



Synergy in the hybrid thermochemical–biological processes for liquid fuel production

Rakesh Agrawal^{a,*}, Navneet R. Singh^a, Fabio H. Ribeiro^a, W. Nicholas Delgass^a, David F. Perkis^b, Wallace E. Tyner^b

^a School of Chemical Engineering and Energy Center at Discovery Park, Purdue University, West Lafayette, IN 47907, United States

^b Department of Agricultural Economics and Energy Center at Discovery Park, Purdue University, West Lafayette, IN 47907, United States

ARTICLE INFO

Article history:

Received 30 October 2008

Received in revised form 14 May 2009

Accepted 22 June 2009

Available online 1 July 2009

Keywords:

H₂CAR process

Hybrid hydrogen–carbon process

Biofuels

Hydrogen

Biomass

Transportation fuels

Thermochemical

Biological processes

ABSTRACT

For a successful large scale implementation of biomass-to-liquid fuel for transportation, it is imperative that production of liquid fuel from biomass be maximized. For this purpose, synergistic processes using energy from sustainable carbon-free energy sources are needed. In this paper, we present such novel integrated processes that, when compared to the known conventional conversion methods, have potential to produce nearly three times more liquid fuel from a given quantity of biomass. The new processes treat biomass predominantly as carbon source and rely on the novel integrations to preserve carbon atoms during biomass conversion to liquid fuel. We have named such approach as hybrid hydrogen–carbon (H₂CAR) process. Furthermore, we propose a novel synergistic integration between H₂CAR and fermentation process where high-level heat from the H₂CAR process is used to supply process heat for the fermentation process and CO₂ produced during the fermentation is converted to liquid fuel using H₂CAR process. This synergy leads to increase in process carbon efficiency (~100%) and higher energy efficiency (65.7% vs. 57.2%), significantly decreasing land area requirement to produce liquid fuel compared to fermentation-based processes. Such synergistically integrated processes provide attractive opportunities for process design, operation and control.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

It is highly desirable to produce liquid fuel in a sustainable manner for the transportation sector in order to overcome the rising concerns of energy security, oil peaking, high crude oil prices and global warming (Goldemberg, 2007; Lewis & Nocera, 2006; Ragauskas et al., 2006). The only sustainable environmentally friendly source of carbon for liquid fuel production is atmospheric CO₂ and plants utilize this source to fix carbon as biomass. Therefore, biomass can be a sustainable source for liquid fuel production. However, a major challenge for biomass-based routes is to economically produce the enormous quantities of liquid fuel needed by the transportation sector.

A recent study states that all the US corn and soybeans can meet only 12% of gasoline and 6% of diesel demand of the USA transportation sector (Hill, Nelson, Tilman, Polasky, & Tiffany, 2006). The billion ton biomass study estimates that 1.36 billion tons of sustainable biomass are potentially available per year in the USA (Perlack et al., 2005) It is also estimated that from this quantity of biomass, cellulosic ethanol or thermochemical methods can only

meet 30% of the US transportation sector's current need of about 13.8 million barrels per day (Mbb/d) (Davis & Diegel, 2007). This still leaves a significant gap between the supply and demand for the US transportation sector. Clearly, there is an urgent need for processes which can produce significantly higher liquid fuel yields from a given quantity of biomass.

In this paper, we propose novel process integration at various levels with the sole purpose of increasing liquid fuel production from a given quantity of biomass. Conventional biomass-to-liquid fuel conversion processes use a major portion of the energy needed for conversion from the biomass itself. Thus, while a portion of the biomass is converted to liquid fuel, a significant portion is converted to CO₂. This is true for corn to ethanol as well as biomass gasification followed by Fischer–Tropsch (FT) processes. As a result, generally less than half of the original biomass energy is recovered as liquid fuel. In the first integrative step, we show the dramatic advantage of supplying energy needed for the conversion processes from a carbon-free energy source such as solar or nuclear. In the second integrative step, we show yet another synergistic integration between a fermentation-based process and a gasification–FT based H₂CAR route. We show the calculated results of such integrations in terms of both the increased liquid fuel yield as well as improved efficiency of the conversion from a given quantity of the biomass. The factors leading to synergistic results are also discussed.

