HYDROGEN AND SYNTHETIC HYDROCARBON FUELS – A NATURAL SYNERGY*

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1. Introduction

Production of synthetic hydrocarbon fuels ("synfuels") can help with the growing shortage of petroleum. Refined petroleum products or synfuels are generically $[CH_2]_n$. Currently, synfuels are made from fossil resources, primarily coal and natural gas. In the coal process, one atom of carbon is produced as CO_2 for every atom produced as CH_2 in the synfuel. This CO_2 must be sequestered or released. If hydrogen is provided from an external, non-fossil source, such as solar, wind or nuclear production of hydrogen from water, the synfuel production process need not produce any CO_2. However, the synfuel, when burned for transportation will produce and release the contained carbon as CO_2. Since the synfuel would be a replacement for petroleum-based fuel, there would be no net increase in the production or release of CO_2. If the hydrogen is provided from an external, non-fossil source, and if the carbon is provided by capture of CO_2 from existing coal-fired power plants or the air, the total U.S. release of CO_2 can be halved. Hydrogen would be used to produce CO from CO_2 in the reverse water gas shift reaction and to produce $[CH_2]_n$ from CO and H_2 in the Fischer-Topsch reaction. Three molecules of H_2 would be needed for every moiety of CH_2 produced.

The production rate of CO_2 from coal power plants in the US is 1875 million metric tons/year. If this CO_2 were captured using proven absorption processes and used with hydrogen produced by solar, wind or nuclear energy to make synfuel, it would provide all the hydrocarbon fuel needed for our transportation economy. Since that transportation economy produces 1850 million metric tons of CO_2 per year, this synfuel process would cut our CO_2 production in half. We could shift from a petroleum-based transportation economy to a synfuel transportation economy. This would reduce our petroleum use by 75%, and reduce our CO_2 production by 50% with no increase in coal use. It would require significant quantities of hydrogen (255 million metric tons/year, or 25 times our current production) that would be produced from water using solar, wind or nuclear energy.

This hydrogen synfuel concept would allow us to significantly reduce our use of petroleum, and cut our CO_2 emissions in half, while still using our existing hydrocarbon-based transportation infrastructure. It could provide a bridge to a pure hydrogen economy.

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2. Petroleum-based Fuels

Although fossil fuels currently provide most of the world's energy, these fuels are in limited supply. About 40% of the U.S. energy demand is met by oil that is converted primarily to liquid fuels (gasoline, diesel, and jet fuel). Today's transportation system depends upon liquid fuels because of their high energy density by weight and volume and their ease of use. However, the world is exhausting its resources (Fig. 1) of the light crude oils [1] used to make liquid fuels, with consumption of oil exceeding discoveries since 1985.

