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Distributed, Integrated Production of Second and Third Generation Biofuels

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1. Introduction

Materials that are burned directly for energy, such as firewood, wood chips, pellets, animal waste, forest and crop residues are considered primary biofuels. First generation biofuels also include bioethanol produced by fermentation of starch (from wheat, barley, corn, or potato) or sugars (from sugarcane or sugar beet), and biodiesel produced by transesterification of oil crops (including rapeseed, soybeans, sunflower, palm, coconut) and animal fats. Second generation biofuels include bioethanol and biodiesel produced from the residual, non-food parts of crops, and from other forms of lignocellulosic biomass such as wood, grasses, and municipal solid wastes (Inderwildi & King, 2009). Third generation biofuels include algae-derived fuels such as biodiesel from microalgae oil, bioethanol from microalgae and seaweeds, and hydrogen from green microalgae and microbes (Aylott, 2010; Dragone, et al., 2010). "Drop in" fuels like "green gasoline," "green diesel," and "green aviation fuel" produced from biomass are considered fourth generation biofuels (Kalita, 2008). Efforts are also underway to genetically engineer organisms to secrete these fourth generation hydrocarbon fuels.

Today, corn is the major source of first-generation bioethanol, with over 12 billion gallons of fuel ethanol produced in 2010 from approximately 4.6 billion bushels of corn (Anon, 2011b) in 190 operating facilities in 26 states. Most are located in the Midwest, near the site of feedstock production (Figure 1), however some are co-located with dairies or beef cattle feeding operations or dairies outside the Corn Belt. The typical size of corn ethanol plants is 50-100 million gallons per year. Table 1 provides a summary of industry growth in the US over the past decade. Ethanol is also the most important biofuel worldwide in terms of volume and market value (Licht, 2006).

In 2007, Congress passed the Renewable Fuels Standard 1 (RFS1), which mandated renewable fuel use of 7.5 billion gallons by 2012. Congress subsequently passed the Energy Independence and Security Act of 2007 (EISA), which made significant changes in the structure and magnitude of the renewable fuel program. The EISA (also called the RFS2) specified use of a total of 15.2 billion gallons/year of renewable fuel by 2012 and 36 billion gallons/year by 2022.[1] Also mandated were maximal amounts of corn-based ethanol,

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[1] Federal Register, March 26, 2010, pp 14670-14904, Final Rule 40 CFR 80; 75 FR 14670;
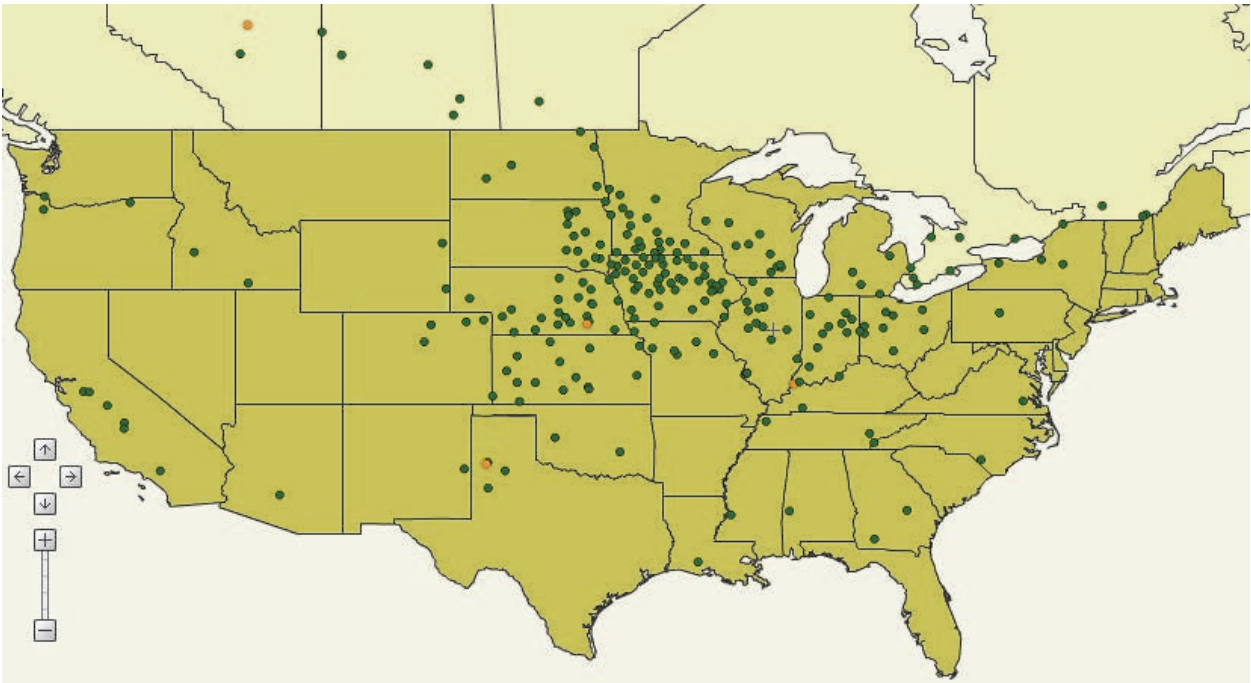http://federalregister.gov/a/2010-3851.

Fig. 1. United States and Canada Fuel Ethanol Plant Map[2]

Year	Total Ethanol Plants	Ethanol Production Capacity (BGY)	Plants Under Construction or Expanding	Capacity Under Construction or Expanding (MGY)	States with Ethanol Plants
1999	50	1.70	5	77	17
2000	54	1.75	6	92	17
2001	56	1.92	5	65	18
2002	61	2.35	13	391	19
2003	68	2.71	11	483	20
2004	72	3.10	15	598	19
2005	81	3.64	16	754	18
2006	95	4.34	31	1,778	20
2007	110	5.49	76	5,636	21
2008	139	7.89	61	5,536	21
2009	170[3]	12.48[4]	24	2,066	26
2010	187[3]	13.03[4]	15	1,432	26

Table 1. United States Ethanol Production Capacity[5]
BGY = Billion gallons per year; MGY = Million gallons per year.

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[2]Anon, 2010b

[3]Operating plants

[4]Includes idled capacity

[5]Anon, 2011a; Federal Register, March 26, 2010, page 14674, Final Rule 40 CFR 80; 75 FR 14670;
http://federalregister.gov/a/2010-3851

cellulosic biofuel, biomass-based diesel, advanced biofuels, and total renewable fuel that must be used in transportation fuel yearly from 2010 to 2022. Table 2 provides the annual renewable fuel volume requirements of RFS2. Other factors driving the demand for biofuels are greenhouse gas standards and regulations. According to EPA's regulatory action, lifecycle greenhouse gas emissions of cellulosic biofuels must be at least 60% less than the baseline lifecycle greenhouse gas emissions (Anon, 2010a). Tax subsidies, government financial support and fuel policies will also significantly affect economic competitiveness, consumption and production.

