Nuclear Hydrogen for Production of Liquid Hydrocarbon Transport Fuels

Charles W. Forsberg
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831
Email: forsbergcw@ornl.gov

Abstract

Liquid fuels (gasoline, diesel, and jet fuel) have major advantages as transport fuels: a high energy density per unit volume and mass, ease of storage, and ease of transport. However, there are major disadvantages: crude oil is increasingly expensive and of value to the petrochemical industry; most of the world's crude oil comes from politically unstable parts of the world; and burning of hydrocarbons releases greenhouse gases to the atmosphere. The alternative explored in this paper is the production of liquid fuels from other carbon feedstocks (heavy oil, tar sands, oil shale, coal, biomass, and other carbon sources) using nuclear energy to produce (1) hydrogen and oxygen from water and (2) heat as required. The use of nuclear energy in this role has the potential to reduce costs and minimize greenhouse gas emissions in the production of liquid fuels. This paper describes the results of initial assessments and planned future studies.

1. Introduction

About 40% of the U.S. energy demand is met by petroleum that is converted primarily to liquid fuels. However, the world is rapidly exhausting its resources of the light crude oils used to make liquid fuels (Fig. 1). To meet our transportation needs, a replacement for crude oil is required.

As oil becomes scarce, liquid fuels will be produced with increasing frequency from natural gas (gas to liquids) and from heavier feedstocks such as heavy oil, tar sands, oil shale, and coal. With current technology, this conversion process can be summarized as follows:

$$\text{Carbon-based feedstock} + \text{Water} + \text{Oxygen } (O_2) \rightarrow \text{Liquid fuels} + \text{Carbon dioxide } (CO_2) \quad (1)$$

Liquid fuels today are made from heavy oils (many countries), tar sands (Canada), and coal (South Africa). In a refinery, heavy oils are converted to liquid fuels by increasing the hydrogen-to-carbon ratio of the feedstock to that of liquid fuels (hydrogen-to-carbon ratio of 1.5 to 2). This requires either thermal cracking to remove carbon or hydrogenation to add hydrogen. The carbon from thermal cracking is ultimately released to the atmosphere as CO_2. Traditionally, hydrogen is produced by steam reforming of fossil fuels, a process that produces hydrogen and CO_2, with the latter being released to the atmosphere.

If we switch from light crude oils to alternative hydrocarbon feedstocks to produce liquid fuels, the CO_2 emissions per vehicle mile traveled will increase, as is shown in Fig. 2. For some options, the CO_2 emissions per mile of vehicle travel will double. In this figure it is assumed that the natural gas and coal are converted to diesel fuel by the classical three-step gasification, water-gas shift, and Fischer-Tropsch synthesis processes. Traditional refining is assumed to produce diesel fuel from crude oils. Because of the expected impacts of greenhouse gases on climate, there are serious questions as to whether traditional technologies should be used to produce liquid fuels from alternative feedstocks.

