Synergistic Routes to Liquid Fuel for a Petroleum-Deprived Future

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When compared with biomass gasification/Fischer-Tropsch synthesis, hydropyrolysis/hydrodeoxygenation (HDO)-based processes have a potential to achieve high biomass carbon conversion to liquid fuel with much lower amounts of supplementary H_2. On the basis of this observation, we suggest a Hydrogen Bio-oil (H_2Bioil) process using fast hydropyrolysis/HDO that has a potential to produce nearly double the amount of liquid fuel when compared with the existing biofuel processes while requiring only modest quantities of supplementary H_2. The optimal operating mode for the H_2Bioil process is suggested to be in an entrained bed mode in presence of H_2 with gas phase HDO of hydropyrolyzed vapors. A remarkable result due to reduced need for the supplementary H_2 is that it provides synergistic integration of the H_2Bioil process with a coal gasification power plant or a small scale steam natural gas (NG) reformer leading to a dramatic increase in the liquid fuel production from biomass and coal or NG. Here, hot synthesis gas ($T>500°C$) from a coal gasifier or methane reformer supplies H_2/CO for hydropyrolysis and deoxygenation as well as heat for the process. This result is exciting, because it presents us with an option to build integrated H_2Bioil processes sooner rather than later when the cost effective H_2 becomes available from a carbon-free energy source such as solar or nuclear. The H_2Bioil process and its integrated version with a small scale NG reformer have strong potential to be attractive on a small scale while being more efficient than any current biomass to liquid fuel process in operation. © 2009 American Institute of Chemical Engineers
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Introduction

A great advantage of using liquid hydrocarbons for the transport sector is their high-energy density and ease of use.[1,2] Currently, almost all the liquid fuel used in the world comes from petroleum crude. In a future scenario, where petroleum crude is not readily available, carbon needed for liquid hydrocarbon fuel will have to come from either other available fossil fuels such as coal, natural gas (NG), etc. or from atmospheric CO_2. In the long run, atmospheric CO_2 is a sustainable source of carbon, and its use in conjunction with a carbon-free energy source, such as solar or nuclear, presents a scenario for net zero carbon emission from the transportation sector.[2] Nature is accustomed to fixing atmospheric CO_2 as biomass, and therefore, use of sustainably available biomass provides an attractive option.[3,4] Because of these plausible scenarios of carbon availability in a petroleum-deprived future, we seek liquid fuel process solutions not only for the long run emanating from the use of sustainably available biomass but also for the immediate future that can exploit synergy with other forms of available fossil

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Additional Supporting Information may be found in the online version of this article.

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fuels. Such solutions will provide us the potential to maintain the current transport infrastructure well into the future by providing a bridge during the transition period.

The energy content of lignocellulosic biomass from switchgrass and poplar trees are 485 MJ/kmol of carbon (17 MJ/kg) and 455 MJ/kmol of carbon (19.6 MJ/kg), respectively. In comparison, the energy density of a high-energy density fuel such as gasoline is 604 MJ/kmol of carbon (32.4 MJ/l). Clearly, conversion of lignocellulosic biomass to high-energy density liquid fuel or chemicals by any conversion process that uses biomass as a sole feedstock is bound to release nearly one-quarter of carbon as CO_2. This release of carbon is not due to any process inefficiencies but simply due to conservation of energy. Any conversion process inefficiency simply leads to release of more lignocellulosic carbon as CO_2. This is a rather undesirable situation, because carbon is delivered to us in a condensed solid state by nature from a source containing 385 ppm of CO_2 at an overall low efficiency of solar energy recovery as biomass of $<1\%$[2,5] (Figure 1). Although a concentration of 385 ppm of CO_2 in air may be deemed high from the perspective of greenhouse effect, it is too low for the design of a low-energy process to recover tonnage quantities of carbon from air. One of the grand challenges in increasing the impact from the use of biomass as high energy density liquid fuel or chemicals is to decrease the use of land area. For any given biomass growth rate, this directly translates into preserving and maximizing the conversion of lignocellulosic carbon to high-energy density liquid fuel or chemical. On the other hand, the recovery of solar energy as heat, electricity or H_2 can be an order of magnitude more efficient than biomass (Figure 1). Therefore, the option to use H_2, heat, or electricity as supplementary energy during the synthesis of liquid fuel to minimize the release of biomass carbon as CO_2 during the conversion process is quite attractive.[2]

It is helpful to briefly examine the characteristics of the existing biomass to biofuel conversion processes to create synergistic solutions for the future. The currently available options to convert biomass to biofuel are summarized in Figure 2.[6–11] These processes have cost, energy, and carbon efficiency limitations. Fermentation-based processes for alcohols from nonsugar portions of the biomass, such as cellulose, hemicellulose, and lignin, are technically challenging and currently not cost effective.[10] Furthermore, for high biomass carbon conversion to liquid fuel, it is essential that all forms of carbon molecules in biomass including lignin be converted to liquid fuel. Thermo-chemical processes not only allow this possibility but are also more to amenable, using supplemental energy as heat or H_2 to increase liquid fuel yield.

