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GREEN FREEDOMTM (PATENT PENDING)

A CONCEPT FOR PRODUCING CARBON-NEUTRAL SYNTHETIC FUELS AND CHEMICALS

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INTRODUCTION

We have developed a low-risk, transformational concept, called Green FreedomTM, for large-scale production of carbon-neutral, sulfur-free fuels and organic chemicals from air and water. Green FreedomTM utilizes carbon-neutral power to

- capture and recover carbon dioxide from the atmosphere,
- split water into hydrogen and oxygen, and
- convert hydrogen and carbon dioxide into synthetic fuels and organic chemicals.

Others have considered the possibility of producing liquid fuels from air and water; however, the published papers are speculative in nature or based on exotic technologies.^{*i,ii,ii,ii,iv*} With Green FreedomTM, our work has progressed beyond speculation to a viable concept. Its viability has been verified by industrial and semi-independent Los Alamos National Laboratory technical reviews.

At the heart of the technology is a new process for separating carbon dioxide from atmospheric air. By integrating this novel process with existing technology, we have developed a practical approach for producing sulfur-free, cabon-neutral liquid fuels and organic chemicals from an abundant and inexpensive source of materials. Initial system and economic analyses indicate the prices of Green FreedomTM commodities would be either comparable with the current market or competitive with that of other carbon-neutral, alternative technologies currently being considered.

Among Green Freedom's[™] compelling advantages, it

- uses benign materials that are in abundant supply as its chemical feeds;
- produces carbon-neutral, sulfur-free liquid fuels and organic chemicals;
- permits continued use of the existing industrial and transportation infrastructure;
- enhances US energy and material security by reducing dependence on imported oil;
- reduces the need for intrusive exploration for and extraction of natural gas, oil, coal, etc.;
- limits the environmental impact to the production facility and power assist waste stream;
- limits pressure on agricultural capacity; and
- has the potential to stabilize energy prices.

CONCEPT OVERVIEW

Green FreedomTM consists of two major parts: synthesis-gas production and synthesis-gas conversion. The new and unique technologies and processes developed for Green FreedomTM reside primarily with synthesis gas production. Synthesis gas production is endothermic, so it requires significant power assistance. Synthesis-gas conversion relies on commercially available technology to convert the synthesis gas into useful products. Most synthesis-gas conversion processes are highly exothermic, so the excess heat can be integrated into the system's operation.

Synthesis-Gas Production

Green Freedom's[™] synthesis-gas process is based on modest, but novel, extensions of current technologies that are in wide use. Novel process integration is also key to Green Freedom[™]. The primary system elements of synthesis-gas production are

- a process to separate carbon dioxide from the atmosphere and produce useful hydrogen as a byproduct,
- a process to generate supplemental hydrogen by splitting water, and
- a carbon-neutral power source.

This collection of elements also makes high-pressure steam available to the conversion process and produces pure oxygen as a useful byproduct that is available for more advanced concepts and commodities.

Synthesis-Gas Conversion

Many useful organic chemicals can be produced from synthesis gas using current commercial technology. Green Freedom[™] integrates its new synthesis-gas production process and power system with existing conversion technology in a way that significantly improves the overall process efficiency and reduces both capital and operating costs of the combined production and conversion processes.

GREEN FREEDOMTM GASOLINE AND METHANOL

We have developed Green FreedomTM concepts for evaluation specifically for production of methanol and gasoline. This includes an 18,000-bbl/day synthetic-gasoline plant and a 5000-tonne/day methanol plant. Figure 1 is an overall process flow diagram of a Green FreedomTM based, synthetic-gasoline plant. The process consists of a supplemental hydrogen production unit and a carbon-dioxide capture and recovery unit, which, together, produce the synthesis gas; and a methanol synthesis unit, and the Mobil methanol-to-gasoline (MTG) process for converting the synthesis gas into gasoline. We'll discuss these elements, power assist, and economics.



Fig. 1. Conceptual diagram of a process for producing synthetic gasoline from air and water.

Carbon-Dioxide Capture and Recovery

The heart of Green FreedomTM is an innovative process for capture and recovery of atmospheric carbon dioxide. Chemically, capturing carbon dioxide from the atmosphere is easy. Carbon dioxide is readily absorbed into a potassium carbonate solution where it reacts with the carbonate ions $(CO_3^{2^-})$ to form bicarbonate ions (HCO_3^{-}) . Furthermore this reaction does not release any noxious odors.

$$CO_2 + CO_3^{2-} + H_2O = 2 HCO_3^{--}$$
 (1)

However, atmospheric carbon dioxide is very dilute (~370ppm), and developing a practical system for capturing and recovering commercially significant quantities has been challenging. Conventional absorption equipment does not process the large volumes of air needed to meet the demands for synthesis gas production and can only capture 73% the carbon dioxide^v from the processed air on a single pass. Green FreedomTM's carbonate scrubbing process can process production quantities of air and capture >95 % of the carbon dioxide on a single pass. The high capture rate reduces process energy consumption by reducing the volume of air per yield that must be processed.