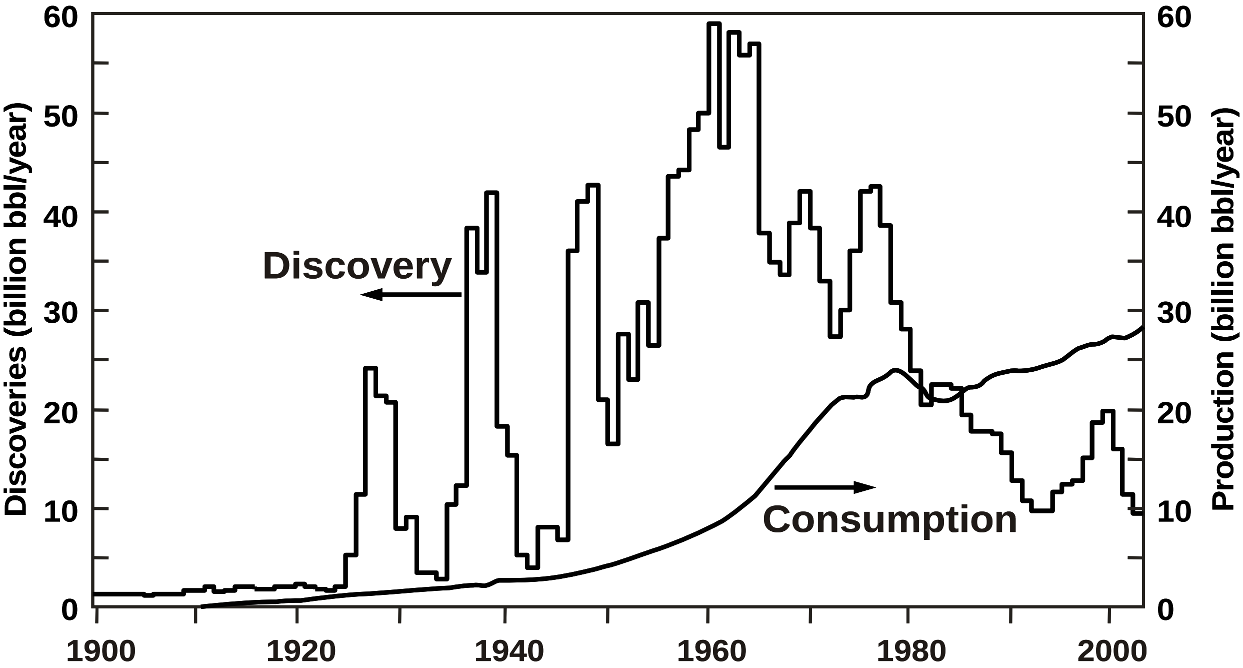

Fig. 1. Rate of Discovery and Consumption of Conventional Crude Oils vs Time (Wells 2005)**.**

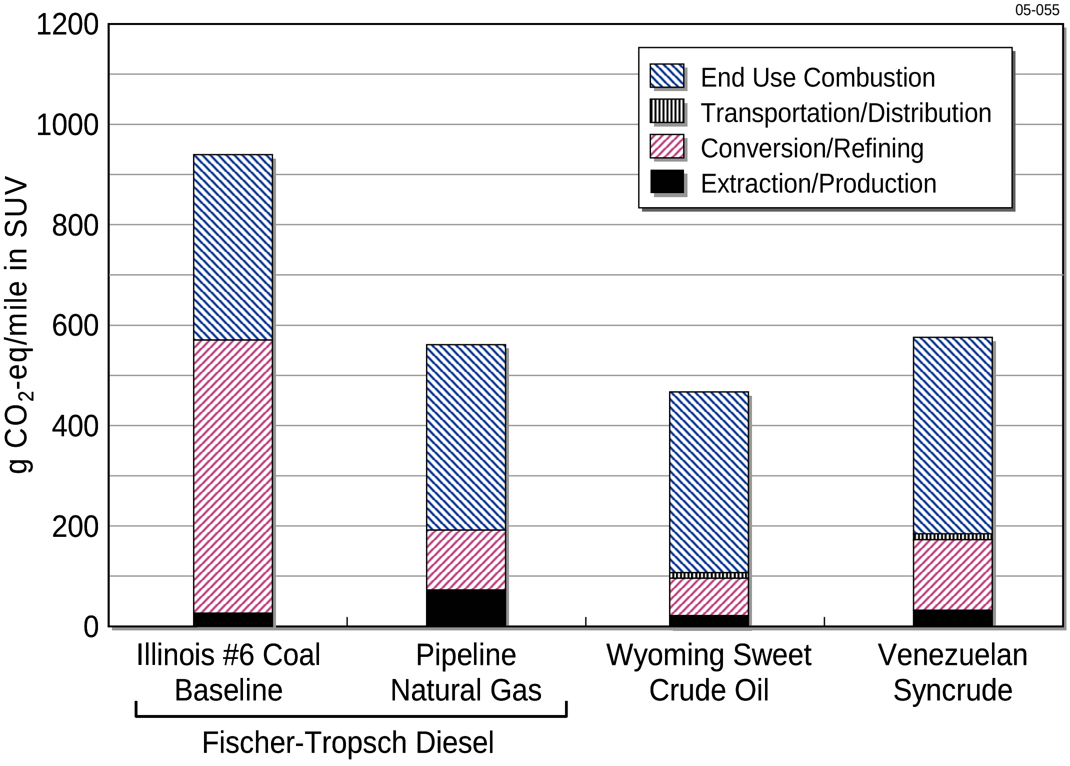

Fig. 2. Equivalent Carbon Dioxide Releases per SUV Vehicle Mile for Diesel Fuel Produced from Different Feedstocks (Marano and Ciferno 2001)**.**

The increased CO_2 emissions from these alternative processes are a consequence of using the carbon feedstock for three purposes within the processes:

- to provide carbon for the liquid fuel;
- to provide energy to operate the conversion process, including O_2 production; and
- to serve as a reducing agent for the production of hydrogen to produce the liquid fuel.

