Solar Energy to Biofuels

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Abstract

In a solar economy, sustainably available biomass holds the potential to be an excellent nonfossil source of high energy density transportation fuel. However, if sustainably available biomass cannot supply the liquid fuel need for the entire transport sector, alternatives must be sought. This article reviews biomass to liquid fuel conversion processes that treat biomass primarily as a carbon source and boost liquid fuel production substantially by using supplementary energy that is recovered from solar energy at much higher efficiencies than the biomass itself. The need to develop technologies for an energy-efficient future sustainable transport sector infrastructure that will use different forms of energy, such as electricity, H_2, and heat, in a synergistic interaction with each other is emphasized. An enabling template for such a future transport infrastructure is presented. An advantage of the use of such a template is that it reduces the land area needed to propel an entire transport sector. Also, some solutions for the transition period that synergistically combine biomass with fossil fuels are briefly discussed.

INTRODUCTION

Biofuel: any liquid fuel from biomass that is used for transportation

Ton of biomass: a metric ton of dry biomass

Ethanol gallon equivalent (ege): gallons of ethanol with same energy content as the given quantity of biofuel

LHV: lower heating value

In 2006, the worldwide transport sector consumed a massive quantity of 97 trillion Mega Joules (1 Mega Joule $=$ 1 MJ $= 10^6$ J) of energy. Of this, 92.3 trillion MJ were derived from liquid fuels (1). Liquid fuels are attractive owing to their high volumetric energy density and ease of use. Historically, the majority of this liquid fuel has come from petroleum crude oil. However, with the recent concern about the eventual decline in the availability of petroleum, alternative energy sources to propel the transport sector are being explored. Indeed, the consumption of bioethanol and biodiesel by the U.S. transport sector climbed from 310 billion MJ in 2004 to 880 billion MJ in 2008 (1). The collection of atmospheric carbon, which is present in the atmosphere at 383 ppm CO_2, in a dense form such as biomass, followed by its conversion to liquid fuel for transportation provides a possible sustainable path. The possibility of supplying liquid fuel sustainably from biomass has a natural appeal, and many studies have been devoted to the estimation of liquid fuel yields from biomass, production economics, and the extent to which these biofuels can meet the needs of a given transport sector (2–7). Many researchers, investors, and policy makers expect that biofuel can take center stage in a sustainable transportation energy future (8).

Although there seems to be a general agreement that biofuel can play a significant role in a future renewable energy–based transport sector, there is a considerable debate regarding the extent to which it will be able to fulfill this need. For the U.S. transport sector, estimates of the annual quantity of biomass that may be available in the future for conversion to biofuel vary from approximately 498 million tons (MT) to in excess of a billion tons (9, 10). Similarly, estimates of biofuel yields from a given land area vary by roughly tenfold (2, 6, 11, 12). Estimates of future biofuel yields from a ton of lignocellulosic biomass also vary from ~84 to 136 ethanol gallon equivalents (eges) (7–9). In this review, we define ege as gallons of ethanol whose energy content in terms of lower heating value (LHV) is the same as that of the quantity of biofuel under consideration. For this purpose, the LHV of ethanol is taken to be 80.14 MJ gal^{-1}. Depending on the source of the estimate, the United States could meet from nearly 20% to slightly more than 50% of its transport fuel need of nearly 13.8 million barrels day^{-1} with biofuel. However, even under the most optimistic scenario, biofuel will not be able to meet the entire U.S. transport sector's need unless large quantities of additional biomass dedicated to fuel use are cultivated and harvested (13).

When additional land is used, the dedicated fuel biomass essentially harnesses a portion of the sunlight falling on the land area. In this scenario, one can choose to harness the solar energy in alternate forms, such as heat, electricity, and H_2, and use them directly or indirectly to drive the transport sector. Furthermore, in a future solar economy, solar energy will be used to meet other needs of the human race, as shown in **Figure 1**. These competing demands will have to coexist harmoniously. It is well known that the amount of solar energy available on Earth is orders of magnitude more than the energy consumed by humans (14). Nevertheless, the total world energy consumption is also quite large. In 2006 it was ~498 trillion MJ and, according to Energy Information Administration estimates, it could reach ~716 trillion MJ by 2030 (1). The corresponding numbers for total energy use by the transport sector are 97 trillion MJ for 2006 and 135 trillion MJ for 2030. Therefore, large inefficiencies in the collection of solar energy and its subsequent use will not only directly impact the required land area but could also have a strong negative impact on the overall cost to society.

This review critically examines the literature regarding the evolution of a sustainable future transport sector that will be driven primarily by renewable energy sources such as solar. In this context, we emphasize three aspects: (*a*) the relative efficiency of growing and using biomass vis-à-vis other alternatives for propelling the transport sector, (*b*) the synergistic use of other forms of energy to augment the production of biofuel from a given quantity of biomass and thus increase the overall recovery of solar energy by increasing the fraction of biomass carbon that is recovered as biofuel from the conversion process, and (*c*) the generation of a template that can be used within the context of a nation or a region to create a future energy-efficient transport sector. The purpose of such an analysis is not to imply that all the steps contained in the template can be implemented in a cost-effective manner, but to indicate the research and development breakthroughs that will be needed for the evolution of an efficient and sustainable transportation infrastructure. In addition, this analysis identifies the challenges that can be met and solutions that can be implemented in the short term as well as those that will require more concerted medium- to long-term effort.

Our review is based on the use of thermochemical processes for the production of biofuel. This by no means implies that thermochemical processes are superior pathways to alternates such as biochemical-based routes. We believe that the results derived are general in nature and applicable to cases in which biofuels are derived using biochemical processing. Also, even though the analysis is conducted using solar energy, it is equally valid when other forms of energy, such as nuclear or wind, are to be used.

Sustainably available waste (SAW) biomass: biomass that is collected as a by-product of existing agricultural and forestry activities

Dedicated fuel (DF) crop: one cultivated on new land not used previously for harvesting biomass

TWO KINDS OF BIOMASS

The supply of biomass for biofuel should not have a negative impact on current or future food, animal feed, and fiber needs (9). Furthermore, when it comes to the availability of biomass for biofuel, it is important to distinguish between two kinds of biomass: sustainably available waste (SAW) biomass and dedicated fuel (DF) crops.

SAW biomass is that which can be collected with sustainable practices from existing agricultural and forestry activities and does not require new land area for cultivation. SAW biomass is collected as agricultural (crop) and forestry (woody) residues, animal manure, and municipal waste (9, 10). These residues are to be collected in an environmentally sensitive manner such as by avoiding increases in soil erosion from wind and water and depletion of the carbon reserves in the soil (15, 16). This requires that a portion of the biomass or crop be left as residue on the field. The goal here is to maximize the collection of SAW biomass within the constraint of environmental sustainability through appropriate changes in agricultural and forestry practices. Plant-related research that will increase the production and collection of SAW biomass with no negative influence on the coproduction of food grains will have a strong impact.

SAW biomass can generally be collected with minimal additional energy input. Furthermore, because it is part of existing product streams, SAW biomass can be treated similarly to other primary energy sources such as fossil fuels. Therefore, SAW biomass can be used akin to a fossil fuel for applications such as electricity generation, H_2 production, liquid fuel for transportation, or heat. However, in this review we will focus on the use of SAW biomass for transportation.

A recent National Research Council (NRC) report estimates a reasonable marginal cost for SAW biomass supplies to be \$77 ton^{-1} for wheat straw, \$93 ton^{-1} for woody biomass, and \$121 ton^{-1} for corn stover (9). These costs translate into \$4.5 to \$7.1 per thousand MJ, which is somewhat higher than coal and natural gas prices but compares favorably with oil at \$12 per thousand MJ (\$70 bbl^{-1}). A low-cost process is thus attractive for the conversion of SAW biomass to liquid fuel (17, 18).

DF crops are cultivated on land that is not attached to use for food, feed, fiber, livestock, or forest products. They require dedicating new land to cultivate and grow perennial crops for biofuel. Some examples of fast-growing DF crops under consideration in the United States are switchgrass and Miscanthus (19, 20). When compared with switchgrass monocultures, a high-diversity mixture of crops is reported to have approximately 200% greater biomass yield (21). The net energy efficiency and economic feasibility of switchgrass grown on reasonably sized marginal croplands was recently demonstrated (22).

Sustainably available (SA) biomass: SAW biomass and DF crops grown with minimal energy input from readily available spare lands

Regulated fuel (RF) crop: a DF crop harvested from constrained land that is regulated and managed for energy use

Consider a case in which spare land to grow DF crops is readily available and DF crops can be cultivated and harvested with energy input that is a small fraction of the energy content of the harvested biomass. From an energy perspective, the biomass thus collected can be treated similarly to SAW biomass. In this review, such DF crops are referred to as sustainably available (SA) biomass. The recent NRC report estimates that by using appropriate land currently available under the U.S. Conservation Reserve Program, 149 MT yr^{-1} of DF crops could potentially be produced by the year 2020 (9). The corresponding estimate for the SAW biomass that can be collected as by-products of agricultural and forestry practices (e.g., corn stover, wheat, grass straw, hay, woody residues, animal manure, and municipal waste) is 349 MT yr^{-1}. If the land potentially used for growing 149 MT yr^{-1} of DF crops is readily available as spare land with no other conflicting demand and the DF crops are collected with minimal additional energy input, then 498 MT yr^{-1} of biomass can be treated as SA biomass in the United States.