Production of 2nd generation biofuels has been a researched for 30 years, with the key impediment being the recalcitrance of the biomass itself (Sjostrom, 1993). Lignocellulose a structural material which nature has designed to resist breakdown. Scientists and engineers have focused on developing pretreatment processes to open the structure of biomass for enzymatic attack (Taherzadeh & Karimi, 2008), while molecular biologists have sought to increase the productivity and efficiency of cellulase enzymes that hydrolyze the fibers into fermentable sugars (Banerjee et al., 2010a; Banerjee et al., 2010b; Jorgensen et al., 2007; Taherzadeh & Karimi, 2007b). Microbes to efficiently convert the mixture of 5 and 6 carbon sugars to ethanol have been yet another technical hurdle (Ballesteros et al., 2004; Olofsson et al., 2008; Saha, 2003).   Many of these systems are now being evaluated in pilot plants (Taherzadeh & Karimi, 2007a; Taherzadeh & Karimi, 2007b). Due to the infrastructure challenges associated with ethanol as a fuel, research efforts in the early 2000s expanded to production of third and fourth generation biofuels that are considered infrastructure compatible. Green gasoline, diesel, and jet fuels can be made from biomass, through either biochemical (enzymatic/fermentation) or thermochemical (gasification or pyrolysis) platforms.

Replacing petroleum-derived gasoline, diesel, and jet fuels with renewable fuels will have a wide range of environmental, societal, and economic impacts. The significance and timing of these impacts will be affected by the pace at which biofuels gain market share. This, in turn, will be affected by market forces (crude oil price and availability, feedstock prices), technology development, political conditions, and regulatory factors (Licht, 2006; Regalbuto, 2009) These impacts will be affected by: 1) the type of fuel produced and its use, 2) the types and locations of the feedstocks, 3) the locations, methods, and scale of conversion systems, 4) the yields of products and co-products from a given feedstock, and 5) the challenges associated with use of these feedstocks (Hahn-Hagerdal, et al., 2006).

To achieve the goal of secure and sustainable bioenergy and biofuel production by the middle of the 21st century, we must build upon on existing infrastructure, but also must make substantial improvements in infrastructure and process technology applied. Much of the challenge will revolve around feedstock supply and logistics, (Sims, 2003) and therefore we envision a decentralized, community-based system with integrated crossover to produce a range of third generation drop-in biofuels (long chain alkenes, alkanes, and alcohols) and bio-derived chemicals. These systems could be developed on green-field sites or built onto first/second generation biofuel (ethanol) facilities. Their smaller size and distributed locations will minimize transport of bulky biomass sources, and will spread the economic impact over a broader landscape.

Advancements are needed in sustainable feedstock production to ensure that plants are bred for rapid growth, minimal inputs, high yield, and desirable composition (Dufey, 2006) Perennial plants able to grow with minimal inputs (fertilizer, pesticides, irrigation water) on lower quality land would be most desirable in terms of sustainability (Ragauskas et al.,

Year	Cellulosic biofuel requirement	Biomass-based diesel requirement	Advanced biofuel requirement	Total renewable fuel requirement
2009	NA	0.5	0.6	11.1
2010	0.1	0.65	0.95	12.95
2011	0.25	0.80	1.35	13.95
2012	0.5	1.0	2.0	15.2
2013	1.0	a	2.75	16.55
2014	1.75	a	3.75	18.15
2015	3.0	a	5.5	20.5
2016	4.25	a	7.25	22.25
2017	5.5	a	9.0	24.0
2018	7.0	a	11.0	26.0
2019	8.5	a	13.0	28.0
2020	10.5	a	15.0	30.0
2021	13.5	a	18.0	33.0
2022	16.0	a	21.0	36.0
2023+	b	b	b	b

Table 2. Renewable Fuel Volume Requirements for RFS2 (billion gallons)
[a] To be determined by EPA through a future rulemaking, but no less than 1.0 billion gallons
[b] To be determined by EPA through a future rulemaking

2006). Crop residues and cover crops could provide dual-use of land, although there are some concerns regarding acceptable sustainability (Lal, 2005; Tilman et al., 2009) An emerging class of feedstocks includes single-celled phototrophs (eg. algae or cyanobacteria) that can fix CO_2 directly into oil (Aylott, 2010). These organisms are also being engineered to produce drop-in fuels or chemicals directly, hence providing a self-contained production/conversion system (Rosenberg, et al., 2008).

Improvements to conversion systems are needed to increase yield and minimize costs, while sizing systems for distributed processing. Efforts to improve the biochemical platform are focused on pretreatment strategies and engineering microbes and enzymes to deconstruct carbohydrate polymers and produce long chain hydrocarbons or alcohols. Thermochemical efforts are being directed towards integrated thermo-catalytic processes that can readily switch between a multitude of feedstocks. Conversion systems of the future must optimize value of products produced, minimize energy and water use, be scaleable to distributed processing networks (to minimize feedstock logistics challenges), and produce minimal wastes.

Can advanced biofuels of the future play a significant role in a world reconfigured to meet energy-related challenges? Many researchers now point to increasing evidence that commercial biofuel production can be reconciled with feeding humanity and preserving the environment, provided that we invest the time and effort needed to make the improvements necessary to achieve this goal (Lynd & de Brito Cruz, 2010). The biofuel production concept described in this chapter has the potential to meet this objective, by combining proven technologies with promising innovations that are currently under development.

2. Feedstock supply

Corn-based ethanol has been periodically criticized for causing high food prices, in spite of the fact that ethanol production uses only the carbohydrate portion of the kernel. The protein, fat, and minerals in corn are concentrated in the distillers' dried grains with solubles (DDGS), and fermentation yeast further improve the quality of this feed for use in livestock rations. Nevertheless, in the late 2000s, ethanol production was blamed for the dramatic increase in corn prices, even though reduced worldwide production and increased grain imports by China were key factors. Ethanol was also blamed for rapidly increasing food costs, even though subsequent analyses pinpointed higher petroleum prices (i.e., transportation costs) and increased profit margins of food manufacturers as the true underlying factors (Henderson, 2008; Perrin, 2008).

The transition from corn to biomass-based feedstocks for bioenergy production should greatly reduce the controversy over food vs. fuel, although some biomass feedstocks (or the landscapes on which they are produced) are currently used for livestock feed (Sims, 2003). For example grasses and some crop residues (e.g., corn stover) are used for cattle feed. Agricultural landscapes that are less productive, subject to erosion, or in more marginal climates are often used to produce livestock forage, and these same landscapes are under consideration for biofuel feedstock production. Therefore, biofuel producers may compete with livestock producers for herbaceous feedstocks (grasses and crop residues).

A further issue with crop residues is their value in providing fertility, tilth, and carbon sequestration when left on the soil. While a certain amount of crop residues (e.g., corn stover, wheat straw) can be sustainably removed, there has been uncertainty over the amounts needed to maintain soil productivity (Lal, 2005; Tilman, et al., 2009). Recently, soil scientists have increased their recommendations for crop residue amounts that should be left on the soil. Current guidance is that 2,500 pounds of organic matter per acre/yr (Gustafson, 2011). For high residue crops like corn and wheat, this would allow removal of substantial amounts of residue (2-3 tons/acre/yr). However, these high residue crops are frequently grown in rotations with low residue crops such as soybeans. Therefore to maintain a sustainable soil profile, some of the high residue crop cover must also be left to average out the low residue crop. For example, in a corn/soybean rotation it has been calculated that less than one ton/acre of residue could be removed from a 200 bushel/acre corn crop. However, major crop genetics companies predict that they will double average yields of corn by 2030, and this will also increase corn stover levels.

