Production of Levulinic Acid in Urban Biorefineries

by

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Submitted to the Engineering Systems Division in partial
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Abstract

The energy security of the United States depends, most experts agree, on the development of substitute sources of energy for the transportation sector, which accounts for over 93% of the nation's petroleum consumption. Although great strides have been made in the development of electric vehicles and associated generation and transmission platforms, technical and economic considerations dictate that the transportation sector will rely preponderately on organic fuels for the foreseeable future. The U.S. Department of Energy and U.S. Department of Agriculture have therefore indicated that integrated cellulosic biorefineries, whose feedstock is abundant lignocellulosic plant matter rather than scarce starch, are a vital area for research, development, and commercialization.

This thesis evaluates the commercial viability of cellulosic biorefineries in and near the nation's urban centers, where significant volumes of carbohydrate feedstock are already concentrated, collected, and hauled as municipal and commercial wastes and therefore available to commercial users at negative cost. The case evaluated is a prospective demonstration-scale facility located in the urban corridor linking New York and Philadelphia, where "tipping fees" received for redirecting urban waste from landfills are the highest in the nation. The chosen conversion platform, a mature technology called the Biofine Process that has not previously been commercialized, uses acid-catalyzed hydrolysis of the carbohydrate feedstock to produce levulinic acid, a noted "platform chemical" that provides three main benefits: (1) convertibility from diverse and heterogeneous carbohydrate feedstocks containing the high moisture levels characteristic of putrescible wastes, (2) high conversion yields using the chosen conversion platform, and (3) a wide variety of downstream synthetic transformations to valuable derivatives, including fuels. Co-products include formic acid and furfural.

In order to evaluate the economic underpinnings of such a facility, the chosen conversion platform is described on the basis of publicly available documents and modeled using a novel domain-specific language (DSL) and symbolic solution library developed for this thesis. This software tool is used to determine the dynamic equilibrium conditions of the process flow of the chemical plant, including net throughput and energy consumption. Such a tool is required because the process flow of the chosen conversion platform feeds back on itself by recycling hydrolysate and acid catalyst, mandating simultaneous solution. A financial model is presented on the basis of the equilibrium process model showing that public support for such a project is required at the vital demonstration scale.

The significant public policy benefits associated with urban biorefineries that can divert putrescible wastes from landfills are therefore shown in this case to depend on public support. In order to estimate the appropriate level of subsidy, external environmental and security benefits are quantified. A study of past federal funding patterns ultimately shows that this level of funding is unlikely to accrue to urban projects without changes in the rural emphasis of current policy and public administration.

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Contents

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This is the second thesis I have written while at MIT. It is also the second having almost nothing to do with my core research responsibilities. For this double measure of freedom, for immeasurable support of all kinds, and for wise guidance and trenchant criticism whenever warranted, I owe a full debt of gratitude to Ken Oye, my advisor. My three years at MIT were intended as, and have turned out to be, a period of unencumbered intellectual exploration and soul-searching. It is Ken who allowed this to be possible. Thank you.

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Finally, my parents have all my gratitude and love. Thank you for endlessly answering the “why” questions and for struggling and sacrificing for my sake every day.

Introduction: Electrical Energy, Organic Fuels, and Federal Energy Policy

The energy needs of the transportation sector remain the greatest impediment to the energy security of the United States. The transportation sector is responsible for 28% of the nation's energy consumption, while over 93% of consumed petroleum takes the form of transportation fuels such as gasoline, diesel distillates, and jet fuel (Alonso et al. 2010a, U.S. Energy Information Administration 2011). Meanwhile, the United States produces less than a third of the petroleum it consumes, a figure in steady decline (U.S. Energy Information Administration 2010). These facts suggest that the nation's energy security is linked tightly to the development of substitute sources of energy for transportation applications.

During the first three years of the administration of President Barack Obama, however, electricity has been the principal concern of federal energy policy. In fiscal year 2011, the Department of Energy budgeted $14.0 billion, including loan guarantees, for projects related to the generation, transmission, and storage of electrical energy (Silverman 2011). Advanced battery manufacturing alone received over $1.5 billion (DOE Report). By contrast, the total budget for research and development of biomass-related technologies, including loan guarantees and grant support for demonstration- and commercial-scale biorefineries, was under $800 million (Silverman 2011). Tellingly, in President Obama's 2011 State of the Union speech, the president set a specific target for market penetration of electric vehicles but neglected mention of vehicles powered by other renewables.

The relationship between an electricity-focused energy policy and the nation's unsustainable petroleum consumption calls for scrutiny. Can an electricity-focused energy policy adequately address the need for substitute transportation technologies? The premise of biofuels development, as well as of this thesis, is that ultimately it cannot. This claim is substantiated in this introductory chapter.

Federal investment in renewable electricity is not without a variety of merits. The technologies involved are relatively de-risked. Solar power plants and wind turbines are reliable assets in the nation's energy portfolio, something that cannot yet be said of advanced biomass and geothermal projects. Renewable generation capacity deployed today can thus begin replacing fossil-fuel power plants immediately for fixed applications. This is the case even if the capacity is never applied to transportation. Moreover, there is a small chance that technological breakthroughs may yet improve the applicability of electricity to transportation. For instance, technologies have been contemplated that would permit the direct conversion of electricity to hydrocarbon fuels.[1]

But ultimately, a successful energy policy will require reversing the nation's dependence on foreign petroleum, and in this respect a federal energy policy focused on electricity has questionable long-run implications. The reason is that such a policy must depend on vehicle batteries as the link between generation and transportation.[2] Despite considerable federal investment in battery technology over many decades and a rise in hybrid- and electric-drive market share from 0.05% to 2.2% of the new vehicle sales between 2000 and 2007 (Beresteanu and Li 2011), the energy density of electric batteries remains insufficient for most transportation applications, even in the theoretical limit of the technology's capability. On account of battery chemistry, the deficit is particularly acute in the wintry climatic conditions prevalent in much of the United States during much of the year. Advanced vehicle batteries also face significant unresolved practical challenges relating to remote charging, cost, maintenance, and thermal runaway, all of which appear intrinsic to the technology.

In this connection it is worth recalling the role that energy density plays in transportation. An autonomous vehicle must displace its energy source in addition to its chassis and any passengers or cargo. The heavier the energy source, holding energy capacity constant, the slower the vehicle or the shorter its range. In the extreme, the vehicle will not move at all. Energy density thus directly affects range and hauling capacity, and its importance increases with the robustness of the application. Large vehicles such as trucks, vans, and aircraft, which together account for more fuel consumption in the United States than small vehicles such as passenger cars, require a more energy-dense energy source than do lighter vehicles (Bureau of Transportation Statistics 2009).

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[1] On April 30, 2010, for instance, the Department of Energy funded 13 “electrofuels” research projects through Advanced Research Projects Agency-Energy. The technology remains distinctly speculative, however, and of dubious economic viability, for even if the appropriate microorganisms could be engineered, the capital expenditure necessary to farm them on a mass scale would be similar to that of algal fuels, which is currently very high.

[2] We assume that commercial success of the aforementioned "electrofuels" programs remains unlikely during the relevant time frame.

Energy source	Energy density	
	Gravimetric (MJ kg^{-1})	Volumetric (MJ L^{-1})
Gasoline	46	32
Butanol	36	29
C.N.G.	51	10
Lithium battery	2.5	(variable)
Lithium battery (metal anodes)	4	(variable)

Table 1: Energy density of sources of energy for vehicle applications (various sources).

The theoretical thermodynamic limitations of battery technology are therefore key to the question of whether batteries and renewable electricity can address the transportation energy crisis. A basic comparison of energy storage potential, rehearsed in Table 1, is discouraging. The energy density of standard gasoline is approximately 46 MJ kg^{-1}. Butanol, an alcohol considered by many to be a promising next-generation renewable replacement for gasoline, exhibits an energy density of approximately 36 MJ kg^{-1}. Compressed natural gas, among the least volumetrically dense of organic fuels, yields 51 MJ kg^{-1} and just over 10 MJ L^{-1} at 3,600 psi. Lithium batteries, by contrast, have a theoretical limit of just 4 MJ kg^{-1}, and then only if advanced research on silicon and other metal or metalloid anodes bears fruit (House 2009). There is no more promising material for battery construction than lithium.

Practically realizable values are even more discouraging than theoretical values. In contrast to already low theoretical value, the battery of the newly released Chevrolet Volt offers an energy density of only 0.18 MJ kg^{-1}, according to industry sources (Petersen 2009), permitting a 35-mile all-electric range. The battery of the Tesla Roadster, a car costing over US$100,000 in 2010 after decades of research into battery technology, yields just 0.424 MJ kg^{-1} (Berdichevsky et al. 2006).[3] In the 2009 DOE Energy Storage Report, the inexpensive production of a 0.35 MJ kg^{-1} battery is set as a highest-priority goal (DOE Storage Report 2009). This is a lower energy density than that of the Roadster and corresponds to an effective all-electric range of just 40 miles.[4]

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[3] This value was calculated as 53 kW h 450^{-1} kg^{-1} based on mass and energy storage values presented in Berdichevsky et al. 2006.

[4] This is not to mention that average source-to-outlet efficiency of electricity generation in the U.S. is only 36%, raising additional questions

Some will reply that electric drivetrains have benefits of their own. Electric motors are typically two to five times more efficient than internal combustion engines at converting energy from the power source into mechanical energy at the wheels, and vehicles running on organic fuels must convey a heavy internal combustion engine in addition to their energy source. While both of these claims are true, neither fundamentally affects the comparison, which is based on a two-orders-of-magnitude difference in energy density that is difficult to overcome.[5] Unsurprisingly, therefore, the mood in battery research has become one of discouragement. Bill Gates, a significant investor in battery technology, has said he believes that electric storage “may not be solvable in any sort of economic way” (Petersen 2010). A 2010 survey of seven leading battery scientists documented their views on the probability of success of several key research targets assuming various levels of federal funding. A majority of the experts believed there was less than a 30% chance of reaching the highest performance target within 10 years, even at the highest level of funding posed as a response point. Discouragingly, this “highest” performance target corresponded to an energy density of only 0.72 MJ kg^{-1}, less than a fifth of the theoretical limit (Baker et al. 2010). These facts together suggest that organic fuels will remain the dominant source of energy for transportation applications, even in a world where the most promising electric battery technologies have come to fruition (see, e.g., Hummel 2011).[6]

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about net cost savings or environmental impact (Smil 2010).

[5] Concerns are magnified under cold-weather conditions, where two additional problems beset battery technology. First, the chemical reactions that take place inside the battery are slowed and impedance increased, diminishing capacity. Second, power draws for cabin heating increase. In combination, these effects halve electric vehicle range, or worse, in wintry conditions of 20°F, compared to 70°F (Dhameja 2002). Another practical concern relates to remote charging. Whereas vehicles powered by liquid organic fuels can simply be "filled up," batteries must be charged over a period of half an hour or substantially more. On-the-fly battery-swapping systems face severe engineering challenges and resistance from industry ("Why car-makers say no to battery-swapping" 2010).

[6] The entire Gates quotation, a response to a question about the applicability of Moore’s law in the energy-storage arena, is worth rehearsing:

> Now and then yes, but we’ve all been spoiled and deeply confused by the IT model. You know chip scaling - exponential improvement - that is rare. Now we do see it; we see it in hard disk storage, fiber capacity, gene sequencing rates, biological databases, improvement in

The foregoing arguments are intended to show that renewable electricity and vehicle batteries are no panacea for the transportation energy crisis.[7] On the contrary, electric power is well-suited to less than half of the nation's transportation applications, even before military applications are taken into account (Bureau of Transportation Statistics 2009, Gaines and Nelson 2009, Becker et al. 2009, Hummel 2011).[8] It is clear that barring an unforeseen energy-storage breakthrough or unprecedented investments in hydrogen infrastructure, organic fuels will continue to represent the most significant component of the nation's transportation energy portfolio.[9] Yet the economics of

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> modeling software - there are some things where exponential improvement is there. If you believe Ray Kurzweil he takes it and says okay all of technology is subject to that and therefore, mankind in 2042 will be replaced by robots. That's the, you know, positive view, which I think goes too far. . . .
>
> The more realistic view is what you'll see in Vaclav Smil in terms of writing about energy. He has Thomas Edison reincarnated and he says OK what would Thomas Edison be surprised about and not surprised about? Light bulbs that screw in? He did that screw-in thing. Lead-acid batteries? Very similar to what Edison did - no surprises. So you say "Oh no, batteries have improved." They haven't improved hardly at all and there are deep physical limits. You know I'm funding five battery start-ups. There's probably fifty out there. That is a very tough problem and intermittent energy sources force you into that problem. And it may not be solvable in any sort of economic way. There is no one that you look at and say has those pieces together (Petersen 2010).

7. This is not to suggest that hybrid powertrains will not become widespread nor that all-electric vehicles will not have success in undemanding applications, only to point out that significant amounts of organic fuel will continue to be required.

8. Navy Secretary Ray Mabus has said, "Whatever fuel we use has got to be a drop-in fuel. We've got the ships and we've got the planes that we're going to have in 2020. [Existing engines must] not know the difference" ("Alternative fuels for the military need to be "drop-in": Navy Sec'y" 2011).

9. Certain quarters have heralded hydrogen fuel-cell technology as a savior. However, fuel-cell technology faces similar challenges to electric battery technology, only these pertain to volumetric energy density rather than gravimetric. Moreover, liquid hydrogen is difficult to store and transport

current-generation renewable organic fuels, such as ethanol, are uninspiring.

* * *

The present thesis studies the possibility of augmenting the nation's biofuels portfolio by manufacturing drop-in transportation fuels and high-value chemicals from urban municipal wastes. The considered technology produces a family of organic fuels known as levulinate fuels, named after their chemical precursor, levulinic acid. Levulinic acid is a noted "platform chemical," meaning that it offers many pathways for conversion to valuable end-products such as fuels, plasticizers, and solvents. The versatility of levulinic acid is one of its central advantages as a commercial biorefinery product.

A central premise of this thesis is that the nation's energy security depends on developing *economical* renewable fuel manufacture. It is for this reason that we will focus heavily on the economics of the chosen conversion technology. We will also quantify the appropriate level of subsidy for such a project in light of its social benefits. Notably, with this subsidy in place, the project is shown to be commercially viable, even at the relatively small demonstration scale. As will be seen, this is because the economics of biofuels manufacture are helped fundamentally by the use of waste streams as a feedstock. Because levulinic acid can be produced efficiently from heterogeneous and relatively wet lignocellulosic feedstock, even the most recalcitrant of waste streams such as food and unrecyclable paper can be used. In the status quo, such wastes pose serious disposal challenges to towns and cities, so that municipalities such as New York, New York, and Trenton, New Jersey, currently pay over \$100 ton^{-1} to transport and dispose of them in landfills (New Jersey Department of Environmental Protection 2011). Such "tipping fees" can serve as an additional and vital source of revenue for a process designed to handle these wastes.

In Chapter 1, levulinic acid and its derivatives are introduced. A history of levulinic acid production is provided and its value as a biorefinery product substantiated. Various production pathways are charted. The Biofine Process, the state of the art of levulinic acid production technology, is introduced. Notable levulinic acid derivatives are cataloged, including levulinate esters of ethanol

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and can take advantage of neither the existing electricity nor existing fuel-distribution infrastructure. A full analysis of fuel-cell technology is outside the scope of this chapter because fuel-cell technology has not been the focus of federal energy policy. In fact, Secretary of Energy Chu has effectively ended funding for most fuel cell development (Wald 2009).

(ethyl levulinate), butanol (butyl levulinate), and linear butenes (butyl levulinate); methyltetrahydrofuran (MTHF); and liquid alkenes derived via γ-valerolactone (GVL). Fuel and chemical applications are discussed and price points surveyed. Feedstock candidates are surveyed for conversion via acid-catalyzed hydrolysis. Municipal solid waste markets in the northeast United States are evaluated as a source of high-volume, negative-cost lignocellulosic material. The composition of this waste is estimated and a range of probable tipping fees (revenues from feedstock delivery) generated. On the basis of this information, a simple operating cash flow is calculated to evaluate the viability of the technology at various levels of capital expenditure.