* Corresponding author. Tel.: +1 765 494 2257; fax: +1 765 494 0805.
E-mail address: agrwalr@purdue.edu (R. Agrawal).

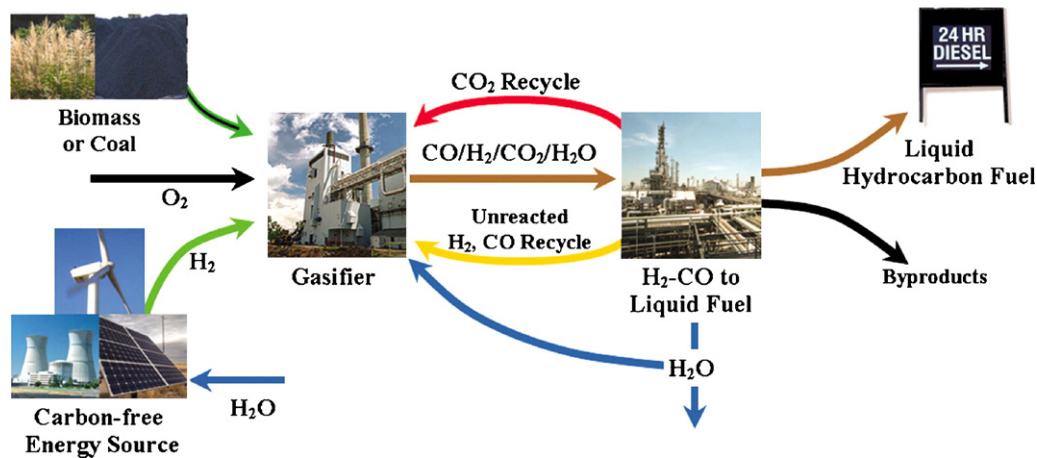


Fig. 1. The H₂CAR process (Agrawal et al., 2007).

2. Integration of a biomass-to-liquid fuel process with a carbon-free energy source (thermochemical process)

Recently, we proposed a novel partnership between biomass and hydrogen derived from carbon-free sources such as solar-thermal, solar PV, wind, and nuclear to produce liquid fuel for the transportation sector (Agrawal, Singh, Ribeiro, & Delgass, 2007). In the conventional processes, a part of the carbon in the biomass is lost as CO₂ and provides the necessary energy required for the conversion process. For example, ethanol production from sugars releases nearly 49% of the total mass as CO₂, and a biomass gasification–FT process has a carbon efficiency of <40% (Agrawal et al., 2007; Huber, Iborra, & Corma, 2006). The proposed partnership is shown in Fig. 1 and results in a significantly higher liquid yield by preserving all the biomass carbon in the final liquid fuel. This H₂–CARbon approach has been nicknamed the H₂CAR process. The H₂CAR approach assures nearly 100% carbon efficiency through recycling of the CO₂ produced during the conversion process to the gasifier operating at higher temperatures where this CO₂ is converted to CO via the reverse water-gas reaction by externally supplying the gasifier with hydrogen from a carbon-free source. This externally supplied hydrogen is also used to adjust the H₂ to CO ratio to about 2 for the FT process and to supply energy for the endothermic gasification reaction and other process losses.

The essential features of the H₂CAR process are: (i) Biomass is primarily a supplier of carbon atoms. (ii) H₂ is supplied from a carbon-free energy source such as solar, wind and/or nuclear. (iii) H₂ is used to convert every carbon atom to liquid fuel. (iv) No CO₂ is released during the biomass-to-liquid conversion process. (v) Solution to H₂ storage problem of the so-called ‘H₂-economy’. This can lead to dawning of a “hybrid hydrogen–carbon economy” (Agrawal & Singh, 2008; Agrawal et al., 2007).

