



ENERGY SOURCES INTEGRATION

Integrating Major Energy Sources With Chemical Conversion Processes for Fossil Fuels

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Executive Summary

Carbon dioxide (CO₂) and other greenhouse gas emissions are already being regulated by the United States and other countries pursuant to climate change mitigation policies. One way to reduce the impact of greenhouse gas regulation is to reduce greenhouse gas emissions from energy and fuel production, as well as from energy consumption (by making more efficient use of fuels and selecting different types of fuels). This white paper addresses greenhouse gas emissions, specifically CO₂, generated by different fuels and the opportunities to reduce CO₂.

Carbon dioxide emissions from fuel use can be reduced by using more hydrogenated fuels, which inevitably produce CO₂, but at lower rates per British thermal unit or kilocalorie. Methane fuel has the highest hydrogen-carbon ratio, yet much of it comes from conventional gas and new shale-gas resources that ultimately are finite. The following analysis suggests ways that integrating renewable resources with existing chemical conversion infrastructure for fossil fuels might reduce CO₂ emissions in a more sustainable way.

To make use of all of the nation's energy resources efficiently and economically, it is important to consider integration of solar, wind, nuclear, and biomass into the nation's existing infrastructure for the chemical conversion of fossil fuels. The advent of large supplies of natural gas in the United States from improved drilling techniques—and the resulting increased price spread between natural gas and crude oil—have also greatly increased the importance of integrating this new shale gas supply with chemical conversion technologies to produce liquid fuels. Adopting this chemical conversion approach will ensure that the resulting liquid fuels will be clean-burning and minimize CO₂ emissions. Such integration could also enhance the value of alternative energy sources, promoting their use and increasing the nation's energy independence, while utilizing the “sunk cost” of the nation's extensive infrastructure of these chemical conversion technologies. For example, various methods for co-processing coal, heavy oils, shale oils, tar sands and biomass could result in more economical routes to cleaner burning fuels, with attendant reduction in carbon dioxide production.

In another example, hydrogen can be obtained from sources that don't produce CO₂ or that produce hydrogen in a thermodynamically favorable way that takes into account total CO₂ emissions in its manufacture and use of these

sources. These resources may be used more economically to upgrade fossil and biofuels chemically, as well as in fuel cells for transportation. This H₂ upgrading route might yield significant carbon dioxide reduction while reducing the need for a new hydrogen delivery infrastructure. In yet another example, biofuels may be processed catalytically to conventional fuels, enabling their unlimited use in engines without incompatibility problems in distribution systems.

The bottom line is that the integration of existing chemical conversion technologies with the nation's various energy sources will enable us to more economically use existing fuels, petrochemical chemical, and engines, while reaping the benefits of lower carbon impact from new, increasing energy sources, such as solar, wind, nuclear, and biomass where they are economically viable.

Introduction

To ensure that U.S. energy policy achieves and maintains optimal coherence, efficiency and economic robustness, it should continually adapt to accommodate technological developments as well as develop a strategy for integrating them with existing chemical conversion technologies. Such integration may allow alternative energy sources to play a potentially greater role in supplying future energy needs by capitalizing on the sunk cost of the nation's current infrastructure for chemical processing of fossil fuels.

Members of the American Institute of Chemical Engineers work in all aspects of the energy industry and have extensive involvement with chemical conversion technologies. Therefore, they can make key contributions to the design of an overall energy strategy.

The need for an overall energy strategy has been recognized by the National Academy of Engineering and the National Academy of Sciences with their initiation of the "American Energy Futures" study, administered by the National Research Council. This two-phase study, chaired by Harold Shapiro, president emeritus of Princeton University (Shapiro, reference 1), should facilitate a productive national discussion of the nation's energy policy and energy future. The study's first phase consists of reports from three panels; one on energy efficiency, another on electricity from renewable sources, and a

third on alternate liquid transportation fuels (Ramage, ref. 2). The second phase focused on strategic, tactical, and policy issues.