Perennial grasses have been proposed as a more sustainable supply for biofuel production, and plants such as switchgrass, big bluestem, prairie cordgrass, and miscanthus yield 5-10+ tons/acre (Ragauskas, et al., 2006; Schmer, et al., 2008). Far less inputs (tillage, fertilization, water, and herbicides/pesticides) are required for production of these feedstocks, compared to that required for corn (ethanol) or soybeans (biodiesel) (Tilman, et al., 2009; Yuan, et al., 2008; Karp, 2008). Many of these plants can be grown on landscapes subject to erosion, periodic flooding, or other factors that would prevent their use for crop production (Schmer, et al., 2008). Yields would likely be lower than could be achieved on highly productive farm ground, but this would avoid the food vs fuel issue. In many locations, perennial grasses are the natural climax community, and would thus provide significant ecosystem benefits in terms of water and soil quality, and wildlife habitat. Even in traditional agricultural regions, perennial grasses could provide an important role as buffer strips to protect water bodies.

Forest and wood processing wastes, and municipal solid waste components are also significant biomass resources that could be used for biofuels production (Isa, et al., 2004; Parikka, 2004). These do not compete for arable lands, nor are they subject to the food vs fuel controversy. Collection and transportation issues have already been resolved, as these feedstocks are byproducts or even negative value wastes of existing processes. Production of fast growing trees in agricultural areas has been suggested, (Schlamadinger & Marland, 1996) but if these landscapes were traditionally used for crop or forage production, then an argument could be made that fuel production would impact food production.

Microalgae offer great potential as a sustainable feedstock for the production of 3rd generation biofuels, as well as 4th generation fuels (Aylott, 2010; Dragone, et al., 2010; Rosenberg, et al., 2008). Recent studies have shown that microalgal biomass is one of the most promising sources of renewable biodiesel that is capable of meeting the global demand for transport fuels (Dragone, et al, 2010). Biodiesel production by microalgae will not compromise production of food, fodder and other products derived from crops. Microalgal biomass contains three main components: proteins, carbohydrates, and lipids (oil). However, several important scientific and technical barriers remain to be overcome before the large-scale production of microalgae-derived biofuels can become a commercial reality. Technological developments, including advances in photobioreactor design, microalgal biomass harvesting, drying, and processing are important areas that may lead to enhanced cost-effectiveness and therefore, effective commercial implementation of biofuel production from microalgae (Greenwell, et al, 2010; Pienkos & Darzins, 2009).

3. Logistics

A critical component of successful commercialization of bioenergy is a secure and reliable supply system for biomass-based feedstocks. In fact this may be the most significant constraint to 2nd/4th generation biofuels. Ample feedstock should be available to biorefineries at the appropriate time and at competitive prices, while assuring reasonable, steady profits to the biomass suppliers. Developing a consistent, economically viable feedstock supply system requires addressing and optimizing diverse harvesting, storage, preprocessing, and transportation scenarios (Kumar & Sokhansanj, 2007).

Unlike corn and other grains, most biomass resources lack a well developed transportation infrastructure. Perhaps the closest would be the logistical infrastructure for wood products industry. Some infrastructure is also present in localized markets for forage crops used for livestock feed. Issues that are problematic for biomass transport include its low bulk density, poor flowability, and susceptibility to physical degradation during storage (especially if moisture is present) (Rentizelas, et al, 2009; Richard, 2010). Therefore, highly efficient harvest, densification, and storage systems for biomass are critical for an efficient biomass-to-biorefinery supply chain that will minimize transportation costs and energy consumption, while maintaining a high quality feedstock for processing (Eksioglu, et al. 2009).

Each of the different types of proposed feedstocks has a unique set of challenges or advantages regarding harvest method and timing, densification, transportation, and storage (Sims, 2003). In the near term (2012~2018), crops residues such as corn stover and forest residues (wood chips) are expected to be the main resource for cellulosic fuels (Perlack, et al., 2005). Several companies (i.e., POET, ICM, Inc) are developing processes which could be "bolted-on" to existing corn biorefineries, to take advantage of synergisms (nutrient and

thermal sharing). These cellulosic processes are being scaled so that readily available corn stover within a reasonable distance of the plant can be efficiently supplied by conventional systems (baling and truck transport). Challenges still remain, however, regarding collection and storage of corn stover bales (Sokhansanj, et al., 2002). Weather conditions during corn harvest are often challenging, and adding a second harvest pass for stover may be unachievable. Thus, farm equipment manufacturers are testing single pass systems that would collect both grain and stover (Shinners & Binversie, 2003) Questions also remain concerning where and how stover bales will be stored. Efforts to re-tool wood pulp operations for biofuel production have the advantage of existing infrastructure for wood harvest and transport, along with the obvious advantage that wood is more storable than herbaceous biomass (Perlack, et al, 2005).

As biomass utilization expands there will be growing pressure to maximize the efficiency at which these raw materials are harvested. Technically, the term woody biomass includes all the trees and woody plants in the forest, woodlands, or rangelands (Parikka, 2004). This biomass includes limbs, tops, needles, leaves, and other woody parts. In practice, woody biomass usually refers to material that has historically had a low value or no economic value and cannot be sold as timber or pulpwood. As markets change over time and from region to region, different kinds of materials may be considered woody biomass. The maintenance of site productivity is perhaps the key non-water quality issue when anticipating the expansion of the use of woody biomass (Groom, et al, 2008. If it is proven that the harvesting of woody biomass actually depletes the nutrients in certain soils, fertilization may become a standard management tool. Soil compaction and excessive rutting can also impact site productivity. Timing harvest operations to avoid wet soil conditions or minimizing equipment travel patterns can prevent such impacts.[6]

Ideally, biomass development will occur in a manner that maximizes efficiencies in energy production and minimizes energy consumption associated with transportation, storage, and raw material processing, while maintaining biodiversity and improving the environment (Perlack, et al., 2005; Rentizelas, et al., 2009). One of the central concerns in woody biomass removal is the reduction of the quantity of dead wood left on site (Kaltschmitt, et al., 1997; Perlack, et al., 2005). Dead wood plays an important role in the ecosystem, from wildlife habitat and nutrient cycling to carbon storage. Woody material on the ground decreases water run-off and erosion. If woody biomass harvesting becomes an issue, specific recommendations can be made to leave a certain amount/number of the desired material on-site. As biomass markets expand, more emphasis and attention may be placed on watershed management. In general, water quality and riparian concerns should not change with the addition of woody biomass removal to a harvest plan. Streams and wetlands should be protected by existing Best Management Practices (BMPs) for Forestry,[7] using the Clean Water Act as a fundamental base (Lynch & Corbett, 2007). The opportunity for forest-derived biomass to be part of the carbon solution is an important consideration in the planning and development of biomass projects, but if management practices are too costly, they are unlikely to be implemented on private lands (Groom, et al., 2008; Kaltschmitt, et al., 1997).

