Environmental Policy: A New Direction in Ethanol Production

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For over twenty years Dartmouth Professor Lee Rybeck Lynd (2007) has led an interdisciplinary research group in biochemical engineering and applied biology relevant to processing cellulosic biomass, winning international recognition as a leader in this field. He recently made the following statement: "Most policy makers I know spend their time predicting how the world is going to respond. They've got a model of the world and the way they evaluate policies is- 'If we do this, this is what we think the world will do.' I don't have a lot of expertise in that. I'm a technical guy: 'Here's what's possible.' And I have found in every policy exercise I've been a part of, there's been a dearth of understanding as to what's possible." He recently testified before Congress that biomass could help reduce the nation's dependence on foreign oil, curb emissions of carbon dioxide, and strengthen America's farm economy. He stated, "Plant biomass is the only foreseeable sustainable source of organic fuels, chemicals, and materials." They have the greatest potential for energy production.

I admit to having less knowledge than Lynd about policy making. As I study the future of energy I find myself in agreement with his statements. It has become clear that significant information gaps exist between social scientists and politicians recommending policy and lab rats like myself. As a plant biomass researcher I will try to partially reduce this information gap, particularly for biomass and ethanol energy generation as I go through one of many typical experiments. To accomplish this I will first review the nature of the growing world energy crisis, and then briefly analyze several often-mentioned alternatives for providing future energy. Any national or international energy policy would have to include each of these alternative solutions to some extent. Finally, I will summarize a recent study analyzing the use of leaves in ethanol production. First, what is the problem? Despite recent declines in petroleum prices, market forces will eventually continue to push prices up. Gasoline reaching over four dollars a gallon a few months back helped to remind us that we have a energy problem, although world economic problems have temporarily cut the price by about a third. If possible output from existing oil wells hasn't already peaked, it is likely to happen soon. Thomas L. Friedman (2008) projected that oil demand will grow from the present 86 million gallons a day to 116 by 2030. About two-fifths of this growth will be in China and India. Unlike Japan, Europe, and other nations, our country did not learn from the 1973-74 oil embargo. For example, Friedman told how France now uses nuclear energy for 78 percent of its electrical generation. Brazil developed a national policy that emphasized ethanol production from sugar cane and new oil exploration. It has become an oil exporter rather than an importer. Meanwhile, this country maintained a policy of encouraging construction of nothing-down, low-interest McMansions in distant suburbs, with three or more garages for trucks and large cars for lengthy daily commutes. It will take decades to move towards a sensible world with higher-density housing, mass transit, and efficient vehicles. Policies and programs that might result in a sustainable high standard of living are needed, and soon.

The problem of future alternative fuel and energy generation is complex. In addition to replacing dirty fossil fuels, there are related challenges that need to be considered when searching for solutions. First, should this country attempt to become energy self-sufficient? Mortimer Zuckerman (2008) discusses this problem reporting that this country produces only about a third of the oil its burns every day. He argues that it is imperative that our economy and way of life not be at the mercy of petroleum producing nations that can be unfriendly. *New Scientist* (Summer, 2008) argues that carbon emissions leading to global warming must be a consideration in the rush to identify new sources of energy. It can be argued that continued warming potentially is an equally serious problem. John Carey (2008) suggests that higher prices might be the best way to gain more energy. Another related argument involves generational justice. How much of the world's fossil fuel energy accumulated over millions of years should be used by this generation? What should be retained for generations to come? Last summer a day rarely passed without articles such as Robert Samuelson's (2008) explaining how high petroleum prices for transportation also result in higher prices for corn and commodities traditionally used for human food. *Newsweek'* (2008) predicts possible shortages of winter heating fuels, also raising living costs. Steve Levine (2008) tells how many accept the argument that the wars in Iraq and Georgia were the consequence of major world powers trying to maintain access to needed petroleum and energy access and distribution. The energy problem and its consequences are extensive. This paper will focus on the initial problem, finding possible prompt solutions to the current energy crisis but will relate back to some of these implications in the process.

Next, there are numerous proposed solutions for meeting this country's energy needs. Each seems to have potential advantages, but clearly no one single answer or solution alone solves the energy problem. "Conservation" is often mentioned as part of the eventual solution, but it has limitations. Can people be persuaded to substantially change life styles? We all want comfortable temperature in our homes, and we will be stuck with the current fleet of gas-guzzling vehicles for at least a decade. People have recently cut back a bit on driving, but this may change as drivers get used to higher prices or if gasoline prices drop even more. Conservation is a popular alternative but can only be a limited part of a long-term solution.

