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Sustainable fuel for the transportation sector

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A hybrid hydrogen-carbon (H_2CAR) process for the production of liquid hydrocarbon fuels is proposed wherein biomass is the carbon source and hydrogen is supplied from carbon-free energy. To implement this concept, a process has been designed to co-feed a biomass gasifier with H_2 and CO_2 recycled from the H_2-CO to liquid conversion reactor. Modeling of this biomass to liquids process has identified several major advantages of the H_2CAR process. (*i*) The land area needed to grow the biomass is <40% of that needed by other routes that solely use biomass to support the entire transportation sector. (*ii*) Whereas the literature estimates known processes to be able to produce ≈30% of the United States transportation fuel from the annual biomass of 1.366 billion tons, the H_2CAR process shows the potential to supply the entire United States transportation sector from that quantity of biomass. (*iii*) The synthesized liquid provides H_2 storage in an open loop system. (*iv*) Reduction to practice of the H_2CAR route has the potential to provide the transportation sector for the foreseeable future, using the existing infrastructure. The rationale of using H_2 in the H_2CAR process is explained by the significantly higher annualized average solar energy conversion efficiency for hydrogen generation versus that for biomass growth. For coal to liquids, the advantage of H_2CAR is that there is no additional CO_2 release to the atmosphere due to the replacement of petroleum with coal, thus eliminating the need to sequester CO_2.

biofuels | coal | hydrogen | oil

The transportation sector relies almost exclusively on liquid hydrocarbons as the energy source. One reason cars, trucks, buses, trains, airplanes, etc. prefer to use liquid hydrocarbons is their high volumetric energy density and convenience of use. However, combustion of liquid hydrocarbon fuels leads to emission of massive quantities of CO_2 with the associated greenhouse effect. In the United States alone, oil consumption in the transportation sector approaches 13.8 million barrels per day (Mbbl/d) (1), corresponding to a release of 0.53 gigatons of carbon per year (GtC/yr) (2). The current global release of carbon from all of the fossil fuel usage is estimated to be at 7 GtC/yr, and the business-as-usual scenario is expected to raise it to ≈14 GtC/yr by 2050 (3–5). The concern over increased carbon release has led to the consideration for the use of alternative carbon-free energy carriers by the transportation sector.

Some of the alternative energy carriers considered for transportation are electricity and hydrogen (6, 7). Both of these energy carriers, when produced from a carbon-free primary energy source such as nuclear, solar, wind, etc. or a renewable source such as biomass, have a potential to eliminate net carbon emission by the transportation sector. However, use of either of these carriers is laden with technical and economical challenges. For the transportation sector, probably the biggest challenge is the storage density of the energy (6). The current energy density of commercial batteries is <175 Wh/kg of battery (8). At a storage pressure of 680 atm (1 atm = 101.3 kPa), the lower heating value (LHV) of H_2 is ≈1.32 kWh/liter. In contrast, the corresponding energy density for gasoline is 8.88 kWh/liter. For a given on-board storage space, the lower storage energy densities of batteries and H_2 severely limit the driving distance (9). Furthermore, energy and cost associated with the delivery of a low-energy density carrier to an automobile is a large fraction of the overall energy and cost (6). Therefore, the convenience of the use of a liquid hydrocarbon fuel through the existing infrastructure is a big deterrent to replacement by batteries or H_2.

Other historical reasons for the use of liquid hydrocarbon fuels have been easy access to primary resources and relatively low cost. However, the recent rise in the petroleum price has refocused the world's attention to the finiteness of this source of energy. By varying accounts, conventional oil production is predicted to peak in as little as the next 10 years to as high as 50 years (10, 11). A large number of developed, as well as developing, nations import oil for the transportation sector to support their economic activities. The looming possibility of the decline in the availability of oil is forcing the nations to consider alternate energy sources such as biomass and coal to supply liquid hydrocarbons for transportation. The use of each of these energy sources brings additional challenges.

The nations rich in coal reserves are actively exploring the option of converting coal to liquid fuels. However, the thermal efficiency of an actual Fischer–Tropsch (FT) process to convert coal to synthetic hydrocarbon liquids is <50% (12). Per unit of transportation energy consumed, the use of coal leads to added carbon release to the atmosphere. For example, about 3 kg of carbon per gallon of gasoline used is released, whereas 6–7 kg of total carbon is estimated to be released with the use of a gallon of synthetic liquid fuel derived from coal. This increase in carbon release has led to intense research for the so-called clean-coal technologies whereby carbon dioxide from the coal-to-liquid conversion process will be captured and then sequestered (13, 14).

