CONTRIBUTED PAPER

The Dual-Fuel Strategy: An Energy Transition Plan

The transition from fossil to renewable and nuclear energy sources is enabled by developing liquid renewable fuels. Electric power and electrochemical energy conversion have central roles.

By William L. Ahlgren

ABSTRACT | Depletion of easily accessible petroleum reserves has created unstable oil supply and price, opening the opportunity to replace oil as an energy source with other fossil sources and ultimately with renewable and perhaps nuclear sources. The dual-fuel strategy is a plan to facilitate the transition from fossil to renewable *sources* by first replacing fossil with renewable *fuels*. It stipulates that all energy sources (fossil, renewable, and nuclear) will be most efficiently monetized by conversion to three primary energy vectors: electric power and two liquid renewable fuels, all compatible with existing infrastructure. One member of a dual-fuel pair is nitrogen-based, for example, ammonia, and the other is carbon-based, for example, methanol. The two are complementary: ammonia is carbon-free, but has high relative toxicity, while methanol has low relative toxicity, but contains carbon. Unlike hydrogen (a *gas*), these *liquid* fuels are compatible with existing infrastructure with only modest modification. Alternatives to ammonia are liquid ammoniates; alternatives to methanol include ethanol, dimethyl ether, and higher alcohols, and alkanes. The two renewable fuels may be called nitrofuel and carbofuel to avoid prejudice as to their exact composition. Renewable fuels are derived from air, and because nitrogen is 2000 times more abundant in air than is carbon dioxide, nitrofuel will be most efficiently produced and at least cost; it will therefore be used whenever possible. In some applications, however, the additional cost of producing carbon-based fuel will be justified by ease of handling. A small number of applications require high energy density fuel; these will be served by a secondary carbon-based fuel vector, derived from primary carbofuel at further cost. The dual-fuel strategy is market-driven. It identifies the sources of competitive advantage for renewable fuels and relies on the force of free enterprise to create a postpetroleum civilization powered by a zero-net-carbon energy system. The strategy enables global carbon emissions to be reduced significantly early in the transition, perhaps by as much as an order of magnitude by 2030, with zero-emissions perhaps as early as 2050.

KEYWORDS | Alternative fuel; ammonia; ammonia fuel; carbofuel; carbon emissions; coal-to-liquid; electric power; electrochemical energy conversion; energy chain; energy policy; energy strategy; energy vector; fuel; gas-to-liquid; greenhouse gases; hydrogen; hydrogen economy; methanol; methanol fuel; nitrofuel; postpetroleum; renewable fuel; sustainable energy; synthetic fuel

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I. INTRODUCTION

With the depletion of easily extractable petroleum reserves, oil supply and price have become unstable, creating an opportunity to replace oil with other fossil sources and ultimately with renewable and perhaps nuclear sources. The dual-fuel strategy is a plan to facilitate the transition from fossil to renewable energy.[1] It is summarized in Section II. In subsequent sections, the ideas behind the plan are elaborated. Although this essay concerns energy strategy, no mention is made of conservation. Here at the beginning let it be acknowledged that energy conservation is the first and foremost component of any future global energy strategy. Given that energy conservation is of first importance, and is taken as far as possible, what else is to be done? That is the question addressed in this essay.

[1] Here (and subsequently) we often use "renewable" as shorthand for "renewable and perhaps nuclear." Nuclear fission energy faces a difficult campaign to re-establish itself as a viable energy source. Nuclear fusion is yet to be demonstrated. Still, either or both might become important, even dominant, as a future energy source. The dual-fuel strategy enables *both* renewable *and* nuclear sources; we sometimes drop the phrase "and perhaps nuclear" only because it is tiresome to repeat it.

Many of the ideas presented here have a long history. As early as 1967 Leon Green, Jr., writing in *Science* magazine [1], formulated a concept for the large-scale use of ammonia as fuel. He observed:

> "The long-term consequences of the greenhouse effect due to CO_2 buildup in the atmosphere are of serious concern. ... To remove the offending elements (carbon and sulfur) from the fuel prior to combustion is a much more efficient and less expensive procedure than trying to clean up the combustion products. ... Outlined below is a concept for energy generation in which the fossil fuels are not burned directly but serve as raw materials for the synthesis of a clean fuel... This clean fuel is ammonia. ... In commercial high-tonnage production of ammonia, natural gas is used as raw material for steam reforming to generate hydrogen for the synthesis reaction. In the course of this process sulfur is removed and recovered in elemental form, and CO_2 is scrubbed from the stream and may be recovered for sale or use. Although current practice is to discharge this CO_2 to the atmosphere, the point is that the CO_2 is under control and can be condensed or caused to react so that the carbon is tied up in some useful form. ...large amounts of CO_2 are recovered per unit of ammonia produced, and the commercial value of this CO_2 will have a major bearing on the economic attractiveness of the concept."

Green's concept, published nearly half a century ago, is stunning in its prescience. Why has it received so little attention? Over three decades ago the U.S. Department of Energy conducted a comprehensive study of liquefied gaseous fuels, including LNG, LPG, hydrogen, and ammonia. The latter alternatives were studied because of the extreme explosion hazard associated with LNG and LPG. Bomelberg and McNaughton coauthored the report on ammonia [2], published in 1980. After a careful comparison of hydrogen and ammonia, they wrote:

> "It is not understandable why hydrogen as a future fuel is widely promoted, whereas ammonia is presently not considered at all. The most likely explanation appears to be that the potential use of ammonia as a substitute fuel is just too unknown, even within the technical community."

In 2012, the potential use of ammonia as fuel remains "just too unknown." Why is this? Perhaps it is because the well-known hazards of ammonia cause its use as fuel to be dismissed out-of-hand. There is also a widely held (but erroneous) notion that nitrogen-based fuels must necessarily produce excessive NOx in their exhaust. These misconceptions must be dispelled; one objective of the present essay is to do so. At the same time, the validity of these concerns must be acknowledged. Ammonia *is* a hazardous substance, and NOx *is* found in the exhaust of ammonia combustion processes. We argue that ammonia can nevertheless be safely used as fuel if it is not required to serve all purposes. We outline a plan—the dual-fuel strategy—that supplements ammonia with a complementary substance, methanol, well known as an alternative fuel. Ammonia and methanol each has strength that compensates the other's weakness: ammonia is carbon-free, but has high relative toxicity;[2] methanol has low relative toxicity, but contains carbon. Their use together yields a good (not perfect) solution for *liquid* renewable fuel, which we assert to be *sine qua non* for a post-petroleum global energy system. Further, we note that ammonia and methanol are but one example of such a dual-fuel pair. Other, better pairs might be found, and must be sought. What we *reject* is hydrogen. Hydrogen is disqualified because it is a *gas*. In our view, the use of hydrogen as an energy vector has been thoroughly explored over a period of half a century, and has failed to come to fruition. It is now time to move on.

A purpose of this essay is to contribute to a discussion initiated in these Proceedings by Bossel [3] and continued by Abbott [4], [5]. Bossel points out the deficiencies of the hydrogen economy, and advocates an electron economy in which batteries play a central role and fuel is unnecessary. Abbott insists that fuel is essential and that the hydrogen economy is the only realistic alternative to business as done now. We agree with Bossel that hydrogen is deficient, and with Abbott that renewable fuel is indispensible. We suggest that *liquid* fuels, ammonia and methanol, answer many of the objections raised by Bossel, while acknowledging Abbott's observation that renewable fuel is an essential component of any future energy strategy.

This essay is an unapologetically rhetorical work. Our purpose is to convince as many readers as possible to adopt the dual-fuel strategy and to adjust their research priorities accordingly. What the reader will find is a mixture of scientific fact, reports on demonstrated technology, speculation about what might be possible, and future-scenario narratives. This mixture is appropriate to the grand scope of our topic. The astute reader will have no difficulty identifying the character of any given statement or passage, and treating it accordingly. Further, we approach the problem at hand—how best to put the global energy system on a sustainable course—as one that cannot be compartmentalized. Issues of energy, environment, and economics are inextricably intertwined yet are traditionally classified in distinct intellectual categories. These three categories cannot be separated; all must be addressed simultaneously. Commercial and financial issues in particular are touched on in this essay. It is essential to do so.

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[2] All liquids other than water are toxic to some degree, or to some organisms. *Relative* toxicity means relative to liquid fuels we are accustomed to, like gasoline. An attempt is made to quantify this notion in Appendix F.

No credible approach to meeting the greatest challenge now facing mankind can ignore these central aspects of the problem.

Last, we provide a substantial list of references, but one which is in no way complete. It is intended as a resource for those readers who want to learn more and are willing to work at it. It contains tertiary literature (monographic books) when available, secondary literature (review papers) as an alternative, and primary sources (original research papers and reports) only when necessary. The subject is of such importance that it deserves a multivolume handbook treatment bringing together this extensive body of knowledge in a more accessible form. This has *not* been done in this brief essay. To say so is to state the obvious; but perhaps by explicitly setting expectations we can avoid disappointing some readers.

II. SUMMARY

Fuels are a crucial component of the global energy system, not to be replaced by a purely electric energy vector. Fuels are indispensable to efficient transport and storage of energy. Further, *liquid* fuels are needed for compatibility with the existing energy infrastructure. Neither the hydrogen economy nor the electron economy meets this requirement; the dual-fuel strategy does. The dual-fuel strategy uses two primary renewable fuels, one nitrogen-based, and the other carbon-based. An example of a dual-fuel pair is ammonia and methanol. A secondary carbon-based fuel, for example dodecane, is also required. "Dual-fuel" is short for "dual ammonia-methanol liquid renewable fuels" *and* "dual fossil-renewable functionality of the existing fuel infrastructure." These two implications of the word *dual* are equally important.

The two primary fuels are *complementary*: ammonia is carbon-free but has high relative toxicity, while methanol has low relative toxicity but contains carbon. Ammonia and methanol have about half the energy density of gasoline, jet fuel, and diesel fuel. The energy density of ammonia and methanol is sufficient, however, to meet 95% of the world's energy requirements. Ammonia can meet 80% of fuel needs, those in which professional fuel handlers specially trained and equipped are employed. Methanol can meet 15%, in which fuel must be handled by persons with no training or safety equipment. The remaining 5% of fuel needs require high energy density, and to meet those specialized needs the higher cost of dodecane (or similar fuel) derived from methanol will be acceptable. Hydrogen is rejected because it is a gas. Liquid fuels are required for *legacy compatibility*: the ability to use the existing energy infrastructure with minimal modification.

Alternatives to ammonia and methanol exist. In particular, ethanol, dimethyl ether or higher alcohols or alkanes can be substituted for methanol to achieve *very* low relative toxicity and high energy density and even better legacy compatibility, but at higher cost. Both members of the dual-fuel pair that ultimately emerges are likely to be blends of several compounds, just like present-day fossil fuels such as gasoline, diesel fuel, and jet fuel. These two nitrogen and carbon-based fuel blends may be called *nitrofuel* and *carbofuel*.

Nitrofuel and carbofuel are renewable fuels to be derived in the long-term from air and water with no supplementary carbon source. Nitrofuel will be the lower cost renewable fuel because air is mostly (78%) nitrogen, thus the feedstock for nitrofuel is easy and inexpensive to extract. Carbofuel will be higher cost because its feedstock, carbon dioxide, is present in air at low concentration, 2000 times less than nitrogen (0.038%); thus it is more difficult and expensive to extract. Carbofuel will be used only in those applications where the low relative toxicity and/or the high intrinsic energy density of carbon-based fuels adds sufficient value to compensate for the higher cost.

Methanol will be the lowest cost carbon-based liquid renewable fuel. It is a primary energy vector to be used whenever low relative toxicity is required and low energy density is acceptable. When high energy density is mandatory then multi-carbon fuels such as dodecane (jet fuel) can be derived from methanol. The additional processing required leads to higher cost which is justified in certain applications such as long-haul air transport. High energy carbofuels such as dodecane are secondary energy vectors. They are high-cost, low-use, specialized products derived from the primary vector (methanol) or perhaps from a methanol precursor such as synthesis gas (carbon monoxide and hydrogen).

Energy is needed to produce renewable fuels. It can be derived from any source: fossil, renewable, or nuclear. *Source-neutrality* is an important feature that distinguishes renewable from fossil fuels. Liquid fossil fuels today come only from oil; liquid renewable fuels can come from any source. Source neutrality enables *agile production*: easily switching between a variety of energy sources to produce a given fuel. This is a key competitive advantage that enables renewable fuels to displace fossil fuels. Renewable fuels *can* be produced from air, water, and renewable or nuclear energy; but they can *also* be produced from fossil sources, or from associated CO_2 exhaust streams. Initially the low-cost energy sources for renewable fuels will be fossil. We retain the name *renewable* for a fuel that *can* be produced sustainably, even when it is temporarily produced in a nonsustainable way; thus ammonia and methanol are "renewable fuels" no matter how they are produced. Temporary nonsustainable production of renewable fuels from fossil sources to achieve low cost is a key element of the dual-fuel strategy.

The transition to renewable fuels will be triggered by competition among gas, coal and oil sources. Fossil chemical energy derived from gas and coal will be converted directly to ammonia and methanol, using well-established petrochemical processes. The cost of conversion is compensated by the lower cost and hazard of transport and storage; this is the gas-to-liquid approach to monetizing natural gas. Natural gas plays a pivotal role in the dual-fuel strategy: in the early stages of the transition it is the energy source and feedstock for the production of low-cost ammonia and methanol.

As the markets for renewable fuels grow, more and more will be supplied by renewable sources. One path will be through excess or stranded electric power. Electric power derived from renewable sources will follow a market-driven economic dispatch protocol. It will be used first to supply immediate load demand and recharge available nonfuel storage. Conversion to chemical energy in the form of renewable fuels will compete with nonfuel storage. Renewable fuel production will be used to capture energy resources located remotely from population centers, especially those located in or across oceans. In these applications the combined benefits of transmission, storage, and the superior system efficiency achieved through distributed generation give a competitive advantage to fuel production over less flexible energy storage systems.

To enable renewable sources to supply renewable fuels, low-cost high-efficiency electrochemical interconversion is a key research and development objective. The technology does not yet exist; its development will be stimulated by rising demand for renewable fuels. Photochemical and thermochemical conversion processes are alternatives by which the dual-fuel strategy can also be implemented.

Renewable fuels can be easily traded over space and time, thus the conversion of electric power to renewable fuels enables an efficient energy marketplace that promotes stable energy supply at low cost. It also promotes a decentralized network of distributed generation-and-load centers (microgrids or energy hubs) that can incorporate combined cooling heat and power (CCHP or trigeneration) and operate on an annual power capture-storage-use cycle. This is an intrinsically robust and *efficient* configuration for the future global energy system. Trading energy in the form of fuel rather than electric power enables CCHP, the efficiency gains of which offset losses incurred in upstream petrochemical or electrochemical conversion processes.

The transition strategy from fossil to renewable and nuclear sources is based on harnessing the power of *market feedback*. The concept of positive feedback is familiar to electrical engineers; it is the operating principle of multivibrators of all kinds, flip-flops in particular. Positive feedback results in rapid transition from an initial to a final state following a trigger stimulus sufficient to drive the system to a metastable threshold state. Market feedback works in the same way for commercial systems. In the dual-fuel strategy the transition is initiated by exploiting an existing technology: the production of ammonia and methanol from natural gas. Gas-to-liquid conversion enables natural gas to compete with oil. Stranded natural gas (and perhaps coal) reserves will be monetized by on-site conversion to the more easily and safely transported liquid renewable fuels. Potential *producers* of ammonia and methanol are easily identified. The major challenge is to identify and empower selected leading-edge *consumers* for these fuels while simultaneously expanding the existing *distribution* networks. Producers, distributors, and consumers must be brought together not only in a traditional commodities-trading context, but also in a broader framework enabling mutually supportive technology development. This trade development organization we name the Dual-Fuel Exchange (DFX). The design and implementation of this institution is the *key element* of the dual-fuel strategy. From the DFX the required technology development will flow. Institutional and technological innovation are equally important to success.

Once renewable fuels become established in the energy system, their production from renewable sources becomes increasingly attractive. The growing market for these fuels stimulates invention to improve conversion efficiency, thus further driving down energy cost and expanding the market for renewable fuels. Positive feedback kicks in. Fossil sources become less and less competitive, and soon (within decades) their use is superseded entirely.

During the transition from fossil to renewable and nuclear sources, the majority of CO_2 generation is centralized at a relatively small number of large plants, located near the gas (or coal) fields. Source concentration, together with development of valuable products that use CO_2 as feedstock, enables profitable carbon capture sequestration and *sale* (CCSS). Examples of ways to derive value from sequestered CO_2 include enhanced gas recovery, production of carbonate-based building materials, and production of carbon-based structural materials. With CCSS global carbon emissions are significantly reduced early in the transition, perhaps by as much as 90% within a decade or two. At completion, fossil sources are no longer in use; we have a zero-net-carbon energy system. Because liquid renewable fuels use the existing energy infrastructure, completion can be achieved within a few decades. Thus, order-of-magnitude reduction of carbon emissions by 2030 and zero emissions by 2050 are goals that can be evaluated for feasibility in scenarios featuring aggressive transformational policies.

III. ENERGY SUPPLY CHAIN

Central to the dual-fuel strategy is the distinction between energy source, vector, and infrastructure. To understand this distinction, consider the energy supply chain. It is a series of processes: extraction, conversion, refinement, transport, storage, and end-use. For example: a forest is an energy source; a stack of split firewood is an energy vector; axe, wheelbarrow, and fireplace are infrastructure.

A. Processes

A link in an energy supply chain is shown in Fig. 1. It is a process that takes an energy vector (the *feed*) as input and

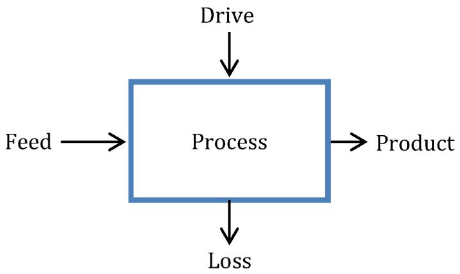

Fig. 1. ***Link in an energy supply chain. Process efficiency is product divided by feed plus drive.***

supplies another energy vector (the *product*) as output. It requires an additional energy input (the *drive*), and it dissipates some energy (the *loss*).

Extraction is the first link in the chain. A producer extracts energy from a source, and converts (or refines) it to a vector. The extraction process has no feed. Its product is an energy vector: something that can be bought and sold. It is characterized by Energy Return on Investment (EROI), a term introduced by Cleveland *et al.* [6], [7]. We define EROI to be the ratio of product to drive. It is a number greater than one, else the energy source will not be exploited. Preferably, it should be ten or more. In the firewood example, the EROI is the ratio of the energy in the firewood (ultimately derived from the Sun) to the energy it took to fell a tree, cut it into logs, and split them.

End-use is the last link in the chain. It has no product; it is merely something someone wants. End-use value cannot be quantified by a physical figure of merit such as EROI or efficiency; it is not measured in joules. Rather, its value is measured in *monetary units* (MU: for example, U.S. dollars, USD) and is whatever someone is willing to pay. In the firewood example, the end-use is a warm room, thanks to a fire in the fireplace. The value of a commodity in monetary units is fundamentally a subjective quantity not accessible to direct physical observation. It is discovered by bringing the commodity to an efficient market which adjusts the price until supply and demand are in balance.

In between extraction and end-use are a series of processes in which energy vectors are refined or converted, transported, stored, and delivered. These intermediate processes are characterized by *efficiency*: the ratio of product to feed plus drive. In the firewood example, one of the processes is transporting the split firewood by wheelbarrow to a woodshed where it is stored. The input feed to this process is the energy in the woodpile in the forest. The output product is the energy in the stack in the woodshed, which might be less than that in the forest woodpile if a few sticks fell out along the way—the process loss. The process drive is the energy it takes to load the wheelbarrow, push it to the woodshed, and unload it. The process efficiency is product divided by feed plus drive: the energy content of the wood in the shed divided by that of the woodpile in the forest plus the energy expended by the wheelbarrow operator.

Value rates are value per amount of commodity. There are two different rates that characterize any market transaction: cost and price. The cost is what the seller paid for the commodity being traded; the price is what the buyer pays. These also apply to the feeds and products in energy chains, in which the relevant value rates are measured in MU/J.

B. Source, Vector, Infrastructure

There are three energy *sources*: fossil, renewable, and nuclear. Fossil sources are classified as coal, oil (petroleum), and gas (natural gas). The renewable category is a broad one, including hydroelectric, wind, solar, tidal, and geothermal. Most renewable sources are ultimately solar in origin. Nuclear sources are fission and perhaps one day fusion. An energy *vector* is anything that carries energy and can be traded (monetized). Although others are possible, the only currently important energy vectors are fuels and electricity. Fuels are chemical energy vectors which can be transported and stored. Electricity is a *power* vector, which can be transported on transmission lines, but must be converted to another form for storage.[3] Energy *infrastructure* is the built environment that enables energy trade. It includes production machinery, transport and storage facilities, and conversion devices such as combustors, engines, and motors. It has been built over the last two centuries. It is the physical layer of the energy marketplace, through which energy vectors flow from source to consumer.

Fossil, renewable, and nuclear energy sources are distinguished by their particular extraction processes. Extraction is characterized by EROI, which determines the competitiveness of the various energy sources. Fossil sources have the highest EROI, and hence dominate the energy marketplace.

C. Fossil Sources Are Not Fossil Fuels

Are coal, oil, and gas energy sources, or energy vectors? At first glance they appear to be both, but a closer look suggests that we divide them into sources and vectors according to the stage of processing. They are sources when in the ground, vectors once extracted. Crude oil is a source when still in the ground, a vector (because it can be traded) after it is in a pipeline or has been loaded onto a tanker and is en route to a refinery. Gasoline, diesel fuel, and jet fuel are vectors. Raw gas is a source, sales gas is a vector. Coal is a source that is most often converted to

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[3] Energy is stored in electric fields in capacitors and in magnetic fields in inductors. Capacitors are used for relatively small-scale, short-time storage. For large-scale energy storage only magnetic fields are under consideration, in the form of SMES (superconducting magnetic energy storage), which has not been deployed commercially. All significant large-scale storage today involves conversion of electric energy to another form.

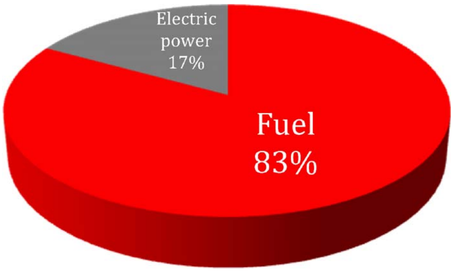

Fig. 2. ***Fuel dominates energy trade. This chart represents the U.S. economy in 2009.***

electricity as a vector, rather than to a fuel; but coal in a train of hopper-cars or waiting in a storage area to be fed into a furnace is a fuel vector. The contemporary global energy infrastructure is designed to handle fossil fuels that are derived from fossil sources. Fuels are energy vectors, not energy sources, but because of this close relation the two are often confounded. In the dual-fuel strategy we propose to derive renewable *fuels* from fossil *sources* for a time as part of our transition plan, so we want to be clear about the distinction. Renewable fuels can be produced using renewable energy sources, and they can *also* be produced using fossil or nuclear sources.

IV. FUEL IS CRUCIAL

Fuels are indispensable, but the fossil sources from which they currently come are not. We can replace fossil sources while keeping renewable fuels as important energy vectors. Fossil fuels will not be replaced by electric power; they will be replaced by renewable fuels. The existing pattern of global energy use, and the energy infrastructure that supports it, has developed over the past two centuries. It is by no means immutable, but neither is its replacement to be taken lightly. We want to work with it, and not against it. Take the U.S. energy system (summarized in Appendix A) as an example. In simplified form it consists of three each of sources, vectors, and end-uses. The sources are fossil, nuclear, and renewable. The vectors are liquid fuel, gaseous fuel, and electricity. The end-uses are transport, production, and habitation. Fig. 2 (based on Table 3 in Appendix A) reveals that 17% of energy commerce in this system is carried by the electric vector, and the remainder—83%—is carried by fuel.[4]

Fuel dominates energy trade. The reason is that fuel is bottled lightning: it is the best way to transport and store energy, and thus to trade it. The share of energy trade carried by the electric vector will grow, but fuel will remain dominant. A future energy system can be envisioned in which essentially all energy is first converted to electric power as part of the extraction process, and then most of it, perhaps 80%, is converted to fuel for trade purposes. Much of that is then reconverted back to electric power where and when needed.

V. ECONOMIC INERTIA

After EROI, the main factor favoring fossil sources is economic inertia. Economic inertia is resistance to change associated with entrenched use. Fossil *fuels* are entrenched in the global economic system. Fossil fuels come only from fossil *sources*, thus the sources are equally entrenched. To compete with fossil sources, renewable sources must supply competing fuel energy vectors that can be traded using the existing infrastructure, which is built around *liquid* fuels. To overcome economic inertia, we must supply liquid renewable fuels.

A. Liquid Fuel and the Legacy Infrastructure

Liquid fuels are preferred energy vectors. Examples are liquid petroleum gas (LPG), gasoline, kerosene, jet fuel, diesel fuel, and fuel oil. Oil is a liquid, easily transported and stored, and easily refined to other liquid fuels. That is why oil (and not natural gas or coal) has the highest EROI and is currently the dominant source of energy. Readily accessible oil supplies are dwindling, however, and the EROI of the remaining supplies is falling. Alternative energy sources can be competitive at the current lower EROI levels. Finding new energy sources and managing an economy with lower EROI are not in themselves great problems. The real problem is that our agility in seeking out and developing new energy sources is compromised by economic inertia, which comes not from the fossil *sources*, but from the fossil *fuels*.

A global energy distribution and use infrastructure has developed in the past two centuries that favors fossil fuels over alternatives. This is the *legacy infrastructure*. It consists of pipelines, tanker fleets, refineries, distribution systems (fuel storage facilities, delivery fleets and dispensing stations), and conversion devices (engines and combustors). Further, fossil fuels are easily produced from fossil sources, but produced only with poor efficiency, hence high cost, from competing sources. It is inefficient and costly to make the complex hydrocarbon mixtures that are fossil fuels directly from renewable or nuclear energy. This leaves only electricity as a viable energy vector for these nonfossil energy sources. As useful as electricity is, it is not likely that it will ever supplant fuels entirely. Thus, much of the existing energy infrastructure—the fuels distribution and use network—is unavailable to nonfossil energy sources. The resulting competitive advantage to fossil sources hampers innovation in energy technology. To promote renewable sources, we need to enable their trade within the legacy infrastructure for fuels. To exploit

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[4] Most electricity is generated from fuel. When energy is traded as fuel then traded again as electricity, we count that energy twice in the total energy trade. Energy trade is measured in dollars, not joules; the conservation of energy does not apply to trade. The same energy traded twice counts as twice as much trade.

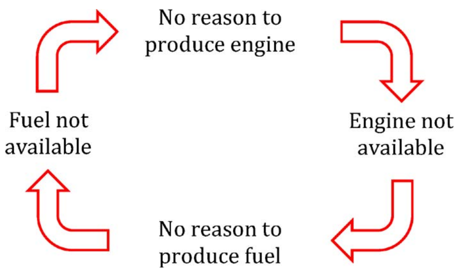

Fig. 3. ***Feedback prevents change until a trigger stimulus is applied.***

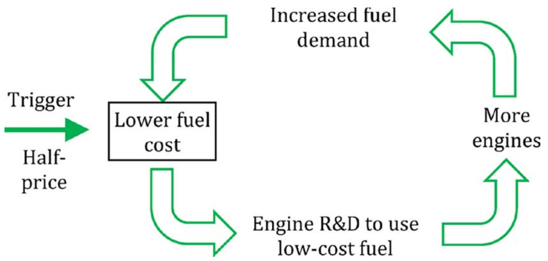

Fig. 4. ***Feedback promotes change after a trigger stimulus is applied.***

the legacy infrastructure, we must respect its preference for *liquid* fuels.

B. Market Feedback

Economic inertia results from an economic *vicious cycle*: a form of positive feedback that opposes change. In the case of fuel, the vicious cycle is illustrated in Fig. 3. It works like this: conversion devices (engines and combustors) that consume alternative fuels are not available, so there is no incentive to produce and distribute alternative fuels; but in the absence of widely available alternative fuels, there is no incentive to develop conversion devices that would consume them. This Catch-22 blocks the adoption of alternative fuels, even if they could be less costly than fossil fuels.

To overcome this vicious cycle, we must replace it with a *virtuous* cycle. The same market feedback mechanism that prevents change will promote it after a use-threshold is crossed; feedback accelerates change once it is triggered. This is illustrated in Fig. 4.

The challenge is to identify the path of least resistance to change and focus financial and technological resources there. This path lies through a few niche markets where renewable fuels have lowest barrier to adoption and compelling competitive advantage. Successful development of these *trigger markets* will lead rapidly to global change once a renewable fuel use threshold is reached.

Some specific suggestions for trigger markets are presented in Section XIX-D. Renewable fuels must be liquids in order to compete. This is true even in those markets currently served by gaseous fuels (e.g., natural gas), because liquids have a competitive advantage over gases. It is precisely that competitive advantage that must be exploited to trigger the transition from fossil to renewable fuel use. In the trigger markets it is necessary to simultaneously develop supply and distribution channels along with end-use conversion devices. A prerequisite is that renewable fuels must be available with more stable supply and at lower cost than their oil-derived competitors. To achieve low cost the intrinsic advantage of liquid fuels over their gaseous competitors must be fully exploited.

VI. RENEWABLE FUELS

To compete with oil, renewable sources need associated renewable liquid fuels.[5] Renewable fuels are made from air and water, and when used they return to air and water. The renewable fuel cycle is illustrated in Fig. 5.

The components of dry air are nitrogen (78.08%), oxygen (20.95%), argon (0.93%), and carbon dioxide (0.04%). These components, plus water, are what we have available to make renewable fuels. The percentage of CO_2 in air is low, and yet sufficient to sustain all plant life on Earth, and enough to profoundly affect the global climate. Still, as a component in a cyclic process such as illustrated in Fig. 5, due to its low concentration CO_2 is not as attractive as N_2, hence carbon-based renewable fuel is not as attractive as nitrogen-based. In the near term, however, we have adequate concentrated supplies of CO_2 to draw on. They are the exhaust streams from large fossil-fuel-fired engines and combustors as well as from a variety of very large petrochemical plants. Such exhaust streams typically offer CO_2 concentrations in the 5%–15% range.

A. Candidate Substances

There are a limited number of substances made from the components of air and water that can serve as chemical energy vectors. Three leading candidates are hydrogen, ammonia, and methanol

$$\mathrm{H_2O} \rightarrow \mathrm{H_2} + \frac{1}{2}\mathrm{O_2}$$

$$\frac{1}{2}\mathrm{N_2} + \frac{3}{2}\mathrm{H_2O} \rightarrow \mathrm{NH_3} + \frac{3}{4}\mathrm{O_2}$$

$$\mathrm{CO_2} + 2\mathrm{H_2O} \rightarrow \mathrm{CH_3OH} + \mathrm{O_2}.$$

[5] An alternative term, *synthetic* fuel, was preempted in the 1970s to mean liquid fossil fuel derived from coal. To avoid confusion with that usage, the term renewable fuel is suggested. If, however, this phrase has already been preempted to signify fuels derived from biomass, then *sustainable* fuel could be used to denote the more general concept intended here.

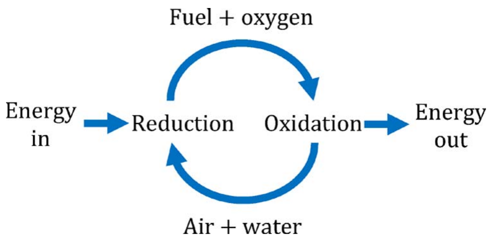

Fig. 5. *Renewable fuel cycle: Fuel is made from air and water by adding energy; it returns to air and water when the energy is extracted.*

In the above reactions, the arrows are in the reduction direction. Reduction is the opposite of oxidation. In the reduction direction, energy is consumed to make fuel plus oxygen. Fuel carries energy—it is an energy vector. When fuel is consumed, the reactions occur in the reverse (oxidation) direction. In the oxidation direction, fuel is combined with oxygen to release energy. The product of the oxidation of renewable fuel is air and water.

In the case of methanol, the process is carbon-neutral if CO_2 from air is used to make the methanol. If carbon from a fossil source is used, then the methanol does not participate in the cycle illustrated in Fig. 5. We refer to methanol as a renewable fuel, however, no matter what the source of carbon, because it *can* be efficiently produced using a renewable energy source. This differs from aromatic and cyclic hydrocarbons (like benzene and toluene) and alkanes (like iso-octane), components of gasoline, which *cannot* be efficiently produced from renewable sources. The unsustainable production of methanol from fossil sources is a temporary measure; ultimately, methanol will be produced from renewable sources.

There are other potential renewable fuels besides hydrogen, ammonia, and methanol. Many of these are listed in Section XV, where further discussion of the attributes of a good renewable fuel will be found. Notable among the alternatives is ethanol in place of methanol. Here we would like to emphasize these points:

- Ammonia and methanol are *examples only*. Other, better renewable fuels can perhaps be found, and should be looked for.
- Hydrogen is *not* what we seek. We need liquid fuels.
- There is no reason whatsoever to insist on a single fuel to meet all needs. On the other hand there is good reason to focus on not too many. Two, or few, is a good target.

B. Air Capture

Air capture is the phrase used in the literature to refer to the extraction of CO_2 from ambient air [8]. Is this process economically feasible? This question is of central importance in developing a strategy for renewable fuels. If CO_2 capture from ambient air emerges as a low-cost option, a global economy that relies *only* on carbon-based renewable fuels will be enabled. Such fuels are carbon-*neutral*, and that is good enough; carbon-*free* fuels such as hydrogen and ammonia are not required.

If air capture succeeds, methanol will emerge as a low-cost fuel to be used whenever relatively low energy density is acceptable. When higher energy density and/or direct compatibility with existing infrastructure and engines is required, processes are available to convert methanol to hydrocarbons that are equivalent to gasoline, jet fuel, and diesel fuel [9]–[11], [286]. Such carbon-neutral hydrocarbon (CNHC) fuels [12] will be more costly than methanol, but the higher cost will be justified by their greater value. This is an attractive scenario; but it depends on the economic viability of air capture.