In Chapter 2, the recurrent nature of the Biofine Process is shown to be resistant to standard simulation methods. Instead, its dynamic equilibrium conditions require simultaneous solution. A simple domain-specific language (DSL) is introduced to allow the easy generation of the required set of symbolic equations on the basis of the process flow description. A solver and graphical user interface are presented to allow engineers to use these equations to inform engineering and costing. Solutions are computed allowing for sensitivity analysis based on key process parameters.

In Chapter 3, federal policy is studied relative to the funding of biorefineries. First, the external (non-appropriable) benefits of an urban biorefinery are quantified. The level of subsidy justified by these benefits is calculated. A study of past funding patterns in the U.S. Department of Energy and U.S. Department of Agriculture is presented to show that the appropriate level of funding is unlikely to accrue to urban projects without changes in the rural emphasis of current policy and public administration.

Chapter 1

Levulinate Fuels and the Economics of Urban Biofuels Production

Levulinic acid ($C_5H_8O_3$, Figure 1.1), also known as 4-oxopentanoic acid, β-acetylpropionic acid, and γ-ketovaleric acid, is a water-soluble acid with two reactive functional groups providing for a variety of synthetic transformations to high-value derivatives (Serrano-Ruiz et al. 2010b, Rackemann and Doherty 2011).[1] It is a compound of principal interest in the fledgling biorefining industry because of (1) its relatively easy production from diverse carbohydrate feedstocks, (2) the potential for high yields in this production, although these are as yet unrealized in the commercial sphere, and (3) its reactivity, which allows it to be transformed into valuable products through a wide variety of pathways. Physical properties of levulinic acid are provided in Table 1.1.

In 2004, staff of the Pacific Northwest National Laboratory, National Renewable Energy Laboratory, and Office of Biomass Program of the Department of Energy evaluated over 300 potential biorefinery products and systematically selected a "Top 10 Building Blocks" on the basis of "estimated processing costs, estimated selling price, . . . technical complexity associated with the best available processing pathway and . . . market potential" (Werpy and Petersen 2004). Levulinic acid was among these top 10 and was said to "offer[] one of the larger families of potential industrial derivatives among the compounds included

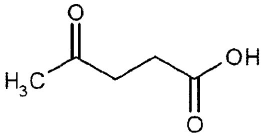

Figure 1.1: Levulinic acid.

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[1] Levulinic acid contains a ketone (-C=O) and carboxyl group (-COOH). According to Hayes et al. (2008), "[levulinic acid] can react as both a carboxylic acid and a ketone. The carbon atom of the carbonyl group is usually more susceptible to nucleophilic attack than that of the carboxyl group."

Property	Value
Dissociation constant (pK_a)	4.59
Density	1.14 kg L^{-1}
Melting point	37°C
Boiling point	249°C
Heat of vaporization	0.58 kJ mol^{-1}
Heat of fusion	79.8 kJ mol^{-1}

Table 1.1: Selected physical properties of levulinic acid (various sources).

in the top 10." The authors furthermore noted that "it could be a building block of central importance within the biorefinery" (Werpy and Petersen 2004). Girisuta (2007) has exhaustively cataloged the various chemical pathways available using levulinic acid as a starting point. These include "functional group transformations involving the carboxylic-, carbonyl- and methyl-group as well as typical oxidation and reduction reactions." Figure 1.2 reproduces a schematic of these pathways.

The availability of multiple downstream pathways is crucial to the commercial viability of levulinic acid production facilities for at least two reasons. First, this flexibility allows levulinic acid to serve multiple purposes in much the same way as petroleum. Petroleum is a complex mixture of hydrocarbons, typically ranging from C_5 to C_{40}, and other organic molecules. The diversity of this mixture allows it to be fractionated and distilled into products ranging from butane and diesel fuel to motor lubricants and asphalt. While levulinic acid is unlikely to share the versatility of petroleum, the ability to displace a range of petroleum-derived products is a significant advantage because it allows for de-risking through diversification and higher volumes through access to multiple markets.

A second advantage of a range of downstream pathways is the possibility of cross-subsidy of commodity products by high-value products during the early stages of commercialization. It is widely acknowledged that renewable biofuels face an uphill battle with respect to displacing relatively inexpensive commodity fossil fuels (Alonso et al. 2010b, Antares Group Incorporated 2001). This disadvantage can be mitigated to the extent that a portion of the biorefinery product can be sold into high-value, non-commodity markets such as markets for industrial chemicals. Typically such markets are low-volume, such that it is unrealistic to expect that the entire biorefinery output could be so directed. However, the financial gains from cross-subsidy may nonetheless be sufficient to carry biorefineries to full commercial scale.

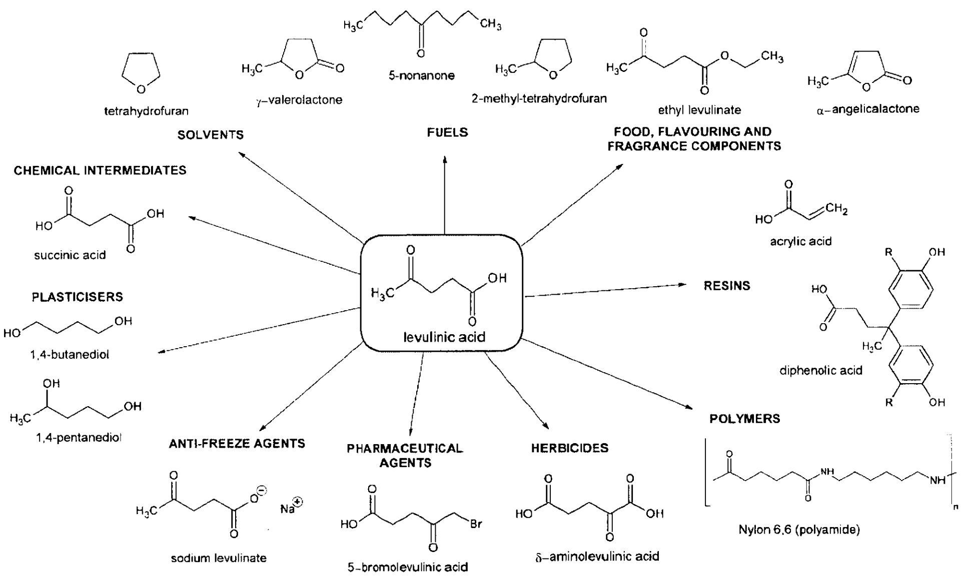

Figure 1.2: Levulinic acid is a platform chemical susceptible to a variety of transformations involving the carboxylic group (producing esters such as ethyl and butyl levulinate, as well as lactones such as α-angelicalactone), nucleophilic additions to the carbonyl group (producing amides), condensation reactions involving the carbonyl group (producing valeric acids such as diphenolic acid), halogenation reactions involving the methyl group (producing organic halides such as 5-bromolevulinic acid and δ-aminolevulinic acid), oxidation reactions (producing, e.g., succinic acid and derivatives such as tetrahydrofuran and 1,4-butanediol), and reduction reactions (producing γ-valerolactone and derivatives such as methyltetrahydrofuran (MTHF)) (Girisuta 2007, Lange et al. 2010). Figure reproduced from Rackemann and Doherty 2011.

1.1 Production of Levulinic Acid

Humans consume only 3-4% of the over 150 billion metric tons of biomass produced by photosynthesis each year (Rackemann and Doherty 2011). This biomass represents the world's only renewable source of fixed carbon, a crucial resource for the production of energy-dense fuels for personal and commercial transportation as well as military applications (Alonso et al. 2010b).

From a chemical perspective, the goal of biorefining is twofold: first, to reduce the oxygen content of the biomass feedstock, thereby increasing the energy density of the material beyond its natural state; and second, to add carbon-carbon bonds so as to reduce the molecular weight of the final product (Alonso et al. 2010b).[2] First-generation biorefineries realize these goals by converting starches, such as those found in corn kernels, to alcohols. The process takes place in two stages, first by subjecting the starches to hydrolysis, typically enzymatic, to convert them into various sugars, then subjecting the sugars to fermentation by the action of micro-organisms. This process is chemically no different from the fermentation of grains to spirits that has been cultivated in human cultures across the millennia. Starches, however, represent a particularly scarce resource insofar as they are a staple of the human diet and can be grown in high volumes in only certain climatic regions.

Alternatively, some first-generation biorefineries have used edible and waste oils for the production of diesel fuel by transesterification or hydrogenation (see Meher et al. 2006 for a review). Edible and waste oils, however, are not presently grown or produced in quantities sufficient for widespread use as a fuel precursor, and the capital costs of using algal technologies to generate the necessary oils on a large scale appear prohibitive. For these reasons, cellulose, the main structural component of plant cell walls, has been targeted by commercial entities as well as federal agencies and executive departments as the feedstock of choice for advanced biorefinery technologies.

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2. During the past decades, the Environmental Protection Agency and other federal agencies and executive departments have promoted the use of fuel oxygenates such as alcohols in an effort to increase the use of renewables such as ethanol and to decrease emissions of carbon monoxide and uncombusted hydrocarbons. Such emissions occur when insufficient oxygen is present to fully combust the available hydrocarbons. However, oxygenation also reduces the energy density of a fuel. It is for this reason among others that the use of fuel oxygenates was opposed by interest groups from consumers to fuel manufacturers.

Cellulose, a polymeric carbohydrate containing hundreds of chained glucose molecules, is a particularly recalcitrant material, especially in its natural crystalline state. Hundreds of millions of years of evolution have produced complex structural and chemical mechanisms that allow plants to fend off structural attacks on their sugars from the microbes and animals. Himmel et al. (2007) have enumerated these defenses on both the macro and molecular level. The core defense that concerns biorefinery operations is the resistance of cellulose to hydrolysis:

> The hydrophobic face of cellulose sheets makes crystalline cellulose resistant to acid hydrolysis because it contributes to the formation of a dense layer of water near the hydrated cellulose surface. The strong interchain hydrogen-bonding network makes crystalline cellulose resistant to enzymatic hydrolysis, whereas hemicellulose and amorphous cellulose are readily digestible. Higher-order structures in plants also contribute to biomass recalcitrance. For example, access to the crystalline cellulose cores of microfibrils is restricted by a coating of amorphous cellulose and hemicellulose. At a microscopic and macroscopic scale, the complex heterogeneous nature of biomass creates mass-transport limitations for delivery of chemical or biochemical catalysts (Himmel et al. 2007, internal references omitted).

Levulinic acid has been known as a potential cellulose and sugar product for many years. It was first synthesized from lignocellulosic biomass using an acid catalyst in the early 19th century (Leonard 1956). According to Girisuta (2007), the first published report comes in the 1840s from the Dutch professor G. J. Mulder, who prepared levulinic acid by heating sucrose with mineral acids. An analysis by Biofine Technology (unpublished) shows that journal references to the compound peaked at approximately 80 per year in the late 1950s and early 1960s. Patent references have appeared at a rate of approximately 15 per year since that time.

In contrast to the remaining nine "Top 10" compounds identified by Werpy and Petersen (2004), levulinic acid can be produced using the exclusively chemical process of dilute acid hydrolysis, wherein a mineral acid such as sulfuric acid is used as a catalyst, most often in the presence of high temperature and pressure.[3] The other compounds identified in the Werpy and Petersen report require instead some sort of partial oxidation reaction (such as

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[3] Other conversion processes reported in the literature include pathways involving hydrolysis of acetyl succinate esters, acid hydrolysis of furfuryl alcohol, oxidation of ketones with ozone, Pd-catalyzed carbonylation of ketones, and alkylation of nitroalkanes (Bozell et al. 2000).

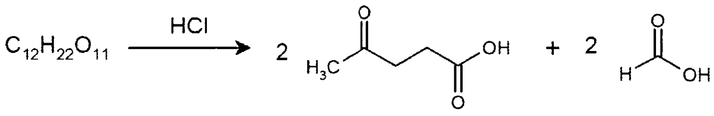

Figure 1.3: Reaction stoichiometry of hexose saccharide (here, sucrose) to levulinic acid ($C_5H_8O_3$) and formic acid (HCOOH).

combustion or gasification), hydrogenation, or a biological processing route such as fermentation in order to be derived from lignocellulosic material (Serrano-Ruiz et al. 2010b). In comparison to these routes, dilute acid hydrolysis is a particularly simple and robust reaction that contributes to the economy of the levulinic acid production process. For instance, hydrogenation requires a source of free hydrogen, which is typically expensive or must be drawn from an otherwise saleable co-product, while fermentation requires significantly more time to complete, approximately one week in most cases. Composting, another aerobic conversion process, requires even more time, sometimes more than two months. Dilute acid hydrolysis requires less than 30 minutes to complete when accelerated by high heat and pressure (Hayes et al. 2008, Bozell et al. 2000). This rapidity translates into short residence times for the incoming material and thus permits the small footprint that can be characteristic of levulinic acid biorefineries.[4]

The theoretical yield of levulinic acid from hexose saccharides is 100 mol % or 64.5 wt % owing to the co-production of formic acid (see Figure 1.3). Production at moderate yields is not difficult, but according to published reports achieving yields close to the theoretical maximum at low cost poses severe challenges (Bozell et al. 2000, Serrano-Ruiz et al. 2010a, Fitzpatrick 2004). Virtually all reported studies involve production of appreciable amounts of chemical side-products that diminish yields. Tables 1.2 and 1.3 reproduce the yields reported across a large number of studies using various feedstocks and acid catalysts, as analyzed by Girisuta (2007). Where yields are substantially below theoretical, the reason is typically that the reacted portion of the carbohydrate feedstock has been converted into a viscous, difficult-to-handle bio-oil containing both levulinic acid and various humic materials, i.e. heterogeneous sugar polymers, lignins, and ash (Paul (unpublished), Bozell 2010). Historically, researchers have found it difficult to separate the levulinic acid product from the side-products.

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[4] Acid-catalyzed hydrolysis is employed by most fermentation processes as a pretreatment step, but in the production of levulinic acid it serves as the only step (Hayes et al. 2008).

Feedstock	Acid	Temperature (°C)	Yield wt %
Cane sugar	HCl	100	15
Glucose	HCl	Room	15
Corn starch	HCl	162	26
Sucrose	HCl	162	29
Glucose	HCl	162	24
Fructose	HCl	162	25
Hydrol	HCl	Room	25
Corn starch	HCl	200	35
Starch	HCl	Room	19
Rice hulls	HCl	160	10.3
Rice straw	HCl	160	5.5
Corn stalks	HCl	160	7.5
Cotton linters	HCl	160	7.4
Sucrose	H_2SO_4	125	30
Sucrose	HCl	125	43
Sucrose	HBr	125	50
Sucrose	Amberlite IR-120	Room	15.6
Fructose	Amberlite IR-120	Room	23.5
Glucose	Amberlite IR-120	Room	5.8
Glucose	H_2SO_4	160-240	35.4
Pulp slurry	HCl	160	40.5
Glucose	HCl	160	41.4

Table 1.2: Levulinic acid yields as reported in the literature (first of two tables). The theoretical yield is 65 wt %. Table adapted from Girisuta 2007.

Feedstock	Acid	Temperature (°C)	Yield wt %
Cotton stems	H_2SO_4	180-190	6.13
Sawdust	HCl	190	9
Oak	H_2SO_4	180	17.5
Bagasse	H_2SO_4	25-195	17.5
Fructose	HCl	100	52
Sucrose	Resin-Dowex	100	17
Fructose	LZY-zeolite	140	43.2
Glucose	Clay-catalyst	150	12
Glucose	HY-zeolite	150	6
Cellulose	H_2SO_4	250	25.2
Various wood	H_2SO_4	200-240	13-18
Cellulose	H_2SO_4	150-250	25.2
Cellulose	HCl	150-250	28.8
Cellulose	HBr	150-250	26.9
Aspen wood	H_2SO_4	150-250	15.5
Aspen wood	HCl	150-250	12.4
Aspen wood	HBr	150-250	13
Newspaper	H_2SO_4	150	12.8
Sorghum grain	H_2SO_4	200	32.6
Extruded starch	H_2SO_4	200	47.5
Wheat straw	H_2SO_4	209.3	19.8

Table 1.3: Levulinic acid yields as reported in the literature (second of two tables). The theoretical yield is 65 wt %. Table adapted from Girisuta 2007.

Two lessons can be drawn from this compilation of studies. First, low yields must be overcome if the already difficult economics of biofuels production are to be improved. According to reports, low yields have contributed to the fact that the market supply price for pure levulinic acid has remained high, over $5 per pound, relative to its effective demand price for most uses (Fitzpatrick 2004).