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[6]http://www.forestry.alabama.gov/PDFs/WoodyBiomassHarvestingIssues.pdf
[7]http://www.fs.fed.us/im/directives/dughtml/fsm2000.html

The Biomass Crop Assistance Program (BCAP) is a program that responds to the added cost of transporting biomass to a certified facility. BCAP is part of the Farm Bill and Recovery Act and is administered by the USDA Farm Service Agency.[8]

In Phase 1, which is active, it provides financial assistance to producers that deliver eligible biomass material to designated biomass conversion facilities for use as heat, power, and/or bio-based products. Initial assistance is for the collection, harvest, storage, and transportation costs associated with the delivery of eligible materials through a direct matching of dollar for dollar of dry ton delivered to qualified facilities, up to $45 maximum over the next two years. The details of Phase 2 have not yet been made public.

Auburn University has received a grant worth up to $4.9 million from the US Department of Energy to design and demonstrate a high productivity system to harvest, process, and transport woody biomass from southern pine plantations.[9] Specific project objectives are to develop design improvements in tree length harvesting machines for energy plantations; configure and assemble a high-productivity, lowest-cost harvesting and transportation system for biomass and demonstrate at full industrial scale; and document performance of the systems.[10]

Over the longer term (2015+), dedicated, perennial bioenergy crops such as switchgrass, prairie cordgrass, and fast growing woody species are expected to become the preferred feedstocks, because of their higher yield and lower input requirements (Perlack, et al, 2005). However, it is also expected that these crops will be grown on marginal soils, leaving the most productive soils for food/feed crop production. Hence, dedicated energy crop production will be distributed across a broader landscape, and this will limit the total tonnage of biomass available in a given region (Kumar & Sokhansanj, 2007). Thus feedstock logistics is the main driver for smaller processing plants or a distributed network of pre-processing-densification plants to support a large centralized processing operation. This latter approach has been promoted by Carolan et al., (2007) in their regional biomass processing center (RBPC) model. Such smaller preprocessing facilities would have a 20-25 mile collection radius, instead of the 75-100+ mile radius common to large corn ethanol plants. These RBPC facilities would collect biomass directly from the farm, pretreat and densify the biomass into more storable and flowable billets, and then provide these to a centralized biofuel production facility. The ammonia fiber expansion (AFEX) treated biomass is also more digestible in livestock feeds, so the RBPC network could support cattle feeding operations and/or biorefineries (Carolan et al., 2007).

Harvest timing and storage are additional concerns for perennial grasses (Marten & Hovin, 1980). In the fall these plants translocate nutrients back down into the root system, to support growth the following year. Hence to maintain plant vigor over the long term, harvest should be delayed until late fall. This will also minimize moisture content in the biomass, enhancing storability. Processing operations will also prefer biomass with reduced mineral content, as this will limit accumulation of these minerals in process fluids and ash (which would need to be disposed of). Unfortunately, fall harvest will eliminate one of the key ecosystem benefits of native grasses, that being winter cover for wildlife (Roth, et al., 2005). Many of these grasses have been used as the backbone vegetation for the USDA

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[8]www.fsa.usda.gov/FSA/webapp?area=home&subject=ener&topic=bcap

[9]http://nrmdi.wordpress.com/2009/09/04/auburn-universitys-center-for-bioenergy-and-bioproducts-awarded-4-9-million-grant-for-bioenergy-research

[10]www.supertrak.com/video/BIOBALER.wmv

Conservation Reserve Program (CRP) which has resulted in a significant boost to wildlife populations over the past 25 years. Early spring harvest of native grasses would be the logical solution, but wet weather conditions typical in spring may make this option very difficult.

Another logistical concern is in transport of biorefinery products to the consumer. Corn based ethanol has faced a significant hurdle, as it is not considered to be an infrastructure compatible fuel. The EPA has limited the concentration of ethanol that can be used in vehicles, originally to 10% and more recently to 15%. Ethanol also cannot be transported in pipelines used for petroleum products, due to its propensity to absorb water. Biomass based ethanol (2nd generation biofuel) will face the same issues. Third and fourth generation biofuels are infrastructure compatible, and should therefore move into the fuel distribution network seamlessly. However, these fuels will be produced in more rural areas, and therefore transport to metropolitan areas will be required.

Use of microalgal biomass has unique issues. Given the relatively low biomass concentration obtainable in microalgal cultivation systems due to the limit of light penetration (typically in the range of 1-5 g/L) and the small size of microalgal cells (typically in the range of 2-20 μm in diameter), costs and energy consumption for biomass harvesting are a significant concern that needs to be addressed (Greenwell, et al., 2010; Pienkos & Darzins, 2009). In this sense, harvesting of microalgal cultures has been considered a major bottleneck towards the industrial-scale processing of microalgae for biofuel production. The cost of biomass recovery from the broth can constitute 20–30% of the total cost of producing the biomass (Borowitzka, 1992). Microalgal biomass harvesting can be achieved in several physical, chemical or biological ways: flocculation, centrifugation, filtration, ultrafiltration, air-flotation, or autoflotation. Generally, microalgae harvesting is a two stage process. First, bulk harvesting is used to separate biomass from the bulk suspension. The concentration factors for this

operation are generally 100–800 times to reach 2–7 % total solid matter. This will depend on the initial biomass concentration and technologies employed, including flocculation, flotation or gravity sedimentation. Second, thickening is used to concentrate the slurry through techniques such as centrifugation, filtration and ultrasonic aggregation. This latter step is generally a more energy than bulk harvesting. Several essential issues must be addressed in photobioreactor (PBR) design, including effective and efficient provision of light; supply of CO_2 while minimizing desorption; efficient mixing and circulation of the culture; and the material used in the construction of the PBR. Light as the energy source for photoautotrophic life is the principal limiting factor in photobiotechnology. In addition, the supply of CO_2 to microalgal mass culture systems is one of the principal difficulties that must be solved. CO_2 must not reach the upper concentration that produces inhibition and, on the other hand, must never fall below the minimum concentration.

4. Conversion and recovery

A wide diversity of biochemical and thermochemical processes are under development for production of 2nd through 4th generation biofuels. Biochemical processes use physical or chemical pretreatments (Alvira, et al., 2010; Chandra, et al., 2007; Dongahai, et al., 2006; Hendriks & Zeeman, 2009; Mosier, et al., 2005; Taherzadeh & Karimi, 2008; Wyman, et al., 2005; Yang & Wyman, 2008), followed by enzymatic hydrolysis of polymers to simple sugars (Dale, et al., 1996; Vlasenko et al., 1997), with subsequent fermentation to fuel

products (Ballesteros, et al., 2004; Saha & Cotta, 2007). Thermochemical processes use high temperatures and pressures to degrade biomass into simple compounds that are then reconstructed into hydrocarbon polymers using chemical catalysis. Some newer approaches link biochemical and thermochemical steps, to take advantage of synergisms.