Alternatively, if economic hydrogen is available from non-greenhouse-emitting sources (solar, wind, nuclear, or steam reforming of fossil fuels with CO_2 sequestration) and the energy for the fuel processing does not release greenhouse gases to the atmosphere, the atmospheric carbon CO_2 emissions from liquid-fuel production per vehicle mile (unit of liquid fuel) can be lower than that available today from light crude oil. With nuclear hydrogen, this conversion process can become the following:

$$\text{Carbon-based feedstock} + \text{Water} + \text{Nuclear energy} \rightarrow \text{Liquid fuels} \qquad (2)$$

When nuclear energy is used (Reaction 2), no CO_2 is released from the fuel production process. All the carbon is incorporated into the fuel, and the carbon in the feedstock is not used as an energy source in the liquid-fuel production process. Carbon dioxide is thus released only from the burning of the liquid fuels.

The option of using nuclear energy to assist liquid-fuel production was first examined in the 1970s. At that time, the incentives were the shortage of oil caused by the Arab oil embargo and the potential for the production of lower-cost hydrogen. These same incentives exist today plus the new incentive to minimize greenhouse gas emissions. This paper is an initial examination of the options and the potential synergisms between nuclear and fossil energy that may ultimately impact economics.

2. Nuclear Energy and Nuclear Hydrogen Characteristics

Hydrogen is the primary feedstock to convert various forms of carbon into liquid fuels. At this conference a full week of sessions are dedicated to production of hydrogen using nuclear energy. The process options include room-temperature electrolysis, hot electrolysis, hybrid cycles, and thermochemical cycles. These options will not be described in further detail herein. However, from the perspective of liquid fuels production, hydrogen production using nuclear energy has two unique characteristics that set it apart from other methods of hydrogen production. These two characteristics are relevant in the context of liquid-fuel production and may provide strong economic incentives to consider nuclear-hydrogen liquid-fuel production.

- *Coproduction of hydrogen and O_2.* All of the nuclear hydrogen production technologies use water as a feedstock and thus produce hydrogen and byproduct O_2. Many of the processes to produce liquid fuels from alternative feedstocks require hydrogen and O_2 (see below). However, oxygen is expensive to produce in terms of capital costs and energy costs.
- *Site independence*. There are increasing incentives to reduce greenhouse gas emissions — including the possibility of taxes on CO_2 emissions or requirements to reduce emissions. If fossil fuels are used in the liquid-fuel-production process as an energy source or to manufacture hydrogen, large quantities of CO_2 will be produced. It may be feasible to sequester this CO_2 in certain types of geological structures. However, in most cases the carbon feedstocks (tar sands, shale oil, coal, etc.) will not be collocated next to suitable geological structures for CO_2 sequestration. Either (1) liquefaction plants must be located next to CO_2 sequestration sites with

shipments of carbon feedstocks or (2) CO_2 must be transported to sequestration sites. There are significant costs associated with either option. In contrast, nuclear plants require only 30 to 50 tons of fuel a year. Unlike other sources of energy, nuclear plants can be built anywhere, without consideration of the cost of fuel transport. High-temperature nuclear reactors can use dry cooling and avoid the need for cooling water. Thus, nuclear plants can be collocated with feedstocks and fuel production plants.

3. Liquefaction Processes

3.1 Process Options

There are multiple processes for the production of liquid fuels using nuclear hydrogen. The fuel production processes can be divided into three categories.

- *Indirect processes*. Carbon feedstocks are converted to syngas [a mixture of hydrogen and carbon monoxide (CO)] and the syngas is subsequently converted to liquid fuels.
- *Direct processes*. Carbon feedstocks such as coal are directly hydrogenated.
- *Other*. These are processes designed for a specific feedstock with specific characteristics. The best-known examples are the processes that convert shale oil to liquids.

All of these processes need to be examined in the context of producing liquid fuels using nuclear hydrogen. Indirect processes were chosen for our initial examination based on several considerations.

- *Feedstock availability*. Because indirect processes can start with any carbon source and produce liquid fuels, they are the most versatile processes.
- *Industrial status*. Indirect processes are today the preferred routes to liquid-fuel production.
- *Product mix*. Improvements in the indirect processes have allowed the production of liquid fuels that better match the market needs and minimize the need for additional refining operations.
- *Clean fuel*. The indirect processes can produce extremely clean fuels relative to liquid fuels produced via crude oil or other liquefaction processes. This is a consequence of two factors: (1) it is relatively inexpensive to clean syngas mixtures to remove sulfur, heavy metals, and other impurities; and (2) the catalysts used to produce liquid fuels from syngas are intolerant of many impurities thus necessitating clean syngas.