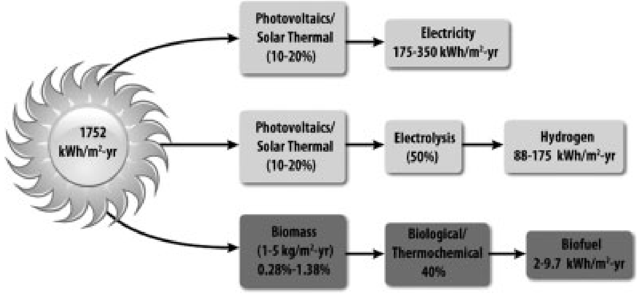

Figure 1. Potential recovery of the annual U.S. solar energy in various forms by currently available processes.

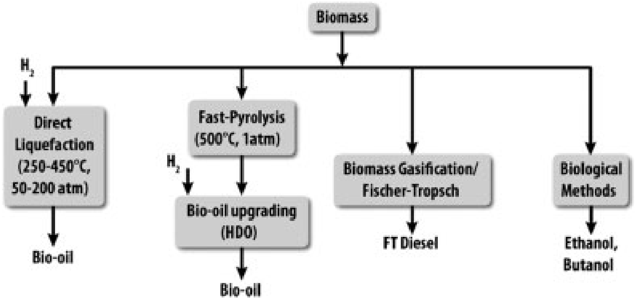

Figure 2. Currently available biomass to biofuel conversion processes.

Among the thermo-chemical routes, the fast pyrolysis processes provide an efficient ($\sim$75%) and low cost method to produce bio-oil,[8] and there are several reactor designs available.[12] However, the resulting bio-oil has extremely high oxygen fraction ($\sim$35–40 wt %), and its energy content is only half that of petroleum and similar to that of the original biomass ($\sim$17 MJ/kg). Furthermore, these bio-oils do not easily blend with petroleum products. This necessitates the subsequent upgrading of the bio-oil by hydrodeoxygenation (HDO) using H_2 in the presence of a catalyst.[10,13,14] However, the bio-oils tend to polymerize and condense with time during shipment and storage and are known to cause coking and gum formation in the HDO reactor and associated lines.[12,15] Direct liquefaction needs very high operating pressure, and the bio-oil produced is expected to be more costly than fast pyrolysis-based systems.[10,16]

Other thermo-chemical processes for biomass conversion to liquid fuel use biomass gasification followed by Fischer-Tropsch (FT) reaction (BG/FT). On the basis of such a process, we recently proposed a hybrid hydrogen-carbon (H_2CAR) process, wherein nearly 100% biomass carbon conversion efficiency is achieved by recycling all the CO_2 formed during the conversion process to the high temperature gasifier and introduction of H_2 from a carbon-free source in the gasifier.[2] However, a major challenge with the H_2CAR process is that the estimated amount of supplementary H_2 needed at 0.33 kg/l of oil produced is quite large. This is especially relevant as the current cost of H_2 from a carbon-free source, such as solar, is quite high. Another challenge stems from the fact that the H_2CAR process uses a gasifier, and a FT reactor and both those unit operations need economy of scale for cost competitiveness. On the other hand, the energy content of biomass is low ($\sim$17 MJ/kg) making it uneconomical for transportation over large distances to feed large size liquid fuel plants. Thus, the use of biomass necessitates finding process solutions that can be built on small scale and distributed over small distances.

In this article, we first examine conversion characteristics of the thermo-chemical processes to identify routes that would require reduced levels of supplementary H_2 while still providing high recoveries of biomass carbon as liquid fuel.

Table 1. Supplementary H_2 Requirement Estimate for Conversion to Deoxygenated Fuel

Representative Molecule	Moles of Supplementary H_2/mole of Representative Molecule	
	Gasification/FT	HDO
Glucose, $C_6H_{12}O_6$	11.1	7
Xylose, $C_5H_{10}O_5$	9.4	6
Coniferyl alcohol, $C_{10}H_{12}O_3$	15	8

On the basis of this insight, we suggest a preferred biomass conversion process that is quite attractive for implementation at small-distributed scale. Next, we suggest novel synergies with NG and coal plants such that these processes can be implemented in the transition time period, until the H_2 from a carbon-free source becomes cost competitive. These short-term solutions are potentially more attractive than the currently available alternate options.