The second lesson to be drawn from the studies is that the acid hydrolysis reaction is indiscriminately effective over a wide variety of feedstocks. Possible feedstocks include essentially any lignocellulosic material, including ordinary vegetable matter, cane sugar, corn starch, rice straw, pulp slurry, various woods, newspapers, pure cellulose, and various sugars, and, importantly, heterogeneous mixtures of these (Serrano-Ruiz et al. 2010b). Feedstock cost thus has the potential to be driven down significantly relative to other biorefinery feedstocks because it is not necessary to secure a specific, homogeneous substrate, as is necessary, for instance, for technologies employing highly tuned microorganisms or gasification (partial combustion) reactions. In fact, to the extent that wastes can be obtained that contain the necessary carbohydrates and meet other necessary criteria, such as lack of certain impurities that may damage the process, the cost of feedstock can be turned negative. The implications of this are discussed later in this chapter.

1.2 The Biofine Process

The Biofine Process, developed by Fitzpatrick in the 1980s and refined during the 1990s and 2000s, has been described as “the most promising commercial process” for the manufacture of levulinic acid and its co-products (Rackemann and Doherty 2011). This hydrolysis process employs a sulfuric acid catalyst and high temperatures and pressures (relative to other levulinic acid production processes) to obtain consistently high yields of levulinic acid in continuous, i.e. non-batch, operation. The Biofine Process has two distinctive features, schematized in Figure 1.4.

The first distinctive feature is the use of a two-stage reactor design intended to overcome low yields associated with formation of side-products such as chars and tars. The first reactor, a plug flow reactor operating at 210-230°C and approximately 25 bar pressure, is designed to provide conditions favorable to the dominant first-order hydrolysis of cellulose but not further degradation to levulinic acid or side-products. Cellulose is converted in this reactor to the intermediate compound hydroxymethylfurfural (HMF). HMF is continuously removed into the second reactor, a continuous stirred reactor operating under less robust conditions designed to favor the reaction sequence from HMF to levulinic acid while minimizing the formation of chars and tars (Fitzpatrick 2004). This reactor operates at a temperature of 195-215°C and approximately 14 bar pressure. Levulinic acid is produced along with the co-product formic acid. Hemicelluloses in the feedstock are converted into furfural. Data on the kinetics of these reactions are available in Hayes et al. 2008.

The second distinctive feature of the Biofine design is the recycling of the lion’s share of the hydrolysate (product-acid mixture) from the end of the process to the beginning (see Figure 1.4). This design creates a recurrent system that both concentrates the product and reduces the need to recover acid. The non-recycled portion of the hydrolysate stream is sent to product extraction. The recurrent design poses analytical challenges because it gives rise to a simultaneity in the determination of magnitudes of the various streams in the process. The feedback from the end of the process to the beginning causes the magnitude and composition of every non-peripheral stream to affect that of every other.

A full technical model of the Biofine Process is described in Chapter 2. The full model depends intimately on a wide range of parameters and is capable of generating estimates of operating conditions such as precise stream magnitudes and total capacity for a given quantity of steam or energy input. For the purposes of Chapter 1, however, the only relevant features of the process

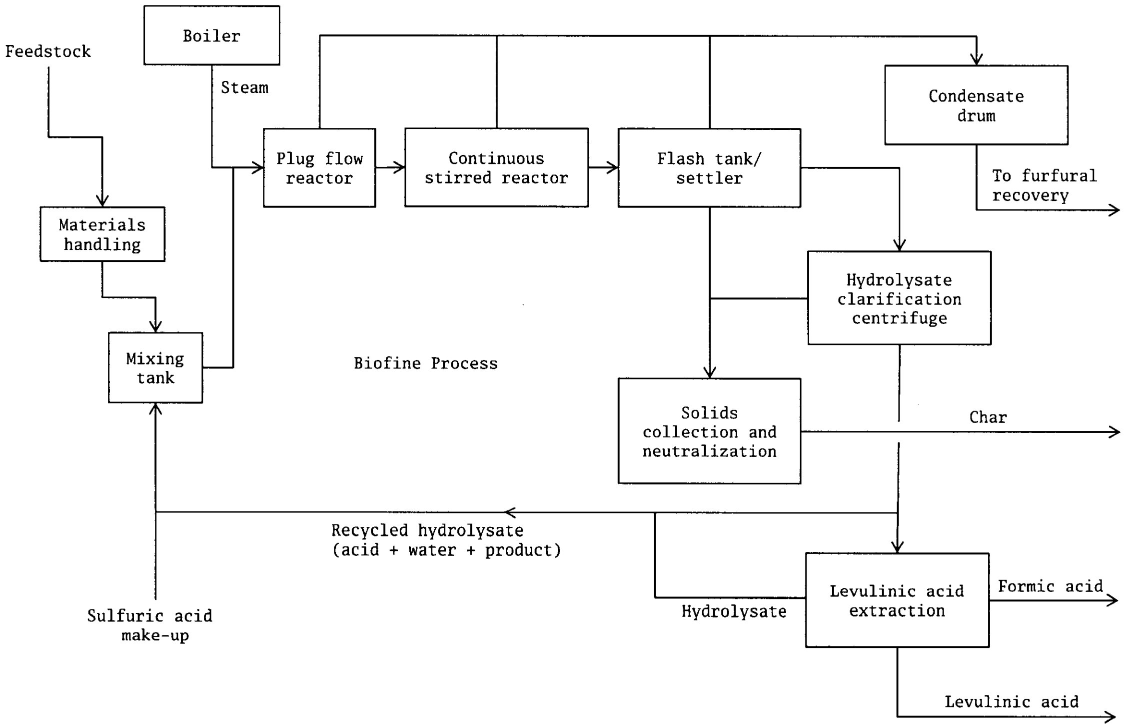

Figure 1.4: Simple schematic of the Biofine process, adapted from Serrano-Ruiz et al. 2010b. The process begins with the mixing of incoming feedstock with recycled hydrolysate, which contains a homogeneous acid catalyst. The slurry is then combined with high-pressure steam and pumped into a plug flow reactor, where it reacts for a short time (15-25 seconds). The aim in this first reactor is to convert celluloses to HMF. The next step is a continuous stirred reactor, where the mixture reacts for a further 25 minutes to produce levulinic acid and formic acid. Hemicelluloses are converted to furfural. A series of clarification and extraction steps yields the final products. A significant portion of the hydrolysate is recycled rather than sent to the extraction unit.

are its typical yields of products from inputs. Yields drawn from public documents are presented in Table 1.4.

The Biofine Process has been piloted at two separate facilities. In 1998 a 1 ton day^{-1} facility was constructed and operated in South Glens Falls, New York, with grant support from the Department of Energy and New York State Energy Research and Development Authority. Subsequently, a 2 ton day^{-1} facility was constructed and operated in Gorham, Maine (pictured in Figure 1.5). Non-public operational data show that the yields obtained at these facilities match those claimed by the developers of the Biofine Process.

Figure 1.5: Biofine pilot facility in Gorham, Maine, operated at 2 tons day^{-1}. Reproduced from public-domain materials published by the Department of Energy.

	To (wt %)				
	Levulinic acid	Formic acid	Furfural	Char/tar	Water
Cellulose	46	18	0	36	0
Hemicellulose	0	0	40	35	25
Lignins	0	0	0	100	0

Table 1.4: Simplified yield matrix of the Biofine Process.

1.3 Commercial Derivatives of Levulinic Acid

At the present time there are a number of derivatives of levulinic acid with the potential for near-term commercial marketability. These include: ethyl levulinate, an ester of levulinic acid with known potential as a plasticizer; butyl levulinate, an ester with compelling fuel properties as a diesel blendstock (Christensen 2011, Janssen et al. 2010);[5] the hydrogenation product methyltetrahydrofuran (MTHF), a gasoline additive with a large potential market (Fitzpatrick 2004); the hydrogenation product γ-valerolactone (GVL), a potential precursor to hydrocarbon fuels (Bond et al. 2010, Schwartz et al. 2010, Serrano-Ruiz et al. 2010c, Gürbüz et al. 2011) and to valeric biofuels (Lange et al. 2010, Rackemann and Doherty 2011);[6] and δ-amino levulinic acid (DALA) (Rackemann and Doherty 2011).

Market research relating to each of these derivatives is outside the scope of this thesis. The most immediately commercializable and high-cost derivative, ethyl levulinate, is selected and used for sensitivity analysis. It is believed that outfits such as Segetis, a Vinod Khosla-funded venture whose business plan is premised on the availability of esters such as ethyl levulinate, would provide a "bankable" offtake for this product.

Ethyl levulinate can be produced from levulinic acid at a rate of 100 mol %, with the addition of 100 mol % ethanol. This corresponds to 39 kg ethanol for each 100 kg levulinic acid, producing a total output of 139 kg ethyl levulinate.

1.4 Economics of Negative-cost Feedstocks

The possibility of negative-cost feedstock, discussed earlier, reverses some of the standard economics of manufacture. It is helpful to consider a few of the

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[5] Note that the production of butyl levulinate requires a source of butanol. At present, the only high-volume source of butanol is petroleum-derived, despite previous assurances to the market from Butamax (a BP-DuPont joint venture) and early-stage outfits such as Cobalt Technologies that high-volume biobutanol would be forthcoming by 2010 or 2011. Note too, however, that linear butenes, which like butanol can also be esterified with levulinic acid to produce butyl levulinate, can in principle be produced directly from levulinic acid (Bond et al. 2010). This pathway is under active development.

[6] According to the hydrocarbon pathway, which is in active development, GVL is further hydrogenated to pentanoic acid, catalytically upgraded to 5-nonanone by ketonization, and hydrogenated to alkanes or alcohols. Alcohols can be dehydrated to alkenes and oligomerized to C6-C27 hydrocarbons.

implications of this. Ordinarily, the objective of manufacture is to (1) maximize the volume of saleable output while (2) minimizing the volume of feedstock and (3) minimizing operating costs (all on the condition that the prices of factors of production are sufficiently low to secure a profit). It will be evident immediately that because a negative-cost feedstock is a source of revenue rather than a cost, item (2) is stood on its head. Roughly speaking, the objective in the case of a negative-cost feedstock is to (1) maximize the volume of saleable output, (2) *maximize* the volume of feedstock, and, once again, (3) minimize operating costs.

In fact, the precise effect of a negative-cost feedstock is slightly more nuanced than this and requires some analysis to explicate fully. To begin, consider a firm as optimizing the following profit function:

$$\pi = f(a)P_b - xP_a - v(a) - c,$$

where π is profit, a is the volume of feedstock (i.e. the plant's feedstock capacity, which the firm chooses), P_a and P_b are the prices of the feedstock and end-product respectively (over which the firm has no control), $v(a)$ is the firm's total variable costs as an increasing function of the quantity of feedstock ($v'(a) > 0$), and $f(a)$ is the firm's output as a function of the quantity of feedstock, i.e. its production function ($f'(a) > 0$). This is quite standard fare and comports with a commonsensical understanding of management's objective.

For simplicity we can adopt the assumption, usually quite accurate, that the production function is linear in a over the relevant interval, such that $f(a) = ya$, which is to say the plant exhibits constant returns to scale in the feedstock (see Sraffa 1926 for a theoretical justification not often enough remembered). Hence the profit function becomes

$$\pi = yaP_b - xP_a - v(a) - c,$$

where y is the yield ($0 < y$), or proportion of feedstock converted into the end-product.[7] Feedstock not converted to end-product is assumed to become waste, which is disposed of at no cost, although costly disposal would not affect the following analysis.

Our object is to determine the ramifications of a negative-cost feedstock versus a positive-cost feedstock, which is to say $P_a < 0$ versus $P_a > 0$. We can proceed quite straightforwardly by taking partial derivatives of the profit function with respect to certain variables of interest. The first observation is

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[7] The variable y is permitted to exceed 1. This is because the feedstock and end-product might be expressed in different units from one another and because mass might be added during processing.

that the partial derivative with respect to y, the yield, has no dependence on P_a, the feedstock price:

$$\frac{\partial \pi}{\partial y} = aP_b > 0.$$

In other words, it always pays to increase yield, holding all else equal, regardless of whether the cost of feedstock is negative or positive. This belies the deceptively intuitive notion that when feedstock is negative-cost "yields don't matter." In fact yields do always matter, the reason being that for any given amount of incoming feedstock, it is better to turn this feedstock into saleable fuel than disposable waste.

The question becomes more complicated, of course, if the *ceteris paribus* condition is violated such that a prospective increase in yield will reduce the capacity of the plant. Such a case amounts to

$$a = a(y), \quad a'(y) < 0$$

i.e. feedstock capacity is a decreasing function of the yield. Again taking the partial derivative with respect to the yield, we now have

$$\begin{aligned}\frac{\partial \pi}{\partial y} &= P_b a(y) + P_b y a'(y) - P_a a'(y) - a'(y)v'(a(y)) \\ &= P_b a(y) + a'(y)(P_b y - P_a) + (-a'(y)v'(a(y))).\end{aligned}$$

On the right side the first and third terms are clearly positive (recall that $a(\cdot)$ is a decreasing function and $v(\cdot)$ an increasing function). Therefore the sign of the entire expression depends on the second term, and, more precisely, on the expression in parenthesis, namely $P_b y - P_a$, for we know that the first component of the second term, $a'(y)$, is negative. Thus if $P_b y - P_a \leq 0$, or, what is the same thing, $P_b y \leq P_a$, then the entire expression turns out to be positive. By contrast, if $P_b y > P_a$, the sign of the entire expression turns out to be indeterminate.

Unfortunately, the latter is the case of interest to us, because $P_b y > P_a$ is always true when the cost of feedstock is negative. This result simply formalizes the intuition that when feedstock is a source of revenue, the desirability of any given tradeoff between capacity and yield will depend intimately on the details of the tradeoff. For instance, if a 1% increase in yield comes at the price of a 5% decrease in feedstock capacity, the tradeoff will be worthwhile only if the savings in variable costs more than offsets the loss of net revenue.

The more important analysis, however, concerns the relationship between yield, product cost, and plant scale when a negative-cost feedstock is available. To see this relationship, we can pose the following question: What should govern plant size in the case of a negative-cost feedstock versus the case of a positive-cost feedstock? To pursue an answer, we can take the partial derivative of the profit function with respect to feedstock capacity:

$$\frac{\partial \pi}{\partial a} = P_b y - P_a - v'(a).$$

Since $P_b y$ is positive, it is clear that the entire right-side expression is positive only if $P_a + v'(a)$ is negative. Thus it is immediately revealed that if P_a, the price of feedstock, is negative and indeed so negative that it exceeds variable costs in absolute value, then expanding further is unconditionally profitable. The meaning of this point bears further explanation. It says that if revenues from feedstock are enough to cover the cost of conversion fully (including amortization of fixed costs), then the yield on which further expansion is conditioned does not depend at all on the price of products. Any yield and any positive product price is sufficient to warrant an increase in scale.

By contrast, if P_a, the price of feedstock, is not quite so negative as to defray costs of conversion, or is positive, as will be the case for the vast majority of manufacturers, then a more complex relationship emerges. Namely, in order for expansion to be profitable on the margin, it must be the case that

$$y > \frac{P_a + v'(a)}{P_b} > \frac{p_a}{p_b}.$$

What is important about this relationship is that the price of the saleable end-product, p_b, plays a crucial role in determining the minimum required yield.

Hence we can see in no uncertain terms what may have been obvious to the astute reader from the start. If a chemicals plant is also a waste disposal plant, and if the tipping fees received for disposing of waste are high enough to pay fully for the operation of the plant, including amortization of fixed costs, then there is no limit to the scale of the plant's profitable operation, no matter how low the price of products may fall. This is in sharp contrast to the case of a biofuels producer who must use agricultural or forestry products as his input material; for such feedstocks are positive-cost and therefore the producer is completely at the mercy of the products' market price. This is the final case considered, above, where the conversion yield y must exceed $\frac{p_a}{p_b}$. So much the worse for such a producer if these markets are commodity fuel markets buffeted by the whims of the petroleum exporters.