A number of alternatives for increased use of fossil fuels have been suggested. For several months, television, radio, and news publications have flooded this country with private advertisements telling us that as a nation we must produce more energy. Most ads related to drilling for more petroleum within this country and along shorelines. T. Boone Pickens (2008) personally encourages us to drill, drill, drill, use natural gas instead of gasoline, and greatly increase use of wind power. It appears coincidental that Mr. Pickens controls huge natural gas reserves and a Texas wind farm that probably is the largest in this country. Converting this country's vehicles from gasoline to natural gas would take years. Considerable expensive new infrastructure for distribution of natural gas for vehicles also would be needed. Additional exploration and drilling for oil and possible use of new techniques for securing old petroleum left in wells would help bridge the gap until new technologies replace our petroleum economy. Additional oil exploration, particularly along seacoasts and in Alaska, appears likely. New oil wells and refineries would probably take at least a decade to come on line. Fossil fuels are not green and would continue to put additional carbon in the atmosphere.

As previously mentioned, many nations such as France have decided to use nuclear energy for a majority of electrical generation. Most estimate it would take us at least a decade for new nuclear production to come on line. It may be possible to expand some current nuclear generation locations. Serious security and disposal issues remain unresolved. For decades nuclear plant expansion has been politically impossible, as this country remains deeply divided on the issue.

One of the most popular proposed energy solutions is clean wind power. In 2007 world wind power capacity increased 27 percent from the previous year, and this growth should continue. An anniversary issue of *Discover* (2008) estimated that as much as 29 per cent of the world's electricity could be produced by wind by 2030. Wind farms would generally be located in the center of this country and California. Population centers with the greatest need for energy are in the east and west, with most people in this country residing near coasts away from the prime wind generation locations. Some coastal areas show promise, but the "not in my backyard" opposition has resulted in formidable political opposition. Estimates start around $60 to $70 billion for infrastructure to eventually transfer electricity from the point of generation to population centers. Other challenges exist. There is wind turbine noise for those near wind farms, and there are environmental safety issues for birds, bats and other wildlife. Also, wind technology generates energy but not capacity. Easton (2008) estimated that there must be winds of at least eight mph to generate power. When there is little wind, as often occurs in the afternoon when power is most needed, there must be back-up sources of electricity. Wind is unpredictable and seasonal. Until adequate storage such as mammoth batteries are developed, wind would still require conventional power plants for back up. Required redundancy is expensive. Solar energy can be evaluated in a similar way. Geographically the sunniest parts of this country are in the southwest far from most major population centers. Solar and wind energy have similar power transmission, energy storage, unpredictability, and redundancy issues. However, both have a part in a long-term solution.

Encouragement for using for biofuels has been debated for the past decade. It is a renewable energy source and could help to promote limited energy independence. Converting crops to ethanol has been used for creating additional markets for farm surpluses, especially corn and soybeans. Biofuels have been my focus for research in the past year. Before discussing this research, a few concerns about biofuel should be addressed. First, is it true that biofuels need more fossil fuel in production than new fuels produced? There is no absolute answer to this. When corn is used, the answer tends to usually be "no." With the cost of planting corn skyrocketing for fuel for planting and harvesting equipment, fertilizer, and transportation, farmers have tried to find ways to conserve on energy. Then, if the corn ethanol can be used locally, there can be a net gain. Another consideration involves net greenhouse emissions savings from biofuels; they apparently do exist. A study in the United Kingdom in a recent issue of *New* Scientist (2008) suggested that there was a 10 per cent gain over conventional fuels when using Brazilian soya oil. Other biofuels were able to do better. Rapeseed saved about 30 per cent, and Asian palm oil saved 40 per cent. Ethanol from Brazilian sugar cane saved 70 per cent, while cooking oil and tallow saved over 80 per cent. However, creating biofuels to reduce less carbon entering the atmosphere can be negative, depending upon the extent of destruction to the natural ecosystem to secure biomass. Using animal waste, damaged trees, algae, food waste, and plants found in nature also greatly reduce emissions. Some estimate that algae remove as much carbon from the atmosphere when growing as is released when it is used as fuel.

