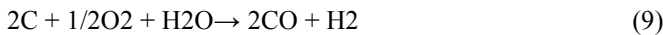
Figure 3: CO₂ Conversion Efficiency in Reverse Water Gas Shift Reaction as a Function of Higher Temperature

(C) FROM CO TO FISCHER-TROPSCH FUELS

FTS is a complex network of parallel and series reactions and is a carbon chain building process wherein CH₂ groups are attached to the carbon chain. It involves catalytic reaction of H₂ and CO to form hydrocarbon chains of various lengths and its major by-product is H₂O.

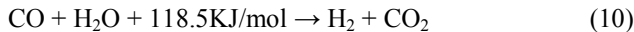
A more thorough examination of the FTS is not required in this paper and focus is given to the FTS net reaction:

For coal, synthesis gas is produced according to the net reaction:



From gasification synthesis gas (2CO + H₂),

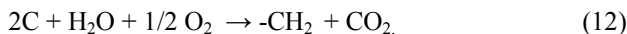
the water-gas shift can be used to produce additional H₂:



leads to the FTS reaction



The net reaction is:



Two carbons produce one FTS product (CH₂) while the other carbon is emitted as CO₂. How to achieve product while limiting CO₂ emissions is the challenge DOD and the

(3) See reference [26]

(4) @ 7.076 (API 35) pounds/gallon diesel

commercial aviation industry must solve. We propose to avoid the CO₂ emissions in the synthesis gas process by utilizing captured CO₂ from the coal-burning power plant and, through the RWGS, deliver the CO directly to the FTS.

A 400 MW SC power plant burning 23.3 MMBtu/ton IL #6 coal operating at 85% online factor and heat rate of 9000 Btu/kWh emitting $\approx 2.3 \times 10^6$ TPY CO₂ (0.7 kg CO₂/kWh) will be used to illustrate the components of the concept.

(D) O₂ and H₂ PRODUCTION

The 400 MW SC plant's 2.3×10^6 CO₂ TPY will be reacted with H₂ to produce CO and H₂O for the FTS plant. HTSE and S-I water splitting will be the technologies used to produce the needed $\approx 1 \times 10^6$ kg H₂. CO₂ emissions are compared for nuclear-powered HTSE and S-I and the conventional electrolysis with electricity derived from a SC plant burning the IL #6 coal. Electrolysis at ≈ 54 kWh/kg H₂ would require about 2000 MW of electric generating capacity to produce the needed $\approx 1 \times 10^6$ kg H₂ and, if fired by coal, emit 2.4×10^6 TPY CO₂. A 2400 MW high temperature nuclear reactor⁽³⁾ (90% online factor and life cycle value of .020-.025 kg CO₂/kWh) would emit $416 \times 10^3 - 520 \times 10^3$ TPY CO₂. [26]

(E) FTS SYN FUEL FROM CAPTURED CO₂

Schultz, et.al. have proposed a novel concept they call "twice burned coal" or "recycled coal", wherein the carbon in the coal is used once for electric power production and the emitted CO₂ captured, hydrogenated and delivered as CO to an FTS plant. This is the essence of their concept:

- SC oxy-combustion power plant burns 1.2 million tons of coal to deliver steam to turbines generating 2.98×10^6 gross MWh/yr with no CO₂ emissions;
- Captured CO₂ will be reacted with H₂
- The resultant CO is then processed in an FTS with no CO₂ emissions – just fuel and lots of H₂O.

Using mass equivalent data provided by Bogart [28] the following is an estimate of the volume of fuel processed.

Several mass equivalents from stoichiometry:

H ₂ to CH ₂	0.429 kg H ₂ / kgCH ₂
CO ₂ to CH ₂	3.143 kgCO ₂ / kg
H ₂ O from FTS	2.571 kgH ₂ O / kg CH ₂

O₂ demand in the SC boiler will be $\approx 2.67 \times 10^6$ tons O₂ TPY. H₂:O₂ ratio for water splitting is 1:8. Thus, $\approx 333 \times 10^3$ TPY H₂ will be available for the RWGS. Calculating the FTS product:

$$\begin{aligned} @ .429 \text{ kg H}_2/\text{kg CH}_2 &= 706 \times 10^6 \text{ kgCH}_2 = 219 \times 10^6 \text{ gal}^{(4)} \text{ CH}_2/\text{YR} \\ @ .85 \text{ on line factor} &= 708 \times 10^3 \text{ gal/day} = 17 \times 10^3 \text{ bbl/day} \\ &= 5.2 \times 10^6 \text{ bbl/YR (compared to Sasol's } 51 \times 10^6 \text{ bbl/YR)} \end{aligned}$$

From Table 4, we can now calculate the gross revenue stream this novel concept can accrue. For electric sale, we use a wholesale price (the average of the weighted average for the first 6 months of 2008 in the Entergy Hub at \$74/MWh) [29] and a \$5-15/ton CO₂ credit to be sold into an emissions trading exchange such as the Chicago Climate Exchange.