Opinions on the viability of air capture vary [13]–[27]. Socolow *et al.* [25] provide an introduction to this technology that is both authoritative and tutorial. They conclude that air capture is likely to be expensive. Nevertheless, four startup companies [28] have made a strong enough case to find investors to commercialize air capture technology. Such enterprises might focus in the near-term on the easier task of CO_2 capture from one of the many available concentrated exhaust streams. This might then provide a development path to a future technology that is economic for ambient air. The controversy over the potential for air capture technology can be summarized in this way: Extensive experience acquired during the past century and captured in the so-called Sherwood plot [29]–[33] suggests that air capture will be expensive. On the other hand, the Sherwood plot is an empirical correlation around which data points cluster; there are outliers. Extreme outliers at low cost are not ruled out by thermodynamics or other physical laws. Therefore, it is possible that air capture technologies can be developed that will be outliers on the Sherwood plot. Perhaps it isn't likely, but neither is it impossible; hence there is scope for controversy, invention, and enterprise.

In this essay, we assume that air capture of CO_2 will prove costly. Then, the relatively easy capture of N_2 (2000 times more abundant in ambient air than CO_2) will favor nitrogen-based renewable fuel. Ammonia (or some other nitrogen-based renewable fuel) will be the low-cost chemical energy vector of the future, with methanol (or one or a few other carbon-based renewable fuels) used as an alternative that is preferred only when specific use factors add sufficient value to justify higher cost. This is the dual-fuel strategy.

C. Cost and Use Factors Set Market Shares

Low-cost ammonia (or nitrofuel) can meet most fuel needs: those where professional fuel handlers can be employed and high energy density is not required. The remaining fuel needs must be met with carbon-based fuel. Of these, most can be met with methanol, but some require a

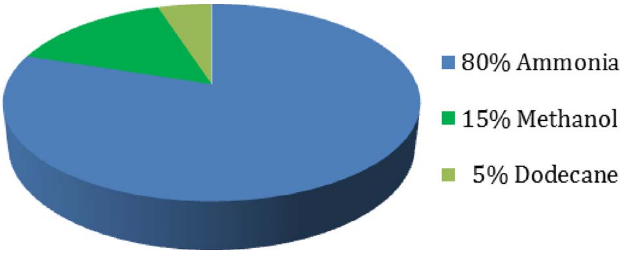

Fig. 6. ***Estimated shares of the renewable fuel market. Ammonia dominates, methanol is important, dodecane is small but essential.***

high energy density fuel such as iso-butanol or n-dodecane. Methanol will be the least-cost carbon-based liquid fuel. When needed, dimethyl ether (DME) can be generated from methanol at high efficiency and negligible additional cost. The conversion is relatively easy and can be accomplished at or near the point of use. Conversion of methanol to higher alcohols or alkanes can also be accomplished, but not as easily. The lower efficiency of conversion to high energy density fuels will result in substantial additional cost. These fuels will therefore be used only when high energy density is essential.

An analysis of contemporary fuel uses is presented in Appendix A, from which we conclude that Fig. 6 represents a reasonable estimate of the way the renewable fuel market will divide: 80% ammonia, 15% methanol, 5% dodecane.

In this estimate we take ammonia and methanol as representative of the primary nitrofuel and carbofuel vectors, and dodecane as representative of a secondary fuel vector. The secondary carbofuel is assumed to be derived from the primary carbofuel by additional processing, resulting in higher energy density and also higher cost. Ammonia, methanol, and dodecane are examples chosen to represent nitrofuel, primary carbofuel, and secondary carbofuel. The substances that actually emerge to function in these roles might be different from the examples chosen; very likely the fuels that ultimately emerge will be mixtures and not pure substances. The examples chosen are intended only as feasible representatives of those future fuels.

D. Production Processes

Processes for the production of renewable fuels are of four kinds:

1) photochemical;
2) thermochemical;
3) electrochemical;
4) petrochemical.

A photochemical process is the direct conversion of solar energy to fuel. A thermochemical process requires intermediate conversion to heat, preferably high-temperature (low entropy) heat, and can be used to convert either solar or nuclear energy to fuel. An electrochemical process requires an intermediate conversion to electric power and is the only kind of process available for wind and water-turbine energy conversion to fuel. Because all forms of energy can be converted to electric power, electrochemical conversion is an option for all energy sources. Petrochemical conversion means converting (or refining) a fossil energy source (gas, oil, or coal) into a renewable fuel. The energy source for petrochemical conversion is not renewable, but the fuel is. The petrochemical conversion route is important, although it is not sustainable, because it provides the trigger that initiates a market feedback mechanism that in turn leads to a sustainable future energy system.

E. Photosynthesis

Nature's own solar conversion system, photosynthesis, can be adapted to human purposes; but it is not the best we can do. The reaction driven by photosynthesis is

$$CO_2 + H_2O \rightarrow HCOH + O_2.$$

The reaction product HCOH represents a carbohydrate building block. Visualize two unsatisfied bonds protruding from the carbon atom, one pointing upward and one downward; they can connect with the unsatisfied bonds on neighboring blocks. These building blocks can be assembled by enzymes into the complex molecules which are the stuff of life. Photosynthesis has evolved to support life: self-assembling, self-replicating organisms that require complex molecules for their machinery. These complex molecules are not optimal energy vectors; that is not their intended function. Biomass *per se* is a poor fuel. Good fuels can be derived from biomass, but the path through biomass is not an efficient one. It may be that biomimetic engineering can be employed to realize organisms (carbon-based self-assembling self-replicating machines) that produce renewable fuels efficiently, and that is a worthy research endeavor. But the production of renewable fuel by first growing and then processing biomass is not sufficiently promising to warrant the attention it currently receives.

F. The Problem With Hydrogen

The problem with hydrogen is that it is a gas. For nearly a half-century hydrogen has received almost exclusive attention as a potential renewable fuel. It is attractive because it is a simple molecule (*the* simplest molecule), has relatively high conversion efficiencies in electro-reduction and oxidation cells,[6] and is environmentally benign. The consequences of a large hydrogen release, as long as there is no explosion or fire, would be small to

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[6] For hydrogen, electro-reduction is electrolysis and electro-oxidation is what happens in a fuel cell. We substitute these less familiar terms because they are more general and apply not only to hydrogen but also to other renewable fuels including ammonia and methanol.

none. A considerable effort has therefore been made to develop hydrogen as an alternative energy vector. Why has there not been more progress in five decades of trying? The most important reason is the high EROI of oil and its derivative fuels, and their consequent low cost. This is now changing. A second fundamental reason stands out: hydrogen is incompatible with the legacy energy infrastructure.[7] This is because hydrogen is a gas.

One might object that another gas, natural gas (methane), is an important part of the legacy infrastructure. But in fact, natural gas is marginal. It is competitively transported over land in pipelines, but its trade over water is difficult, dangerous, and relatively expensive. This is because it is a gas. Hydrogen is an even more volatile gas, more difficult to compress and liquefy. If natural gas is marginal as an energy vector, hydrogen is noncompetitive. Liquid fuels are superior.

This point of view has recently been endorsed by J. O'M. Bockris, who for decades was one of the most forceful advocates for the hydrogen economy. In [35] he states:

> "Methanol synthesized from hydrogen. . .would then remove the problem of the cost of storage, transportation and reconversion to electricity which hangs on to the use of hydrogen itself. . . Its use would provide, in practice, a 'liquid form' of hydrogen."

To this we add the question: why bring hydrogen into the picture at all? If using hydrogen as an intermediate in the production of methanol from sunlight (or other energy sources) turns out to be the most efficient process, then let it be used. If not, there is no need to involve hydrogen in any way, not even in the fuel production process. Plants make carbohydrates [$(HCOH)_n$, something quite like methanol] directly from sunlight without going through hydrogen as an intermediary. Why shouldn't we do the same? Further, methanol is not the only "liquid form of hydrogen;" there is also ammonia, which in many ways is even more advantageous as an energy vector.

G. The Benefits of Ammonia and Methanol

Methanol is liquid at room temperature and atmospheric pressure. It can be handled just like gasoline. Ammonia is liquid at room temperature at a pressure of about ten atmospheres. This is a low pressure, the pressure to which a racing (narrow) bicycle tire is inflated using a hand pump. Ammonia and propane have similar vapor pressures and similar equipment is required to handle them. Both ammonia and methanol can be stored, distributed, and converted in engines and combustors with equipment currently used in the legacy infrastructure, requiring only modest modification. This advantage is decisive.

Like hydrogen, ammonia and methanol each has a long history of development as a potential alternative fuel. An entry into the extensive literature of ammonia and methanol as fuel is provided in Appendix B. Like hydrogen, the low cost of oil has been a principal barrier to adoption. Unlike hydrogen, each has the advantage of being liquid. But each also has a disadvantage: ammonia that it has high relative toxicity; methanol that it contains carbon.

VII. COMPLEMENTARY FUELS

Ammonia is carbon-free, but has high relative toxicity; methanol has low relative toxicity,[8] but contains carbon. They are *complementary*: each has strength that compensates the other's weakness. The dual-fuel idea is to use both, each in its proper domain. Ammonia can be safely used to meet about 80% of all fuel needs, namely, all those applications in which it is feasible to employ professional fuel handlers who are provided with training and protective gear. This is not to be construed as burdensome or excessive; what is required is very modest. Any farmer today who applies anhydrous ammonia to his or her fields should have this kind of modest training and protective gear. The majority of fuel use, 80%, is by persons with this level of professionalism. The remaining 20% of fuel use is mostly what might be called residential—heating and cooking and also operating personal and family cars for general purposes. For these uses, it is not practical to require even a modest level of professionalism. The fuel that serves these uses must lend itself to safe handling by persons with no training or safety equipment whatsoever. Methanol can be used to meet this requirement. Where a more easily vaporized fuel is needed (e.g., as a substitute for propane or natural gas currently used in home heating and cooking) methanol can be inexpensively and efficiently converted to dimethyl ether (DME) at or near the point of use.

Because it contains carbon, the use of methanol is to be minimized; it is to be restricted to only those applications where fuel is handled by nonprofessional persons. Methanol has about half the carbon intensity of the fuels it would displace,[9] thus if it or its derivatives (e.g., dodecane) account for 20% of fuel use the equivalent carbon emission is 10%. Ammonia displaces the remaining 80% of fossil

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[7] For an argument in favor of building a new fuel infrastructure, see Ogden [34]. Ogden concludes that the infrastructure requirements for hydrogen fuel present a barrier, but not an insurmountable one. That may be, but apparently the barrier is formidable enough. Else, why hasn't more progress toward the hydrogen economy been made in the last four decades? The cost to build a hydrogen fueling station is measured in M$; that to modify an existing gasoline station to also dispense methanol is measured in K$; the cost differential between the vehicles that would use those stations is equally impressive.

[8] The toxicity of methanol is like that of gasoline: you shouldn't drink it, breathe the vapor, or get it on your skin, but it is easy enough to handle safely without special equipment or training. Environmental and health and safety (EHS) issues for fuels are reviewed in Section XVIII.

[9] This statement represents a rough guess; fuel carbon intensity (FCI) is not a unique and easily specified quantity; see Appendix D.

fuel use at zero carbon emission, thus there is a potential 90% reduction—an order of magnitude—in carbon emissions by switching to these complementary alternative fuels.

If the energy needed for methanol production is derived from renewable sources, and if the carbon needed comes from air, then methanol is a carbon-neutral fuel and there is no need to restrict its use. It will always, however, be less efficient and more costly to produce than ammonia, and will therefore only be used when ease of handling justifies higher cost. It is also important to reserve the possibility that for some time the carbon needed might come from a CO_2 exhaust stream produced by the combustion of fossil fuels, in which case the methanol produced is not carbon-neutral and its use must be restricted as much as possible. Further, to trigger the adoption of renewable fuels it is likely that fossil sources such as natural gas and perhaps coal must serve as both carbon *and* energy sources for methanol production for some period of time. In the near term, the most competitive source for both ammonia and methanol will be natural gas. We need to devise a strategy that enables us to use that source while still effecting a major reduction in carbon emission. This can be accomplished if most energy is carried by ammonia and carbon capture sequestration and sale is implemented at the point of production.

VIII. NITROFUEL AND CARBOFUEL

It is likely that ammonia and methanol can be improved on as fuels. Perhaps superior alternatives will be identified, or perhaps the pure substances can be improved upon by blending with other substances, or perhaps with each other. Nowadays when we speak of fuel we mean complex blends like gasoline, diesel fuel, and jet fuel. Gasoline is often represented[10] by iso-octane, but actually contains a variety of hydrocarbon and nonhydrocarbon substances. Likewise diesel fuel is often represented by hexadecane (cetane) and jet fuel by dodecane, but in reality all are complex blends. In the future, when we speak of fuel we will mean *nitrofuel* and *carbofuel*, a pair of liquid renewable fuels. Nitrogen, the main component of the atmosphere, must be the basic component of carbon-free liquid fuel; hence the term nitrofuel.[11] Nitrofuel is likely to be ammonia or a blend of ammonia with other compounds; but whatever it is, it must be nitrogen-based. Carbofuel is carbon-based: it is methanol, or ethanol, or dimethyl ether (DME), or a blend, perhaps with yet other compounds. Possibilities for nitrofuel and carbofuel are discussed further in Section XV. The precise compositions of nitrofuel and carbofuel are not important at this time; they will emerge. In this essay we use ammonia and methanol as a specific example of a dual-fuel pair. It is an example only; very likely a better pair will emerge.

IX. THE DUAL-FUEL STRATEGY

The dual-fuel strategy is a plan to facilitate the transition from fossil to nonfossil energy. The word *dual* has two meanings: *dual* renewable fuels; and *dual* functionality of the legacy infrastructure. Dual renewable fuels are needed because there is no single renewable fuel that can meet all requirements. Dual functionality of the legacy infrastructure means it can accept both fossil and renewable fuels, and thus overcome the economic inertia associated with that infrastructure. Renewable fuels must be designed to be compatible with the existing infrastructure with minimal modification; this is *legacy compatibility*. "Dual-fuel" is short for "dual ammonia-methanol liquid renewable fuels and dual fossil-renewable functionality of the legacy fuel infrastructure."

The essence of the strategy is to focus first on replacing fossil with renewable *fuels*; the *sources* will then follow. To replace fossil with renewable fuels the inherent competitive advantage of renewable fuels in the energy marketplace must be recognized and exploited. The sources of that competitive advantage are threefold: 1) legacy compatibility; 2) agile production; and 3) risk mitigation. Legacy compatibility enables energy suppliers and consumers who make a modest investment in infrastructure to reap a large return on that investment in the form of stable, low-cost energy supplies. Renewable fuels are chosen to be compatible with existing infrastructure so massive new investment is *not* required to use them. Because the investment is modest, the return on investment can be high. Agile production, a consequence of source-neutrality, enables energy carried by renewable fuels to be low-cost, and the supply to be stable. If one source becomes scarce, producers can switch to an alternative source with minimal disruption to the down-stream energy chain. Renewable fuels further enable users to manage not only energy cost and supply risks, but also the risks associated with global warming. The evidence for anthropogenic global warming is convincing to many, but not to all. Those who are not convinced will agree, however, that the risk is of such magnitude that it is prudent to consider mitigation plans. Further, there is another risk that entrepreneurs must consider. Whether or not global warming is real, governments might act on the assumption that it is, and adopt policies to limit carbon emission. That risk also can be managed by adopting the dual-fuel strategy.

The dual-fuel strategy relies on market feedback to set in motion an economic virtuous cycle. A virtuous cycle is a positive feedback loop. Once market feedback is triggered, change is rapid and results in a new post-petroleum stable state within a period of a few decades. Concomitantly,

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[10] More accurately, gasoline is *compared to* iso-octane, for test purposes.

[11] There are proposals to use nonatmospheric elements such as boron and aluminum for this purpose. We reject such proposals in favor of the renewable fuel cycle based on atmospheric components, as described in Section VI.

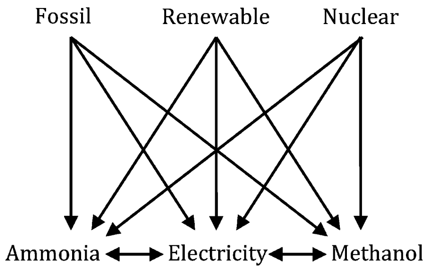

Fig. 7. ***Source neutrality: any source supplies any vector. Ammonia and methanol are liquid renewable fuels that can be produced from any source—including a fossil source.***

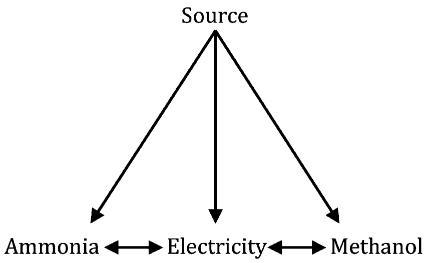

Fig. 8. ***The dual-fuel energy triangle. Interconversion between electric power and liquid renewable fuels forms the base.***

global carbon emissions are reduced by an order of magnitude early in the transition, and eliminated entirely at completion. To implement this strategy it is necessary that renewable fuels be supplied early in the transition at significantly lower cost than competing oil-derived fuels. To enable this, renewable fuels will first be derived from gas or coal sources, and only later from renewable sources.

X. SOURCE NEUTRALITY

Any of the dual-fuel energy vectors can be produced from any energy source. This is source neutrality, illustrated in Fig. 7.

The highly interconnected web of Fig. 7 makes for an efficient and robust energy market, with consequent stable supply and low cost, resistant to fluctuations in the supply available from any one source. Contrast this with business as done now: fossil fuels come only from fossil sources. The electric power vector is source-neutral, but fuels are not; that is why we are drawn to electric vehicles *despite* the difficulties with energy storage in batteries. Were source-neutral clean and safe fuels available, we would not be developing all-electric vehicles; we would be interested only in hybrid-electric vehicles that store energy as fuel. Source-neutral chemical energy vectors are what we really want.

A. Dual-Fuel Energy Triangle

Fig. 7 is simplified by merging all the sources, resulting in the dual-fuel energy triangle shown in Fig. 8. Fig. 8 is a symbolic summary of the dual-fuel strategy. At the apex of the triangle is *any* energy source; the three energy vectors are at its base. The arrows forming the *sides* of the triangle are conversion processes from source to fuel. The arrow down the *center* of the triangle is conversion from source to electric power. The two way arrows that form the *base* of the triangle represent preferably high-efficiency electrochemical interconversion processes between electric power and fuel; but can also represent conventional thermomechanical-electrical conversions such as fuel-fired heat engines driving electric generators.

The side (source-to-fuel) processes are petrochemical if the source is fossil. If the source is nuclear, they are thermochemical processes. If the source is renewable, they may be either photochemical or thermochemical processes. The center (source-to-electric power) process may be an electromechanical conversion driven directly by a wind or water turbine; or the electromechanical convertor may be driven by a heat engine that derives its energy from fossil, solar, or nuclear sources:[12] or there can be no electromechanical converter, the process then being one of direct conversion (such as photovoltaic or thermoelectric). The base processes are preferably electrochemical interconversion (electro-oxidation and electro-reduction) systems. A system comprised of electrochemical cells that can carry out both oxidation and reduction is often called a regenerative fuel cell; regenerative fuel converter (RFC) is more accurate terminology for a system built around cells. The electrochemical conversion processes that form the base of the dual-fuel triangle are of such importance that they deserve a rationalized nomenclature.

B. Electrochemical Converter and Related Terminology

Electrochemical converter refers to any one of the broad class of devices that directly interconvert electric power and chemical energy. They are to be contrasted with generators and motors which are electromechanical converters, and heat engines that are thermomechanical converters. Electrochemical converters are classified into two broad categories: batteries and electrochemical fuel converters (EFCs). Batteries are self-contained units carrying both fuel and oxidizer in a single package; they are like rocket engines. By contrast, EFCs are air-breathing. When operating in fuel-consuming mode they carry fuel with them, and rely on oxygen from the air as oxidizer.[13] EFCs

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[12] A thermomechanical process converts heat to mechanical energy; an electromechanical process then converts mechanical to electrical energy. Using conventional electric generators and motors, mechanical and electrical energy are interconvertible at high efficiency, often greater than 95%. Mechanical and electrical energy are therefore sometimes regarded as equivalent.

[13] According to this system of terminology, a zinc-air battery is an EFC that consumes zinc as fuel.

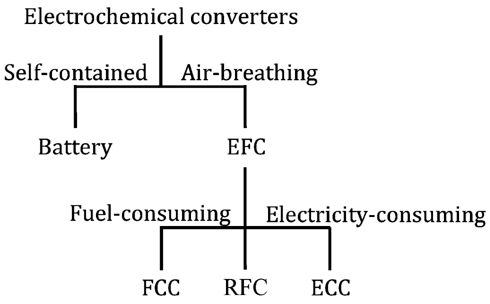

Fig. 9. *Taxonomy of electrochemical converters. Batteries carry their own oxidizer; electrochemical fuel converters (EFCs) use air.*

are further classified into three sub-categories that in common usage are referred to as fuel cells, electrolyzers, and regenerative fuel cells. Fuel cell systems we name fuel-consuming converters (FCCs); electrolyzer systems we name electricity-consuming converters (ECCs); regenerative fuel cell systems perform both FCC and ECC functions; we name them regenerative fuel converters (RFCs). This taxonomy of electrochemical energy converters is summarized in Fig. 9.

The word regenerative rather than reversible is used to avoid confusion with the thermodynamic usage of reversible, meaning a process carried out with zero entropy *generation* (but possibly with entropy *transfer*) and thus with zero (or small) gradients of all intensive variables. Small gradients mean slow processes; thus reversible processes set the benchmark for efficiency, but do so at low power, and thus are not optimal for practical purposes. Regenerative energy conversion processes can be optimized to achieve the best balance between efficiency and power. Regenerative in this context means two-way (duplex is a better word, but regenerative is established usage). An RFC is a device that can convert fuel to electric power *or* electric power to fuel; a *reversible* RFC can do so with maximal efficiency.

Fuel is the reduced form of a chemical energy carrier and exhaust is the oxidized form:

$$\text{Fuel} + O_2 \underset{\text{Reduction}}{\overset{\text{Oxidation}}{\rightleftarrows}} \text{Exhaust}$$

Fuel is *full* of energy; exhaust is *exhaust*ed of energy. Hydrogen has water as exhaust; ammonia has nitrogen and water; methanol has carbon dioxide and water.

Substances that participate in the oxidation and reduction processes but are avoidable and usually undesirable are named *impurities* if they appear on the left side of the oxidation-reduction equation and *emissions* if on the right. Sulfur is a common impurity in fuels, and in conventional fuels nitrogen is an impurity rather than an exhaust. Sulfur dioxide (SO_2) and nitrogen and carbon monoxide (NO and CO) are commonly-occurring emissions. Fuels are themselves emissions when they appear on the right, as in fuel slip that occurs especially under nonstoichiometric fuel-rich conditions.

EFC (electrochemical fuel converter) denotes a complete system comprised of multiple cells and ancillary subsystems. Individual cells are always two-way (regenerative) to some degree although never truly reversible. We use FC (fuel cell or fuel-consuming) to refer to the *mode of operation* of an individual cell. The reverse mode is EC (electrolysis cell or electricity-consuming). In FC mode fuel is *consumed* in an electro-oxidation process that produces both electric power and exhaust; in EC mode fuel is *produced* in an electro-reduction process that consumes both electric power and exhaust. Complete systems are most often designed to operate in one mode or the other: an FCC produces electric power from fuel, an ECC produces fuel from electric power. An RFC is a single system that can operate in both modes; such systems are comparatively rare, despite the fact that at the cell level electrochemical processes are inherently two-way. We retain electrochemical engine (ECE) as a synonym for FCC because it is convenient when a distinction is to be drawn between an electrochemical and an internal combustion engine (ICE). The engine of the ECE produces electric power, whereas the ICE produces mechanical power; using engine for both is reasonable since electric and mechanical power are thermodynamically equivalent.

C. Scenario Based on Efficient Electrochemical Conversion

If electrochemical processes can be accomplished with high efficiency, they will be preferred over alternatives, and the future energy system will look like Fig. 10.

In this scenario, the use of fossil sources has been eliminated. Energy from renewable and perhaps nuclear sources is first converted to electric power, and then any excess power not needed to meet immediate load demand or recharge high-efficiency storage assets is used to produce fuel.

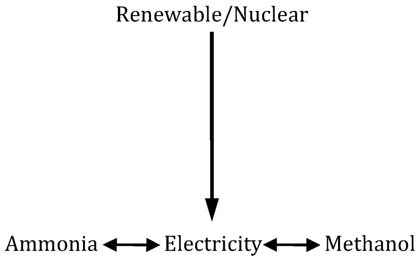

Fig. 10. *Future energy scenario given high electrochemical conversion efficiencies. EFCs form the base.*

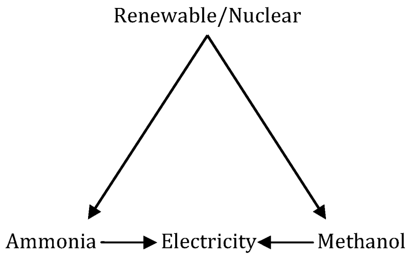

Fig. 11. ***Future energy scenario given high direct-to-fuel conversion efficiencies. Fuel-fired heat engines form the base.***

D. Photochemical and Thermochemical Alternatives

If electrochemical processes with sufficiently high interconversion efficiencies do not emerge, but direct conversion to renewable fuels proves most efficient, then the future energy system will look like Fig. 11.

Here again fossil sources have been eliminated. In this scenario energy from nonfossil sources is used to produce fuels directly by photochemical and thermochemical processes, and electricity is produced by conventional processes. The arrows along the base of Fig. 11 point from fuel to electric power, representing conventional fuel-to-heat-to-mechanical-to-electrical conversion. This is the scenario in which we simply replace fossil with solar fuels, leaving most of the electric power infrastructure unchanged. The prospects for bringing this vision to reality are greatly enhanced by focusing on the photochemical production of *liquid* renewable fuels, ammonia and methanol, and not hydrogen.

Between the two extreme scenarios shown in Figs. 10 and 11 lies the most probable future path: a combination of high-efficiency conversion processes both electrochemical and photochemical, and perhaps also thermochemical. This is the scenario illustrated in Fig. 8.

E. Source-Neutral Fuels Empower Renewable Sources

The central idea of the dual-fuel strategy is to replace fossil fuels with renewable fuels, first in niche applications, then generally. Fossil fuels come only from fossil sources, but renewable fuels are source-neutral: they can be generated from any energy source. By converting to source-neutral *vectors* we empower renewable *sources* to compete with fossil sources.

XI. EFFICIENT ELECTROCHEMICAL CONVERSION

Of the four processes (photo-, thermo-, electro-, and petrochemical) the electrochemical process is the most agile. Any energy source can be used to generate electric power, thus electrochemical conversion provides a path to fuel from any source. Further, efficient (in the energetic sense) interconversion between electric power and fuel makes for an efficient (in the economic sense) energy market. When energy vectors can be easily transformed back and forth, buyers and sellers can be easily brought together across space and time, enabling an efficient market which in turn produces stable energy supply at low cost. If electrochemical interconversion can be made highly efficient, it will be widely adopted, and the future energy system will be represented most closely by Fig. 10.

A. Conversion Efficiency

The electrochemical route to fuel production is often criticized as inefficient. Electrolytic production of hydrogen, for example, is compared to the charging of secondary batteries, and is deemed to be less efficient as a conversion process from electrical to chemical energy. This criticism is valid. We should ask, however, whether the relatively low conversion efficiency of electrolysis (or more generally, electro-reduction) is an intrinsic characteristic? Is it dictated by fundamental physical laws that cannot be circumvented? If not, then we should ask first, which do we prefer: chemical storage as fuel, or chemical storage in batteries? The answer is clear: we prefer fuel. Therefore, we should work to improve conversion efficiency rather than abandon fuel in favor of batteries.

B. Disruptive Technology

Efficient low-cost electrochemical conversion is a *disruptive technology*: one that may be difficult to achieve, but if achieved, will radically transform civilization. Efficient low-cost electrochemical conversion decisively solves the storage issue of renewable energy sources. If achieved, it will rapidly displace competing storage technologies. But its impact will be much broader. It will enable renewable to displace fossil sources, fundamentally changing the nature of the global economy. Old industries will be eliminated, and new ones created. The largest segment of our current global economy—petrochemicals—will undergo radical change. It will be downsized to a (still large) chemical products business. The shift of energy production away from fossil sources will engender new enterprises serving enormous markets with limitless opportunities for entrepreneurs.

One approach to efficiency improvement is high-temperature electrochemical conversion (HTEC) based on proton-conducting solid electrolytes, shown schematically in Fig. 12.[14] This is known technology that needs further development to improve efficiency and reduce cost. Fig. 12 shows the direct production of ammonia or methanol in a single electro-reduction cell (electric power is consumed and fuel is produced). This has been demonstrated for

[14] An entry into the literature of HTEC is provided by [36]–[39]. See [40]–[44] for general background in solid-state electrochemistry. Examples of contemporary works on ammonia conversion using HTEC are [45]–[55]. This list is representative only and not comprehensive.

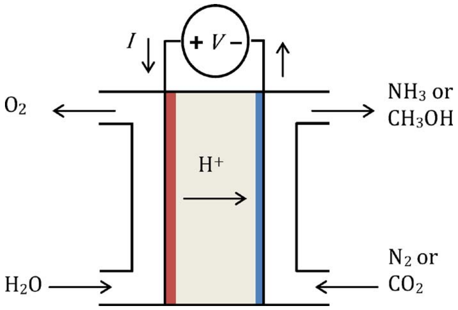

Fig. 12. ***Disruptive technology: High-efficiency interconversion between electric power and liquid renewable fuels.***

ammonia, but not (so far as we know) for methanol. Production of CO from CO_2 has been demonstrated, and can be a step in a methanol production process. If the direction of all the arrows in Fig. 12 is reversed, the device is then operating as a fuel cell (fuel is consumed and electric power is produced).

HTEC is offered only as an example of a possible technology path; there are many others. Electrochemical conversion can be implemented using cells that incorporate either solid or liquid electrolytes, both of which have many forms distinguished especially by operating temperature. High-temperature solid electrolytes are mostly oxides. These in turn are usually either proton or oxygen-ion conductors. At lower temperature, the solid electrolytes used are polymers, usually proton conductors. Liquid electrolytes at high temperature are molten salts, or if also at high pressure may be aqueous solutions. Liquid electrolytes at low temperature are most often aqueous solutions, which may be either acid or alkaline (proton or hydroxyl conductors). Other variations have to do with what happens at the negative electrode, where it might be that oxygen or chlorine or something else is formed. Further variation comes from combining energy sources. Photoelectrochemical and thermo-electrochemical conversion are hybrid processes in which an additional energy input supplements (or conserves) electric power. Both are well-known; HTEC, in which heat energy supplements electric power, is an example of a thermo-electrochemical hybrid process. All the foregoing and others as well need to be explored. The exact technology path to low-cost high-efficiency electrochemical interconversion is a matter of tactics, not strategy.

C. Photochemical and Thermochemical Alternatives

It may be that high-efficiency electrochemical conversion technology cannot be developed, and that efficient and low-cost direct photochemical[15] or thermochemical processes will emerge instead. In that case the future energy system will look more like Fig. 11 instead of Fig. 10. This too is a good outcome. Photochemical, thermochemical, and electrochemical conversion technologies all should be explored, and should compete with each other to provide the best path to the future energy vectors: electric power and liquid renewable fuels.

XII. NONFUEL STORAGE

Nonfuel storage is an important adjunct to the electric power vector, but is not a substitute for fuel. To store electromagnetic energy, it is first converted to another form.[16] For stationary storage on a large scale it is currently most cost effective to convert to the gravitational potential energy of water (pumped hydroelectric storage, PHES) or the internal energy of a gas (compressed air energy storage, CAES). For small-scale or portable storage, conversion to chemical energy in a rechargeable battery is competitive today. Large-scale storage in batteries is feasible and will compete with electrochemical fuel production in future.

A. Round-Trip Efficiency

The round-trip efficiency of the conversion process is a key characteristic of any electric energy storage system.[17] For PHES, CAES, and batteries, this can be in the 70%–90% range. A regenerative fuel converter (or cell), RFC, can be used as an energy storage device. Such systems currently have low round-trip efficiencies, in the range of 15%–25%; therefore they are not now deployed in commercial use. Bossel [3] concludes from this that batteries are the preferred electrochemical energy converters. On the other hand, improving the round-trip efficiency of RFCs would give them the advantage, since storing energy as fuel in a bottle is intrinsically simple and inexpensive. If there is no fundamental reason why RFCs cannot be made more efficient, then it is worthwhile to make the effort.

Both RFCs and batteries have, in principle, similar ultimate limits on efficiency. Both require that we eliminate, insofar as possible, the sources of entropy generation in electrochemical processes. Is there a fundamental reason why entropy generation in a fuel cell must be more than in a battery? If not, then achieving high efficiency in the former is merely a matter of technology development, and we should get on with it. This is a subject that deserves close analysis. In batteries we have the opportunity to select oxidation-reduction reactions optimized for minimum entropy generation, whereas in fuel cells we have a limited choice of fuels and oxidants. If we reject hydrogen as impractical for other

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[15] An example which seeks to produce methanol directly from solar radiation can be found in the Helios project at Lawrence Berkeley National Laboratory [56].

[16] SMES development to commercial viability would falsify this statement. We mean long-term storage, not short-term storage such as that provided by ultra-capacitors to improve the responsiveness of battery storage systems, or very short term storage as in the inductors and capacitors of electronic power convertors.

[17] Other factors such as cost and weight are determinative in specific applications.

reasons, we are limited to ammonia and methanol (or nitrofuel and carbofuel) as fuels, and to air as the oxidant. This is a big difference and may be decisive. At present, it is an open question.

B. Batteries as Energy Vectors

Any nonfuel storage device that is portable is potentially an energy vector, but never as convenient (hence valuable) as liquid fuel. Examples of alternatives to liquid fuel are batteries, flywheels, and small CAES systems; and also gaseous fuels in compressed form (e.g., CNG). Let us take batteries as representative of this group. Batteries might evolve into a second chemical energy vector.[18] To do so, they must overcome some problems. Both batteries and fuel cell systems (fuel consuming converters, FCCs; also known as electrochemical engines, ECEs) have low-specific energy, but for batteries this problem is more pronounced because they must carry their oxidizer with them. Further, batteries cannot be rapidly recharged,[19] so they have to be replaced if rapid turn-around is required. The fundamental problem with batteries is that they are not only energy storage devices, but are also conversion devices. This is not convenient for trade. We want to trade energy without having to trade our conversion devices at the same time. If energy is to be stored in chemical form, it is inherently more convenient to store it as fuel rather than batteries.