Experimenting with new sources for biofuel using native plants has been my interest. My research has focused on plants that will have minimal environmental impact and not diminish the world's food supply. I initially chose to work with leaves gathered in yards and parks each fall and later moved on to other possible sources like cattails, trees, and algae. One hopes that biochemical engineering can eventually develop the biofuels needed for sustaining quality human life in a cost efficient and green manner. As stated in the opening quotation by Lynd, progress is coming in small steps. Policy makers usually hope for instant results to meet voters' political and economic concerns. However, considerable additional biofuel research and development is needed. Some of the most advanced and promising results not involving corn and possible human foods were recently summarized by Roger Mandelbaum (2008). A company named Range Fuels recently started construction a next-generation commercial ethanol plant in Soperton, Georgia. It is estimated that the surrounding geographic area has enough biomass from wood products to make 10 to 15 billion gallons of fuel a year. It supposedly has a simplified gasification process that can convert biomass into a gas in just 20 minutes. Another company, Coskata, in Warrenville, Illinois, claims to have an even more efficient process by enlisting bacteria to ferment syngas into ethanol. Both firms will face challenges. Water is essential for ethanol production, often limiting locations for new biofuel plants. It also can be difficult to find a local plentiful source of biomass, find an efficient method of collecting it, and then ensure having the source for years to come. The ethanol industry is in its infancy. New ideas appear in popular and scientific literature daily.

To demonstrate the many small steps that go into developing and improving ethanol production, I will present an example of the type of research that I conduct, this time involving tree leaves that have left trees in the autumn. It seems like a promising source for producing some ethanol. It is estimated that approximately 60 gallons of ethanol could be produced per ton of leaf litter. In comparison to other cellulose sources, leaf litter has less sugars and will produce less ethanol. However, energy is already being expended to harvest leaf litter whereas addition energy would be consumed to harvest other cellulose sources. This is why this research was conducted.

Introduction

Let me first review some ideas that might help one to better understand my study. Ethanol is ellulosic ethanol is one possible alternative.[1,2,3] Cellulosic ethanol is made by breaking down cellulose in plants and certain bacteria into glucose. The glucose can then be fermented into ethanol.

Cellulose is an important component of plant cell walls[4] and the main carbohydrate in plants.[5] Cellulose is composed of up to 15,000 glucose molecules connected by b-1,4 glycosidic bonds.[5] Cellulose forms a rigid crystalline structure due to hydrogen bonding within and outside the molecule.[5] Cellulose fibers are formed by intermolecular hydrogen bonds connecting strands of glycan. Glycan chains are then stacked, and further hydrogen bonding holds the whole structure together. Cellulose is responsible for the rigidity and strength of the plant.[5] Figure 1 shows the crystalline structure of cellulose.

(See Figure 1)

In nature, enzymes from microorganisms break down cellulose into glucose by cleaving the b-1,4 bonds.[1,5,6,7] Figure 2 shows the conversion of cellulose to individual glucose molecules. Once cellulose has been broken down, the glucose can be used in the production of ethanol. Work has been done manipulating microorganisms to produce decent yields of ethanol. In a study by Alterthum, et al. Escherichia coli were genetically altered with genes from Zymomonas mobilis.[8] Zymomonas mobilis produces enzymes that can convert sugar into ethanol.[8] The study involved turning multiple sugars such as glucose, xylose, and galactose, into ethanol.[8] A genetically altered strain of E. coli effectively converted all sugars into ethanol better than traditional bacteria strains.[8]

(See Figure 2)

Breaking cellulose into glucose is difficult as cellulose is usually associated with hemicellulose and lignins.[4,5] Lignins are a plastic-like, phenolic polymers that prevent enzymes from degrading cellulose and hemicellulose.[5]

The purpose of this experiment is to characterize leaf litter for the amount of sugars, lignins, and other components within the plant material. Leaf litter was chosen for two reasons. First, leaf litter requires little additional fuel to harvest for ethanol production as it is already has to be harvested in the fall when we rake our yards and transport the leaves to compost facilities. The second reason is that leaf litter is not currently used for anything productive other than production of mulch. For these two reasons, leaf litter is an attractive source for ethanol production.

Materials and Methods

The method used was slightly modified from the protocol developed by the National Renewable Energy Laboratory (NREL).[9]

Pre-treatment

Leaves collected in Fall 2007 were ground into a powder. Samples were prepared in triplicate. Three hundred mg samples were weighed and 3 mL of 72% sulfuric acid were added to each sample. Samples were incubated at 30^{o}C in a shaking water bath for approximately one hour. Eighty-four grams of water were added to each sample before they were autoclaved at 121^{o}C for 1 hour. The residual solid was collected in a filtering crucible by vacuum filtration. Solid and liquid materials were analyzed separately.