Now consider a second case in which the availability of land is constrained. The available limited land will be regulated and managed for energy use by optimizing the use of incident solar energy. The total energy need will be in excess of that which could be supplied by growing DF crops on the available land. Therefore, the recovery of solar energy as DF crops will compete with other possible recovery forms such as electricity, heat, and H_2. In this review, we will refer to a DF crop grown on such regulated and managed land as a regulated fuel (RF) crop.

Despite some initially successful demonstrations of growing DF crops, a remaining question is whether the sunlight falling on the land where the DF crop is grown could be harnessed for the transport sector more efficiently in some other form. As discussed in the next section, differences in the efficiencies of collecting and using solar energy can have a profound impact on the land area needed to support the transport sector. Furthermore, in a solar economy, other human needs may compete for the use of available land.

ENERGY EFFICIENCIES OF COMPETING METHODS

In this section, we will first compare the energy efficiencies of harvesting the solar energy falling on a given land area as various secondary forms of energy such as RF crops, heat, electricity, and H_2. Based on these observations, synergistic and efficient pathways will then be further reviewed.

A crop growing at the rate of 1 kg m^{-2} yr^{-1} in the United States, with an energy content of ~17 MJ kg^{-1}, captures only 0.28% of the average incident solar energy of 6307 MJ m^{-2} yr^{-1} (1752 kWh m^{-2} yr^{-1}) (13). In this review, unless specified, we report the calorific content of biomass as well as any liquid product derived from it in terms of its LHV. The quantity of biomass refers to dry biomass. The fast growing DF crop of Miscanthus is expected to have a growth rate of ~3.7 kg m^{-2} yr^{-1} (23). Even the highly efficient sugarcane crop stores only ~1% of the annual incident light as biomass (24, 25). Zhu et al. have estimated that the maximum conversion efficiency of solar energy to biomass under today's atmospheric CO_2 concentration of ~383 ppm and at 30°C is 4.6% for C3 photosynthesis and 6% for C4 photosynthesis (26, see also 27). The highest efficiencies observed across a full growing season for C3 and C4 crops are 2.4% and 3.7%, respectively (26). The observed efficiencies across a full growing season will be higher than those that could be achievable on an annual basis if biomass cannot be grown for the rest of the year.

Algae are considered efficient collectors of solar energy. Under ideal growing conditions of proper pH and controlled temperatures, yields in the range of 3–7 kg m^{-2} yr^{-1} have been reported (28). The joint venture between ExxonMobil and Synthetic Genomics Inc. plans to produce 2000 gal of fuel $acre^{-1}$ yr^{-1} (~1.86 liter m^{-2} yr^{-1}) (29). This presumably high oil production

Table 1 Demonstrated efficiencies to harvest solar energy in various secondary forms of energy

Secondary energy	Demonstrated efficiencies
Heat	Up to 70%
Electricity	10–42%
Hydrogen	5–15%
Crops for energy use	0.3–2%

rate still corresponds to recovery of ~0.9% of the annual incident solar energy as oil. According to recent projections, it may be possible to grow algae at an exceptionally high growth rate of ~12 kg m^{-2} yr^{-1} with 30 wt% oil content (30). Assuming that the oil portion of the algae has the high energy density of 33 MJ kg^{-1}, the resulting annual solar energy conversion efficiency of 4.2% is more than twice that of the demonstrated annual efficiencies; however, it seems to be the highest estimate of what may be achievable.

Algae should be considered a RF crop because the sunlight falling on the pond or the land that is to be converted to the pond could be used to generate other secondary forms of energy. In summary, fast growing crops such as sugarcane and Miscanthus have annual solar energy conversion efficiencies of ~1%, and we have not found a reference that shows actual annual conversion efficiencies for algae to be much greater than 2%.

Table 1 lists the solar energy conversion efficiencies that either have been demonstrated on a lab scale or are currently commercially available for the production of heat, electricity, and H_2 (31). Depending on the processing temperature, solar heat can readily be recovered at efficiencies of 40–70% (32, 33). Solar electricity can be generated either by a solar-thermal process or a photovoltaic module with efficiencies in the range of 10 to 42% (34–36). Commercial photovoltaic modules with efficiencies approaching 20% are already available, and lab-scale multijunction tandem cells have shown efficiencies slightly greater than 40%. H_2 can be produced from water by an electrolyzer with electricity to H_2 efficiency in the neighborhood of 50% (37, 38). Diver et al. (32) recently made calculations for a thermochemical water-splitting ferrite cycle heat engine with a net solar power into the reactor to H_2 conversion efficiency of 29.9% [based on the high heating value (HHV) of H_2]. They also estimate that cycle thermal efficiencies of up to ~50% are possible. After assuming that at a reactor temperature of 2300 K, 60% of the incident solar radiation will be absorbed, and correcting for the LHV of H_2, the net efficiency from solar energy to H_2 for the ferrite cycle will be in the vicinity of 16% with a potential to approach 27% (32). It should be noted that the efficiencies in **Table 1** do not include the energy needed to build the device to capture solar energy as heat, electricity, or H_2. The numbers shown are for the percentage of solar energy recovered when the conversion device is already available and all the solar energy from a given land area is used for conversion. In **Table 1**, we also list the annualized demonstrated efficiencies for RF crops.

Inspection of **Table 1** reveals that the demonstrated recovery of annual incident solar energy on a given land area for a RF crop is generally at least an order of magnitude lower than that for electricity or H_2. Furthermore, conversion of RF crops to biofuel will encounter additional losses that can be in the range of 20–50% (9, 13, 39). The efficiency numbers in **Table 1** for RF crops can be further corrected to account for the efficiency of converting RF crops to liquid fuel to provide sun-to-fuel (S2F) efficiencies (31). These efficiencies must be coupled with the fact that the energy effectiveness of different fuels in providing mechanical energy to an automobile varies greatly. What are of interest are sun-to-wheel (S2W) efficiencies (31). The S2W metric is similar to well-to-wheel efficiency (40, 41) and is a useful criterion to measure the efficiency of competing

Sun-to-fuel (S2F) efficiency: percent of incident solar energy recovered as fuel energy

Sun-to-wheel (S2W) efficiency: percent of incident solar energy recovered as mechanical energy driven technologies when solar energy is the primary driver for light duty vehicles (LDV), i.e., the cars, light trucks, minivans, etc., used by the general population. The S2W efficiency, in addition to S2F efficiency, must account for inefficiencies associated with distribution, transmission, on-board delivery, storage, and driving use. A unit of on-board energy either as electricity or H_2 will potentially provide longer driving distance through an electric LDV or an H_2 fuel cell vehicle (FCV) than a unit of on-board energy as liquid fuel using an equivalent internal combustion engine (ICE) vehicle because the ICE is generally less efficient (37, 38, 42). This fact, coupled with the magnitude of differences in **Table 1**, tells us that the S2W efficiency for RF crops will be much lower than that for alternate routes of using solar electricity or H_2.

Self-contained process: a process in which biomass is the main energy feedstock and any nonbiomass energy used is a small fraction of the biomass feedstock's energy content

Because RF crop–based liquid fuels, when compared with electricity or H_2, have so much lower S2F efficiencies, we encounter a liquid fuel conundrum. The high energy density [~32–36 MJ liter^{-1} (43)] of liquid fuels has historically provided us with relative ease of handling during distribution and delivery of the fuel as well as the convenience of on-board storage of large amounts of energy in a relatively small volume. It is the high energy density of liquid fuels that has made it possible for heavy duty vehicles (HDVs) such as trucks and airplanes to travel long distances. The energy density for electricity storage in Li ion–based batteries is ~1 MJ liter^{-1} (44) and in H_2 at 700 bar pressure is ~4.7 MJ liter^{-1} (45). With such low storage energy densities for electricity and H_2, there will always be a need for a high energy density fuel for certain parts of a transport sector such as some HDVs.

EFFICIENT SOLUTIONS FOR THE LIQUID FUEL CONUNDRUM

In a sustainable solar economy, there are at least three possible methods for producing liquid fuels: (*a*) conversion of SA biomass to biofuels, (*b*) cultivation of RF crops and their subsequent conversion to biofuels, and (*c*) direct separation of CO_2 from air and its conversion to liquid fuel by using H_2 and other forms of energy from the sun. Because SA biomass is akin to a primary energy source, its use will be on par with any method that uses additional land area with constrained availability to harvest solar energy. As a result, SA biomass is the primary choice for supplying liquid fuel to a sustainable transport sector. As a side note, in light of the higher efficiencies for the direct production of electricity and H_2 in **Table 1**, as long as there is a need for liquid fuel, on an energy efficiency basis, the use of SA biomass to provide H_2 or electricity should be avoided. However, as stated earlier, for countries such as the United States, the supply of SA biomass is limited and provides only a fraction of the liquid fuel needed by the transport sector.

Owing to the low efficiencies for collecting solar energy as RF crops, it becomes important to maximize biofuel production from SA biomass. We will first examine the literature to guide us through the amount of biofuel that can potentially be produced from a given quantity of biomass by self-contained processes. Then the need for augmented processes that use supplemental energy to boost biofuel production will be presented. Finally, we will compare all these processes with the possibility of direct separation of CO_2 from air and its conversion to liquid fuel.