To use batteries as a chemical energy vector, a new infrastructure must be built to enable exchange. For electric vehicles, this is a feasible but capital-intensive approach, requiring significant new investment by both the supplier (who must build and operate a network of battery charging and exchange stations) and the consumer (who must buy an electric car compatible with the supplier's network).[20] For large-scale energy trade, we must imagine the equivalent of oil-carrying supertankers which have been converted to giant batteries, plying the trade routes of the world. It is not impossible; but wouldn't fuel be better? All that is needed to contain liquid fuel is a bottle; it is the ideal energy vector.

C. Fuel Production Versus Energy Storage

Storage and fuel production functions must be distinguished. As part of an electric energy storage system, for which electric power is both input and output, only the round-trip efficiency matters. On the other hand, when used for fuel production, the one-way efficiency of the electrolysis (or electro-reduction) system is of secondary importance. Of primary importance for electrolysis cell systems [electricity-consuming converters (ECCs)] is the relative value of electric power and fuel. If electric power is cheap and fuel is expensive, fuel production using electric power makes sense.

The electric power and fuel vectors each have their own markets that determine their value. Even at relatively low efficiency, fuel production using electric power will be economical as a means to monetize excess electric capacity that must be used or lost. Today, most electric power is generated from fuel, hence electric power is a value-added product. It makes no sense to convert it back again to fuel, which only degrades its value. When, however, electric power is generated from renewable or nuclear sources, then it is fuel that is the value-added product, and not electric power. Using electric power to produce fuel will then make perfect sense. This will happen sooner rather than later if the interconversion efficiency between electric power and fuel can be improved.

Currently the principle renewable source for electric power is hydroelectric. Both hydroelectric and nuclear sources have built-in storage, which diminishes the motivation to produce fuel from the generated electric power. This will change as more electric power is generated from wind and solar, which are stochastic sources lacking an intrinsic storage mechanism. To provide reliable electric power service using stochastic sources, excess generating capacity must be built. There will then be more and more opportunities to purchase off-peak-load power at low cost. As fossil fuel supply and price become more erratic, fuel production will become an increasingly attractive use for excess power. The choice between nonfuel storage and fuel production devolves to an economic dispatch protocol: electric power is first used to meet immediate load demand, then used to recharge high-efficiency nonfuel storage, and last used for fuel production. We anticipate a future in which this last use will be the largest of the three.

A possible scenario is this: High-efficiency nonfuel storage (e.g., PHES and CAES) will be built first, to enable renewable energy sources to surpass 30% of the global energy supply. Meanwhile, renewable fuel use will spread, supplied mainly by production from natural gas. As the market for renewable fuel grows, innovation to improve the efficiency and lower the cost of ECCs will be stimulated. The challenge is to develop an ECC that can run intermittently with high efficiency and is sufficiently low

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[18] Primary (disposable) batteries are already an alternative energy vector, but not competitive except in very limited niche applications. Secondary (rechargeable) batteries are not yet energy vectors. They are conversion devices that might become vectors if an infrastructure is developed to trade them [57].

[19] Quite high recharge rates are achievable. Electric vehicle battery packs can be recharged in as little as 10 minutes [58]. But can battery packs remain under 10-year/10 000-cycle warranty when charged at such high rates? Even if they can, the same amount of energy can be transferred in 10 seconds by filling a tank with a liquid fuel. Battery recharging will never be competitive with liquid fuel refilling for simplicity, speed, and convenience. Vehicles powered by batteries only (so-called all-electric vehicles) will become a quaint memory as soon as low-cost renewable fuel becomes widely available. Hybrid electric vehicles (HEVs), however, will continue to thrive in all scenarios. The goal of HEV design should be to make the battery pack as small as possible, consistent with an all-electric drive, and to store most of the required energy as renewable fuel.

[20] This is the business model of the company Better Place [57], which is conducting a large-scale experiment to determine if this mode of energy trade can gain public acceptance.

cost. The cost must be low enough to make it an attractive investment even at low capacity factor.[21] Achieving this technology goal will enable electrochemical fuel production to displace nonfuel storage entirely.

D. Distributed Generation and Energy Hubs

Fuel has an additional inherent advantage over electric power: it enables much higher overall efficiency in the energy chain. Energy transmission and distribution as fuel instead of as electric power enables distributed generation (DG) and combined cooling heat and power (CCHP).[22] When electric power is generated near the end-use, low-grade heat produced as a by-product can be used, rather than wasted.

An example is the microgrid architecture proposed for future energy systems. A microgrid is a subdivision of the electric power grid formed by loads and generators aggregated together into a single dispatchable (controllable) unit that can seamlessly disconnect from and reconnect with the macrogrid. Not all the loads comprising a microgrid can be controlled, nor can all the generators, since some are powered by more-or-less unpredictable renewable sources. But enough of each is controllable so that significant demand-side management (DSM) and distributed generation (DG) flexibility is available. This flexibility is exercised by a local system operator (LSO), possibly robotic or semi-autonomous. The LSO allocates internal generating resources to internal loads and also controls the interaction of the microgrid with the macrogrid in which it is embedded. The microgrid can trade energy with the macrogrid, or it can disconnect (or be disconnected) if either becomes dysfunctional. Each microgrid exercises the DG/DSM flexibility under its control in response to market pressures and opportunities.

The microgrid concept can be extended to include renewable fuel as well as electric power; the microgrid then becomes an *energy hub*. Hubs located in densely populated areas where energy consumption is intense will exceed locally available renewable energy resources and will need to import energy; that energy can be imported either as fuel or as electric power. When energy is imported as fuel, and locally converted to electric power as needed, CCHP enables higher efficiency usage than is achievable when the energy is imported directly as electric power. Therefore, we expect that in future, most energy will be traded amongst energy hubs in the form of renewable fuel, and not as electric power.

Energy hubs, like microgrids, are vehicles for evolving the electric power grid toward a decentralized structure. The purpose of this restructuring is threefold: 1) to promote the use of renewable energy sources (inherently distributed in nature); 2) to enable high system-level efficiency; and 3) to enhance the reliability and security of electric power supply.

E. Energy From Remote Regions

We want to design a global energy system, whether its architecture includes DG in microgrids or not, that can be supported by massive renewable fuel production in remote areas such as oceans and deserts. For example, the blue-water tropical oceans of the world, far from land, are attractive locations for massive marine solar energy plants, perhaps based on ocean thermal energy conversion (OTEC).[23] Such plants could satisfy a large fraction of the planetary energy requirement. As electric power, this energy is stranded in the middle of the ocean; but in the form of liquid renewable fuel it is easily delivered where and when needed. This is true also for very large solar photovoltaic or thermal power plants that may be built in the remote desert regions of Africa, Central Asia, Australia, and the Americas. The same applies to nuclear as well as renewable sources. Nuclear fission reactors, if they are built in the future, will most likely be sited in locations remote from population centers. The best way to enable very large but remote renewable and nuclear energy sources is to deliver their product as fuel, rather than as electric power. Nonfuel storage is an important adjunct to the electric power vector, enhancing market efficiency and reducing cost. It is, however, not a substitute for fuel. To promote renewable sources, we need renewable fuels.

XIII. NATURAL GAS AS A TRANSITION SOURCE

Both ammonia and methanol are currently produced most cost-effectively from natural gas, using conventional petrochemical processes. An infrastructure and market for renewable fuels can be developed using this source. This does not supplant the need for high-efficiency fuel synthesis from renewable energy sources. On the contrary, it *enables* it, by generating a rising tide of market demand for renewable fuel products.

A. Which Comes First?

The technology for efficient low-cost conversion of renewable energy sources to renewable fuels needs development. There is weak incentive to do so prior to the widespread adoption of renewable fuels. Conversely, there is weak incentive to adopt renewable fuels if there is not an inexpensive supply. Which comes first? To break this conundrum, a bootstrap procedure is called for. First expand the range of end-uses using already existing technology: the petrochemical production of ammonia and methanol.

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[21] Capacity factor is the fraction of a plant's full productive capacity that is actually used. A plant with low capacity factor is one that sits idle much of the time.

[22] CCHP is also known as tri-generation.

[23] OTEC is sometimes denigrated for its low Carnot efficiency. What matters, however, is not efficiency but EROI. The ocean is a massive solar collector that costs nothing to build. Extracting energy from it, even at low efficiency, might be a profitable enterprise.

B. Stranded Natural Gas

Stranded natural gas fields—those separated from markets by oceans or located in regions hard to reach by pipeline—can be developed most economically by gas-to-liquid conversion. The cost of conversion is compensated by lower transport and storage cost, and also by opening new markets. Stranded natural gas is a resource that can be used to produce ammonia and methanol fuels at sufficiently low cost to attract early adopters of renewable fuels.

C. Prerequisites

Two prerequisites are needed to start the process of opening these markets.

- Plans, kits and services to convert existing infrastructure to renewable fuel must be available.
- The existing ammonia and methanol distribution systems, originally developed to serve nonenergy consumers, must be expanded to accommodate the new fuel market.

The development of these two prerequisites must proceed in parallel, a difficult but not impossible challenge. Electrochemical conversion is *not* the focus of this initial technology development; rather, conversion of conventional engines and combustors to run on renewable instead of (or in addition to) fossil fuels is the first objective. Growing the market for renewable fuels and developing the associated fuel distribution infrastructure will provide the necessary economic incentive for further development of electrochemical conversion technology in the future.

D. DFX: The Dual-Fuel Exchange

Financial engineering is required to meet the challenge. We must design a market, the dual-fuel exchange (DFX), capable of bringing buyers and sellers together. There is an entry barrier to participation in the DFX, but that barrier is low, and the rewards of membership are high. Energy buyers must be willing to invest in a moderate level of equipment modification. Engineering entrepreneurs must be willing to invest in development of products and services to meet that need. Energy sellers (in the beginning, natural gas producers) must be willing to expand their production of ammonia and methanol. Distributors of ammonia and methanol must be willing to expand their operations. All this will be possible because the investment is low and the reward high for all DFX participants. Financial engineering is required to create the DFX and set it in motion. The DFX, once operative, will deliver energy with better reliability and lower cost than business as done now. As a bonus, it will do so with much smaller carbon footprint.

XIV. CARBON EMMISSION

The dual-fuel strategy enables low to zero carbon emission in the long term. When natural gas or coal is the feedstock, however, neither ammonia nor methanol are carbon-free; this strategy then offers no near-term reduction in CO_2 emissions. *It is still worth doing*. The purpose is then to provide a transition to a dual-fuel infrastructure and energy market which will enable renewable to displace fossil sources and thus ultimately lead to a zero-carbon energy system.

It might be possible, however, to do still better. The dual-fuel strategy can potentially enable an order-of-magnitude reduction in carbon emission in the near-term. To enable near-term reduction, however, CO_2 generated from fossil sources must be dealt with. The problem is enormous in scale. The solution, a global economy based on 100% renewable energy, requires development on a commensurate scale. This can be done.

A. Centralized CO_2 Generation Enables CCSS

Converting fossil sources to ammonia promotes near-term reduction in carbon emission by concentrating CO_2 production at centralized locations. Doing so enables processes for carbon capture sequestration and sale (CCSS) to be profitable. It will be more likely that such processes can be successfully developed and deployed if they are concentrated in a hundred *large* sources (petrochemical fuel processing plants), rather than dispersed throughout a hundred thousand *medium* sources (central-station electric base-load power plants), and a thousand million *small* sources (mostly vehicles—air, water, rail, and road transport). Conversion of fossil sources to ammonia enables CCSS by *not* requiring that it be accomplished at a large number of dispersed sources.

For reviews of approaches to CCSS, see [59] and [60]. A dissenting view holds that CCSS is not feasible. For example, Page *et al.* [61] argue that CCSS is excluded by thermodynamic considerations. We find their analysis valuable, but their conclusion mistaken. Their analysis "focuses on post-combustion capture of CO_2 from direct fired [electric power] plants." They conclude that "the value of further investment in CCS . . . is questionable." This conclusion is wrong. It is based on a very narrow usage of the phrase "carbon capture," which Page *et al.* take to mean capture at the exhaust stack of an electric power generating station. We use CCSS in a much broader sense, including the sequestration and sale of CO_2 that has already been captured in the course of petrochemical processes such as ammonia production. Instead of being an argument against CCSS, the analysis presented in [61] supports the view that natural gas should be converted to ammonia at the gas fields; the CO_2 that is naturally captured while doing so should be sequestered in a valuable product; ammonia rather than natural gas should then be distributed as fuel to electric power plants; and the CO_2-based product should be sold to other customers.

Another objection to CCSS holds that the amount of CO_2 generated is so vast (what Mikkelsen *et al.* [60] call the "teraton challenge") that there is no possible way to use it. On the other hand, building and maintaining (rebuilding) the global transportation and energy infrastructure is also a vast project. If we can create CCSS products for land- and sea-based energy farm construction and transportation projects, we will be able to absorb a very large amount of carbon. The new renewable energy infrastructure will need to cover one to two percent of the Earth's surface. We can well afford to set aside this relatively small fraction of our planet in exchange for solving our energy problem; but it is nonetheless a very large area that we will be building on. Accomplishing this will require vast resources on a scale similar to the CO_2 we will be capturing from fossil sources while that new infrastructure is being built. What better place to put this captured CO_2 than in the very system that will enable us to stop generating it? When we are done building the new renewable energy infrastructure for Planet Earth, in about 2050, we'll stop using fossil sources. Meanwhile, the CO_2 generated will go to good use in a number of global-scale grand projects. All that is needed to enable this is creativity in developing building materials that use carbon or CO_2 as a feedstock, or that sequester CO_2 as part of a process to enhance extraction of other feedstock materials.

B. Examples of CCSS

Enhanced gas recovery and mineral carbonation are two approaches to grand-scale use of carbon dioxide that are particularly attractive. We review them briefly in the following subsections. A third approach to CCSS that avoids carbon dioxide generation altogether is then proposed.

1) Enhanced Gas Recovery: Value can perhaps be derived from the CO_2 generated by fuel processing at natural gas fields by using it on-site to enhance production. This process is named carbon sequestration with enhanced gas recovery (CSEGR). In the CSEGR process, CH_4 is extracted from its natural underground storage vault and combined with O_2 to produce H_2 and CO_2. The H_2 is used for NH_3 synthesis and the CO_2 is pumped back into an adjacent nearly empty reservoir. There it is used to pressurize the reservoir so that the remaining natural gas can be squeezed out. When no more CH_4 can be extracted, the CO_2 is left in place and the gas field sealed. The underground CH_4 is simply replaced with CO_2; all else remains unchanged. This process has no environmental impact if all goes well. Two ways things can go wrong are that the injected CO_2 gets into the water supply, or all of the injected CO_2 escapes. In the first event we have carbonated water; in the second we are no worse off than if we had released it into the atmosphere in the first place. These are relatively benign consequences. Further, both are unlikely if the underground reservoir is uncompromised by fracturing. An unaltered reservoir has (by definition) been stable for millions of years, and can confidently be predicted to remain so.

The main drawback of CSEGR is that it depends on the availability of an adjacent "mature" reservoir and the formation of a sufficiently sharp interface between the incoming carbon dioxide "bubble" and the outgoing natural gas in that nearly-empty field. This interface must be stable throughout the multiyear period during which the gas remaining in the mature field is extracted. It is currently unknown whether this can happen. Further, CSEGR is not applicable to all gas fields, but only when new and old gas fields can be paired. An entry into the literature of CSEGR is provided in Appendix C. As attractive as CSEGR is, alternatives must be sought; one such is mineral carbonation.

2) Mineral Carbonation: Mineral carbonation is the capture of CO_2 in carbonate solids that can be used as building materials. This process starts with an abundant mineral feedstock that contains CaO or MgO and adds carbon dioxide to form the carbonate

$$\mathrm{MO} + \mathrm{CO_2} \rightarrow \mathrm{MCO_3}$$

where $\mathrm{M} = \mathrm{Ca}$ or Mg. For example $CaCO_3$ is limestone and $MgCO_3$ is magnesite. These are materials that could be used in place of petroleum-derived asphalt to pave roads or to build structures. As such, they are valuable products (like concrete, cinder blocks, and bricks) that can be sold to compensate the petrochemical plant operator for the cost of making them. Feedstock for the mineral oxide reactant comes from naturally occurring minerals in land or sea-based deposits, or perhaps industrial waste products. In the latter case, there is value also in the disposal of the waste.

Lackner suggested this approach in 1995 [62]. Subsequently a great deal of work has been done to develop mineral carbonation for CCSS. Mineral carbonation is a natural process (weathering) which happens spontaneously. The key challenge is to make the carbonation reaction go at a high enough rate to be commercially viable. At least one commercial enterprise is already in pilot-scale trials [63]. Appendix C includes further discussion and references to the literature.

3) Carbon–Nitrogen Displacement: Perhaps the most elegant solution to carbon emission is to simply displace the carbon in natural gas with nitrogen

$$3\mathrm{CH_4} + 2\mathrm{N_2} \rightarrow 4\mathrm{NH_3} + 3\mathrm{C}.$$

Carbon on the right-hand side of this reaction is in the form of graphite, or carbon black, a stable solid that can be used to make structural components, building materials, and a host of other products. We will call this the carbon–nitrogen displacement, or CND, reaction. The standard Gibbs energy change of the CND reaction is −5.6 kJ/mol NH_3. This is a small number, 1.5% of the enthalpy of combustion. Thus, the CND reaction can in principle proceed spontaneously with little loss of stored chemical energy. Ammonia as fuel has half the energy density of methane; but the carbon black produced along with the ammonia retains its energy which is available for production of nonfuel products. There are 1 1/4 reactant gas molecules for every product gas molecule, thus equilibrium yield can be increased by raising the pressure. If an effective catalyst can be found, this is a feasible process.

Aside from a few reports of reactions in methane-nitrogen plasmas, there appears to be no prior work exploring the possibility of implementing the CND reaction. Thermolysis of methane in the absence of any other reactant to yield hydrogen and carbon black is an alternative which has received some attention. This reaction is endothermic and requires energy input from a solar or nuclear source. The CND reaction, by contrast, is exothermic and could in principle be self-driven, consuming a small portion of the energy contained in the natural gas feedstock. Although speculative, the CND reaction deserves attention since successful development would have revolutionary impact.

C. Near-Term Order-of-Magnitude Reduction in CO_2 Emissions

When combined with CCSS, ammonia derived from natural gas is a carbon-free fuel. Ammonia replaces about 80% of fossil fuel use. This replacement eliminates 80% of carbon emissions. Methanol and its derivatives such as DME and dodecane replace about 20% of fossil fuel use. Methanol is the liquid equivalent of natural gas as a low-carbon fuel, with about one-half the carbon intensity of oil-derived fuels.[24] Taking one-half to be the improvement in carbon intensity, a 10% reduction in carbon emission is achieved. The overall result is a 90% reduction in carbon emission—an order-of-magnitude improvement.

But even if CCSS cannot be successfully developed and deployed, the conversion of natural gas to ammonia and methanol is still worthwhile because it is a path to build a market for renewable fuels that can in future be derived from zero-carbon renewable sources. Building this market is essential to enabling renewable sources to compete with fossil sources. The goal is to replace fossil with renewable *sources*; replacing fossil with renewable *fuels* is only a means for getting there.

XV. FUEL DESIGN

To simplify the energy infrastructure, the smallest possible number of primary fuels should be implemented.[25] The hydrogen economy plans for just one; the dual-fuel strategy requires two. The essential features of these two fuels are that they are *renewable* and *liquid*. Renewable fuels are source-neutral; they are not linked to any particular energy source, as fossil fuels are. Rather, they can be generated from any source—including fossil sources. A desirable (but not essential) feature of a renewable fuel is that it should be interconvertible with electricity with high efficiency. Then, any energy source that can be converted to electricity can also be converted to fuel. Hydrogen, the simplest of molecules, is the best for interconvertibility. But hydrogen has a fatal flaw: it is a gas. Polar molecules are preferred because they condense (liquefy) easily; they are liquid at room temperature and moderate pressure. It is this feature that confers compatibility with the legacy energy infrastructure. Further, we speculate that simple (i.e., small) molecules are best for high conversion efficiency.[26] Thus, we seek simple polar molecules.

Let us ask: Starting with air and water, what can we make that might serve as renewable fuel?

A. Carbon-Free Substances

If we wish to avoid carbon, ammonia is the first thought. After that comes a list of exotic possibilities.[27] A substance that might be considered "simpler" than ammonia is nitrosyl hydride, or nitroxyl: HNO. A more "complicated" molecule is hydrazine: N_2H_4. There is also hydroxylamine (NH_2OH), nitramide (NO_2NH_2), hydrogen azide (HN_3), hydrazoic acid ($2H_2O \cdot HN_3$), and ammonium azide ($NH_3 \cdot HN_3$). Further, there is nitric acid (HNO_3), ammonium nitrate ($NH_3 \cdot HNO_3$), and so on.

Solid nitrogen-based fuels have been proposed. Examples are metal amines [65], ammonia borane [66], and guanidine [67].[28] The motivation for inventing such fuels is to mitigate the toxicity hazard of ammonia, especially in transportation applications involving nonprofessional fuel handlers. Solid fuels, however, are to be avoided. The use of carbofuel in those applications where toxicity is unacceptable is a superior approach. It is more consistent with existing infrastructure, thus easier to implement.

None of the substances listed above appear to be useful as fuel, except perhaps as solutes in liquid ammoniates (see below, and Appendix H). A comprehensive review of nitrogen compounds with a view to use as fuel has not, however, been done; such a review is needed.

B. Carbon-Containing Substances

If we are willing to admit some carbon into our fuel, the range of possibilities expands enormously.

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[24] Roughly; see Appendix D on fuel carbon intensity.

[25] In addition, there will always be secondary fuels for special purposes. Such special fuels are likely to be more expensive than the primary fuels, but that extra expense will be justified by other considerations that we cannot (and need not) foresee.

[26] At present, this is speculation; it is a question for theoretical investigation.

[27] Useful guidance is provided by Ashcraft and Green [64].

[28] All of these, strictly speaking, belong in a separate category since they contain elements beyond H–N–O; guanidine belongs in the following subsection.

Carbon monoxide (CO) is the simplest fuel that can be derived from CO_2. Formaldehyde (H_2CO) is next, followed by formic acid (HCOOH). Methanol (CH_3OH) is next, then dimethyl ether [DME, $(CH_3)_2O$] and ethanol (C_2H_5OH). Continuing toward more complex molecules, there are higher alcohols, $H(CH_2)_nOH$, and alkanes, $H(CH_2)_nH$. There is probably no reason to consider molecules more complex than these latter two categories, which attain the most desirable fuel properties: low relative toxicity, high energy density, and compatibility with existing infrastructure. Extending the usage of Zeman and Keith [12], we refer to both higher alcohols and alkanes as carbon-neutral hydrocarbon (CNHC) fuels. The choice between methanol and CNHC fuels revolves around production and use efficiencies. Methanol is closest to H_2O and CO_2, and will therefore most likely have the highest production efficiency from renewable energy sources. Probably it will also have the highest use efficiencies in engines of all kinds (very likely in ECEs and perhaps also in ICEs and CTs if one factors out the cost of engine modification). The lower production and use efficiencies of CNHC fuels will make them relatively more costly than methanol; but this may be acceptable since they are also more valuable. They are more valuable because they can be used in existing engines with no modification whatsoever, and because they have twice the energy density. An analysis of the relative costs of producing and using the foregoing fuel options is needed.

Allowing both carbon *and* nitrogen opens yet more possibilities. The simplest is hydrogen cyanide, HCN; next is cyanamide, or cyanimide (H_2NCN); next is ammonium cyanimide ($NH_3 \cdot H_2NCN$). Amines are an extensive family of H–C–N compounds, the first member of which is methylamine (NH_2CH_3). Examples of two-nitrogen compounds are monomethyl and dimethyl hydrazine (CH_3NHNH_2 and $CH_3NHHNCH_3$), unsymmetrical dimethyl hydrazine [$(CH_3)_2NNH_2$], and so on. Adding oxygen one has isocyanic acid (HNCO); and urea, or carbamide [$(NH_2)_2CO$]; ammonium cyanate ($NH_3 \cdot HNCO$); nitromethane (CH_3NO_2).[29] Ammonium bicarbonate (also known as ammonium hydrogen carbonate; $NH_3 \cdot H_2CO_3$, or NH_4HCO_3) is the analog of ammonium nitrate. The list goes on; here we cite only some leading examples. Fuels containing both carbon and nitrogen present additional challenge for control of NOx generation due to the extra complexity of combustion processes.

C. Mixtures and Blended Fuels

It is likely that future fuels, like present ones, will be blends and not pure substances. Knowledgeable chemists will dismiss most of the substances listed above for use as fuel, in pure form. But should they be dismissed as fuel *additives*? Many of these substances are miscible with each other, enabling properties to be tailored. Physical properties such as melting and boiling points, vapor pressure, viscosity, ignition energy, adiabatic flame temperature, flame propagation velocity, and the like can be manipulated and optimized. Mixtures, especially with anhydrous ammonia, might make an improved nitrofuel.

The leading example is Divers' solution (DS), a solution of ammonium nitrate in ammonia [71]. It has significantly lower vapor pressure than ammonia, so is easier to transport and store. Because it contains oxygen, its energy density is less than that of pure ammonia, but it also has improved ignition properties for use in ICEs. The utility of DS mixtures as fuel was noted by Davis in [72] and [73]. Combustion properties were studied by Farber and Darnell [74]. Ganley and Bowery [75] report recent tests using DS mixtures as fuel in a modified diesel engine. These reports show that the mixture is not explosive, is easily handled, and has useful combustion characteristics.

In addition to DS, there are many other nitrogen-based energetic materials that might be components of a nitrofuel blend. Further, there are many carbon-containing solutes that can be mixed with ammonia to produce fuel. Fuel-blending using solid solutes in ammonia is discussed in Appendix H.

In addition to solid solutes there are liquid and gaseous solutes. Ammonia and methanol or ethanol are miscible and such mixtures can be evaluated as fuel, although as far as we know it has not yet been done. The properties of mixtures of ammonia and methanol are reported in [76] and [77] and related works cited therein. According to [76], a solution of 40 mol% ammonia in methanol has a boiling point (vapor pressure of 1 bar) at 10 °C. Ammonia-acetylene blends were developed as an alternative fuel in Europe during World War II (see [2] and [78]–[82]). These mixtures have improved ignition characteristics compared to pure ammonia, but they also have higher vapor pressure [83]; blends with lower vapor pressure are preferred. The list of ammonia mixtures with carbon-containing solutes may not be endless, but there are very many possibilities to be evaluated.

Azeotropes are mixtures for which vapor and liquid phases have the same composition. This is a desirable feature because it enables the fuel to be stored as a liquid and used as a vapor.[30] We would like the stored liquid phase to maintain constant composition as it is vaporized for use.[31] Azeotropes occur for mixtures of some of the above compounds, including ammonia and DME [84]–[86]. This particular azeotrope, discovered by refrigeration

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[29] Nitromethane is already well established as an engine fuel; see [68]–[70].

[30] In most existing ICEs the fuel is "atomized," i.e., converted to small liquid droplets that are sprayed into a combustion chamber where they vaporize completely. Use of an azeotrope would enable the fuel to be vaporized before entering the combustion chamber.

[31] The azeotropic composition varies with temperature. For R723 the composition varies by 30% as the temperature varies from −20 °C to +60 °C. The composition of the liquid will tend to the azeotropic composition at any given temperature as vapor is removed.

engineers and given the designation R723,[32] has also been mentioned for use as fuel [87]. Use of a nonazeotropic ammonia-DME mixture as fuel has been reported [88]. Like the ammonia-acetylene mixture, R723 has a higher vapor pressure than pure ammonia. This is no problem for a refrigerant, but is an undesirable characteristic for a fuel. Nevertheless, we can learn from refrigeration scientists who have developed sophisticated methods to search for useful azeotropes. These methods can be employed in the search for the optimum renewable fuels.

D. Perspective on Renewable Fuels

The dual-fuel strategy assumes two fuels, nitrofuel and carbofuel. The objective is to minimize, but not necessarily *immediately* eliminate, CO_2 emissions. It is enough to start on a path that leads to zero-carbon fuels the in future. The key feature of a renewable fuel is that it can be produced using renewable or nuclear sources. It is this feature that enables zero fuel carbon intensity ultimately, even if that is not realized immediately.

A liquid alternative to hydrogen is required. Ammonia and methanol are not the only choices for renewable fuels, but they are the simplest. The leading alternative to this pair replaces methanol with ethanol.[33] Methanol has low relative toxicity, like that of gasoline; ethanol has *very* low relative toxicity, almost like water (you can drink it). If a very low toxicity fuel is mandatory, ethanol is a good choice. It is already in widespread commercial use, with established distribution channels.[34] That fact alone may give it a decisive advantage. Ethanol is fully compatible with the dual-fuel strategy.

Is there a penalty associated with using ethanol rather than methanol as a chemical energy vector? One recent study [89] suggests that there is; but the question does not have a straightforward and definitive answer. Ethanol production using renewable energy is most often associated with biomass. Biomass production based on arable land is not viable because it competes with food production. Production based on nonarable land or ocean-based biomass (e.g., algae) might be viable despite low efficiency if coupled with a valuable coproduct such as sewage treatment. Here we do not debate biomass versus other modes of renewable energy conversion. The question is: do simpler molecules have an advantage over more complex ones as chemical energy vectors, independent of the method of synthesis? A theoretical investigation is called for. Lacking that, we speculate that simpler molecules are easier to synthesize; thus, we provisionally favor methanol.

XVI. AMMONIA/NITROFUEL

Noncarbon fuels are preferred to provide the most options for the reduction of CO_2 emissions. Ammonia, NH_3, is attractive because it reacts with oxygen to form nitrogen and water vapor, both benign atmospheric components.[35] It has relatively low vapor pressure, similar to propane, and is thus easy to transport and store. Like propane, ammonia is a liquid at room temperature under moderate pressure—about that of a racing bicycle tire. It has, however, the disadvantage of high relative toxicity. Nevertheless, ammonia has a proven record of safe use. It is already one of the most manufactured and used industrial chemicals. The U.S. Environmental Protection Agency (EPA) provides a balanced assessment of the hazards of ammonia [90]:

> "[Ammonia's] toxicity and high production volume prompted EPA to list ammonia as an extremely hazardous substance. . . [and] . . . require that facility employees who could potentially be exposed to ammonia in any form be trained in the safe use and potential hazards posed by this chemical. *EPA stresses that although mishandling of ammonia can cause harm, there is no cause for undue alarm about its presence in the community. Ammonia is typically handled safely and without incident*" [emphasis added].

Currently, ammonia is primarily used as fertilizer, and as a working fluid in refrigeration plants. As a fuel, it can be safely used in all applications where professional fuel handlers are employed. The special training and equipment required to handle ammonia is very modest. For an idea of the training required, consult [91]. Required special equipment is rubber gloves and gas-tight goggles. Contact lenses must be removed before handling ammonia. Recommended is complete body-covering (i.e., shoes and head covering, long pants, long sleeved shirt) and face-covering (a transparent shield). Additional protection can be kept at the ready, perhaps clipped to one's belt (an "escape" breathing mask with activated carbon canisters). Safety showers capable of providing high-volume water flow must be available at refueling sites.

Professional fuel handlers with appropriate training and equipment can be employed in the majority of fuel applications. These include central station power generation, where ammonia displaces natural gas; surface transport (sea, river, rail, and road trucking), where it displaces diesel fuel; and perhaps short-haul aviation, where it displaces jet fuel. These are summarized below; Appendix B can be consulted for more information.

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[32] Refrigeration engineers refer to anhydrous ammonia as R717.

[33] Still other alternative carbofuels are listed in Sections XVII-B/C. The considerations discussed here in the context of ethanol apply to those other alternatives as well.

[34] This is all the more true if alkanes are used for carbofuel; see Section XVII-C

[35] At high temperature, nitrogen monoxide can also form. Counterintuitively, this is actually *less* of a problem for ammonia as fuel than for other fuels, even including hydrogen; see Section XVIII-C.

A. Base-Load Electric Power and Industrial Process Heat

Ammonia is currently transported in liquid form through pipelines of 2000+ km in length. The existing natural gas pipeline infrastructure can be gradually converted to ammonia, certainly with dual pipes sharing the same right-of-way, perhaps even using the existing pipes. Ammonia requires much lower pressure than natural gas, so existing gas pipelines are more than adequate. Ammonia has good materials compatibility with iron and steel. Some materials will have to be replaced and some components modified, for example compressors. Even if these have to be completely replaced, much of the existing natural gas infrastructure can remain intact.

One of the most straightforward and low-cost near-term conversions will be central-station electric power generation. Natural gas and coal can be replaced with ammonia in this application, which today is a major source of GHG emissions. Steam turbines account for the majority of base-load central station electric power generation plants throughout the world. In these plants, coal, oil, or natural gas is used as fuel for boilers in which steam is generated. The steam is then supplied to the rest of the plant, which is independent of the boiler. In such plants, only the boiler unit need be modified to convert to ammonia.[36] It may have to be replaced; even so, the majority of the plant remains intact. Most electric power generating plants already have a supply of anhydrous ammonia, used to control NOx emissions. Thus, the electric power generation professional community is already familiar with the techniques and equipment for handling this material safely.

Industrial process heat is another very large energy sector that, like base-load electric power, requires only combustors (furnaces) as fuel conversion devices. An example is the production of Portland cement, which consumes a great deal of energy and is responsible for substantial CO_2 emission. Both steam generation for electric base-load power and industrial process heat can be supplied in the near-term by ammonia with minimal modification to existing facilities and equipment. Only burner design and replacement is required.

B. Peaking Power, Distributed Generation, and Transportation

Ammonia can be used to power any engine or combustor currently run on fossil fuels. These include combustion turbines (CTs, also known as gas turbines GTs), internal combustion engines (ICEs, both SI and CI), and fuel cells (both indirect and direct). These devices are used in electric power systems for peaking power, as components in combined cycle generation systems, and for distributed generation. They are used throughout the transportation sector, to propel aircraft, ships, trains, and trucks. All portions of that sector that employ professional operators can use ammonia as fuel. Modification of CTs and ICEs of various kinds to run on ammonia has been widely demonstrated. Commercial enterprises developing both kits and services for modification of existing engines and also purpose-built engines are beginning to appear [93], [94]. Like other hydrogen-bearing fuels, ammonia can be used indirectly in fuel cells by first passing through a reformer, a device that converts ammonia to nitrogen and hydrogen. The hydrogen then is fed to the fuel cell. Preferable for simplicity is to feed the fuel cell directly with ammonia, an option that has been demonstrated and is under development; see reviews by Wojcik [47] and Ni [53].

