AFTER PETROLEUM IS GONE, WHAT THEN? ORGANIC CARBON SOURCES FOR ALTERNATIVE TRANSPORTATION FUELS

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INTRODUCTION

Dire predictions regarding the availability of petroleum and continuation of our present civilization, are indicated by the title of a recent presentation "The Peak of World Oil Production and the Road to the Olduvai Gorge," which predicts the crash of civilization in 2030.[1] There are other more conservative predictions for just a peak in petroleum production in 2005.[2] In a previous paper at this conference I projected the peak in oil production to 2040.[3] Recently the Energy Information Administration projected a 2.2 % annual increase in oil production through the year 2020.[4] Continued improvements in exploration, drilling and production technologies provide the capability for continued oil production rate increases.[5] On this basis, petroleum engineers and petroleum engineering students can count on ample job opportunities for the foreseeable future.

Still, it is obvious that there is a finite amount of petroleum on that planet Earth, which can be produced for a reasonable price. That reasonable price for petroleum is the price at which liquid fuels can be produced from sources other than petroleum. These alternative sources of liquid fuels are the topic of this paper. All reasonable liquid fuels contain carbon, hence the subtitle for this paper "Organic carbon sources for alternative transportation fuels." These alternative sources of organic carbon are numerous and far more abundant than petroleum. Technologies for conversion of alternative organic carbon sources into transportation fuels range from "proven and ready to use" to "wishful and uncertain." The price for this conversion to liquid fuels ranges from "almost competitive today" to "outrageously high."

The logic for ignoring global warming in this study, and relationship of alternative carbon sources to the proposed use of hydrogen as an alternative transportation fuel will be given in the later portion of this paper.

ALTERNATIVE ORGANIC CARBON SOURCES

The following alternative sources of organic carbon for transportation fuels will be considered in this paper:

- Natural gas
- Coal and lignite
- Western (Greenriver) oil shale
- Devonian shale (OH, KY, TN, IN)
- Natural gas hydrates
- Biomass residues
- Intentionally grown biomass

These organic carbon sources will now be discussed, followed by a discussion of the chemical processes by which organic carbon can be converted into liquid transportation fuels.

Natural gas Natural gas is the most convenient fuel for small-scale stationary uses. For this reason there is a long-term logic for conserving natural gas for this purpose. Long-term logic and medium-term economics result in different decisions, and in a free society medium-term economics wins. In this circumstance, natural gas has become an attractive fuel for large-scale generation of electricity, and at the time of writing this paper gas prices have become chaotic — $9/thousand cubic feet.[6] Still, natural gas is abundant. Its world-wide reserves approximate that of petroleum. Natural gas is a very excellent engine fuel, but also is very inconvenient to carry on the vehicle using it. For this reason conversion of natural gas into liquid transportation fuels will be discussed later in this paper.

Coal and lignite Coal and lignite are our most abundant and usable domestic organic carbon sources. The technologies for large-scale, environmentally-benign mining are already proven, since coal is still the dominant fuel for electric utilities. It is estimated that 2,800 billion tons of coal potentially are available in the US.[7] On a heating value basis, this is equivalent to about 9,650 billion barrels of petroleum.

Western (Greenriver) Oil Shale Western oil shale is abundant in Colorado, Utah and Wyoming. Considerable investment has been made in mining and processing technologies. In the period of about 1940 to 1980, oil shale was thought to be the next source of liquid transportation fuels. The environmental problems associated with mining the shale, and then disposal of the spent shale are immense. In this circumstance, permitting for commercial shale utilization would be difficult and expensive. The amount of oil shale that exists is large: 2,000 billion barrels domestically and 12,000 billion barrels on our planet.[8,9]

Devonian shale Devonian shale is also known as eastern shale or black shale. This resource is located in Ohio, Kentucky, Tennessee, and Indiana. It is exceedingly abundant, 800 billion-barrels equivalent have been identified just near outcrops, and the deeper resources have not been estimated.“’ Utilization of this shale has not been demonstrated on a large scale, since the pyrolysis processes used for Greenriver shale do not provide an adequate yield of liquid products.