Lynd et al. (2005), in their strategic analysis of biorefineries list the advantages of integrated multi-product biorefineries. First, integrated biorefineries enable maximizing the value generated from heterogeneous feedstocks, making use of component fractions. Second, revenues from high-value coproducts reduce the selling price of the primary product. Third, the economies of scale provided by an integrated biorefinery lowers the processing costs of low-volume, high-value coproducts, because common process elements are involved in producing fermentable carbohydrates, regardless of whether one or more products are produced, and coproduction can provide process integration benefits (e.g. meeting process energy requirements with electricity and steam cogenerated from process residues).

We propose that such an integrated biochemical/thermochemical process would be best suited for distributed, smaller scale production of biofuels (Fig 2). This design would facilitate use of multiple feedstocks which are likely to be the norm in smaller operations. We assume these feedstocks could include crop residues, forestry residues, components of municipal solid waste, or dedicated biomass sources such as fast growing trees or native grasses. The process design would also provide the flexibility to produce a broad range of products, which could be adjusted to meet market demands and generate the highest level of income.

The initial unit operations in this process would be similar to that in current dry mill corn ethanol plants (i.e., size reduction, fractionation, and hydrolysis). The primary difference will be in the size of these facilities. Instead of the 100-120 million gallon/yr (MMGY) corn ethanol plants, 2nd-4th generation biofuel facilities will be in the 10-40 MMGY range. The upper size limit will likely be determined by the amount of biomass that can be economically delivered to the plant gate (Carolan, et al., 2007; Eksioglu, et al., 2009). This will be affected by biomass yields per acre, competing uses/markets, price, and feedstock logistic issues.

Feedstocks would first be subject to particle size reduction, followed by a continuous solvent-based fractionation process to disrupt the protective matrix of lignin that surrounds the cellulose and hemicellulose fibers, and separate these three streams. NREL developed the clean fractionation process in the 1990s, and several companies and university research teams are working to develop alternative, lower cost solvents to make this process economical (Emmel, et al., 2003; Kim & Lee, 2006; Lee, et al., 2009; Li, et al., 2010; Moxley, et al., 2008; Pan, et al., 2006; Zhang, et al., 2007). We anticipate this could be commercialized by the late 2010s. Upstream fractionation of biomass would maximize downstream reactor productivity, since lignin would not dilute the sugar titer in cellulose and hemicellulose hydrolysates (Zhang, 2010b). Removing lignin will also prevent lignin from binding to and inactivating hydrolytic enzymes (Berlin, et al., 2006; Mes-Hartree & Saddler, 1983; Palmqvist & Hahn-Hagerdal, 2000), and will reduce production of chemicals inhibitory to yeast metabolism (Pfeifer, et al., 1984). Plus it will help ensure that each component is used for its highest value.

Lignin is an abundant, renewable, and amorphous natural polymer consisting of phenylpropane units (Boudet, et al., 2003). The units, primarily syringol, guaiacol, and p-hydroxyphenol, are linked together by ether and carbon–carbon inter-unit bonds to form a very complex three-dimensional polymer matrix. The lignin fraction contains a multitude of
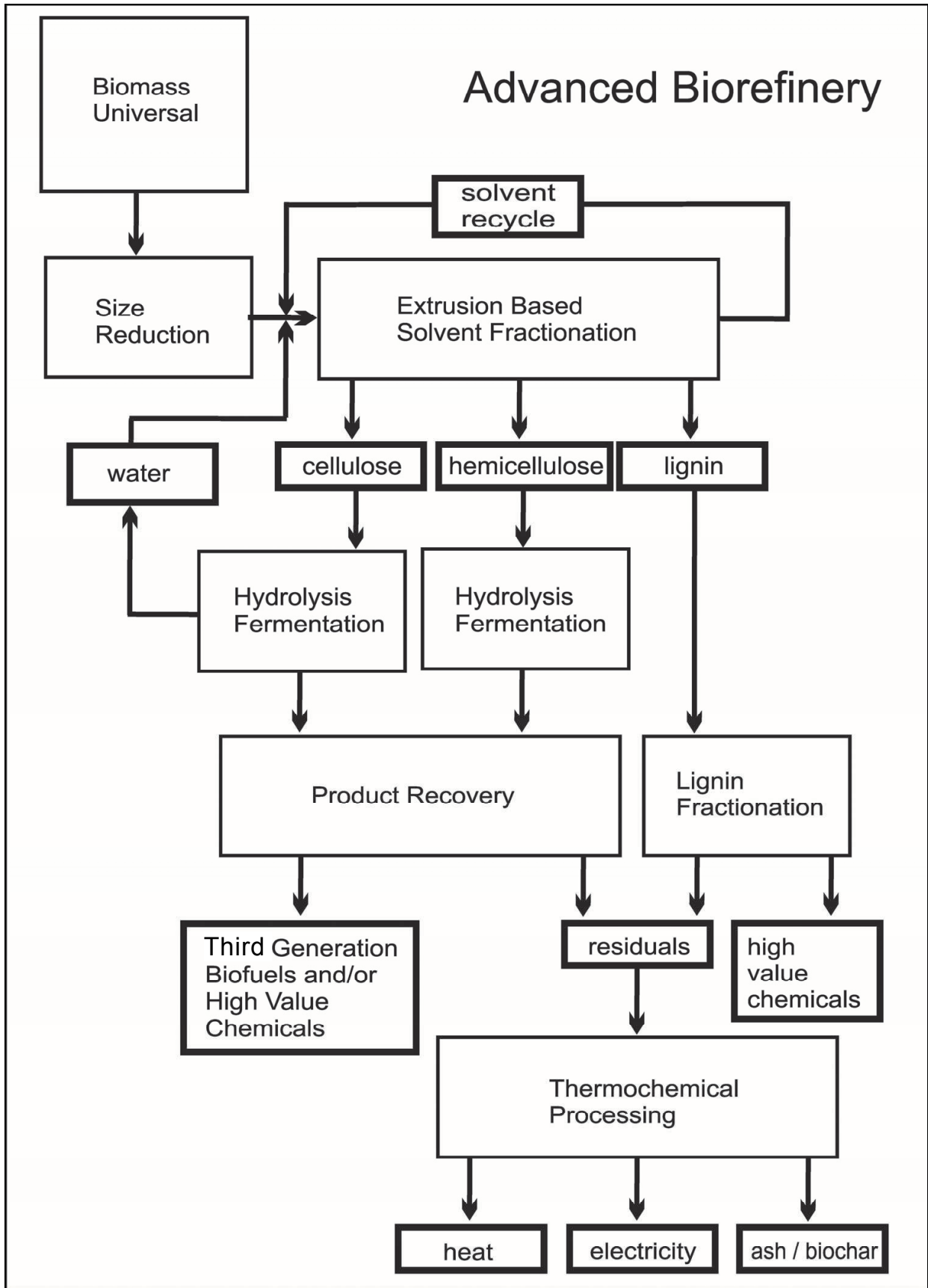
Fig. 2. Integrated advanced biorefinery platform

important and high value chemicals, (Taherzadeh & Karimi, 2008; Thring, et al., 2000) and researchers are developing separation methods (Pan et al., 2005). If these techniques become available at an appropriate scale, the lignin fraction would first be processed to recover these products (Katzen, et al., 1995; Sun & Cheng, 2002). Residual lignin would be thermochemically processed (combustion, pyrolysis, or gasification) to generate combined heat and power for the operation (as opposed to natural gas or other fossil fuels typically used in 1st generation biofuels). This will improve the carbon balance of 2nd-4th generation biofuels. Additional coproducts could be ash and/or biochar, which would be returned to the land to provide nutrients and carbon sequestration (Lehmann, et al., 2006). Alternatively, biochar could be converted into higher value products such as activated carbon.