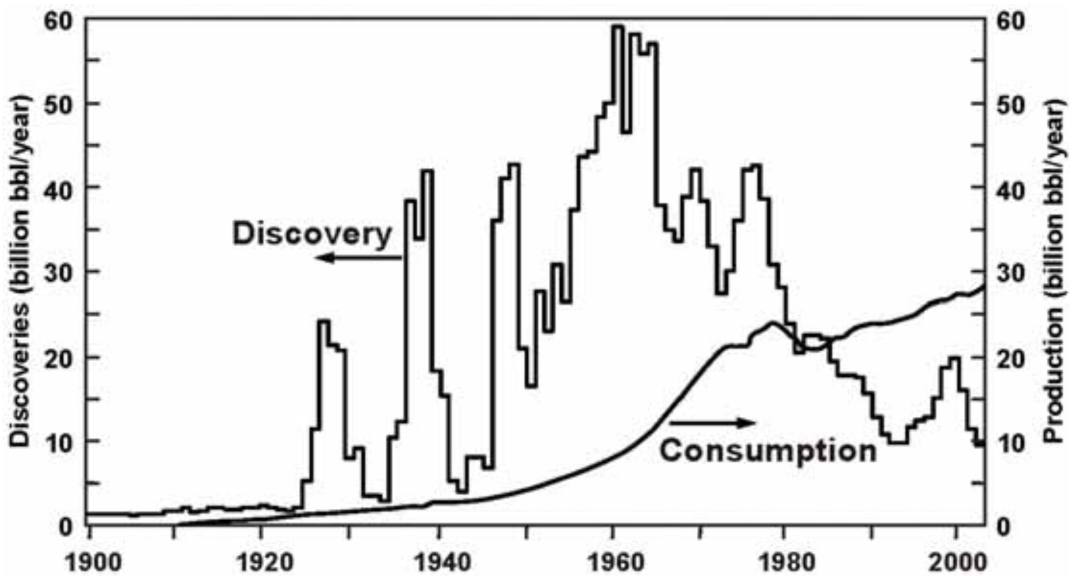

Figure. 1. Rate of world discovery and consumption of conventional crude oils vs. time. [1]

A half-century ago, M. King Hubbert developed a phenomenological model to forecast the peaking of oil production in the lower forty-eight of the United States. This model was principally based on the certainty that the production of a finite resource, e.g., petroleum, will follow a family of bell-shaped curves depending on different initial production rates and estimates of the ultimate size of the resource. He predicted that the year of peak US oil production would be about 1970. [2] In 1970, US oil production in fact did peak, confirming the prediction made some fifteen years earlier. According to more pessimistic sources [3, 4], about half of the world's oil has already been consumed (Fig. 2), while the remaining oil will be increasingly difficult to recover. Natural gas can be converted to liquid synthetic hydrocarbon fuel and is more plentiful than oil but still limited. The US DOE Energy Information Agency shows US consumption at 22.3 trillion cubic feet (TCF) per year, with proven reserves of 198 TCF (9 years' worth) and unproven but expected reserves of 1430 TFC (65 years' worth at the current rate of consumption) [5]. Increasing consumption is already pushing prices up and projected lifetimes down. Coal is plentiful, with supplies to last hundreds of years, but the environmental costs of mining, transporting, and using coal are severe. In addition, the use of fossil fuels generates CO_2. To reduce the risk of catastrophic global climate change predicted by many climate scientists, this CO_2 will have to be captured and sequestered, using currently undeveloped and unproven technologies. Although humankind will continue to rely heavily on fossil fuels for much of its energy needs for the rest of this century, the challenge during that time must be to find and develop acceptable alternatives.