Supplementary H_2 Usage by Thermo-Chemical Processes

For all the thermo-chemical processes, one can envision operating conditions whereby supplementary H_2 is used to preserve biomass carbon during conversion to liquid fuel. However, our goal is to identify thermo-chemical processes that would maximize preservation of biomass carbon with lower quantities of H_2. For discussion, thermo-chemical processes can be divided into two categories: one where biomass is first gasified to smaller molecules CO and H_2 and then, followed by a FT process (BG/FT); and second where a biomass is broken initially into smaller monomeric or oligomeric fragments, and then, HDO is used to substitute O atom with H atoms. To estimate relative quantities of H_2 needed for 100% carbon conversion by each category, instead of biomass, we used representative molecules such as glucose for cellulose, xylose for hemicellulose, and coniferyl alcohol for lignin. Thus, our calculations do not account for the energy needed to break biomass into these smaller molecules. During the gasification step of the representative molecules, enough supplementary H_2 is added to convert all the carbon into CO and furthermore to obtain a H_2/CO ratio of 2 for the subsequent FT process. For the HDO reactions, all the O atoms were substituted with H atoms, and the displaced O atoms were converted to H_2O molecules. Net process heat for both the gasifier and the HDO reactors was kept similar through oxidation of some additional H_2 in the gasifier. This led to gasification efficiencies for glucose and coniferyl alcohol of about 85% and that for xylose to be nearly 77%. The calculation steps are presented in the supplementary information, and the results are summarized in Table 1. The supplementary H_2 requirement numbers for gasification/FT processes are 1.6 to 1.9 times higher than for the HDO process. It should be cautioned that the actual differences in H_2 consumption will depend on the real efficiencies of various processing steps in each category. For example, with the realistic biomass gasification efficiency of about 70% or lower, the difference between the H_2 requirements between the two categories will be even larger. On the other hand, the deoxygenated fuel from the HDO-based route may require further processing to make it more suitable for an internal combustion engine and could lead to additional H_2 demand. It is also possible that there may not be a need to completely deoxygenate the liquid fuel in a HDO process, leading to lower H_2 demand than in Table 1. Despite these unknown factors, the relative difference in the supplementary H_2 demand between the two categories listed in Table 1 is substantially large to favor the HDO-based processes. Thus, we will focus on identifying HDO-based processes that will potentially maximize biomass carbon conversion to liquid fuel with lower supplementary H_2 demand.

Novel Process with Low Supplementary H_2 Usage

Although most of the HDO-based processes such as direct liquefaction and fast pyrolysis followed by bio-oil upgrading are suitable candidates, we will focus on creating offshoots from the fast pyrolysis-based processes. The reason being that fast pyrolysis-based processes are easier to build on small scale at low cost and are becoming commercially viable.[8–10,12,15] As discussed earlier, the associated challenge is related to subsequent handling of bio-oil before and during the HDO process. To overcome this problem, the fast pyrolysis reactor exhaust could be passed through a HDO reactor before total condensation to bio-oil. However, a preferred operating mode would be to replace fast pyrolysis with fast hydropyrolysis in presence of a suitable catalyst, i.e., co-feed H_2 and a suitable catalyst along with biomass to an entrained or fluidized bed short contact time reactor (Figure 3). The operating conditions are to be chosen with the goal to produce bio-oil that is distillable directly from biomass, without need for a separate hydrotreating reactor. In addition to H_2, additional energy from a carbon-free source can be supplied potentially as either heat and/or electricity. If needed, the exhaust from the fast hydropyrolysis reactor, after char removal and subsequent temperature adjustment, can be send through a fixed bed reactor to allow greater contact time with a HDO catalyst at a temperature more suited for HDO. We emphasize, however, that the bio-oil product is cooled

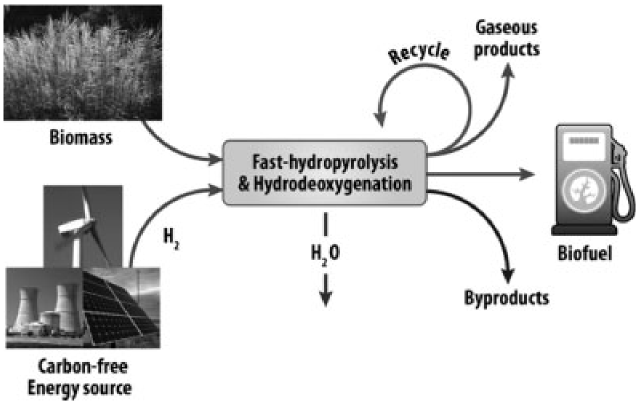

Figure 3. H_2Bioil process where biomass fast hydropyrolysis and HDO are conducted in a single step, and H_2 from carbon-free energy is used.

only to the HDO reaction temperature, not cooled and reheated as in many current processes. We have named such a process as hydrogen bio-oil (H_2Bioil).