Process simulations using ASPEN have shown the thermodynamic feasibility of the process. For a biomass gasifier operating at 70% efficiency and a biomass growth rate of 1.5 kg/m²/yr, nearly 0.92 million km² land area is needed to produce 13.8 Mbbbl/d as against 2.5 million km² needed for the corresponding conventional biomass gasification–FT process. About 269 billion kg of H₂ per year from solar energy will be needed for this scenario but this represents a significantly lower land area requirement as compared to the land area needed for the biomass growth. The carbon efficiency of the H₂CAR process is expected to be nearly 100% as against 37% for the conventional process. Another interesting aspect is that the energy efficiency based on the energy content of the biomass and hydrogen fed to the conversion plant is expected to be higher for the H₂CAR vs. the conventional approaches (~57% vs. ~41%).

The reason for the dramatic increase in the liquid fuel production from a given quantity of biomass for the H₂CAR process can be

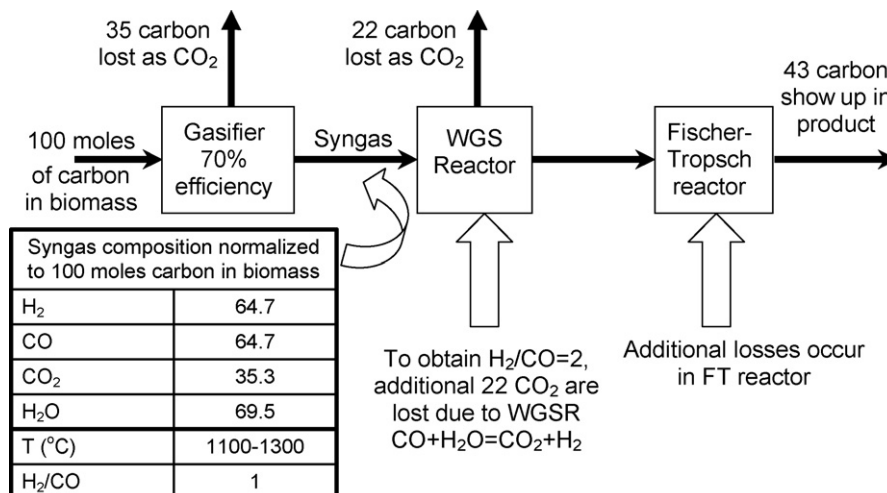


Fig. 2. The process of loss of carbon atoms as CO₂ during the conventional biomass gasification/FT process.

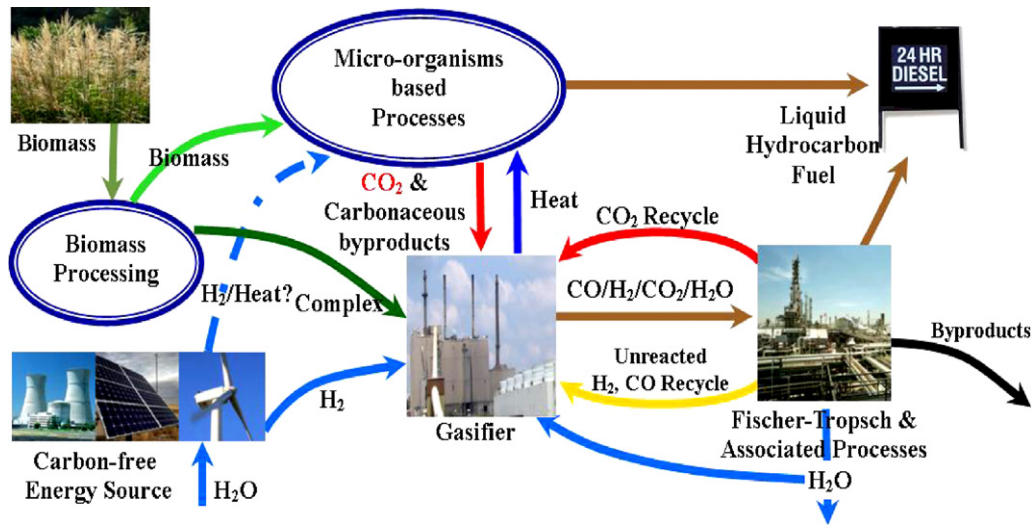


Fig. 4. A plausible integrated configuration of the H₂CAR-biological processes.