Solid Analysis

Solid material was dried in the crucible at 105^{o}C until a constant weight was measured. This measurement gave the combined mass of acid insoluble lignin and acid insoluble ash. The solid material was heated at 570^{o}C until constant weight. The remaining, solid material was acid insoluble ash.

Liquid Analysis

Acid soluble lignins were determined by measuring the UV absorbance at 198 and 240 nm. One mL of filtrate was diluted with 10 mL of water for absorbance measurements. Average absorbances and %ASL (Acid Soluble Lignin) were determined. The %ASL was determined with the following equation[9]:

% ASL= {[(Avg UV abs) x filtrate volume x dilution]/ [E x Sample Weight]}

The extinction coefficients, E, were based on those reported for bagasse[9].

Carbohydrates in the liquid portion were analyzed by High Performance Liquid Chromatography (HPLC). HPLC conditions were:

Column: Kromasil Amino Column (25 cm length x 4.6 mm diameter

Mobile Phase: 75% Acetonitrile 25% Water

Flow rate: 2 mL/minute
Refractive index detection

Sugar standards were used to determine the retention times of the sugars and to prepare standard curves for quantification of sugars found in the filtrates. Sugar standards were made for arabinose, xylose, glucose, galactose, mannose, and cellobiose. Standard curves were made for each sugar by plotting HPLC peak areas versus sugar concentrations in the standards.

Results

Solid Material

Analysis of the solid material in the filtering crucible determined that an average of 27.6% of the initial 300 mg leaf powder sample was acid insoluble lignin while 2.6% was acid insoluble ash.

Liquid Material

Table 1 shows the results for measuring the acid soluble lignins in the liquid material. Amount of acid soluble lignins in 300 mg of leaf litter was determined to be 23.4+/-1.1% using the absorbance 240 nm and 21.2+/-0.8% using the absorbance at 198 nm. An average of these two values is 22.3+/-1.0% Table 1: Acid soluble lignin data from absorbance measurements at 198 and 240 nm

(See Table 1)

Standard sugar and filtrate samples were analyzed by HPLC. Standard curves for xylose, arabinose, mannose, galactose, glucose, and cellobiose were created. Sugar peaks in the filtrate were identified by comparing their retention times with the sugar standards. The amount of each sugar in the filtrates was determined by inserting the peak area from the HPLC chromatogram into the standard curve line equation of that particular sugar. The measured amount of each monosaccharide was corrected to its anhydro mass to reflect the amount of the corresponding polysaccharide in the original plant material. Cellulose (23.8+/- 1.6%), xylan (7.4+/- 0.7%), and arabinan (7.9+/- 0.8%) were found in significant quantities. Other sugars found were negligible. The observation that cellobiose was negligible indicated that the acid hydrolysis was essentially complete.

Table 2 summarizes the overall amount of lignins, ash, and polysaccharides found in the leaf litter samples. A column for cattails was included for comparison (Lama, Rife and Marg, unpublished results).

(See Table 2)

Discussion

A large portion of leaf litter is made up of lignins. Acid insoluble lignins and acid soluble lignins make up as much as 50% of leaf material. Cellulose, arabinan, and xylan were found in significant quantities within leaf litter. Cellulose (23.8+/-1.6%) makes up nearly a quarter of the leaf followed by arabinan and xylan at significantly lower amounts. Galactose, mannose, and cellobiose amounts in leaf litter samples were negligible. Based on overall calculations, fall leaf litter has the potential to yield approximately 60 gallons of ethanol per ton of leaves. Table 2 shows that cattails have significantly higher amounts of cellulose, arabinan, and xylan. Cattail material can be made into nearly twice as much ethanol/ton. It is important to note that although cattails can be made into a higher amount of ethanol per ton, cattails have to be harvested. This will require energy that will decrease the overall net yield. Leaf litter is still a good source of cellulosic ethanol because much of the energy needed to harvest and transport the leaves is already being expended. Future work for leaf litter will involve maximizing the amount of sugars recovered from leaf litter as well as optimizing the fermentation