1.5 Regional Feedstock Availability and Composition

The foregoing analysis makes clear that evaluating the suitability of waste materials as a feedstock is an important order of business, for if the possibility of obtaining feedstock at a negative cost exists, we can be assured that, although no economic questions will be resolved fully until the fixed and variable costs of a production facility have been characterized, the economics at least remain favorable toward the construction of urban levulinic acid production facilities.

On a regional basis, New England's tipping fees are the highest in the nation, but those of the State of New Jersey are roughly on par with New England's and have been for some time (see Table 1.5) (Iowa Association of Naturalists 1998). New Jersey's particularly high tipping fees are due largely to the addition of a large volume of waste from greater New York City to other waste streams passing through to southern and western disposal sites.

Location	Year	Mean tipping fee ($ ton^{-1})	Source
Northeast	2004	70.53	Repa 2005
Mid-Atlantic	2004	46.29	Repa 2005
South	2004	30.97	Repa 2005
Midwest	2004	34.96	Repa 2005
South Central	2004	24.06	Repa 2005
West Central	2004	24.13	Repa 2005
West	2004	37.74	Repa 2005
National	2004	34.29	Repa 2005
New Jersey	2005	60-80	N.J. D.E.P. 2005

Table 1.5: Tipping fees by U.S. region for municipal solid waste, with New Jersey included for comparison.

Among New Jersey counties, Mercer County has the highest tipping fees at $125 per ton as of late 2010 (Stratton 2011, Princeton Township Newsletter 2010). Table 1.6 provides a summary of the counties with the highest tipping fees. Business partners of the author believe that this price level represents the highest in the nation, although an exhaustive county-by-county has not been conducted. The values reproduced in the table correspond to the tipping fee paid to dispose of standard municipal solid waste, which is referred to by the New Jersey Department of Environmental Protection as Type 10 waste. Other types of waste, such as medical waste, naturally carry a higher disposal price (N.J. D.E.P. 2011).

The suitability of municipal wastes streams as a biorefinery feedstock depends on the biorefinery conversion process in question, as discussed earlier, as well as the precise composition of the stream in question and its price (possibly negative). This section considers composition and price. As Table 1.7 shows, municipal solid waste is an extremely heterogeneous substance and can be broken down into a variety of sub-streams, such as food waste and leaves. The

Location	Year	Mean tipping fee ($ ton^{-1})	Source
Essex County	2011	92.33	N.J. D.E.P. 2011
Hudson County	2011	93.75	N.J. D.E.P. 2011
Mercer County	2010	125.00	Stratton 2011, Princeton Township 2010
Morris County	2010	94.00	Morris County Transfer Station 2010
Union County	2011	97.48	N.J. D.E.P. 2011
Warren County	2011	95.00	N.J. D.E.P. 2011

Table 1.6: N.J. counties with highest tipping fees for N.J.D.E.P. Type 10 waste (municipal solid waste).

characteristics of the aggregate stream, including its chemical composition, will depend on the stream's "macro composition," which is to say its composition in terms of sub-streams, as well as the chemical composition of each of the sub-streams. The methodology adopted here is to characterize both the macro composition of the aggregate MSW stream in terms of sub-streams and the chemical composition of each sub-stream, and then use these data to calculate the chemical composition of the aggregate stream. This methodology, no more intricate than a dot-product on a mathematical level, permits revised calculations to be performed easily should the macro composition of a stream change whether as a result of unforeseen shifts in supply or as a result of an intentional decision on the part of the recipient. This last point is important because depending on the way in which waste is separated and hauled in a given region, a recipient may find it possible to select precise sub-streams for delivery without meaningfully affecting tipping fee revenue. Composters, for instance, select a stream of organic materials that here we will call the compostable MSW stream.

The four MSW streams we consider (see, e.g., Table 1.7) are the full, unseparated MSW stream, which may include metals, plastics, and other non-organics in addition to the organic components; and three organic-only subsets thereof, each a subset of the last. These are: (1) the compostable MSW stream, which is a combination of food waste, paper waste, and yard waste (the paper waste in question is the unrecyclable variety, including waxed cardboard, food-contaminated paper, low-value newsprint, and so forth); (2) the compostable MSW stream with no yard waste, which excludes tree cuttings, grass, and leaves but includes paper and food wastes; and finally (3) the food waste stream, which contains only organic food matter such as vegetable food scraps and starches such as potatoes and corn. These three organic waste streams are associated with a particularly low value (high tipping fee) because they are moist, tend to putrify and smell, and have low suitability for recycling. Thus to the extent that this chapter characterizes the tipping fee of these streams as equivalent to the prevailing MSW tipping fee, tipping fee revenue estimates are likely to be conservative. All three organic streams are suitable for levulinic acid production because they are rich in cellulose on a dry basis and because the acid hyrolysis production process, which occurs in an aqueous medium, is capable of processing feedstocks with relatively high moisture levels.

In order to characterize chemically the three organic MSW streams, we must first characterize chemically the various sub-streams. Table 1.8 reports these results on a dry basis, drawn from Eleazer et al. (1997). Table 1.9 displays a conversion to the wet basis. These tables also display the methane generation potential of the various sub-streams, data that will be used later in the calculation of the climate change mitigation potential of an urban biorefinery such as this.

As the foregoing data show, food waste and paper waste are the predominant components of the compostable stream and of the compostable stream exempting yard waste. Food waste and paper waste have similar chemical compositions to each other on a dry basis, but food waste tends to be significantly wetter. This difference will lead us to an interesting optimization problem in the next chapter. This is because on one hand it may pay (*prima facie*) to seek out predominantly paper waste, on the argument that paper waste contains the higher fraction of the core input chemical in question, cellulose. On the other hand, it may pay to seek out predominantly food waste, on the argument that tipping fees received for taking a material made predominantly of water go straight to the bottom line. What will be revealed in Chapter 2 is that the optimal mixture of food and paper waste can be characterized precisely and depends on the relative magnitudes of tipping fees and end-product prices.[8]

Given the foregoing data, it is a straightforward matter of dot products to generate the chemical composition of the various MSW streams. These compositions are presented in Table 1.10. A “food only” stream is now included for the sake of comparison. The starkness of the difference between food waste on the one hand and food waste mixed with paper waste on the other hand is clear in this table. It is also notable that the subtraction of yard waste from the compostable stream raises the cellulose concentration of the resulting stream relative to the compostable stream. This is because yard waste has higher lignins content and lower cellulose content, on average, than the remainder of the compostable stream, as shown in Table 1.9. Table 1.11 is a similar table

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[8] Time constraints have unfortunately made it impossible to publish these results in Chapter 2.

Sub-stream	Share of MSW stream (wet %)					
	Data from E.P.A. study			Data from state studies		
	Unseparated	Compostable	Compostable, no yard waste	Unseparated	Compostable	Compostable, no yard waste
Grass	3.5	6.3		3.0	4.9	
Leaves	3.5	6.3		3.0	4.9	
Tree branch	7.3	13.0		3.4	5.6	
Food	17.7	31.6	42.4	13.6	22.4	26.5
Coated paper	0.9	1.6	2.2	2.2	3.6	4.3
Old newsprint	0.9	1.6	2.2	4.2	6.9	8.2
Old corrugated containers	5.7	10.2	13.7	9.3	15.3	18.1
Office and other paper	16.5	29.5	39.6	22.0	36.2	42.9
Non-compostable	44.0			39.3		

Table 1.7: Macro composition of municipal solid waste streams in the United States. “Unseparated” column is as reported in a meta-analysis of E.P.A. and state studies conducted by Staley and Barlaz (2009). Other columns were derived from these values. The “Compostable, no yard waste” stream is a subset of the “Compostable” stream, which is in turn a subset of the “Unseparated” stream. The E.P.A. study was conducted in 2007. State studies were conducted between 1998 and 2007, inclusive, and relied on 150 to 1,185 samples per study of at least 90.7 kg per sample. All figures exclude materials diverted to recycling but include materials later diverted to waste-to-energy plants. Columns may not add up to 100% because of rounding errors.

Sub-stream	Composition (dry wt %)			Methane generation
	Cellulose	Hemicellulose	Lignin	(mL g^{-1}, dry basis)
Grass	26.1	12.5	25.0	136
Leaves	15.3	10.5	43.8	30.6
Tree branch	35.4	18.4	32.6	62.6
Food	55.4	7.2	11.4	300.7
Coated paper	42.3	9.4	15.0	84.4
Old newsprint	48.5	9.0	23.9	74.3
Old corrugated containers	57.3	9.9	20.8	152.3
Office and other paper	87.4	8.4	2.3	217.3

Table 1.8: Chemical composition of municipal solid waste sub-streams in the United States (dry basis). Data are from Eleazer et al. (1997), who collected and experimentally analyzed material from local waste processing facilities and residences. Methane generation was analyzed over a period sufficient for decomposition to complete, up to 700 days in the case of office paper. Results are averaged for grass, where two observations were reported.

Sub-stream	Moisture %	Composition (wet wt %)			Methane generation
		Cellulose	Hemicellulose	Lignin	(mL g^{-1}, wet basis)
Grass	60.0	10.4	5.0	10.0	54.4
Leaves	60.0	6.1	4.2	17.5	12.2
Tree branch	20.0	28.3	14.7	26.1	50.1
Food	70.0	16.6	2.2	3.4	90.2
Coated paper	6.0	39.8	8.8	14.1	79.3
Old newsprint	6.0	45.6	8.5	22.5	69.8
Old corrugated containers	6.0	53.9	9.3	19.6	143.2
Office and other paper	6.0	82.2	7.9	2.2	217.3

Table 1.9: Same as Table 1.8, except wet basis.

showing the net methane generation of these MSW streams.

The data in Table 1.10 allow us to answer the question of how much input of each chemical compound (cellulose, hemicellulose, and lignin) is associated with a given plant capacity as expressed in, say, wet tons per day of feedstock. Assuming conversion yields are in hand, it therefore becomes a straightforward matter to calculate the volume of output, which can be combined with price data to produce net revenue from sales. For the purposes of the current chapter, the conversion yields presented in Table 1.4 will be assumed.

1.6 Provisional Financial Model

Given the data provided in the foregoing sections, it is possible to construct a provisional financial model showing the internal rate of return (IRR) of an urban levulinic acid production facility given a range of assumptions regarding end-product price and total capital cost.

The first step in the construction of this model is the development of a set of fixed parameters not subject to sensitivity analysis. These parameters are displayed in Table 1.12. First, the plant size is fixed at 300 wet ton day^{-1}, or 109500 wet ton year^{-1}. This size corresponds to a relatively small but commercial facility taking in 25-35 garbage trucks per day of material. In fact, as will be shown in Chapter 2, the assumption that plant size is fixed irrespective of the MSW stream chosen as the feedstock is unrealistic. For a given size of boiler or a given energy input to the plant (either of which is a sound way of fixing the size of the plant), the feedstock capacity varies considerably with the feedstock's composition, particularly its moisture content. However, for the sake of simplicity it will be assumed in this chapter that the feedstock capacity of the plant is fixed irrespective of feedstock.

Second, the operating cost per unit of product is assumed to be constant. This, again, is unrealistic, as the amount of energy and labor required to produce a pound of product will depend on the make-up of the feedstock and on the precise scale of the plant. Once again, however, it is helpful for the sake of this provisional model to assume that variable costs per unit of product are constant. This assumption will also be relaxed in the next chapter.

The foregoing parameters allow us to construct the operating statement, displayed as Table 1.13, and the operating income statement, displayed as Table 1.15. Prices used for the "worst," "mid," and "best" cost cases are displayed in Table 1.14, drawn from discussions with colleagues and market research (Formic Acid Research 2008, Kimera 2010, Kimera 2011). The "mid" assumptions are believed to be the most reflective of current prices.

Based on the cash flows presented in the operating income statement, it is possible to compute an all-equity internal rate of return (IRR) assuming various

Compound	Share of MSW stream (wet %)					
	Data from E.P.A. study			Data from state studies		
	Compostable	Compostable, no yard waste	Food only	Compostable	Compostable, no yard waste	Food only
Cellulose	41.0	48.8	16.6	48.8	54.8	16.6
Hemicellulose	6.7	5.7	2.2	7.0	6.7	2.2
Lignins	9.4	5.8	3.4	9.4	7.8	3.4
Water	34.8	33.2	70.0	26.5	23.0	70.0
Other	8.0	6.6	7.8	8.4	7.7	7.8

Table 1.10: Chemical composition of various municipal solid waste streams in the United States, as computed from data in Tables 1.7 and 1.9.

Compound	Methane generation (mL g^{-1})			
	Data from E.P.A. study		Data from state studies	
	Dry basis	Wet basis	Dry basis	Wet basis
Compostable	178.5	116.4	176.8	130.0
Compostable, no yard waste	212.3	141.9	190.3	146.6
Food only	300.7	90.2	300.7	90.2

Table 1.11: Methane generation of various municipal solid waste streams in the United States, as computed from data in Tables 1.7, 1.8, and 1.9.

Parameter	Value	Source
Scale of plant	109500 tons year^{-1} (300 tons day^{-1})	Assumption
Operating cost including labor, overhead, energy inputs	\$300 ton^{-1} (\$0.15 pound^{-1})	Biofine DOE Report 2002 (\$0.10 pound^{-1}), inflated by CPI growth since 2002 (25%) and margin of error (20%)

Table 1.12: Assumptions used in provisional financial model.

Operating condition	Value (tons year^{-1})			Source
	Compostable	Compostable, no yard waste	Food waste	
Feedstock in	109500	109500	109500	Plant size parameter
Cellulose in	53384	60050	18198	Feedstock in, Table 1.10
Hemicellulose in	7617	7355	2365	Feedstock in, Table 1.10
Levulinic acid produced	24556	27623	8371	Cellulose in, conversion rate parameter
Ethanol reacted	9743	10959	3321	Levulinic acid produced, reaction stoichiometry
Ethyl levulinate produced	34300	38583	11692	Levulinic acid produced, ethanol produced
Formic acid produced	9609	10809	3275	Cellulose in, conversion rate parameter
Furfural produced	3046	2942	946	Hemicellulose in, conversion rate parameter

Table 1.13: Operating statement for a 300 ton day^{-1} facility based on chemical composition data presented in Table 1.10 and yields presented in Table 1.4.

	US$ ton^{-1}			US$ gallon^{-1}		
	Worst	Mid	Best	Worst	Mid	Best
Tipping fee	60.00	80.00	125.00	n/a	n/a	n/a
Formic acid	725.75	816.47	1360.78	3.69	4.16	6.93
Ethyl levulinate	600.00	1200.00	2400.00	2.54	5.09	10.17
Furfural	650.00	750.00	900.00	3.15	3.63	4.36
Ethanol (input)	911.23	708.63	607.49	3.00	2.33	2.00

Table 1.14: Price assumptions used in worst, mid, and best case. These values will be used to construct the operating income statement (Table 1.15). The “mid” assumptions are believed to reflect current market prices most accurately.

Financial flow	Million US$ year^{-1}								
	Compostable			Compostable, no yard waste			Food waste		
	Worst	Mid	Best	Worst	Mid	Best	Worst	Mid	Best
Sales (tipping fees)	6.57	8.76	13.69	6.57	8.76	13.69	6.57	8.76	13.69
Sales (ethyl levulinate)	20.58	41.16	82.32	23.15	46.30	92.60	7.02	14.03	28.06
Sales (formic acid)	6.97	7.85	13.08	7.84	8.83	14.71	2.38	2.67	4.46
Sales (furfural)	1.98	2.29	2.74	1.91	2.21	2.65	0.61	0.71	0.85
Net sales	36.1	60.05	111.83	39.48	66.09	123.64	16.58	26.18	47.06
Ethanol expense	8.88	6.90	5.92	9.99	7.77	6.66	3.03	2.35	2.02
Cost of goods sold	8.88	6.90	5.92	9.99	7.77	6.66	3.03	2.35	2.02
Total operating expenses	7.56	7.56	7.56	7.56	7.56	7.56	7.56	7.56	7.56
Net operating income	19.67	45.59	98.35	21.93	50.77	109.43	6.00	16.27	37.49
Net operating income w/ 10% margin of error	17.7	41.03	88.52	19.74	45.69	98.49	5.40	14.64	33.74

Table 1.15: Operating income statement. Figures are drawn from the operating statement (Table 1.13) and the price assumptions (Table 1.14).

capital expenditure amounts for plant construction. These IRR figures, which assume a two-year construction period and an eight-year usable life with no salvage value (very conservative assumptions), are displayed in Table 1.16.