ferent unit operations. Specifically, a thermochemical gasification route (H₂CAR process) is added in parallel to the biological pathway (fermentation). The aim is to convert the portion of biomass that cannot be easily converted through the biological route to liquid fuel via the thermochemical route. In Fig. 3, we present the framework used to carry out systems analysis using the proposed integration scheme. The essential features of this scheme are:

- (i) Biomass is split into two fractions. First fraction is sugar fraction or the fraction that can be easily converted to biofuel through the use of micro-organisms, enzymes, etc. The second fraction is complex carbohydrate or a biomass that cannot be converted to biofuel through the use of micro-organisms.
- (ii) The first fraction is sent to a reactor analogous to fermenter where most of it is converted to desired biofuel.
- (iii) The second fraction is sent to a chemical processing system where it is hydrogenated with H₂ from a carbon-free energy

source. This unit can be a direct biomass-to-liquid conversion (similar to say coal to liquids). An alternative is to replace direct biomass hydrogenation unit with a two-step process of gasification followed by CO and H₂ reaction. For this analysis, we use the H₂CAR process for the fraction of biomass which cannot be utilized by micro-organisms.

- (iv) CO₂ and any undesirable carbonaceous by-product from the fermenter (or any reactor containing micro-organism) are sent to the H₂CAR process. The major advantage of the framework shown in Figs. 1 and 3 is that the carbon efficiency of the entire process will be ~100% implying much reduced land area to support the entire US transportation sector.

An attractive feature of this concept is that as new biomass species along with new enzymes and microbes for conversion to alcohol are developed, various mass and heat flows through each of the pathways depicted in Fig. 3 will be adjusted in tandem

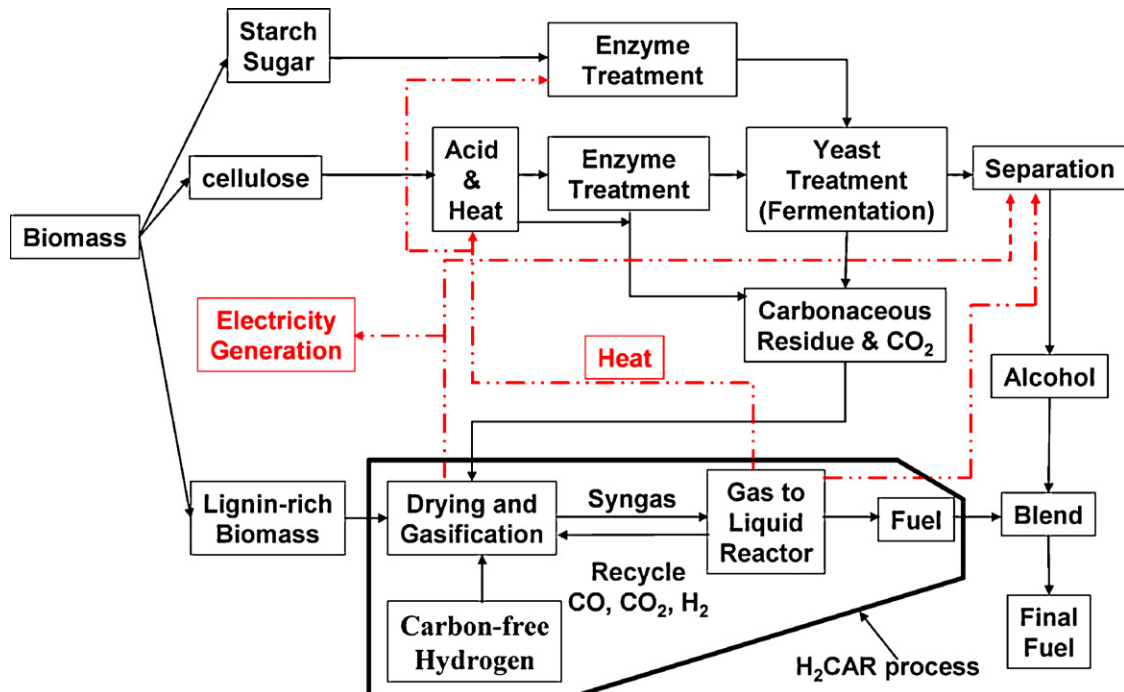


Fig. 5. Detailed schematic of an integrated framework for biomass-to-liquid fuel conversion process.

