MA 205
Bioreactors in Every Day Life
Ethanol and the Maize Craze
Instructor Handout

Major Silas Bowman
Lieutenant Colonel Alex Heidenberg

December 6, 2007

Contents

1 Motivation **2**

1.1 BACKGROUND ON BIOREACTORS . . . 2

2 Introduction to the Maize Industrial Maze **4**

2.1 Industrial Corn . . . 4

2.1.1 The Plant . . . 4

2.1.2 The Farm . . . 6

2.1.3 The Elevator . . . 9

2.2 The Feedlot and other Consumers of Corn . . . 10

2.2.1 Cattle Metropolis . . . 10

2.2.2 Industrial: Garden City, Kansas . . . 11

2.3 The Processing Plant . . . 11

2.3.1 Taking the Kernel Apart: The Mill . . . 11

2.4 The Consumer - Us . . . 13

2.5 The Meal - Fast Food . . . 14

3 Finding Our Way Through the Maize Maze! **16**

3.1 National Geographic - Green Dreams . . . 16

3.2 Questions to Ponder Regarding Ethanol . . . 16

4 Bioreactor Math **18**

4.1 Phases of bacteria growth: . . . 18

4.2 Rate Laws . . . 18

4.3 Stoichiometry . . . 19

4.4 Mass Balances . . . 21

4.4.1 *Cell* . . . 21

4.4.2 *Substrate / Nutrient* . . . 22

4.4.3 *Product* . . . 22

4.5 Ethanol Bioreactor Model . . . 22

4.6 The Problem . . . 24

4.7 Sample Solution . . . 25

Chapter 1

Motivation

Bioreactors are any cell that given a food or substance creates something else. An example is Ecoli Virus cell that has been genetically altered to produce insulin when fed glucose. Another example is the production of fuel grade ethanol from glucose using an organism such as Saccaromyces cervisiae.

Corn farmers have found over the last 40 years a huge increase in the volume of corn being produced. We use corn in almost everything we do. Corn is converted into food, plastics, sweeteners, oils, alcohol, chemicals, and fuel additive. Many of these conversions are done with various bioreactors. The conversion of corn to alcohol, usually ethanol, is done with a well known bioreactor called yeast in a process called fermentation. The question is can we start using more ethanol than fossil fuels and is it worth it. Some say the conversion from seed in the ground to fuel in the tank takes more energy than it produces. On top of that the government has been subsidizing corn farmers since the early 70s to the tune of 5 billion a year.

Brewer's yeast is also a bioreactor that converts the sugar in grains to alcohol and carbon dioxide producing beer. Micro-breweries benefit greatly from cultivating different yeasts and reusing them in each batch of beer. The flavor, alcohol content, color, and carbonation of beer relies heavily on the type of yeast used and the size of the initial population. American style beers are lighter in alcohol and flavor which in part is due to the yeast and part due to the amount of grain or sugar content of the beer. By limiting the time the yeast has to act and the amount of available sugar a brewer can reduce the alcohol content. One can also save a lot of money when starting a micro-brewery by having a few robust cultures of yeast to use.

1.1 BACKGROUND ON BIOREACTORS

The use of living cells to produce marketable chemical products is becoming increasingly important and has resulted in some amazing second and third order effects. Chemicals, agriculture products, and food products produced by biosynthesis have risen from the 1990 market of $ 275 million to over $ 25 billion and continues to grow. Microorganisms and mammalian cells are being used to produce a variety of products such as insulin, most antibiotics, and polymers. In the future we hope to use bioreactors to create a vast number of organic chemicals currently produced using petroleum.

Chapter 2

Introduction to the Maize Industrial Maze

We as humans are different from most of nature's other eaters. We have acquired the ability to substantially modify the food chains we depend on, by means of such revolutionary technologies as cooking with fire, hunting with tools, farming, and food preservation.

The industrial revolution[1], following the close of World War II, has changed the fundamental rules of the food chain. Industrial agriculture has supplanted a complete reliance on the sun for our calories with something new under the sun: a food chain that draws much of its energy from fossil fuels instead. Yes, we rely on corn, a natural plant, but our massive processing of this sun fueled plant from seeds in the ground to ethanol in the gas tank requires enormous amounts of fossil fuel.

Chapter 2 is a condensed version of the first portion of Michael Pollan's book the Omnivoure's Dilemma. [Pol06]

2.1 Industrial Corn

2.1.1 The Plant

Corn in the Supermarket

If one follows the industrial food chain - the one that now feeds us most of the time and typically culminates either at a supermarket or a fast-food - one might expect the chain to lead to a wide variety of places. Though you might travel through many states and cover a great many miles, at the very end of these food chains (which is to say at the very beginning), one will invariably find themselves almost in the exact same place: a farm field in the American Corn Belt. The great variety of food found in the supermarket turns out to rest on a narrow biological foundation comprised of a tiny group of plants that is dominated by a single species: Zea mays, the giant tropical grass most Americans know as corn.

Corn is what feeds the steer that becomes the steak. Corn feeds the chicken and pig, the turkey and the lamb, the catfish and the tilapia and, increasingly, even the salmon, a carnivore by nature

[1] Pollan, Omnivore's Dilemma, [Pol06] page 5

that the fish farmers are re-engineering to tolerate corn. The eggs are made of corn. The milk and cheese and yogurt, which once came from dairy cows that grazed on grass, now typically come from Holsteins that spend their working lives indoors tethered to machines, eating corn.