The conventional thermal stripping process for recovering the captured carbon dioxide from the absorbent, consumes too much energy to be practical. Green FreedomTM uses a newly-developed electrolytic stripping processes that is very selective. It also produces hydrogen as a byproduct that reduces supplemental hydrogen production requirements by 33%. These are key enabling features for Green FreedomTM.

Figure 2 is a process flow diagram of an integrated, carbon-dioxide capture and recovery process. To reduce operating costs and capital investment of capturing carbon dioxide, we have combined the absorption process with existing evaporative cooling systems employed by large power plants, a nuclear power plant in this case, in a compatible way.



Fig. 2. Process flow diagram for a CO2 capture and recovery process based on the electrolytic stripping process.

Cooling and capture would both be performed in a single cooling tower enhanced to increase air/water contact a modest amount. When compared with the use of a separate absorber tower that is solely dedicated to capturing carbon dioxide, this novel process-integration scheme reduces capital costs by \sim 90%, capture energy requirements by \sim 98%, and evaporative water losses by a significant amount.

The new electrolytic stripping cell drastically reduces the energy needed for stripping carbon dioxide from the carbonate solution so that stripping is practical. We estimate that the process would consume ~410 kJ/mole CO₂ of electricity and ~100 kJ / mole CO₂ of low-level heat energy. Taking credit for supplemental hydrogen production avoidance due to the cell's hydrogen byproduct, the net electrical energy consumption is ~55 kJ/mole CO₂ recovered. The new stripping process requires ~96% less energy than a conventional thermal-stripping process. Furthermore, new materials are emerging that would reduce the capital cost of electrolytic stripping cells substantially,^{vi} below what we assumed in our economic analysis.

The technical risks associated with the new carbon-dioxide capture and recovery process, are related to unverified performance characteristics of the unit operation. Data exist that confirm operability, but additional data are needed to verify efficiency, determine side-stream demineralization requirements, and identify ultimate life-limiting aspects.

Supplemental Hydrogen Production

Separate hydrogen production is needed to supplement the hydrogen produced as a byproduct from carbon dioxide recovery. Green Freedom[™] supplemental hydrogen production could be based on any water-splitting technology. We chose water electrolysis for our baseline process design as the lowest technical risk. Water electrolysis is mature technology, and recent advances in electrolyzer construction materials could further reduce the capital costs.^{vi} Water electrolyzers have no unusual power requirements and can be driven by current pressurized water reactor (PWR) or boiling water reactor (BWR) technology. Some water splitting technologies require high-temperature nuclear powered heat sources, which are not currently available. Because water electrolysis can be powered by PWRs and BWRs, a potentially source of technical risk associated with high-temperature reactors can be avoided in the initial deployments.

Steam electrolysis has more attractive economics but is a developing technology.^{vii} It utilizes a solidoxide membrane to split steam into hydrogen and oxygen at high temperatures. We analyzed steam electrolysis for use in Green FreedomTM and developed an energy integration scheme that enables a steam-electrolysis cell to operate at high temperatures without requiring a high-temperature energy source. Because of the effective resistive heating, the electrolyzer heats the hydrogen and oxygen products to a temperature greater the inlet steam. Therefore, the natural heat build up in the products can be used to superheat the steam. As such, it too can be powered by existing PWR or BWR technology and circumvent the technical risk of a high-temperature reactor.

Power Assist

Green FreedomTM is based on a carbon-neutral power source to assist production. We have limited our studies to nuclear power because its capital costs are lower than wind and solar-electric power, and it has significant environmental advantages over fossil energy sources, which are not carbon-neutral. Figures 3 and 4 illustrate some of the environmental advantages of nuclear power for hydrogen production, which are valid for Green FreedomTM hydrogen production as well. Figure 3 shows the lifecycle carbon-dioxide emissions for various methods of production. Lifecycle carbon-dioxide emissions associated with a nuclear-powered steam electrolysis plant are lower than all other options listed except wind and hydroelectric.