Biomass to Biofuel: Yield from Self-Contained Processes

A self-contained process is one in which the primary energy source for the operating plant is biomass itself and the process uses only a small quantity of nonbiomass energy. Only a brief description of biomass conversion routes is provided here. Because different processes provide different biofuel molecules, the biofuel produced per ton of biomass is converted to customary ege units to compare yields of alternate processes. Note that a yield of 100 ege ton^{-1} of biomass is equivalent to production of biofuel with an energy content of 8.014 MJ from a kilogram of biomass.

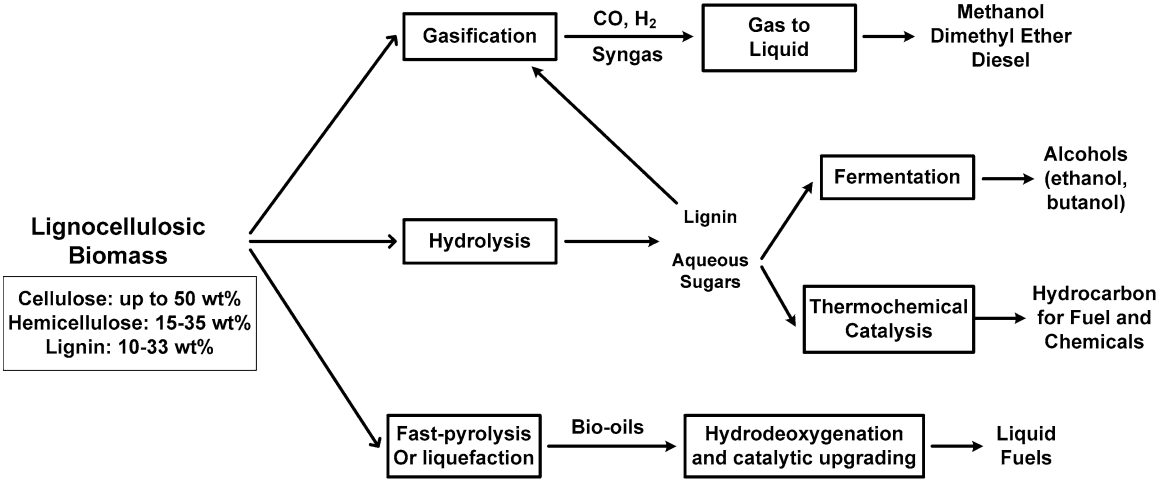

Figure 2

Alternative methods for conversion of lignocellulosic biomass to biofuels. Adapted from Huber et al. (46).

Although an extensive literature describes conversion processes for biomass to biofuel, two recent review articles by Huber et al. and Mohan et al. provide an excellent overview of the state of the art (46, 47). A general block diagram depicting alternative conversion processes is shown in **Figure 2**.

The structure of a typical biomass is made up of cellulose, hemicellulose, and lignin. Cellulose is a high molecular weight linear crystalline polymer that is solely made from C6 glucose, whereas hemicellulose is an amorphous polymer of shorter chain length containing five different sugars of both C5 (xylose and arabinose) and C6 (glucose, galactose and mannose) (46). Lignin is a highly branched polyphenolic polymer that contains hydroxyl- and methoxy-substituted phenylpropane units (47). Woody biomasses have a relatively higher lignin content. One distinguishing feature of biomass is that, unlike fossil fuels, it has a high oxygen-to-carbon atomic ratio that varies from 0.4 to approximately 0.8 depending on the source of the biomass (48). This results in an oxygen content of 40–45 wt% and leads to lower energy content of the lignocellulosic biomass. For all the modeling results reported in this article, we have taken biomass energy content to be 17 MJ/kg of biomass. For reference, this specific energy is ~40% of that of a kilogram of liquid petroleum.

There are thermochemical- and biochemical-based routes for converting biomass to biofuel. In one method, biomass is gasified at high temperatures (~1000°C) and high pressures (greater than 30 bar) in the presence of steam and oxygen to produce synthesis gas (syngas) containing a mixture of CO and H_2 (49, 50). Generally, the H_2 to CO ratio of the syngas is then adjusted to approximately 2 through a water-gas-shift reaction and then fed to a gas-to-liquid reactor(s) for further processing. Technology exists to produce many liquid fuels, such as linear alkanes or diesel through the Fischer-Tropsch (FT) process, methanol and other alcohols, and gasoline (51–53). Detailed technical and economic modeling shows that the cost to produce diesel via gasification/FT is high (54). Leckel provides an interesting overview of several FT refineries with particular emphasis on diesel fuel production (55). An advantage of the gasification-based process is that all of the biomass is first converted to the common gaseous molecules CO and H_2; therefore, the composition of the final liquid product can be independent of variability in the composition of the biomass used. FT reactions are exothermic, and ~21% of the energy in the syngas appears as heat and is therefore not stored as energy in the diesel fuel (31). With the biomass gasification efficiency in the range of 50–75% and the FT efficiency of 70–75%, the net gasification/FT process efficiency is 41–50% (50, 56, 57). This translates into diesel production of 87 to 106 ege/ton of biomass.

Biochemical routes using hydrolysis to produce aqueous sugars and then fermentation to produce alcohols and other chemicals are described in an extensive body of literature (4, 5, 7, 58, 59). Basically, in this process the cellulose and hemicellulose components of the biomass are broken into individual sugars in the presence of excess water, acids, bases, or enzymes. Microorganisms then convert the sugars to ethanol or butanol.

Interestingly, in spite of a large volume of published work, production of ethanol from lignocellulosic biomass using biochemical methods has yet to be demonstrated on a commercial scale yield from large-scale plants (9). Estimates vary from the currently expected yield of 75 ege/ton of biomass to a near future yield, with R&D-driven advances, of ∼105 ege/ton of biomass (7, 8, 60).

The biological route is at present unable to convert the lignin portion of the biomass to liquid fuel. Therefore, a substantial portion of the biomass is recovered as unconverted organic residue. The combination of a biochemical process producing alcohols from cellulose and hemicellulose with the organic residue used in a gasification/FT process to produce additional quantities of gasoline and diesel has been suggested (2, 7). Such a hybrid process is estimated to produce the equivalent of 77 gallons of gasoline and 11 gallons of diesel per ton of total biomass (∼136 ege/ton of biomass), which corresponds to ∼64% net process efficiency. This increment in yield will come with a substantial cost increase because of the use of an FT process.

Recent pioneering work by Dumesic's group uses novel thermochemical catalytic chemistry in place of fermentation to produce fuels and chemicals from aqueous sugars (61–63). This chemistry has been shown to produce interesting fuel molecules such as furan derivatives, branched alkanes and olefins, and alkylated aromatics. These molecules can provide replacements for gasoline and diesel. Future developments in this route will have a strong impact on how biofuel could be produced from sugars.

Among the thermochemical routes, fast-pyrolysis is an efficient method developed in the 1970s that converts biomass to a low energy density liquid (64). In this process, finely ground biomass is rapidly heated in the absence of oxygen to a temperature in the vicinity of 500°C for a short period of approximately one second. The evolved gases are rapidly quenched to yield a liquid that is an emulsion of water and oil generally referred to as bio-oil. The advantages of fast-pyrolysis processes are that they are energy efficient (∼75%), and high biomass carbon recoveries in the 65–75% range are feasible (65, 66). Both energy efficiency and carbon recovery refer to fractions of energy and carbon in the biomass that show up in the carbon-containing molecules of the bio-oil. Fast-pyrolyzers can also be built on the small scale. This characteristic is particularly beneficial as the low energy density of the biomass limits the economical distance for its transportation to a processing plant to 35 to 105 km (9, 67). In fast-pyrolysis, approximately 30% of the biomass carbon is roughly equally split between permanent gases (CO_2, H_2, CO, CH_4, C_2H_4, C_3H_6 etc.) and char by-products. The combustible components are generally combusted to supply heat and electricity for the fast-pyrolysis reactor and other process needs of the plant. Several reactor designs are available for fast-pyrolysis (64, 68), and several companies have built demonstration fast-pyrolyzers with biomass feeds up to 50 ton day^{-1} (69).

However, the properties of the bio-oil from fast-pyrolyzers have limited their use. Typical compositions (in wt%) of bio-oils derived from wood are 54–58% C, 5.5–7% H, 35–40% O, 0–0.2% N, 0–0.2% ash; solid content is 0.2–1 wt% (69). Owing to the high oxygen content, the HHV of bio-oil is in the range of 16–19 MJ kg^{-1}. In contrast, a heavy fuel oil typically has an oxygen content of ∼1 wt% and HHV of 40 MJ kg^{-1} (69). Furthermore, bio-oils do not easily blend with petroleum products. They tend to polymerize and condense with time during shipment and are known to cause coking and gum formation in downstream processing reactors (46, 69, 70). This necessitates the upgrading of bio-oil before it can be used as fuel.