to maximize fuel production. Furthermore, the process will allow simultaneous handling of diverse species of biomass making our process ecologically friendly. In one of the possible configurations, the chemical processing system referred to in Fig. 3 can be represented by the H₂CAR process of Fig. 1 and the resulting process is shown in Fig. 4. The H₂CAR process reaches a carbon efficiency of 100% by recycling all the CO₂ formed during the conversion process and feeding it back to the gasifier where the high temperature prevalent in the gasifier favors reverse water-gas shift reaction reducing CO₂ concentration by using external H₂. So, as long as CO₂ is available for feeding to the gasifier, use of external H₂ can be used to convert this CO₂ to CO which can be further converted to liquid fuel by Fischer–Tropsch process.

The essential features of proposed integrated H₂CAR-fermentation process shown in Fig. 5 are: (i) Optimal conversion route for all forms of carbon such as sugar, cellulose, hemicellulose, and lignin contained in the biomass-to-liquid fuel. (ii) Conversion route for the entire carbon residue from the unit operations contained within the biological process through gasification. (iii) Conversion of all the CO₂ from the fermenter to liquid fuel using H₂CAR. (iv) Use of high-level heat from the gasifier and gas-to-liquid conversion reactor for the digestion of lignocellulosic mass and the separation of alcohol from the fermenter effluent. (v) Use of the low-level heat from the gasifier as well as gas-to-liquid conversion reactor to dry the biomass prior to gasification. (vi) Use of any excess high-level heat from the gasifier to co-produce electricity. (vii) Heat from carbon-free energy sources such as nuclear reactors or concentrated solar thermal to supplement requirements for the fermentation process.

4. Calculation details

A descriptive process model which incorporates a fair amount of detail on costs and conversion efficiencies at each step of the ethanol production process is used. The model can calculate energy requirements and capital and operating costs for ethanol plants varying in size from 10 to 100 million gallons per year (Dale & Tyner, 2006a, 2006b). We selected an ethanol plant size of 100 million gallons per year for integration with the H₂CAR process. The ethanol plant needs 106,300 kg corn grain/h and produces 34,123 kg/h ethanol, 32,640 kg/h CO₂ and 34,074 kg/h DDGS. The product formation nearly follows the one-third rule, where 1/3 of the corn grain is converted to ethanol, 1/3 to CO₂ and 1/3 to DDGS by mass (Rosentrater, 2005). Fossil energy required for this plant is 12.8 MJ/l ethanol produced, in agreement with a number of literature studies (Hill et al., 2006; Morey, Tiffany, & Hatfield, 2006), whereas the energy content of ethanol is 21.1 MJ/l. Ethanol yield in our model is 107.5 gal per metric ton corn (0.41 l/kg corn). Biomass gasifier data is obtained from DOE H2A analysis and calculation details are explained in Supporting Information.

5. Results and discussion

Detail calculations were done for the integrated process of Fig. 4, and the salient results are summarized in Table 2. Due to the utilization of entire carbon in corn grain by gasifying DDGS, corn stover and recycle of CO₂ from fermenter to the gasifier such that biomass is treated as source of carbon atoms and hydrogen from a carbon-free energy source is used, significant decrease in biomass requirement for producing a given quantity of liquid fuel. In addition, supplying energy from the high-level heat of gasifier or Fischer–Tropsch (FT) reactor decreases significantly or completely eliminates the energy requirement in the bio-refinery stage. We present a comparison of these integrations in terms of carbon efficiency, energy efficiency and carbon-free hydrogen requirement to

Table 2

Carbon, energy efficiency and H₂ requirement of integrated H₂CAR–corn ethanol processes.