Natural gas hydrates Natural gas hydrates are a significant problem in pipelining natural gas, but a problem that has been effectively managed. Natural gas hydrates as found in nature, in deep permafrost and deep ocean sediments are an immense opportunity for energy production. The amount of natural gas contained in the hydrates is truly vast relative to conventional natural gas resources.“ No process has been demonstrated to recover natural gas from these hydrates. In addition the potential impact on the environment may be large. In this circumstance, natural gas hydrates remain a “wishful” but still vast source of fuels.

Biomass residues Biomass residues are available in small scattered amounts. Forestry and lumber production residues are already effectively used as boiler fuel. Municipal solid waste and most agricultural residues are still not an economic source of energy. **A** tipping fee is necessary for their disposal. These residues could be converted to liquid fuels, but it is more expedient to use them as a local boiler fuel using existing technologies, when economic.

Intentionally grown biomass Since by-product biomass residues are not economic as a bulk energy sources, it would not be expected that intentional growth **of** biomass for energy would be economic either. Intentionally grown biomass for energy must compete for land and irrigation water resources directly with more profitable food and fiber crops. In addition the potential amounts of intentionally grown biomass are small relative to transportation fuel demand.[12]

PROCESSES FOR CONVERSION OF ORGANIC CARBON TO LIQUID TRANSPORTATION FUELS

The carbon conversion processes to be considered in this section include the following:

- Conventional petroleum refining
- Gasification and reforming
- Pyrolysis
- Hydrogenation
- Fermentation

The review of these processes will be very brief, just to indicate the nature of the process, and its state of development.

Conventional petroleum refining Conventional petroleum refining is mentioned as a carbon conversion process since proven modifications of the existing refining process potentially can convert all the carbon present in petroleum into liquid transportation fuels. When petroleum prices were relatively low, petroleum refiners found that it was cost effective to produce liquid transportation fuels with coking and cracking processes. In this circumstance, the “excess” organic carbon in petroleum was rejected as coke and then gasified along with refinery wastes. The resulting synthesis gases can be burned for boiler fuel, as well as for production of petrochemicals and hydrogenation of petroleum products.” Refiners even market excess electricity that results from cogeneration. Significant increases in petroleum prices serve to change this circumstance, and so make it desirable to increase the yields of liquid transportation fuels from petroleum. This task is accomplished by using hydrogenation and hydrotreating for production of liquid transportation fuels. In addition, the potential exists for using coal or lignite as both a source of fuel and of hydrogen for a petroleum refinery. By this means, it will be possible to produce more than one barrel of transportation fuel per barrel of crude petroleum processed. For this reason conventional petroleum refining is listed as a means of converting organic carbon to transportation fuels. The proposed modification of petroleum refineries will happen on an incremental basis as the price of oil is perceived to stabilize at a moderately high level, perhaps $30/bbl. The incentives to refine heavy oil and tar will also increase as the price for conventional petroleum stabilizes at a higher level.

Gasification and reforming The objective of gasification and reforming processes is to convert organic carbon into synthesis gas, a mixture of carbon monoxide and hydrogen. This synthesis gas can then be reacted to produce a variety of liquid fuels, and also "petrochemicals." The essence of the gasification process is the reaction of carbon with water:

$$C + H_2O \rightarrow CO + H_2$$

This reaction is written in an overly simplified form to stress the fact the gasification reaction is "unbuming" water. When hydrogen containing fuels are burned to release energy, water is a product of combustion. When water is converted to hydrogen by gasification, approximately the same amount of energy must be supplied. In terms of thermochemistry, gasification is a strongly endothermic process, and this fact is a central feature in designing gasification processes. The necessary energy for the gasification reaction is frequently supplied by adding pure oxygen to the reaction mixture. The stated equation is also oversimplitied because carbon dioxide is also produced and the reaction is reversible. Chemical equilibrium is reached among the species present, so the immediate yields are not 100% of the desired products. The endothermic nature of the gasification process makes the overall thermal efficiency of gasification processes to liquid fuels and petrochemical about 50%, in spite of energy conservation efforts.