Augmented process: one that uses supplemental nonbiomass energy to substantially boost liquid production from a given quantity of biomass

One method that has been extensively studied for upgrading bio-oil is hydrodeoxygenation (HDO) in the presence of a catalyst to reduce the oxygen concentration (69–72). A typical bio-oil contains more than 300 compounds, and almost all of them include oxygen. Besides water, major compounds include hydroxyaldehydes, sugars, hydroxyketones, carboxylic acids, and phenolics (69). Owing to the presence of so many diverse molecules, HDO catalysis and reactor processing research is evolving into a challenging but useful activity. The amount of oxygen present in bio-oil is far greater than that of the sulfur or nitrogen removed in the hydrodesulfurization (HDS) or hydrodenitrogenation (HDN) of crude petroleum. However, the sulfided as well as unsulfided Co-Mo and Ni-Mo catalysts typical of HDS and HDN have been used in several HDO studies (70, 73, 74). Zeolite-based catalysts, especially those based on ZSM-5, have also been used for thermal stability improvement (46). Researchers at Pacific Northwest National Laboratory (PNNL) have developed a two-step process in which bio-oil is first hydrotreated at low temperatures (∼270°C) followed by a second treatment at higher temperatures (∼350°C). Both stages are run at substantially high pressures of ∼140 bar (70). Although some light components are formed during the HDO step of bio-oil processing, carbon recoveries in the upgraded hydrotreated oil exceed 80%. The oxygen content in the hydrotreated oil can be reduced to below 1 wt%. Because H_2 needs to be supplied to this process, it is important to avoid unwanted side reactions of the oxygenated hydrocarbon molecules in the bio-oil, especially to light molecules such as methane, that will increase H_2 demand and reduce selectivity to the desired hydrotreated oil molecules. The H_2 consumption has been found to vary in the range of 27–31 gmol liter^{-1} of bio-oil processed (70, 72).

The hydrotreated oil is hydrodeoxygenated and has an energy content in the range of 39–43 MJ/kg of upgraded oil and can easily be converted to gasoline and diesel fractions with further hydrocracking (66). Jones et al. have estimated that if a portion of the biomass is gasified to provide the H_2 for HDO of the bio-oil obtained from the remaining biomass, then one could produce gasoline/diesel quality liquid fuel at a yield of 110 ege/ton of total biomass (66).

To summarize, we find that the diverse set of self-contained processes is 40–64% efficient and that their expected liquid fuel yield per ton of biomass varies from the mid-70s to just less than 140 ege. For comparison, if we take biomass with a carbon content of ∼510 kg/ton of biomass and hypothetically convert all the carbons to gasoline-type molecules, the net liquid yield would be ∼320 ege. Thus, the expected yield from the self-contained process is roughly only one-third of the maximum possible, which is reflected in the release by these processes of more than half of the biomass carbon to the atmosphere as CO_2. When the SA biomass supply is limited and more liquid fuel is needed, it is worthwhile to explore augmented processes that will use a nonbiomass form of solar energy to increase liquid fuel production. The next section compares the efficiency of producing additional liquid fuel from such processes using SA biomass with the efficiencies of growing RF crops and converting them to liquid fuel via self-contained processes.

Biomass to Biofuel: The Case for Augmented Processes

Examination of **Table 2** quickly reveals why nearly half of the carbon in biomass is released as CO_2 during its conversion to biofuel by a self-contained process (75). On a per carbon atom basis, as compared with gasoline molecules, biomass sources such as switchgrass, poplar, and sugar have roughly two-thirds the amount of energy. Therefore, even if the conversion to high energy density fuel molecules such as gasoline were 100% efficient, nearly one-third of the biomass carbon would be lost in a low-energy state such as CO_2. With reasonable conversion process efficiencies, one would expect to lose nearly 50% of the biomass carbon as CO_2.

Table 2 Estimated carbon loss for biomass to high energy density liquid fuel with the energy content of gasoline

Biomass	Energy content (MJ kg^{-1})	Energy content (kJ/mol C)	Carbon loss with 100% efficient conversion (%)	Assumed conversion efficiency (%)	Total carbon loss (%)
Switchgrass	17.2	485	24.7	75	43.5
Poplar	19.6	455	32.9	75	49.7
Sugar	14.1	423	43.0	97	44.7

Note: Energy content of gasoline = 605 kJ/mol C. Data from Singh et al. (75).

As shown in the schematic of **Figure 3**, Agrawal et al. envisioned tailoring an augmented conversion process with supplemental energy to decrease and even eliminate the release of CO_2 during this step (13). As our subsequent discussion shows, all the self-contained thermochemical processes can be tailored to use supplemental energy and increase biofuel production from a given quantity of biomass. The addition of supplemental H_2 to a biomass gasifier exhaust stream to produce larger quantities of methanol that is then shipped to a biorefinery has been suggested independently (76). The possibility of producing methanol or ethanol and some of their derivatives by adding H_2 to biomass has also been contemplated separately (77).

Because heat and H_2 are recovered at much higher efficiencies from solar energy (**Table 1**), use of these as supplemental energy increases the overall S2F efficiency for liquid fuels. A properly augmented process can produce incremental biofuel at a much higher S2F efficiency than growing additional RF crop and converting it to biofuel by a self-contained process.

Modeling results are available for the gasification/FT-based H_2CAR process shown in **Figure 4** (13). The word H_2CAR refers to a conversion process that uses H_2 from a nonbiomass energy source with biomass carbon to increase biofuel yield (13). There are two novel features of this process: first, H_2 is directly fed to the biomass gasifier, and second, unconverted CO_2 along with any CO_2 from downstream processes is recycled to the gasifier. At the high temperatures (~1000°C) of the gasifier, the reverse water-gas-shift reaction is thermodynamically preferred, and a large fraction of the CO_2 reacts with the injected H_2 to form CO. The exhaust stream from the gasifier has an H_2/CO ratio close to two, which is needed for the FT reactor. The novel features of the process enable ~100% carbon recovery as liquid hydrocarbon fuel, and the only loss of carbon is through purge streams. Depending on the product distribution in the oil produced, this process is capable of providing 310–330 ege/ton of biomass (13). This yield is three times that of a self-contained gasification/FT process. However, the calculated H_2 consumption, which is based on the total diesel production, is 0.33 kg/liter of oil and could be considered quite high (78).

To identify processes with a lower supplemental H_2 demand, estimates of H_2 consumption to hydrodeoxygenate representative model compounds such as glucose ($C_6H_{12}O_6$), xylose ($C_5H_{10}O_5$), and coniferyl alcohol ($C_{10}H_{12}O_3$) via gasification/FT as well as HDO were made (78). For the HDO reaction, all the C–O bonds were substituted by C–H bonds and the displaced O atoms were converted to water. For the gasification/FT process, the model compounds were first gasified and then reacted with the supply of additional H_2 to yield the same molecules as the HDO process. According to estimates, the supplemental H_2 requirement for the gasification/FT route is 1.4–1.9 times more than the HDO route. These calculations do not account for the potential H_2 involved in the breaking of biomass into smaller monomeric or oligomeric fragments. However, the difference in H_2 demand for the two routes with representative model compounds is large enough to favor the HDO-based processes for lowering the supplementary H_2 demand while maximizing the biomass carbon conversion to liquid fuel.

It is straightforward to envision a fast-pyrolysis-based process in which oxygenated bio-oil is hydrodeoxygenated using solar H_2. Because carbon recovery during the HDO step is in excess of 80% and the energy content of the upgraded oil can be as high as ~42 MJ kg^{-1} (~31 MJ $liter^{-1}$), which is similar to that of gasoline, it should be possible to increase the high energy density oil yield per ton of biomass (70). Indeed, a recent report from PNNL models a three-step process in which gasoline and diesel are produced via fast-pyrolysis, HDO, and hydrocracking using H_2 primarily from natural gas (66). Depending on the value of the energy content of the upgraded oil (38–43 MJ/kg of oil) used for estimation, the oil yield can be in the range of 169–192 ege/ton of biomass (66, 70, 75). This expected oil yield range is substantially higher than that from any self-contained process and also provides a good estimate for the case in which solar H_2 would replace natural gas–derived H_2.

Recently, the concept of introducing a catalyst and cofeeding H_2 to a fast-pyrolysis reactor to allow fast-hydropyrolysis and some HDO has been suggested and termed H_2Bioil (78). **Figure 5** shows the overall concept. Ideally, one would like to choose a reactor design, catalyst, and operating conditions to directly produce deoxygenated high energy density liquid fuel in one step. However, it is likely that a much higher temperature, most likely in excess of 400°C, and a much shorter contact time (~1 s) will be needed for the fast-hydropyrolysis step, and these may not be optimal conditions for the level of deoxygenation needed. Therefore, if needed, the exhaust from the fast-hydropyrolysis reactor, after removal of any char present and temperature adjustment, can be directly sent through an HDO reactor to allow the needed contact time with the HDO catalyst at its preferred operating conditions. The aim is to avoid some of the steps associated with fast-pyrolysis such as total condensation of bio-oil, the associated problems with subsequent handling, and the revaporization for HDO. Bridgwater & Peacock describe a large number of fast-pyrolysis reactor configurations, many of which can be adapted for fast-hydropyrolysis (64).

A few groups have reported lab-scale hydropyrolysis of biomass in a fixed-bed reactor (79–86). These early experiments provide a favorable conceptual proof for hydropyrolysis to produce oil with low oxygen content. However, fast-pyrolysis experiments are not conducted in a fixed-bed mode owing to rapid heating-cooling and the need for a very short residence time in the reactor. Because all the reported hydropyrolysis literature data are for the fixed-bed mode, there is a need to conduct experiments in a fast-hydropyrolysis mode with a possibility of immediate downstream HDO. Because most HDO reactors operate at elevated pressures, this implies that unlike in fast-pyrolysis, the preferred operating pressure for the fast-hydropyrolysis reactors will also be much higher than 1 bar.