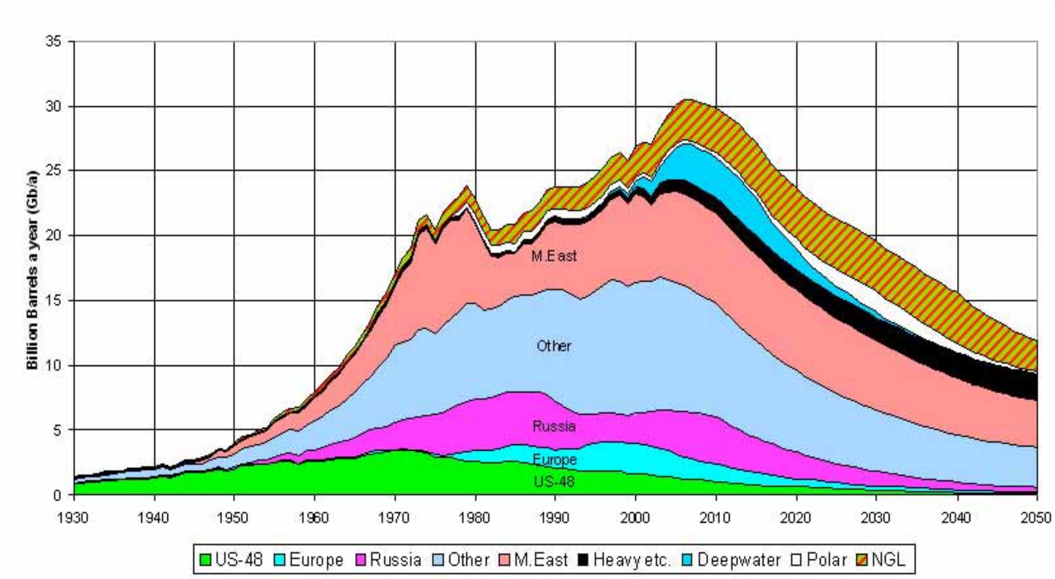

Figure 2. A prediction of the world oil supply [3]. The peak of the conventional oil supply is predicted to occur in 2008. Although other sources predict the peak to occur later, most predictions vary by only a few decades. For a report on this issue commissioned by the U.S. Department of Energy, see [4].

3. Synthetic Hydrocarbon Fuels – "Synfuel"

Synthetic liquid hydrocarbons have been synthesized for more than three-quarters of a century from non-liquid feedstocks — principally coal but also natural gas in recent years. The leading process is the Fischer Tropsch (F-T) process which uses synthesis gas — hydrogen and carbon monoxide — as its feed and produces a synthetic "crude" that undergoes further processing to a range of commercial finished products. [6] The synthesis gas is produced by coal gasification and by reforming of natural gas. Both of these feed preparation processes (in addition to the cost of the feed) can represent a significant cost component of the entire synthesis process. For coal, synthesis gas is produced according to the reaction: $2C + 1/2O_2 + H_2O \rightarrow 2CO + H_2$. The Water-Gas Shift reaction can be used to produce additional H_2: $CO + H_2O \rightarrow H_2 + CO_2$ The reaction for producing Fischer-Tropsch products from synthesis gas (CO and H_2) is : $CO + 2H_2 \rightarrow CH_2 + H_2O$. Thus, the simultaneous Fischer-Tropsch and Water-Gas Shift reactions in the reactor leads directly to the complete reaction: $2C + H_2O + 1/2O_2 = CH_2 + CO_2$. Note that two carbons are required to produce one Fischer-Tropsch CH_2 product; the other carbon being emitted as carbon dioxide.

Synfuel by Coal Gasification:

Gasification	$2C + 1/2O_2 + H_2O \rightarrow 2CO + H_2$
Water gas shift	$CO + H_2O \rightarrow H_2 + CO_2$
F-T reaction	$CO + 2H_2 \rightarrow CH_2 + H_2O$
Net reaction	$2C + H_2O + 1/2O_2 \rightarrow CH_2 + CO_2$

The extra hydrogen that is provided by the Water-Gas Shift can be provided by water-splitting with energy supplied from a nuclear reactor or other non-CO_2-emitting source. In this case, we still provide synthesis gas as above: $C + 1/4O_2 + 1/2H_2O \rightarrow CO + 1/2H_2$ and then provide the extra hydrogen by water-splitting: $3/2H_2O = 3/2H_2 + 3/4O_2$, for a net reaction of $C + H_2O + \text{Energy} \rightarrow CH_2 + 1/2O_2$.

Synfuel by Coal Gasification + Hydrogen from Water-splitting:

Gasification	$C + 1/4O_2 + 1/2H_2O \rightarrow CO + 1/2H_2$
Water-splitting	$3/2H_2O + \text{Energy} \rightarrow 3/2H_2 + 3/4O_2$
F-T reaction	$CO + 2H_2 \rightarrow CH_2 + H_2O$
Net reaction	$C + H_2O + \text{Energy} \rightarrow CH_2 + 1/2O_2$

In comparison with the conventional gasification and Fischer-Tropsch sequence, only half the carbon is required, and there is no CO_2 produced in the conversion process. Further, oxygen is provided by the water-splitting, which avoids the need for an external oxygen supply to the gasification process, and even has some excess oxygen for potential sale. Figure 3 illustrates the complete block diagram for the idealized process.