Service points to the potential dangers associated with the sequestration of CO_2 in depleted oil/gas reservoirs, unmineable coal beds, and deep saline aquifers (15). If CO_2 leaks out, it can lead to leaching of dangerous trace elements in freshwater aquifers due to lowering of the pH and can impact soil chemistry. Clearly, massive quantities of CO_2 would be sequestered during a century's-long production of liquid fuels from coal. This would place extreme demands on CO_2 capture, storage, and monitoring systems. An alternative route whereby liquid fuels from coal can be produced without any CO_2 sequestration, as well as with no additional CO_2 emission (as compared with petroleum use), would be highly desirable.

Biomass is another energy source that has increasingly drawn attention as a source of liquid hydrocarbon fuels (16, 17). It can also be a solution to the problem of CO_2 emission from the transpor-

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Abbreviations: GtC, gigatons of carbon; H_2CAR, hybrid hydrogen-carbon; FT, Fischer–Tropsch; LDVs, light-duty vehicles; LHV, lower heating value; Mbbl/d, million barrels per day; NRC, National Research Council; PHEVs, plug-in hybrid electric vehicles; PV, photovoltaic; WGS, water–gas shift.

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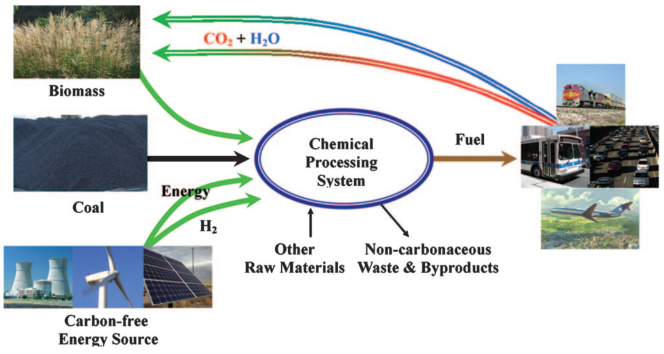

Fig. 1. Schematic of the proposed process. Some images courtesy of Department of Energy/National Renewable Energy Laboratory.

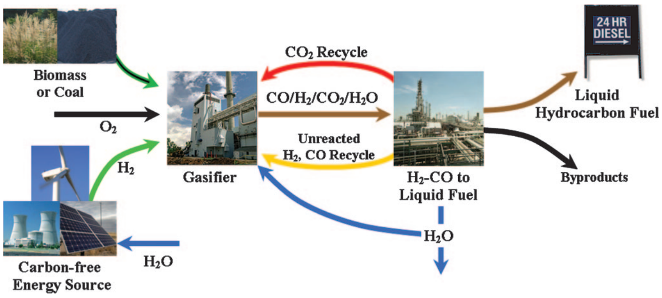

Fig. 2. One of the possible configurations of the proposed H_2CAR process. Some images courtesy of Department of Energy/National Renewable Energy Laboratory.

tation sector because CO_2 released from vehicle exhaust is captured during biomass growth from atmosphere. However, it has been estimated that the United States can fulfill only 12% of its total gasoline and 6% of its diesel demand by converting all corn and soybeans currently produced in the country to ethanol and biodiesel, respectively (18). Other options include gasification of biomass to obtain synthesis gas (syngas), a mixture of CO and H_2, and its conversion to liquid fuels using the FT process. A quick estimate can be made for the land area required to support total current oil consumption of 13.8 Mbbl/d by the United States transportation sector. Using the "current case" biomass growth and gasification data provided in the recent National Research Council (NRC) report on H_2 (6) and assuming that the conversion of syngas to diesel is 100% selective, one can estimate the optimistic land area requirement to be ≈5,296,000 km^2. This required land area is 58% of the total United States land area. Just to put the numbers in perspective, the currently used cropland area in the United States is 1,792,000 km^2 (6), which is roughly 20% of United States land area. It will be challenging, if not impossible, to supply the energy need of the total United States transportation sector by using bioenergy crops as a sole source of energy.

A Solution

To overcome the environmental challenges associated with coal and the land limitations with the bioenergy crop, we suggest an alternative pathway where neither coal nor biomass is treated as a sole source of energy to produce liquid hydrocarbon fuel. In our proposal, the primary purpose of either coal or biomass is to provide carbon atoms needed for the production of liquid hydrocarbons. Thus, the goal is to accomplish the complete transformation of every carbon atom contained in either of the feed stocks to liquid fuel by supplementing the conversion process with a carbon-free energy source. We propose to generate H_2 from a carbon-free primary energy source such as solar, nuclear, wind, etc. and then use it to supply the hydrogen atoms needed for the chemical transformation. While not necessary, a portion of this H_2 could also be used to provide the energy needed for the transformation and, thus, further improve the carbon efficiency. A schematic of the proposed process is depicted in Fig. 1.