Most studies of future energy strategy focus on a specific energy source, such as solar, wind, nuclear, or biomass. They look at the impact of these specific sources on future transportation and electrical needs, such as electric cars and the hydrogen economy, without considering how the source could be integrated with existing chemical conversion technologies. Reuel Shinnar (Shinnar, ref. 3) was among the first to recognize the potential advantages of integrating alternative energy sources with existing chemical conversion technologies. Robert Williams (ref. 4) has shown that synergies are possible in the co-gasification of coal and biomass when coupled with Fisher Tropsch and ZSM-5 processing. Recently, the Alternate Liquid Transportation Fuels panel of the Shapiro Report (Ramage, ref. 2) completed a comprehensive study of the economics of integrating chemical conversion technologies for biomass and coal.

Another very recent paper (ref. 5) published in *Computers and Chemical Engineering* using Figure 1 below, described the key optimal economic path in the integration involves the direct cascade of Fisher-Tropsch (FT) effluent to processing with a ZSM-5 zeolite to make conventional gasoline and diesel fuel without the need for an expensive separate facility to upgrade the FT effluent. The route through methanol, directly cascaded to ZSM-5, also offers a similar economic path to conventional fuels. There likely will be a decades-long period when fossil fuels remain the main source of liquid fuels, while electric/hybrid cars, for example, may gain market share. It's also likely that some of the current liquid fuels, such as jet, diesel, and marine fuels, may still be important well into the next century. It is also unlikely that petrochemicals, particularly aromatics and olefins, will be displaced by alternates in any reasonable timeframe. During this long transition period, it could be important to integrate alternate fuel sources with existing fossil fuel chemical conversion technologies to increase efficiency and reduce carbon dioxide emissions.

The goal of this AIChE briefing paper is to provide an overview of the broadest possible range of energy sources and related chemical transformation technologies, and suggest broad strategies for their efficient and economic integration.

Processes for Integrating Existing Chemical Conversion Technologies with Alternate Energy Sources

Electricity and Hydrogen Manufacture

Figure 1 demonstrates how electricity and hydrogen (H_2) can be made from a number of sources. The advantage of making electricity from nuclear, solar, wind, and geothermal sources is that it can be produced with no attendant carbon dioxide (CO_2) production. By employing electrolysis, some of this electricity could be used to make H_2 , which could be used in upgrading fossil fuels or employed in fuel cells to power cars and light trucks. However, due to thermodynamic losses and process inefficiencies, the electrolysis step will consume 20 to 25 percent of the electrical energy. Making H_2 from fossil fuels is cheaper, but the attendant CO_2 production must be traded off against the lower cost. The H_2 fuel cell is about 60 percent efficient, so that the overall efficiency (with the electrolysis step) is about 45 to 50 percent, which is similar to an efficient diesel engine (Ramage, ref. 2).

Since a combined electric motor and battery is 80 to 85 percent efficient, an all-electric car may offer more energy efficiency compared to an H_2 fuel cell powered car. Therefore, it may possibly be cheaper to feed this electricity directly to the grid, where it can be used to charge the batteries in electric cars or plug-in hybrids. An important future study would be to determine if the electric car or plug-in hybrid will offer a lower cost transportation system than H_2 fuel cells, since expanding the existing electrical grid will probably be much cheaper than building a new H_2 infrastructure.

Most fossil fuels can be gasified and the resulting carbon monoxide (CO) and H_2 can be Water Gas Shifted to produce more H_2 , but at the expense of more CO_2 production. Herbert Cooper (ref. 6) has recently explored the economic advantages of the gasification/methanol route in co-producing electricity and methanol from coal. Natural gas can also be steam reformed to produce CO and/or H_2 . In addition, lighter fractions of crude oil (naphtha) can be catalytically converted to higher-octane components as well as H_2 . Finally, biomass can be gasified to CO and H_2 or shifted to all H_2 . Biomass is considered essentially CO_2 neutral, because the resulting CO_2 will be balanced by replacement plant growth.