C. Environmental and Safety Advantages

Ammonia has significant environmental and safety advantages. The fire and explosion hazard of ammonia[37] is very low, much less than that of natural gas, propane, or gasoline—or hydrogen. The consequences of anhydrous ammonia spills are serious, but far less devastating than similar petroleum-related incidents. Compared to unintended releases of other major industrial chemicals (e.g., petroleum, sulfuric acid and chlorine), the environmental impact of a major ammonia release is mitigated and self-healed within a relatively short time. Ammonia is a lighter-than-air gas that disperses readily. An ammonia spill is therefore difficult to contain, but also rapidly self-diluting. Ammonia combines readily with atmospheric water vapor to form ammonium hydroxide, a strong base. In high concentration it is toxic, but it is rapidly diluted to become fertilizer. In a relatively short time the diluted residue will promote plant growth. The short-term consequences of major ammonia spills can be devastating, but in the midterm (one growing season) the consequences are relatively benign.

Despite its toxicity, ammonia is less hazardous than petroleum, perhaps even less hazardous than hydrogen. Not only fire and explosion hazard *per se*, but also secondary hazards such as the explosion-triggered release of other chemicals must be considered in making a comparison. Ammonia is unique among high-energy materials (fuels and explosives) in being immune to accidental ignition. The ignition barrier for ammonia combustion is high[38] and is one of the reasons why engines designed for use with petroleum fuels need modification to use ammonia fuel. This is an advantage, not a drawback. In exchange for minor equipment modifications, we get a fuel that will not burn or explode accidentally.

D. Pipes Versus Wires and Liquids Versus Gases

Ammonia transport in pipelines is superior to electric transmission on high-voltage overhead lines for moving large amounts of energy over long distances. The

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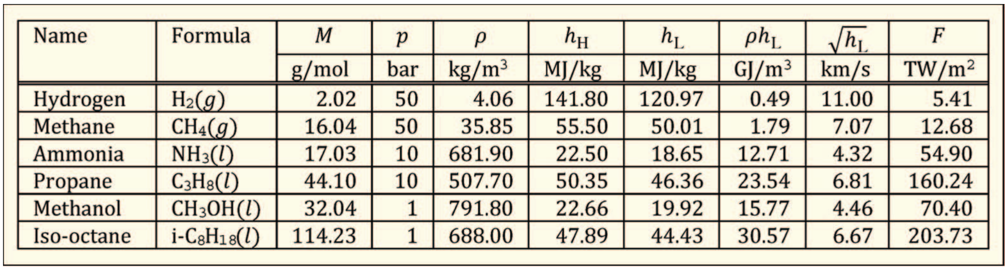
[36] For an account of current boiler technology, see [92].

[37] It is important to emphasize that anhydrous ammonia is not ammonium nitrate. Ammonium nitrate is associated with severe explosion hazard, such as the famous Texas City disaster of 1947.

[38] As measured by AIT, MIE or MIC ratio.

Table 1 Figures of Merit for Pipeline Transport of Representative Fuels



Name	Formula	M	p	ρ	h_H	h_L	ρh_L	$\sqrt{h_L}$	F
		g/mol	bar	kg/m^3	MJ/kg	MJ/kg	GJ/m^3	km/s	TW/m^2
Hydrogen	$H_2(g)$	2.02	50	4.06	141.80	120.97	0.49	11.00	5.41
Methane	$CH_4(g)$	16.04	50	35.85	55.50	50.01	1.79	7.07	12.68
Ammonia	$NH_3(l)$	17.03	10	681.90	22.50	18.65	12.71	4.32	54.90
Propane	$C_3H_8(l)$	44.10	10	507.70	50.35	46.36	23.54	6.81	160.24
Methanol	$CH_3OH(l)$	32.04	1	791.80	22.66	19.92	15.77	4.46	70.40
Iso-octane	$i\text{-}C_8H_{18}(l)$	114.23	1	688.00	47.89	44.43	30.57	6.67	203.73

environmental and view-shed impact is reduced and the transmission efficiency is higher. By transmission efficiency we mean the efficiency associated with transmission losses alone, not including losses associated with conversion from electrical to chemical form. Transmission losses associated with pipeline transport favor liquid fuels, as discussed by Leeth [95] and Ahlgren [96], [97]. In [97] a figure of merit, the fuel power density, is proposed for comparing alternative fuels as vectors for pipeline transport of energy. Fuel power density is $F = \rho h\sqrt{h}$, where ρ is the density and h the specific enthalpy of combustion of the fuel. It should be large for a good fuel. Table 1 exhibits these quantities for several representative fuels.

The fuel power density displayed in the last column of Table 1 underscores the advantage of high-density liquid renewable fuels such as ammonia and methanol over gaseous fuels such as hydrogen and natural gas. Gasoline (represented by iso-octane) is the best. Although not listed, kerosene (dodecane) and diesel fuel (hexadecane) are even better. Propane is not as good as gasoline, but is still quite good. This confirms that long-chain alkanes are superior fuels—except that they are in short supply and cause global warming. The alternative renewable liquid fuels, ammonia and methanol, are good too. Importantly, they are much better than either hydrogen or natural gas (methane). That is because they are liquids and not gases. The fact that ammonia and methanol are four-to-five times better than methane as a pipeline energy vector is one reason why it is worthwhile to convert natural gas to these liquid renewable fuels prior to transmission over long distances in pipelines.

Savings in transmission losses partly compensate losses incurred in petrochemical conversion from gas or coal to ammonia. Further efficiency gains accrue if CCHP is implemented at the point of use. Consider for example the transmission of electric power from Utah to Los Angeles. Currently this is done by generating electric power at the coal fields and transporting it on an HVDC transmission line. The waste heat generated at the power plant must be disposed of in Utah. If, instead, the coal were converted to ammonia in Utah by standard petrochemical processes (augmented by CCSS to eliminate CO_2 emission) and transported in a pipeline, it could then be converted to electricity in Los Angeles. The conversion of fuel to electricity could be done using distributed generators (perhaps hybrid SOFC-GT CCHP units) capable of recovering and using much of the heat generated. All of that heat is wasted in Utah; worse, its disposal wastes or degrades other resources as well.

Compared to natural gas or hydrogen transmission, ammonia is more efficient and less costly. Cost savings result from lower initial cost for both pipelines and storage since both can operate at much lower pressure, and lower operational cost since less energy is needed to operate pumps and compressors.

E. Monetizing Stranded Gas, Solving the LNG Problem, and Enabling Carbon Capture

Ammonia transport by sea (in tanker ships) is superior to using compressed natural gas (CNG) or liquefied natural gas (LNG) for bringing stranded natural gas to market. Natural gas is the principle energy source for electric power generation in many regions, including California. No community in California is willing to accept an LNG terminal due to the high explosion risk. Therefore the Energìa Costa Azul terminal was built in Baja California, Mexico, and the gas shipped north by pipeline. By contrast, there is no problem delivering ammonia directly to the communities where it is needed. California currently imports about 100–300 kt[39] of ammonia per year, mostly for agricultural purposes. It arrives through the ports of Stockton and West Sacramento, in the center of California. Ammonia is thus an easily imported replacement for natural gas as the principal supply for electric power generation in California and elsewhere.

Using ammonia for electric power generation enables zero-carbon emissions at the generating plants. The CCSS process required to mitigate CO_2 emission is shifted from the generating plant, where it is an awkward addition, to the gas or coal fields that are the source of the ammonia, where it can be efficiently integrated with the large-scale petrochemical processes that are already there.

The advantages of liquids are well-known in the natural gas industry, which takes great interest in gas-to-liquid (GTL) conversion technology as a way to monetize stranded gas fields. Less energy is required for transport and storage of liquids, thus there is less expense, and also

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[39] The unit symbol "t" stands for tonne (or metric ton) and is 1000 kg; thus 1 kt = 1 Gg.

less risk. The only barrier to expanding production of ammonia and methanol as fuels is that the back-end distribution and end-use infrastructure needs modest modification. Much of the required technology is well-established, and the remainder is straightforward and can be developed rapidly.

XVII. METHANOL/CARBOFUEL

Although noncarbon fuels are preferred, no substance has yet been discovered that can replace gasoline as a liquid fuel of low relative toxicity that is also carbon free. In lieu of that ideal substance, methanol is suggested to replace gasoline. Methanol can substitute for gasoline with relatively minor modification of existing distribution and use infrastructure. Choosing methanol as a replacement for gasoline offers a factor of two (perhaps; see Appendix D) reduction in CO_2 emissions, while allowing the existing transportation physical plant to remain mostly intact. This is a good trade.

A. Easy Replacement for Gasoline

Conventional vehicles and engines can be converted to run on methanol, or to accept either methanol or gasoline, with relatively minor modification. The conversion of an engine to run on methanol [98], [99] involves at least three tasks:[40] 1) parts made of materials that are incompatible with methanol must be replaced; 2) control functions (e.g., electronic control of fuel-injectors) must be adjusted; and 3) exhaust processors (catalytic converters) must be modified or replaced. This is not trivial; the cost is hundreds or even thousands of dollars. But this is one or two orders of magnitude less than the cost to accommodate hydrogen, which requires that the engine and the infrastructure that serves it be completely replaced. Automakers can produce flex-fuel versions of new vehicles that can run on either gasoline or methanol at quite modest increased cost, less than two percent of the total cost of a typical vehicle.

Gasoline distribution stations also can be modified at low cost. All that is required is to provide an additional storage tank and pump for methanol, to supplement the three kinds of gasoline and one or two kinds of diesel fuel that are already there. A U.S. Department of Energy study [101] examined the requirements to modify the gasoline distribution system to handle methanol. The details were worked out in the California methanol demonstration project and summarized in [102] and [103]. An independent study is reported in [104].

Future automotive engines might be based on electrochemical engines (ECEs), and methanol can be used there as well. The same comments made regarding ammonia ECEs apply to methanol: they can be either indirect (incorporating a reformer), or direct. Honoring the general engineering principle that simpler is better, we expect the latter to result in more efficient and less costly systems. Critics point out that ECEs are not currently competitive with ICEs. This is true; it is because ECEs are surface conversion devices, whereas ICEs are volume conversion devices. Nanotechnology will enable fractal-constructal structures that emulate similar surface conversion devices in biological organisms (e.g., the human lung). By packing a large surface area into a small volume, this technology will enable ECEs to overcome what has historically been their fundamental limitation, the inherent kinetic disadvantage of a surface (versus a volume) process. Biomimetic engineering is the breakthrough that will propel ECE performance past that of ICEs in the 21st century. One need not endorse this prognostication, however, to embrace liquid renewable fuels, which can be used in all kinds of engines.

B. Ethanol and DME

Ethanol, C_2H_5OH, and dimethyl ether or DME, $(CH_3)_2O$, are two alternative carbon-based fuels. Ethanol and DME molecules are composed of the same atoms, differently arranged. The different molecular structure confers very different physical properties on these two substances. At standard temperature and pressure, ethanol is a liquid and DME is a gas. DME is like propane (or ammonia) in its handling attributes: gas at room temperature and atmospheric pressure, liquid under moderate pressure. Both ethanol and DME have in common a desirable characteristic: very low relative toxicity.

Ethanol is the best known alternative to methanol. Its safety features are excellent; it is the only fuel one can drink as well as burn. DME is a preferred fuel for CI engines,[41] to which it is well-suited because it has a high cetane number. Methanol, by contrast, has a high octane number and is suited to SI engines. Thus, methanol and DME are complementary. In numerous studies ([105]–[109] are a selection) DME has been injected in ICEs along with methanol to improve performance. To our knowledge, neither methanol-DME [110] nor ethanol-DME mixtures have been investigated as fuel blends; perhaps this is a worthy project. In the dual-fuel scenario, future fuel distribution stations are expected to offer different blends and grades of fuel, just as gasoline distribution stations do today.

Both ethanol and DME have higher energy density than methanol because of their greater carbon-hydrogen ratio. Either can be adopted as the primary carbofuel if methanol proves problematic for reasons of toxicity.

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[40] The same applies to ammonia [94], [100]; but ammonia conversion is more challenging, and requires further research before conversion kits and services can be made commercially available. This could be done very rapidly for methanol; see Appendix B.

[41] That is, CI engines operated by nonprofessionals. Ammonia (or nitrofuel) should replace diesel fuel for CI engine applications involving professional fuel handlers.

C. Higher Alcohols and Alkanes

An advantage of methanol as a transportation fuel is that it is easily substituted in the existing infrastructure with minimal modification. Ethanol is even better in this regard, and higher alcohols are better yet. Higher alcohols have the formula $H(CH_2)_nOH$. Butanol ($n = 4$) is an example that has received some attention as an alternative fuel. Increasing n improves both compatibility with existing engines and also energy density, both attractive features.

Taking this line further we may ask, why not use alkanes as the primary carbofuel? The use of alkanes as fuel permits the use of the existing infrastructure with no modification whatsoever. Alkanes are hydrocarbons with the molecular formula $H(CH_2)_nH$. The primary reference fuels for gasoline, kerosene (jet fuel) and diesel fuel are alkanes with $n = 8$, 12, and 16 respectively. These alkanes are direct substitutes for their corresponding fossil fuels; no engine or infrastructure modifications are needed. Further, the energy density is the same as we are accustomed to with contemporary fossil fuels.

Adding some oxygen content to fuels is advantageous to improve combustion characteristics, and is done in contemporary blended fuels such as gasoline. Higher alcohols might therefore be preferred to, or might be blended with, alkanes. If produced from renewable energy and air using atmospheric CO_2 then both higher alcohols and alkanes are carbon-neutral fuels. When produced in this manner, we refer to both as carbon-neutral hydrocarbon (CNHC) fuels. They are source-neutral renewable fuels. As carbon-rich fuels they have the intrinsic advantage of higher energy density, as well as the incidental advantage of being compatible with existing ICEs, CTs and fuel distribution infrastructure.

Why not use one of these desirable CNHCs as primary carbofuel? Because they will be produced less efficiently and at higher cost than the simplest liquid carbofuel substance: methanol. Methanol will be preferred whenever it can be used because it will have the lowest cost per unit energy.

D. Cost Versus Range

CNHC fuels have energy density the same as the fossil fuels they replace. In stationary (nontransportation) applications, this is not a big advantage; and many transportation applications also can manage with lower energy density than current fossil fuels offer. In a few transportation applications, however, the low energy density of ammonia and methanol is a serious disadvantage. Ammonia and methanol have about half the specific energy or energy density of the fossil fuels they replace (gasoline, diesel fuel, jet fuel). This disadvantage must be compensated by significantly lower cost. If a trip costs half as much using methanol instead of gasoline, or ammonia instead of diesel fuel, most travelers will accept refueling more often to gain that cost advantage. In comparing fuels, we must compare cost per unit energy and not cost per unit mass or volume. We hypothesize that if renewable fuels are available at half the cost per unit energy (one-fourth the cost per mass or volume) compared to their fossil competitors, they will succeed in most sectors of the energy market.

More frequent refueling might be compensated by developing more efficient engines. If renewable fuels enable electrochemical engines (ECEs) with twice the efficiency of ICEs, then the range advantage of fossil fuels disappears and renewable fuels are in every way superior. Alternatively, in some transportation applications it is possible to double the fuel carrying capacity of vehicles for very little cost. This might be the case for ships and trains, for example. In such cases the range between refueling is maintained simply by doubling the size of the fuel tank.

For those cases where long range between refueling is essential and compact low-weight storage is required, carbon-rich fuels must be used. On the battlefield, maximum range without refueling is a life-or-death advantage, and cost is no object. Therefore for military purposes carbon-rich fuels will continue to be used for their inherent higher energy density. Some segments of the commercial air transport sector also demand high energy density fuel; but some may be more competitive using lower energy density fuel if it is also low cost. The choice depends on consumer preference and system-level considerations. For example, if a nonstop flight from Los Angeles to New York costs twice as much as one that has to stop to refuel in Denver, customers might prefer the less expensive flight; but they probably won't consider a flight that has to stop two or three times. Short-range flights, such as Los Angeles to San Francisco and Washington to New York, can adopt low-energy-density renewable fuels since they don't need the range. The aviation sector already tends toward specialized aircraft for specific markets; specialized fuels are only an extension of current practice. Outside the aviation sector, most commercial transport will be cost-driven, and will convert to the fuel-engine-system combination that delivers the best range per unit cost.

XVIII. ENVIRONMENTAL AND HEALTH AND SAFETY HAZARDS

Environmental and health and safety (EHS) hazards and risks must be evaluated in relative terms. Fuels are, by definition, high-energy materials. As such, they are intrinsically hazardous. This is true for fossil fuels, for hydrogen, and for all others. The perfectly safe and environmentally benign fuel does not exist. The best we can do is to choose from available alternatives the option with the fewest or least serious problems. Renewable fuels are not without risk. Rather, the risk they bear is less than that of the fossil fuels they replace.

Advocates for the hydrogen economy often cite the superior qualities of hydrogen fuel with regard to EHS issues. They are correct. If we compare ammonia and methanol to hydrogen with respect to EHS, we conclude that hydrogen is preferable. Such comparisons are pointless, however, because hydrogen cannot displace fossil fuels for reasons unrelated to EHS. What we must do is to compare ammonia and methanol to fossil fuels. Ammonia must be compared to LNG and methanol to gasoline. In that comparison, ammonia and methanol are superior on EHS criteria. We review these issues in the following.

The overriding question is that of CO_2 emission. How can we dramatically lower fuel-related CO_2 emission in the near term, and eliminate it in the long term? To achieve this goal we are prepared to accept some moderate increase in other EHS risks to mitigate the really enormous risk posed by the prospect of anthropogenic climate change.

A. Methanol Safety and Spill Remediation

Methanol is a preferred liquid fuel for safety. Although toxic, it is less so than gasoline.[42] Methanol is today a minor component in many gasoline blends. The toxicity of gasoline and its components is reviewed in [111]–[115]. See Appendices F and G for discussion and additional references. Of the many components of gasoline, methanol is among the *least* toxic. Replacing the other more toxic components of gasoline with methanol, we arrive at a less toxic fuel. The toxicity of methanol is reviewed in [115]–[124]. Breathing methanol vapor in typical (low) concentration causes no harm. Its fire and explosion safety is superior to gasoline; see [125] and [126]. Unlike gasoline and other petroleum-derived fuels, methanol is miscible with water; thus methanol fires can be extinguished by dousing with water. For that reason, and because it is a high-octane fuel, delivering high power in SI engines, it is used in race cars.

Like any alcohol, methanol is closely related to glucose, and is thus relatively easily processed by organisms. The negative impact of a methanol spill is significantly less than a comparable crude oil or gasoline or diesel fuel spill. More importantly, the environmental impact of exhaust fumes from methanol use is far less than that of gasoline and diesel fuel. The environmental impact of using methanol as fuel is reviewed in [123] and [124]. A quotation from [124] summarizes the EHS advantages:

> "Methanol is more environmentally benign than gasoline, as well as safer. . . . Methanol is less prone to contribute to ozone formation than gasoline. This is because the unburned hydrocarbons from methanol-fueled SI vehicles contain fewer constituents that react photo-chemically to form ozone. . . . In CI engines. . .nitrogen oxides and particulate emissions are lower compared to diesel-fueled vehicles. . . . In addition, methanol contains no sulfur and does not contribute to atmospheric sulfur dioxide. . . . The impacts of methanol spills on drinking water and aquatic ecosystems are relatively milder, shorter, and more localized than for equal quantities of gasoline or diesel spills. Terrestrial ecosystems affected by a methanol spill will recover within weeks. Gasoline spills, in contrast, can cause extensive, long-term damage. . . . Short-term exposures to methanol below certain threshold values do not pose major health hazards. Overall, gasoline is considered more hazardous to health than neat methanol. . . . Fire hazards [of methanol are] a far less significant risk than gasoline. Neat methanol's ignitability in ventilated areas is between that of gasoline and diesel [i.e., safer than gasoline]."

The drawback to methanol is that burning it creates CO_2, a greenhouse gas. This is not a problem if methanol is derived from atmospheric CO_2 using renewable energy sources. But we want to devise a strategy that enables us to use fossil energy sources as a temporary (unsustainable) measure, while still reducing CO_2 emissions in the near-term.

B. Ammonia Environmental Benefits and Costs

Use of ammonia as fuel avoids direct emission of CO_2; this is a benefit. While suppressing CO_2 emission, however, widespread adoption of ammonia as fuel will inevitably be accompanied by an increase in the inadvertent release of ammonia to the atmosphere. This is a cost. The cost/benefit trade needs to be assessed.

Nitrification is a serious environmental problem associated with fertilizer use. It will become more severe, and other negative environmental consequences will result, from increased ammonia production and use as fuel. The toxicity of ammonia to aquatic organisms, for example, is well-known. These negative consequences must be evaluated, and plans made to minimize them.

The environmental hazards of ammonia are reviewed in [2], [127] and [128]. There is need for an updated work similar to [128], focusing on ammonia as fuel and emphasizing a comparison with other options. The larger work of which [2] and [128] are a part is an excellent example of such a comparative study. Here we only make some observations. Ammonia is a fertilizer. It encourages plant growth, so has the possibility of being relatively benign in not-too-high concentrations. When high concentrations do occur, as a result of accidental release, the environmental damage done is relatively easily and rapidly self-repaired by natural processes. An example in which alfalfa was used to remediate an ammonia spill is reported in [129]. The environmental impact of ammonia spills is characterized by

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[42] If relative toxicity trumps carbon intensity and cost, then methanol can be replaced with ethanol, DME, or CNHCs. That tradeoff is a topic for further study. All such fuels are entirely consistent with the dual-fuel strategy; any can serve as carbofuel.

the U.S. Department of Health and Human Services in a 2004 Public Health Statement [143]:

> "Ammonia does not last very long in the environment. Because it is recycled naturally, nature has many ways of incorporating and transforming ammonia. In soil or water, plants and microorganisms rapidly take up ammonia. After fertilizer containing ammonia is applied to soil, the amount of ammonia in that soil decreases to low levels in a few days."

It is likely that the risks associated with ammonia as fuel are substantially less than those associated with fuels in use today, and that they are acceptable. This is, however, an important open question that requires the attention of the environmental science and engineering community. The undesirability of higher atmospheric ammonia levels is incontrovertible. What needs study is the *relative* undesirability, compared to the consequences of fossil (or other) fuel use. Nothing is problem-free; we must choose the least problematic.

C. Nitrogen Oxides

It is sometimes objected that excessive NOx emissions result when ammonia is burned. This objection is based on the reasonable but wrong assumption that more nitrogen in fuel necessarily means more NOx in the exhaust. This misconception is encouraged by the fact that NOx is in fact found in the exhaust of ammonia combustion processes (just as in all other combustion processes that use air as oxidant), and that *under some conditions* it can be excessive. In evaluating the problem of NOx emission due to ammonia combustion, bear in mind the following points:

- when carbon-based fuels are burned, the Gibbs energy change of the reaction demands the formation of CO_2;
- by contrast, when nitrogen-based fuels are burned the Gibbs energy favors N_2 formation and not NOx;
- air is a mixture of nitrogen and oxygen; when air is heated *by any means*, NOx will form;
- the amount of NOx remaining when the air cools *can* be zero.

NOx generation is a matter of kinetics and not thermodynamics. It is therefore complicated, but the possibility of eliminating NOx emission through combustion engineering exists. Contrast this with the formation of CO_2 when carbon-based fuels are burned: no amount of combustion engineering will make this CO_2 go away; one must look instead to post-combustion capture and sequestration.

Nitrogen oxides are *not* a problem with ammonia combustion. Or rather, they are not *more* of a problem than they are with any other fuel. At room temperature, thermodynamics favors nitrogen, and not nitrogen oxides, as the most stable reaction product of ammonia oxidation. Nevertheless, nitrogen monoxide still forms: it is the result of high temperature combustion in air, independent of the chemical composition of the fuel used. The formation of nitrogen oxides in combustion processes is a consequence of using *air* as the source of oxygen. It is the air that supplies nitrogen, and not the fuel

$$N_2 + O_2 \rightarrow 2NO.$$

This reaction was studied by Nernst in 1906 [130]. It is endothermic; it absorbs heat. Therefore, according to the principle of Le Chatelier and Braun, in mixtures of nitrogen and oxygen the equilibrium concentration of nitrogen monoxide increases with temperature.[43] In a combustion process in which the high-temperature exhaust gases are rapidly quenched to room temperature, these concentrations become locked-in by kinetic barriers. This also happens if air is passed through an electric furnace in which no fuel is present at all, because air itself is the source of the nitrogen. Replacing a hydrocarbon fuel with one containing nitrogen does not necessarily increase NOx generation. To the contrary, ammonia is injected into the exhaust of carbofuel combustion processes today to *suppress* NOx emission. The "thermal de-NOx" process was patented by Lyon in 1975 [131], [132] and reviewed by him in 1987 [133], [134]. A recent review has been given by Zaslonko *et al.* [135]. The essence of the process is the reaction

$$NH_2 + NO \rightarrow N_2 + H_2O.$$

The key reactant, NH_2, is a radical that derives from ammonia under combustion conditions. Most fossil-fired electric power plants have a thermal de-NOx system and use a supply of anhydrous ammonia to implement it. Similar results can be obtained in ICEs; for example, Kanao [136] shows that ammonia added to gasoline in correct amount reduces NOx emissions. Counter-intuitively, ammonia used as fuel can generate *less* NOx than hydrocarbon *or even hydrogen* fuel.

It remains true that minimization of NOx emission is an issue that must be addressed for ammonia combustion processes, just as for any other combustion process carried out using air rather than pure oxygen. It is also true that fuel-bound nitrogen *might* lead to more NOx emission than air-nitrogen.[44] It is an engineering problem to design a

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[43] The principle of Le Chatelier and Braun says that if you supply something that a reaction consumes on the left, it will go further to the right. In this case, the reaction consumes heat, so if heat is supplied, thus raising the temperature, more product (NO) results.

[44] Air-nitrogen is N_2, in which the triple bond is very strong and hard to break; thus formation of NO from N_2 and O_2 requires high temperature. Fuel-bound nitrogen, by contrast, occurs in compounds where the nitrogen is bound most often by single bonds. These bonds are relatively easy to break; thus NO can form at lower temperature. High concentrations of NOx might then be present in the exhaust stream if the combustion process is improperly designed.

combustion process that ensures that NOx is not generated; thermodynamics assures us that it is possible to do so. There is an extensive knowledge base on the use of ammonia as fuel in combustion processes, much of it acquired by the U.S. Army's Energy Depot project carried out in the 1960s. A guide to this literature is provided in Appendix B. The general conclusion from a study of this body of work is that ammonia combustion is intrinsically no worse than hydrocarbon or even hydrogen combustion as a source of NOx, and can be engineered to be better. Careful attention to combustion process design is called for in all cases in which air is used as the oxidant. Ammonia combustion is exceptional only in that it has an inherent NOx suppression mechanism built-in.

The recent work of Lee *et al.* [137] is instructive. They study NH_3/H_2/air flames at different relative amounts of fuels[45] and air, and different degrees of flame stretch.[46] The results show how NOx formation can be suppressed, essentially by providing ammonia-rich conditions leading to sufficient NH_2 radical formation, just as in Lyon's thermal de-NOx process. At the same time, the work of Lee *et al.* emphasizes that NOx suppression does not happen without effort; it requires careful design of the combustion process. [137] deals with premixed flames fed by ammonia-rich NH_3/H_2 fuel mixtures, including pure ammonia. Companion works deal with hydrogen-rich fuel mixtures [138] and with more realistic nonpremixed flames [139]. Lee *et al.* combine experimental flame structure measurements with detailed chemical kinetic modeling. Their NOx concentrations, however, are only calculated and not measured. The next step is to combine modeling and computer-aided design of combustors with NOx exhaust measurements.

The picture emerging from current research on ammonia combustion is this: NOx formation is suppressed by an ammonia-rich (i.e., fuel-rich) mixture; but then there is ammonia slip (NH_3 emission). Conversely, an ammonia-lean mixture results in NOx emission. To suppress both NH_3 and NOx emissions requires precise tuning of the fuel-air ratio entering the combustor. This means incorporating active feedback control of the combustion process, incorporating NH_3 and NOx sensors. These have yet to be developed in suitable form, i.e., in a form equivalent to the so-called lambda sensors widely used in vehicular combustion systems today. A research and development program carried out along these lines will soon achieve the low-NOx combustion processes needed for near-term commercialization of ammonia as fuel.

Yet another perspective on NOx is that perhaps it is not a bad thing, but a good thing. When generated in substantial quantity by a central source from which it can be captured, NOx has value. The "fixing" of atmospheric nitrogen in a form that can be absorbed by crops is an end in itself—it is the objective of the fertilizer industry. NOx can be used as a feedstock from which to produce ammonium nitrate, urea, and other fertilizers. Thus a possible path to ammonia utilization as fuel is to accept and even enhance NOx generation and then capture and sequester it as a salable product: a fertilizer or fertilizer-precursor. Most likely this would only be economic for large centralized sources such as base-load electric power generation. The idea of this approach is to extend the renewable fuel cycle illustrated in Fig. 5. Rather than returning nitrogen to the air immediately upon fuel oxidation, it is returned through the natural nitrogen cycle that includes growth and decay of vegetation. As far as we know, this approach to NOx mitigation has not been analyzed for economic viability. It is likely to be more feasible for fuel-bound nitrogen in the form of ammonia than for nitrogen as found in typical coals currently used for electric power generation. In this approach, one seeks to *maximize* NOx as a product of ammonia combustion rather than to minimize it. This is in essence the problem that has been already solved by the nitric acid manufacturing industry.[47] The technical problem then shifts to economic capture of NOx from the downstream exhaust.

D. Ammonia Toxicity

Ammonia is a toxic substance and there is significant safety hazard associated with its use. That ammonia can be safely handled, however, is proven by the fact that it is done routinely. Ammonia is one of the highest volume industrial chemicals on the planet today, used primarily for food production (fertilizer) and distribution (refrigeration). Because it is toxic, however, its handling should be restricted to professionals, properly equipped and trained. It should not be used for nonprofessional transportation and residential purposes. That still leaves 80% of all fuel requirements that can be met by ammonia.

Ammonia hazards and safety issues are reviewed in [128] and in [141]–[144]. Appendix A of [128], "Accidental spills," is particularly valuable. It consists of brief narratives of what happened in a variety of incidents in the 1969–1979 time period. These narratives give a better feel for the relative hazards of ammonia than do numerical indices alone.[48]

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[45] Lee *et al.* investigate ammonia–hydrogen fuel mixtures. Ammonia and hydrogen are opposites in many ways, representing the extremes of fuel behavior; see the fuel properties summaries in Appendix E. The mixture of the two is therefore an interesting topic for combustion and flame research, even aside from the important practical applications.

[46] Flame "stretch" is what happens on your camp stove when you open the propane valve wider. In [137] it is measured by a dimensionless parameter (the Karlovitz number) that increases with flow velocity; see Glassman and Yetter [140].

[47] For further information see Appendix B and [157] and [211].

[48] Such indices include LC50, PEL, TLV, REL, IDLH, and so on. They are used by regulatory agencies and professional organizations such as NFPA, OSHA, ACGIH, and NIOSH. To delve into this alphabet soup, one needs only Internet access and time. We do not quote the numbers here as they are meaningless without some way to calibrate oneself as to their significance. We recommend the narratives provided in [128].

E. Fire and Explosion Safety Advantage

Compensating for the high relative toxicity of ammonia is its very low fire and explosion hazard. Ammonia is superior to all other known fuels for safety in this regard. The NFPA uses a scale of 0 to 4 to rate the fire and explosion hazard of materials. On this scale anhydrous ammonia is rated 1: slight fire hazard. This is the lowest rating possible for a fuel. Consequently, the NFPA gives anhydrous ammonia a "nonflammable gas" shipping label [126]. The main reason why ammonia is such a safe fuel is that it has a very high minimum ignition energy (MIE).[49] High MIE means difficult to initiate combustion (ignite). The range of values reported in the literature for the MIE of ammonia in air is quite broad, from 8 to over 1000 mJ.[50] The low end of this range, ~10 mJ, is still very much more than any other fuel: methanol is 0.14, methane 0.30, propane 0.26, and hydrogen 0.017. Another figure of merit, designed to account for flammability limits and energy density, is the RF index of Kondo [150]. This number is low for low hazard. Among all known fuels, it is the lowest for ammonia. The RF numbers of selected fuels are: ammonia 7, methanol 29–41, methane 40, propane 52, hydrogen 402. The very high value of MIE (and related figures of merit such as AIT and MIC ratio) and the very low value of RF number for ammonia is unique among potential fuels.

From a fire safety point of view another very desirable property of ammonia is that its flame is efficiently extinguished with water alone. This is to be contrasted with petroleum-derived fuels in use today that require special foam extinguishing agents to fight fires. These facts underscore a very desirable feature: ammonia is a fuel with exceptionally low fire and explosion hazard.

Consider this scenario: You are in an airplane fully loaded with fuel and it is about to crash. If the fuel is kerosene (jet fuel), it will explode on impact and you will be burned to a cinder. If it is ammonia, you can put on a face-mask with activated-carbon-canisters that will protect you from the fumes for up to an hour; and you can cover your body with clothing and perhaps even apply protective lotion to your skin. If you survive the initial impact, you will be able to escape from the cloud of toxic ammonia vapor, which will disperse rapidly and upward, because ammonia is lighter than air. Consequently, you won't have to go too far before the ambient ammonia concentration is much reduced. Further, the antidote to exposure to ammonia is water; something you have a good chance of being able to get to. If you have to choose between kerosene and ammonia, would you not prefer the ammonia scenario?

A nonexplosive fuel opens an additional possibility: impact-tolerant fuel tanks. In a crash, some fuel will escape from the most vulnerable portions of the aircraft, such as the engines and fuel lines. Explosion of this initial leaked fuel ruptures the fuel tanks, and their contents in turn explode. If the initial fuel release does not result in explosion, but only dissipates into the air, the fuel tanks might remain intact. Then not only fire and explosion has been avoided, but also containment of most of the fuel has been preserved. It is easier to design a crash-tolerant fuel container if the impact is all that must be absorbed, without the additional complication of an explosion.

The toxicity of ammonia is a drawback, but it must be weighed against the drawbacks of alternative fuels. Ammonia has a very low fire and explosion hazard, lower than hydrogen or fossil fuels, especially the extremely dangerous liquefied gas fuels, LPG and LNG. Ammonia's excellent fire and explosion safety comes primarily from its high ignition energy—a high activation barrier to the initiation of the combustion reaction. This makes ammonia an almost ideal fuel: difficult to ignite accidentally, but sufficiently ignitable in the controlled environment of a purpose-built combustor. Its only drawback is toxicity, which can be mitigated with proper precautions.