There are a number of important consequences of Fig. 1. First, there is no CO_2 emission from the chemical processing system, and the only CO_2 released to the environment is from the transportation engine. Therefore, for coal, it eliminates the need to sequester CO_2 produced in the liquefaction process. Second, an associated benefit of the absence of CO_2 release from the chemical processing system is that ≈40% of the amount of coal or biomass is needed to deliver the same quantity of liquid fuel. This is a great advantage in prolonging the life of the known coal reserves as well as in reducing the land area needed for the bioenergy crop. The large reduction in land area provides an opportunity for sustainable production of hydrocarbon fuel for the transportation sector. Third, by providing open-loop H_2 storage, this solution addresses one of the grand challenges of the H_2 economy. The addition of H_2 atoms to carbon atoms from coal or biomass provides a high-density method for storage of massive quantities of H_2. Fourth, on a carbon atom basis, the energy content of the liquid fuel is higher than that of coal or biomass. Moreover, conversion of the 60–70% of the carbon atoms normally lost from a given amount of coal or biomass into liquid fuel provides a further means to store large quantities of carbon-free energy in a usable form for the transportation sector. The proposed solution provides an important step toward meeting the goal of generating 10 TW of carbon-free power by 2050 (3).

We recently found two sources that mention the reaction of H_2 from renewable sources with biomass to produce liquid fuel (19, 20). However, our proposal is expected to have much broader impact because it is more encompassing due to the judicious inclusion of coal and nuclear energy. More importantly, we suggest a number of processing steps in Fig. 2 that make this processes technically viable and also provide quantitative assessment of the relative benefits.

Although optimal configurations for the chemical processing system shown in Fig. 1 are yet to be defined, we chose the gasification route to provide guidance for the benefits. In a typical gasifier, oxygen and steam are supplied along with a carbon-containing feed stock. The resulting combustion energy not only provides heat for the endothermic gasification reaction, a majority of which is stored in the CO and H_2 exiting the gasifier, but also compensates for the energy losses from the system. CO_2 is formed in the gasifier from the combustion reaction and through the water–gas shift (WGS) reaction in post-gasifier processing. Whereas in the past it has been common to talk about the possibility of sequestering the resulting CO_2, in the H_2CAR process we plan to either suppress the formation of this CO_2 or react it with H_2 from a carbon-free energy source such as solar, nuclear, etc. to produce liquid fuel. The reverse WGS reaction of CO_2 with H_2 to form CO and H_2O is an endothermic reaction and requires high temperatures to obtain a reasonable conversion. To simplify the overall process, we propose to recycle CO_2 from the H_2-CO to liquid conversion processes such as an FT process to a suitable location in the gasifier (Fig. 2). Furthermore, to help drive the thermodynamic equilibrium to the favorable H_2/CO ratio of near two, the proposed process directly feeds H_2 from the carbon-free energy source to the gasifier.

To our knowledge, such a gasifier with a recycle CO_2 stream and H_2 co-feed has never been built. The advantage of this configuration is that at steady-state operation, there is no CO_2 buildup and therefore no net or little CO_2 formed in the gasifier. This means that nearly all of the carbon atoms fed to the gasifier from coal or biomass are converted to CO. Of course, CO_2 will be present in the gasifier effluent stream. Under typical operating conditions of

Table 1. Production of 13.8 Mbbl/d of synthetic oil by using biomass

Case	Gasifier efficiency, %	Biomass land area, million km^2	Required H_2, billion kg/yr	H_2 land area, thousand km^2	Carbon efficiency, %	Energy efficiency, %
Conventional–I	50	5.30	0	0	26.2	29
Conventional–II	70	2.51	0	0	36.7	40.6
H_2CAR–I	50	1.41	276	62	≈100	52.7
H_2CAR–II	70	0.92	239	54	≈100	58

conventional gasifiers, the gas composition of gaseous effluent stream is found to be close to thermodynamic equilibrium (21, 22). Similarly, for the proposed gasifier, we expect CO_2 concentration to be determined by equilibrium considerations at the high temperatures of 800–1,300°C prevalent in the gasifier. Therefore, the formation of CO_2 in the presence of added H_2 will be greatly reduced. As a result, CO_2 acts as an inert that is simply circulated through the overall process. For simplicity, we have named the hybrid H_2-carbon process of Fig. 2 as the H_2CAR process.

In the H_2CAR process, addition of sufficient quantity of H_2 along with oxygen to the gasifier may be thought of as providing energy for the gasification of the biomass or coal to CO. The oxidation of H_2 is an exothermic reaction, and conversion of some H_2 to water results in the net contribution of energy needed for gasification. Alternatively, high-temperature heat from a nuclear reactor or solar concentrators can be used to supply energy for the gasification.