Estimates of oil yield and H_2 consumption for the H_2Bioil fast-hydropyrolysis-based process described above have recently been made (75, 78). In the absence of data for the fast-hydropyrolysis operation mode, it is difficult to predict a precise oil yield. However, the fixed-bed studies do report a decrease in char production that could lead to higher oil yield (81, 82, 86). Also, less intense degradation reactions have been reported under H_2 than under an inert atmosphere (85). However, the possibility exists that the formation of lighter C_1–C_3 components might increase slightly. Furthermore, the eventual performance will depend on finding optimal catalysts. In light of these factors, by assuming the carbon yield in the high energy density liquid fuel (42 MJ/kg of oil) for H_2Bioil to be the same (~70%) as for the bio-oil from a fast-pyrolyzer (65), a yield of 215 ege/ton of biomass, using 0.11 kg H_2/liter of high energy density oil, is produced (75). This calculated yield is higher than the 169–192 ege/ton of biomass estimated for the earlier described three-step process owing to the slightly higher biomass carbon recovery figure used here. Although the potential exists to optimize operating process conditions, catalysts, and the use of H_2 to obtain biomass carbon recovery from a fast-hydropyrolysis/direct downstream HDO process in excess of

70%, which would result in further increase in oil yield, currently 215 ege/ton of biomass provides a reasonably good experimental target.

Estimates for a self-contained fast-hydropyrolysis/HDO process can also be made. A novel process concept, wherein a portion of the biomass is gasified and the hot exhaust gas containing H_2 and CO from the gasifier section is directly used for fast-hydropyrolysis of the remaining biomass fraction, is shown in **Figure 6** (75). If needed, the temperature in the hydropyrolysis zone can be adjusted by injecting an appropriate stream at a proper temperature after the gasification zone in the reactor. Incorporation of a high temperature water-gas-shift catalyst is expected to provide in-situ conversion of CO to H_2. Such an integrated process is expected to provide high heat efficiency. This self-contained process was termed H_2Bioil-B (75). At a higher gasifier efficiency, a lower fraction of biomass is directed to the gasifier section because the generation of H_2 and CO is more efficient. Depending on the gasifier efficiency (in the range of 50% to 75%), 42% to 32% of the biomass is fed to the gasifier resulting in 126 to 146 ege/ton of total biomass. This estimated yield range is at the upper end of the self-contained processes.

Thus far we have discussed the use of H_2 in augmented processes. Direct solar heat can also be used to augment a thermochemical process in which biofuel is produced in a hydrothermal medium using external heat. A recent review article describes several such processes (87). One of the earlier studies by Lawrence Livermore National Laboratory researchers describes experimental results using concentrated solar heat to gasify a coal and biomass mixture (88). A handful of papers have since been published reporting experimental results in which biomass or biomass-derived char is gasified using steam and concentrated solar heat (89–91). The exhaust gaseous stream has a H_2/CO ratio of less than two. Therefore, it is possible to further enhance the liquid yield of such processes by using solar H_2 to adjust the H_2/CO ratio prior to the gas-to-liquid reactor (13, 92). Use of solar heat is also reported for fast-pyrolysis (93). Because these processes use at least some direct solar heat, the S2F efficiencies can potentially be higher than those for augmented processes that solely use H_2.

The use of augmented thermochemical processes in conjunction with the processing of residue from a biochemical pathway process has also been suggested (94, 95). Such integrated processes allow better heat management and lead to high oil yields, similar to that of the H_2CAR process.

As a side note, in place of solar energy, the use of nuclear energy to supply the needed H_2 or heat for the augmented processes is also possible (13, 96, 97). The advantage of using nuclear energy is that it overcomes the issues related to the intermittent availability of solar energy.

S2F Efficiencies for RF Crops

Now that we have estimates of biofuel yields for several self-contained as well as augmented processes, it is informative to compare the fraction of the solar energy that is eventually recovered as biofuel via the cultivation and then conversion of RF crops through these processes. **Figure 7** shows the estimated annual biofuel yields from sunlight falling on 1 m^2 of land area (75). These numbers were calculated using the U.S. average annual solar incidence of 6307 MJ m^{-2} yr^{-1} and a biomass collection rate at a biomass processing plant of 1.86 kg m^{-2} yr^{-1} (98). With an energy content of 17 MJ/kg of biomass, 31.7 MJ m^{-2} yr^{-1} of solar energy is delivered as dense biomass for conversion to liquid biofuel. In this figure, bio-oil from the fast-pyrolysis process is not a high energy density biofuel and is shown for information only. For the augmented processes, sunlight from a fraction of the 1 m^2 land area is used to make supplemental H_2 at a net efficiency of 7.6%, and the rest of the land is used to grow RF crops.

The S2F yield numbers reported in **Figure 7** do not account for the auxiliary energy input needed to grow, collect, and then deliver biomass to the gate of a processing plant. Generally the agricultural energy input needed to grow and harvest biomass can be 10 to 20% of the total biofuel produced from the harvested biomass via a conventional self-contained process (21, 22, 98). If the biofuel produced from the harvested biomass is to supply this energy, then a corresponding correction must be made to the numbers reported here. Whereas this will decrease the S2F numbers in **Figure 7** by approximately 10 to 20% for the self-contained processes, the corresponding decrease will be smaller by a factor of two to three for the augmented processes because of the higher biofuel yield per ton of biomass from these processes. However, if a large fraction of this agricultural input is provided through the efficient means of direct electricity, H_2, or heat from the sun, then the fraction of land area dedicated to supplying the agricultural energy input will be small. Furthermore, if small distributed processing plants were to be built, thus avoiding long delivery distances for biomass, then the amount of energy consumed in the delivery of the biomass to a processing plant will be a small fraction of the energy content of the delivered biomass. In such situations, the actual S2F yields from a given land area will be similar to those reported in **Figure 7**, especially for the augmented H_2Bioil and H_2CAR processes. Within a processing plant, all the major energy needs, such as for drying biomass, and any electrical or heat demands are provided from the energy content of the incoming biomass and H_2 when used. Any excess by-product in the form of electricity or heat from a processing plant is not credited in the energy yield as biofuel. Similarly, the energy used to build a biomass processing plant or a plant to produce solar hydrogen is taken to be a small fraction of the total biomass energy processed over the life of the processing plant. The carbon efficiency refers to the fraction of biomass carbon arriving at the processing plant that is recovered in the biofuel product.

Five important observations can be drawn from this figure: (*a*) In existing self-contained processes, generally less than 50% of the energy contained in biomass is recovered as biofuel. Even for the conceptual H_2Bioil-B process, the estimated efficiency from biomass to biofuel is less than 68%. (*b*) Owing to lower efficiencies from biomass to biofuel, S2F efficiencies are quite low for the self-contained processes. For the case shown in **Figure 7** with the assumed RF crop collection rate, the biomass provides solar energy with an efficiency of 0.52%, which results in S2F efficiencies less than 0.34%. This number is an order of magnitude lower than the recovery of solar energy as electricity or hydrogen (**Table 1**). (*c*) The augmented processes can potentially produce two to three times more biofuel per unit of land area than the self-contained processes. (*d*) When augmented processes are used, the energy content of the biofuel can be substantially greater than that of the starting biomass. This is an important observation as it shows that a large fraction of biomass carbon is used to store solar energy in the form of high energy density biofuel. (*e*) For a process such as H_2CAR in which nearly 100% of biomass carbon is recovered as biofuel, the energy content of the supplemental H_2 can be slightly greater than the energy content of the biofuel produced. This means that a substantial portion of the H_2 energy is lost due to inefficiencies during the conversion step. Interestingly, due to higher efficiency for H_2 production, this process still has the highest S2F efficiency of all the processes shown in **Figure 7**.

These observations provide insights that bring us closer to finding solutions to the liquid fuel conundrum in a solar economy. We will now address the next question: when liquid fuel is needed, is it better to use solar energy for an augmented process with SA biomass or to grow a RF crop?

Incremental Biofuel via an Augmented Process with SA Biomass versus Cultivation of RF Crop for Biofuel

When liquid fuel is needed and SA biomass is available for processing with an augmented process, one can use sunlight from an available land area to process the SA biomass with an augmented process or to grow a RF crop and convert it to liquid fuel. On one hand, from **Figure 7** the maximum estimated amount of biofuel than could be produced from a RF crop using a self-contained process is ∼22 MJ m^{-2} yr^{-1}. Even if the RF crop collection rate were increased from 1.86 kg m^{-2} yr^{-1} to a high growth and collection rate of 6 kg m^{-2} yr^{-1}, the biofuel yield would be less than 72 MJ m^{-2} yr^{-1}. On the other hand, for the process efficiencies used in **Figure 7**, sunlight from 1 m^2 of land dedicated to making H_2 would produce ∼479 MJ m^{-2} yr^{-1} worth of H_2. This amount of H_2, when compared with the H_2 amounts used in the augmented processes of **Figure 7**, will supplement processing of much larger quantities of SA biomass and produce an incremental amount of liquid fuel that is far in excess of what could be produced by growing a RF crop. Thus, the carbon contained in biomass at hand is precious because if it is released to the atmosphere during the biofuel conversion process, then the collection of the same amount of carbon by growing a RF crop is quite energy inefficient. Also, biomass should not be viewed simply as a source of energy, but more importantly as a source of carbon. Furthermore, this carbon can be used for storing additional solar energy to provide the greatly increased quantities of biofuel much needed for the transport sector.