XIX. BUSINESS MODEL

Competitive advantage is inherent in the dual-fuel strategy. This advantage must be recognized and exploited to expand the use of renewable fuels in trigger markets. A trade organization, in Section XIII-D named the Dual-Fuel Exchange (DFX), is needed to facilitate this. The DFX is an alliance of energy consumers, producers, and servicers with mutual interest in low-cost stable energy supply. The investment barrier required to join the DFX is low; the benefits to members are high. These benefits flow from the competitive advantage inherent in liquid renewable fuels.

A. Sources of Competitive Advantage

Competitive advantage for the DFX comes from: 1) legacy compatibility; 2) agile production; and 3) risk mitigation. *Legacy compatibility* means that the existing energy infrastructure can be used with minimal modification. This translates to easy entry to the dual-fuel energy market. Participation in the DFX requires some initial investment, but this barrier is low because existing physical plant can be used with minimal modification. *Agile production* means that market participants can draw not only on oil as a source of energy, but also on coal and gas and eventually on renewable and nuclear sources. Producers can diversify their sources and methods; and if they do not, distributors and customers can turn to other producers who do. *Risk mitigation* is against two major risk categories: petroleum supply and global-warming-related business factors. The DFX provides a hedge against the risk that declining conventional oil reserves will lead to erratic

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[49] Related quantities are auto-ignition temperature (AIT) and minimum igniting current (MIC) ratio. All these are figures of merit that should be high for a safe fuel—one that is not easily ignited accidentally. All are exceptionally high for ammonia; see Appendix E or [126].

[50] Note that there is a typographic error in NFPA 497, reproduced in [126]. The decimal point in the entry for the MIE of ammonia should be removed. The MIE of ammonia is reported in [145]–[149].

supply and price. It is also a hedge against the risk that the reality of global warming will compel government-mandated carbon taxation (or other forms of carbon restriction) in the near future. Such an eventuality, if it transpires, will give dual-fuel producers and consumers an overwhelming advantage over competitors who engage only in business as done now.

B. Half-Price Goal

The principal benefits of renewable fuel use are lower cost and more reliable supply compared to oil-derived fossil fuels. Renewable fuel at a price point about half that of the competing fossil fuel will be sufficient to capture substantial market share.

To be precise: currency per energy content (C/E) is the cost or price of fuel on an energy basis, $\mathrm{VMU} \cdot \mathrm{GJ}^{-1}$, where VMU represents currency[51] and the energy content of the fuel is taken to be its HHV.[52] Relative fuel C/E is normalized to a benchmark against which the fuel competes. The one-half price-point goal means that the relative C/E of ammonia against LNG, CNG, or diesel fuel must be one-half. Likewise, that of methanol against gasoline must be one-half. Alternatives to C/E for valuing fuels are currency per mass (C/M) and currency per volume (C/V). C/V (e.g., $\mathrm{VMU} \cdot \mathrm{L}^{-1}$) is common for trading liquid fuels. The relative C/V of ammonia against LNG or diesel fuel and methanol against gasoline must be about one-*quarter* to achieve a relative C/E of one-half, because ammonia and methanol have only about half the energy density of the fossil fuels against which they compete.

C. Triggering the Energy Transition

The notion of an economic *virtuous cycle*, illustrated in Fig. 4, is central to the dual-fuel strategy. Renewable fuel use and renewable source development interact with each other in a positive feedback loop: as each grows, it promotes the growth of the other. This mechanism requires a trigger to initiate. The trigger will be provided by niche applications in which the countervailing force of economic inertia is weakest, so that the natural competitive advantage of renewable fuels can overcome it. A relative cost-per-energy of one-half is the main driver. Identifying potential trigger markets is the next step.

D. Near-Term Projects

Trigger markets are leading-edge applications of renewable fuels. They are applications for which the required modification to existing infrastructure is least, and the benefits to be gained are greatest. Five opportunities are: 1) marine propulsion for ammonia and methanol tankers; 2) ammonia-powered railway locomotives; 3) methanol-powered local-use road vehicle fleets; 4) small-to-midsize integrated power systems or energy hubs; and 5) base-load electric power and other industrial plants with boilers and furnaces. In the following we discuss each of these in turn.

1) Marine Propulsion: Commercial shipping will be converted to renewable fuels to gain competitive advantage as the use of low-grade marine diesel fuel-oils is phased out. Replacing these fuels with ammonia will be less costly than converting to CNG. Ammonia and methanol tankers are likely first candidates for conversion since they already are rigged to handle these commodities, which can thus become both cargo and fuel. Shipping converted to renewable fuel will consume twice the mass or volume of fuel compared to the fossil requirement. The circumstance under which that is acceptable must be analyzed.

Consider for example commercial ammonia tankers. The space taken up in a tanker by the fuel that propels it is a fairly small fraction of the total capacity of the ship, but if multiplied by two (for a fuel of half the energy density) or four (for a round-trip using the low-energy-density fuel) the space requirement is significant. Examples of ammonia tanker ships can be found in [151]. In [151, p. 45(a)], one finds a ship owned by Harland and Wolff PLC, capable of carrying 59 000 m^3 of ammonia and provided with a fuel-oil capacity of 3717 t (approximately the same as m^3). In [151, p. 83(a)] one finds a ship owned by Odense Staalskibsvaerft A/S, capable of carrying 15 000 m^3 of ammonia and provided with a fuel-oil capacity of 1807 m^3. If the volume required for fuel be doubled, it is 13% in the first case and 24% in the second; if quadrupled these numbers become 26% and 48%. This suggests that the use of ammonia as fuel for shipping will be economic only for large tankers (not a problem since increasing tanker size is the trend in any case) and that for new shipping designs that optimize propulsion energy efficiency should be implemented (also not a problem as it will be done in any case). Under such circumstances we can expect that less than 20% of the ship's carrying capacity must be devoted to fuel. This will be acceptable if the renewable fuel has half the cost-per-energy of the fossil fuel it displaces.

Ammonia and methanol can compete on cost with diesel fuel already today. At present, however, very low-cost low-grade fuel-oil is used by much of the world's shipping, and it might be difficult to compete on cost with these. Pollution from burning these fuels is, however, a major concern in many parts of the world; for example the Baltic Sea. Shipping in these regions will not continue to use marine diesel fuel oils, but must be converted to a cleaner fuel, perhaps CNG. It is then CNG with which renewable fuels must compete, and the logic of gas-to-liquid applies: the cost of fuel storage is high and the energy per unit volume is low for CNG, so it is worth the extra expense to first convert natural gas to liquid

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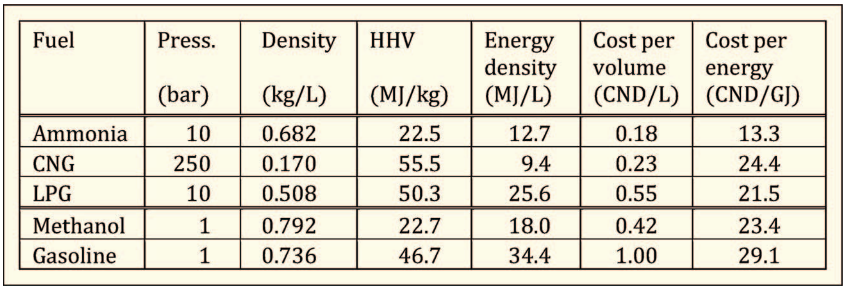
[51] A VMU, variable monetary unit, is unadjusted for inflation; it is the face value of currency. Examples of VMUs are U.S. dollars ($ or USD) or Euros (euro or EUR). A CMU, constant monetary unit, is a VMU adjusted by an inflation factor to a value at a specified reference date; thus one might specify a CMU2000 as a unit of value referenced to the year 2000 by means of an agreed upon consumer price index (CPI).

[52] HHV is the standard Gibbs energy of combustion with product water in the liquid (standard) state.

Table 2 Fuel Price per Unit Energy 2009



Fuel	Press. (bar)	Density (kg/L)	HHV (MJ/kg)	Energy density (MJ/L)	Cost per volume (CND/L)	Cost per energy (CND/GJ)
Ammonia	10	0.682	22.5	12.7	0.18	13.3
CNG	250	0.170	55.5	9.4	0.23	24.4
LPG	10	0.508	50.3	25.6	0.55	21.5
Methanol	1	0.792	22.7	18.0	0.42	23.4
Gasoline	1	0.736	46.7	34.4	1.00	29.1

anhydrous ammonia. There is an added bonus if the CO_2 generated in the conversion can be sequestered and perhaps sold, or if carbon credits can be obtained; but that might not be necessary to achieve an economically competitive fuelling system.

Table 2 shows the price per unit energy cited in [152].[53] The salient points are as follows:

- ammonia is already at a price point close to one-half its fossil competitors;
- methanol, although lower in cost than its fossil competitor, still has a way to go to reach the half-price point.

This cost analysis is cited, not as definitive, but as an example. There are issues that need further investigation. In Table 2 the listed cost-per-volume (C/V) of methanol is 2.3 times that of ammonia. This is surprising because the price-setting feedstock for both is natural gas. We need to understand where the large cost differential between ammonia and methanol comes from. Another issue is the low cost of ammonia compared to CNG. The authors state that "the compression work is significant and this raises the CNG price about three times." This observation is crucial, as it accounts for the entire competitive advantage of ammonia. [152] is focused on road transport; further study in the context of shipping is needed. The same prices for CNG may not be applicable to the marine transport application. The data on which this and similar analyses is based needs to be reviewed and refined as a first step in evaluating the viability of this project. If favorable, the next step is technology development to demonstrate and commercialize ship propulsion systems. Technology development of ammonia for marine fuel applications must focus on the requirements that there be very low risk of fuel spills and that no NOx be generated in the ammonia combustion process; else the environmental benefits sought by banning the use of low-grade fuel oils would be lost.

Simultaneously it will be necessary to work with regulatory agencies. Safety regulations promulgated by the International Maritime Organization (IMO) will require modification. Ammonia is currently forbidden on most shipping. An ammonia tanker is attractive as a first project because it should be possible to obtain a waiver of these regulations for a ship whose entire purpose is to transport ammonia. For other shipping it might be advisable to concentrate on methanol-powered marine propulsion in the near term, to avoid confrontation with regulatory agencies. But that confrontation must come; ammonia makes sense for marine propulsion, and its use in that application must be allowed. Maritime transport employs professional fuel handlers and engine operators, thus is an appropriate application for ammonia. Ammonia has very desirable fire and explosion safety features and manageable toxicity—especially in an environment where there is plenty of water close at hand. The logistical problem is minimal since fuel resupply for ships is not required too often and can be planned for at a relatively small number of ports worldwide. Further, there is an urgent need for nonpolluting shipping. Given these circumstances, the use of ammonia in this application must be vigorously promoted, despite the need for changes in current safety regulations.

2) Railway Locomotives: Conversion of railway locomotives powering trains with all kinds of cargoes can be relatively easily accomplished because (like ships) they can bring their fuel with them. For rail transport, a separate fuel car or cars would accompany the locomotive. Ammonia can be used as fuel since professional fuel-handlers are employed. Ammonia is already carried in railway cars, so is familiar.[54] Rail transport conversion might be easier to effect than sea transport, in which case it becomes the top choice for a leading edge demonstration. Selection factors have to do with scale (locomotives are smaller than ships) and industry and regulatory agency cooperation. Interest on the part of regulatory officials in innovation and in promoting alternative fuels is crucial. Currently rail locomotives are powered by diesel fuel, with which ammonia is already competitive just as it is with CNG (according to

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[53] The authors of [152] subtract from the HHV of methanol the energy required to reform it to produce hydrogen. In Table 2 we undo that adjustment. The monetary unit in Table 2 is Canadian dollars (CND). Note that 1 gal = 3.8 L. At the time this table was compiled, gasoline in North America was selling for about 3.80 CND per gallon.

[54] Transport of ammonia in railway tankers is widely practiced, yet remains controversial. We suspect that the controversy has to do mainly with legal issues: who assumes the risk associated with accidental spills, and is that party adequately compensated for that risk, or shielded from lawsuits arising from circumstances beyond the party's control? These are not technology but policy issues that must be resolved through legislation.

Table 2, assuming diesel fuel and gasoline are similar in price).

Of the four transport sectors (air, sea, rail, road), the conversion of air transport is the most challenging technically, and road transport is most challenging logistically. Air transport is a particularly attractive application for nitrofuel because the fuel distribution and handling system is relatively compact and completely under the control of professionals already trained and equipped to handle hazardous substances. Of all the engine conversion demonstrations carried out to date, however, aircraft propulsion is the least developed (see Appendix B). This is a very important area for research, but not yet ready as a trigger market. It may be that research will confirm what many suspect: that the primacy of specific energy as a figure of merit for aviation fuels will dictate that CNHCs will dominate this sector.

3) Road Transport Local Fleets: Solving the logistics problem for road transport amounts to restarting the California methanol project of the 1980s and 1990s (see Appendix B). As then, an initial market opportunity is presented by government and corporate fleets with vehicles used only for local trips. These vehicles can be refueled from private depots. Methanol can be supplied to these depots in bulk shipments, thus circumventing the distribution problem. This is a particularly attractive target for a near-term large-scale project since the groundwork has already been done. All that is needed is to restart a program the success of which has already been proven. The California methanol project ended when oil and gasoline prices declined sharply in about 1987. This project can be restarted now. Its continuing viability will be assured by a strategy to maintain the price of methanol (on an energy basis) at half that of gasoline. Thus, an analysis such as that illustrated in Table 2 is crucial. There the relative C/E of methanol against gasoline is 0.8. It must be brought down to 0.5, and a strategy must be developed to make sure it stays there as future gasoline prices fluctuate. An economic and financial analysis of the prospect for doing so is the first step in evaluating this project.

4) Midscale Energy Hubs: For stationary engine markets a near-term project is an integrated energy system, an energy hub as described in Section XII-D. First application might be for a small rural community already familiar and comfortable with ammonia through agricultural use. The system can incorporate microturbines or perhaps ICEs as prime movers for electric power generation. SOFC-GT hybrid generators are likely to be commercially available soon and will perhaps be the preferred generation system. Ammonia fuel will be supplied through the existing fertilizer distribution network. Ammonia will be used not only as fuel, but also as a refrigerant and as a working fluid for heat pumps and other subsystems intended to make maximal use of low-grade heat that would otherwise be wasted. This will enable very efficient district heating and cooling for habitation as well as production purposes. The latter might perhaps include refrigeration for food storage in an agricultural community. A complete system targeted to an appropriate size, such as a university campus or a small-to-midsize rural farming community, should find a near-term market. First customers will be those located near ammonia terminals; there are many such communities.

5) Base-Load Electric Power: Natural gas-fired boilers generating steam for base-load electric power production are a target with the potential for very significant GHG emission reduction in the near term. Industrial process heat (e.g., Portland cement manufacture) is an equivalent alternative target. Ammonia is easier and safer to transport and store than is natural gas, especially if transport is over water. Ammonia has zero point-of-use emissions. These advantages will drive conversion from natural gas to ammonia. Boilers and furnaces can be readily converted as soon as low-NOx burners are commercially available, and no other part of the plant needs to change. Plants located near existing ammonia pipelines, or near seaports with terminals capable of handling ammonia tankers, are natural choices since relatively short and inexpensive pipeline construction will be able to supply them. Power plants or other industrial plants meeting this geographical criterion and in need of boiler or furnace upgrade or replacement are prime candidates. There may or may not be an incentive for owners of candidate plants to make the change in order to achieve zero CO_2 emissions; but there will certainly be an incentive if fuel cost can be cut in half and supply at that cost made stable and predictable. It is up to the DFX to make this happen.

Projects involving methanol as fuel need little additional technology development. For those which rely on ammonia as fuel, the demonstration of low-NOx ammonia combustion processes and engines is prerequisite. It will not take long to reach this goal once a sufficient effort is undertaken; there is already in place a solid foundation of scientific and technical knowledge, acquired over the past century, on which to build. After this research goal is achieved, development and demonstration of production-ready engine models can follow rapidly.

E. Role of the DFX

Triggering the transition to a postpetroleum energy system requires institutional and technological innovation. An institution is needed that can unite energy consumers, distributors and producers around the dual-fuel energy vectors. Producers of ammonia and methanol are easily named, and will be happy to expand their markets. The major challenge is to identify and empower selected leading-edge *consumers* for these fuels while simultaneously building a distribution network. To accomplish this, the DFX must be more than a commodities market; it must be a technology development alliance. It must be capable of creating a strategic roadmap and promoting research and development following that roadmap. Models for such organizations are EPRI, SEMATECH, and USCAR.

The core of the alliance will be the consumers. Consumers have an interest in avoiding the high cost and unreliable supply that increasingly characterizes oil-derived energy. The driving force for the DFX must come from these consumers. They need to create an anticartel to counter attempts by such producer's organizations as OPEC and GECF to exert market power. Producers will be persuaded to participate in the DFX to increase their sales. Distributors, equipment manufacturers, and servicers will want to offer services to the producers and consumers. These groups all have a natural mutual interest, thus there is the basis for an alliance. Alliance members will include all those who seek to replace oil with natural gas or coal. As a by-product of accomplishing that objective they will also build the foundation of a future energy system based on renewable sources, in which the exploitation of natural gas or coal is no longer required.

The DFX will use existing commodities exchanges for its financial machinery. Beyond that, a shared vision and willingness to engage in precompetitive cooperative R&D investment is required. This can be aided by the public sector (governments), but need not be dependent on it. The nucleus for the DFX can be found in existing industry organizations, starting with the trade associations of major energy consumers.[55] These energy consumers must come together to fund research and development, and invite their suppliers to join with them. This is the first task of the DFX.

XX. CONCLUSION

Business as done now relies predominantly on fossil energy sources with fossil fuels and electric power as vectors. This is unsustainable; fossil sources must be replaced by renewable and perhaps nuclear sources. We have three choices for our global energy future, differentiated by energy vectors, as follows:

1) the hydrogen economy: electric power and hydrogen fuel as vectors;
2) the electron economy: electric power the *sole* vector—no fuel;
3) the dual-fuel strategy: electric power and two (or few) liquid renewable fuels as vectors.

The dual-fuel strategy is the best choice. In this plan electric power plays a central but not exclusive role. Fossil fuels are replaced with low-carbon (ultimately, zero-carbon) alternatives: ammonia (or nitrofuel) and methanol (or carbofuel). Because they are liquids, both of these renewable fuels are compatible with existing infrastructure. This enables the transition to be triggered using low-cost fossil sources (probably natural gas, perhaps coal) at the beginning; they are phased out later. The transition is gradual at first, but accelerates as market feedback kicks in. Innovation is encouraged by enabling competition between all energy sources. Entrepreneurs adopting the dual-fuel strategy harness the same market feedback that creates economic inertia to overcome it and drive the transition to a new global economy. They will supplant their fossil competitors by developing a more efficient energy market. This will enable them to offer a superior product: carbon-free energy with more stable supply and at lower cost. They will be able to do so because they are more agile. They can take advantage of low-cost fossil sources, including petroleum, when available; and they can equally well turn to alternative fossil and nonfossil sources of energy when petroleum is not available. The dual-fuel strategy provides a hedge, not only against the risk of unstable oil supply, but also against the risk of global warming. Because it uses the existing energy infrastructure, the transition to a post-petroleum system can be accomplished in a relatively short time, a few decades. The dual-fuel strategy enables an order of magnitude reduction in global carbon emissions early in the transition period, perhaps by 2030, and zero net carbon at its completion, perhaps by 2050. The dual-fuel strategy is a feasible plan to make the transition to a postpetroleum zero-carbon global energy system as rapidly as possible, perhaps by mid-century. ■

APPENDIX A
U.S. ENERGY USE PATTERNS

The purpose of this Appendix is to provide justification for the use of two rough 80–20 rules:

- 80% of energy trade is carried by fuel, 20% by electric power;
- 80% of fuel use is by professional operators, 20% by nonprofessionals.

To justify these approximate rules, we first give a brief summary of the U.S. energy system. We focus on the U.S. system because the EIA provides detailed data in Excel spreadsheet format, thus easy to analyze. The flow of energy from source, through vector, to end-use, is represented by Lawrence Livermore National Laboratory's (LLNL) energy flow charts,[56] derived from EIA data. There are nine sources and four end-uses (not including rejected energy) shown in the LLNL diagram. One gets a sense of the energy vectors, but only electricity is called out explicitly. It is possible, however, to aggregate liquid and gaseous fuels using the same EIA data[57] on which the LLNL diagram is based. We further simplify the LLNL

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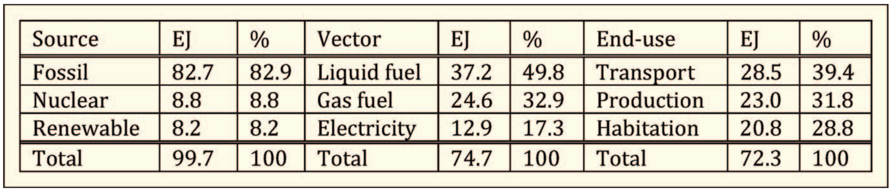
[55] For the electric power industry, that means such organizations as the Edison Electric Institute and the Electric Power Research Institute.

[56] LLNL Energy Flow Diagram for 2009 is available from the Lawrence Livermore National Laboratory [153].

[57] EIA Annual Energy Review for 2009 is available from the U.S. Energy Information Agency [154].

Table 3 U.S. Energy Flow by Source, Vector, and End-Use, for 2009



Source	EJ	%	Vector	EJ	%	End-use	EJ	%
Fossil	82.7	82.9	Liquid fuel	37.2	49.8	Transport	28.5	39.4
Nuclear	8.8	8.8	Gas fuel	24.6	32.9	Production	23.0	31.8
Renewable	8.2	8.2	Electricity	12.9	17.3	Habitation	20.8	28.8
Total	99.7	100	Total	74.7	100	Total	72.3	100

chart to three each of sources, vectors, and end-uses. The result is summarized in Table 3.

The sources are fossil, nuclear, and renewable. The vectors are: liquid fuel (mainly gasoline, diesel, and jet fuel, but also including kerosene and fuel oil);[58] gaseous fuel (mainly natural gas);[59] and electricity. The end-uses are: transportation (road, river, rail, sea, air); production (all economic activity in which energy is required to make something, including manufacturing, materials processing, and food production—industry and agriculture);[60] and habitation (energy for buildings, both residential and commercial—mainly heating, cooling, and lighting).[61]

The dual-fuel strategy is to use ammonia (or nitrofuel) whenever professional fuel handlers (people with special training and equipment) can be employed. Applications involving nonprofessional fuel handlers are to be served by methanol (or carbofuel). What are the relative sizes of these two fuel market segments? Two ways to estimate this division in the existing system are by fuel type and by fuel use.

First, by fuel type. It is estimated that 74% of fuel use is professional, 26% is nonprofessional. This estimate is obtained as follows. Consider all coal, all natural gas, and all diesel and jet fuel use to be professional. Then the remaining liquid fuel use (LPG, gasoline, kerosene and heating oil) is nonprofessional. Clearly, this is not exactly right. Some natural gas is used in residences, and not all LPG and fuel oil is used in residences. These errors balance each other. The EIA data lists all electrical generation and the losses associated with it. This is reduced by 23% to exclude nuclear and renewable sources; the remainder, 77%, is from fossil sources. The 2009 EIA data are displayed in Table 4.[62]

Second, by fuel use. It is estimated that 71% of fuel use is professional, 29% is nonprofessional. In the professional category, we include fuel use for electric power generation; for any kind of production (food, manufacturing, processing—the industrial sector); for air, sea, river, and rail transport; for road transport using heavy trucks; and for habitation of large buildings (the commercial sector). In the nonprofessional category, we include fuel use for road transport by light trucks and cars, and for habitation of small buildings (the residential sector). The 2009 EIA data are displayed in Table 5.[63]

The two methods of breaking out fuel use into nonprofessional and professional fuel-handler categories are in reasonably good agreement, given the crudeness of the assumptions. In Tables 3–5, there is uncertainty as to where loss terms in the energy chains belong. EIA data is not explicitly organized around energy chains, leading to ambiguity. Further, double-counting can occur when breaking out energy components according to different categories than those chosen by the EIA. Nevertheless, the consistency of these tables with each other is good enough to suggest that the estimates derived from them are usable. They are rough estimates, good enough for the present purpose. In future, the fraction of energy trade carried by the electric vector will increase, which will also increase the fraction of fuel use by professional handlers. For example, increased use of either natural gas or coal for electric power generation is use by professional fuel handlers, who could equally safely handle ammonia. Therefore as an estimate for the near-term future we assume a division skewed toward professional handlers:

professional handlers 80%
nonprofessional 20%

This is the division assumed in the dual-fuel strategy.

APPENDIX B
LITERATURE OF AMMONIA AND METHANOL AS FUEL

Non-fuel ammonia technology is the topic of a monograph by Appl [156]. A monograph somewhat broader in scope is [157]. The first textbook to include a chapter on

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[58] Most of the flow from the petroleum source (dark green) in the LLNL diagram is carried by liquid fuel vectors.

[59] Most of the flow from the natural gas source (dark blue) in the LLNL diagram is carried by gaseous fuel vectors.

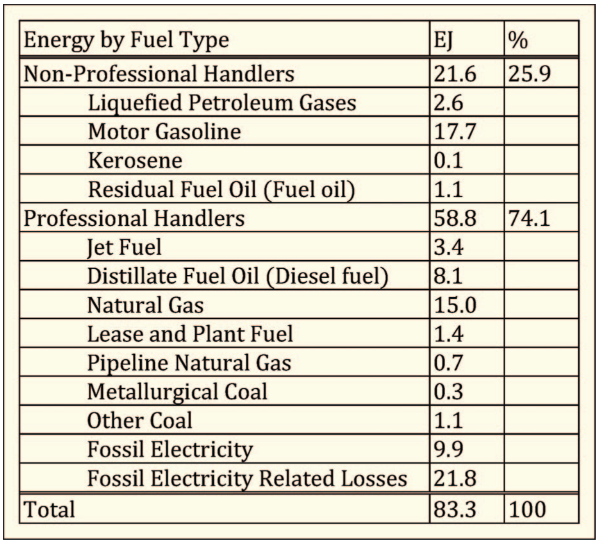
[60] This is the industrial category of the LLNL diagram.

[61] This is the residential and commercial categories of the LLNL diagram, combined.

[62] EIA Annual Energy Outlook for 2010, Supplemental Tables; Table 10, Energy Consumption by Sector and Source. Table 85, Electric Power Generation, was used to estimate the fraction of electric power generated from fossil sources. See [155].

[63] See [155]. Table 45, Transportation Sector Energy Use by Mode and Type, was used to break out the nonprofessional versus professional components of the transportation sector.

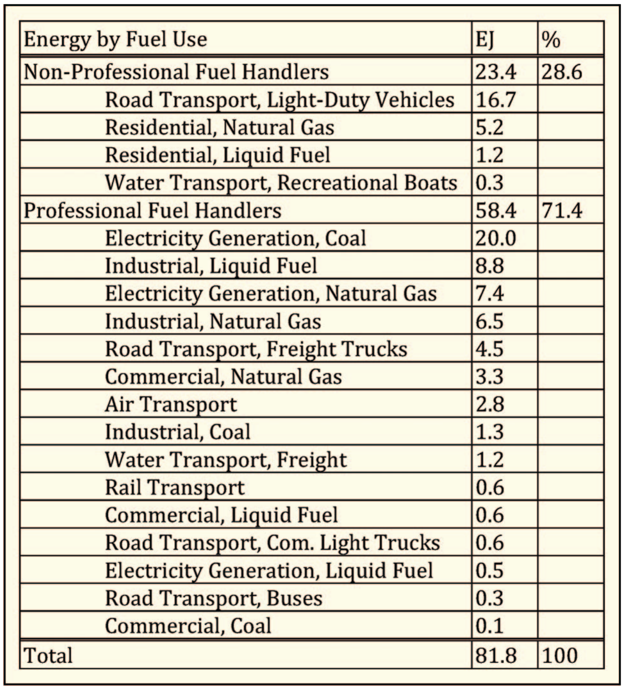
Table 4 Fuel Energy Consumed, by Type



Energy by Fuel Type	EJ	%
Non-Professional Handlers	21.6	25.9
Liquefied Petroleum Gases	2.6	
Motor Gasoline	17.7	
Kerosene	0.1	
Residual Fuel Oil (Fuel oil)	1.1	
Professional Handlers	58.8	74.1
Jet Fuel	3.4	
Distillate Fuel Oil (Diesel fuel)	8.1	
Natural Gas	15.0	
Lease and Plant Fuel	1.4	
Pipeline Natural Gas	0.7	
Metallurgical Coal	0.3	
Other Coal	1.1	
Fossil Electricity	9.9	
Fossil Electricity Related Losses	21.8	
Total	83.3	100

the use of ammonia as fuel has recently been contributed by Dincer and Zamfirescu [158]. Ammonia as fuel was comprehensively reviewed in 1980 by Bomelberg and McNaughton [2] and [159]. Their review is particularly useful for an overview of work in Europe prior to and during World War II, and also the work done during the 1960s as part of the U.S. Army's Nuclear Powered Energy Depot program. Much of this work is available online through the U.S. Defense Technical Information Center (DTIC) Web site [160]. The Society of Automotive Engineers (SAE) Digital Library [161] must also be consulted for a complete review of this early work. A thorough review updating work since 1980 is provided by Bartels and Pate [162]. Anyone interested in the use of ammonia as fuel should consult the Web sites of the Iowa Energy Center [163] and the NH3 Fuel Association [93]. Reviews [164]–[184] are of more or less broad scope and provide further perspective. Many researchers view ammonia as just another hydride, a hydrogen carrier, to be converted back to hydrogen in a reformer prior to use as fuel. This is the perspective, for example, of Thomas and Parks [175] and Lipman and Shah [177]. This viewpoint reflects an entrenched commitment to the use of hydrogen as a key energy vector, a strategy that must be reexamined. Hydrogen should be viewed not as an energy vector, but at most, as a process intermediate in the production of ammonia and methanol. Even that role should be eliminated if possible, in the interest of process simplification.

Table 5 Fuel Energy Consumed, by Use



Energy by Fuel Use	EJ	%
Non-Professional Fuel Handlers	23.4	28.6
Road Transport, Light-Duty Vehicles	16.7	
Residential, Natural Gas	5.2	
Residential, Liquid Fuel	1.2	
Water Transport, Recreational Boats	0.3	
Professional Fuel Handlers	58.4	71.4
Electricity Generation, Coal	20.0	
Industrial, Liquid Fuel	8.8	
Electricity Generation, Natural Gas	7.4	
Industrial, Natural Gas	6.5	
Road Transport, Freight Trucks	4.5	
Commercial, Natural Gas	3.3	
Air Transport	2.8	
Industrial, Coal	1.3	
Water Transport, Freight	1.2	
Rail Transport	0.6	
Commercial, Liquid Fuel	0.6	
Road Transport, Com. Light Trucks	0.6	
Electricity Generation, Liquid Fuel	0.5	
Road Transport, Buses	0.3	
Commercial, Coal	0.1	
Total	81.8	100

Using the references cited above as pointers, the interested reader will find a large number of reports on the use of ammonia as fuel in modified ICEs (both SI and CI) and CTs. Recent work not covered by those reviews are [100] and [185]–[187]. Most of the engines used as experimental platforms were intended originally for either road transport or stationary applications (electric power generation or water pumping). There is need for further work in all areas, but especially development work targeting air and marine transport. These are applications which contribute significantly to global air pollution, and in which professional fuel handlers are always employed. As such, they are target markets for ammonia fuel. We have found no report of sea trials of an ammonia-powered ship, although some of the engines tested could have served this purpose. There is one report of tests at the United States Merchant Marine Academy on the use of an ammonia-diesel fuel emulsion in marine engines [187].

There is a famous instance of aerospace application of ammonia as fuel, that of the X-15 rocket plane, which was powered by liquid oxygen and ammonia [188], [189]. Although the X-15 was a rocket, a study of the engines that powered it is a starting point for evaluating the feasibility of using ammonia for aircraft propulsion. A selection of relevant reports are [190]–[202]. Chapter 4 of [189], titled "The Million-Horsepower Engine," describes the development of the X-15's liquid-propellant rocket engines, mainly the XLR99. Operational experience with this ammonia-burning engine is summarized in these terms:

> "In retrospect, the engine still casts a favorable impression. The XLR99 pushed the state-of-the-art further than any engine of its era, yet there were no catastrophic engine failures in flight or on the ground."

It is interesting to read at the end of this chapter the experience of converting the X-15 rocket plane to use a

XLR11 engine powered by oxygen and ethanol. The conversion from ammonia to ethanol is described as:

> "...[requiring] some modifications to the system, but none of them were major—fortunately, the two liquids [ammonia and ethanol] had a similar consistency and temperature. ...there were no modifications to the fuel tanks. North American had already built and sealed them by the time NASA decided to use the XLR11s. It was determined that both the metal and the sealant were compatible with alcohol, so there was no need to reopen the tanks. ...considering that North American had designed the airplane with no intention of installing anything but the XLR99, the changes were of little consequence...."

The experience with the X-15 rocket plane mirrors that with more mundane machinery: engines of all kinds designed to operate using liquid fuels can be modified relatively easily to operate on *other* liquid fuels, even quite different ones such as ammonia and ethanol. "Relatively" means relative to conversion to hydrogen. Conversion of the X-15 from ammonia to hydrogen propellant was never contemplated; it would have been prohibitively difficult.

We are aware of just one report on ammonia as aviation fuel [203]. It is purely a design study with no accompanying experimental demonstration, conducted in the 1960s as part of the U.S. Army Energy Depot program cited previously. Severely reduced range between refueling due to low specific energy of the fuel was cited as the main reason for recommending that "Because of limited performance of ammonia-fueled aircraft, this task be dropped...." Contemporary researchers should not be discouraged by this recommendation, as the context in which it was arrived at is very different from the objectives that drive present and future commercial development. The negative recommendation of [203] does, however, underscore a very important disadvantage of ammonia: low specific energy, about one-half that of kerosene. To achieve commercial viability, this disadvantage must be balanced by significantly lower cost and better supply reliability.