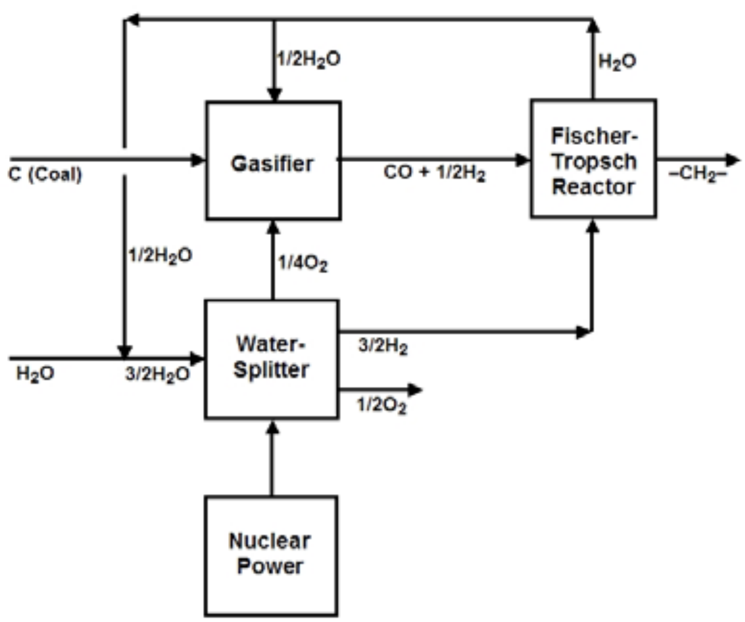

Figure 3. Coal Gasification and Fischer-Tropsch Processes Augmented with Externally Provided Hydrogen Produced by Water-Splitting.

Fossil-fired power plants produce CO_2 which could be captured and converted to CO for production of synthetic fuels. CO_2 can be converted to CO by the Reverse Water Gas Shift Reaction, $CO_2 + H_2 \rightarrow CO + H_2O$. CO could then be used in the F-T reaction with additional hydrogen from water-splitting to produce synfuel.

Synfuel by CO_2 Capture + H_2 from Water-splitting:

Reverse Water Gas Shift	$CO_2 + H_2 \rightarrow CO + H_2O$
F-T reaction	$CO + 2H_2 \rightarrow CH_2 + H_2O$
Water-splitting	$3H_2O + \text{Energy} \rightarrow 3H_2 + 3/2O_2$
Net reaction	$CO_2 + H_2O + \text{Energy} \rightarrow CH_2 + 3/2O_2$

In this case, no coal is needed at all, and CO_2 is consumed rather than produced. The excess O_2 would be used in the fossil power plant that provides the CO_2, simplifying CO_2 capture. There is currently considerable effort underway on developing CO_2 capture systems for new and extant power plants. The increasing concern with Global Climate Change suggests that there is a reasonable likelihood of such plants operating in the timeframe associated with synthetic fuel from carbon dioxide. Such a synergistic system, dubbed “twice burned coal” or “recycled coal”, has the potential to significantly reduce our current emissions of CO_2 since the carbon in the coal is used once for power production and then again for liquid hydrocarbon fuel synthesis.

4. CO_2 Capture

Work on the extraction of environmental CO_2 for synthetic hydrocarbon fuel production was performed by Drs. Meyer Steinberg and Vi-Duong Dang in the mid 1970s. [7] Among the variety of techniques evaluated, one utilizing the absorption of CO_2 by potassium carbonate with thermal solvent regeneration offered the most promise. However, research since then has produced a number of alternative CO_2 extraction methods. Our current technology choice is a membrane system using gas absorption by chemical means with either amine or inorganic solvents. There exist applications for these systems, principally in the area of ocean platform natural gas cleanup, but there could be a potential application for the removal of CO_2 from power plant stack-gas. The common name for such systems is Membrane Gas Absorption (MGA) which is investigated mainly by European organizations such as the Paul Scherrer Institute (Switzerland) [8], Aker Kvaerner (Norway) [9], and TNO Environment, Energy and Process Innovation (Netherlands) [10]. Examples of their systems and concepts are presented in Figure 4. Our analysis indicates that these MGA systems can be cost effective, and might even be extended to recovery of CO_2 from the atmosphere in the future.