Use of H₂ in Chemical Conversion Processes

H₂ produced by any of the above methods can also be used in a number of processing steps. Coal can be fed to the Bergius process, in which the finely divided coal can be liquefied catalytically at high H₂ pressure. The subsequent heavy coal liquid can be upgraded with a number of catalysts and high H₂ pressure. For example, catalytic hydro-cracking and catalytic desulfurization and denitrogenation are widely used to upgrade coal liquids to conventional fuels. These same routes can also upgrade heavy oils and tar sands. However, due to the high H₂ pressure required, direct liquefaction may be more expensive than the indirect route, i.e. gasification/Fischer-Tropsch.

Coking, another conversion process, is used extensively in petroleum refining. Through a thermal soaking process, it converts heavy fractions to lighter olefinic products and solid petroleum coke. These lighter products must be upgraded with H₂ processing to reduce the olefin content and increase product quality. The coke produced can be either gasified to CO and H₂ or disposed of as easily sequestered solid carbon. Since coking, with coke sequestration, competes directly with gasification, more work is required to assess the relative economics.

In shale retorting, another thermal process, shale is partially burned to heat the petroleum-like material locked in the rock and then capture it as shale oil. This liquid must be upgraded by catalytic H₂ processing to reduce its high nitrogen content and yield useful fuels. The spent shale, with its high carbon content, can then be buried in landfills or in the mines where it originated.

During the coming transition period, when fossil fuels will continue to be used alongside growing alternate energy sources, it may make economic sense to use some of the H₂ produced from the non-CO₂ sources to upgrade fossil fuels, and reduce their carbon impact. Not only do the H₂ upgraded fossil fuels produce less CO₂, they can use the existing fuel distribution system. If H₂ is made from fossil fuels, then, stoichiometrically, the H₂ used in a fuel cell or used in upgrading fossil fuels, will give equivalent overall CO₂ reduction. The overall economic impact of how much H₂ to use in upgrading fossil fuels as opposed to direct use in fuel cells should be an important future study.

A large part of the nation's transportation sector (i.e. over-the-road diesel trucks, heavy construction equipment, airplanes, and trains) will continue to require H₂ upgraded hydrocarbon fuels. In addition, the

manufacture of petrochemicals and polymers will still require the chemical conversion technologies outlined above (Shinnar, ref.3).

Co-processing of Biomass and High-carbon Fossil Fuels

As you can see in Figure 1, the heavier fossil fuels (i.e. coal, tar sands, heavy oils, shale oil) can be integrated with biomass (i.e. wood, plant stalks) through gasification and water-gas-shift technologies. Both Williams (ref. 4) and Ramage (ref. 2) have outlined comparative economics for co-gasification of coal and biomass. All the feed materials are linked to conventional fuels through the CO and H₂ produced in gasification and subsequently being converted in either the Fischer Tropsch process or the methanol process. George Huber (ref. 7) has presented a comprehensive review of various routes to biomass fuels.

With its flexibility to make a broad range of products, including conventional fuels, alcohols and oxygenates, lubes, waxes and petrochemicals, the Fischer Tropsch (FT) process, coupled with ZSM-5 processing, will play a key role in any integration effort. The FT process, proven in large-scale plants in Germany during World War II, as well as in subsequent use in South Africa, Borneo, and Qatar, yields very pure products. That's because all impurities must be removed from the H₂ and CO feed to protect the FT catalyst. For example, FT-based fuels used in Germany's zeppelins were so pure the exhaust-gas condensates could be used for showers and dishwashing. The diesel fuel has a very high cetane number with no sulfur and can make an excellent blending stock for conventional diesel.

The methanol produced can go directly to market or be converted by ZSM-5 to high-octane gasoline or olefins for petrochemicals. This technology has been demonstrated in a large-scale plant in New Zealand. FT products require fairly extensive upgrading using conventional petroleum refining technology, so, when only gasoline or diesel is required, part or all of the FT effluent can be fed directly to ZSM-5 processing for conversion directly to high-octane gasoline or high-quality diesel. Depending on process conditions, the ZSM-5 step can convert FT effluent and methanol to light olefins for use in polymers and petrochemicals (Weisz, ref. 8).