To assess the benefits of H_2Bioil process, we modeled the entire process based on data available for conventional fast pyrolysis followed by HDO of bio-oil.[17,18] It should be pointed out that some limited literature experimental results provide us favorable indications for the H_2Bioil process.[19–22] These authors used a packed bed of biomass with a catalyst that was subjected to rapid heating in presence of H_2. The reactor exhaust provided upgraded fuel with low oxygen content. These studies provide us with the proof of concept that biomass when heated in presence of H_2 and a suitable catalyst can yield the desired high-density liquid fuel. However, we are unable to use the literature results from fixed-bed reactors operating in semibatch mode for our modeling calculations of a continuously fed biomass entrained or fluidized bed reactor. Also, these experiments do not report the H_2 consumption during the biomass fast hydropyrolysis process. For calculation purposes, we assumed that the carbon efficiency of the H_2Bioil process was similar to that for the conventional fast pyrolysis process, and char and light gases were burnt to supply heat for reaction. It is worth noting that the HDO reaction is exothermic, and the heat requirement from the char or light gases could be substantially lower for the H_2Bioil process than for conventional fast pyrolysis, leading to higher overall carbon efficiency.

To determine the quantity of H_2 needed for the H_2Bioil process, we took an upper limit by requiring two molecules of H_2 per atom of oxygen removed from the biomass. It should be noted that this requirement of H_2 for the H_2Bioil process is much higher than the one estimated in Table 1. For example, for biomass molecules similar to glucose and xylose (from cellulose and hemicellulose), we are using nearly 70% more $H_{2,}$ and for aromatics such as coniferyl alcohol from lignin, we are using 25% less H_2. However, because lignin content of biomass is typically less than 25%, our use of H_2 provides us an overestimate of the H_2 demand. Indeed, our estimated H_2 requirement of 1024 liter H_2/l of bio-oil for the H_2Bioil process seems to be conservative as it is higher than the highest H_2 consumption of 881 l H_2/l bio-oil reported in the literature to upgrade a bio-oil from a fast pyrolysis reactor.[13,23] Furthermore, for these calculations, the product composition was taken to be similar to that from the earlier work on hydrodeoxygenated bio-oil from fast pyrolysis and also hydropyrolysis.[13,17,23] The main result is high energy density fuel, which is a mixture of various molecules with varying H/C ratio and each having little to no oxygen. The detailed heat and mass balances are described in the Supporting Information and are based on the modeling results provided by Ringer et al.[17] We estimate from our process an unprecedented yield of approximately 230 ethanol gallon equivalent (ege) per ton of biomass. This production rate is compared with those from other biomass to liquid fuel processes in Table 2 and unequivocally shows the tremendous benefit of the H_2Bioil process. This liquid fuel yield is more than twice that of the current gasification/FT and cellulosic ethanol processes!

Table 2. Comparison of Liquid Fuel Yields from Various Biofuel Technologies

Biofuel Technology	Carbon Efficiency (%)	Process Energy Efficiency (%)	Liquid Fuel Yield (ege*/ ton biomass)
Biomass gasification/FT	36.7	40.6	86
Cellulosic ethanol	36.8	35–57	74–121
Biomass fast-pyrolysis	69.7	77	163
H_2Bioil	69.7	81.7	230
H_2Bioil-C	66.3	78.7	218
H_2Bioil-NG	57.6	76.2	230
H_2CAR	100	58	330

*Ege: ethanol gallon equivalent.

From Table 2, it is observed that the H_2CAR process with nearly 100% carbon conversion efficiency is better in terms of liquid fuel yield than H_2Bioil or any other biofuel options. Indeed, one of the process optimization goals for the H_2Bioil process will be to increase carbon efficiency beyond the estimated 70% by minimizing the formation of char and light gases. When compared with fast pyrolysis, the presence of H_2 during pyrolysis in the H_2Bioil process is expected to decrease the char formation, but operating conditions will have to be chosen to limit the formation of the light gases. Even with the estimated level of carbon recovery, H_2Bioil has the potential to play major role in providing transportation fuel. For example, in the United States with the 1 billion tons of annual sustainable biomass and solar H_2, the H_2Bioil process has a potential to produce 8.7 million bbl/d of biofuel.[24] This amount of biofuel, when supplemented with plug-in hybrid cars that could be driven for 64 km per battery charge using electricity from carbon-free energy sources, will be able to support the entire U.S. transportation sector.