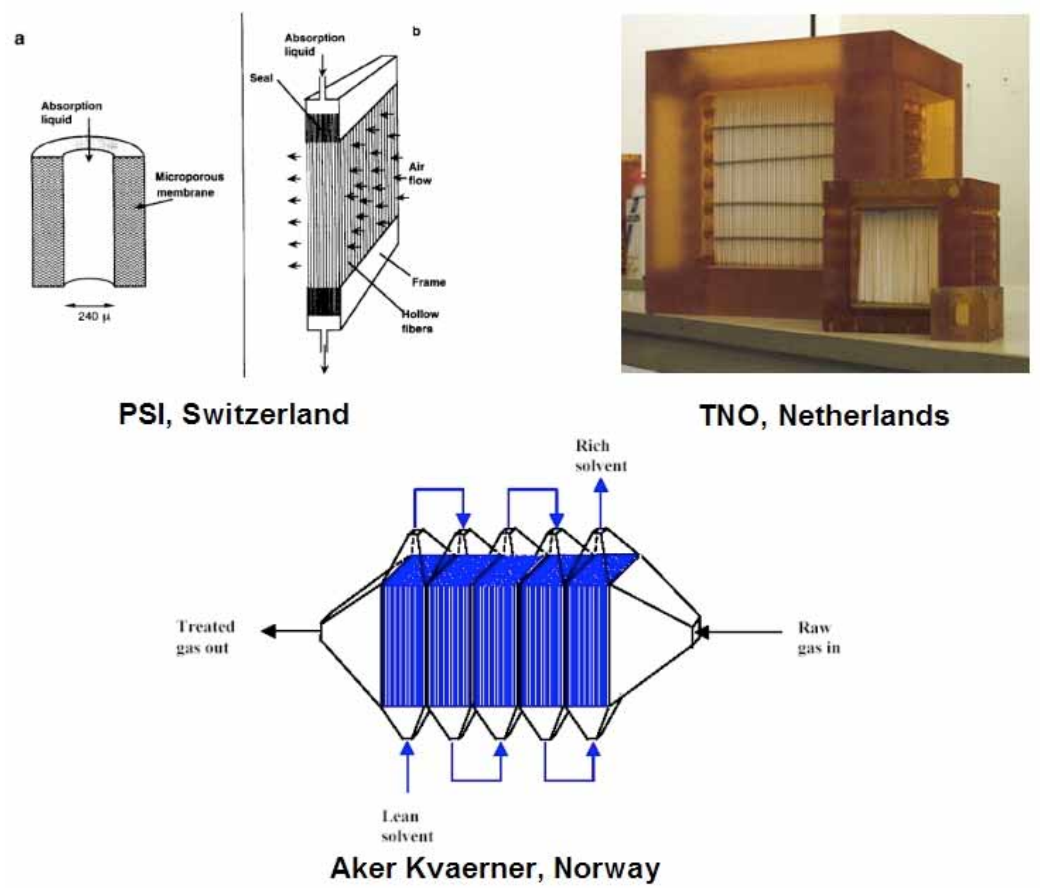

Figure 4. Sample Membrane Gas Absorption Systems and Concepts

5. Economics Estimates

While the concept of using an external source of hydrogen to reduce or even eliminate CO_2 production while making synfuel is exciting, the economics have to be reasonable. We did some simple economics analyses to explore the economics. A leading developer of coal-based synthetic hydrocarbon production is Rentech, Inc. of Denver, CO. They carried out a scoping study for the state of Wyoming of synthetic diesel fuel production from Powder River Basin coal using coal gasification and the Fischer-Tropsch synthesis process. [11] For their baseline economic assumptions, they estimate the cost of synfuel production, including both capital and operating costs, at $0.95/gallon. The baseline assumptions include coal at $5.00/ton and a 6.5% cost of capital. Adjusting these to more realistic values of $30/ton for coal and 10% interest raises the cost of synfuel to $1.85/gallon, still a reasonable cost. We then estimated the impact of getting the hydrogen needed for the F-T process from nuclear power. The amount of coal needed is reduced in half. The cost of the hydrogen was estimated for production using the Sulfur-Iodine thermochemical water-splitting process coupled to the Modular Helium Reactor [12], and also for production by standard low temperature electrolysis using electricity from a Light Water Reactor. For our nominal assumptions, which include \$30/ton coal and 10% interest rate, we estimate a synfuel cost of \$2.06/gallon (MHR) and \$2.36/gallon (LWR), respectively. If we get a \$30/ton credit for each ton of CO_2 not released compared to the coal-based case, these costs fall to \$1.32/gallon and \$1.61/gallon, respectively.

If we get the carbon in the form of CO_2 captured from coal-fired power plants, process it using the Reverse Water Gas Shift reaction to CO and then produce synfuel by the F-T process, we eliminate the need for any additional coal and actually consume all of the CO_2. In this case, the production costs at a 10% interest rate are \$2.75/gallon and \$3.31/gallon for hydrogen from the MHR and LWR, respectively. If we get \$30/ton credit for CO_2 not produced and consumed, these costs fall to \$1.72/gallon and \$2.28/gallon, respectively. These results are summarized on Table 1.