Schultz, et.al. calculated FTS fuel costs (\$2002) using their concept and derived an estimate below \$2.00/gal. Detailed consideration of their economic analysis is beyond the scope of this paper and reference 24 is recommended for their thorough treatment of costs.

Table 4.

REVENUE STREAM POTENTIAL

Gross Revenue: FTS; MWh/YR; CO ₂ Offset Credits @ (\$5-15/ton)		
400 MW coal-Oxy-Combustion SC plant, .85 on line factor		
	\$5/ton CO ₂	\$15/ton CO ₂
MWh @ \$74/MWh	\$198 x 10 ⁶	\$198 x 10 ⁶
Avoided tons CO ₂	\$11,500,000	\$34,500,000
FTS Side @ \$2/gal	\$438 x 10 ⁶	\$438 x 10 ⁶
Total Gross Revenue	\$647 x 10⁶	\$670 x 10⁶

VIII. AN ALTERNATIVE TO THE CONCEPT

An alternative concept which utilizes coal directly into the FTS process using HTR as a heat source for efficient HTSE or SI to produce the required H₂ for FTS. Figure 4 offers a block diagram of a coal-to-FTS which derives O₂ for gasification of the coal and H₂ for the FTS process from nuclear power-driven HTSE or SI and, thereby, limiting CO₂ to that attributed to the life cycle CO₂ emissions from utilizing a HTR.

It eliminates the SC coal-fired oxy-combustion electric power plant and its revenue flow and ignores future electricity demand. U.S. Department of Energy’s 2008 Annual Energy Outlook projects electricity sales increase from 3.6x10¹² kWh in 2006 to 4.7 x10¹² kWh in 2030 at a rate of 1.1 %/YR with coal’s share increasing from 49 to 54%. [30]

A 2400 MW HTR would be adequate to provide the necessary mass of H₂ from HTSE or SI water splitting. A portion of the co-produced O₂ is fed into the gasifier but the remainder would have little or no commercial application and likely vented to the atmosphere. It would be more prudent to utilize the O₂ in the SC coal burning furnace and capture the CO₂ emissions. That would accrue carbon credits as well as revenue from marketing the generated electricity to the grid while providing power to the RWGS and FTS processes. That revenue flow could be applied to the overall economics of the CO₂ to liquid fuels process.

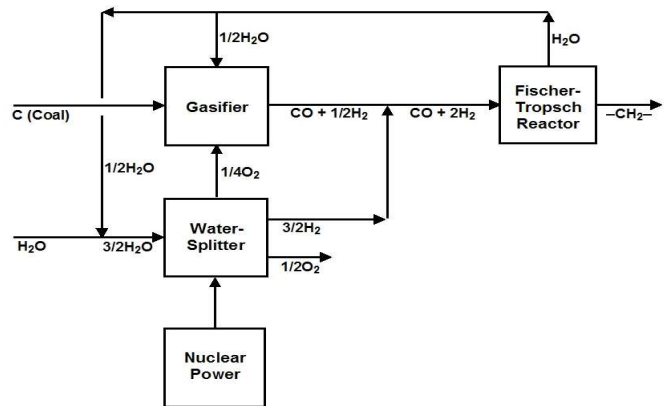


Figure 4. Coal gasification and FTS reliant upon H₂ provided by HTR driven HTSE or SI. [31]

IX. CONCLUSION

DOD is reacting to tightening world oil supplies and rising fuel prices. It also has a program to identify a single fuel to operate its entire battle space fleet. Alternative fuels such as coal-to-liquids, oil shale and tar sands are obvious candidates. However, each emits huge amounts of carbon dioxide. When the U.S. enters binding regulation of CO₂, those fuels will carry significant economic penalties.

The FTS process appears to be suited to providing DOD quality synthetic fuel. We proposed a novel concept: CO₂ from an oxygen-fired coal generating plant would be hydrogenated to produce CO, which is fed into an FTS to produce non-CO₂ synfuels. A high temperature nuclear reactor would be used to drive HTSE or SI water splitting.

By avoiding CO₂ emissions, the concept would accrue tradable emission credits for sale into carbon exchange markets. Their market value and sale of electric power from the coal plant would bring down the production cost of the synthetic fuel and give DOD assured supply of a single fuel.

While some components of this concept are commercially available (the FTS process and oxy-combustion power plant) the O₂ and H₂ production process coupled to high temperature reactors are not available, though the chemical and physical principles are well known.

An international consortium of partners from the U.S., U.K, Japan, China, South Korea or India would have the capital and technical skills needed to undertake that analysis. Each share similar economic challenges to their military and civilian aviation fleets as world oil prices continue to rise and supplies diminish. Given the very limited options for alternatives to aviation fuel, it is imperative that an approach such as offered herein be given due consideration.

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