Another remarkable result for the H_2Bioil process is that the required amount of supplementary H_2 at 0.09 kg/l of biofuel is far lower than the 0.33 kg/l of biofuel for the H_2CAR process. This large difference in H_2 requirement primarily steams from the following two reasons: (i) as carbon efficiency of a process is increased, the H_2 requirement per liter of fuel increases sharply. For example, biomass gasification/FT process in Table 2 has carbon efficiency of 36.7% and requires no supplementary H_2. As carbon recovery is increased, less carbon is released as CO_2. This means, the energy that was available due to formation of CO_2 must now be supplied by H_2. Furthermore, we need H_2 to be substituted on additionally recovered carbon. Therefore, the H_2Bioil process with carbon efficiency of 69.7% benefits in terms of H_2 demand per liter of liquid fuel when compared with nearly 100% carbon efficient H_2CAR process. (ii) The overall efficiency of H_2Bioil process is based on fast pyrolysis and high efficiency of a HDO process. In contrast, biomass gasification efficiency for the H_2CAR process was taken to be 70%. The dramatic reduction in the H_2 requirement coupled with reasonably high carbon recovery makes the H_2Bioil process quite attractive.

Clearly, demonstration of the H_2Bioil process will have a major impact. Along with solar H_2, it will provide a sustainable solution for a foreseeable future. However, currently, the cost of H_2 from solar or nuclear energy is quite high, and it is worthwhile to search for synergistic extensions of the H_2Bioil processes that are attractive enough to be built in the transition period.

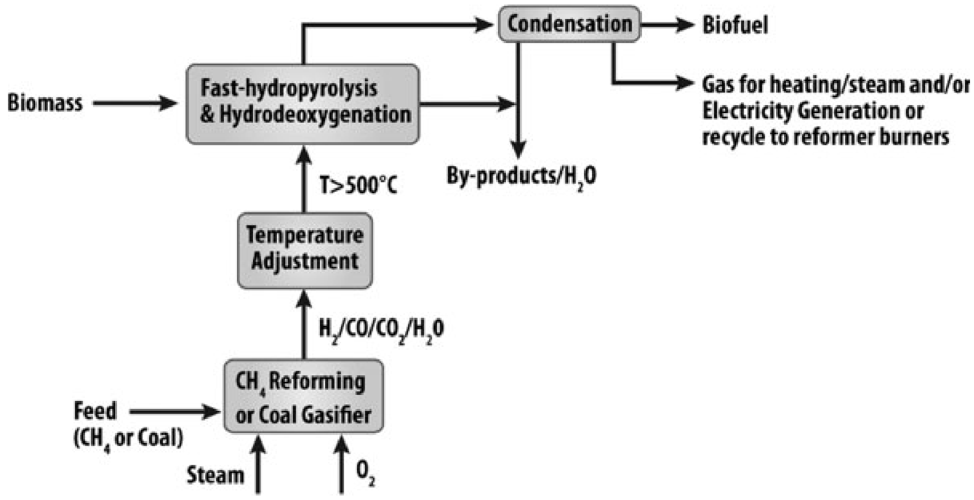

Figure 4. H_2Bioil integration using direct hot syngas from a coal gasifier or a natural gas reformer.

Synergistic Solutions for the Transition Period

The elegance of H_2Bioil is that the key elements of the process can be developed and put into commercial use much before the economical availability of hydrogen from solar. We propose a novel concept whereby hot gas (T>500°) from a coal gasifier or methane reformer containing H_2 along with CO, CO_2, and H_2O will be directly used for fast hydropyrolysis and HDO (Figure 4). Direct use of hot gas has a potential to make the overall process more energy efficient. It will also eliminate equipment and associated cost needed to purify H_2 before the fast hydropyrolysis/HDO. We will now present modeling results demonstrating synergistic aspects of this novel integration.

Integration of H_2Bioil with coal gasification (H_2Bioil-C)

An integrated coal gasification combined cycle (IGCC) power plant is an efficient method to generate electricity from coal. Figure 5 shows our proposed integration of H_2Bioil plant with an IGCC plant. We have named the process resulting from this integration as H_2Bioil-Coal (H_2Bioil-C).