The energy density of renewable fuel can be increased if we settle for low-carbon rather than insisting on zero-carbon fuel. Further, if such a fuel leads to improved engine efficiency compared to kerosene, its lower energy density is partly offset. The use of ammonia as an additive or auxiliary fuel in jet engines burning fossil fuels has been reported to improve their performance [204]. Use of ammonia combined with $LiBH_4$ as a primary jet fuel is the subject of a patent [205]. The purpose of the $LiBH_4$ additive is to lower the vapor pressure of the fuel blend, an issue cited also in [204]. Both suggest a line of research seeking to develop a blended fuel such as mixtures with a carbon-containing component (see Section XV and Appendix H). It is not necessary to remove *all* carbon from the fuel. If a fuel with one-tenth or even one-fifth the carbon intensity of jet fuel is a commercially viable competitor, whereas a fuel with zero carbon intensity is not, the former will do more to mitigate anthropogenic climate change than the latter. It might be, however, that fuels equivalent to kerosene are essential to aviation. Then CNHCs will be the renewable fuels that must be used in this application. They will be more costly than ammonia or methanol, but their higher energy density will justify the higher cost for air transport.

Ammonia as fuel for burners is a topic of particular significance for electric power generation using steam turbines. Ammonia is today injected into natural gas burners for steam generation plants as a NOx mitigation measure. An example can be seen in [206], where equipment for NOx reduction by selective catalytic reduction (SCR) is displayed. It is expected that boilers incorporating natural gas burners can be relatively easily modified to burn ammonia as the primary fuel instead. Preliminary investigations of ammonia flames in open burners are reported by Brandhorst *et al.* [207] and Grannell [100]. A comprehensive study is underway under the supervision of Meyer, [208]–[210]. In this work, ammonia is mixed with methane and the fuel blend is used in burners designed for natural gas. Meyer reports that "near 100% replacement [of CH_4] with NH_3 seems feasible with near zero emissions [of NOx]." This study confirms that the engineering of the ammonia combustion process is challenging, but can be done. The outcome will be commercially available low-NOx ammonia combustion systems for steam generation and process heat.

Ammonia burner technology has been most thoroughly developed as part of the production process for nitric acid [157], [211]. This is a very large industrial sector with over a century of technology experience. The burners for this process are unique. Combustion must be enhanced with platinum gauze catalysts under conditions precisely calibrated to enhance NO production. Fortunately for the prospects of ammonia as fuel, NO production is difficult to achieve. To *maximize* NO production, careful design of the combustion process is required. In support of that objective an extensive foundation of scientific and technological knowledge has been developed over the past century; examples are [212]–[214]. This same knowledge base can be used to accomplish the easier task of developing burners that *minimize* NO production. Ammonia combustion has also been studied in the context of flaring unwanted emissions; see [215]–[217]. Readers interested in accessing the literature of ammonia combustion may begin with the classic reviews of Miller and Bowman [218] and Lindstedt *et al.* [219] and the recent work of Lee *et al.* [137]–[139], Zieba [220] and Duynslaegher *et al.* [221].

Methanol as fuel is the topic of a monograph by Olah *et al.* [222], which should be consulted for an entry into the very extensive literature on this topic. A recent update is provided in [223]. Two older reports that remain very useful are those by Hagen [224] and Lowell *et al.* [225]. A recent survey by Bromberg and Chang is available [226]. The Methanol Institute is a source of additional information [227]. An important large-scale experiment on replacing gasoline with methanol was carried out in California between 1979 and 1997. The results up until 1986 are reported by Blaisdell *et al.* [228]. A related study of the feasibility to scale up production of methanol for fuel use is reported by Bechtel Corporation [229]. The California experiment proved the economic feasibility of replacing gasoline with methanol. The low oil prices that followed the financial crisis of 1987 prevented this project from expanding to a broader commercial base at that time. As oil prices trend upward and supply becomes more unstable in the second decade of the 21st century, the business model developed in these reports will look ever more attractive to entrepreneurs. The California experiment wound down in the late 1980s, but continued reduced in scope into the 1990s. Summary reports can be found in [103] and [230]–[232].

A very useful series of reports were prepared by the U.S. Department of Energy under the series title *Assessment of Costs and Benefits of Flexible and Alternative Fuel Use in the U.S. Transportation Sector*. Fourteen reports in this series were published between 1988 and 1996. Unfortunately not all of these reports are easily accessible. Readers with serious interest should nevertheless hunt them down and study them. A selection is [101], [124] and [233]–[235]. Ammonia is regrettably not covered explicitly, but methanol receives extensive and very valuable coverage. Further, issues related to the existing energy infrastructure, relevant to all fuels, are treated extensively.

APPENDIX C

ENHANCED GAS RECOVERY AND MINERAL CARBONATION

Carbon sequestration by enhanced gas recovery (CSEGR) is inspired by a process that is known and works for enhancing petroleum production: carbon dioxide is injected into oil reservoirs to increase the pressure and force the oil out. This works well since CO_2 and oil do not mix. Can it work with natural gas? Any two gases mix very well in an open space, but in the porous medium that is an underground natural gas reservoir, it may be that the mixing is slow enough for the process to be practical. This idea was first proposed by van der Burgt, Cantle and Boutkan in 1992 [236]. Their study analyzed the most obvious potential problem: the formation of a preferential flow path resulting in an early CO_2 breakthrough, thus reducing the overall sweeping efficiency. Blok *et al.* took up the analysis in 1997 [237]. Their abstract expresses very clearly the strong appeal of this process:

> "When hydrogen is produced from natural gas, a concentrated stream of CO_2 is generated as a by-product. If manufacture is carried out near a depleted natural gas field, the separated CO_2 can be compressed and injected into the field and securely sequestered there. The incremental cost of the produced hydrogen (for CO_2 compression plus transport, injection and storage) would typically be about 7% relative to the case where the separated CO_2 is vented. Moreover, CO_2 injection leads to enhanced natural gas recovery as a result of reservoir repressurization. Though the extra natural gas is somewhat contaminated with CO_2, it is a suitable feedstock for hydrogen production. Taking credit for enhanced natural gas recovery reduces the penalty for sequestration to a net incremental cost of typically 2%. These cost penalties are much lower than those typical of CO_2 removal schemes associated with electricity production."

The acronym CSEGR was coined by Oldenburg and coworkers, who conducted further analysis both physical and economic [238], [239]. Recently Singh, Goerke and Kolditz have taken up the study [240]. They summarize the issue:

> "The extent to which carbon dioxide could mix with natural gas is a primary concern for technical and economic feasibility of carbon sequestration with EGR."

They calculate "breakthrough curves" showing concentration of gas injected at inlet well to that at outlet well versus time. They find significant concentrations in times on the order of years. This seems to be too short a time to be useful for exploitation of all but very mature gas fields that are about to cease production. It could be useful if a relatively new gas reservoir adjacent to a mature, nearly exhausted gas reservoir is to be exploited. In general, however, alternative CCSS processes will be needed. Mineral carbonation is the most appealing.

Carbon sequestration by mineral carbonation is reviewed by Krevor and Lackner [241]. The physics and chemistry of several processes have been established. Commercial viability remains to be determined. Process efficiency and cost are central considerations. Examples of studies addressing these issues are [242]–[244]. In at least one instance mineral carbonation has transitioned from research to precommercial trials. A mineral carbonation CCSS process is in pilot-plant demonstration at the Moss Landing power plant in California, under development by Calera Corporation [63]. This process is intended to remove CO_2 from the exhaust stacks of the power plant. It relies on extracting calcium and magnesium oxides from seawater to provide the feedstock for carbonate formation. The Calera process is proprietary, but appears to be similar to processes described by House [245] and Li [246]. Whether or not this experiment turns out to be successful, it is important to bear in mind that capturing and sequestering CO_2 in a petrochemical conversion plant where natural gas or coal is used as a feedstock for ammonia production is far easier and thus more economical than doing it at the exhaust stacks of an electric power plant. It will be more profitable to do CCSS at the gas or coal fields, and then distribute ammonia as fuel to the power plants.

APPENDIX D

FUEL CARBON INTENSITY

Fuel carbon intensity (FCI) is a figure of merit for comparing fuel production and use processes. The smaller a process FCI is, the better. FCI is the ratio of the mass of C or CO_2 emitted into the atmosphere to the useful energy output of the process. The units of FCI are kgC/GJ or $kgCO_2/GJ$. In the literature the amount of CO_2 may be given as $kgCO_2e$, the e standing for "equivalent," signifying that the emission of other GHGs (primarily CH_4 and N_2O) is also accounted for. These other GHGs are emitted into the atmosphere as part of the production and use processes of the fuel; they are accounted for by replacment with an amount of CO_2 that has an equivalent effect on global warming.

FCI is the correct way to quantify the merit of a fuel production and use *process*. Carbon-free fuels such as hydrogen and ammonia can have high FCIs and carbon-containing fuels such as methanol and iso-octane can have low FCIs, depending on how they are produced. CHR and IFCI are two figures of merit that are *intrinsic* characteristics of fuels, independent of how they are produced. They are defined in the following. These figures of merit are useful if their limitations are recognized.

The simplest measure of something similar to the fuel carbon intensity is the C/H ratio (CHR). This means the ratio of the number of carbon atoms to the number of hydrogen atoms in a fuel molecule. We would like it to be as low as possible. For hydrogen and ammonia it is zero. For methane and methanol it is 0.25. For ethane, ethanol, and dimethyl ether it is 0.33. For most constituents of gasoline and similar fossil fuels it is about 0.5. For coal it can be very much higher, up to 0.9 for high-quality anthracite.

The CHR is a poor estimator of fuel carbon intensity. Much better is the inverse carbon-specific[64] standard enthalpy of combustion, proportional to the intrinsic fuel carbon intensity (IFCI) defined below. Let h_c^0 be the specific standard enthalpy of combustion. It corresponds to the higher heating value (HHV) of the fuel, i.e., the energy retrieved by burning the fuel with water in standard state (liquid phase at room temperature) as one of the combustion products. Let c_F be the mass fraction of fuel that is carbon, sometimes called the specific carbon content. It is a dimensionless number defined as nM_C/M_F, where n is the number of carbon atoms in a fuel molecule, M_C is the molecular weight of carbon ($12.01\ \mathrm{g \cdot mol^{-1}}$), and M_F is the molecular weight of the fuel. Then $\mathrm{IFCI}' = c_F/h_c^0$, with units kgC/J. To make an intrinsic figure of merit with units $kgCO_2/GJ$, comparable to FCI, we define $\mathrm{IFCI} = \mathrm{IFCI}' \cdot (M_{CO_2}/M_C) \cdot (HHV/LHV) \cdot (10^9\,\mathrm{J/GJ})$. The definition of FCI uses LHV (rather than HHV) of the fuel as this more closely conforms to energy available when fuel is burned in most combustion engines. For hydrogen and ammonia IFCI is zero. For carbon-based liquid fuels it shows remarkably little variation: 69.0 for methanol, 73.2 for ethanol and gasoline, and 75.3 for jet and diesel fuel. The range of values of IFCI for these fuels is about 9% from best (lowest) to worst (highest). Among the carbon-based fuels methane has the lowest IFCI value, 54.9 $kgCO_2/GJ$; but methane is not a liquid, it is a gas. Methane is used mainly for electric power generation industrial process heat, where its renewable competitor is ammonia, with zero IFCI. Methanol has an IFCI advantage of about 6% over ethanol and gasoline, its main competitors. These facts are worth noting, but bear in mind that the intrinsic fuel properties CHR or IFCI do not much matter. It is FCI, a path (system) property, that is important.

IFCI is a better approximation to FCI than is CHR, but it is still not the real thing. Whereas liquid carbon-based fuels have IFCI in the neighborhood of 75 $kgCO_2e/GJ$, their FCI using default values from [247] is in the neighborhood of 90 $kgCO_2e/GJ$. Hydrogen has an IFCI of zero, but its default FCI value is 92 $kgCO_2e/GJ$, the highest of any liquid or gaseous fuel! This is because the most common production and distribution processes for hydrogen generate carbon emissions. Correct assessment of carbon intensity requires analysis not only of the chemical compound that is used as fuel, but also its production, distribution, and use processes. CHR and IFCI focus attention only on the chemical compound itself.

To compute FCI we need the entire fuel path, or life cycle, specified by the chain of processes described in Section III. For any given fuel this is obviously not unique. The very high value of FCI for hydrogen comes from assuming it is generated from natural gas and then a lot of energy from other fossil fuels is used to get it to where it will be used, and to manufacture the equipment used in producing, storing, transporting, and using it. One can most definitely construct alternative scenarios in which this number is very much smaller. Hydrogen produced by electrolysis of water can possibly have an FCI approaching zero. The same is true of methanol, although the molecule contains carbon, if the source of that carbon is CO_2 extracted from the air.

A relatively simple way to structure FCI calculations is offered by Cleeves [248]. For any given fuel, 12 sources of carbon emissions are identified as follows:

1) carbon dioxide and hydrogen sulphide removed from natural gas;
2) carbon from air incorporated in fuel;
3) coproducts production;
4) direct land use change;
5) feedstock production and recovery;
6) feedstock transport;
7) fertilizer and pesticide manufacture;

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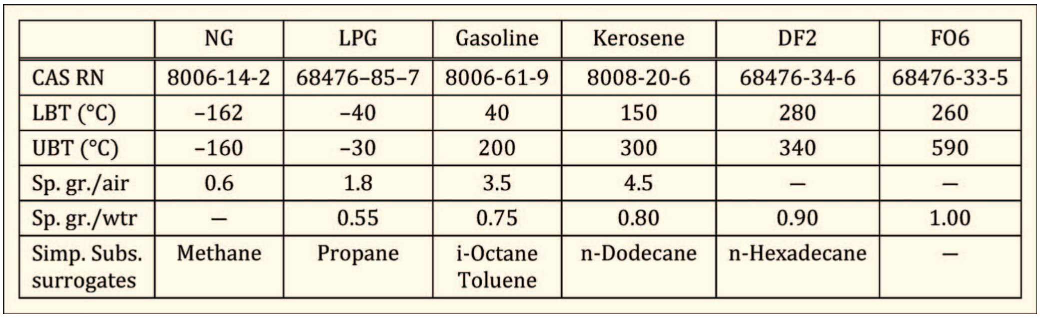
[64] The modifier *specific* means "per unit mass of substance"; the modifier *carbon-specific* means "per unit mass of carbon contained in the substance."

Table 6 Common Fuel Blends



	NG	LPG	Gasoline	Kerosene	DF2	FO6
CAS RN	8006-14-2	68476–85–7	8006-61-9	8008-20-6	68476-34-6	68476-33-5
LBT (°C)	–162	–40	40	150	280	260
UBT (°C)	–160	–30	200	300	340	590
Sp. gr./air	0.6	1.8	3.5	4.5	–	–
Sp. gr./wtr	–	0.55	0.75	0.80	0.90	1.00
Simp. Subs. surrogates	Methane	Propane	i-Octane Toluene	n-Dodecane	n-Hexadecane	–

8) fuel dispensing;
9) fuel production;
10) fuel storage and distribution;
11) leaks and flaring;
12) vehicle or vessel operation.

The FCI is the sum of the contributions from each component:

$$\mathrm{FCI} = \sum_{i=1}^{12} \mathrm{CI}_i$$

where components 2 and 3 are zero or *negative*. By this computation scheme, ethanol produced from sugar cane has FCI 24.4 $\mathrm{kgCO_2e/GJ}$ [248]. Using the same scheme Bryce [249] computes the following (all in $\mathrm{kgCO_2e/GJ}$): ethanol from corn, 62–74; ethanol from wheat, 40.9; methanol from natural gas, 76.2; methanol using electrolytic hydrogen and CO_2 from petrochemical process exhaust stream: 31.7 if average grid power with high hydroelectric content; 14.3 if wind power. These last two values are below the IFCI of methanol (69.0) because component 2 is negative.

The pathway through the energy chain determines FCI. That pathway is not an intrinsic property of the fuel. If renewable fuel is made from CO_2 drawn from the atmosphere (or from an exhaust stream into the atmosphere) then component 2 of FCI is a negative number. In comparing two potential renewable fuels such as methanol and ethanol, attention must be focused on component 9, fuel production. We need to keep this as small as possible. If the simpler molecule (methanol) can be produced most efficiently, it will also have the lowest FCI.

APPENDIX E

PROPERTIES OF FUELS

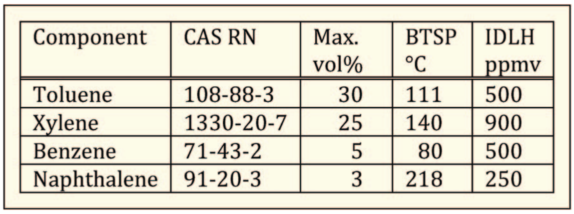
Renewable fuels must be compared to the fossil fuels they will displace. This comparison is complicated because the fossil fuels in widespread use are not simple substances, but are complex and poorly defined blends. Table 6 lists six representative common fuel blends (CFBs) representing the range of fossil fuels in use today.

NG is natural gas; LPG is liquid petroleum gas; gasoline is the common fuel for light surface transport vehicles; kerosene represents jet fuels; DF2 (diesel fuel no. 2) represents fuel oils used for heavy surface transport vehicles; FO6 (fuel oil no. 6) represents the residual fuel oils sometimes used for heating and marine transport. The compositions of CFBs vary widely. For comparison of thermochemical properties and toxic threat they can be represented by simple substance surrogates. Table 6 lists such surrogates for all the CFBs but FO6, for which we have not as yet had occasion to choose one. For gasoline we use two simple substance surrogates: i-octane and toluene. Either can be used for comparison of thermochemical properties, but i-octane is preferred. More accurate surrogates for gasoline are mixtures of simple substances, for example n-heptane, i-octane, and toluene [250]. For relative toxicity it is necessary to use toluene because alkanes are simple asphyxiates that can in no way represent the toxic threat presented by gasoline.

Table 7 lists the four toxic components that are sometimes found in significant concentrations in the liquid CFBs, especially gasoline and kerosene.

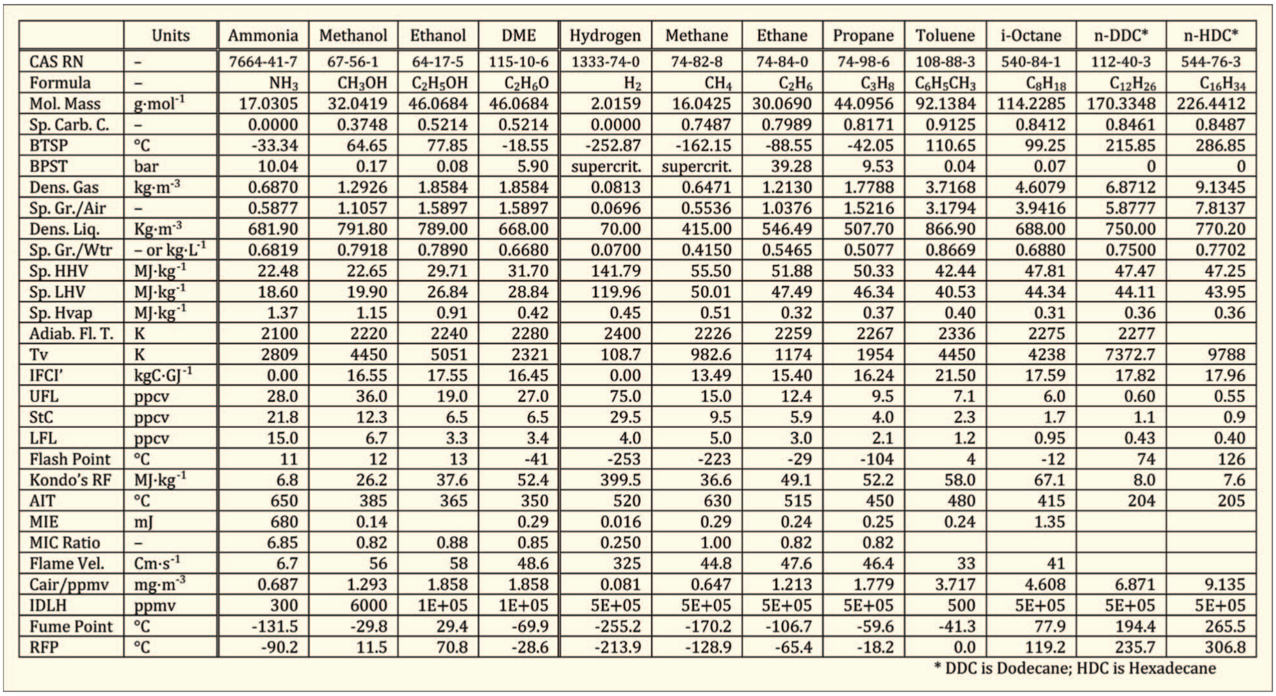
The third column lists the maximum percent by volume that the component might comprise in a gasoline or kerosene fuel blend, determined by consulting several dozen materials safety data sheets. Diesel fuel appears to be much less likely than gasoline or kerosene (jet fuel) to contain these toxic components. The fourth column lists the boiling temperature at standard pressure (BTSP) of the pure component. The activity of the component in the actual fuel blend is relevant but unavailable. For

Table 7 Toxic Components of Liquid CFBs



Component	CAS RN	Max. vol%	BTSP °C	IDLH ppmv
Toluene	108-88-3	30	111	500
Xylene	1330-20-7	25	140	900
Benzene	71-43-2	5	80	500
Naphthalene	91-20-3	3	218	250

Table 8 Fuel Properties



	Units	Ammonia	Methanol	Ethanol	DME	Hydrogen	Methane	Ethane	Propane	Toluene	i-Octane	n-DDC*	n-HDC*
CAS RN	–	7664-41-7	67-56-1	64-17-5	115-10-6	1333-74-0	74-82-8	74-84-0	74-98-6	108-88-3	540-84-1	112-40-3	544-76-3
Formula	–	NH_3	CH_3OH	C_2H_5OH	C_2H_6O	H_2	CH_4	C_2H_6	C_3H_8	$C_6H_5CH_3$	C_8H_{18}	$C_{12}H_{26}$	$C_{16}H_{34}$
Mol. Mass	g·mol^{-1}	17.0305	32.0419	46.0684	46.0684	2.0159	16.0425	30.0690	44.0956	92.1384	114.2285	170.3348	226.4412
Sp. Carb. C.	–	0.0000	0.3748	0.5214	0.5214	0.0000	0.7487	0.7989	0.8171	0.9125	0.8412	0.8461	0.8487
BTSP	°C	-33.34	64.65	77.85	-18.55	-252.87	-162.15	-88.55	-42.05	110.65	99.25	215.85	286.85
BPST	bar	10.04	0.17	0.08	5.90	supercrit.	supercrit.	39.28	9.53	0.04	0.07	0	0
Dens. Gas	kg·m^{-3}	0.6870	1.2926	1.8584	1.8584	0.0813	0.6471	1.2130	1.7788	3.7168	4.6079	6.8712	9.1345
Sp. Gr./Air	–	0.5877	1.1057	1.5897	1.5897	0.0696	0.5536	1.0376	1.5216	3.1794	3.9416	5.8777	7.8137
Dens. Liq.	Kg·m^{-3}	681.90	791.80	789.00	668.00	70.00	415.00	546.49	507.70	866.90	688.00	750.00	770.20
Sp. Gr./Wtr	– or kg·L^{-1}	0.6819	0.7918	0.7890	0.6680	0.0700	0.4150	0.5465	0.5077	0.8669	0.6880	0.7500	0.7702
Sp. HHV	MJ·kg^{-1}	22.48	22.65	29.71	31.70	141.79	55.50	51.88	50.33	42.44	47.81	47.47	47.25
Sp. LHV	MJ·kg^{-1}	18.60	19.90	26.84	28.84	119.96	50.01	47.49	46.34	40.53	44.34	44.11	43.95
Sp. Hvap	MJ·kg^{-1}	1.37	1.15	0.91	0.42	0.45	0.51	0.32	0.37	0.40	0.31	0.36	0.36
Adiab. Fl. T.	K	2100	2220	2240	2280	2400	2226	2259	2267	2336	2275	2277	
Tv	K	2809	4450	5051	2321	108.7	982.6	1174	1954	4450	4238	7372.7	9788
IFCI'	kgC·GJ^{-1}	0.00	16.55	17.55	16.45	0.00	13.49	15.40	16.24	21.50	17.59	17.82	17.96
UFL	ppcv	28.0	36.0	19.0	27.0	75.0	15.0	12.4	9.5	7.1	6.0	0.60	0.55
StC	ppcv	21.8	12.3	6.5	6.5	29.5	9.5	5.9	4.0	2.3	1.7	1.1	0.9
LFL	ppcv	15.0	6.7	3.3	3.4	4.0	5.0	3.0	2.1	1.2	0.95	0.43	0.40
Flash Point	°C	11	12	13	-41	-253	-223	-29	-104	4	-12	74	126
Kondo's RF	MJ·kg^{-1}	6.8	26.2	37.6	52.4	399.5	36.6	49.1	52.2	58.0	67.1	8.0	7.6
AIT	°C	650	385	365	350	520	630	515	450	480	415	204	205
MIE	mJ	680	0.14		0.29	0.016	0.29	0.24	0.25	0.24	1.35		
MIC Ratio	–	6.85	0.82	0.88	0.85	0.250	1.00	0.82	0.82				
Flame Vel.	Cm·s^{-1}	6.7	56	58	48.6	325	44.8	47.6	46.4	33	41		
Cair/ppmv	mg·m^{-3}	0.687	1.293	1.858	1.858	0.081	0.647	1.213	1.779	3.717	4.608	6.871	9.135
IDLH	ppmv	300	6000	1E+05	1E+05	5E+05	5E+05	5E+05	5E+05	500	5E+05	5E+05	5E+05
Fume Point	°C	-131.5	-29.8	29.4	-69.9	-255.2	-170.2	-106.7	-59.6	-41.3	77.9	194.4	265.5
RFP	°C	-90.2	11.5	70.8	-28.6	-213.9	-128.9	-65.4	-18.2	0.0	119.2	235.7	306.8

* DDC is Dodecane; HDC is Hexadecane

comparison, methanol boils at 65 °C, ethanol at 78 °C, and i-octane at 99 °C. Gasoline has a boiling range from 40 °C to 200 °C. This gives an idea of volatility. The last column lists a toxicity figure of merit, IDLH (Immediately Dangerous to Life or Health) determined by the U.S. National Institute of Occupational Safety and Health (NIOSH) [222]. For purposes of toxicity comparisons, we take toluene as a surrogate for gasoline. Iso-octane has no listed IDLH and is classified as a simple asphyxiate. As such, it cannot represent gasoline insofar as toxicity characteristics are concerned. In Appendix F we define the relative fume point (RFP) based on toluene. RFP conflates both toxicity and volatility into a single figure of merit that we use to characterize the relative toxic threat posed by different fuels. The objective is to compare unfamiliar fuels with a simple substance surrogate for gasoline, a fuel with which we are familiar.

Table 8 is a compilation of some of the properties of ammonia, methanol, ethanol, and DME most relevant to their use as fuels. The same properties of hydrogen and a range of hydrocarbons (including CFB simple substance surrogates) are presented for comparison. In compiling this table we take standard temperature and pressure (STP) to be 25 °C (298.15 K) and 1 bar (100 kPa or 0.9869 atm). We assume that gases are ideal and liquids are incompressible. "Air" means dry air composed of 78 mol% nitrogen, 1 mol% argon, and 21 mol% oxygen, with average molecular weight $M_A = 28.98$ g/mol and density $\rho_A = 1.1684$ kg/m^3 at STP. Specific carbon content is $c_F = nM_C/M_F$, where n is the number of carbon atoms in a molecule, M_C is the atomic mass of carbon (12.0107 g/mol), and M_F is the molecular mass of the fuel. BPST is the boiling pressure at standard temperature, calculated using the Antoine equation with coefficients from [253]. This is the pressure at which the substance will condense (liquefy) at 25 °C. Gas densities are determined assuming they are ideal: $\rho_F = p_s M_F/(RT_s)$. Specific gravity of gaseous fuels with respect to air is calculated as M_F/M_{air}. Liquid densities are nominally at STP, but some of the values quoted were determined at other conditions and are assumed not to change with temperature and pressure. Note that the specific gravity of a liquid with respect to water is numerically the same as that liquid's density expressed in kg/L, since water at STP has a density of exactly 1 kg/L. Specific HHV, LHV, and Hvap refer to the mass specific enthalpies of combustion and vaporization. HHV is the the higher heating value which corresponds to product water in the liquid (standard) state. Thus, HHV is the standard specific enthalpy of combustion (often denoted h_c^0). LHV is the lower heating value that corresponds to product water in the gas state. Specific Hvap is often denoted h_{vap}^0. The corresponding molar enthalpy of vaporization at standard pressure is $\bar{h}_{\text{vap}}^0 = Mh_{\text{vap}}^0$. Tv is the vaporization temperature defined by $T_v = \bar{h}_{\text{vap}}^0/R$. IFCI′ is the inverse carbon-specific standard enthalpy of combustion as defined in Appendix D: $\text{IFCI}' = c_F/h_c^0$. LFL, StC and UFL are the lower flammability limit, stoichiometric concentration, and upper flammability limits. Kondo's RF number is a figure of merit to assess fire hazard [150], high for high hazard, defined by RF $= (\sqrt{\text{UFL}/\text{LFL}} - 1) \cdot \text{LVH}$. The adiabatic flame temperature T_{ad} is the solution to the equation: $h_c(T_{\text{ad}}) = h_c^0$, assuming pressure constant at 1 bar and stoichiometric fuel/

air ratio. It is the temperature of the combustion products if they retain all the energy released when the reactants combine with air, at standard temperature initially, and at constant standard pressure. AIT is the auto-ignition temperature, the temperature at which the most easily ignitable mixture will ignite on its own. This mixture is assumed also in determining MIE and MIC. MIE is the minimum ignition energy supplied by a capacitive spark discharge, and MIC is the minimum igniting current required from an inductive spark discharge. The MIC ratio is formed by normalizing the MIC for any fuel to the value for methane. Kondo's RF, AIT, and MIE are indicators of relative fire/explosion hazard. The superior relative fire/explosion safety of ammonia is reflected by its low value of RF and high value of AIT, MIE, and MIC ratio. These are better indicators than flash point of the relative fire/explosion hazard of ammonia. The exceptionally high value of MIE for ammonia is particularly noteworthy. Flash point is good for comparing fuels of different volatility but similar characteristics otherwise. Ammonia is very different from hydrocarbon fuels, especially with respect to MIE, thus a comparison based on flashpoint is misleading. The flammability properties of ammonia were summarized by Buckley and Husa [145] very simply: "ignition is difficult and flame propagation in air mixtures is slow."

Next comes toxicity data. Cair/ppmv is a conversion factor to obtain concentration in air expressed as mass per volume. IDLH is the concentration deemed by NIOSH to be immediately dangerous to life or health [251]. NIOSH gives IDLH values for some nontoxic but flammable substances by specifying a value based on the LFL; we ignore these in order to separate the evaluation of toxicity and fire/explosion hazards. Instead, we assign an IDLH of 500 000 ppmv (i.e., fuel vapor comprising half of the atmosphere one must breathe) to all fuels that are simple asphyxiates, regardless of their flammability. This includes fuels for which NIOSH assigns an IDLH based on LFL, and also all fuels for which NIOSH assigns no IDLH. Fume point and relative fume point (RFP) are defined in Appendix F. RFP is the basis on which we compare the relative toxic threat posed by different fuels. By this measure, just as concluded in the toxicity review literature [115]–[124], methanol is safer than gasoline.

The data sources for this table are [126], [140], [145]–[149], and [251]–[256]. There is need for a critical review of the primary literature to verify and update this information.

APPENDIX F

RELATIVE FUME POINT

How to quantify toxicity? This question, like all questions involving CFBs, is complicated by the fact that the substances we wish to characterize are ill-defined. We would like to use a familiar substance, gasoline, as the benchmark with which we compare proposed alternative fuels. To do so we first need to know how toxic gasoline is. Official documents (for example [251] and [252]) do *not* provide an answer. This is because the substance commonly known as gasoline does not have a precisely-defined composition. The problems with specifying the composition and toxicity of gasoline are described in [257]–[264]. We propose that, for purposes of establishing a benchmark for comparing the relative toxicities of fuels, toluene be used as the reference substance. This approximation suppresses the complexity presented by gasoline while retaining the essential features of the health threat that it presents. A fuel that is like toluene is also like gasoline: it has some toxicity, but it can nonetheless be safely handled by persons with no special training or protective gear.

We seek to capture in a single number two aspects of concern in assessing the toxic threat posed by fuels: toxicity and volatility. Toxicity *per se* is not so dangerous; a substance with low vapor pressure may be safely handled even if it is a deadly poison. A substance is dangerous when it is both toxic and also volatile. It is this combination that we wish to characterize. We propose to use for this purpose a temperature, the *fume point*. The fume point is analogous to the flash point; it characterizes toxic hazard just as the flash point characterizes fire and explosion hazard. A lower fume point means higher threat, just as with flash point.

Toxicity is specified by a concentration which if exceeded becomes dangerous. The concentration of a fuel in air is closely tied to its volatility, expressed directly by vapor pressure, or indirectly by boiling point and enthalpy of vaporization. Accordingly we seek to combine a concentration in air expressing toxicity with these volatility parameters. The relevant relation is the Clausius–Clapeyron equation:

$$\ln\left(\frac{p_2}{p_1}\right) = T_v\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where $T_v = \bar{h}^0_{\text{vap}}/R$. To understand this equation, imagine a pool of liquid fuel at the bottom of a box containing an inert gas, with which the fuel vapor mixes. Inert gas is a surrogate for air in the thought experiment; it will not condense at temperatures required for low boiling point substances such as hydrogen, methane, and ammonia. The total pressure is maintained at 1 bar, perhaps by a sliding piston closure. The temperature of the box can be set to whatever value we wish. With the temperature low (say, 10 K) all the fuel is liquid (or maybe solid) at the bottom of the box. As the temperature is raised, the fuel evaporates and mixes with the inert gas. At temperature T_1 the partial pressure of fuel is p_1; at T_2 it is p_2. As we raise the temperature, the partial pressure of fuel vapor in equilibrium with the liquid increases. Let T_b be the boiling temperature at standard pressure (BTSP); this is the temperature at which the vapor pressure of the fuel is 1 bar. T_v and T_b together characterize the volatility of a substance.