Now that the energy preference for developing augmented processes for SA biomass over growing RF crops is clear, the next logical question is once all the SA biomass has been processed by augmented processes, what is the efficient source of carbon for additional liquid fuel?

Direct Atmospheric CO_2 to Liquid Fuel versus Use of RF Crops

The current concentration of CO_2 in the air is ∼383 ppm by volume (99). One can use the available solar energy from a given land area to extract CO_2 from air and convert it to liquid fuel via a chemical process using solar heat and H_2. For example, a reverse water-gas shift reactor may be used to adjust the H_2/CO ratio, followed by a FT process to make diesel fuel. Several studies provide experimental results and energy estimates for directly extracting CO_2 from air (100–104). For example, Zeman reports that 225 kJ of thermal energy and 121 kJ of electrical energy are needed to extract one mole of CO_2 (101). Our recent study provides S2F efficiency estimates for this direct CO_2 extraction route (31). For estimation purposes, solar energy was assumed to be first recovered as electrical energy and then converted to H_2 using an electrolyzer efficiency of 50.7% based on the H_2 LHV. The estimated S2F results, as a function of the efficiency of solar energy conversion to electricity, are reproduced in **Figure 8** (31). For direct CO_2 extraction, the energy associated with extraction was assumed to be solely supplied as electrical energy and was taken to be 20 times the minimum work of separation of CO_2 from air. This extraction energy requirement as solar energy is nearly twice that reported by Zeman (101). Because the maximum S2F efficiency for a RF crop is obtained when the augmented H_2CAR process is used (**Figure 7**), in **Figure 8** the S2F efficiency for the RF crop is estimated using this process. However, even at a high RF crop collection rate of 6.25 kg m^{-2} yr^{-1} and sun-to-electricity efficiencies of 40%, the S2F efficiency is approximately 2%, which is much lower than the range of 4% to nearly 11% for the direct CO_2 extraction route. This means that RF crops including algae will have much lower energy efficiencies than the direct CO_2 extraction route. In **Figure 8**, S2F efficiencies for SA biomass treat SA biomass as a primary energy source, and therefore its energy content is not included in the efficiency calculations. As a result, from the perspective of utilizing additional solar energy, augmenting a SA biomass conversion process is the most energy efficient of the three alternatives.

These results clearly demonstrate that if there is still a need for the liquid fuel when all the available SA biomass has been processed through augmented processes, then it is more energy efficient to separate CO_2 from air and convert it to liquid fuel than to grow a RF crop. However, the direct CO_2 extraction route could face other challenges such as the development of a cost-effective process to separate extremely low concentrations of CO_2 from air at an unprecedented scale.

TOWARD A FUTURE SUSTAINBLE TRANSPORT SECTOR

In a future world, when convenient-to-use primary energy sources such as fossil fuels cease to be readily available and substantial costs are associated with the conversion of primary energy sources, such as solar, to usable forms of energy, an inefficient use of such forms of energy will likely be an economic burden on society. This not only necessitates the identification of pathways that will be energy efficient but also the development of technologies that will support them.

From a review of the literature on the energy efficiency of liquid fuel production from solar energy, the following points can be summarized:

1. SA biomass is akin to a primary energy source and should be the primary resource for liquid fuel production.
2. When enough SA biomass is not available to supply all the needed liquid fuel, the next most efficient method is to use an appropriate augmented process with supplemental energy such as heat, H_2, or electricity, which are also derived from sunlight but at a much higher efficiency than RF crops.
3. When all the available SA biomass has been converted through augmented processes and there is still a need for liquid fuel, then it will be more efficient to directly extract CO_2 from air and convert it to synthetic fuel using solar heat and H_2 than to grow RF crops for biofuel.

The above hierarchical order provides us an efficient route to supply liquid fuel to that portion of the HDV sector that must use on-board high energy density fuel. However, in this review we have not accounted for the energy that will be consumed to manufacture equipment and plants for biomass processing to biofuel or to harvest solar energy as electricity or H_2. Therefore, it is implicit that the energy associated with the manufacture of a plant, when distributed over the lifetime for which plant is expected to be in operation, is a small portion of the total energy processed beneficially by the plant over the same time period. Similarly, the energy and resources used in cultivating and harvesting RF crops have not been included in this discussion.

For LDVs, however, the use of electricity along with SA biomass needs to be explored. Once all the available SA biomass has been converted to biofuel by the self-contained processes and consumed, then the use of electricity to drive the LDV should be maximized within the constraints of the feasibility of on-board electricity storage. Electricity is recovered at a much higher efficiency from solar energy than a RF crop and most likely will also be more efficient than H_2 generation (**Table 1**). Furthermore, if both electricity and H_2 were to be recovered at the same efficiency from solar energy, the S2W efficiency of electric cars would be greater than that of H_2 FCVs (42).

If the use of solar electricity has been explored and fuel is still needed to drive LDVs, then use of additional liquid fuel production from SA biomass using augmented processes should be explored vis-à-vis H_2 FCVs. In this case, which of the two alternatives is used will depend on the S2W efficiency of each route. The efficiency by which solar energy is used to augment production of incremental biofuel and the efficiency by which ICE vehicles use this biofuel will need to be compared with the efficiency of H_2 production and its use by H_2 FCVs (31).

Clearly, in a future sustainable solar economy, liquid fuel in conjunction with solar electricity and H_2 will propel the entire transport sector of a nation or a region of the world. A large fraction of the liquid fuel will most likely be produced from SA biomass using augmented processes that use solar heat and/or H_2 as supplemental energy to increase liquid fuel production.

BRIDGE TO THE FUTURE

The implementation of an efficient solution to fuel a sustainable transport sector will take some breakthroughs in research, the development of innovative technologies, and policy decisions that will encourage and enable the solution's use without causing major economic disruptions. However, while long-term solutions are being developed, it is desirable to seek and develop technologies that can synergistically and economically use currently available energy sources in conjunction with SA biomass. Implementation of such technologies will provide much needed experience and knowledge for the long-term solutions as well as the bridge needed to reach a sustainable future. In the interim, large-scale use of such technologies will also provide environmental benefits (31).

Recently, a synergistic small-scale augmented process was suggested for the transition period using H_2 from natural gas until low-cost solar H_2 becomes available (78). In this process, the natural gas reformer tubes are integrated with the fast-hydropyrolysis reactor so that the hot gases exiting the reformer tubes are sent directly to the fast-hydropyrolysis reactor. Such integration eliminates equipment associated with H_2 separation and simplifies that needed to supply heat to the fast-hydropyrolysis reactor. Portions of the uncondensed gases that are coformed with biofuel are recycled to the natural gas reformer burners. The process synergy is reflected in the fact that the integrative process is expected to produce 1.45 times more liquid fuel than could be produced from the same quantities of biomass and natural gas if each were using its own self-contained process. The integrated process is estimated to require ~7903 MJ of natural gas per ton of biomass and to produce high energy density oil of ~215 ege/ton of biomass. The numbers reported here have been recalculated for the LHV of 48.6 MJ/kg of carbon in oil (42 MJ/kg of oil) and are different from those reported in Agrawal & Singh, which inadvertently used a slightly higher value (78). The integrative aspect of the process eliminates equipment and is expected to contribute to the compactness of the plant; therefore, a successful experimental demonstration could enable it to be built in large numbers on a distributed scale.

A similar synergistic solution can be obtained by integrating the exhaust of a coal gasifier with a fast-hydropyrolyzer for biomass (78). Here the possibility exists to draw a hot side stream from a coal gasification-based power plant and directly inject it into the fast-hydropyrolysis reactor. Similarly, the uncondensed gases that are coproduced with the biofuel can be sent to the gas turbine. The integrative aspects are estimated to provide much higher biofuel yields while keeping power production unchanged.

There is clearly a need not only for experimental demonstration of such integrative solutions but also development of many more innovative solutions that will accelerate the wide-scale production of biofuel from SA biomass and take us closer to a sustainable future.

SUMMARY POINTS

1. Upper theoretical limits of the efficiencies by which RF crops can harvest solar energy are much lower than the demonstrated efficiencies of solar energy conversion to electricity or H_2. Furthermore, currently the conversion to mechanical work is the most energy efficient for electricity, followed by H_2 with a fuel cell, and then oil. Therefore, along with sustainable oil, these other forms of energy will also play an important role in propelling a sustainable transport sector.
2. There will always be a transport sector that requires high energy density fuel similar to the current liquid hydrocarbon fuels.