The range of IRRs computed using the “worst” and “mid” price assumptions and the intermediate capital cost assumptions ($60 and $80 million) indicate an extremely healthy return by the standards of a mature industry yet may not provide sufficient return to compensate for the technology and integration risk of an early-stage venture. The typical hurdle rate for venture capital investments is 30-50%, rising slightly higher for energy investments due to illiquidity and size. Wüstenhagen and Teppo (2006) find that the lowest energy hurdle rate is approximately 50%. These facts suggest that government involvement may be called for to the extent that the positive externalities of urban levulinic acid production facilities justify public assumption of the relevant risks.

Capital expenditure (million US$ year^{-1})	Internal rate of return (%)								
	Compostable			Compostable, no yard waste			Food waste		
	Worst	Mid	Best	Worst	Mid	Best	Worst	Mid	Best
40	24.94	54.77	96.07	29.31	61.57	106.38	1.41	24.27	53.23
60	14.38	38.93	72.28	18.03	44.45	80.58	-5.66	13.83	37.68
80	7.93	29.49	58.27	11.16	34.28	65.39	-10.12	7.44	28.4
100	3.41	23.01	48.76	6.37	27.31	55.1	-13.33	2.96	22.02

Table 1.16: Internal rate of return (IRR) over a 10-year period assuming a two-year construction period and an eight-year usable life with no salvage value. Given the technology and integration risk inherent in a project of this scope, investors are likely to demand a 2-4 year payback. Wüstenhagen and Teppo (2006) find that the hurdle rate for energy projects rarely falls below 50%.

Chapter 2

Tools for Technical Modeling of Levulinic Acid Manufacture

This chapter presents a computational tool developed to model and symbolically solve the steady-state conditions of a recurrent chemical process. Precisely this sort of system is created by the hydrolysate recycle loop of the Biofine Process described in Chapter 1. The tool presented here could equally be applied to any system composed of stocks and flows, such as a standard systems-dynamics model or the circular production system of Sraffa or of Quesnay. In this thesis only the chemical-plant application is developed.

The tool is demonstrated on a pared-down version of the Biofine Process. The model output is shown to confirm the operating model presented in Chapter 1. It should be noted that a significantly more complex version of the model, based on proprietary rather than public data, is in use in a production setting.

2.1 Purpose of Domain-Specific Language and Solver

Data-flow programming environments such as spreadsheets are ideal tools for modeling simple systems with no feedback loops. In such a system, components affect each other noncyclically. In a spreadsheet representation of such a system, the final output cells of interest are computed from a chain of previous cells with the same noncyclical dependency structure.

Feedback loops throw the data-flow modeling approach for (as it were) a loop. If cell A depends on cell D (perhaps indirectly) and cell D depends on cell A (perhaps indirectly), then spreadsheets and other data-flow programming tools are no longer appropriate.

One method of modeling systems with feedback loops is to develop a system of interrelated differential equations. This is the approach taken by systems dynamics. A wide variety of simulation tools exist for this purpose. Using one of these tools or a general-purpose simulator such as Matlab or Mathematica, one can study the dynamic evolution of such a system based on some set of initial parameters. Under certain conditions, certain models will approach a steady state. This convergence to equilibrium will be observable in a trace of the simulation.

In the case of a chemicals plant, however, the goal of modeling is not to determine whether a set of initial parameters will generate a steady state, nor to experiment with out-of-equilibrium dynamics. The goal instead is to *assert* a steady state and a set of exogenous parameters (a chemical plant must operate in mass balance and with certain fixed pieces of equipment) and from this work backwards to the values of key endogenous variables. For instance, the steady state of interest might be one in which the plant uses 5000 kg of steam each hour, this being the maximum output of the boiler. An endogenous variable of interest might then be the volume of feedstock the plant can process. The goal, in other words, is not dynamic simulation, but static solution.

One method of "solution" is to use a dynamic simulation to perform trial and error until the desired steady-state is obtained. However, this method is not elegant, and as degrees of freedom grow it becomes impractical.

The alternative approach is to solve the relevant set of simultaneous equations. This set of equations will contain one equation for each equilibrium condition and each fixed parameter. Equilibrium conditions in this context are the equations describing the conservation of mass in the system. No mass can be created or destroyed in any stream or vessel (except, in an open system such as a chemicals plant, at specially designated "input" and "output" locations such as feedstock hoppers). Additional fixed parameters are used to describe such features as the reaction stoichiometry in reactors and the distribution of each vessel's contents to downstream streams.

It is impractical to write down and solve such a system of equations by hand. In even small process models the number of equations can quickly grow into the hundreds or thousands. Rather, an automated method must be devised to generate the necessary equations on the basis of a human-readable description of the system. Such a description will ideally be written using a language designed expressly for this purpose (a domain-specific language, or DSL) so as to make the process as painless for the modeler as possible. Then, the generated equations must be solved for the appropriate free parameters.

Solution algorithms for this final step can be numeric or symbolic. The vast majority of programming languages and mathematics toolkits employ numeric algorithms only. Some software, however, has the ability to solve systems of equations using a computer algebra system (CAS). This allows more variables to be introduced than the number of equations in the system, so that the solutions will be expressed in terms of the excess variables. This is an extraordinarily powerful approach because it opens the door to symbolic rather than Monte Carlo optimization.

2.2 Conceptual Design of Domain-Specific Language

Greatly simplified, a chemical plant consists of three basic building blocks: compounds, streams, and vessels. Compounds are the various kinds of "stuff" that can move through the system, for instance water and levulinic acid. Streams are physical linkages between vessels through which mixtures of compounds can flow. Vessels are the locations where streams come together and intermix their contents, and where reactions can take place. In real life, types of vessels might include tanks, reactors, centrifuges, settlers, heat exchangers, and so forth. However, for the purposes of our DSL, models will be characterized solely in terms of their functional properties. There are a total of v vessels, s streams, and c compounds.

We can characterize each instance of the building blocks in terms of a small set of properties. These properties are listed in Table 2.1 along with the dimensionality of each.

Compounds (c in total)

- Name (scalar)
- Molecular weight (scalar)

Streams (s in total)

- Name (scalar)
- Source (scalar)
- Destination (scalar)
- Distribution array (vector of length c)

Vessels (v in total)

- Name (scalar)
- Conversion matrix (matrix of size $c \times c$)
- Exogenous inflows (vector of length c)
- Exogenous outflows (vector of length c)

Table 2.1: Model building blocks.

The precise definition of the properties of vessels, streams, and compounds is described in the tool documentation. The following is an illustration of the characterization of a stream on the basis of its properties. Suppose one stream is known as stream "s5." This is its *name* property. This stream might carry material from vessel v2 (the *source*) to vessel v5 (the *destination*). The *distribution array* of this stream would refer to the fraction of effluent from vessel v2 that enters this stream (versus other streams whose source is also v2). This fraction is allowed to vary by compound, so that *distribution array* is of length c. For instance, if the relationship between stream s5 and vessel v2 is such that 50% of the water in vessel v2 enters stream s5, but no other products do, then the distribution array of stream s5 would consist of $c-1$ zeros and 1 one-half, with the one-half located in the vector element corresponding to water. (The sum of all distribution arrays associated with a given source vessel must be a vector of ones, in order to be consistent with mass balance.) Thus if exactly one other stream (say, "s9") had vessel v2 as a source, stream s9 would necessarily have a distribution array opposite that of stream s5, in this case consisting of $c-1$ ones and 1 one-half.

2.3 Domain-Specific Language Interface

As described above, three types of building block are sufficient to characterize a chemical plant model. For purposes of human input, these building blocks are most usefully arranged in arrays such that the rows of the arrays correspond to individual building block instances and the columns correspond to parameters. Because there are three types of building block, three arrays are used: a compounds array (dimensions: $c \times 2$), a streams array (dimensions: $s \times 4$), and a vessels array (dimensions: $v \times 4$).

These arrays and the syntax of their contents constitute the domain-specific language for specifying the design of the chemicals plant. The DSL has been implemented in Mathematica. The interpreter is a set of instructions that transforms a plant description in terms of these arrays into an internal description in terms of a list of steady-state equations. A user-interface is also provided by the system allowing the non-technical user to manipulate operating parameters and re-solve the system. The user-interface generates an interactive process flow diagram (PFD) that the user may use to "zoom in" on certain streams and vessels of interest.

An example screen capture of the streams array is shown in Figure 2.1. This screen capture displays only the first several streams out of several dozen. As is clear in the screen capture, there are four columns in the array, each corresponding to one of the four properties of the stream building-block. The first column is the stream name, the second column the stream source, the third column the stream destination, and the fourth column an abbreviated representation of the distribution array. Similar tabular entry formats are used for the vessels array and the compounds array.

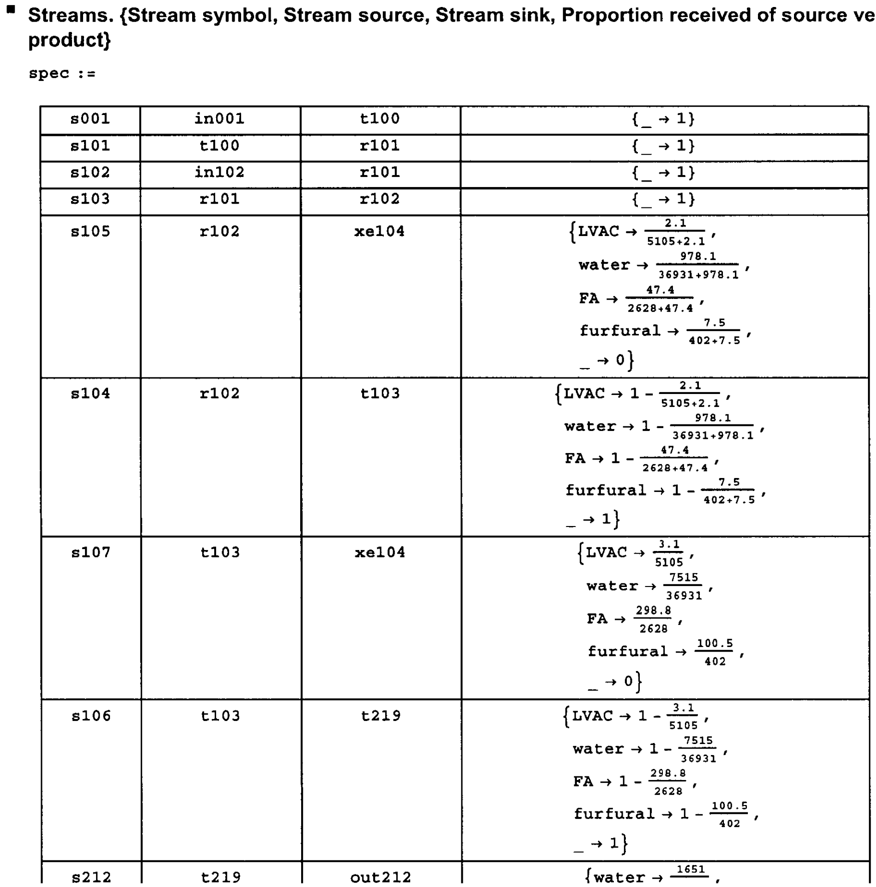
A micro-type listing of the generated equation system is shown in Figure 2.3. The full set of equations numbers over 500. Screen captures showing the graphical user interface and interactive process flow diagram are displayed in Figures 2.3 and 2.4. As mentioned above, the interface enables clicking on individual vessels and streams in the process flow diagram to receive a read-out of the operating conditions associated with the chosen element. The final screen capture shows a level of levulinic acid output commensurate with that of the model presented in Chapter 1, given commensurate levels of energy and feedstock inputs.

2.4 Solver and Symbolic Optimization

Generation of the relevant equilibrium equations within a symbolic mathematics platform such as Mathematica, as we are now doing, permits powerful and novel types of analysis. For instance, the relevant equations can be solved in more variables than there are equations. The result is that degrees of freedom are added to the system and the final outputs - say, product volume or net operating cash flow - are computed not as numbers but as expressions in terms of certain symbolic variables of interest. This approach makes it possible to conduct symbolic, rather than numeric, sensitivity analysis. Calculus can replace Monte Carlo analysis, and visualizations can be generated from analytic expressions rather than simulation data.

A specialized solver has been developed to process these underdetermined systems properly. It ensures that, of all the variables in the system, solutions are expressed in terms of the variables of interest and not others. In other words, the solver allows the user to designate certain variables as exogenous for the purpose of the solution algorithm. The solver also ensures that the user does not specify more degrees of freedom than he or she intends. If too many degrees of freedom are specified, a symbolic solution can become computationally infeasible.

The type of visual analysis that this approach makes possible is exhibited in Figures 2.5, 2.6, and 2.7. These figures show contour plots of gross revenue (tipping fees plus end-product sales, excluding operating costs) subject to changes in certain variables of interest, which are displayed on the axes. Variables of interest used to construct these plots include: solids loading, which is an operating parameter of the plant; boiler output, which is a variable in the long run because it is possible to perform upgrades on boiler machinery; and MSW percentage, which is the percent of the incoming feedstock composed of



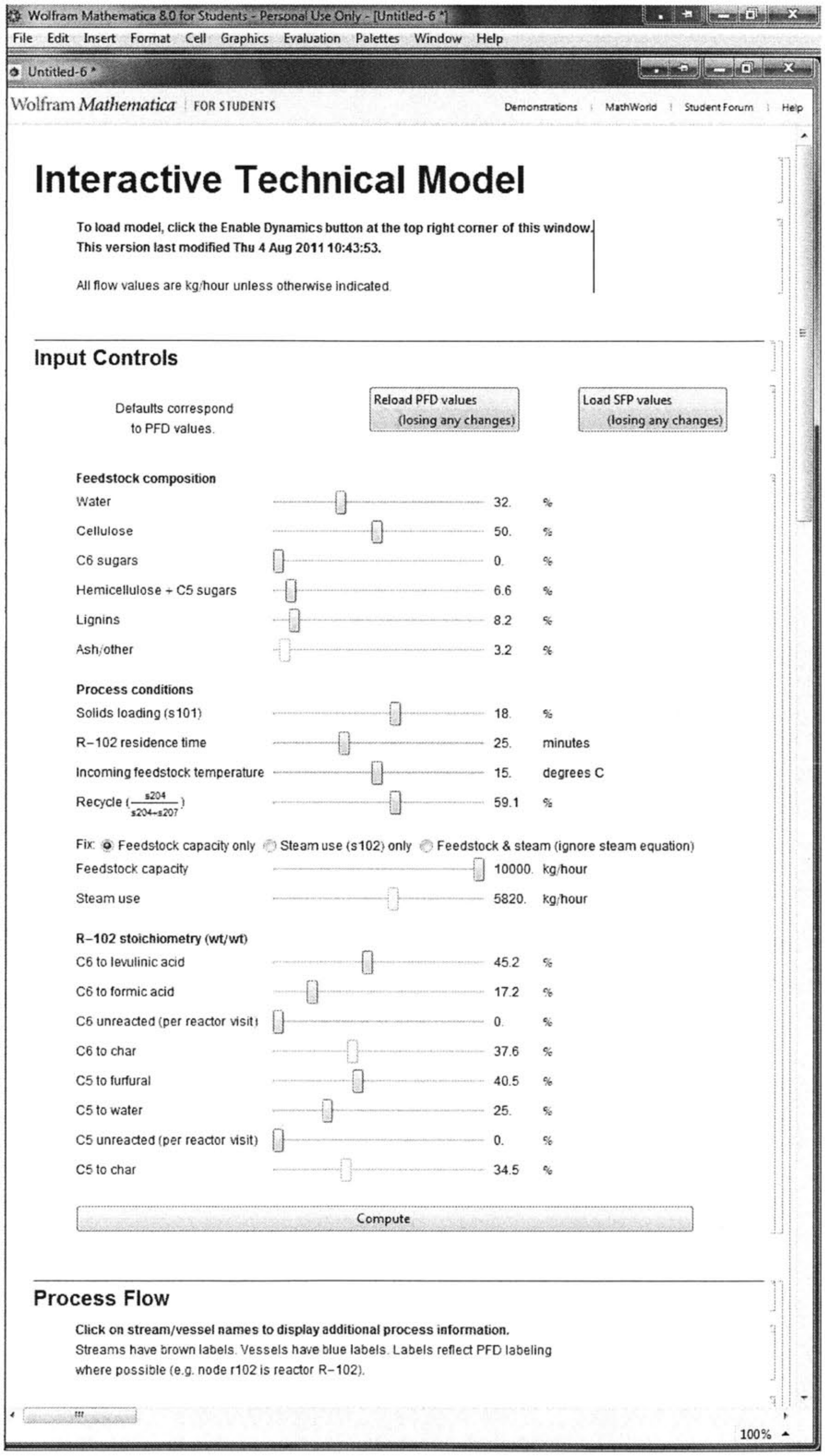
- **Streams. {Stream symbol, Stream source, Stream sink, Proportion received of source vessel product}**

spec :=

s001	in001	t100	$\{\_ \to 1\}$
s101	t100	r101	$\{\_ \to 1\}$
s102	in102	r101	$\{\_ \to 1\}$
s103	r101	r102	$\{\_ \to 1\}$
s105	r102	xe104	$\{\text{LVAC} \to \frac{2.1}{5105+2.1},$ $\text{water} \to \frac{978.1}{36931+978.1},$ $\text{FA} \to \frac{47.4}{2628+47.4},$ $\text{furfural} \to \frac{7.5}{402+7.5},$ $\_ \to 0\}$
s104	r102	t103	$\{\text{LVAC} \to 1-\frac{2.1}{5105+2.1},$ $\text{water} \to 1-\frac{978.1}{36931+978.1},$ $\text{FA} \to 1-\frac{47.4}{2628+47.4},$ $\text{furfural} \to 1-\frac{7.5}{402+7.5},$ $\_ \to 1\}$
s107	t103	xe104	$\{\text{LVAC} \to \frac{3.1}{5105},$ $\text{water} \to \frac{7515}{36931},$ $\text{FA} \to \frac{298.8}{2628},$ $\text{furfural} \to \frac{100.5}{402},$ $\_ \to 0\}$
s106	t103	t219	$\{\text{LVAC} \to 1-\frac{3.1}{5105},$ $\text{water} \to 1-\frac{7515}{36931},$ $\text{FA} \to 1-\frac{298.8}{2628},$ $\text{furfural} \to 1-\frac{100.5}{402},$ $\_ \to 1\}$
s212	t219	out212	$\{\text{water} \to \frac{1651}{\ },$