The advantage of feeding H_2 from a carbon-free energy source and recycling CO_2 to the high-temperature gasification step is that it decouples the reverse WGS reaction requirement from the catalyst in H_2-CO to liquid conversion reactor. Generally, the H_2-CO to liquid conversion reactors operate at temperatures below 350°C, where the reverse WGS reaction is not favorable. The H_2CAR process takes the advantage of the preferable high temperature range prevalent in the gasifier to run reverse WGS reaction. This allows a degree of freedom to tailor the FT synthesis catalyst specifically for the desired liquid hydrocarbon molecule. Another advantage of this process configuration is that net CO_2 formation is minimized. Therefore, the cost associated with CO_2 handling is reduced.

To quantify the impact of the proposed H_2CAR route, we have done order of magnitude calculations for both biomass and coal as the carbon source. In the year 2005, the United States transportation sector alone consumed nearly 13.8 Mbbl/d of the world's total oil consumption of 82.5 Mbbl/d (10). Therefore, calculations were done to displace 13.8 Mbbl/d of oil with a synthetic fuel such as diesel. It is believed that the magnitude of the United States transportation sector is large enough to provide clear insight into the pros and cons of the proposed pathway. H_2CAR results for biomass are presented first followed by those for coal.

Biomass to Liquid Fuels

Initial calculations for biomass were done for the two biocrop cases described in the NRC report (6). In case I, the "current scenario" of the NRC report, the biomass was presumed to grow at a rate of 1 kg of dry biomass/m^2/yr (corresponding to 4 ton/acre/yr) with a carbon content of 0.425 kg of C/kg of dry biomass. The gasifier efficiency is 50% (based on LHV). For case II, the "future scenario" of the NRC report, the biomass growth rate was 1.5 times the current growth rate, and the gasifier efficiency was 70%. In our calculations for the conventional process, we assumed 100% conversion and selectivity in the FT reactor to the desired diesel ($C_{15}H_{32}$) fuel molecules. This provides an optimistic scenario for the biomass requirement and land area needed to grow the biomass. For the H_2CAR process of Fig. 2, conversion in the FT reactor was taken to be 90% with 100% selectivity to diesel fuel molecules, and the unconverted reactants, along with CO_2, were recycled to the gasifier. ASPEN (23) simulations were done for all of the cases, and the results are summarized in Table 1. Both of the conventional cases use 15% of the biomass to dry the rest of the biomass (6), whereas in the H_2CAR processes, this drying energy is provided through combustion of additional H_2. This increases the H_2 requirement for the proposed cases but requires less land area to grow the biomass. In Table 1, H_2 is produced from solar energy, and the required land area for H_2 was calculated by using the conversion efficiency from solar to H_2 of 8.5% (based on LHV of H_2). The energy efficiencies in Table 1 are based on the energy content of biomass and H_2 arriving at the plant. The relevant results for biomass are the following. (*i*) The estimated land areas for both the conventional processes are too large. Even with the anticipated advancements, the land area for the conventional–II case is 27.5% of the total United States land area. This land area is greater than the current United States cropland area. (*ii*) The land area requirements for the proposed processes, especially for the H_2CAR–II case, are substantially lower and have a potential to be manageable. (*iii*) The carbon efficiency for the conventional biomass process is quite low. Nearly two-thirds of the carbon contained in the biomass is lost as CO_2. (*iv*) The addition of H_2 in the H_2CAR process improved the overall efficiency of the process. (*v*) Another associated benefit of H_2CAR process is that diversity of crops can be maintained because any type of biomass can be gasified, and Tilman *et al.* (24) have shown that plant diversity enhances the biomass yield by 180% over monocultures. Also, a diverse biomass growth has a better chance of survival in droughts. (*vi*) The ability to use diverse biomass also provides an additional degree of freedom to tailor biomass growth for the maximization of carbon pickup from the atmosphere without the constraints of relative quantities of lignin, cellulose, hemicellulose, starch, oil, sugar, etc. in a plant. (*vii*) Land area radius decreases to support a given size of plant. (*viii*) Less space is required for storage of biomass. (*ix*) Less fertilizers and pesticides would be required for the same quantity of liquid fuel production, if any. (*x*) There would be less wear and tear to the land. (*xi*) Less biomass demand to produce same quantity of transportation fuel implies less energy and water input to grow the required amount of biomass.