Let x_f be the molar (or volume) concentration of fuel in the vapor phase at the threshold of toxicity. If specified by IDLH in ppmv, then $x_f = \text{IDLH} \times 10^{-6}$. It is related to pressures by $x_f = p_f/p_s$, where p_s is the total pressure, taken to be the standard pressure of 1 bar. Let T_f be the temperature corresponding to x_f. This is the fume point; it is the temperature at which the vapor in equilibrium with a pool of fuel reaches a concentration designated as the threshold of toxicity. The Clausius–Clapeyron equation can be rewritten:

$$\frac{1}{T_f} = \frac{1}{T_b} + \frac{1}{T_v}\ln\frac{1}{x_f}.$$

Given a threshold toxicity level (e.g., IDLH), the fume point can be calculated from the thermochemical characteristics of the fuel. This has been done in Table 8. Also listed is the *relative fume point*

$$T_{\text{RFP}} = T_f - T_{\text{ref}}.$$

The RFP is appropriate for comparing the toxic threat posed by different fuels. If RFP < 0, there is a threat that will require special precautions such as training and protective gear for fuel-handlers. The more negative is the RFP, the more dangerous is the fuel. If RFP > 0, the threat is less than that posed by gasoline. The more positive the RFP, the safer is the fuel. Referring to Table 8, ammonia presents a significant toxic threat, but methanol is relatively safe, and ethanol is safer still. DME is dangerous; this is because DME is a gas and not a liquid. DME is a simple asphyxiate and thus presents only a suffocation threat; still, that is a threat, and it is captured by the RFP figure of merit. Referring to Table 8, note that hydrogen and methane have the worst RFPs of any fuels, including ammonia. This is because they are high vapor pressure gases. They are simple asphyxiates, hence the risk is of suffocation only; still it is a risk. Note that the RFP of propane is -18 °C, compared to the RFP of ammonia which is -90 °C. These two fuels have similar volatility, so the difference between them is toxicity. Propane is a simple asphyxiate, whereas ammonia is a toxic substance with low IDLH. Note also that toluene, the surrogate for gasoline, has an IDLH not much more than ammonia. The main difference between toluene and ammonia is volatility; the much lower volatility of toluene makes it less of a threat. Methanol is safer than toluene (and gasoline) primarily because it has a much higher IDLH. The RFP figure of merit captures the combined effect of toxicity and volatility in determining the relative threat posed by different fuels.

APPENDIX G
RISKS OF COMPLEXITY, ADVANTAGE OF SIMPLICITY

Not captured by IDLH is risk associated with long-term low-level exposure, notably the risk of cancer. The cancer risk of methanol has recently been assessed by Cruzan [116], who concludes:

> "The data from genotoxicity studies, the inhalation and drinking water oncogenicity studies of methanol in rats and mice, and mode of action considerations support a conclusion that methanol is not likely to be carcinogenic in humans."

By contrast, the cancer risk of gasoline and similar complex fuel blends is well-documented. One of the most dangerous components of gasoline and other complex petroleum-derived fuels is benzene, a potent carcinogen; see [265]–[271], [287]. Deschamps [269] emphasizes that benzene is a genotoxic carcinogen, a substance that reacts directly with DNA [270]. A single such molecule has lethal potential for persons whose DNA happens to be vulnerable to this particular threat. A panel convened by the British government to recommend an air pollution standard for benzene [271] concluded:

> ". . . benzene is a genotoxic carcinogen and therefore no absolutely safe exposure level can be defined. Nevertheless, for practical purposes we believe that a concentration may be proposed at which the risks are exceedingly small. . ."

To achieve an "exceedingly small" risk, an exceedingly small number was settled on: 1 ppb. The NIOSH IDLH value for benzene is 500 ppm, 5 1/2 orders of magnitude greater than the panel's recommendation. IDLH means what it says: *immediately* dangerous. It does not try to quantify the more insidious threats posed by cancers and the like that take years or decades to manifest. Recognizing this threat, current-day gasoline producers attempt to minimize benzene content. Apparently, however, this is difficult or expensive to do: MSDSs for gasoline still list up to 5% benzene as a component. It is likely that atmospheric benzene concentrations exceeding 1 ppb are routine in the neighborhood of gas stations and engines fueled by gasoline. This risk has been deemed acceptable for decades. It will probably be eliminated only when gasoline is replaced by simple renewable fuels such as ammonia and methanol.

What other health risks are associated with gasoline? There is an extensive literature, much of which has to do with the combustion products, exhaust fumes and particulates. A fundamental issue with gasoline toxicity is that the actual content of gasoline remains unknown, for all practical purposes. Fuels derived from petroleum are inherently complex. They are distillation cuts; whatever is separated in a given temperature range is included. This uncertainty about what is contained in fossil fuels is itself a risk factor. By contrast, even blended renewable fuels (nitrofuel and carbofuel) will be well-defined, relatively simple substances. The risks of these well-defined fuels can be determined and appropriately mitigated with confidence. Methanol has health risks, but they are less than those of gasoline, and can be understood and managed more effectively.

APPENDIX H

DIVERS' SOLUTION AND RELATED MIXTURES

The properties of NH_3–NH_4NO_3 mixtures were first reported by Edward Divers in 1873 [71]. Divers' solution (DS) refers to the composition containing the maximum concentration of ammonium nitrate. DS sometimes goes by the name liquid ammoniate of ammonium nitrate [272].

The composition of chemical mixtures can be specified in more than one way. Most fundamentally we specify the components as atoms. DS mixtures are part of the ternary system: H–N–O. Another view uses stable compounds as components. Thus the H–N–O ternary system can be specified as NH_3–HNO_3–NH_4NO_3 [273], [274].

We give the name DS mixtures to the quasi-binary system: $(NH_3)_{1-x}(HNO_3)_x$. The phase diagram of the ammonium-rich side of this system was first systematically studied in [275] and more recently in [276]. Ammonium nitrate ($NH_3 \cdot HNO_3$, usually written NH_4NO_3 to emphasize the actual structure of the adduct) is the 1 : 1 mixture in this quasi-binary system. An adduct is formed when a hydrogen ion is transferred from HNO_3 to NH_3, creating an ionic bond: $(NH_4)^+(NO_3)^-$. Think of HNO_3 as $HONO_2$. Adduct formation occurs when the two molecules adopt a preferred orientation with respect to each other: H_3N–$HONO_2$. The HO bond is then stretched so that the hydrogen ion moves away from its oxygen partner and toward the nitrogen in the ammonia molecule.

Stoichiometric solid ammonium nitrate has $x = 0.5$ and is in equilibrium at STP with a liquid phase of composition $x = 0.42$. Thus, at a temperature slightly greater than 25 °C this composition is a liquid with vapor pressure 1 bar. For comparison, the vapor pressure of pure ammonia is ten times higher. DS mixtures have significantly lower vapor pressure than pure ammonia.

The liquid-phase ammonia-rich mixtures with $0 < x < 0.42$ have lower vapor pressure and improved combustion compared to pure ammonia. The improved combustion comes from the oxygen in the mixture; fuel with its own oxygen doesn't have to get it from the air, so can burn more easily. Oxygenated fuels, however, have lower specific energy since the oxygen content adds to their mass without increasing their energy content. Property trade-offs can be made by varying the composition of the blend to optimize for a given application. For example stationary applications such as steam generators for electric power plants do not place a premium on high specific energy and may prefer a fuel with low vapor pressure for ease of storage. The same might be true for sea and rail transport and perhaps even for road transport. Air transport, however, requires the highest achievable specific energy and will be unlikely to adopt DS mixtures as fuel.

Lower specific energy is one consequence of using an oxygenated fuel; increased explosion hazard is another. Ammonium nitrate is famously a component in various explosive compositions. One of the worst industrial accidents of all time, 1948 Texas City disaster, occurred when a ship loaded with ammonium nitrate exploded. Despite this, pure ammonium nitrate is safe to handle, and is rendered even safer in DS mixtures. A best practices guide published by the European Fertilizer Manufacturer's Association [277] states:

> "Ammonium nitrate is especially difficult to detonate and neither flame, spark nor friction is known to cause detonation. . . . Strongly acidic conditions and the presence of contaminants should be avoided to counter the explosion hazard in ammonium nitrate solutions. Explosions can occur when ammonium nitrate is heated under confinement in pumps. . . . A number of materials have a strong catalytic effect on the thermal decomposition of ammonium nitrate. These include acids, chlorides, organic materials, chromates, dichromates, salts of manganese, copper and nickel and certain metals such as zinc, copper and lead. The decomposition of ammonium nitrate is suppressed or prevented by an alkaline condition. Thus the addition of ammonia offers a major safeguard against the decomposition hazard."

Nevertheless, ammonium nitrate is a component of explosives, therefore its use in fuel blends must be evaluated very carefully. Studies on the explosion hazard of ammonium nitrate were carried out in the 1950s [278] following the Texas City disaster. [279] describes DS mixtures to which powdered metals are added, thus creating an explosive material used to manufacture blasting caps. Contamination increases the explosion risk, as noted in the forgoing quote and also in [280]:

> "The sensitivity to detonation . . . is increased with temperature . . . and contamination. Contamination of material by fuel and/or hydraulic oil is more likely with bulk material, and care must be exercised to avoid this."

Further research is called for to determine under what conditions exactly DS mixtures are safe. A recent review [281] provides a starting point.

Other carbon-free ammonia-based mixtures that, like DS, are liquid under normal conditions can be envisioned. Rocket fuels and explosives are often nitrogen-based. The list in Section XV-A contains some of these substances. Most are too hazardous in pure form to serve as fuels, but might be safe as additives at low enough concentration. Liquid ammoniates [272] and [282]–[285], perhaps using such materials as solutes, are a class of materials that deserve study.

It may be that fuels for air transport must contain some carbon to achieve adequate specific energy. Fuels that contain some carbon, but are much less carbon-intensive than current-day jet fuels, would still be very useful for reducing the carbon footprint of air transport. This might be achievable, for example, with carbon-containing analogs of DS mixtures. For example, ammonium nitrate ($NH_3 \cdot HNO_3$) can be replaced with the analogous carbonate, ammonium hydrogen carbonate (also known as ammonium bicarbonate), $NH_3 \cdot H_2CO_3$. Like ammonium nitrate, this contains too much oxygen to achieve high specific energy. Carbon-containing solutes with less collateral oxygen can be explored to find a mixture suitable for aviation fuel. Ammonium acetate, $NH_3 \cdot HCO_2CH_3$, contains less oxygen and more "fuel" atoms: hydrogen, nitrogen and carbon. It has a higher solubility in anhydrous ammonia than any other salt except for ammonium nitrate. Ammonium acetate is an adduct of ammonia and acetic acid, just as ammonium nitrate is an adduct of ammonia and nitric acid. Ammonia forms adducts of this kind with a great many compounds, all of which might form quasi-binary systems that could be useful as nitrofuel blends. A systematic search for suitable liquid fuel blends based on ammonia with solutes both carbon-free and carbon-containing has not yet been done, and is needed.

NOMENCLATURE

ACGIH	American Council of Governmental and Industrial Hygienists.
AIT	Auto-ignition temperature.
BTSP	Boiling temperature at standard pressure.
BPST	Boiling pressure at standard temperature.
CAES	Compressed air energy storage.
CARB	California Air Resources Board.
CAS RN	Chemical abstract service registry number.
CCHP	Combined cooling heat and power.
CCSS	Carbon capture sequestration and sale.
C/E	Currency/energy equivalent (VMU $\cdot$ J^{-1}).
CFB	Common fuel blend.
CHR	Carbon–hydrogen ratio.
CI	Compression ignition.
C/M	Currency/mass equivalent (VMU $\cdot$ kg^{-1}).
CMU	Constant monetary unit (inflation adjusted).
CND	Canadian dollar; also carbon–nitrogen displacement.
CNG	Compressed natural gas.
CNHC	Carbon–neutral hydrocarbon.
CPI	Consumer price index.
CT	Combustion turbine (same as GT).
C/V	Currency/volume equivalent (VMU $\cdot$ L^{-1}).
DF2	Diesel fuel number 2.
DFX	Dual-Fuel eXchange.
DG	Distributed generation.
DME	Dimethyl ether.
DS	Divers' solution.
DSM	Demand-side management.
EC	Electrolysis cell *or* electricity consuming.
ECC	Electricity-consuming converter, an electrolyzer or fuel generator.
ECE	Electrochemical engine, same as FCC, a fuel cell system.
EFC	Electrochemical fuel converter.
EHS	Environmental and health and safety.
EIA	Energy Information Agency.
EPA	Environmental Protection Agency.
EROI	Energy return in investment.
FC	Fuel cell *or* fuel consuming.
FCC	Fuel-consuming converter, a fuel cell system.
FCI	Fuel carbon intensity.
FO6	Fuel oil number 6.
GECF	Gas exporting countries forum.
GT	Gas turbine (same as CT).
GTL	Gas-to-liquid.
HEV	Hybrid electric vehicle.
HHV	Higher heating value.
HTEC	High-temperature electrochemical conversion.
HVDC	High-voltage direct current.
ICE	Internal combustion engine.
IDLH	Immediately dangerous to life or health.
IFCI	Intrinsic fuel carbon intensity.
INL	Idaho National Laboratory.
LC50	Lethal concentration 50%.
LHV	Lower heating value.
LLNL	Lawrence Livermore National Laboratory.
LNG	Liquefied natural gas.
LPG	Liquefied petroleum gas.
LSO	Local system operator.
MIC	Minimum igniting current.
MIE	Minimum ignition energy.
MSDS	Materials safety data sheet.
MTSP	Melting temperature at standard pressure.
MU	Monetary unit.
NFPA	National Fire Protection Association.
NG	Natural gas.
NIOSH	National Institute for Occupational Safety and Health.
NOx	Nitrogen oxides.
OPEC	Organization of Petroleum Exporting Countries.
OSHA	Occupational Safety and Health Administration.
OTEC	Ocean Thermal Energy Conversion.
PEL	Personal exposure limit.
PEM	Polymer electrolyte membrane.

PHES	Pumped hydroelectric storage.
PNNL	Pacific Northwest National Laboratory.
PRF	Primary reference fuel.
REL	Reference exposure level.
RFC	Regenerative fuel converter, or regenerative fuel cell system.
RFP	Relative fume point.
SCR	Selective catalytic reduction.
SI	Spark ignition.
SMES	Superconducting magnetic energy storage.
SOFC	Solid oxide fuel cell.
STEL	Short-term exposure limit.
STP	Standard temperature and pressure.
TLV	Threshold limit value.
TWA	Time-weighted average.
USD	U.S. dollar.
VMU	Variable monetary unit (currency, no inflation adjustment).

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REFERENCES

[1] L. Green, Jr., "Energy needs versus environmental pollution: A reconciliation?" *Science*, vol. 156, pp. 1448–1450, 1967.

[2] H. J. Bomelberg and D. J. McNaughton, "Ammonia as a fuel," U.S. Department of Energy, DOE/EV-0085, Report X in Liquefied Gaseous Fuels Safety and Environmental Control Assessment Program: Second Status Report, 1980, vol. 3.

[3] U. Bossel, "Does a hydrogen economy make sense?" *Proc. IEEE*, vol. 94, pp. 1826–1837, 2006.

[4] D. Abbott, "Hydrogen without tears: Addressing the global energy crisis via a solar to hydrogen pathway," *Proc. IEEE*, vol. 97, pp. 1931–1934, 2009.

[5] D. Abbott, "Keeping the energy debate clean: How do we supply the world's energy needs?" *Proc. IEEE*, vol. 98, pp. 42–66, 2010.

[6] C. J. Cleveland, R. Costanza, C. A. S. Hall, and R. Kaufmann, "Energy and the U.S. economy: A biophysical perspective," *Science*, vol. 255, pp. 890–897, 1984.

[7] C. J. Cleveland, "Net energy from the extraction of oil and gas in the United States," *Energy*, vol. 30, pp. 769–782, 2005.

[8] K. S. Lackner, P. Grimes, and H.-J. Ziock, "Capturing carbon dioxide from air," *Sourcebook*, vol. 57, no. 9, pp. 6–20, 1999.

[9] C. D. Chang, *Hydrocarbons From Methanol*. New York: Marcel Dekker, 1983.

[10] C. D. Chang and A. J. Silvestri, "MTG—Origin, evolution, operation," *ChemTech*, vol. 10, pp. 624–631, 1987.

[11] T. Mokrani and M. Scurrell, "Gas conversion to liquid fuels and chemicals: The methanol route—Catalysis and processes development," *Catalysis Rev.*, vol. 51, pp. 1–145, 2009.

[12] F. S. Zeman and D. W. Keith, "Carbon neutral hydrocarbons," *Phil. Trans. R. Soc. A*, vol. 366, pp. 3901–3918, 2008.

[13] H. J. Herzog, *Assessing the Feasibility of Capturing* CO_2 *From the Air*. Cambridge, MA: MIT Laboratory for Energy and the Environment, 2003, Publication LFEE 2003-002 WP.

[14] K. S. Lackner, "Guide to CO_2 sequestration," *Science*, vol. 300, pp. 1677–1678, 2003.

[15] R. Baciocchi, G. Storti, and M. Mazzotti, "Process design and energy requirements for the capture of carbon dioxide from air," Chem. Eng. Process., vol. 45, pp. 1047–1058, 2006.

[16] J. K. Stolaroff, "Capturing CO_2 from ambient air," Ph.D. dissertation, Carnegie Mellon Univ., Pittsburgh, PA, 2006.

[17] F. Zeman, "Energy and material balance of CO_2 capture from ambient air," *Environ. Sci. Technol.*, vol. 41, pp. 7558–7563, 2007.

[18] H. J. Herzog, J. Meldon, and A. Hatton, "Advanced post-combustion CO_2 capture," MIT Laboratory for Energy and the Environment, Clean Air Task Force Report, 2009.

[19] K. S. Lackner, "Capture of carbon dioxide from ambient air," *Eur. Phys. J. Special Topics*, vol. 176, pp. 93–106, 2009.

[20] R. A. Pielke, Jr., "An idealized assessment of the economics of air capture," *Environ. Sci. Policy*, vol. 12, pp. 216–225, 2009.

[21] K. Heidel, G. Holmes, A. Singh, and D. Keith, *Process Design and Costing of an Air-Contactor for Air-Capture*. Calgary, AB, Canada: Carbon Engineering Ltd., 2010.

[22] D. W. Keith, K. Heidel, and R. Cherry, "Geo-Engineering Climate Change: Environmental Necessity or Pandora's Box?" in *Capturing* CO_2 *From the Atmosphere: Rationale and Process Design Considerations*, B. Launder and J. M. T. Thompson, Eds. New York: Cambridge Univ. Press, 2010.

[23] M. Ranjan, "Feasibility of air capture," M.S. thesis, MIT, Cambridge, MA, 2010.

[24] M. Ranjan and H. J. Herzog, "Feasibility of air capture," *Energy Procedia*, vol. 4, pp. 2869–2876, 2011.

[25] R. Socolow, M. Desmond, R. Aines, J. Blackstock, O. Bolland, T. Kaarsberg, N. Lewis, M. Mazzotti, A. Pfeffer, K. Sawyer, J. Siirola, B. Smit, and J. Wilcox, "Direct air capture of CO_2 with chemicals," in *A Technology Assessment for the APS Panel on Public Affairs*. New York: APS.

[26] S.-J. Han, M. Yoo, D.-W. Kim, and J.-H. Wee, "Carbon dioxide capture using calcium hydroxide aqueous solution as the absorbent," *Energy Fuels*, vol. 25, pp. 3825–3834, 2011.

[27] T. Wang, K. S. Lackner, and A. Wright, "Moisture swing sorbent for carbon dioxide capture from ambient air," *Environ. Sci. Technol.*, vol. 45, pp. 6670–6675, 2011.

[28] Global Thermostat, Kilimanjaro Energy, Carbon Engineering Ltd., and Air Fuel Synthesis. [Online]. Available: globalthermostat.com; www.kilimanjaroenergy.com; www.carboengineering.com; www.airfuelsynthesis.com

[29] G. Astarita, D. W. Savage, and A. Bisio, *Gas Treating With Chemical Solvents*. New York: Wiley, 1983.

[30] C. J. King, *Separation and Purification: Critical Needs and Opportunities*. Washington, DC: National Academy Press, 1987.

[31] T. M. Duncan and J. A. Reimer, *Chemical Engineering Design and Analysis: An Introduction*. New York: Cambridge Univ. Press, 2001.

[32] R. D. Noble and P. A. Terry, *Principles of Chemical Separations With Environmental Applications*. New York: Cambridge Univ. Press, 2004.

[33] B. R. Bakshi, T. Gutowski, and D. Sekulic, *Thermodynamics and the Destruction of Resources*. New York: Cambridge Univ. Press, 2011, (see especially Chapter 4, "Material separation and recycling").

[34] J. M. Ogden, "Prospects for building a hydrogen energy infrastructure," *Annu. Rev. Energy Environ.*, vol. 24, pp. 227–79, 1999.

[35] J. O'M. Bockris, "Would methanol formed from CO_2 from the atmosphere give the advantage of hydrogen at lesser cost?" *Int. J. Hydrogen Energy*, vol. 35, pp. 5165–5172, 2010.

[36] H. Wendt, *Electrochemical Hydrogen Technologies, Electrochemical Production and Combustion of Hydrogen*. New York: Elsevier, 1990.

[37] S. C. Singhal and K. Kendall, *High Temperature Solid Oxide Fuel Cells*. New York: Elsevier, 2003.

[38] B. Yu and J. Xu, *High Temperature Electrolysis in Large-Scale Hydrogen Production*. Hauppauge, NY: Nova Science, 2010.

[39] I. Garagounis, V. Kyriakou, C. Anognostou, V. Bourganis, I. Papachristou, and M. Stoukides, "Solid electrolytes: Applications in heterogeneous catalysis and chemical cogeneration," *Ind. Eng. Chem. Res.*, vol. 50, pp. 431–472, 2011.

[40] H. Schmalzried, *Chemical Kinetics of Solids*. New York: Wiley-VCH, 1995.

[41] J. Maier, *Physical Chemistry of Ionic Materials*. New York: Wiley, 2004.

[42] V. V. Kharton, *Handbook of Solid State Electrochemistry*. New York: Wiley-VCH, 2009.

[43] R. A. Huggins, *Advanced Batteries—Materials Science Aspects*. New York: Springer-Verlag, 2009.

[44] R. A. Huggins, *Energy Storage*. New York: Springer-Verlag, 2010.

[45] R. D. Farr and C. G. Vayenas, "Ammonia high temperature solid electrolyte fuel cell," *J. Electrochem. Soc.*, vol. 127, pp. 1478–1483, 1980.

[46] G. Marnellos and M. Stoukides, "Ammonia synthesis at atmospheric pressure," *Science*, vol. 282, pp. 98–100, 1998.

[47] A. Wojcik, H. Middleton, I. Damopoulos, and J. Van Herle, "Ammonia as a fuel in solid oxide fuel cells," *J. Power Sources*, vol. 118, pp. 342–348, 2003.

[48] R.-Q. Liu, Y.-H. Xie, Z.-J. Li, J.-D. Wang, and Y.-G. Sun, "Application of proton conductors (CeLa) CaO_2 in synthesis of ammonia," *Acta Phys.-Chim. Sin.*, vol. 21, pp. 967–970, 2005.

[49] J. J. Vajo, "Ammonia fuel cell," U.S. Patent 7 157 166, Jan.2, 2007.

[50] N. Sammes, G. Restuccia, and J. C. Ganley, "Ammonia synthesis in a modified IT SOFC system," presented at the Ammonia Fuel Conf., Minneapolis, MN, Sep. 29–30, 2008.

[51] J. C. Ganley, "Concept model: A regenerative ammonia fuel cell system," presented at the Ammonia Fuel Conf., Kansas City, MO, Oct. 12–13, 2009.

[52] A. Skodra and M. Stoukides, "Electrocatalytic synthesis of ammonia from steam and nitrogen at atmospheric pressure," *Solid State Ionics*, vol. 180, pp. 1332–1336, 2009.

[53] M. Ni, M. K. H. Leung, and D. Y. C. Leung, "Ammonia-fed solid oxide fuel cells for power generation—A review," *Int. J. Energy Res.*, vol. 33, pp. 943–959, 2009.

[54] J. H. Holbrook and J. C. Ganley, "Method and apparatus for anhydrous ammonia production," U.S. Patent 7 811 442, Oct. 12, 2010.

[55] W. B. Wang, X. B. Cao, W. J. Gao, F. Zhang, H. T. Wang, and G. L. Ma, "Ammonia synthesis at atmospheric pressure using a reactor with thin solid electrolyte $BaCe_{0.85}Y_{0.15}O_{3-\alpha}$ membrane," *J. Membrane Sci.*, vol. 360, pp. 397–403, 2010.

[56] E. Chamberlin, "Developing artificial photosynthesis," Lawrence Berkeley National Laboratory, Helios Solar Energy Research Center, Berkeley, CA, 2009.

[57] Better Place Company. [Online]. Available: www.betterplace.com

[58] C. Botsford and A. Szczepanek, "Fast charging vs. slow charging—Pros and cons for the new age of electric vehicles," presented at the Int. Battery, Hybrid and Fuel Cell Electr. Veh. Symp., Stavanger, Norway, May 13–16, 2009.

[59] R. Zevenhoven, S. Eloneva, and S. Teir, "Chemical fixation of CO_2 in carbonates: Routes to valuable products and long-term storage," *Catalysis Today*, vol. 115, pp. 73–79, 2006.

[60] M. Mikkelsen, M. Jørgensen, and F. C. Krebs, "The teraton challenge: A review of fixation and transformation of carbon dioxide," *Energy Environ. Sci.*, vol. 3, pp. 43–81, 2010.

[61] S. C. Page, A. G. Williamson, and I. G. Mason, "Carbon capture and storage: Fundamental thermodynamics and current technology," *Energy Policy*, vol. 37, pp. 3314–3324, 2009.

[62] K. S. Lackner, "Carbon dioxide disposal in carbonate materials," *Energy*, vol. 20, pp. 1153–1170, 1995.

[63] Calera Corporation. [Online]. Available: calera.com

[64] R. W. Ashcraft and W. H. Green, "Thermochemical properties and group values for nitrogen-containing molecules," *J. Phys. Chem. A*, vol. 112, pp. 9144–9152, 2008.

[65] C. H. Christensen, T. Johannessen, R. Z. Sørensen, and J. K. Nørskov, "Towards an ammonia-mediated hydrogen economy?" *Cat. Today*, vol. 111, pp. 140–144, 2006.

[66] F. H. Stephens, V. Pons, and R. T. Baker, "Ammonia-borane: The hydrogen source par excellence?" *Dalton Trans.*, pp. 2613–2626, 2007.

[67] J. A. Van Vechten, "Hydrogen fueling via guanidine," presented at the APS Meeting, Denver, CO, Mar. 5–9, 2007. [Online]. Available: http://meetings.aps.org/link/BAPS.2007.MAR.S39.10

[68] A. Makovky and L. Lenji, "Nitromethane—Physical properties, thermodynamics, kinetics of decomposition, and utilization as fuel," *Chem. Rev.*, vol. 58, pp. 627–644, 1958.

[69] E. Boyer and K. K. Kuo, "Characteristics of nitromethane for propulsion applications," presented at the 44th AIAA Aerosp. Sci. Meeting Exhibit, 2006, Paper AIAA 2006-361.

[70] E. Boyer and K. K. Kuo, "Modeling of nitromethane flame structure and burning behavior," *Proc. Combust. Inst.*, vol. 31, pp. 2045–2053, 2007.

[71] E. Divers, "On the union of ammonium nitrate with ammonia," *Phil. Trans. Roy. Soc. Lond.*, vol. 163, pp. 359–376, 1873.

[72] C. O. Davis, "Ammonium nitrate in liquid ammonia as fuel," *Sci. Newslett.*, vol. 49, no. 6, p. 93, 1946.

[73] C. O. Davis, "Operation of internal combustion engines," U.S. Patent 2 393 594, 1946.

[74] M. Farber and A. J. Darnell, "Spectroscopic examination of the NH_3-HNO_3 and NH_3-NO_3 diffusion flames," *J. Chem. Phys.*, vol. 22, p. 1261, 1954.

[75] J. C. Ganley and M. S. Bowery, "Engine-ready carbon-free ammonia fuel," *Ammonia Fuel Conf.*, 2010.

[76] S. Kudo and T. Toriumi, "Total pressure for binary systems of liquid ammonia-alcohol. I. Liquid NH_3-CH_3OH systems and liquid $NH_3-C_2H_5OH$ systems," *Bull. Chem. Res. Inst. Non-Aqueous Solutions*, vol. 8, pp. 27–33, 1959.

[77] D. Schäfer, J. Xia, M. Vogt, A. Kamps, and G. Maurer, "Experimental investigation of the solubility of ammonia in methanol," *J. Chem. Eng. Data*, vol. 52, pp. 1653–1659, 2007.

[78] G. Claude and A. Hess, "Sur un nouveau mode d'enmagasinement de l'actélyène," *Comp. Rend.*, vol. 124, pp. 626–628, 1897.

[79] G. Claude, "Un nouveau succédané de l'essence, l'ammoniaque acétylénée," *Comp. Rend.*, vol. 212, pp. 585–588, 1941.

[80] J. L. M. Fréjacques, "L'ammoniac acétyléné," *Chimie Industrie*, vol. 46, pp. 579–589, 1941.

[81] A. Kufferath, "Die Lösung von Acetylen in Ammoniak als Austausch-Kraftstoff für Benzin," *Oel und Kohle*, vol. 11, pp. 275–278, 1942.

[82] J. L. M. Fréjacques, "Fuel for motor vehicles," U.S. Patent 2 357 184, 1944.

[83] A. Vetere, A. Cojutti, and M. A. Scaramucci, "Vapor-liquid equilibria of the acetylene-ammonia system," *Chem. Eng. Sci.*, vol. 30, pp. 301–315, 1975.

[84] H. Lippold and R. Heide, "Dimethylether als Kältemittelkomponente," *KI Luft—Und Kältetechnik*, vol. 33, pp. 202–205, 1997.

[85] H. Lippold, "Wärmeübergangs-koeffizienten bei der Verdampfung von NH_3 und NH_3-Dimethylether-Gemisch," *KI Luft—Und Kältetechnik*, vol. 37, pp. 78–82, 2001.

[86] D. Krauss and J. Schenk, "Ammonia/dimethyl ether (R723) as a new refrigerant blend," in *Proc. IIR Conf., Ammonia Refrigerating Syst. Renewal Improvement*, 2005.

[87] E. J. Drouilly, "Fuel mixture for internal-combustion engines," U.S. Patent 2 559 605, 1951.

[88] S.-C. Kong, "Performance of a compression-ignition engine using direct injection of liquid ammonia/DME mixture," in *Proc. Ammonia Fuel Conf.*, 2011.

[89] F. Hasegawa, S. Yokoyama, and K. Imou, "Methanol or ethanol produced from woody biomass: Which is more advantageous?" *Bioresource Technol.*, vol. 101, pp. S109–S111, 2010.

[90] *Chemical Emergency Preparedness and Prevention Advisory—Ammonia*, U.S. Environmental Protection Agency, U.S. EPA Chemical Emergency Preparedness and Prevention Office Report Number OSWER 91-008.2, Jun. 1990.

[91] P. A. Froehlich, "A guide for developing a training program for anhydrous ammonia workers," U.S. Department of Health, Education, and Welfare, National Institute for Occupational Safety and Health, Publication Number 79-119, Dec. 1978.

[92] *Steam—Its Generation and Use*, 41st ed. Charlotte, NC: The Babcock & Wilcox Company, 2005.

[93] Ammonia Fuel Association. [Online]. Available: http://www.nh3fuelassociation.org/

[94] Gillespie Stack Grannel L.L.C. (GSG). [Online]. Available: www.gillespiellc.com

[95] G. G. Leeth, "Energy transmission systems," *Int. J. Hydrogen Energy*, vol. 1, pp. 49–53, 1976.

[96] W. L. Ahlgren, "Pipe flow—A tutorial for electrical engineers," California Polytechnic State University Digital Repository. [Online]. Available: http://digitalcommons.calpoly.edu/eeng_fac/297

[97] W. L. Ahlgren, "Fuel power density," *J. Pressure Vessel Technol.*, 134:000000, 2012.

[98] *Methanol Innovation: Technical Details of the 1989 Methanol Marathon*. Washington, DC: SAE Publication SP-804, 1990.

[99] S. Unnasch, "Development and demonstration of a bus retrofit kit for methanol-ignition improver fuel," California Energy Commission Rep. P500-92-016, 1992.

[100] S. Grannell, "The operating features of a stoichiometric, ammonia and gasoline dual fueled spark ignition engine," Thesis, Univ. Michigan, Ann Arbor, MI, 2008.

[101] U.S. Department of Energy, "Vehicle and fuel distribution requirements," Assessment of costs and benefits of flexible and alternative fuel use in the U.S. Transportation Sector, Rep. DOE/PE-0095P, 1990.

[102] B. Doss, D. Tate, and S. Klughers, "Methanol fueling system: Installation and maintenance manual," California Energy Commission, P500-96-002, 1996.

[103] A. C. Argentine, "ABCs of AFVs—A guide to alternative fuel vehicles," California Energy Commission, Rep. P500-99-013.

[104] *Methanol Refueling Station Costs*. Alexandria, VA: American Methanol Foundation, 1999.

[105] K. H. Kozole and J. S. Wallace, "The use of dimethyl ether as a starting aid for methanol-fueled SI engines at low temperatures," *SAE Trans.*, vol. 97, 1988, Paper 881677.

[106] M. E. Karpuk, J. D. Wright, J. L. Dippo, and D. E. Jantzen, "Dimethyl ether as an ignition enhancer for methanol-fueled diesel engines," SAE Publication SP-889, Paper 912420, 1991.

[107] N. Bhana and D. Cipolat, "Optimization of the performance of a methanol/dimethyl ether fuelled compression ignition engine," *SAE Trans.*, vol. 115, 2006, Paper 2006-01-1986.

[108] Y. Yan, Y. S. Zhang, Y. T. Chen, Z. D. Chen, and G. Xiao, "Study on HCCI combustion and emission characteristics of diesel engine fueled with methanol-DME," SAE Publication SP-2280, Paper 2010-01-0578, 2010.

[109] C. Liang, C. Ji, and X. Liu, "Combustion and emissions performance of a DME-enriched spark-ignited methanol engine at idle condition," *Appl. Energy*, vol. 88, pp. 3704–3711, 2011.

[110] E. Chang, J. C. G. Calado, and W. B. Streett, "Vapor-liquid equilibrium in the system dimethyl ether/methanol from 0 to 180 °C and at pressures to 6.7 MPa," *J. Chem. Eng. Data*, vol. 27, pp. 293–298, 1982.

[111] L. Caprino and G. Togna, "Potential health effects of gasoline and its constituents: A review of current literature (1990–1997) on toxicological data," *Environ. Health Perspect.*, vol. 106, pp. 115–125, 1998.

[112] E. Reese and R. D. Kimbrough, "Acute toxicity of gasoline and some additives," *Environ. Health Perspect. Suppl.*, vol. 101, pp. 115–131, 1993.

[113] T. M. Burbacher, "Neurotoxic effects of gasoline and gasoline constituents," *Environ. Health Perspect.*, vol. 101, pp. 133–141, 1993.