Coal gasification is commercial now, in spite of the above factors, and the difficulty of processing solids at high pressures. Eastman Chemicals in Kingsport, Tennessee built their initial coal gasification plant in 1983, and then expanded it in 1991, proving the attractiveness of coal gasification in their circumstances. They process 2.1 million tons of coal per year for production of acetic anhydride. Coal gasification is also accomplished at the Great Plains Synfuels Plant in Beulah, South Dakota, where 6.3 million tons of lignite are converted into 5.4 billion SCF of synthetic natural gas. When South Africa was economically isolated due to their apartheid policies, they built their SASOL coal gasification facilities to provide them an internal source of liquid transportation fuels. The SASOL facilities continue in operation today.[14]

Gasification of natural gas and other light hydrocarbons is termed "reforming." Natural gas is much easier to convert to synthesis gas than coal, since coal is a solid containing considerable ash. The energy required for gasification either can be supplied by partial oxidation of the natural gas, or by heating a natural gas and steam mixture in a furnace called a reformer. Production of ammonia, methanol, acetic acid, etc. is accomplished in many national and international facilities today by means of these steam reformers producing synthesis gas.

Synthesis gas can be processed into a wide variety of liquid fuels. Most directly, Fischer-Tropsch, FT, synthesis can be used to produce liquid transportation fuels, particularly diesel fuels. Shell is producing premium diesel fuel in Malaysia from natural gas liquids; FT synthesis is also employed in South Africa SASOL facilities. Methanol is produced directly from synthesis gas today. In theory, methanol is a very good SI engine fuel, but it is not widely used. Methanol can be converted directly to high octane gasoline by the Mobil M-gasoline process. This process was to be commercialized in New Zealand but low petroleum prices have confused the situation. Synthesis gas can be converted into dimethyl ether which is a good diesel fuel, whereas methanol is not." Currently, announcements for new natural-gas-to-liquid fuel plants are frequent. One example is the 75,000 barrel-per-day plant for Egypt, to begin operation in 2005 using Shell's middle distillate synthesis process.[16]

It should be noted that wood and other organic materials can be gasified, and the synthesis gas used to produce liquid fuels, and so have environmentally-friendly and renewable liquid fuels. It could also be noted that in WWII that civilian vehicles were operated directly with gas generated by wood gasifiers mounted on the car. This use of solid fuel to operate a vehicle was very inconvenient, and the on-car gasifiers were rapidly abandoned when WWII was over, again illustrating the need for convenient liquid transportation fuels.

In summary, gasification can convert both coal and natural gas to good liquid transportation fuels by commercially proven processes. Long-term projections of petroleum prices, and uncertainties associated with these price projections are crucial concerns with regard to the construction of synthetic liquid fuel facilities using gasification technologies.

Pyrolysis Pyrolysis is superficially a very simple process. Heat any material containing organic carbon in the absence of oxygen, and it will be converted into three products; liquid oils, combustible gases, and char. Pyrolysis is also known **as** "destructive distillation." Manufacture of metallurgical coke and production of charcoal are examples of commercial pyrolysis processes. Coal tar from the pyrolysis of coal for coke was the major source of simple organic chemicals now known as ''petrochemicals'' before petrochemicals existed.

Pyrolysis of Greenriver oil shale, termed "retorting," is the process of choice for production of shale oil. At least two oil shale processes have been demonstrated in a reasonably large-scale: the Union, now Unocal, retort and the gas combustion retort. Unocal closed its commercial, but still federally subsidized, 10,000 barrel-per-day oil shale plant near Parachute Creek, Colorado, June 1, 1991.[17] It is expected that the economics of oil shale retorting will be less attractive than coal gasification, although some individuals might question that point. The environmental impact of mining oil shale and then disposing of the spent shale ash containing such toxic residues as arsenic is considerable. In addition, significant amounts of water are required for the overall retorting process.

Pyrolysis can also be applied to coal, prior to burning the remaining char in electric power plants. By this means organic hydrogen and carbon will be conserved for liquid fuels, and only the remaining carbon would be burned for electric power production. Superficially this is an attractive concept, and it has received minimal testing. I attempted to facilitate further development of this process without success in the 80's.[18] Coal pyrolysis may become more attractive as our petroleum reserves decrease. The economics of coal pyrolysis versus coal gasification for liquid fuels are not obvious at this time.