Even though the amount of H_2 needed is large, the land area needed to produce it by using solar energy is a small fraction of the land area to grow the biomass. However, the intermittent nature of the H_2 from solar energy will have strong repercussions on how the biomass gasifier will be operated and will require further innovations. H_2 from nuclear reactors will not face this challenge because H_2 will be available at a steady production rate around the clock. For this reason, it is likely that initial H_2CAR plants may be built by using H_2 from nuclear reactors.

It should be emphasized that the proposed "sun to wheels" solution is successful in providing a viable sustainable route to meet the hydrocarbon fuel need for the total United States transportation sector. The interesting aspect is that it does so with a reasonable land-area requirement. The potential attractiveness of our proposal will improve with further advancements in the production, distribution, and end-use technologies.

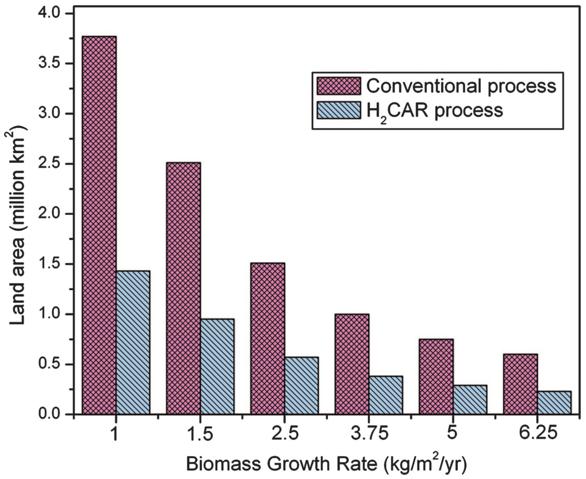

Fig. 3. Effect of biomass growth rate for 70% gasifier efficiency on the total land-area requirement for conventional and H_2CAR processes. Total oil production = 13.8 Mbbl/d (1 kg/m^2/yr ≡ 4 ton/acre/yr).

For the results in Table 1, the biomass growth rates used are relatively modest. Recently, switchgrass yields as high as 2.5 kg of dry biomass/m^2/yr (equivalent to 10 dry tons/acre/yr) have been reported (25). Fig. 3 shows the decrease in total land area due to improvements in biomass growth rate for conventional and H_2CAR processes. From Fig. 3, it is evident that the H_2CAR process requires significantly less land area than the conventional process at any level of biomass growth rate. For a biomass growth rate of 2.5 kg/m^2/yr, the land area required for the H_2CAR process at 0.57 million km^2 is only 6.2% of the total United States land area. It must be brought to notice that improvement in biomass gasifier efficiency will decrease the land-area requirement for conventional processes but will have small effect on H_2CAR. This is because irrespective of gasifier efficiencies, H_2CAR has a carbon efficiency of nearly 100%, and hence, the land-area requirement for biomass remains the same.

Why Does the Concept Work?

The main reason that the H_2CAR process is so effective in reducing the land-area requirement is that the overall average efficiency to convert solar energy to H_2 via the photovoltaic (PV)/electrolyzer route is much greater than that for solar to biomass. To demonstrate this point, annualized efficiencies were calculated for each case and are shown in Fig. 4.

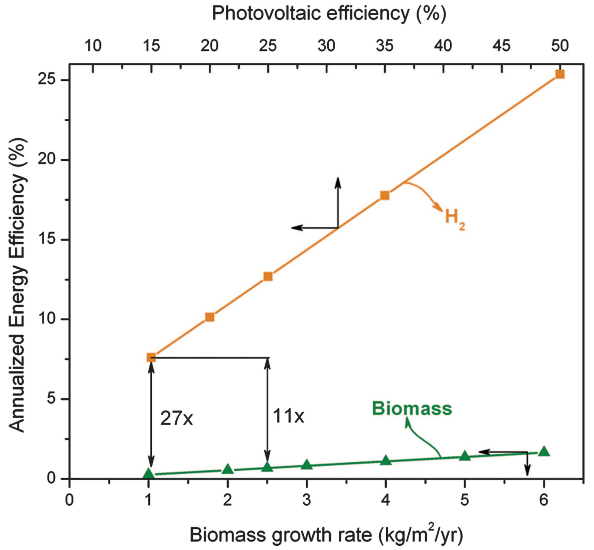

Fig. 4. Annualized energy efficiency comparison for biomass at different growth rates and H_2 production at different PV efficiency with a fixed electrolyzer efficiency of 50.7% (LHV).