3.2 Fischer-Tropsch Processing

Fisher-Tropsch is the most widely used indirect method for the production of liquid fuels. The Fisher-Tropsch process is described, and methods for integration into a nuclear coal-liquefaction plant are discussed. More-detailed studies are required to understand the preferred options.

3.2.1 Chemistry

There are three major reactions in production of liquid fuels from carbon sources (coal, etc.) using the indirect Fischer-Tropsch liquefaction process:

Oxidation of carbon: $$2C + O_2 \rightarrow 2CO \qquad (3)$$

Water-gas-shift reaction: $$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (4)$$

Fischer-Tropsch: $$(n/2 + m)H_2 + mCO \rightarrow C_mH_n + mH_2O \qquad (5)$$

The overall reaction converts carbon, O_2, and water into liquid fuels and CO_2. The major process operations (Fig. 3) are described with coal as the feedstock.

Syngas Production (Gasifier)

The first step is the production of syngas (a mixture of hydrogen, CO, and other gases) from the carbon source, water, and O_2. Chemical reactions 3 and 4 occur in the gasifier. Depending upon temperature, pressure, and feed composition, some mixture of hydrogen, CO, CO_2, and water will be produced as the raw syngas. The carbon oxidation process (reaction 3) is highly exothermic and can be considered a one-way process. The water-gas-shift reaction (reaction 4) is an equilibrium reaction where the degree of completion of the reaction is strongly sensitive to temperature and gas composition. The feedstock can be almost any carbon-containing material. Gasifiers currently operate on coal, petrocoke, garbage, natural gas, biomass, and a wide variety of other feeds.

Fischer-Tropsch Liquid-Fuel Production (Syngas Conversion)

For production of liquid fuels, syngas is fed to a Fisher-Tropsch conversion reactor that produces the liquid fuel (C_mH_n). Reactions 4 and 5 occur in the Fisher-Tropsch conversion process. The choice of pressure, temperature, residence time, and feed gas composition determines the products.