3. It is important to distinguish between SA biomass and RF crops. SA biomass is akin to a primary energy source and will be the main supplier of sustainable liquid fuel.
4. A self-contained biomass to biofuel process will generally not recover more than 50% of biomass carbon. However, the carbon in a given quantity of biomass is precious because once it is released as a low-energy molecule such as CO_2 during the conversion process to liquid fuel, the replacement carbon to produce additional fuel is recovered at much lower energy efficiencies as either RF crops or direct extraction of CO_2 from air. Basically, a given quantity of biomass is not only an energy source but more importantly a carbon source.
5. From a given quantity of biomass, as compared with a self-contained biomass to biofuel conversion process, augmented processes can produce two to three times more liquid fuel. This additional liquid is a result of the use of supplemental solar energy as heat, H_2, or electricity, which translates into higher biomass carbon recoveries.
6. Of the two options, production of liquid fuel via direct extraction of CO_2 from air is estimated to be more energy efficient than that via cultivation of RF crops. However, both routes are inferior in energy efficiency to an augmented process that can produce more fuel than a self-contained process.
7. For LDVs, once liquid fuel from SA biomass using a self-contained biofuel conversion process is insufficient, the use of electricity within the constraints of on-board storage should be maximized. After that, the choice of whether to use additional liquid fuel from the processing of SA biomass through augmented processes or an H_2 FCV will depend on S2W efficiencies. This means that the efficiencies of ICEs and FCVs will also play a role.

FUTURE ISSUES

1. Agricultural and forestry practices will need to be tailored to maximize production as well as collection of SA biomass in an environmentally responsible manner.
2. A shift from treating biomass primarily as an energy source to treating it as a carbon source needs to be made. Efficient augmented processes for conversion of SA biomass to liquid fuel using supplemental solar energy for high biomass recovery need to be developed. This implies that efficient processes for the recovery and storage of solar heat and hydrogen to supply the supplemental energy will also be needed.
3. Technical breakthroughs will be needed to build self-contained as well as augmented biomass conversion processes on a small, distributed scale to avoid transportation of low energy density SA biomass over long distances. Such plants may be mobile so they can be moved according to the availability of biomass at different locations at different times of the year.
4. A future transportation infrastructure will likely use other forms of energy, such as electricity and H_2, along with sustainable oil. Evolution of such an infrastructure that is energy

efficient and hence sustainable will require careful planning and policy decisions. For this purpose it is essential to first create several future energy-efficient scenarios that encompass harvesting, transformation, distribution, and usage of different forms of energy in a synergistic interaction with each other. This will help us to identify the technological developments/breakthroughs needed to build a sustainable transportation system. More importantly, it will help us to plan and implement the research and development as well as policies needed for the transition.

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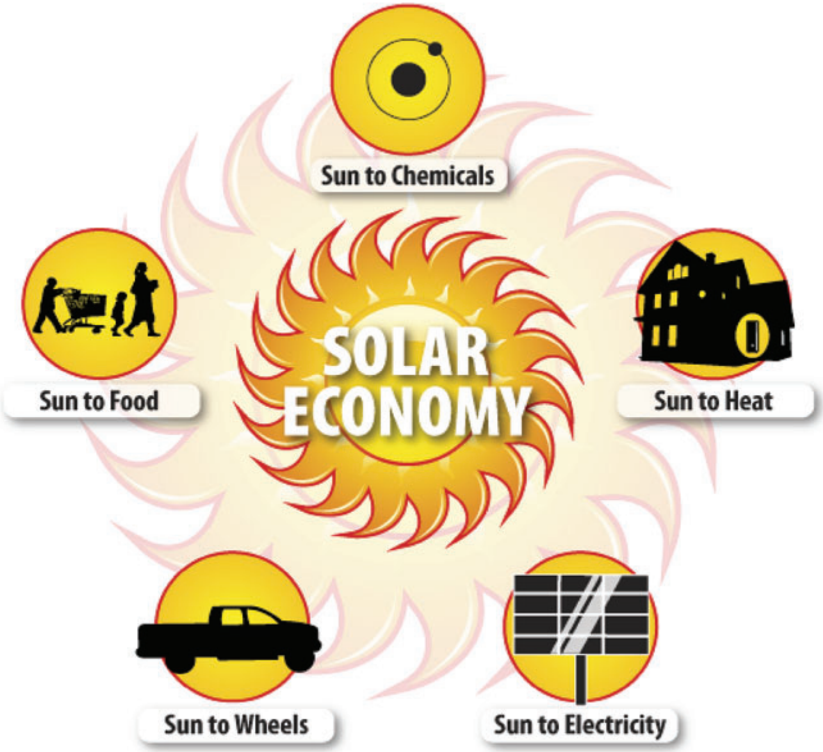

Figure 1

Use of solar energy to meet major human needs.

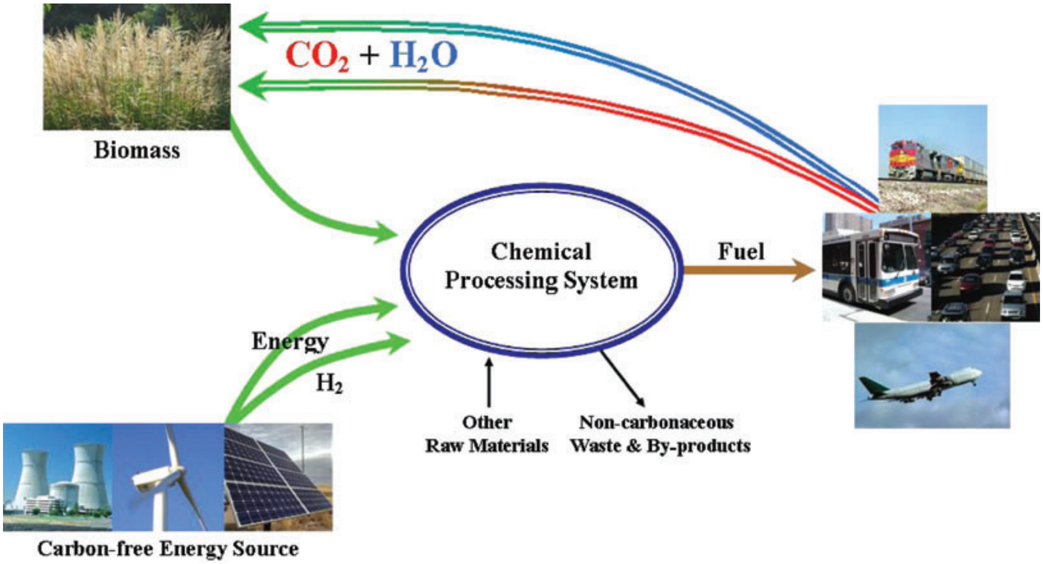

Figure 3

The input of supplementary energy to processes that convert biomass to biofuel. Adapted from Agrawal et al. (13).

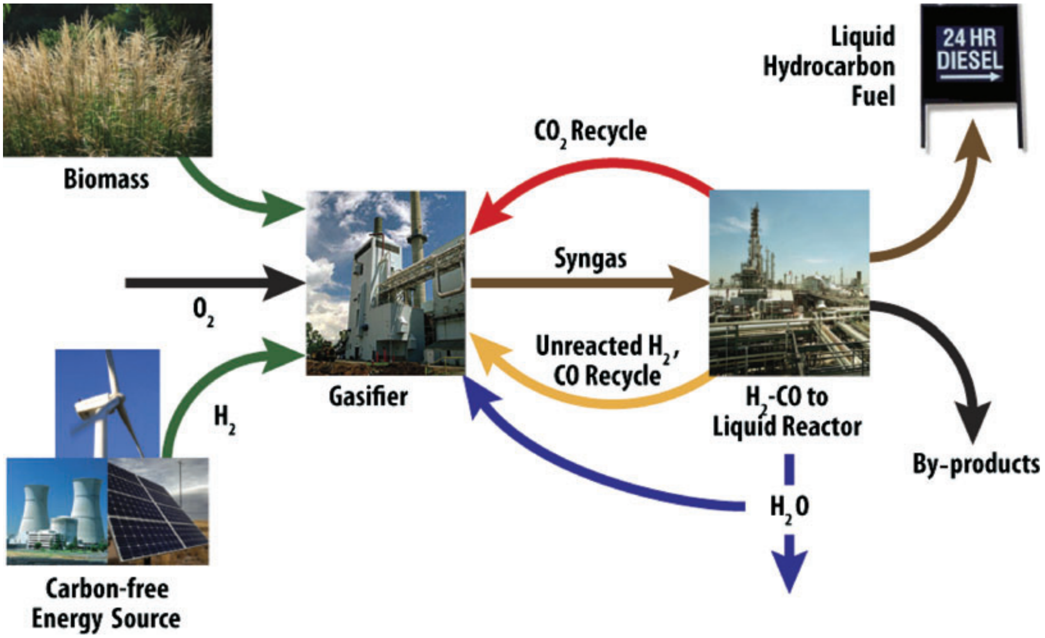

Figure 4

An augmented H_2CAR process based on gasification/Fischer-Tropsch (FT) for increased biofuel production. Source: Agrawal et al. (13).