For biomass, energy content generally varies from 16.5 to 19 MJ/kg of dry biomass (26). In our calculations, we used LHV of dry biomass to be 17.5 MJ/kg (6). For a biomass growth rate of m kg/m^2/yr, the solar energy stored per m^2 per yr in the biomass will be $17.5m \times 10^3$ kJ. With solar insolation of 1 kW/m^2 at an annual average of 20% per day, the total solar energy per m^2 per yr is 6.3×10^6 kJ. It is the ratio of these two numbers that is plotted as annualized efficiency for biomass growth as a function of biomass growth rate in Fig. 4. Similar efficiency for H_2 production is calculated by multiplying PV efficiency for conversion of solar energy to electricity by a factor of 0.507. This factor was calculated by correcting the 60% electrolyzer efficiency that is based on the higher heating value (HHV) of H_2 to its LHV (LHV/HHV of H_2 = 0.845). For the currently available crystalline- and polycrystalline-silicon-based PV cell efficiency of 15%, this translates into annualized energy efficiency for H_2 production of 7.6%. For biomass growth rates of 1, 1.5, and 2.5 kg/m^2/yr, the corresponding annualized efficiencies are 0.28%, 0.42%, and 0.69%. Similar photosynthesis efficiencies have been reported in the literature (4, 27–29). At the projected improved biomass growth rate of 2.5 kg/m^2/yr, the H_2 generation efficiency is an order of magnitude better than photosynthesis efficiency. Even at a futuristic biomass growth rate of 6.25 kg/m^2/yr, the annualized efficiency for biomass growth of 1.73% is less than a quarter of the current H_2 annualized efficiency. This proves that the proposed partnership between H_2 and biomass for the H_2CAR process will always be effective in reducing land-area requirements. Furthermore, as shown in Fig. 4, we expect additional improvement in H_2 generation efficiency with improvement in PV cell and electrolyzer efficiencies. For example, the suggested electrolyzer efficiencies of 75–85% in the NRC report are higher than the corresponding value of 60% used in Fig. 4.

A corollary result may also be derived from Fig. 4. There have been suggestions to either generate electricity (30, 31) or produce H_2 from biomass (6). It is clear from Fig. 4 that such endeavors are an inefficient utilization of solar energy resulting in increased demand for land. It is a better utilization of land to generate electricity or hydrogen from solar cells or an alternative carbon-free energy source and use biomass as a carbon source to store this energy as synthetic fuels.

Comparison with Biological Routes

To compare the land-area requirement for the H_2CAR process with the one projected for biological routes (17) using enzymes and microbes, we used the results of a recent billion ton annual biomass study (25). The billion ton biomass study estimates that currently 1 billion tons of dry biomass/yr is available in the United States, and with some modifications in agricultural practices, 1.366 billion tons of dry biomass per year (1.366 trillion kg/yr) is recoverable. The study also projects that this quantity of dry biomass is needed to meet 30% of the United States daily transportation fuel through biological routes. We first notice that this number is not much different from conventional–II case in Table 1. For the case in the table, the amount of biomass needed is 3.77 trillion kg/yr. For the assumptions made in Table 1, 1.366 trillion kg/yr of dry biomass will produce ≈36% of the daily transportation fuel need. However, to get a lower bound of the land area for the conventional gasification route, conversion and selectivity from H_2-CO to liquid fuels were assumed to be 100% in Table 1. For a reasonable selectivity of 70–85%, we expect that 25–31% of the daily transportation fuel need could be met from 1.366 billion tons of dry biomass by using a conventional gasification route with gasifier efficiency of 70%. Indeed, the projected production numbers from the biological and gasification routes are quite similar.

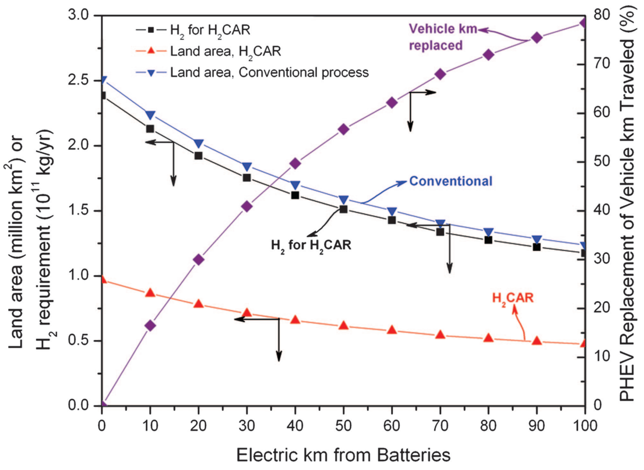

Fig. 5. Land-area and H_2 requirement for conventional and H_2CAR process using PHEVs as a function of drivable distance traveled per single full charge of batteries.

With the added verification in the estimated production from the conventional gasification route, we estimate that from 1.366 trillion kg of dry biomass/yr, the H_2CAR process can produce liquid fuels for 99.6% of the United States transportation sector. This is indeed a remarkable result for the proposed "sun to wheels" H_2CAR process that takes us closer to meeting the needs of the entire United States transportation sector.