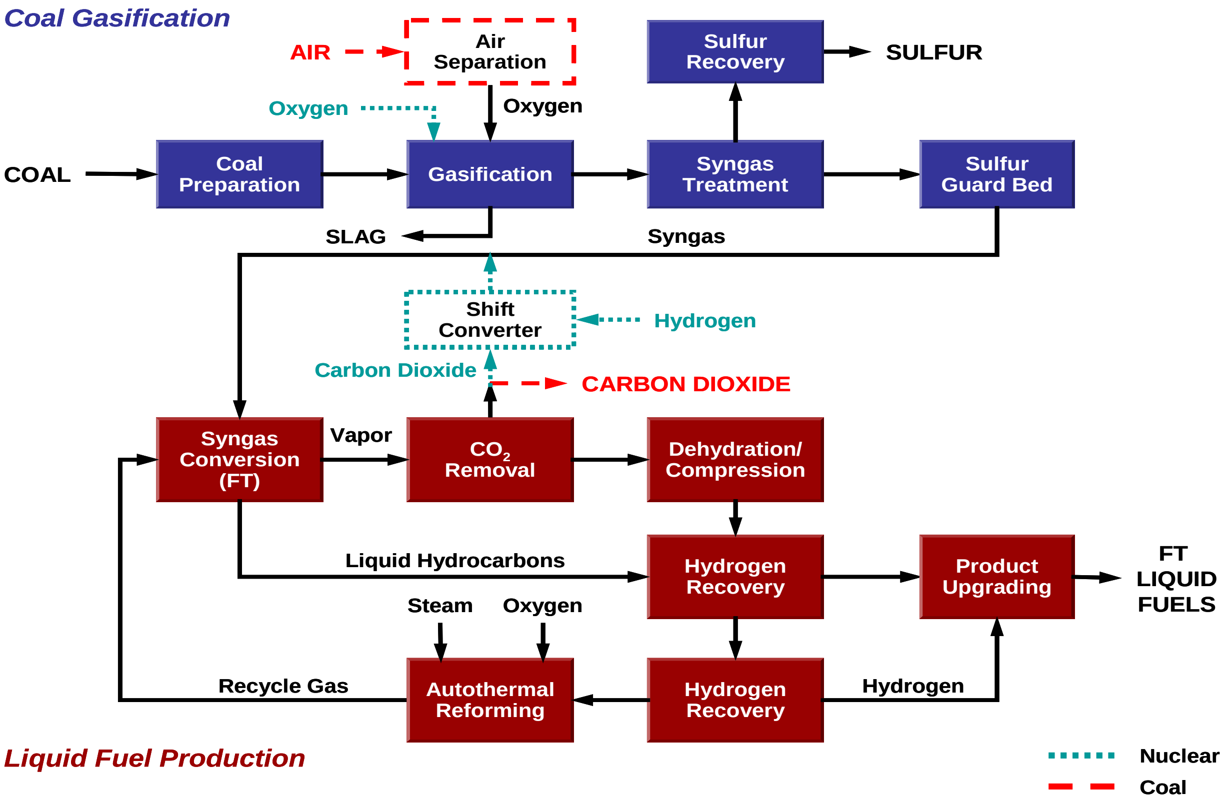

Fig. 3. Nuclear Coal Liquefaction and Coal Liquefaction by the Indirect Coal-Gasification Fischer-Tropsch (FT) Process.

Nuclear Syngas Fisher-Tropsch Liquid-Fuel Production

The nuclear variant involves supplying O_2 for the gasification step and hydrogen to avoid the need for the water-shift reaction (reaction 4) for hydrogen production. In practice, CO_2 is produced in the process, thus creating the need to recycle that CO_2 back to CO by the reverse-water-shift reaction.

3.2.2 Flowsheet

The plant is divided into two sections: coal gasification and liquid-fuel production. Modifications required for a nuclear coal-liquefaction plant are shown by dotted lines in Fig. 3 and in italic text in the description below.

Coal Gasification

Coal preparation. Coal is ground.

Air separation. High-purity O_2 is produced. For conventional plants, O_2 is obtained from air using standard cryogenic air separation techniques. *For a nuclear coal-liquefaction plant, the* O_2 *is from the splitting of water in the nuclear hydrogen plant.*

Gasification. Coal with a carrier fluid is combined with oxygen and fed into the gasifier, a process that creates syngas (chemical reactions 3 and 4). If a Shell gasifier is used, the carrier is CO_2 gas. If a Texaco gasifier is used, the carrier is water. This operation includes high-temperature gas cooling, slag handling, and solid waste handling.

Syngas treatment. This is a set of purification steps that remove sulfur and other compounds.

Sulfur recovery. This process converts the various sulfur compounds from syngas treatment into sulfur for sale or disposal.

Fisher-Tropsch Conversion

Syngas conversion (Fischer-Tropsch). This reactor converts the syngas mixture (primarily CO and H_2) into a liquid fuels stream and a gas stream via reactions 4 and 5.

Carbon dioxide removal (gas processing). The CO_2 is selectively removed from the off-gas. If a Shell gasifier is used, a fraction of the stream is sent back to the gasifier to act as a carrier gas to bring the coal into the gasifier. The remainder of the CO_2 is then released to the atmosphere. *In a nuclear coal-liquefaction facility, the excess* CO_2 *is recycled. Options include (1) the combination of* CO_2 *with the hydrogen in a shift reactor (reaction 4) to produce CO and water, (2) recycle to the gasifier with added hydrogen, and (3) use of the Fischer-Tropsch reactor by recycle of* CO_2 *with added hydrogen.*

Dehydration/Compression (gas processing). The moisture is removed from the gas stream and subsequently compressed.

Hydrocarbon recovery (gas processing). Useful hydrocarbons are recovered and sent to the product-upgrade system.

Hydrogen recovery (gas processing). Hydrogen is recovered from the gas stream, which is then reheated with the hot liquid from the syngas conversion step.

Product upgrading. The product-upgrading section is a simplified refinery that separates and converts the Fischer-Tropsch products into gasoline, diesel, and jet fuel.

Autothermal reforming. The remaining gases (CH_4, C_2H_2, and C_2H_6) are converted to syngas and sent back to the syngas conversion step. This requires the input of steam and oxygen. *In a nuclear-coal-liquefaction plant, the oxygen is produced by the nuclear hydrogen plant.*

3.2.3 Issues

An optimized flowsheet would likely result in a variety of changes in parts of the flowsheet and may add the hydrogen and recycled CO_2 at different locations within the plant. Studies are under way to understand how the flowsheets would be modified.

3.3 Other Liquefaction Processes

The implications of nuclear hydrogen for other liquefaction processes are being examined. However, it is observed that many other processes (direct liquefaction, flash heating of coal for liquids recovery, etc.) produce high-carbon by-product streams. If these other processes are adapted, indirect liquefaction is likely to be used to convert these secondary carbon-rich product streams to liquid fuels.