The cellulose and hemicellulose fractions would then be subjected to chemical (Lavarack, et al., 2002; Torget, et al., 1991) or enzymatic (Banerjee, et al., 2010a; Banerjee, et al., 2010b; Banerjee, et al., 2010c; Fan, et al., 1980; Grethelin, 1985; Ragauskas, et al., 2006; Sun & Cheng, 2002), hydrolysis to convert the fiber polymers into fermentable sugars (Jorgensen et al., 2007). Having separate hydrolysates of glucose and xylose will provide the advantage of allowing for separate fermentations by organisms specifically adapted for these substrates. The glucose solution could be fermented by traditional yeast into ethanol (2nd generation biofuel) or by bacteria such as *Clostridium* into butanol (4th generation biofuel) (Qureshi & Ezeji, 2008). Researchers and companies such as Solazyme are developing other microbes (native or genetically modified) to ferment glucose into a range of infrastructure compatible, energy dense 4th generation biofuels such as longer chain alcohols, alkanes, and alkenes. The xylose fractions present a greater challenge, as fewer microbes have the needed metabolic machinery (Saha & Cotta, 2007). However, certain yeast strains (e.g., Pichia) are able to ferment xylose to ethanol, and research groups have engineered *Saccharomyces* for xylose fermentation. Other teams are using bacteria to convert xylose to ethanol (Ahring, et al, 1996). Perhaps the greater value for xylose would be fermentation by bacteria such as *Clostridium* into butanol or long chain length hydrocarbons.

One of the challenges with biomass hydrolysate fermentation is the low bulk density of biomass, which results in a high viscosity when solid loadings exceed 15-20% dry matter. This limits product concentrations that can be achieved in traditional submerged bioreactors, which in turn results in higher costs and energy consumption for downstream product recovery. It has been calculated that fermentation broth must contain at least 4% (w/w) ethanol for distillation to be economically viable (Larsen et al., 2008; Zhang, et al., 2010a). For many types of biomass this will mean a solid loading rate of at least 20% (w/w). At these high solid levels the high viscosity prevents traditional submerged bioreactors from achieving sufficient mixing and mass transfer, while resulting in localized solids build-up or caking. Low water activity and high concentrations of sugars, end products, and/or inhibitory chemicals can also inhibit enzymes and fermentation organisms.

Using a biomass fractionation pretreatment upstream will minimize viscosity problems and maximize solids loading during SSF, because the hydrolysate streams will consist primarily of cellulose and hemicellulose, respectively. For example, Zhang et al (2010c) conducted SSF of a pretreated corncob fraction at 19% solids and achieved 69 g/L ethanol. Fed-batch feeding of solids is another method to increase net solids loading (Hodge, et al., 2009; Hoyer, et al., 2010; Varga, et al., 2004). Intermittent feeding of a fractionated cellulose or hemicellulose stream can achieve higher overall solids loadings, while still maintaining low viscosity, because the substrate is continuously degraded to soluble sugars. This also prevents the buildup of sugars which can otherwise inhibit some fermentation organisms

(Hodge, et al., 2009; Olofsson, et al., 2008. Fed-batch feeding also effectively reduces enzyme dosage. Zhang et al., (2010c) conducted fed batch SSF, achieving a final solid loading of 25% and ethanol titer of 84.7 g/L.

To further increase product concentration, various types of high solids bioreactors have been proposed (Varga et al., 2004; Zhang, et al., 2010a). These have included gravitational tumbling in roller bottle reactors (Roche, et al., 2009a; Roche, et al., 2009b), horizontal paddle type bioreactors (Jorgensen, et al., 2007; Roche et al., 2009a;), scraped surface bioreactors (Dasari, et al., 2009), and stirred helical bioreactors (Jorgensen et al., 2007; Zhang et al. 2010a). Jorgensen et al. (2007) achieved 35% solid loading and 62 g/L ethanol in a bioreactor with a horizontal rotating shaft with paddles, and this design provides sufficient mixing at very low rotation rates, meaning less power consumption (Zhang et al., 2010a). Scraping blades can be used to prevent "dead zones," and keep the reactor surface clean to maximize heat/cooling transfer (Dasari, et al., 2009). Zhang et al (2010a) used a helical stirring system to 64.7 g/L ethanol from 30% solid loading of steam exploded corn stover.

Many of these sugar fermentation processes will produce CO_2 as a byproduct. In the case of ethanol fermentation, one third of the carbohydrate carbon is released as CO_2. The integrated process (Fig 2) could be adapted to include photobioreactors in which engineered microalgae or cyanobacteria would convert this CO_2 into 3rd generation fuels or solvents (Greenwell, et al., 2010; Pienkos & Darzins, 2009). In addition, these microalgae could be used to sequester CO_2 from flue gases emitted from fossil fuel-fired power plants and other sources, thereby reducing emissions of a major greenhouse gas (1 kg of dry algal biomass utilize about 1.83 kg of CO_2). The utilization of microalgae for biofuels production also offers the advantages that they: 1) synthesize and accumulate large quantities of neutral lipids (20–50 % dry weight of biomass) and grow at high rates; 2) are capable of year-round production, therefore, oil yield per area could greatly exceed the yield of oilseed crops; 3) need less water than terrestrial crops thus reducing the load on freshwater sources; 4) do not require herbicide or pesticide application; 5) bioremediate wastewater by removal of nitrogen from a variety of sources (e.g. agricultural run-off, concentrated animal feed operations, and industrial and municipal wastewaters); and 6) can be cultivated in saline/brackish water/coastal seawater on non-arable land, and do not compete for resources with conventional agriculture. Production would occur in recirculating photobioreactors, which would be located in adjacent greenhouses. Low grade heat from the biorefinery operations would maintain appropriate temperatures inside the greenhouse during cold weather.

Recovery of ethanol or butanol from fermented solutions would likely occur via the time-tested process of distillation. However, advancements in membrane technology may eventually allow for lower energy processes such as pervaporation (Lipnizki et al., 1999). Longer chain alcohols and hydrocarbons can be recovered from fermentation solutions by phase separation, if sufficiently high concentrations are produced. Non-fermentable solids in the residual fermentation broth would be separated by centrifugation or filtration and used to generate process steam and electricity via thermochemical processes, while process water would be recycled to the greatest extent possible.

5. Technology development and deployment

Projected costs for biomass ethanol (>$2-3/gal) have been substantially greater than actual costs ($1-1.50/gal) for corn-based ethanol (Eisentraut, et al., 2010; Sanderson & Ad, 2008).