Effect of Improvement in Other Technologies

Currently, light-duty vehicles (LDVs) consume 8.9 Mbbl/d of the 13.8 Mbbl/d used by the entire United States transportation sector. If all of the LDVs were to be replaced with gasoline hybrid electric vehicles (GHEVs), then the demand for gasoline would decrease, resulting in reduced biomass demand. Assuming that GHEVs are 1.45 times more fuel-efficient than nonhybrid gasoline vehicles (6), the daily United States gasoline demand would decrease from 8.9 to 6.2 Mbbl/d. This means that the amount of biomass needed to meet the needs of the United States transportation sector would be reduced to nearly 1.1 trillion kg per yr.

However, in the current scenario, an overall better picture emerges with the use of plug-in hybrid electric vehicles (PHEVs). Rechargeable batteries provide short-range driving capability to PHEVs. The long-range driving still depends on liquid fuels. If LDVs were replaced with PHEVs, then electricity from a PV grid could be directly used to charge the vehicles. Unlike the usual wisdom of charging the PHEVs at night by using electricity from grid, now they would be charged during the day by using solar energy. There are two immediate benefits. One is that the batteries in millions of automobiles become a very large amount of storage for solar energy. The second is that reduction in the amount of liquid fuel results in the reduced biomass and H_2 requirement for the H_2CAR process. Fig. 5 shows some pertinent results based on Argonne National Laboratory estimates of the relationship between the range of batteries in kilometers and the vehicle kilometers traveled that could be replaced with the electric kilometer capability of PHEVs. Thus, if all LDVs were replaced with PHEVs containing batteries that can provide driving distance of 48 km between two successive charges, then nearly 56% of total distance driven by LDVs in the United States could be powered by batteries. Only 44% of the total driven distance would require liquid fuel. Therefore, the demand for liquid fuel for the LDVs would decrease from ≈8.9 to 3.9 Mbbl/d. Even with 1.5 kg/m^2/yr biomass growth rate, only 6.4% of the United States land area will be needed with H_2 consumption, decreasing from nearly 239 billion kg/yr to 149 billion kg/yr. For the overall sustainable energy scenario, it will clearly be better to use PHEVs with the capability for reasonable driving distance by using rechargeable batteries.

Because the H_2CAR process in conjunction with GHEVs and/or PHEVs leads to a large reduction in the amount of biomass required, one can envision a scenario where more biomass is available than is needed for the transportation sector alone. In such a scenario, a strong potential exists for supply of synthetic biofuel to other energy sectors such as residential and commercial, effectively extending the capability for storing solar energy for use around the clock. This also presents an intriguing possibility of the United States becoming a net exporter of oil.

One of the drawbacks of the H_2CAR process as described is that H_2 generation from solar is a two-step process, which cuts the conversion efficiency to nearly half of the PV efficiency (Fig. 4). Of course, one could improve the process by devising a more efficient, direct one-step solar-to-H_2 process.

Clearly, the H_2CAR process provides an exciting possibility to supply sustainable liquid fuel for the much needed transportation sector with manageable land area. Now we will briefly explore its beneficial extension for coal-to-liquid processes.

Coal to Liquid Fuels

Unlike biomass gasifiers, coal gasifiers are much more advanced. FT processes in conjunction with WGS reaction to convert synthesis gas (syngas) to diesel are also fairly well developed. Therefore, it is relatively easy to assess the benefit of the H_2CAR process in the context of coal to liquid fuel. For calculations with coal as the carbon source, we used the coal and the associated gasifier data available in the NRC report (6). The NRC's "current case" with gasifier efficiency of 75% was considered. Other assumptions were similar to those described for the biomass cases, and the results are summarized in Table 2.

Several observations can be made from these simulations. (*i*) For the conventional process, the amount of coal needed is greater than the current rate of 1.128 trillion kg/yr of coal consumption in the United States and will have a huge impact on the coal reserves. (*ii*) Additional CO_2, >3 trillion kg/yr, will be emitted. If not sequestered, this corresponds to additional contribution of >0.9 GtC/yr to the current global release of 7 GtC/yr from fossil fuels. (*iii*) The proposed H_2CAR process is thermodynamically feasible and reduces the coal requirement to ≈40% of that of the conventional process. There is no associated additional CO_2 release to the atmosphere. (*iv*) United States coal is expected to last for 244 years if used at the current consumption rate. However, if coal is used to produce liquid fuels by conventional process, this coal will last for ≈89 years. The use of the H_2CAR process to make liquid fuels will increase the life of coal to 144 years. (*v*) For the proposed process to be adopted, huge quantities of H_2 from carbon-free energy