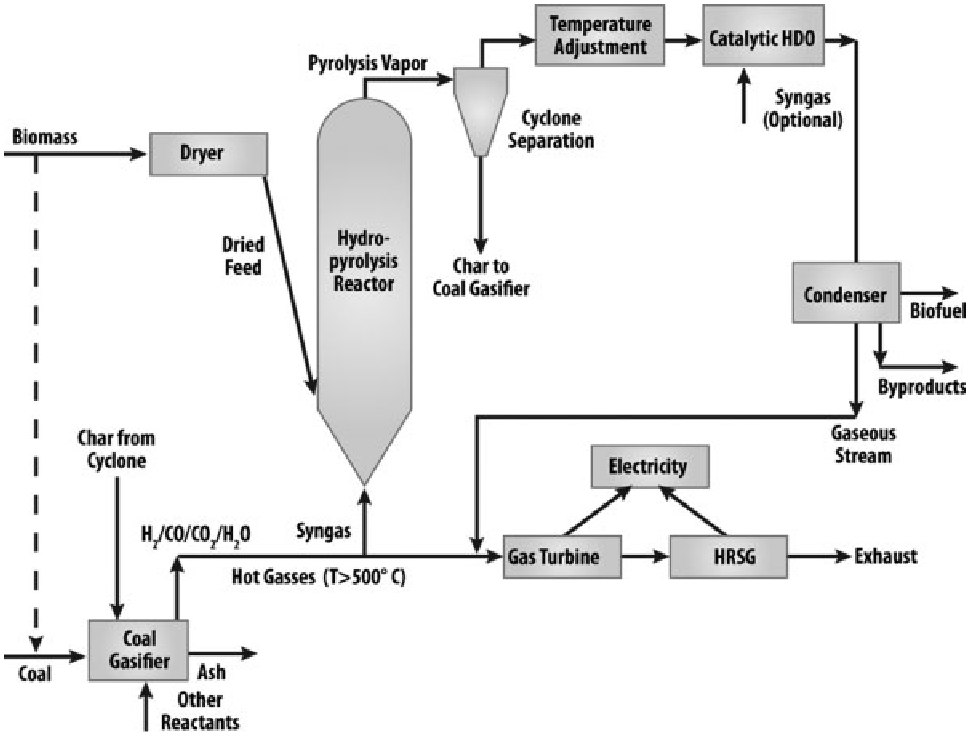

Figure 5. Novel H_2Bioil-C process configuration where hot syngas from a coal gasifier is used to supply H_2 and process heat for biomass fast hydropyrolysis.

A pressurized slipstream of hot exhaust gas containing H_2/CO/CO_2/H_2O from the coal gasifier is used for the fast hydropyrolysis and HDO with the following benefits:

1) Direct utilization of hot synthesis gas (syngas) from the coal gasifier supplies H_2 for the HDO reaction and process heat for the hydropyrolysis process. This results in improved energy efficiency.

2) Low capital and operating cost are achieved for the biomass portion of the plant, because no additional combustor is needed and no separate mechanism, such as sand recirculation, for heat transfer to the biomass hydropyrolysis reactor is needed.

3) Char and noncondensable gases formed during biomass fast hydropyrolysis process can be used in the coal gasifier and gas turbine, respectively, providing synergistic integration.

4) A fraction of total biomass can be co-fed to the coal gasifier to compensate for any decrease in power generation due to utilization of H_2 and process heat for the biomass fast hydropyrolysis/HDO.

An important advantage of this process over conventional HDO is that it will avoid the need for pure hydrogen, and thus save the capital cost associated with hydrogen purification and recovery. Of course, the use of in-situ water-gas shift (WGS) catalysts in the fast hydropyrolysis, and the HDO reactors can provide an effective means to control the H_2 partial pressure during biomass conversion. Furthermore, an interesting but as yet unanswered question is whether CO can play a direct role in pyrolysis or deoxygenation.

H_2Bioil-C was modeled using the data available from the National Renewable Energy Laboratory (NREL) biomass fast pyrolysis process[17] and the Wabash coal gasifier power plant.[25] A slip stream equal to 10.5% of the coal gasifier exhaust stream was fed to the fast hydropyrolysis reactor at 800°C. Nearly 5% of the incoming biomass to the plant was co-fed to the coal gasifier to maintain the current electricity production of the Wabash power plant. The expected process energy efficiency of overall biomass to deoxygenated biofuel conversion based on the biomass energy content was calculated to be ~79%, which is much higher than hitherto known processes. In terms of liquid fuel yield, H_2Bioil-C process has a potential to produce 218 ege/ton of biomass feed (Table 2). This is a highly synergistic result as the total electricity production from the IGCC facility is kept unchanged.