4. Future Fuel Transitions

The approach herein allows for evolution to a system that has no greenhouse gas impacts.

- *Tar sands, coal, and shale oil*. With these feedstocks, a nuclear-hydrogen liquid-fuel system limits greenhouse gas emissions to those from burning the clean fuel. There are no significant greenhouse impacts from fuel production itself.
- *Garbage and sewage solids*. Society produces many carbon-containing wastes—many of which were originally made from fossil fuels. Ultimately, the carbon in most of these wastes is oxidized, with the CO_2 released to the environment. If these feedstocks are used for liquid-fuel production, there are no additional greenhouse gas emissions beyond what would ultimately occur via the oxidation of these waste streams.
- *Biomass*. Biomass is used today to produce liquid fuels such as alcohol by fermentation. Because the CO_2 used to make the biomass comes from the atmosphere, no greenhouse gas impacts result. However, only a fraction of the biomass becomes a liquid fuel. For example, the conversion of corn to ethanol results in roughly one-third of the carbon from the original corn in the ethanol, one-third in the by-product animal feed, and one-third in the form of CO_2 released to the atmosphere from respiration of the yeast. Biomass is used as an energy source, with much of the energy used to make the fuel. If the biomass is directly converted into liquid fuels by Fischer-Tropsch or a similar process, all the carbon is incorporated into liquid fuels. With this option, biomass is used primarily as a carbon source, not an energy source. The quantities of liquid fuels measured in terms of energy value increase by factor of 3 or more per unit of biomass input.

- *Air*. Liquid fuels can be made from hydrogen and CO_2 extracted from (1) the atmosphere or (2) the ocean. A modified Fischer-Tropsch synthesis process is used. The hydrogen is used (1) as a feedstock to make the liquid fuels and (2) as an internal energy source to drive the process of producing the fuel. Because the CO_2 is recovered from the atmosphere or seawater, no greenhouse impacts occur. About 80% of the total energy input required to produce the liquid fuel is used to produce the hydrogen. Carbon dioxide extraction from air or water is not the primary energy cost.

The direct production of liquid fuels from air and water is the ultimate option for liquid-fuel production. This option (Forsberg 2005) has been studied for both commercial liquid-fuel production and military fuel production, where a nuclear-powered tanker makes aviation and diesel fuel for naval ships and thus eliminates the logistic challenges of fueling aircraft carriers and other naval vessels. For several reasons, this is an important endpoint option for liquid-fuels production whether or not it is implemented.

- *Liquid-fuel impacts.* This option provides unlimited liquid fuels with no greenhouse impacts as long as the hydrogen and energy come from non-greenhouse-emitting energy sources.
- *Ultraclean liquid fuel*. The feedstocks contain no sulfur or heavy metals; thus, ultra clean liquid fuels are produced.
- *Hydrogen economy*. From an economic perspective, this technology places an upper economic limit on the allowable costs for using hydrogen directly as a transport fuel compared with those for using liquid fuels. The production costs of liquid fuels using hydrogen and CO_2 from the atmosphere are significantly higher than the production costs of hydrogen. However, the costs of distributing and storing liquid fuels are much lower than those for distributing and storing hydrogen. Either approach can provide the fuel for the transport system without increasing atmospheric greenhouse concentrations. Economics would determine the preferred option.

5. Conclusions

The end of the age of oil is approaching. Because liquid fuels have major advantages as transport fuels (a high energy density per unit volume and mass, ease of storage, and ease of transport), they remain major options as future transport fuels. However, the growing worldwide constraints on CO_2 emissions may partly determine the replacement for liquid fuels derived from traditional crude oils. Nuclear hydrogen, and the by-product O_2, create multiple options for the manufacture of liquid fuels from multiple feedstocks. These options are now being investigated to understand their characteristics and potential. However, these options are only partly understood at the present time.

6. References

Wells, P., 2005. “Oil Supply Challenges—1: The Non-OPEC Decline,” *Oil Gas J.,* 20-28 (Feb 21).

Marano, J. J., and Ciferno, J. P., 2001. *Life-Cycle Greenhouse-Gas Emissions Inventory for Fischer-Tropsch Fuels,* Energy and Environmental Solutions, LLC, for the U.S. Department of Energy National Energy Technology Laboratory.

Forsberg, C. W., 2005 “Hydrogen Markets: Implications for Hydrogen Production Technologies,” *International Journal of Hydrogen Energy* (in press).