Vegetable oils and animal fats can be upgraded to biodiesel by hydrogenation and purification, or fed directly to ZSM-5 processing for conversion to conventional fuels (Weisz, ref. 8). Since upgrading these liquid

biofuels will be expensive, it may be more cost-effective to use the one-step ZSM-5 route to produce high-quality conventional fuels.

Research to find an economical route to fermenting cellulosic material to alcohol is ongoing. Depending on its success, gasifying this cellulosic material and using the FT/ ZSM-5 route may make more economic sense. Additionally, because ZSM-5 can convert almost any alcohol, oxygenate, or biodiesel to conventional fuel, attention should be paid to the comparative cost and impact of transporting alcohol cross-country for blending purposes, as opposed to converting it to gasoline or diesel and shipping it via existing pipelines. With this approach, an unlimited amount of alcohol or biodiesel could be used as a fuel, without affecting current engine performance.

In Conclusion

A possible future route to meet the nation's energy needs is integration of solar, wind, nuclear, and biomass into the nation's existing infrastructure for the chemical conversion of fossil fuels. Doing so may translate into more efficient and economical use of all of the nation's energy resources and ensure that the resulting liquid fuels will be cleaner-burning, thereby further reducing regulated CO₂ emissions.

Such integration will enhance the nation's ability to use alternative energy sources and promote their use, increasing the nation's energy independence and security, while taking advantage of the nation's very substantial infrastructure for chemical/fuel conversion technologies.

References

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Appendix

Commercial Chemical Conversion Processes for Energy Integration

Catalytic Liquefaction

Feed: coal, biomass, heavy oils, tar sands, shale, peat, H₂

Products: all conventional fuels

Gasification

Feed: coal, biomass, heavy oils, tar sands, shale, peat, natural gas, oxygen, air

Products: CO₂ and H₂

Thermal Conversion (coking, retorting)

Feed: coal, heavy oils, biomass, shale, tar sands, peat

Products: coke, all conventional fuels, C₁ to C₃ gases, olefins

Catalytic Water Gas Shift

Feed: CO, H₂, H₂O

Products: H₂

Catalytic Reforming of Natural Gas

Feed: natural gas, C₁ to C₅ gases, C₁₂

Products: CO₂ and H₂

Methanol Production

Feed: CO and H₂

Product: methanol

Fischer-Tropsch Process

Feed: CO and H₂

Products: higher alcohols, paraffins, light olefins, diesel, gasoline, waxes, lubricating oils

Alcohol Conversion to Hydrocarbons (ZSM-5)

Feed: methanol, ethanol and higher alcohols, raw Fischer-Tropsch effluents, bio alcohols, bio olefins, bio oils

Products: all conventional fuels, olefins

Catalytic Naphtha Reforming

Feed: C₅ to C₂₀ hydrocarbons

Products: high-octane gasoline, H₂, petrochemicals

Fermentation

Feed: grains, cellulosic parts of plants, sugar cane,

Products: ethanol

Thermal and Catalytic Olefins Production

Feed: C₂ to C₄₀ paraffins

Products: C₂ to C₄₀ olefins, petrochemicals, H₂

Catalytic Methanation

Feed: CO₂, CO, H₂

Products: CH₄, some higher hydrocarbons

Catalytic Hydrocracking

Feed: heavy hydrocarbons, H₂

Products: low-sulfur conventional fuels

Catalytic Desulfurization and Denitrogenation

Feed: fuels high in sulfur and nitrogen, H₂

Products: low-sulfur conventional fuels

Catalytic Isomerization

Feed: C₁₀ to C₆₀ hydrocarbons, H₂

Products: higher octane and cetane fuels, low pour point diesel, high viscosity index lubricating oils