Figure 4 shows the lifecycle acid production potential for the same methods of hydrogen production. The acid co-production potential for a nuclear-powered steam-electrolysis plant is also lower than all other

options except wind and hydroelectric. Finally, the environmental impact of a nuclear-powered syntheticgasoline production plant is limited to the plant's footprint and the disposal of a relatively small volume of radioactive waste. We also expect the total land area affected by a Green Freedom[™] plant to be much less than the combined area affected by fossil-fuel extraction and the refining facility of comparable capacity.







Fig. 4. Lifecycle acid production potential for various hydrogen production methods.^{viii}

Even though the next generation (Gen III) of PWR and BWR technologies are the preferred choice for powering Green FreedomTM, a high-temperature reactor or other advanced reactor concepts currently under development could power Green FreedomTM when they become commercially competitive. Green FreedomTM could also use other alternative energy sources, such as wind power, if they become economically competitive as well. Hydroelectric power is attractive but its availability is inherently limited.

Conversion to Synthesis Fuel

Our baseline conversion process for evaluating Green Freedom[™] gasoline production is based on existing technology: methanol synthesis and the Exxon Mobil MTG process. Current methanol-synthesis technology is well established and uses copper/zinc/alumina catalysts that convert a mixture of hydrogen, carbon monoxide, and carbon dioxide into methanol.^{ix} Catalysts, similar to the existing methanol synthesis catalysts, also exist for direct conversion of carbon dioxide and hydrogen into methanol.^x The MTG technology has been commercialized and is being licensed by Exxon Mobil. The first commercial MTG plant went into operation in 1985 in New Zealand and produced 14,500 barrels/day of gasoline until it was shut down in 1997 for economic reasons. Other plants are currently being designed or are under construction.

Although the baseline conversion is based on methanol synthesis and the MTG process, Green FreedomTM is not limited to this set of conversion technologies. For example, a Fischer-Tropsch process in combination with a refinery could be used to produce gasoline, jet, and diesel fuels.

Green Freedom Gasoline Production Economics

We performed economic analyses on a partially optimized baseline concept based on a single Gen III PWR to provide power for the process. The analyses estimated a capital cost of \$5.0 billion for an 18,400-bbl/day synthetic-gasoline plant and \$4.6 billion for a 5,000 tonne/day methanol plant. Nuclear power accounts for more than 50% of the total plant capital investment. The estimated operating cost is \$1.40/gal for synthetic gasoline and \$0.65 for methanol. Because the capital investment is high, a profit margin of \$0.50 per \$1.00 of sales or more is needed to yield an acceptable return on investment.

Therefore, the price of gasoline at the pump must be about \$4.60/gal, and price of methanol at the plant gate must be \$1.65/gal for these base cases.

A number of new technologies of varying technical risks (not considered in our economic analyses) offer promising opportunities for lowering these prices in the future. These include innovations in material science, reactor technology, and compressor technology.

- Electrolytic cells account for ~20% of the total capital investment required for a synthetic gasoline plant. General Electric can fabricate alkaline electrolyzers from Noryl[®] plastic for a significant cost savings.^{vi} Use of this material for both the hydrogen electrolyzers and electrolytic stripping cells could result in substantial savings.
- Advances in material science that make steam electrolysis commercially feasible could reduce both capital costs and energy consumption as well.

If just these improvements are realized, the price of gasoline at the pump would be reduced to \$3.40/gal and the price of methanol at the plant gate would be reduced to \$1.14/gal. Using new nuclear reactor designs based on standardized, prelicensed designs could result in additional cost savings.

CONCLUSIONS

Making gasoline from air and water sounds exotic, but now practical technology has been developed to implement known chemical pathways for producing fuel from these abundant raw materials. Others have considered the possibility of producing methanol from air and water, but the published papers are either speculative in nature or based on exotic technologies.^{i,ii,iii,iv} With Green FreedomTM, this possibility has progressed beyond speculation to a realistic, low-risk concept because it is based on novel process integration and modest extensions of existing technology. The largest uncertainties associated with Green FreedomTM are the capital and operating costs. Those cost uncertainties cannot be reduced until performance data is generated for the carbon-dioxide capture and recover process and more detailed designs and analyses are developed.

The results of the initial economic analysis are very encouraging. Although the estimated gasoline price for the baseline process is above current market levels, several promising technological developments could reduce costs significantly and market pressures are likely to increase gasoline prices to the point where Green FreedomTM gasoline is competitive, even without resorting to a "green premium." In addition, with modest improvements to the process, nuclear-powered production of methanol could be competitive with existing technology in the near future.

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