For this reason the US DOE initiated the "Demonstration of Integrated Biorefinery Operations" program in 2006 to help cost-share construction costs for pilot or demonstration scale facilities to convert biomass to ethanol. Three rounds of grants have since been awarded, and the initial awardees are expected to begin production in 2011-2012. Six proposals were funded in 2007 at a federal investment of $385 million. Biochemical processes included POET, which is constructing a 25 MMGY corn cob/stover conversion facility adjacent to one of its 100 MMGY corn ethanol plants in Emmetburg, IA. Abengoa (Kansas) is constructing an 11.4 MMGY facility to use corn stover, wheat straw, and other feedstocks, while Iogen is establishing a similar facility in Idaho. In 2008, DOE announced that 9 second round awardees would receive a total of $240 million. Biochemical processes included Verenium's 1.5 MMGY facility in Louisiana, and Zeachem's 0.25 MMGY facility in Oregon. In 2009, DOE announced funding of $482.7 million for 18 pilot and demonstration scale facilities. Awardees planning biochemical processes included Amyris Biotechnologies (California), ADM (Illinois), ICM, Inc (Missouri) and Logos Technologies (California). These facilities are expected to begin operation in 2013-2014.

Production of 3rd and 4th generation biofuels from biomass is further behind, with butanol being the leading candidate. A British Petroleum and DuPont joint venture (Butamax) has refurbished an ethanol facility in Great Britain to make butanol from sugar using engineered yeast. Gevo has acquired the Agri-Energy corn ethanol plant in Luverne, MN and is pursuing a similar strategy. Companies such as Chevron and Weyerhaeuser are also exploring butanol production. Various research teams are working to develop improved microbes for butanol production, with pilot scale facilities already in operation, or scheduled for startup in 2011-2012. Besides butanol, other companies are exploring options to produce drop-in replacements for currently used fuels. For example, Flambau River Biofuels (WI) received funding in the second round of DOE's biorefinery program to construct a 6 MMGY wood-to-diesel facility that should be operational in 2012-2013. The company LS9 is engineering bacteria to produce other 3rd generation biofuels and plans to test pilot scale systems in the next 12-24 months.

Initial deployment of 2nd generation biofuel processes using corn stover is already occurring at certain corn-based ethanol facilities. Co-locating allows for several synergistic opportunities (Khanna, 2008). For example, lignin from the biomass plant can provide all its thermal energy, as well as meeting part of the needs for an adjacent corn-based plant. Excess nutrients from the corn ethanol plant can help enhance fermentation of biomass-derived sugars. Furthermore, downstream unit operations for ethanol recovery, purification, storage and shipping can be shared by the two processes. Similarly, some woody biomass conversion processes are being co-located at pulp mills to take advantage of delivery and pretreatment infrastructure.

6. Job opportunities in the bioeconomy

Production of 2nd – 4th generation biofuels is a sequential outgrowth of 1st generation biofuel production, and will have a substantial impact on jobs and market opportunities (Carr, et al., 2010). In areas such as biomass production and logistics, many additional jobs in traditional areas will be created to supply biorefineries with needed feedstock (DOE estimates 200,000 jobs nationwide). Similarly, the biorefineries themselves will create a significant number of additional jobs. Industries providing enzymes, microbes and other supplies for these facilities will create new and expanded job opportunities as well. These

biorefineries will also increase job opportunities in traditional mechanical and plastic industries for manufacturing required equipment, instruments, and materials. These positions will require novel training and education program for workers currently employed in the 1st generation biorefinery industry and future or potential workers in labor pool.

A significant aspect of 2nd and 4th generation biofuel production will be the infrastructure to harvest, collect, storage, and transport of biomass (Table 3). The DOE has projected that at least 200,000 new jobs could be created for biomass logistics. This would be in addition to jobs that could be re-directed from providing woody wastes or forage materials to less competitive markets. Although there are only a few small demonstration-scale cellulosic ethanol plants in the U.S. presently, cellulosic ethanol and drop-in biofuel facilities will increase in number as costs decrease. Therefore, to supply feedstock to a 2nd and 4th generation biofuel facilities, jobs will be needed for feedstock production, harvesting, gathering, storing, transportation by road or rail, and quality monitoring. To achieve sustainable biomass production, agricultural workers, scientists, biochemists and engineers, who are in charge of operating or monitoring those biomass production and logistics processes will be needed. They should have education backgrounds in biochemistry, plant science, biological science, biochemical engineering or/and analytical sciences

Production stages	Instruments/Materials	Job positions	Jobs per plant
Biomass harvesting, densification, and storage	Agricultural machines such as harvesters, planters, irrigation systems (pump and piping), trucks, and hay balers, hydraulic compressor or extruder	Mechanic industries for producing needed equipment. Customized harvesters and planters may be needed. Mobile grinding, compression, or extrusion equipment for biomass densification.	15
Biomass transport	Trucking	Truck drivers, forklift operators	5-10
Biomass quality control, impact of removal	Testing instruments for quality and composition	Agricultural or Chemical Engineers	2

Table 3. Natural resource harvesting jobs for 2nd/4th generation biofuels produced via biochemical route

In the mid-2000s, there were dozens of design/engineering firms, each with hundreds of employees, that built out the corn ethanol industry. It is anticipated that these same firms, as well as those involved in chemical and other fuel related processes, will be the key suppliers of this technology to the 2nd – 4th generation biofuel industry. These firms will have the additional advantage that their intimate knowledge of ethanol production facilities will allow them to design-in adjacent 2nd – 4th generation biofuel systems to take the greatest advantage of potential synergies. These firms would also have the advantage of being able to provide on-going maintenance and repair services as they do now for 1st generation biofuel plants. Positions critical to these firms included: engineering and construction

managers, mechanical engineers, electrical engineers, chemical engineers, civil and environmental engineers and technicians, computer control programmers and operators, tool and die makers, metal and plastic fabricators, forming/extruding/drawing machine operators, boilermakers, pipefitters, construction equipment operators and laborers, quality control inspectors and others. It is reasonable to expect that expansion of the 2nd – 4th generation biofuel industry will employ a similar number of people. The jobs impact for site preparation and construction of a 10-30 MMGY facility would be 300-500 positions.

As noted previously, the size of the biofuel facilities will be limited by the amount of feedstock that can be economically delivered to the plant gate. The consensus at this point is that 10-30 MMGY facilities will be the norm, and thus we based our labor projections on this size plant. Because these systems will generally mirror the conversion process used in corn ethanol, it is reasonable to use labor requirements of corn ethanol to estimate biomass fuel labor needs. On this basis a 10-30 MMGY 2nd/3rd generation biofuel facility would have 40-50 employees.