Table 2. Production of 13.8 million bbl/d of synthetic oil by using coal with 75% gasifier efficiency

Case	Amount of coal, trillion kg/yr	Required H_2, billion kg/yr	CO_2 sequestered, GtC/yr	Carbon efficiency, %	Energy efficiency, %
Conventional	1.97	—	0.9	39.9	50.7
H_2CAR	0.79	211	0	≈100	65.2

sources will be needed. It is no surprise that for the H_2CAR process, the heat content (LHV) of the H_2 used is 1.2 times the corresponding value of the coal fed to the gasifier. Energy in the H_2 goes toward producing 1.5 times more liquid product for the same amount of coal. (*vi*) Although the energy needed to produce H_2 is large, as discussed for the biomass case, the land area to produce it by using solar energy is quite manageable. Alternatively, H_2 could also be produced by using nuclear energy. (*vii*) The amount of synthetic oil produced contains ≈105.4 billion kg of H_2/yr. This is nearly half of the H_2 required by the H_2CAR process. If we think of the synthetic oil as a medium for storing H_2, then the large quantities of H_2 stored in the high energy density fuel by H_2CAR will solve the grand challenge problem of H_2 storage associated with the H_2 economy (6). (*viii*) Even under the best FT reaction conditions, ≈27% of the energy contained in the final liquid fuel product is liberated as thermal energy rather than being stored as fuel. This coproduction of thermal energy has a large negative impact on the H_2 demand for the H_2CAR process. There is clearly a need for better alternate chemical pathways that can use energy from carbon-free sources in conjunction with carbon moieties contained in coal to efficiently produce synthetic liquid for the transportation sector. (*ix*) Another advantage of the H_2CAR process is the decreased annual rate of release of pollutants like Hg. (*x*) The overall energy efficiency of the H_2CAR process based on the energy content of coal and H_2 is ≈65% and is higher than the conventional process's energy efficiency of nearly 51%. Similar to the biomass cases in Table 1, we find that the H_2CAR-based processes have higher efficiency.

Conclusions

In summary, the proposed hydrogen-carbon economy and associated H_2CAR process provide compelling alternatives. The primary function of biomass or coal is envisioned to provide carbon atoms for the much-needed hydrocarbon liquid to propel the transport sector. The required H_2 for the hydrogenation process is supplied by carbon-free energy sources such as solar, nuclear, wind, etc. To preserve the carbon atoms, the energy need for the transformation process is also supplied from the alternate source. In some cases, this energy need could be met through the combustion of additional H_2. A big advantage is that, with recycle to the gasifier, there is no additional CO_2 released to the atmosphere due to the replacement of petroleum with coal. Probably the greatest benefit is achieved with the use of biomass as the carbon source. This approach has the potential to provide a sustainable route to transportation fuel with much lower land area than hitherto seen for the cultivation of the bioenergy crop. The reduction to practice of this route could provide the transportation sector with a high density liquid energy source for the foreseeable future of the human race without a net CO_2 emission to the environment. A final and very important advantage of H_2CAR is that it uses the existing fuel distribution infrastructure.

The proposed H_2CAR-based processes also have a strong impact on the future areas of research. The primary research emphasis needs to be on cost-effective H_2 production from a carbon-free energy source such as solar or nuclear. In addition, efficient, low-cost, and easy-to-operate methods are needed for the conversion of biomass through reaction with H_2 to a suitable hydrocarbon liquid fuel. In the short term, the same is true for the conversion of coal to liquid. The current conversion route of gasification followed by a H_2-CO liquid conversion reaction is quite inefficient, and an alternative efficient hydrogenation process is highly desirable. In the mean time, until such alternate processes are discovered, the preservation of carbon atoms in the current gasification and H_2-CO liquid conversion reaction is essential. A proposed solution in this work is to co-feed H_2 and recycle CO_2 from the H_2-CO liquid conversion reactor to the gasifier. Feasibility and development of such gasifiers especially for biomass will require extensive research. Needless to say, if we are going to continue with the current transportation fuel infrastructure, the efficiency improvement in the internal combustion engine will be highly beneficial. Clearly, the proposed concepts deemphasize research in CO_2 sequestration as well as on-board H_2 storage. The synthesized liquid hydrocarbon fuel provides the H_2 storage in an open-loop system. Indeed, we face a number of challenging but highly rewarding possibilities through the proposed hybrid hydrogen-carbon economy for a sustainable future.

Methods

Well known process system analysis methods in conjunction with the commercial software ASPEN were used to perform various material and energy balances. The calculation details and results are provided in supporting information (SI) *Appendix*.

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