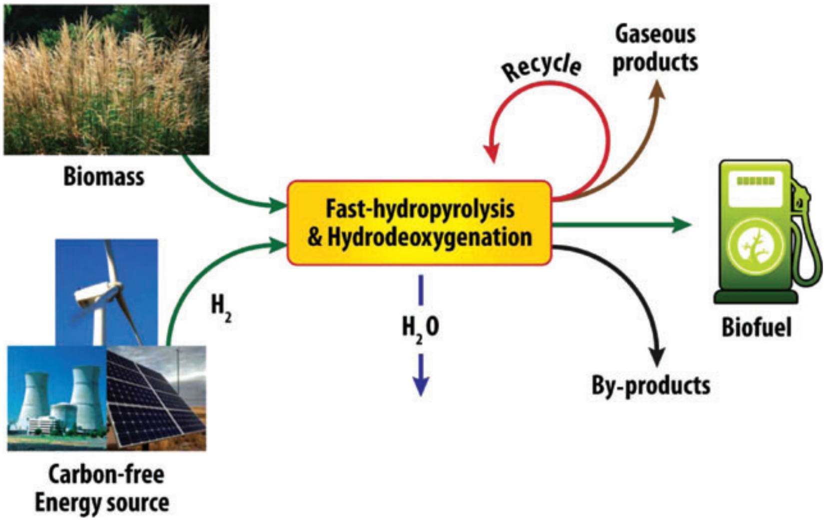

Figure 5

A fast-hydropyrolysis-based process in which hydropyrolysis and hydrodeoxygenation (HDO) are conducted in a single step. Source: Agrawal & Singh (78).

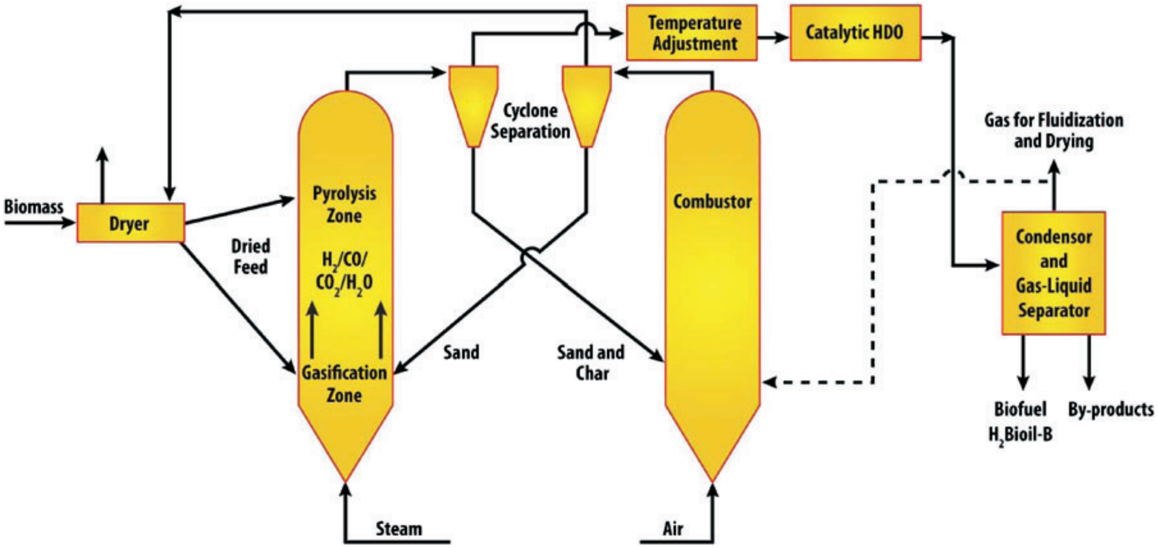

Figure 6

The H_2Bioil-B process in which a portion of biomass is gasified to provide H_2 for fast-hydropyrolysis and HDO. Source: Singh et al. (75).

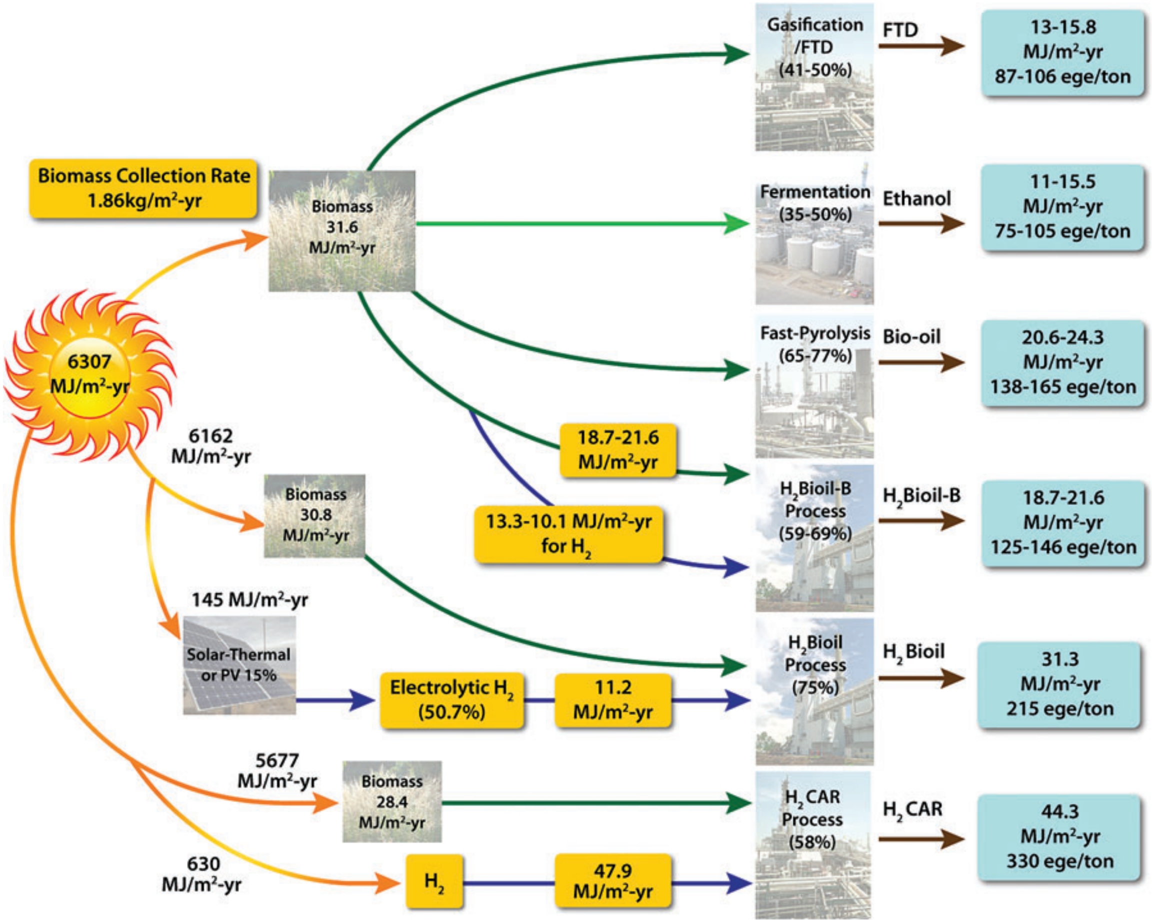

Figure 7

Estimated values of the overall annual biofuel yield from 1 m^2 of land area with annual solar incident energy of 6307 MJ m^{-2} yr^{-1}. For each process, literature reported or estimated conversion efficiency values are shown in parentheses. Adapted from Singh et al. (75). FTD: Fischer-Tropsch Diesel, PV: photovoltaic, ege: ethanol gallon equivalent.

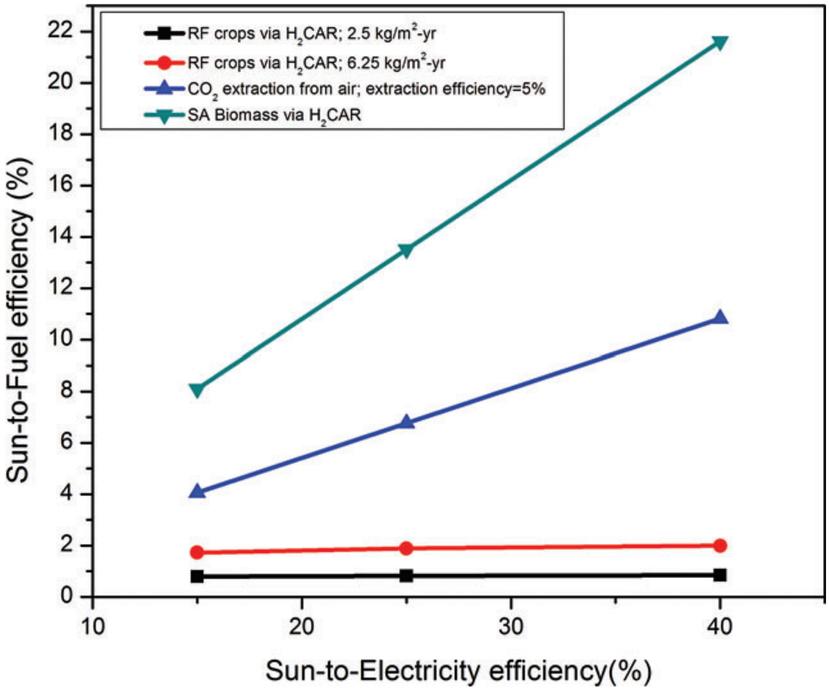

Figure 8

Sun-to-fuel (S2F) efficiency comparison for four options: regulated fuel (RF) crops collected at 2.5 and 6.25 kg m^{-2} yr^{-1} and processed via the H_2CAR augmented process, CO_2 extraction from air, and sustainably available (SA) biomass processed via the H_2CAR augmented process. Source: Singh (31).

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Contents

Errata

An online log of corrections to *Annual Review of Chemical and Biomolecular Engineering* articles may be found at http://chembioeng.annualreviews.org/errata.shtml