Table 1. Estimated Cost of Synfuel, \$/gallon
(with/without \$30/ton CO_2 credit)

Process	External Hydrogen Source		
	None	Modular Helium Reactor + S-I Process	Light Water Reactor + Electrolysis
Coal gasification + F-T	1.85	-	-
Coal gasification + H_2 from water + F-T	-	1.32 / 2.06	1.61 / 2.36
CO_2 capture + H_2 from water + F-T	-	1.72 / 2.75	2.28 / 3.31

From these estimates we see that the addition of hydrogen obtained from water by thermochemical or electrolytic water-splitting to reduce the amount of coal needed and CO_2 produced in synfuel production, may actually reduce the total production cost of the synfuel, depending on the size of the CO_2 credit that is obtained for non-release or consumption of CO_2. If the carbon is obtained from CO_2 captured from flue gas, the need for additional coal can be eliminated and the net CO_2 production can be negative for only modest cost penalty. Finally, if CO_2 can be extracted from the atmosphere – as our studies have shown to be a little more costly than for CO_2 extracted from coal-fired power plants – then the carbon fuel cycle will have been closed.

6. Systems Analysis

The overall impact of alternative sources of transportation fuels can be seen by examining the CO_2 flows resulting from energy consumption [13]. Our current US petroleum-based transportation economy releases 1811 million metric tonnes (MMt) of CO_2 per year. Approximately another 100 MMt of CO_2 are released in the production and processing of that petroleum. If that fuel were produced from coal by gasification and F-T processing, 1113 MMt of carbon from coal would be needed and 2046 MMt of CO_2 would be produced. Added to the 1811 MMt that is released when the fuel is burned, the net CO_2 release would be 3857 MMt/yr. Comparing these numbers to our current use of coal for electricity production of 565 MMt/yr of carbon as coal and release of 2070 MMt/yr of CO_2, we can see that reliance on coal-based synfuels for our transportation fuel needs would require tripling the amount of coal we use and increasing by half the total amount of CO_2 we produce.