An option that is often cited is to co-feed biomass to a coal gasifier and then, convert the resulting syngas to liquid fuel.[26] Up to 20% of biomass has been co-fed successfully to a coal gasifier.[26] As shown in Table 2, gasification of biomass at efficiency comparable with that of a coal gasifier and then subsequent use of a FT process will result in about 86 ege/ton of biomass. Thus, we expect to obtain an increase by a factor of 2.6 in bio-fuel production by the H_2Bioil-C process! This result is quite significant as it demonstrates the potential advantage of a fast hydropyrolysis/HDO process over a gasification/FT process.

An additional reason for the high efficiency of the H_2Bioil-C process is due to the fact that the H_2 and CO available in syngas are used for their respective chemical value, whereas in the stand-alone power production they are combusted to generate power. To maintain constant power output, the light gases formed during hydropyrolysis are fed to the turbine. When compared with the biomass gasification/FT process, H_2Bioil-C also benefits from the lower H_2 demand as shown in Table 1.

Integration of H_2Bioil with natural gas reforming (H_2Bioil-NG): A case for small size plants

First, let us examine if it makes sense to produce H_2 from NG and use it for a carbon containing moiety's (Biomass) gasification followed by a FT process to produce liquid fuel. We must keep in mind that methane has carbon that can also be used to build liquid hydrocarbon molecules. The first issue at hand is to determine if there are excess H_2 molecules available beyond what could be used by carbon already present in CH_4 for biomass gasification/FT to produce liquid fuel.

Consider the partial oxidation of CH_4:

$$CH_4 + 0.5O_2 = CO + 2H_2 \quad \Delta H_{1000^\circ C} = -23\,\mathrm{kJ/mol},$$

and compare its heat of reaction with complete methane combustion reaction:

$$CH_4 + 2O_2 = CO_2 + 2H_2O \quad \Delta H_{1000^\circ C} = -803\,\mathrm{kJ/mol}$$

If we could run the partial oxidation reaction with the loss of only −23 kJ/mol of heat, then the reactor would be said to have an energy efficiency of 97%. However, actual efficiency of similar processes is generally in the 75% to 85% range. This means that in an actual CH_4 partial oxidation reactor, slightly excess oxygen will have to be supplied to provide the energy for the process inefficiency leading to the formation of CO_2 and H_2O molecules. This means that after the H_2/CO ratio of a partial oxidation reactor has been adjusted to 2 through WGS reaction, there will be CO_2 and H_2O molecules resulting from CH_4. This implies that all the carbon contained in CH_4 is not converted to liquid fuel, and a fraction is lost as CO_2. Indeed an actual gas to liquid (GTL) plant provides about 7.9 ege/GJ of NG (process efficiency of GTL is 63%) vs. a value of 9.5 ege/GJ of NG for a theoretical case where all the carbon atoms have been converted to diesel. So, NG does not generate enough H_2 to convert its own carbon atoms to liquid fuel through a partial oxidation and FT process. A GTL process has to be supplemented with solar or nuclear H_2 to convert all of its own carbon atoms to liquid fuel. Steam reforming processes produce H_2 by converting almost all of carbon in CH_4 to CO_2. Clearly, use of this H_2 in conjunction with alternative CO_2 molecules that have been obtained by a parallel process of partial oxidation of another carbon containing moiety (biomass gasification) to produce liquid fuel via FT process will not provide a synergistic solution.

However, we present a scenario where it is synergistic to use H_2 containing gas directly from the exhaust of steam-methane reformer (SMR) for biomass fast hydropyrolysis/HDO. We have named this process as Hydrogen Bio-oil-NG (H_2Bioil-NG). This integration of the H_2Bioil process is similar to the one shown in Figures 4 and 5. In the process of Figure 5, the coal gasifier is replaced with a SMR such that all the hot exhaust gas from the reformer tubes is directly sent to the fast hydropyrolysis reactor. If needed, the temperature of the exhaust stream maybe adjusted to a desired value by making steam through heat exchange before sending it to the fast hydropyrolysis reactor. Similarly, additional steam needed for reforming can be produced by heat exchange with the exiting streams from the fast hydropyrolysis and the catalytic HDO reactors. After the exhaust stream from the HDO reactor has been cooled and liquid biofuel collected, a significant portion of the uncondensed gases is sent to burners to supply heat needed for the methane reforming. Any char made in the process could be burnt either to supply heat or steam to the reformer. In the simplest version of the H_2Bioil-NG process, no gas turbine, etc will be used to coproduce electricity.