Hydrogenation Hydrogenation is inherently an expensive process, requiring hydrogen at high pressures and special catalysts. It is basically a known process, and it is applied to petroleum products as needed, particularly to remove unwanted constituents such as sulfur and aromatics. Hydrogenation has been considered for direct liquefaction of coal, Hydrogenation has been tested on a small-scale to get increased yields of oil from the eastern, Devonian oil shale: the HTORT process. The process developers estimated that 400 billion barrels of oil could be made available from Devonian shale using their HTORT process.[19] For large-scale production of liquid fuels from alternative carbon sources, hydrogenation is not considered economically attractive. I am not aware of the HYTORT process being reconsidered in recent years.

Fermentation Ethanol is a good fuel for SI engines. Producing ethanol via fermentation makes it a renewable and environmentally friendly fuel. It also perceived as supporting the rural economy when the fermentation feed stock is starch or sugar. I doubt that a statistical analysis of corn price and volume would verify that this perception is true. The costs for ethanol are rather high relative to gasoline and food quality materials are being used for their fuel value. In spite of these inherent disadvantages tax incentives have been provided for use of ethanol in gasoline. Commercially, ethanol for solvent and industrial usage is produced as an ordinary petrochemical, the hydration of ethylene directly with water.

In another proposed fermentation process, cellulose is hydrolyzed by either acids or enzymes into sugars. The sugars are then fermented into ethanol. This process uses an economical non-food starting material, cellulose as contained in wood or even municipal solid waste. Cellulose hydrolysis has been tried for over fifty years without sustained commercial success. There are inherent reaction rate and reaction yield constraints that prevent its success. The concept has been reviewed relatively recently.[20]

While it is not a fermentation process, another source of biomass based transportation fuel should be noted in this paper. That source is vegetable oils and animal fats that can be converted into a good diesel fuel by a relatively simple chemical process, transesterification with methanol. Transesterification reduces the viscosity of vegetable oils so it becomes a good diesel fuel frequently called biodiesel. The major problem with biodiesel is that the primary raw material, vegetable oil, costs on the order of $3 per gallon. Used cooking oils and inedible tallow are available for about half that cost. They are available in limited amounts, and they also have value in animal rations and in pet foods.

THE HYDROGEN ECONOMY

Hydrogen for fuel cells is receiving increasing attention as a potential route for transportation fuels. It should be noted that the most economic source of hydrogen is reforming of natural gas as discussed earlier in this paper. This concept is already being used for fuel cell powered buses in California,?' but there is little mention of cost on an unsubsidized basis. Coal gasification is also a potential source of hydrogen for fuel cells. Low molecular weight hydrogen would be a more difficult fuel to transport on a vehicle than even natural gas, which is already considered inconvenient for use as a transportation fuel. Hydrogen also has special safety issues. For this reason, on-board reforming of hydrocarbons to produce hydrogen is being considered. Designing an economic miniaturized reformer on-vehicle hydrogen production would seem to a very difficult, if not impossible task.

GLOBAL WARMING

Global warming has not been considered in this paper, for a good reason. The limited reductions in emissions of fossil carbon dioxide, which might be specified by the Kyoto accord, are more easily accomplished at electric power generation facilities, not on vehicles. There are several options to reduce fossil carbon dioxide emissions associated with electric power production as follows:

- Expand nuclear power usage.
- Develop deep-hot-rock geothermal (conventional geothermal and hydroelectric have limited opportunities to expand).
- Use additional renewable resources such as wind-power and solar.
- Use biomass fuels that have no net carbon dioxide emissions.
- Sequester carbon dioxide produced from utility plants and coal gasification plants in geologic formations or on the deep ocean floor.

The discussion of the above CO_2 management options would require another paper. Using a selection of the above options for reduction of fossil carbon dioxide emissions associated with electric generating facilities is far more easily accomplished than constraining the use of carbon containing liquid transportation fuels.

CONCLUSIONS

The following conclusions can be drawn:

- Premium transportation fuels from natural gas via gasification are commercial now in some locations, and these facilities are expected to increase.
- Proven commercial technology exists for coal gasification, to produce premium transportation fuels.
- Other sources of organic carbon for transportation fuels are more difficult to process economically, and so they will not be developed for the foreseeable future.
- The rate at which facilities for gasification/reforming natural gas and coal are built will depend upon companies and independent investor’s perception of stable, relatively high prices for petroleum.

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Dr. Parker has been involved in energy related research at many levels:

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