If a CO_2-free source of hydrogen, such as nuclear or solar energy, is provided, production of synfuels could be done using 556 MMt/yr of carbon as coal and producing 1905 MMt/yr of CO_2. This would mean doubling our current consumption of coal but with no increase in our current production of CO_2. If the carbon needed for synfuel were provided from CO_2 captured from flue gas of our current coal-fired power plants, the mass flows match well. About 565 MMt/yr of carbon is used and released in the form of CO_2, and about 565 MMt/yr is needed for synfuel production. We could provide all of our transportation fuel using CO_2 captured from our current coal-fired power plants. This would require no additional coal use and would actually cut our current release of CO_2 in half. Both these scenarios would require a significant increase in the amount of hydrogen that would have to be produced, and would require development on non-CO_2 emitting techniques, such as water splitting, for its production. These alternate scenarios are summarized on Table 2. The dramatic difference in CO_2 production of the scenarios is illustrated on Fig. 5.

Table 2. Fuel Needed and CO_2 Released for Alternate Transportation Fuel Sources

Units: MMt/yr	Transportation Fuel From			
	Oil	Coal	Coal + H_2 from water	CO_2 + H_2 from water
Oil needed	612	--	--	--
Coal needed	--	1113	556	0
H_2 needed	--	--	130	260
CO_2 produced	~100	2046	104	-1811
CO_2 released on use	1811	1811	1811	1811
Net CO_2 released	1911	3857	1905	0
Current C as coal use/CO_2 produced: 565/2070 MMt/yr, H_2 use: 10 MMt/yr				