Figure 2.1: Tabular representation of stream data serving as input to the DSL interpreter. First column: stream name. Second column: stream source. Third column: stream destination. Fourth column: abbreviated distribution array. The underscore character in this abbreviated representation means “all compounds not otherwise specified.

Figure 2.2: Approximately 500 equations generated by DSL interpreter for a pared-down model of the Biofine process as reconstructed from public documents.



Interactive Technical Model

To load model, click the Enable Dynamics button at the top right corner of this window.
This version last modified Thu 4 Aug 2011 10:43:53.

All flow values are kg/hour unless otherwise indicated.

Input Controls

Defaults correspond
to PFD values.

Feedstock composition		
Water	32.	%
Cellulose	50.	%
C6 sugars	0.	%
Hemicellulose + C5 sugars	6.6	%
Lignins	8.2	%
Ash/other	3.2	%
Process conditions		
Solids loading (s101)	18.	%
R-102 residence time	25.	minutes
Incoming feedstock temperature	15.	degrees C
Recycle ($\frac{s204}{s204+s207}$)	59.1	%

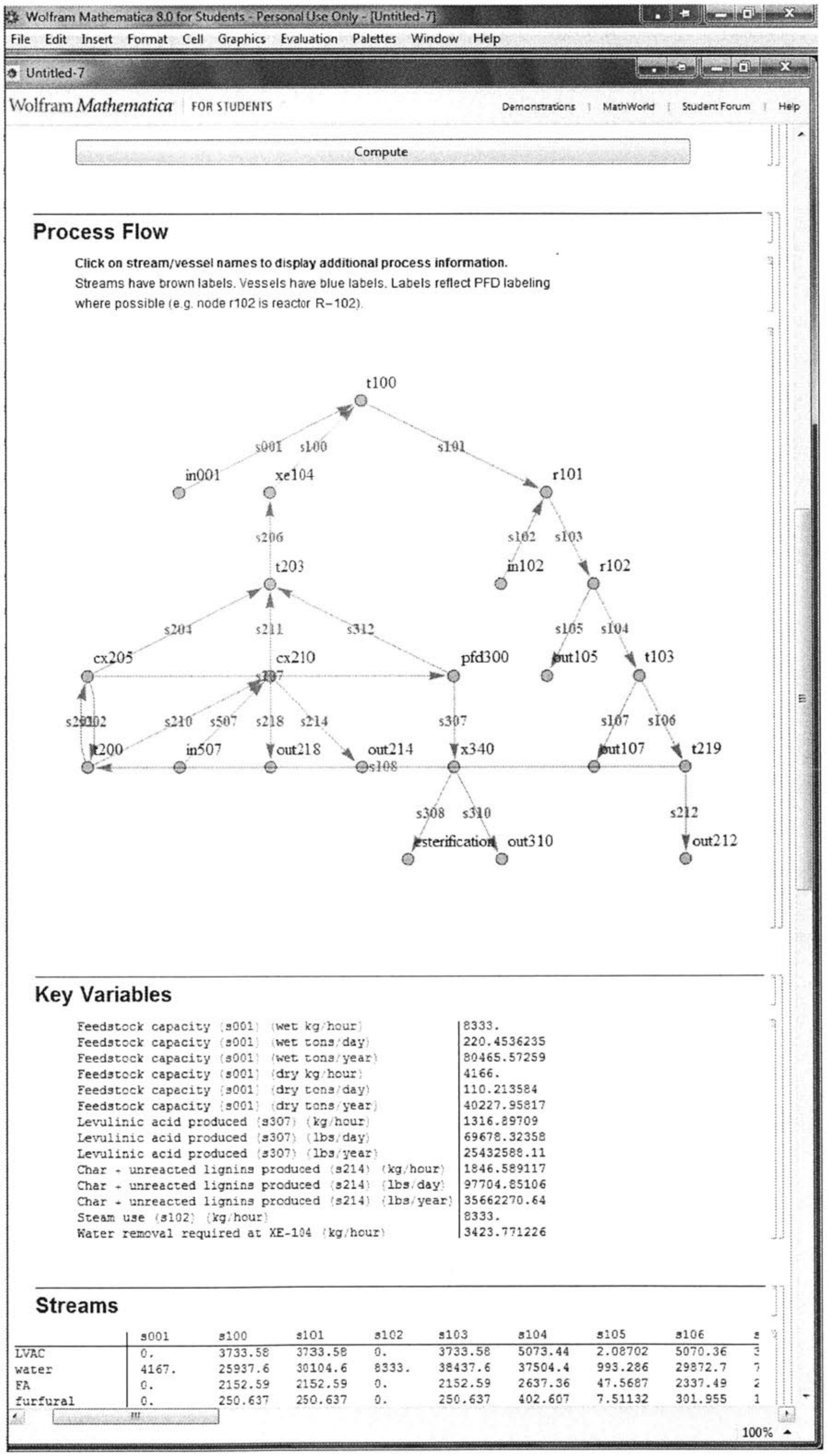
Fix: ● Feedstock capacity only ○ Steam use (s102) only ○ Feedstock & steam (ignore steam equation)

Feedstock capacity	10000.	kg/hour
Steam use	5820.	kg/hour
R-102 stoichiometry (wt/wt)		
C6 to levulinic acid	45.2	%
C6 to formic acid	17.2	%
C6 unreacted (per reactor visit)	0.	%
C6 to char	37.6	%
C5 to furfural	40.5	%
C5 to water	25.	%
C5 unreacted (per reactor visit)	0.	%
C5 to char	34.5	%

Process Flow

Click on stream/vessel names to display additional process information.
Streams have brown labels. Vessels have blue labels. Labels reflect PFD labeling where possible (e.g. node r102 is reactor R-102).

Figure 2.3: First screenshot of equilibrium process flow model, showing parameter sliders.



Process Flow

Click on stream/vessel names to display additional process information.

Streams have brown labels. Vessels have blue labels. Labels reflect PFD labeling where possible (e.g. node r102 is reactor R-102).

Key Variables

Feedstock capacity (s001) (wet kg/hour)	8333.
Feedstock capacity (s001) (wet tons/day)	220.4536235
Feedstock capacity (s001) (wet tons/year)	80465.57259
Feedstock capacity (s001) (dry kg/hour)	4166.
Feedstock capacity (s001) (dry tons/day)	110.213584
Feedstock capacity (s001) (dry tons/year)	40227.95817
Levulinic acid produced (s307) (kg/hour)	1316.89709
Levulinic acid produced (s307) (lbs/day)	69678.32358
Levulinic acid produced (s307) (lbs/year)	25432588.11
Char + unreacted lignins produced (s214) (kg/hour)	1846.589117
Char + unreacted lignins produced (s214) (lbs/day)	97704.85106
Char + unreacted lignins produced (s214) (lbs/year)	35662270.64
Steam use (s102) (kg/hour)	8333.
Water removal required at XE-104 (kg/hour)	3423.771226

Streams

	s001	s100	s101	s102	s103	s104	s105	s106
LVAC	0.	3733.58	3733.58	0.	3733.58	5073.44	2.08702	5070.36
water	4167.	25937.6	30104.6	8333.	38437.6	37504.4	993.286	29872.7
FA	0.	2152.59	2152.59	0.	2152.59	2637.36	47.5687	2337.49
furfural	0.	250.637	250.637	0.	250.637	402.607	7.51132	301.955

Figure 2.4: Second screenshot of equilibrium process flow model, showing interactive process flow diagram updated to reflect dynamic equilibrium process conditions.

the mixed compostable MSW stream (which includes paper) rather than food waste only.

Contour plots such as these allow for easy visualization of the bottom-line effect of changes in important operating conditions. One interesting application is the question addressed by Figures 2.6 and 2.7. These figures are distinguished by the level of tipping fees: Figure 2.6 has them set at \$70 ton^{-1}, Figure 2.7 at \$125 ton^{-1}. The slope of the contour lines indicates which feedstock stream is more valuable. Upward sloping lines indicate that pure food waste is more valuable, whereas downward sloping lines indicate that the mixed stream is more valuable. Thus, the change in slope as between the two figures shows that the optimal ratio of mixed MSW to pure food waste is a function of tipping fees, or, more precisely, the ratio of tipping fees to the applicable weighted average of end-product prices. As tipping fees rise from \$70 ton^{-1} to \$125 ton^{-1} (Figure 2.6 to Figure 2.7), the contour lines flatten, showing that the ratio of the value of general compostable waste to the value of pure food waste is decreasing. If tipping fees were to rise higher, the slope of the lines would turn positive.

This type of analysis is would be extraordinarily computationally taxing using Monte Carlo methods. This is because each instance of solving the system (a system of approximately 500 equations even in this pared-down model) takes approximately 15 seconds on a top-end personal computer. Thus, it would require a few hours of processor time to perform a high-resolution Monte Carlo analysis over the entire parameter space displayed in just, say, Figure 2.5. The symbolic solution also offers a degree of interpretability that cannot be obtained from simulation results.

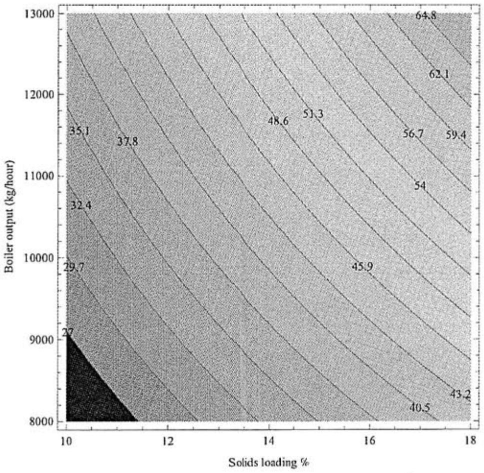


Figure 2.5: Gross revenue by solids loading and boiler output. Tipping fees are fixed at \$125 ton^{-1}.

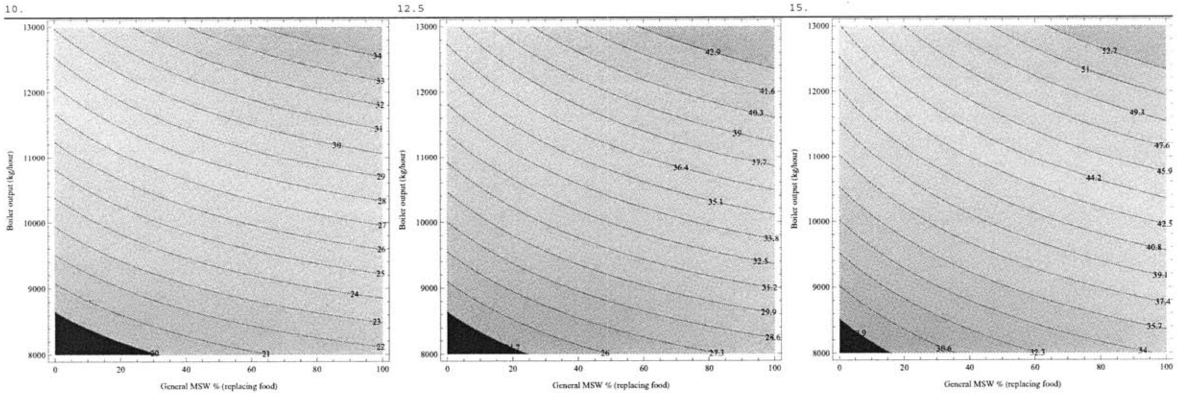


Figure 2.6: Gross revenue in $ millions, by general compostable MSW proportion and boiler output. Tipping fees are fixed at $70 ton^{-1}. Left plot: solids loading at 10%. Center plot: solids loading at 12.5%. Right plot: solids loading at 15%.

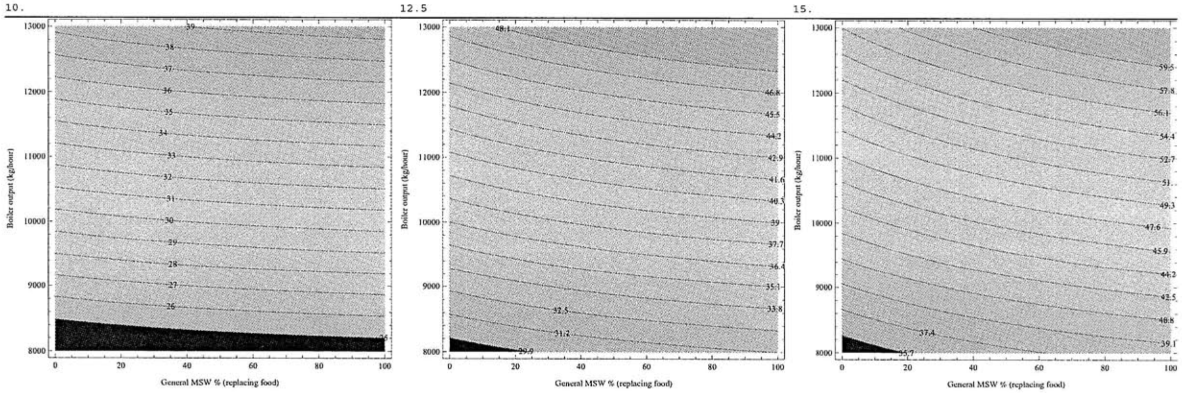


Figure 2.7: Gross revenue in $ millions, by general compostable MSW proportion and boiler output. Tipping fees are fixed at $125 ton^{-1}. Left plot: solids loading at 10%. Center plot: solids loading at 12.5%. Right plot: solids loading at 15%.

Chapter 3

Federal Policy for Urban Biorefineries

The previous two chapters have constituted an existence proof of the viability of a 300 ton day^{-1} commercial levulinic acid biorefinery operating on municipal waste streams. As has been shown, the expected returns of such a facility, while healthy, are not expected to justify private investment at this small commercial scale, at least not on the all-equity basis that typically characterizes risky projects.[1] The question thus arises: in what respect, if at all, ought the federal government to step in to improve the prospects of such a project?