Case (in all cases, mass equivalent to DDGS is subtracted)	Carbon efficiency (%)	Energy efficiency (%)	H ₂ requirement (billion kg/yr)
Corn ethanol	67	57.2	–
H ₂ CAR	~100	57.3	269
H ₂ CAR + fermentation (heat and CO ₂ integration)	~100	65.7	200

produce a given quantity of liquid fuel in Table 2. All the case studies are explained in Supporting Information (SI).

One reason for higher efficiency of conversion of CO₂ from fermenter to diesel via reverse water-gas shift is because there is no need to supply energy for drying of biomass. On the other hand, large quantity of energy is required for the drying process. Potential exists to achieve higher efficiency by reducing the inefficiency of the process. In our calculations (refer SI), we assumed a water-gas shift reactor efficiency of 80%, comparable to CH₄ reforming (NRC, 2004).

From Table 2, we observe that integration is much better for the H₂CAR-fermentation as compared to stand-alone fermentation or H₂CAR process (nearly 8.2% higher). This improvement in energy efficiency increases the ethanol life cycle energy balance from 1.25 to 3.32 and simultaneously, decreases the hydrogen requirement from 269 to 200 billion kg/yr. However, looking at the energy efficiency values of the integrated H₂CAR-fermentation process (65.7%) with stand-alone H₂CAR process (62.3%) after accounting for the electricity production in Table 2, one may think that there is not much gain in the integrated process as compared to H₂CAR. However, our aim is to maximize the energy stored in the liquid fuel as compared to the energy in original biomass. Conversion of one form of energy to another leads to significant losses in the process. Prins et al. have shown that the major exergy losses in biomass gasification and subsequent conversion to liquid fuel are in gasification (23% loss), steam generation (9% loss), and power generation (24% loss) (Prins, Ptasiniski, & Janssen, 2005). Direct use of heat generated during the H₂CAR process for the fermentation process removes inefficiencies involved with steam and power generation for electricity production. This is the reason for synergy in the integration process. In addition, if cheap electricity is available for H₂ production from carbon-free energy sources, it is desirable to use heat available from gasifier for liquid fuel production instead of producing electricity solving the storage problem of the carbon-free energy sources. So, comparison should be on the basis of the energy efficiency for liquid fuel production from a given quantity of biomass in the integrated process (65.7%) as compared to H₂CAR (57.3%) or fermentation (57.2%).

6. Conclusions

In this paper, we have demonstrated that biomass alone cannot support the entire US transportation sector. To overcome this scenario, we suggest a novel partnership between biomass and hydrogen from a carbon-free energy source to produce biofuels having three times higher yield per unit mass of biomass as compared to the conventional processes. The H₂CAR process can potentially meet the need for the entire US transportation sector with 1.37 billion tons of biomass as against 3.77 billion tons of biomass required for conventional gasification–FT process. Furthermore, this approach solves the hydrogen storage problem of the so-called hydrogen economy. In addition, we describe a novel integration of the H₂CAR process with the conventional fermentation-based processes leading to even higher process energy efficiencies. This

synergistic process results in a decrease in H₂ requirement as compared to the stand-alone H₂CAR process and a significant decrease in the land area as compared to the stand-alone fermentation-based processes. High-level heat from the gasifier and FT reactor can be used to supply energy for the bio-refinery, where CO₂ and corn stover can be converted to liquid fuel using H₂CAR process. The ethanol life cycle energy balance improves from 1.25 to nearly 3.32 without any CO₂ release during the conversion process, implying an environmentally friendly way of producing ethanol.

For biomass-to-liquid fuel production for the transportation sector, it is essential to have high carbon conversion and energy efficiencies to minimize biomass use and, hence, the land area requirement. It is apparent from our discussion that this can be achieved through the development of a synergistically integrated biomass-to-liquid fuel conversion processes. We presented two such examples in this paper. From a process engineering perspective, this presents unique opportunities for the process design, operation and control.