This was a sample of current research. So, what would this lab rat prefer to see as energy policy? The bottom line is that an immediate energy policy should be flexible and sustainable. It should not expect to rush things. Research takes time, and policy makers and researchers need to have on-going and better communication. A few apparent suggestions for a future national energy policy should be listed. First, the government should continue to support research and production of biofuels. This support should be reduced for corn and beans and instead focus on biomass not needed for food. Next, a new policy should encourage diverse sources of energy. Financial assistance is needed for research, development and production of all new sources of energy including solar, wind, nuclear, biofuels, and new sources of petroleum. Encouraging diversity should include encouraging different sources of biomass, depending upon vegetation in different regions of the country. Switch grass may be used to make ethanol in dry areas, annual grasses and plants in another, trees in others, and possibly algae or less well-known sources of energy in special situations. At this time, biofuels appear to best meet immediate and continuing energy needs as they can be used in the most needed ways. It would be hoped that financial assistance could lessen and then cease once new industries are fully developed. Finally, an energy policy must also include other obvious steps that would help during the gap period until there are new clean long-term methods of producing energy. There should be limited drilling on our continental shelves and Alaska, increased gas taxes to encourage efficient cars, a fix our mass transit system, greater financial assistance to better insolate homes and businesses, and increased tax credits or other means of financial assistance for those with low incomes.

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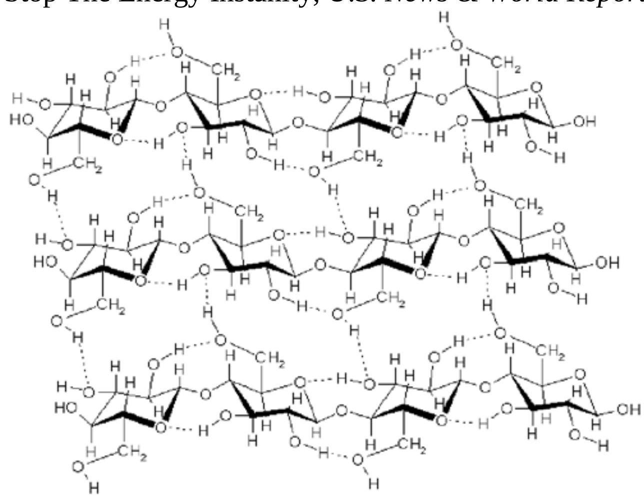

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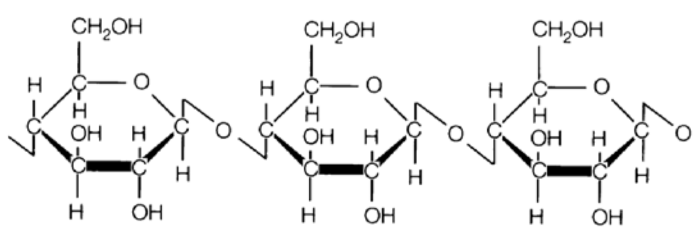
Figure 1: Structure of cellulose. This figure comes from http://www.doit-poms.ac.uk/tlplib/wood/figures/cellulose.png.



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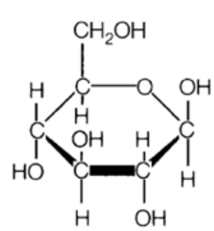

Figure 2:† Cellulose to glucose.† Structures come from http://www.greenspirit.org.uk/Resources/cellulose.gif.

†

Sample	198 (1+10)	240 (1+10)
A1	2.9348	1.1623
A2	2.8622	1.1941
A3	2.897	1.1903
Avg	2.898	1.18223
Dilution	11	11
%ASL	0.2264	0.2463
B1	2.6974	1.098
B2	2.6751	1.1045
B3	2.6974	1.1122
Avg	2.68996	1.1049
Dilution	11	11
%ASL	0.2121	0.2323
C1	2.6539	1.0577
C2	2.6974	1.0616
C3	2.6751	1.0666
Avg	2.67546	1.06196
Dilution	11	11
%ASL	0.2117	0.2241

Table 1

Substance	Leaf Litter Percent	Cattail Comparison
Acid Soluble Lignin	22.3 +/- 1.0%	3.7 +/- 0.1%
Acid Insoluble Lignin	27.6%	22.1 +/- 0.3%*
Acid Insoluble Ash	2.6%	Not Available
Cellulose	23.8 +/- 1.6%	37.4 +/- 4.4%
Xylan	7.4 +/- 0.7%	24.5 +/- 7.0%
Arabinan	7.9 +/- 0.8%	11.5 +/- 5.3%

Table 2: Percentage results for leaf litter and cattails for acid insoluble lignins, acid insoluble lignins, acid insoluble ash, cellulose, xylan, and arabinan.