Indeed a simple version of the H_2Bioil-NG is quite amenable to be built on small scale. Small scale SMRs producing H_2 in the range of 40 to 1600 Nm^3/hr are now quite cost effective.[27,28] Modification of such small scale SMRs to allow for the suggested integrations of the H_2Bioil-NG process will result in small scale biofuel processes that will be quite attractive from the capital cost perspective. It should be noted that the integrative aspect of the H_2Bioil-NG is accompanied with process simplification. There is no need to separate H_2 from the reformer exhaust gas, which eliminates equipment and saves cost for SMRs. The use of direct hot gas eliminates the need for a separate mechanism to provide heat for the fast hydropyrolysis reactor leading to lower capital investment for fast hydropyrolysis/HDO. The elimination of equipment and process integration will lead to the reduction in cost and contribute to the compactness of the H_2Bioil-NG equipment.

Modeling calculations to estimate the synergistic gain from the H_2Bioil-NG process were performed. For every ton of biomass, 7170 MJ of NG is required on the basis of LHV. The overall process efficiency of the H_2Bioil-NG, based on dry biomass and NG input, is estimated to be 76.2%, and 229.6 ege of biofuel is produced per ton of biomass. A stand-alone biomass gasification/FT process is estimated to produce 86 ege/ton of biomass, and a GTL plant operating solely with NG will yield about 56.6 ege from 7170 MJ worth of NG. This means that the combined yield from these individual plants each using the same quantity of biomass and NG, respectively, will be about 142.6 ege. In contrast, the 229.6 ege/ton of biomass from H_2Bioil-NG represents an increase by a factor of 1.6! Indeed, H_2Bioil-NG provides a synergistically integrated small scale biofuel process for the transition period until low-cost solar or nuclear H_2 becomes available.

Conclusions

The current processes to provide transportation liquid fuel from biomass are limited severely due to low utilization of carbon in the biomass and low overall process efficiency. Therefore, to provide replacement liquid fuel for the massive quantities of petroleum crude currently used, it is essential to find the processes with extremely high biomass carbon conversion to liquid fuel. In the long run, this goal can be achieved potentially by using H_2 from a carbon free energy source such as solar or nuclear. However, to have an immediate impact, it is desirable to maximize biomass carbon conversion to liquid fuel with modest amounts of H_2.

We accomplish the goal of modest H_2 consumption by observing that at high biomass carbon recoveries, processes based on HDO will require substantially less supplementary H_2 than the processes where biomass is first gasified to syngas and then converted to liquid fuel through the FT reaction. On the basis of this observation, we suggest the use of a process called H_2Bioil whereby biomass is hydropyrolyzed and hydrodeoxygenated using H_2. We envision an entrained or fluidized-bed fast hydropyrolysis in presence of suitable catalysts followed by an immediate downstream HDO before the total condensation of liquid fuel product. Modeling estimates indicate that the high process energy efficiency and carbon recovery of the H_2Bioil process leads to more than double the deoxygenated liquid fuel production per ton of biomass when compared with any currently practiced process. Another major advantage of this process is that it can be built at small to medium size and distributed over relatively short distances to avoid transportation of biomass over long distances. With a modest H_2 demand of 0.09 kg H_2 per liter of biofuel, the H_2Bioil process will be quite attractive once low-cost solar or nuclear H_2 becomes available.

Probably, the most remarkable offshoot of the reduced H_2 need of the H_2Bioil process is that it provides synergistic integration with a coal gasification power plant and also with a small steam NG reformer. In these integrative plants, process and equipment simplifications are achieved by directly using the hot gas from the exhaust of a coal gasifier or a steam methane reformer containing H_2 along with CO, CO_2, and H_2O for fast hydropyrolysis and HDO. The synergistic integration results with coal and NG plants are indeed quite exciting as they result in dramatic increase in the liquid fuel production. As a result, they provide a bridge to the long-term sustainable solution, while cost of H_2 from solar energy becomes economical. The H_2Bioil-NG process has a potential to be economically built in the small to medium size range while still being more efficient than any current biomass to liquid fuel process in operation. This implies that a large number of distributed plants can be built. The logistics and environmental benefits because of the use of lower quantities of biomass and its transport over short distances to produce a given quantity of biofuel will be immense. Indeed, the demonstration of the H_2Bioil based processes will have a huge impact on the liquid fuel-based transport sector for any foreseeable petroleum-deprived future.

Methods

Well-known process system analysis methods in conjunction with a commercial software ASPEN were used to perform various material and energy balances. The calculation details and results are provided in the Supporting Information.

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