[114] G. K. Raabe, "Review of the carcinogenic potential of gasoline," *Environ. Health Perspect.*, vol. 101, pp. 35–38, 1993.

[115] M. G. Costantini, "Health effects of oxygenated fuels," *Environ. Health Perspect.*, vol. 101, pp. 151–160, 1993.

[116] G. Cruzan, "Assessment of the cancer potential of methanol," *Crit. Rev. Toxicol.*, vol. 39, no. 4, pp. 347–363, 2009.

[117] J. D. Pritchard, "Methanol," U.K. Health Protection Agency, HPA Compendium of Chemical Hazards, 2011.

[118] S. Barone, A. Davis, J. Gift, A. Iannucci, and P. Schlosser, "IRIS toxicological review of methanol," U.S. Environmental Protection Agency, Rep. EPA/635/R-09/013 (2009) and EPA/635/R-11/001A, 2011.

[119] T. B. Starr and J. L. Festa, "A proposed inhalation reference concentration for methanol," *Regul. Toxicol. Pharmacol.*, vol. 38, pp. 224–231, 2003.

[120] B. L. Carson, J. L. McCann, J. V. Ells, B. L. Herndon, and L. H. Baker, "Methanol Health Effects," U.S. Environmental Protection Agency, NTIS Accession PB82-160797, 1981.

[121] *Automotive Methanol Vapors and Human Health: An Evaluation of Existing Scientific Information and Issues for Future Research*. Cambridge, MA: Health Effects Institute, May 1987.

[122] R. Kavet and K. Nauss, "The toxicity of inhaled methanol vapors," *Crit. Rev. Toxicol.*, vol. 21, pp. 21–50, 1990.

[123] *Analysis of the Economic and Environmental Effects of Methanol as an Automotive Fuel*, U.S. Environmental Protection Agency Rep., 1989.

[124] *Environmental, Health, and Safety Concerns*, U.S. Department of Energy, Rep. DOE/PE-0100P, 1991, Assessment of Costs and Benefits of Flexible and Alternative Fuel Use in the U.S. Transportation Sector, Technical Report Seven.

[125] *Methanol Fuels and Fire Safety*, U.S. Environmental Protection Agency, Rep. EPA 400-F-92-010, 1994, Fact Sheet OMS-8.

[126] *NFPA Fire Protection Guide to Hazardous Materials*, 13th ed. Quincy, MA: National Fire Protection Association, 2002.

[127] Ammonia, National Research Council Subcommittee on Ammonia, 1977, Report to the U.S. Environmental Protection Agency, NTIS Accession Number PB-278 182.

[128] D. J. McNaughton and D. L. Brenchley, "Ammonia: An introductory assessment of safety and environmental control information," U.S. Department of Energy, Report W in Liquefied Gaseous Fuels Safety and Environmental Control Assessment Program: Second Status Report, Volume 3, DOE/EV-0085, 1980.

[129] M. P. Russelle, J. F. S. Lamb, B. R. Montgomery, D. W. Elsenheimer, B. S. Miller, and C. P. Vance, "Alfalfa rapidly remediates excess inorganic nitrogen at a fertilizer spill site," *J. Environ. Quality*, vol. 30, pp. 30–36, 2001.

[130] W. Nernst, "Über die bildung von Stickoxyd bei hohen Temperaturen," *Zeitschrift für anorganische und allgemeine Chemie*, vol. 49, pp. 213–228, 1906.

[131] W. K. Lyon, "Method for the reduction of the concentration of NO in combustion effluents using ammonia," U.S. Patent 3 900 554, 1975.

[132] R. K. Lyon, "The NH_3-NO-O_2 reaction," *Int. J. Chem. Kin.*, vol. 8, pp. 315–318, 1976.

[133] R. K. Lyon and J. E. Hardy, "Discovery and development of the thermal DeNOx process," *Ind. Eng. Chem. Fundam.*, vol. 25, pp. 19–24, 1986.

[134] W. K. Lyon, "Thermal DeNOx: Controlling nitrogen oxides emissions by a noncatalytic process," *Env. Sci. Tech.*, vol. 21, pp. 231–236, 1987.

[135] I. S. Zaslonko, A. M. Tereza, O. N. Kulish, and D. Yu. Zheldakov, "Kinetic aspects of the lowering of the level of nitrogen oxide in combustion products using admixtures of ammonia (De-NOx) (A review)," *Chem. Phys.*, vol. 11, pp. 2120–2153, 1994.

[136] M. Kanao, "Fuel composition," U.S. Patent 4 166 724, 1979.

[137] J. H. Lee, J. H. Kim, J. H. Park, and O. C. Kwon, "Studies on properties of laminar premixed hydrogen-added ammonia-air flames for hydrogen production," *Int. J. Hydrogen Energy*, vol. 35, pp. 1054–1064, 2010.

[138] J. H. Lee, S. I. Lee, and O. C. Kwon, "Effects of ammonia substitution on hydrogen-air flame propagation and emissions," *Int. J. Hydrogen Energy*, vol. 35, pp. 11 332–11 341, 2010.

[139] S. Lee and O. C. Kwon, "Effects of ammonia substitution on extinction limits and structure of counter-flow non-premixed hydrogen-air flames," *Int. J. Hydrogen Energy*, vol. 36, pp. 10 117–10 128, 2011.

[140] I. Glassman and R. A. Yetter, *Combustion*, 4th ed. New York: Academic, 2008.

[141] J. Withers, W. ten Berge, J. Gordon, C. Harris, I. Hymes, and J. Jolley, *Ammonia Toxicity Monograph*. London, U.K.: The Institution of Chemical Engineers, 1988.

[142] N. J. Duijm, F. Markert, and J. L. Paulsen, *Safety Assessment of Ammonia as a Transport Fuel*, Risø National Laboratory, Denmark, Risø-R-1504(EN)," 2005.

[143] N. Roney, F. Llados, S. S. Little, and D. B. Knaebel, *Toxicological Profile for Ammonia*, U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, 2004.

[144] *Comparative Quantitative Risk Analysis of Motor Gasoline, LPG, and Anhydrous Ammonia as an Automotive Fuel*, Quest Consultants, Iowa Energy Center, 2009.

[145] W. L. Buckley and H. W. Husa, "Combustion properties of ammonia," *Chem. Eng. Prog.*, vol. 58, pp. 81–84, 1962.

[146] J. M. Kuchta, "Investigation of fire and explosion accidents in the chemical, mining, and fuel-related industries—A manual," in *U.S. Bureau of Mines Bulletin*, vol. 680, 1985.

[147] L. G. Britton, "Using material data in static hazard assessment," *Plant/Oper. Progr.*, vol. 11, no. 2, pp. 56–70, 1992.

[148] D. L. Fenton and K. S. Chapman, "Combustion of Ammonia With and Without Oil Vapor," Kansas State University, Final Report for Research Project 682-TRP, 1995.

[149] D. L. Fenton, A. S. Khan, R. D. Kelley, and K. S. Chapman, "Combustion characteristics review of ammonia-air mixtures," *ASHRAE Trans.*, vol. 101, no. 2, pp. 476–485, 1995.

[150] S. Kondo, A. Takahashi, K. Tokuhashi, and A. Sekiya, "RF number as a new index for assessing combustion hazard of flammable gases," *J. Hazardous Mater.*, vol. A93, pp. 259–267, 2002.

[151] R. Scott, *Standard Ship Designs—Bulk Carriers and Tankers*. Surrey, U.K.: Fairplay Publications, 1985.

[152] C. Zamfirescu and I. Dincer, "Ammonia as a green fuel and hydrogen source for vehicular applications," *Fuel Processing Technology*, vol. 90, pp. 729–737, 2009.

[153] Lawrence Livermore National Laboratory, *Energy Flow Diagrams*. [Online]. Available: publicaffairs.llnl.gov/news/energy

[154] U.S. Energy Information Agency, *Annual Energy Reviews*. [Online]. Available: www.eia.doe.gov/emeu/aer

[155] U.S. Energy Information Agency, *Annual Energy Outlook Supplement*. [Online]. Available: www.eia.doe.gov/oiaf/aeo/supplement

[156] M. Appl, *Ammonia, Principles and Industrial Practice*, Wiley-VCH, 1999.

[157] G. Maxwell, *Synthetic Nitrogen Products—A Practical Guide to the Products and Processes*. New York: Kluwer Academic Publishers, 2004.

[158] I. Dincer and C. Zamfirescu, *Sustainable Energy Systems and Applications*. New York: Springer, 2011.

[159] H. J. Bomelberg, "Use of ammonia in energy-related applications," *Plant/Oper. Progr.*, vol. 1, pp. 175–180, 1982.

[160] DTIC, Search "ammonia fuel" to retrieve 45 reports. [Online]. Available: http://www.dtic.mil

[161] The Society of Automotive Engineers (SAE) Digital Library, Search "ammonia fuel" to retrieve 45 reports. [Online]. Available: http://store.sae.org

[162] J. A. Bartels and M. B. Pate, *A Feasibility Study of Implementing an Ammonia Economy,* Iowa Energy Center, 2008.

[163] Iowa Energy Center. [Online]. Available: www.energy.iastate.edu/renewable/ammonia

[164] S. Baron and M. Steinberg, "The economics of production of liquid fuel and fertilizer by the fixation of atmospheric carbon and nitrogen using nuclear power," in *Proc. 10th Intersoc. Energy Eng. Conf.*, 1976, vol. 1975, pp. 842–848, IEEE.

[165] M. Dubey, "Technical and economic feasibility of making fertilizer from wind energy, water, and air," in *Sun, Mankind's Future Source of Energy, Proc. Int. Solar Energy Soc. Congr.*, 1978, vol. 3, pp. 1812–1821.

[166] D. Richards and R. W. Henderson, "OTEC produced ammonia—An alternative fuel," in *Proc. 8th Ocean Energy Conf.*, 1981, pp. 665–673.

[167] H. Silla, "Possible Future Marine Fuels," National Maritime Research Center, Rep. NMRC-KP-164, 1977.

[168] G. L. Dugger, R. W. Henderson, E. J. Francis, and W. H. Avery, "Projected costs for electricity and products from OTEC facilities and plantships," *J. Energy*, vol. 5, pp. 231–236, 1981.

[169] W. H. Avery, D. Richards, and G. L. Dugger, "Hydrogen generation by OTEC electrolysis, and economical energy transfer to world markets via ammonia and methanol," *Int. J. Hydrogen Energy*, vol. 10, pp. 727–736, 1985.

[170] L. Green, Jr., "Ammonia energy vector for the hydrogen economy," *Int. J. Hydrogen Energy*, vol. 7, pp. 355–359, 1982.

[171] J. J. MacKenzie and W. H. Avery, "Ammonia fuel: The key to hydrogen-based transportation," in *Proc. 31st Intersoc. Energy Conv. Eng. Conf.*, 1996, vol. 3, pp. 1761–1766.

[172] A. R. Miller, "Ammonia fuel-cell vehicles," in *Proc. World Car Conf. '96*, 1996, pp. 491–501.

[173] R. B. Steele, "A proposal for an ammonia economy," *CHEMTECH*, vol. 29, no. 8, pp. 28–34, 1999.

[174] T. Saika, M. Nakamura, T. Nohara, and S. Ishimatsu, "Study of hydrogen supply with ammonia fuel," *JSME Int. J. B*, vol. 49, pp. 78–83, 2006.

[175] G. Thomas and G. Parks, *Potential Roles of Ammonia in a Hydrogen Economy, A Study of Issues Related to the Use of Ammonia for On-Board Vehicular Hydrogen Storage,* U.S. Department of Energy, 2006.

[176] P. J. Feibelman and R. Stumpf, *Comments on "Potential Roles of Ammonia in a Hydrogen Economy"*, Sandia National Laboratories, 2006.

[177] T. Lipman and N. Shah, "Ammonia as an Alternative Energy Storage Medium for Hydrogen Fuel Cells: Scientific and Technical Review for Near-Term Stationary Power Demonstration Projects, Final Report," University of California at Berkeley, Institute for Transportation Studies, 2007.

[178] J. Holbrook, "The (green) ammonia energy cycle," in *Proc. 5th Int. Energy Conv. Eng. Conf. (IECEC)*, 2007.

[179] A. Mozafari-Varnusfadrani, "Predictions and Measurements of Spark-Ignition Engine Characteristics Using Ammonia and Other Fuels," M.S. Thesis, Queen Mary College, The University of London, London, U.K., 1988.

[180] C. Zamfirescu and I. Dincer, "Using ammonia as a sustainable fuel," *J. Power Sources*, vol. 185, pp. 459–465, 2008.

[181] C. B. Panchal, P. P. Pandolfini, and W. H. Kumm, "Ocean Thermal Plantships for Production of Ammonia as the Hydrogen Carrier," Argonne National Laboratory, Argonne, IL, Rep. ANL/ESD/09-6, 2009.

[182] H. Vrijenhoef, "Ammonia, fuel for the future," *3rd International Seminar of Torres Vedras,* 2010.

[183] A. Klerke, C. H. Christensen, J. K. Nørskov, and T. Vegge, "Ammonia for hydrogen storage: Challenges and opportunities," *J. Mater. Chem.*, vol. 18, pp. 2304–2310, 2008.

[184] C. Duynslaegher, H. Jeanmart, and J. Vandooren, "Use of ammonia as a fuel for SI engine," in *Proc. Eur. Combustion Meeting*, 2009.

[185] A. J. Reiter and S.-C. Kong, "Combustion and emissions characteristics of compression-ignition engine using dual ammonia-diesel fuel," *Fuel*, vol. 90, pp. 87–97, 2011.

[186] C. S. Mørch, A. Bjerre, M. P. Gøttrup, S. C. Sorenson, and J. Schramm, "Ammonia/hydrogen mixtures in an SI-engine: Engine performance and analysis of a proposed fuel system," *Fuel*, vol. 90, pp. 854–864, 2011.

[187] V. Agosta, "Use of ammonia-fossil fuel emulsions in a diesel engine," *Proc. Ammonia Fuel Conf.,* 2008.

[188] W. H. Stillwell, "X-15 Research Results With a Selected Bibliography," NASA Report Number SP-60, 1965.

[189] D. R. Jenkins, "X-15: Extending the Frontiers of Flight," NASA Rep. SP-2007-9-001-HQ, 2007.

[190] W. P. Munger and R. W. Seaman, "XLR99-RM-1 Rocket Engine for the X-15," NACA Report Number H87-28722, 1956, pp. 215–235, Research Airplane Committee Rep.

[191] B. O. Wagner, "X-15 Airplane Engine Installation," NACA Rep. H87-28722, 1956, pp. 225–235, Research Airplane Committee Report.

[192] R. W. Seaman, "XLR99-RM-1 engine for the X-15 airplane," in *Proc. 1958 Res.-Airplane-Committee Rep. Conf. Progr. X-15 Proj.*, 1958, pp. 275–283, NACA Report.

[193] J. W. Gibb, "X-15 propellant system description," in *Proc. 1958 Res.-Airplane-Committee Rep. Conf. Progr. X-15 Proj.*, 1958, pp. 285–292, NACA Report.

[194] R. W. Seaman and D. S. Smith, "Flight rating test demonstration of the XLR-99-RM-1 rocket engine," in *Amer. Rocket Soc. (ARS),* Paper 1409-60, 1960.

[195] H. A. Barton and G. R. Cramer, "Rocket engines for manned vehicles," *Missile Des. Develop.*, vol. 46, no. 58, p. 14, Nov. 1960.

[196] R. G. Leiby, D. R. Bellman, and N. E. DeMar, "XLR99 Engine Operating Experience," 1961 Research Airplane Committee Report, NASA Rep. N71-75460, 1961, pp. 215–226.

[197] L. N. Hjelm and B. R. Bornhorst, "Development of improved ceramic coatings to increase the life of the XLR99 Thrust Chamber," 1961 Research Airplane Committee Report, NASA Report Number N71-75460, 1961, pp. 227–253.

[198] M. J. Luperi and S. J. Tick, "Vibration and combustion investigation of the LR-99 engine," in *Proc. ARS Propell., Combust., and Liquid Rockets Conf.*, 1961, American Rocket Society (ARS) Paper Number 1720-61.

[199] H. Davies, "The design and development of the Thiokol XLR-99 rocket engine for the X-15 aircraft," *J. Royal Aeronaut. Soc.*, vol. 67, no. 626, pp. 79–91, 1963.

[200] F. H. Winter and P. Cosyn, "The XLR-99 pioneer rocket engine—Powering the X-15 rocket plane into air and space in the 1950s–60s," presented at the 60th International Astronautical Congress, 2009, Paper 5046.

[201] R. L. Wiswell, P. Olekszyk, and J. W. Gibb, "X-15 Propulsion Subsystem Component Development," 1961 Research Airplane Committee Report, NASA Rep. N71-75460, 1961, pp. 265–276.

[202] R. Wiswell, *X-15 Propulsion System,* AIAA Paper 97-2682, 1987.

[203] N. C. Kailos, "Utilization of Ammonia as an Alternate Fuel in Army Aircraft Engines," U.S. Army Aviation Materiel Laboratories Technical Report 66-52, 1966, DTIC Accession AD-0638360.

[204] M. M. Johnson and R. M. Schirmer, "Jet engine combustion process," U.S. Patent 3 049 872, 1962.

[205] D. L. Armstrong and W. P. Knight, "Method of producing thrust for propulsion by combusting a reaction product of $LiBH_4$ and NH_3 with an oxidant," U.S. Patent 3 198 431, 1963.

[206] Peerless Mfg. Company. [Online]. Available: bmrthermal.com/peerless_boilers

[207] H. Brandhorst, Jr., M. Baltazar-Lopez, B. Tatarchuk, D. R. Cahela, and T. Barron, "Ammonia—It's transformation and effective utilization," presented at the 6th International Energy Conversion Engineering Conference (IECEC), 2008, Paper AIAA 2008-5610.

[208] T. R. Meyer, "Ammonia combustion with near-zero pollutant emissions," Iowa Energy Center 20th Anniversary Celebration, 2010.

[209] T. R. Meyer, "Combustion of ammonia for reduced CO_2 in heating and power generation systems," presented at the Ammonia Fuel Conf., Kansas City, MO, Oct. 12–13, 2009.

[210] T. R. Meyer, "Ammonia combustion with near-zero pollutant emissions," presented at the Ammonia Fuel Conf., Portland, OR, Sep. 18–21, 2011.

[211] *Production of Nitric Acid,* Best Available Techniques Booklet 2, Published 2000 by the European Fertilizer Manufacturer's Association, Brussels, Belgium

[212] A. P. Oele, "Technological aspects of the catalytic combustion of ammonia with platinum gauze elements," *Chem. Eng. Sci.*, vol. 8, pp. 146–157, 1958.

[213] T. Shimizu, O. Imai, Y. Sakakibara, and T. Ohrui, "Models for the catalytic oxidation of ammonia over a platinum gauze pad," *Int. Chem. Eng.*, vol. 22, pp. 329–337, 1982.

[214] T. Shimizu, O. Imai, Y. Sakakibara, and T. Ohrui, "Stability of ammonia burners," *Int. Chem. Eng.*, vol. 23, pp. 486–493, 1983.

[215] J. J. Shepherd, "Ammonia flares: Incinerators-oxidizers—A proven safe and readily used method for disposing of ammonia in industrial applications," in *Proc.*

Int. Inst. Ammonia Refrigeration 10th Meeting, 1988, pp. 211–223.

[216] J. J. Shepherd, "Ammonia flares: Costs, codes, installation and design considerations," in *Proc. Int. Inst. Ammonia Refrigeration 12th Meeting*, 1990, pp. 111–125.

[217] S. L. Lopes, J. A. Carvalho, Jr., B. K. Alves, A. R. M. Borges, T. Morimoto, and H. S. Couto, "Formation of pollutants in an industrial ammonia vapour combustion system," *J. Inst. Energy*, vol. 71, pp. 47–54, 1998.

[218] J. A. Miller and C. T. Bowman, "Mechanism and modeling of nitrogen chemistry in combustion," *Prog. Energy Combust. Sci.*, vol. 15, pp. 287–338, 1989.

[219] R. P. Lindstedt, F. C. Lockwood, and M. A. Selim, "Detailed kinetic modelling of chemistry and temperature effects on ammonia oxidation," *Combust. Sci. and Tech.*, vol. 99, pp. 253–276, 1994.

[220] M. Zieba, A. Brink, A. Schuster, M. Hupa, and G. Scheffknecht, "Ammonia chemistry in a flameless jet," *Combustion and Flame*, vol. 156, pp. 1950–1956, 2009.

[221] C. Duynslaegher, H. Jeanmart, and J. Vandooren, "Ammonia combustion at elevated pressure and temperature conditions," *Fuel*, vol. 89, pp. 3540–3545, 2010.

[222] G. A. Olah, A. Goeppert, and G. K. S. Prakash, *Beyond Oil and Gas: The Methanol Economy*. New York: Wiley-VCH, 2006.

[223] G. A. Olah, G. K. S. Prakash, and A. Goeppert, "Anthropogenic chemical carbon cycle for a sustainable future," *J. Am. Chem. Soc.*, vol. 133, pp. 12 881–12 898, 2011.

[224] D. L. Hagen, "Methanol: Its Synthesis, Use as a Fuel, Economics, and Hazards," U.S. Energy Research and Development Administration, Rep. NP-21727, 1976.

[225] D. D. Lowell, C. B. Moyer, S. Unnasch, and M. D. Jackson, "Methanol as a Motor Fuel: Review of the Issues Related to Air Quality, Demand, Supply, Cost, Consumer Acceptance, and Health and Safety," California Energy Commission Rep. P500-33-902, 1989.

[226] L. Bromberg and W. K. Cheng, *Methanol as an Alternative Transportation Fuel in the US: Options for Sustainable and/or Energy-Secure Transportation*. Cambridge, MA: Sloan Automotive Laboratory, MIT, 2010.

[227] The Methanol Institute. [Online]. Available: www.methanol.org

[228] T. B. Blaisdell, M. D. Jackson, C. B. Moyer, and S. Unnasch, "California's Methanol Program, Evaluation Report, Volumes 1, 2, and 3," (California Energy Commission, P500-86-012, Nov. 1986; P500-86-012a, Jun. 1987; P500-86-012b, Aug. 1987).

[229] Bechtel, Inc., *California Fuel Methanol Cost Study, Volumes 1, 2, and 3*, Managing sponsor: Chevron USA, Inc., 1990.

[230] P. F. Ward and J. M. Teague, "Fifteen years of fuel methanol distribution," in *Proc. 11th Int. Symp. Alcohol Fuels*, 1996, California Energy Commission Rep. CEC-999-1996-017.

[231] T. MacDonald, "Alcohol fuel flexibility—Progress and prospects," in *Proc. Fifteenth Int. Symp. Alcohol Fuels*, 2005, California Energy Commission Rep. CEC-600-2005-038.

[232] R. J. Nichols, "The methanol story: A sustainable fuel for the future," *J. Sci. Ind. Res.*, vol. 62, pp. 97–105, 2003.

[233] *Methanol Production and Transportation Costs*, U.S. Department of Energy, Rep. DOE/PE-0093, 1989, Assessment of Costs and Benefits of Flexible and Alternative Fuel Use in the U.S. Transportation Sector, Tech. Rep. Three.

[234] *Analysis of Alternative-Fuel Fleet Requirements*, U.S. Department of Energy, Rep. DOE/PE-0103P, 1992, Assessment of Costs and Benefits of Flexible and Alternative Fuel Use in the U.S. Transportation Sector, Tech. Rep. Ten.

[235] *Market Potential and Impacts of Alternative Fuel Use in Light-Duty Vehicles: A 2000/2010 Analysis*, U.S. Department of Energy, Rep. DOE/PO-0042, 1996, Assessment of Costs and Benefits of Flexible and Alternative Fuel Use in the U.S. Transportation Sector, Tech. Rep. Fourteen.

[236] M. J. van der Burgt, J. Cantle, and V. K. Boutkan, "Carbon dioxide disposal from coal-based IGCC's in depleted gas fields," *Energy Conv. Manag.*, vol. 33, pp. 603–610, 1992.

[237] K. Blok, R. H. Williams, R. E. Katofsky, and C. A. Hendriks, "Hydrogen production from natural gas, sequestration of recovered CO_2 in depleted gas wells and enhanced natural gas recovery," *Energy*, vol. 22, pp. 161–168, 1997.

[238] C. M. Oldenburg, S. H. Stevens, and S. M. Benson, "Economic feasibility of carbon sequestration with enhanced gas recovery (CSEGR)," *Energy*, vol. 29, pp. 1413–1422, 2004.

[239] Y. Zhang, C. M. Oldenburg, S. Finsterle, and G. S. Bodvarsson, "System-level modeling for economic evaluation of geological CO_2 storage in gas reservoirs," *Energy Conv. Manag.*, vol. 48, pp. 1827–1833, 2007.

[240] A. K. Singh, U.-J. Goerke, and O. Kolditz, "Numerical simulation of non-isothermal compositional gas flow: Application to carbon dioxide injection into gas reservoirs," *Energy*, vol. 36, pp. 3446–3458, 2011.

[241] S. C. Krevor and J. S. Lackner, "Enhancing process kinetics for mineral carbon sequestration," *Energy Procedia*, vol. 1, pp. 4867–4871, 2009.

[242] R. N. J. Comans, W. J. J. Huijgen, and G.-J. Witkamp, "Cost evaluation of CO_2 sequestration by aqueous mineral carbonation," *Energy Conv. Manag.*, vol. 48, pp. 1923–35, 2007.

[243] W. K. O'Connor, D. C. Dahlin, G. E. Rush, S. J. Gerdemann, and L. R. Penner, "Energy and economic evaluation of ex situ aqueous mineral carbonation," in *Greenhouse Gas Contr. Technol.*, vol. 7, E. S. Rubin, Ed. New York: Elsevier, 2005, pp. 2011–2015.

[244] W. K. O'Connor, D. C. Dahlin, G. E. Rush, S. J. Gerdemann, L. R. Penner, and D. N. Nilsen, *Aqueous Mineral Carbonation*, U.S. Department of Energy, DOE/ARC-TR-04-002, 2005.

[245] K. Z. House, C. H. House, D. P. Schrag, and M. J. Aziz, "Electrochemical acceleration of chemical weathering as an energetically feasible approach to mitigating anthropogenic climate change," *Environ. Sci. Technol.*, vol. 41, pp. 8464–8470, 2007.

[246] W. Li, W. Li, B. Li, and Z. Bai, "Electrolysis and heat pretreatment methods to promote CO_2 sequestration by mineral carbonation," *Chem. Eng. Res. Design*, vol. 87, pp. 210–215, 2009.

[247] *Determination of Carbon Intensity for the Renewable and Low Carbon Fuel Requirements Regulation*, BC, Canada: British Columbia Ministry of Energy, 2010.

[248] M. Cleeves, *How to Determine and Report the Carbon Intensity of Fuels*. BC, Canada: British Columbia Ministry of Energy, 2010.

[249] A. Bryce, *Low-Carbon Methanol from Renewable Electricity*. Victoria, BC, Canada: Blue Fuel Energy Corporation, 2010.

[250] M. Chaos, Z. Zhao, A. Kazakov, P. Gokulakrishnan, M. Angioletti, and F. L. Dryer, "A PRF+toluene surrogate fuel model for simulating gasoline kinetics," *5th U.S. Combustion Meeting*, The Combustion Institute, 2007.

[251] *NIOSH Pocket Guide to Chemical Hazards, 3rd Printing*, U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, NIOSH Publication 2005-149, Sep. 2007

[252] International Chemical Safety Cards (ICSC), United Nations, International Labor Organization. [Online]. Available: http://www.ilo.org/safework/info/databases/lang–en/WCMS_113134/index.htm

[253] NIST Chemistry Web Book. [Online]. Available: http://webbook.nist.gov/chemistry/

[254] D. P. Gregory and R. J. Dufour, "Utilization of Synthetic Fuels Other Than Hydrogen," U.S. Department of Energy, Rep. DOE/OR/21400-T76, 1972.

[255] V. F. Zakaznov, L. A. Kursheva, and Z. I. Fedina, "Determination of normal flame velocity and critical diameter of flame extinction in ammonia-air mixture," *Combust. Explosion Shock Waves*, vol. 14, pp. 710–713, 1978.

[256] V. Babrauskas, *Ignition Handbook*. Issaquah, WA: Fire Science Publishers and the Society of Fire Protection Engineers, 2006.

[257] H. J. McDermott and S. E. Killiany, "Quest for a gasoline TLV," *Amer. Ind. Hyg. Assoc. J.*, vol. 39, pp. 110–117, 1978.

[258] "Toxicology update," *J. Appl. Toxicology*, vol. 9, pp. 203–210, 1989.

[259] C. Harper and J. J. Liccione, *Toxicological Profile for Gasoline*, U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, 1995.

[260] B. Hamilton and R. J. Falkiner, "Fuels and Lubricants Handbook: Technology, Properties, Performance, and Testing," in *Motor Gasoline*, G. F. Totten, Ed. West Conshohocken, PA: ASTM International, 2003.

[261] A. M. Hochhauser, "Gasoline and other motor fuels," in *In Kirk-Othmer Encyclopedia of Chemical Technology*, vol. 12, New York: Wiley, 2005, pp. 386–435.

[262] J. W. Weaver, L. Jordan, and D. B. Hall, "Predicted Ground Water, Soil and Soil Gas Impacts from US Gasolines, 2004 First Analysis of the Autumnal Data," U.S. Environmental Protection Agency, Rep. EPA 600/R-05/032, 2005.

[263] J. W. Weaver, L. R. Exum, and L. M. Prieto, "Gasoline Composition Regulations Affecting LUST Sites," U.S. Environmental Protection Agency, Rep. EPA/600/R-10/001, 2010.

[264] J. Borak, C. A. Fields, and G. Sirianni, "Toxicology Principles for the Industrial Hygienist," in *Toxicology of Complex Chemical Mixtures*, W. E. Lutrell, W. W. Jederberg, and

K. R. Still, Eds., American Industrial Hygiene Association, 2008.

[265] G. S. Parkinson, "Benzene in motor gasoline—An investigation into possible health hazards in and around filling stations and in normal transport operations," *Ann. Occup. Hyg.*, vol. 14, pp. 145–153, 1971.

[266] M. A. Mehlman, "Dangerous properties of petroleum-refining products: Carcinogenicity of motor fuels (gasoline)," *Teratogen. Carcinogen. and Mutagen.*, vol. 10, pp. 399–408, 1990.

[267] M. A. Mehlman, "Causal relationship between chronic myelogenous leukemia and benzene-containing solvents," *Ann. N.Y. Acad. Sci.*, vol. 1076, pp. 110–119, 2006.

[268] D. J. Praustenbach, R. D. Bass, and P. Price, "Benzene toxicity and risk assessment 1972–1992: Implications for future regulation," *Environ. Health Perspect.*, vol. 101, pp. 177–200, 1993, (Suppl. 6).

[269] F. Deschamps, "Unleaded gasoline-continuing hazard," *Occupational Medicine*, vol. 45, no. 1, p. 55, 1995.

[270] F. Deschamps, A. Pfohl-Leszkowicz, and T. Trenque, "Risk for occupational cancers. Effect of deoxyribonucleic acid adducts," *Presse Med*, vol. 23, pp. 991–4, 1994.

[271] *Report of the Expert Panel on Air Quality Standards—Benzene*, U.K. Department of the Environment, 1994.

[272] A. Persona, J. Penar, and J. Reszko-Zygmunt, "Liquid ammoniate of ammonium nitrate as a supporting electrolyte," *Bull. Electrochem.*, vol. 13, pp. 366–369, 1997.

[273] E. Nemitz and M. A. Sutton, "Gas-particle interactions above a Dutch heathland: III. Modelling the influence of the $NH_3-HNO_3-NH_4NO_3$ equilibrium on size-segregated particle fluxes," *Atmos. Chem. Phys. Discuss.*, vol. 4, pp. 1567–1621, 2004.

[274] R. T. Rewick, "Calorimetry Studies of Ammonia, Nitric Acid, and Ammonium Nitrate," U.S. Army Armament Research and Development Command, Rep. ARLCD-CR-79017, 1979DTIC Accession Number AD-A-078229.

[275] B. Kuriloff, "Gleichgewichtsverhältnisse zwischen Ammoniumnitrat und Ammoniak," *Zeitschrift für physikalische Chemie*, vol. 25, pp. 107–111, 1898.

[276] E. A. Worthington, R. C. Datin, and D. P. Schutz, "Physical properties of ammonia solutions: Ammonium nitrate-ammonia-water and urea-ammonia-water," *Ind. and Eng. Chem.*, vol. 44, pp. 910–913, 1952.

[277] *Production of Ammonium Nitrate and Calcium Ammonium Nitrate*, European Fertilizer Manufacturer's Association, Best Available Techniques Booklet Number 6, 2000.

[278] R. M. Hainer, "Study of Ammonium Nitrate Materials, Progress Report Number 11," U.S. Coast Guard, DTIS Accession Number AD-786334.

[279] J. R. Hradel and C. K. Bjork, "Ammonium nitrate explosive composition containing ammonia," U.S. Patent 3 094 443, 1959.

[280] *Handbook for the Safe Storage of Ammonium Nitrate Based Fertilizers*, International Fertilizer Industry Association and European Fertilizer Manufacturer's Association, 1992.

[281] C. Oommen and S. R. Jain, "Ammonium nitrate: A promising rocket propellant oxidizer," *J. Hazardous Mater. A*, vol. 67, pp. 253–281, 1999.

[282] H. Smith, *Chemistry in Anhydrous Liquid Ammonia*. New York: Interscience, 1963.

[283] J. Jander, *Chemie in wasserfreiem flüssigem Ammoniak*. Berlin, Germany: Vieweg, 1966.

[284] D. Nicholls, *Inorganic Chemistry in Liquid Ammonia*. New York: Elsevier, 1979.

[285] J. J. Lagowski, "Liquid ammonia," *Synth. Reactivity in Inorgan. Metal-Organ. and Nano-Metal Chem.*, vol. 37, pp. 115–153, 2007.

[286] C. D. Chang, "Hydrocarbons from methanol," *Cat. Rev.-Sci. Eng.*, vol. 25, pp. 1–118, 1983.

[287] M. A. Mehlman, "Dangerous properties of petroleum-refining products: Carcinogenicity of motor fuels (gasoline)," *Teratogen. Carcinogen. Mutagen.*, vol. 11, pp. 213–226, 1991.

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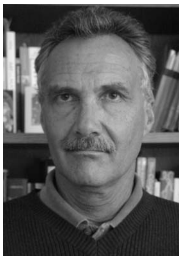

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