Generally a new process comes with its own challenges and integrated H₂CAR-fermentation process is no exception. Following are some of the major challenges: (i) Finding an 'optimum' biomass for the integrated process. (ii) Cost-effective production of H₂ from carbon-free energy source. (iii) Design of a novel chemical processing unit for complex biomass. (iv) Design and operation of novel gasifier. This becomes even more challenging when wet carbonaceous residue from fermenter and any other unit operation is to be sent to the gasifier. (v) Novel separation processes to maximize advantage of heat integration. (vi) More selective conversion of CO and H₂ to desired synthetic liquid fuel (fermenter fuel could be blended with this fuel leading to optimization of the blended properties).

Acknowledgments

We sincerely thank Purdue University's Energy Center, Indiana Center for Coal Technology Research (CCTR), Hartley Foundation and Center for Advanced Manufacturing at Purdue University for partial support of this work.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.compchemeng.2009.06.026.

References

- Agrawal, R., & Singh, N. R. (2008). *System and process for producing synthetic liquid hydrocarbon*. US Patent Application 20080115415A1.
- Agrawal, R., Singh, N. R., Ribeiro, F. H., & Delgass, W. N. (2007). Sustainable fuel for the transportation sector. *Proceedings of the National Academy of Sciences of the United States of America*, 104, 4828–4833.
- Dale, R. T., & Tyner, W. E. (2006a). *Economic and technical analysis of ethanol dry milling: Model description*. <http://ideas.repec.org/p/pae/wpaper/06-04.html>.
- Dale, R. T., & Tyner, W. E. (2006b). *Economic and technical analysis of ethanol dry milling: Model user's manual*. <http://ideas.repec.org/p/pae/wpaper/06-05.html>.
- Davis, S. C., & Diegel, S. W. (2007). *Transportation energy data book* (26th ed.). <http://cta.ornl.gov/data/download26.shtml>, ORNL-6978.
- Goldemberg, J. (2007). Ethanol for a sustainable energy future. *Science*, 315, 808–810.
- Hill, J., Nelson, E., Tilman, D., Polasky, S., & Tiffany, D. (2006). From the cover: Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels. *Proceedings of the National Academy of Sciences of the United States of America*, 103, 11206–11210.
- Huber, G. W., Iborra, S., & Corma, A. (2006). Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering. *Chemical Reviews*, 106, 4044–4098.
- Levene, J. I., Mann, M. K., Margolis, R., & Milbrandt, A. (2005). An analysis of hydrogen production from renewable electricity sources. In *Conference paper for ISES 2005 Solar World Congress Orlando, FL*.
- Lewis, N. S., & Nocera, D. G. (2006). Powering the planet: Chemical challenges in solar energy utilization. *Proceedings of the National Academy of Sciences of the United States of America*, 103, 15729–15735.
- Morey, R. V., Tiffany, D. G., & Hatfield, D. L. (2006). Biomass for electricity and process heat at ethanol plants. *Applied Engineering in Agriculture*, 22, 723–728.
- NRC. (2004). *The NRC report—The hydrogen economy-opportunities, costs, barriers, and R&D needs*. Washington, DC: The National Academies Press.
- Perlack, R. D., Wright, L. L., Turhollow, A. F., Graham, R. L., Stokes, B. J., & Erbach, D. C. (2005). *Biomass as feedstock for a bioenergy and bio-products industry: The technical feasibility of a billion-ton annual supply*. http://feedstockreview.ornl.gov/pdf/billion_ton_vision.pdf, DOE/GO-102995-2135 ORNL/TM-2005/66.
- Prins, M. J., Ptasiński, K. J., & Janssen, F. J. J. G. (2005). Exergetic optimisation of a production process of Fischer-Tropsch fuels from biomass. *Fuel Processing Technology*, 86, 375–389.
- Ragauskas, A. J., Williams, C. K., Davison, B. H., Britovsek, G., Cairney, J., Eckert, C. A., et al. (2006). The path forward for biofuels and biomaterials. *Science*, 311, 484–489.
- Rosentrater, K. A. 2005. Expanding the role of systems modeling: considering byproduct generation from biofuel production. *Ecology and Society* 11(1): r2. [online] URL: <http://www.ecologyandsociety.org/vol11/iss1/resp2/>.