7. Technology development and incorporation constraints

The primary constraints to 2nd/4th generation biofuel production will be feedstock and water availability, and transportation infrastructure. In most cases, facility siting and size will be determined by the amount of feedstock available within an economical transportation radius (Rentizelas, et al., 2009; Richard, 2010). There is a diverse pool of un- or under-utilized biomass resources that could be directed to production of 2nd/3rd generation biofuels with minimal impact on other industries or interest groups (Perlack, et al., 2005). For example, forestry and wood wastes may not compete directly with food crops for land, but production of fast growing trees for biofuels could compete with production of timber for lumber markets. The DOE has estimated that over 1 billion tons of biomass would be available each year (Perlack, et al., 2005). Further expansion of 2nd/3rd generation biofuels may create some level of competition for feedstocks and/or land use. For example, use of crop residues (stover, straw) could compete with uses for livestock bedding or feed. Similarly, converting grasses to biofuels could compete with livestock feed use, or expanded grass production could displace crop production in some locations (Kumar & Sokhansan, 2007). Use of margin land or wildlife habitat for biomass production could significantly impact wildlife (Roth, et al, 2005). To minimize this, biomass sources and harvesting strategies that minimize negative impacts on wildlife systems will need to be employed. Diverse plantings of biomass crops would also be preferred over monocultures. Competition for these land and biomass resources will drive up prices for all users.

Production of feedstocks for 2nd and 4th generation biofuels will have fewer environmental constraints than corn production, however there are still potential issues (Eisentraut, 2010; Kaltschmitt, et al., 1997). Water is often a limiting resource, and biomass plants should be selected for drought and salt tolerance. In addition, the impacts of planting and harvesting practices on water resources and water quality need be evaluated. Biomass feedstocks are generally more nutrient efficient compared to corn, and do not require the same degree of annual fertilization. However, as with all plants, biomass feedstocks will respond favorably to fertilization. To minimize fertilizer use, several approaches are under development: 1) specific strains that require less minerals and nutrients, 2) recycling nutrient-rich coproducts and/or process water after biofuel production, to recycle most nutrients back to field, 3) integrating biomass production with animal or municipal waste water treatment systems to

provide nutrients, 4) developing specific harvest strategies to allow the plants to re-mobilize nutrients back into the roots before harvest of the above-ground parts of plants.

As with 1st generation biofuels, energy and chemical use are significant issues for 2nd – 4th generation biofuel processes. There are several key issues to address: 1) energy efficient densification technology and systems, 2) energy efficient pretreatment processes, which can produce fermentable sugars from lignocellulosic biomass with lower environmental footprint, 3) novel microbial strains with high product tolerance and expression levels, and 4) energy-saving product separation and recovery systems, which depend on development of new separation methods and materials. An additional concern is presenting the escape of genetically modified organisms that could be used in processing. Technologies such as high efficient air filtration systems, in-line chemical sterilization, steam in-place and sterile filtration will be necessary to maintain containment.

8. Summary

The DOE has estimated that 1.3 billion tons of un- or under-utilized biomass is available annually for use in producing biofuels (Perlack, et al., 2005). One resource is municipal solid waste, which is cheap, abundant, and available where the fuels would be used. Corn stover, cereal straws and other agricultural residues are being evaluated widely in the Midwest, for potential co-processing at corn ethanol plants. Elsewhere in the U.S., forest thinnings, pulp and paper mill waste, and yard waste are significant resources that could be converted into biofuels. Moreover, significant work is being conducted to develop dedicated energy crops such as switchgrass, cane, sorghum, poplar, and miscanthus. In addition to their high yield, some of these energy crops are perennial plants that can be grown on less productive sites, so as not to directly compete with food production. These feedstocks will be critical to achieving the renewable fuel production requirements set forth in RFS2.

Industry and the DOE have invested millions of dollars in designing and constructing the first cellulosic bioethanol demonstration and commercial scale plants. Most of these operations are being co-located with either wood pulping or corn-based ethanol plants, to take advantage of feedstock availability and process syngergies. These 2nd generation biofuel facilities are expected to begin operation in 2011-2013, and will serve as proving-grounds to help improve productivity and reduce costs. If successful, these facilities will encourage additional investment in lignocellulosic ethanol production. Based on current U.S. energy policy, it would appear that ethanol, derived from corn and lignocellulose, will be the main renewable liquid transportation biofuel through 2020.

Cellulosic ethanol will contribute significantly to RFS2 and the broader U.S. goals of creating a sustainable energy supply, reducing greenhouse gas emissions, assuring energy security, and promoting rural economic development. However, the infrastructure for distributing and using ethanol is limited, and expansion of the biofuel market share above 20% will likely involve production of advanced, drop-in biofuels (i.e., liquid hydrocarbons). Therefore the focus of many in industry and government has shifted to production of these infrastructure compatible biofuels that can also be produced from the same feedstocks being investigated for cellulosic ethanol production. Systems for producing these advanced biofuels will also take advantage of the feedstock logistic solutions that will be resolved by 2nd generation biofuels (Lynd & de Brito Cruz, 2010).

Algal oil can be produced by metabolizing biomass sugars or by fixing CO_2 via photosynthesis. These lipids (oils) can then be converted into 3rd generation biofuels such as

biodiesel or JP8. Alternatively, algae and cyanobacteria can be engineered to directly produce fuel compounds, instead of oil. Hydrocarbons and long-chain alcohols (4th generation biofuels) can be made from biomass sugars through microbial fermentation or liquid-phase catalysis, or directly from biomass via catalytic pyrolysis or gasification and Fisher Tropsch reactions. These biofuel replacements for gasoline, diesel, and jet fuel will give higher mileage than ethanol and biodiesel, and will work in existing engines and fuel distribution networks.

Logistical challenges of transporting, storing, and maintaining acceptable quality biomass will restrict the size of future biorefineries. These biorefineries are also likely to be most economical and energy efficient if they are able to produce a multitude of high value fuels and chemicals. Therefore we anticipate that a distributed, integrated platform technology for community-based production of advanced biofuels will prevail. This platform can be used in any location, due to its self-contained and autonomous design. The primary inputs will be biomass, CO_2, sunlight for photosynthesis, and solar or wind power to provide electricity. The integrated, community-based design would produce energy in an environmentally and socially sustainable manner.

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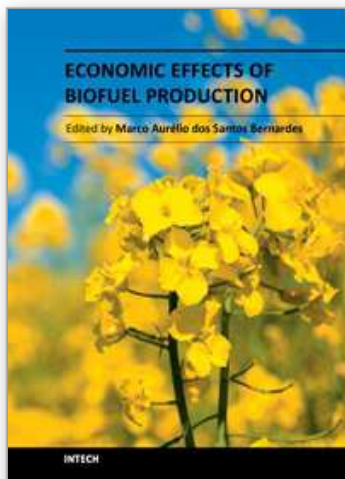
Economic Effects of Biofuel Production

Edited by Dr. Marco Aurelio Dos Santos Bernardes

This book aspires to be a comprehensive summary of current biofuels issues and thereby contribute to the understanding of this important topic. Readers will find themes including biofuels development efforts, their implications for the food industry, current and future biofuels crops, the successful Brazilian ethanol program, insights of the first, second, third and fourth biofuel generations, advanced biofuel production techniques, related waste treatment, emissions and environmental impacts, water consumption, produced allergens and toxins. Additionally, the biofuel policy discussion is expected to be continuing in the foreseeable future and the reading of the biofuels features dealt with in this book, are recommended for anyone interested in understanding this diverse and developing theme.

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