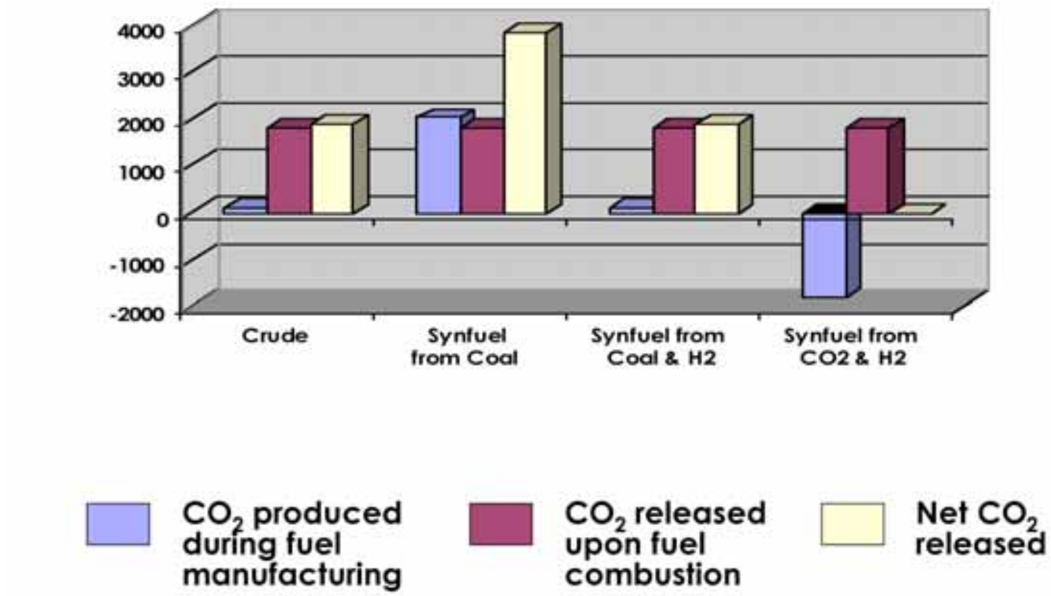

Figure 5. CO_2 released by alternative sources of transportation fuels, MMt/yr

7. Conclusions

Production of synthetic hydrocarbon fuels can help with the growing shortage of petroleum. In production of synfuels from coal, one atom of carbon is produced as CO_2 for every atom produced as CH_2 in the synfuel. If hydrogen is provided from an external, non-fossil source, such as solar, wind or nuclear production of hydrogen from water, the synfuel production process need not produce any CO_2. However, the synfuel, when burned for transportation will produce and release the contained carbon as CO_2. Since the synfuel would be a replacement for petroleum-based fuel, there would be no net increase in the production or release of CO_2. If the hydrogen is provided from an external, non-fossil source, and if the carbon is provided by capture of CO_2 from existing coal-fired power plants, the total U.S. release of CO_2 can be halved. Hydrogen would be used to produce CO from CO_2 in the reverse water gas shift reaction and to produce $[CH_2]_n$ from CO and H_2 in the Fischer-Topsch reaction. Three molecules of H_2 would be needed for every moiety of CH_2 produced.

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Our economics estimates indicate that use of hydrogen in the synfuel production process would reduce the consumption of coal by a factor of two and actually may result in a cheaper synfuel product. Capture of CO_2 from flue gas instead of using coal as the source of carbon for the synfuel appears to be practical (and may be required to help mitigate climate change), and would allow synfuel to be produced with only minor cost increase over coal-based synfuel production.

This hydrogen synfuel concept would allow us to significantly reduce our use of petroleum, and cut our CO_2 emissions in half, while still using our existing hydrocarbon-based transportation infrastructure. The hydrogen production infrastructure needed for synfuel production could be used to produce hydrogen for direct application via fuel cells in the future. A hydrogen-synfuel economy would provide a bridge to a pure hydrogen economy.

8. References

1. P. R. A. WELLS, "Oil Supply Challenges—1: The Non-OPEC Decline," *Oil and Gas Journal*, 20–28 (February 21, 2005).
2. M. King Hubbert, "Nuclear Energy and the Fossil Fuels," Publication No. 95, Shell Development Company, 1956.
3. Association for the Study of Peak Oil, available at http://www.peakoil.net.
4. R.L. Hirsch, R. Bezdek and R. Wendling, "Peaking of World Oil Production: impacts, mitigation and risk management," Feb. 2005, available at http://www.netl.doe.gov/otiic - "World Oil Issues".
5. U.S. DOE Energy Information Agency: http://www.eia.doe.gov - "Natural Gas"
6. For an exhaustive review of the Fischer-Tropsch process, Syntroleum Inc. sponsors a website: http://www.fischer-tropsch.org/.
7. Meyer Steinberg and Vi-Duong Dang, "Production of Synthetic Methanol for Air and Water Using Controlled Thermonuclear Reactor — I. Technology and Energy Requirement," Energy Conversion, Vol. 17, pp 97-112, Pergamon Press, 1977.
8. Samuel Stucki, et. al, "Coupled CO_2 Recovery From the Atmosphere and Water Electrolysis: Feasibility of a New Process for Hydrogen Storage," International Journal of Hydrogen Energy, Vol. 20, pp. 653-663, 1995.
9. K.A. Hoff, H.F. Svendsen, O. Juliussen, O. Falk-Pedersen, M.S. Grønvold and D. B. Stuksrud, "The Kvaerner/Gore Membrane Process for CO_2 Removal — Mathematical Model and Experimental Verification," AIChE annual meeting 2000, Los Angeles.
10. Paul H.M. Feron, "CO_2 Removal Using Membrane Gas Absorption," presented at Euromembrane, Hamburg, Germany, 30 September 2004.
11. http://www.rentechinc.com/process-technical-publications.htm Presentation to the Wyoming Governor's Office and the Wyoming Business Council, April 14, 2005 Cheyenne, Wyoming
12. K. R. Schultz, et. al, "Large-Scale Production of Hydrogen by Nuclear Energy for the Hydrogen Economy," National Hydrogen Association Annual Meeting, 2003.
13. http://eed.llnl.gov/flow/ "US 2002 Carbon Dioxide Emissions from Energy Consumption," Lawrence Livermore National Laboratory