In this chapter, the desirability of federal subsidy is addressed. The externalities and coordination problems associated with urban biorefinery projects are described and where possible quantified. Next, a descriptive account is provided of federal energy policy toward biomass and biorefineries. This account examines the statutes and regulations in force and concludes that federal biorefinery assistance remains oriented nearly exclusively toward rural and ethanol projects despite clear legislative efforts to diversify. On the basis of this evidence it is argued that financial support for urban facilities commensurate with their social benefits is unlikely to be forthcoming.[2] Reasons for this state of affairs are sought. It is concluded that four factors play a significant role. These are: (1) bureaucratic politics within and among the applicable federal agencies and executive departments; (2) bureaucratic inertia attributable to uneven public-private information asymmetries (i.e. ethanol's "track-record" advantage); (3) the policy of the Department of Energy to

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1. If debt finance could be obtained it would serve much the same purpose as government support. Indeed, this is the premise of a federal loan guarantee.

2. Tax credits, in contrast to up-front financial support, have been available for any cellulosic biorefinery, urban or rural, but the likely expiration of these credits at the end of 2012, and the perennial fickleness of tax credits in any case, would appear to do little to encourage private investment. This dynamic is discussed in detail later in the chapter.

micro-manage the funded development pathways ("picking winners"); and (4) the lobbying power of the rural and agriculture lobbies.

3.1 Desirability of Federal Subsidy for Urban Biorefineries

Standard welfare economics holds that resolution of coordination problems and internalization of externalities are the two main justifications available for government intervention in the private markets (Pigou, Coase).[3] In this section positive externalities associated with an urban biorefinery are examined in the categories of environmental remediation and energy security. The abatement of infrastructure degradation, another potential positive externality, is ignored, as it is assumed to be best addressed by marginal fee-collection or taxation of all road-users rather than waste haulers in particular. Discussion of externalities is followed by a discussion of the coordination problem facing regulators and fragmented sources of capital in the evaluation of early-stage, capital-intensive projects. Altogether, the picture that emerges is one of significant public benefit associated with even a relatively small, 300 ton day^{-1} urban biorefinery. Quantitative results suggest that at least $5 million per annum of public support is justified. More support may be warranted for technologies exhibiting a greater ratio of external benefit to privately appropriable gain.

3.1.1 Environmental Benefits

Environmental benefits from the displacement of landfills fall into three categories: (1) abatement of greenhouse gas emissions from hauling, notably emissions of carbon dioxide and nitrogen oxides; (2) abatement of methane emissions from the decomposition of waste; and (3) reduction of the risk of groundwater contamination due to leeching. For our purposes groundwater contamination will not be considered, as its site-specific character makes it difficult to quantify generally. Nor will we consider emissions of nitrogen oxides, as the level of these is also difficult to quantify, contingent as it is on combustion conditions and other factors not directly related to distance traveled. Ignoring these two potential sources of environmental damage will

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[3] Internalization of externalities encompasses the subsidy of public goods, as these are goods whose privately appropriable benefit is negligible compared to the positive externalities of their production. To be sure, heated debates exist over putative justifications besides these two, such as the enforcement of morality (George) and the stabilization of the economy or the currency (Friedman, Keynes, Pasinetti), but these need not detain us.

result in conservative final estimates of the environmental benefit associated with the technology.

Methods used for the calculation of hauling externalities are as follows. Emissions due to hauling depend on the distance to the applicable disposal site as well as the volume of waste hauled. The level of emissions abatement associated with the substitution of a 300 ton day^{-1} biorefinery for a landfill therefore depends on the difference in distances traveled. Table 3.1 calculates this difference in the context of an urban biorefinery located at the center the Northeast Corridor of the United States, roughly halfway between New York City and Philadelphia, such as in the city of Trenton, NJ. Travel distances are calculated taking the waste source to be New York City. The displaced landfill is taken to be located in central Pennsylvania or northern Virginia, a conservative assumption for New York City waste, which is increasingly hauled as far as Ohio (New York City Comptroller 2002). Reasonable values are assumed for carbon dioxide emissions per mile traveled (assumed to be proportionate to fuel economy) and for truck capacity, based on EPA and industry data.

Methods used for the calculation of methane-related externalities follow a similar framework. Emissions due to decomposition depend on the volume of feedstock. Using data calculated in Chapter 1, it is possible to quantify on a weight/weight basis the methane generation of a unit of feedstock. This value is displayed in Table 3.2 for each of the familiar MSW streams. These values are used to calculate methane abated and the equivalence in carbon dioxide abated. As a greenhouse gas, methane is 72 times more potent than carbon dioxide on a weight basis over its lifetime of 20 years, after which time it decomposes principally to carbon dioxide. It is assumed that landfill gas is not captured. Currently only 558 of the approximately 2,400 operating or recently closed landfills in the United states capture a portion of their emitted methane, and this type of remediation remains voluntary and costly (EPA Landfill Methane Outreach Program 2011). It is assumed, importantly, that the biorefinery is carbon-neutral in its operation, in the sense that the petroleum displaced by its end-products has a higher carbon content than the fossil fuel required to run the plant. Based on the operating costs outlined in Chapter 1, which include energy costs, this assumption is realistic.

Abatement of emissions from hauling and from decomposition can both be expressed, for the sake of easy interpretation, in terms of the number of passenger vehicles removed from the road. This equivalence is presented in the final rows of Table 3.1 and Table 3.2. The tables show that carbon dioxide abatement from hauling is equivalent to the removal of approximately 1,000 cars, whereas methane abatement is equivalent to the removal of 83,000 to 131,000 cars, depending on the feedstock used. Decomposition-related externalities thus outpace those due to hauling by a factor of 100. This is a remarkable finding, because the cost of waste hauling is single-handedly driving many municipalities to budgetary lamentation, quite irrespective of environmental costs (New York City Comptroller 2002). The combined external and private costs of landfill disposal are thus seen to be doubly enormous.

It would also be helpful for the sake of interpretation to be able to express abated emissions in terms of currency. Such an enterprise can be perilous on account of the necessary proliferation of assumptions, but we can proceed cautiously by following the approach of West et al. (2006), who perform the translation by estimating only the net present cost of premature methane-related mortality, mostly mediated by ozone exposure. In particular, West and colleagues do not attempt to assess the risk of catastrophic climate effects. West and colleagues estimate that the social value of one ton of methane abated is US$240 according to their metric. This value comports with similar studies considered by Pearce (2003). Using this value to monetize the results described earlier, we find that the social benefit of biorefining relative to landfilling is $1.5 to $2.5 million year^{-1}, depending on feedstock (Table 3.2). It should be noted again that this amount accounts for only those benefits directly related to human health. Benefits related to the avoidance of catastrophic climate change and its effects have been excluded.

3.1.2 Security Benefits

Part of the social benefit of an urban biorefinery is the displacement of petroleum products predominantly sourced from overseas. The overseas origin of petroleum contributes to a variety of direct and indirect security costs, including the incremental military costs of protecting shipping lanes, the reputational risks inherent in supporting extractive and often exploitative regimes, and the commercial risks of temporary supply disruptions.

Benefits from security enhancement are more difficult to quantify than benefits from environmental remediation because of problems of cost attribution. For instance, it would appear nearly impossible to estimate how much of the military's budget is attributable to the defense of shipping lanes. Yet a number of researchers have taken up this task and produced estimates, which must be taken with due caution, framed in terms of dollars of "security cost" per unit of oil or per unit of liquid fuel (gasoline, diesel, jet fuel, etc.). A selection of this research is displayed in a common unit measure on the left-hand side of Table 3.3.

These results can be combined with our previous results regarding production volumes to generate total security-related social savings associated with urban biorefining on a 300 ton day^{-1} scale. These are displayed on the right side of the table. The average is $0.9 to $2.6 million year^{-1}, depending on

			Value	Source
(1)	Feedstock in	(tons $year^{-1}$)	109500	Table 1.13
(2)	Truck trip equivalence	(trips $year^{-1}$)	7821	(1), Truck capacity: 14 tons
(3)	Distance to landfill (round-trip)	(miles)	600	Assumption
(4)	Distance to urban biorefinery (round-trip)	(miles)	140	Assumption
(5)	Travel savings	(million miles $year^{-1}$)	3.60	(2), (3), (4)
(6)	Typical CO_2 production for heavy diesel truck	(g $mile^{-1}$)	1479	EPA data
(7)		(ton $million^{-1}$ $mile^{-1}$)	1630	(6)
(8)	CO_2 abated	(tons $year^{-1}$)	5866	(5), (7)
(9)	Passenger vehicle equivalence abated	(# vehicles)	1025	(8), EPA data (passenger vehicle average: 5.725 tons CO_2 $year^{-1}$)

Table 3.1: Greenhouse gas abatement due to reduction in transportation of waste. The waste source is assumped to be New York City. Landfill location and biorefinery location are assumed to be central Pennsylvania and Trenton, NJ, respectively. Garbage truck fuel economy is assumed to be 6 miles $gallon^{-1}$. Garbage truck capacity is assumed to be 14 tons.

			Compostable	Compostable, no yard waste	Food only	Source
(1)	Landfill methane generation per unit feedstock	(mL g^{-1})	116	142	90	Table 1.11
(2)		(wt %)	7.8	9.5	6.0	(1)
(3)	Feedstock in	(tons $year^{-1}$)	109500	109500	109500	Table 1.13
(4)	Methane abated	(tons $year^{-1}$)	8511	10380	6599	(2), (3)
(5)	CO_2 equivalence abated	(tons $year^{-1}$)	612810	747330	475092	(4), EPA data (methane equivalency: 72 × CO_2 over 20 years)
(6)	Passenger vehicle equivalence abated	(# vehicles)	107041	130538	82986	(5), EPA data (passenger vehicle average: 5.725 tons CO_2 $year^{-1}$)
(7)	Present marginal value of health benefits (ignoring climate change)	\$US million $year^{-1}$	2.04	2.49	1.58	(6), West et al. 2006

Table 3.2: Greenhouse gas abatement due to reduction in methane emissions. Landfill gas is assumed uncaptured (capture is in effect at less than one quarter of U.S. landfills (EPA)). Methane generation figures are drawn from Table 1.11. Plant capacity is assumed constant at 300 tons day^{-1} (109500 tons $year^{-1}$) regardless of feedstock type.

feedstock.

As with our environmental findings, it is likely that the presented values represent conservative estimates. This is because the cost estimates in the literature (those reproduced on the left side of Table 3.3) are point-in-time estimates of direct and indirect security costs, but do not incorporate the risk of total exhaustion of reserves. Many consider the total exhaustion of economically recoverable reserves to be the most threatening aspect of “energy insecurity.” Should this depletion occur, energy prices for transportation applications would shift to reflect the supply cost of the next most abundant source of liquid fuel, no matter how high this price might be. Needless to say, our estimate of security benefits would be larger if the risk-discounted cost of such an event were included.

3.1.3 Resolution of Coordination Problems

A third justification for federal financial support is its role as a device to coordinate regulatory bureaucracies and private investors around particular projects. Regulators and investors face cognitive limitations and severe uncertainty as to which among many prospective technologies is worth regulatory attention and private due diligence (see, e.g., Heller 2008). A regulator has little interest in conducting approval and endorsement of a project that will not see the light of day because of funding limitations. Likewise, private investors have little interest in allocating due-diligence attention or capital to a project that is unlikely to meet regulatory approval or enjoy sufficient funding from other investors. This coordination problem can contribute, together with unrealized economies of scale, to the “valley of death” that is reputed to face high-capital cost, high-risk ventures.

A credible coordination device can partially ameliorate coordination gridlock insofar as it focuses the attention of all relevant parties on a single project at once. The coordination signal ought to be contingent on project merit lest market participants disregard it, but in principal no financial assistance need be involved (although this is likely to improve the signal’s visibility and credibility). The role of coordination signals can be seen in federal agencies’ practice of announcing their grant recipients in celebratory fashion, with press releases, conference calls, and award galas, rather than in private. If coordination were perfect, it would in principle make no difference whether these public steps were taken; but in fact they do draw additional attention to winning projects and thereby attract private due diligence in a crowded, uncertain, and cognitively limited marketplace and regulatory environment.

It is not impossible to conceive of a long-term experiment that a federal agency could construct to quantify the role of its endorsements as coordination

Social cost of fossil fuel use (nominal US$, unadjusted, gallon^{-1})	Source	Biorefinery social savings (million US$ year^{-1})		
		Compostable	Compostable, no yard waste	Food only
1.32	Copulos 2003	6.2	7.4	2.5
0.14	Parry and Darmstadter 2003	0.7	0.8	0.3
0.14	NRC 2002	0.7	0.8	0.3
0.29	Leiby et al. 1997	1.3	1.6	0.5
0.40	Ketcham and Komanoff 1992	1.9	2.2	0.8

Table 3.3: Left: Security cost associated with foreign petroleum use, per gallon of liquid fuel (gasoline, diesel, jet) consumed regardless of geographic source. Note that historical values have not been deflated. Right: Social savings associated with construction of a 300 ton day^{-1} urban biorefinery at production levels displayed in Table 1.13. Replacement of petroleum-derived fuels is computed by energy equivalence. Ethyl levulinate is 31% less energy dense than ultra-low sulfur diesel on a volume basis (Christensen 2011).

devices, but no attempt to do so will be made here. This benefit is naturally left qualitative.

3.1.4 Summary of Social Benefits

Summing the quantifiable costs calculated above, we can now estimate conservatively that the annual external benefit of the technology studied in this thesis to be \$2.4 million to \$5.1 million year^{-1}. Within this range, the precise realized value will depend on operating conditions. It can be assumed that a rational plant operator will choose the feedstock that maximizes private gain (maximum cellulose throughput), which in our case is also the feedstock that maximizes social gain.

Therefore, the policy stance most commensurate with the realizable social benefit of a 300 ton day^{-1} urban biorefinery is some form of subsidy of at least \$5.1 million per annum during the plant's operating life (or the net-present-value equivalent at the time of construction). This amount would have to be reevaluated at different plant scales. It is assumed that the merit review process conducted by the DOE would ensure that subsidy would be bestowed only on projects with social benefits at least as great as those presented here.

A second question is whether this level of subsidy, which is based on consideration of external benefits, would be sufficient to raise the return on equity of the levulinic acid project of Chapters 1 and 2 above the relevant hurdle. The answer is that it is probably is. Table 3.4 displays new IRRs calculated using the subsidized cash flows. As a comparison to Table 1.16 shows, these IRRs are in general 5 to 10 percentage points higher. At lower end-product prices the gains are larger; at higher end-product prices the gains are smaller. A 5 to 10 percentage point increase would be sufficient in many of the considered cases to cross the applicable hurdle rate of 50%, although this depends on the precise relationships between end-product prices, tipping fees, and capital costs. Considerations such as coordination problems, the "valley of death," and catastrophic climate change that were excluded from previous analysis might play a role here by tipping the scale in favor of larger subsidy as required.

3.2 Federal Policy for Biorefinery Assistance

We have now established that federal support of urban biorefineries is warranted on welfare grounds and that at least once type of urban biorefinery is economically viable if subsidized at, or even below, the socially optimal level. It is now possible to turn to the question of whether this level of subsidy is likely to be forthcoming given existing institutions and policies.

Capital expenditure (million US\$ year^{-1})	Internal rate of return (%)								
	Compostable			Compostable, no yard waste			Food waste		
	Worst	Mid	Best	Worst	Mid	Best	Worst	Mid	Best
40	33.87	60.88	100.4	37.66	67.28	110.43	15.57	33.31	59.44
60	21.81	43.89	75.77	24.94	49.07	83.84	6.5	21.34	42.72
80	14.51	33.79	61.26	17.26	38.28	68.18	0.89	14.1	32.78
100	9.43	26.88	51.43	11.94	30.91	57.58	-3.08	9.05	25.97

Table 3.4: Subsidized internal rate of return (IRR) over a 10-year period assuming a two-year construction period and an eight-year usable life with no salvage value. Compare with table 1.16.

The federal government has been extraordinarily active in its support of biofuels. Indeed, U.S. ethanol subsidies bear significant notoriety for their scale and scope. Twelve different pieces of legislation have been involved in ethanol subsidy at the federal level. Many states have their own additional complexes of fuel standards and producer incentives supporting corn ethanol (Tyner 2008, Tyner 2007). Over the past decade, however, a variegated landscape has arisen wherein not just corn ethanol but a wide range of other biorefinery projects have been supported to various degrees, by various agencies, and using various policy instruments. By one count, there have been a total of 22 separate federal programs - current, expired, or pending as of 2011 - that provide direct or indirect subsidies to non-starch biofuels (Yacobucci 2011). This diversification is largely a result of the criticism starch ethanol has received for its effect on food prices and its net energy balance.

In order to understand how this broad constellation of federal policies might interplay with the development of urban biorefineries, this section makes an effort to describe the landscape of federal programs on both a detailed and a holistic level, which is to say on the basis of individual provisions as well as combined effect.

It is helpful first to develop one distinction that will be of service going forward. Federal assistance programs can be hewn into the categories of "ambient" and "up-front." Ambient programs are those that provide benefits during the operational lifetime of a project. In other words, funds are received at the same time as commercial revenue. Tax credits are an example of an ambient program. Another example is the EPA's Renewable Fuel Standard (RFS), which functions as a price support.[4] Up-front programs, by contrast, provide initial funding for construction in the form of grants or loan guarantees. The DOE's biorefinery grant programs and the USDA's loan guarantee programs are examples.

Up-front programs have two features that make them more attractive than ambient programs from the viewpoint of recipients. First, once awarded, there is no risk of repeal, which can be catastrophic for a project premised on them. The

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4. Note that the effect of the RFS is not considered in any depth for the purposes of this largely backward-looking study. The RFS has elaborated the tax credit model in ways that have the potential to ameliorate some of its drawbacks. For instance, the RFS is intended to lock in price supports for many years via mandated volumes and tradeable credits ("RINs"). However, the unpredictability and politicization of the EPA's "mandates," which have been lowered for each of the last three years, are discouraging and suggest that the RFS will fare no better than production tax credits at inspiring business confidence (see, e.g., Reuters 2011).

uncertainty associated with potential repeal (or failure to renew) severely diminishes the effectiveness of ambient programs. Another advantage of up-front programs from the perspective of recipients is that funds are not tied directly to project success. While it may appear commonsensical from a policy perspective to condition funds on success, the reason for federal support is to absorb downside risk. Up-front funds do this by providing funds at the time of construction. Funds are typically spent before any project failure can materialize. Ambient programs, by contrast, reward fuel produced on a dollars-per-gallon basis (whether this be through a tax credit or the price support implicit in the Renewable Fuel Standard). The effect is to magnify up-side risk while doing nothing to dampen down-side risk. From the perspective of investors, the reward profile created by the up-front approach is significantly more attractive. Catastrophic down-side technology risk is a main concern of biofuels projects. Market risk is significantly less important, for fuels are commodity products with predictable markets.

3.2.1 Global Statutory Analysis

What becomes clear upon examination of the menagerie of federal programs is that nearly all federal biorefinery assistance programs remain restricted to very specific categories of conversion technology, feedstock, or location as a matter either of statute or of bureaucratic practice. The only programs not restricted in this way are those that fall into the category of ambient programs, such as tax credits, which as discussed a moment ago do too little to the typical project's risk profile to affect the chances of private investment. In fact, they add uncertainty by virtue of the possibility of repeal. As a consequence, biorefinery programs outside the ambit of the traditional rural ethanol platform, while not excluded formally, are excluded in practice.

The statutory analysis begins with the data presented in Tables 3.5 and 3.6. Table 3.5 outlines the important characteristics of each federal program operating in the area of biorefinery support. Table 3.6 evaluates each program in terms of its ability to contemplate an urban biorefinery. The aim is to outline the ways in which each program's statutory or *de facto* limitations may exclude an urban biorefinery project operating on municipal waste feedstock.

Before moving on, the columns of Table 3.5 call for some explanation. The "time-course" column displays whether a given program provides ambient or up-front incentives. This has already been discussed. The "scale" column describes the size of the program in comparable terms. For up-front programs such as grants and loan guarantees, scale refers to the total amount of funds available during the most recent obligated fiscal year. This amount bears no necessary relationship to the annual amount allocated to the program over its

	Drafted	(Amended) [Extended]	Expiry	Statute	Scale	Time-course		Type				Agency/ department			
						Up-front	Ambient	Volume floor	Tax credit	Grant	Loan g'tee	DOE	USDA	IRS	EPA
Volumetric Ethanol Tax Credit	2004	(2008) (2008) [2010]	2011	PL 108-357	\$0.45 gallon^{-1}		X		X					X	
Small Ethanol Producer Tax Credit	1990	[2004] (2005) (2008) [2010]	2011	PL 101-508	\$0.10 gallon^{-1}		X		X					X	
Biodiesel Tax Credit	2004	[2005] (2008) [2010]	2011	PL 108-357	\$0.50-\$1.00 gallon^{-1}		X		X					X	
Small Agri-Biodiesel Producer Credit	2005	(2008) [2010]	2011	PL 109-58	\$0.15 gallon^{-1}		X		X					X	
Renewable Diesel Tax Credit	2005	(2008) [2010]	2011	PL 109-58	\$1.00 gallon^{-1}		X		X					X	
Credit for Production of Cellulosic Biofuel	2009		2012	PL 110-246	\$1.01 gallon^{-1}		X		X					X	
Special Depreciation Allowance for Cellulosic Biofuels	2006	(2008)	2012	PL 109-432/ PL 110-343	N/A	X			X					X	
USDA Biorefinery 9001 Assistance	2008		2012	PL 110-246	\$691 million (loans) year^{-1}	X					X		X		
Biomass Research and Development	2000	[2002] [2005] (2008)	2015	PL 106-224	\$28 million (grants) year^{-1}	X				X		X	X		
Biorefinery Grants	2001		2012	Various	\$220 million (grants) year^{-1}	X				X		X			
DOE Loan Guarantee Program	2005		None	PL 109-58	\$10 billion (loans) year^{-1}	X						X			
Renewable Fuel Standard	2005	(2007)	None	PL 109-58	N/A		X	X							X

Table 3.5: Active federal biorefinery assistance programs. Some data adapted from Yacobucci 2011.

	Scale	Time-course		Statutory limitations			De facto limitations
		Up-front	Ambient	Chemical	Feedstock	Region	
Volumetric Ethanol Tax Credit	\$0.45 gallon^{-1}		X	Ethanol			
Small Ethanol Producer Credit	\$0.10 gallon^{-1}		X	Ethanol			
Biodiesel Tax Credit	\$0.50-\$1.00 gallon^{-1}		X	FAME (\$1 gallon^{-1} and \$0.50 gallon^{-1})	Agricultural (\$1 gallon^{-1})		
Small Agri-Biodiesel Producer Credit	\$0.15 gallon^{-1}		X	FAME	Agricultural		
Renewable Diesel Tax Credit	\$1.00 gallon^{-1}		X				
Credit for Production of Cellulosic Biofuel	\$1.01 gallon^{-1}		X				
Special Depreciation Allowance for Cellulosic Biofuels	N/A	X					
USDA Biorefinery 9001 Assistance	\$691 million (loans) year^{-1}	X				Rural	
Biomass Research and Development	\$28 million (grants) year^{-1}	X					R&D only; too small for demonstration and commercial projects
Biorefinery Grants	\$220 million (grants) year^{-1}	X					Rural; Sugar or gasification platform
DOE Loan Guarantee Program	\$10 billion (loans) year^{-1}						Generation and transmission; no biofuels
Renewable Fuel Standard	N/A		X				

Table 3.6: Restrictions on the applicability of federal assistance programs to an urban biorefinery project operating on waste feedstock and producing levulinic acid.

lifetime, nor to the average annual amount allocated (some programs receive wildly fluctuating allocations year-to-year); but it nevertheless provides a useful basis for comparison. For loan programs, the amount displayed is the annual loan amount to be underwritten under the program, not the expected value of losses and foregone interest on which a budgetary charge would be assessed. This measure of loan volume provides an intuitive apples-to-apples comparison with the grant programs. For the production tax credit programs, the amount listed is the rate of subsidy per unit produced.

3.2.2 Tax Credit Programs

The various producer tax credits deserve our attention as a barometer of legislative intent. This is because the Washington lawmakers who write tax credits into statute do so directly, without an intervening regulatory bureaucracy. The first thing that stands out in the legislative history is the decrease over time in the specificity of the programs. In the two decades after the enactment of the 1990 Small Ethanol Producer Tax Credit, for which only ethanol producers were eligible, a series of new programs was implemented. These new programs had the collective effect of opening biofuels tax credits to a broader range of biofuels producers. First admitted were fatty-acid methyl ester (FAME) biodiesel producers (2004), then all biodiesel producers (2005), and finally all cellulosic biofuels producers (2009).

This pattern is notable because it is a reflection of the overall evolution of federal policy with respect to biofuels. As new technology developed and the policy drawbacks of starch ethanol became apparent, it became incumbent upon Washington lawmakers and their staff to craft broader incentives. The amendment history of the Special Depreciation Allowance for Cellulosic Biofuels shows the same pattern. At its enactment in 2006, only enzymatic hydrolysis processes were permitted, but its amendment in 2008 opened the doors to all processes.

The pattern of change in the producer tax credit programs suggests that Washington lawmakers intend a catholic approach to biorefinery assistance. The newer, most inclusive tax credit programs are no less generous in terms of credit per gallon of fuel than their older, more restrictive brethren. In other words, the legislative establishment has gone to the pain of amendment to avoid picking winners in this sphere.

Producer tax credits also deserve our attention, however, as a model of uncertainty. As quintessential ambient programs, tax credits are subject to the risk of non-renewal and indeed repeal at any time. Thus any project whose economic viability depends on the future existence of tax credits must price political risk as well as technology and market risk into the cost of capital. It is difficult to imagine convincing investors to bet on this trifecta of risk for any real-world project. In principle the political risk of repeal could be hedged, but no markets are known to exist for trading in the relevant derivatives. The lack of stable incentives in this area has been roundly criticized by Kenkel and Holcomb (2009).

The picture that emerges of the federal tax credits in place is one of inclusiveness with respect to project types but irrelevance with respect to commercial impact. As we turn to other federal programs we should ask if a better approach is possible.

3.2.3 Grant and Loan Guarantee Programs

The Department of Energy's biorefinery grant program and the Department of Agriculture's loan guarantee program are the 800-pound gorillas, as it were, of federal biorefinery funding. In fiscal year 2010 alone, these two programs allocated nearly one billion dollars of funds on an up-front, competitive basis. Such awards are extremely attractive to prospective recipients because they are large, sometimes over $100 million, because they mitigate down-side risk by involving the government at the earliest stage, when equity is riskiest, and because they serve to coordinate private capital in service of new "rock star" projects.

For urban projects, however, the prospect of receiving either DOE or USDA funds is dim. By statutory mandate, no program enacted by the Farm Bill is permitted to allocate funds outside of rural areas; the USDA loan guarantee program is among these. Although the DOE grant program has no similar mandate, an investigation of the recipients of DOE funds reveals that, in practice, no DOE grant recipient at the demonstration- or commercial-scale has ever been located in an urban or suburban area. Table 3.7 displays a list of these projects along with various technical details and, importantly, the size of the municipality where the facility is located.

It is impossible to know the candidate pool from which these DOE awardees were drawn. While many biorefinery projects do rely on agricultural feeds and gravitate to rural areas accordingly, there are a number of biorefinery technologies suited to urban areas. These would collectively be expected to have some representation among the awardees. Biodiesel and renewable diesel facilities, for instance, can re-purpose waste oils that are concentrated in cities. Acid hydrolysis and gasification processes can convert municipal wastes. In fact, two past DOE awardees, Enerkem and INEOS, are in the business of processing relatively dry municipal wastes using proprietary gasification technologies. This is an approach perfectly suited to certain urban wastes. Moreover, tipping fees for this feedstock would be twice as high in urban areas as in the rural Mississippi and Florida locations where these projects were

Name	Location	Pop'n	Urban/suburban/ rural	Product	Conversion method	Type
Mascoma	Kinross, MI	5922	Rural	Ethanol	Fermentation	Commercial
BlueFire	Fulton, MS	3882	Rural	Ethanol	Fermentation	Commercial
Verenium	Jennings, LA	10968	Rural	Ethanol	Fermentation	Demonstration
Pacific Biogasol	Boardman, OR	3220	Rural	Ethanol	Fermentation	Demonstration
Lignol	Ferndale, WA	11415	Rural	Ethanol	Fermentation	Demonstration
RangeFuels	Soperton, GA	2824	Rural	Ethanol	Gasification	Commercial
Enerkem	Pontotoc, MS	5253	Rural	Ethanol	Gasification	Demonstration
POET	Emmetsburg, IA	3958	Rural	Ethanol	Other	Commercial
Abengoa	Hugoton, KS	3904	Rural	Ethanol	Other	Commercial
INEOS	Vero Beach, FL	16939	Rural	Ethanol	Other	Demonstration
Flambeau	Park Falls, WI	2793	Rural	Hydrocarbons	Gasification	Commercial
New Page	Wis. Rapids, WI	18435	Rural	Hydrocarbons	Gasification	Demonstration
Sapphire	Columbus, NM	1765	Rural	Hydrocarbons	Other	Demonstration
RSA	Old Town, ME	8130	Rural	Butanol	Fermentation	Demonstration
Myriant	Lake Providence, LA	5104	Rural	Chemicals	Fermentation	Demonstration

Table 3.7: Locations of commercial- and demonstration-scale facilities funded through the DOE biorefinery grant program.

ultimately located. These facts suggest that the firms had federal assistance in mind when choosing their site.

One other piece of evidence supports this interpretation. First, Enerkem and INEOS were recipients of *both* DOE and USDA funds. Receiving funds from both sources is a common pattern. In fact, award announcements are often jointly emceed by Secretary of Energy Chu and Secretary of Agriculture Vilsack. This degree of coordination on such a wide range of projects suggests that the availability of USDA "leverage" affects DOE's own internal deliberations about whether to fund a project. If this political-bureaucratic dynamic is indeed in place, the statutory rural mandate of the USDA is likely to spill over into the DOE's own funding pattern.

3.3 Conclusion and Future Work

As has been shown in this final chapter, there are two major categories of federal biorefinery assistance in force. The first category is the "ambient" programs, which includes the Internal Revenue Service's producer tax credits and the EPA's Renewable Fuel Standard. These programs effectively offer their subsidy at the same time as revenues, that is, after a project has successfully come on-line, if it ever comes on-line. Such programs do not affect down-side risk. Grant and loan programs, by contrast, are "up-front" programs in the sense that funds are received prior to construction. An advantage of up-front programs from the perspective of award recipients is the government's assumption of a significant portion of the project's down-side risk. Another advantage is the confidence these one-shot games engender relative to repealable tax credit programs and lowerable fuel standards, both of which are ultimately subject to the whims of Washington ("what the government gives, the government can take away").

This chapter has also described the various social benefits of an urban biorefinery based on the technology outlined in Chapters 1 and 2. The quantifiable portion of these benefits amounts to approximately $5 million year^{-1}. This level of subsidy is small by comparison to the $50 million and $100 million grants and loan guarantees that the Department of Energy and Department of Agriculture routinely award through their flagship programs. The $5 million year^{-1} level of support is not only commensurate with social benefit, but it also offers a reasonable chance of raising the the IRR of an urban biorefinery such as the one considered in this thesis above the necessary hurdle for private funding. Despite these facts, an analysis of the statutory basis, award record, and bureaucratic politics of the various award programs suggests that funding for an urban project of this sort would not be forthcoming if existing statutes and administrative norms remained in place.

The results of this study suggest multiple areas for further study. One area for further study is the relationship between the Department of Energy and Department of Agriculture. It was suggested above that norms and constraints may bleed from the programs of one department into those of the other insofar as funding decisions are made in concert. Case studies or statistical analysis of this effect would be useful for addressing this question more comprehensively.

Another key area for future research is the determinants of administrative decisions about the Renewable Fuel Standard and similar programs. The RFS, like producer tax credits, is necessarily technology-neutral and region-neutral in its administration, thus avoiding problems of administrative neutrality in grant administration. As mentioned earlier, however, the annual standard promulgated under this program is subject to review and decrease by the EPA. In fact, the standard for cellulosic biofuels has been lowered or eliminated in each of the last three years. A sustained lack of commitment mechanisms surrounding these decisions may cause the program to lose a portion of its incentive effect. Therefore, an analysis of the existing decision-making procedures within this program would be helpful in understanding how the credibility of technology-neutral, location-neutral federal funding programs might be enhanced.

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