Heading over to the processed food and you find ever more intricate manifestations of corn. A chicken nugget, for example, piles corn upon corn: what chicken it does contain consists of corn, of course, but so do most of a nugget's other constituents, including the modified corn starch that glues the thing together, the corn flour in the batter that coats it, and the corn oil in which it gets fried. Much less obviously, the leavening and lecithin, the mono-, di-, and triglycerides, the attractive golden coloring, and even the citric acid that keeps the nugget "fresh" can all be derived from corn.

To wash down your chicken nuggets with virtually any soft drink in the supermarket is to have some corn with your corn. Virtually all sodas are sweetened with high-fructose corn syrup (HFCS). Grab a beer and you'd still be drinking corn, in the form of alcohol fermented from glucose refined from corn.

Read the ingredients on the label of any processed food and if you know what chemical name it travels under, corn is what you will find. For modified or unmodified starch, for glucose syrup and maltodextrin, for crystalline fructose and ascorbic acid, for lecithin and dextrose, lactic acid and lysin, for maltose HFCS, for MSG and plyols, for the caramel color and xanthan gum, read: corn. Corn is in the coffee whitener and Cheez Whiz, the frozen yogurt and TV dinner, the canned fruit and ketchup and candies, the soups and snack and cake mixes, the frosting and gravy and frozen waffles, the syrups and hot sauces, the mayonnaise and mustard, the hot dogs and bologna, the margarine and shortening, the salad dressings and the relishes and even the vitamins. There are some forty-five thousand items in the average American supermarket and more than a quarter of them now contain corn. This goes for the non-food items also - everything from the toothpaste and cosmetics to the disposable diapers, trash bags, cleansers, charcoal briquettes, matches, and batteries, right down to the shine of the cover of the magazine that catches your eye by the checkout: corn. Even in produce you will find corn: in the vegetable wax that gives the cucumbers their sheen, in the pesticide responsible for the produce's perfection, even in the coating on the cardboard it was shipped in. The supermarket itself - the wallboard and joint compound, the linoleum and fiberglass and adhesives out of which the building has been built - is in no small measure a manifestation of corn.

And us? Are we what we eat?

Corn Walking

At its most basic, the story of life on earth is the competition among species to capture and store as much energy as possible[2] - either directly from the sun, in the case of plants, or in the case of animals, by eating plants and plant eaters. The energy is stored in the form of carbon molecules and measured in calories. The calories we eat, whether in an ear of corn or a steak, represents packets of energy once captured by a plant.

[2] Pollan, Omnivore's Dilemma, [Pol06] page 10

The Rise of Zea Mays

Corn won over the wheat people because of its versatility, prized especially in new settlements far from civilization. This one plant supplied settlers with a ready-to-eat vegetable and a storable grain, a source of fiber and animal feed, a heating fuel and an intoxicant. Corn could be eaten fresh of the cob ("green") within months after planting, or dried on the stalk in fall, stored indefinitely, and ground into flour as needed. Mashed and fermented, corn could be brewed into beer or distilled into whiskey; for a time it was the only source of alcohol on the frontier. (Whiskey and pork were both regarded as "concentrated corn," the latter a concentrated form of protein, the former of its calories; both had the virtue of reducing corn's bulk and raising its price.) No part of the big green grass went to waste: The husks could be woven into rugs and twine; the leaves and stalks made good silage for livestock; the shelled cobs were burned for heat and staked by the privy as a rough substitute for toilet paper. Corn then as today was the all purpose plant.

2.1.2 The Farm

One Farmer, 129 Eaters

After following one farmer we will find the complexity and diversity of corn and the corn farmer[3]. George Nayler's farm provides enough sustenance for 129 people. There is no way of knowing whether George Naylor is literally growing the corn that feeds the steer that becomes their steak, or sweetens their soft drink, or that supplied the dozen or so corn-derived ingredients from which a chicken nugget is constructed. But given the complexly ramifying fate of a bushel of commodity corn, the countless forking paths followed by its ninety thousand kernels as they're dispersed across the nations sprawling food system, the odds are good that at least one of the kernels grown on the Naylor farm has, like the proverbial atom from Caesar's dying breath, makes its way to us.

Planting the City of Corn

In one day George Nayler can plant 160 acres of corn. A week or two after this he will start planting soybeans. The two crops take turns in the fields year after year, in what is known as the classic Corn Belt rotation since the 1970s. (Since that time soybeans have become the second leg supporting the industrial food system: It too is fed to livestock and now finds its way into two-thirds of all processed food.) In Iowa only 2 percent of the state's land remains of what used to be (tall-grass prairie), every square foot of the rest having been completely remade by man.

Vanishing Species

The strange phenomenon with corn is that one might think the falling corn prices would lead farmers to plant less of it, but the economics and psychology of agriculture are such that exactly the opposite happened. Beginning in the fifties and sixties, the flood tide of cheap corn made it profitable to fatten cattle on feedlots instead of grass, and to raise chickens in giant factories rather than in farmyards. Iowa livestock farmers couldn't compete with the factory-farmed animals, so chickens and cattle disappeared from the farm. In their place the farmers planted more corn.

[3] Pollan, Omnivore's Dilemma, [Pol06]

Whenever the price of corn slipped they planted a little more of it, to cover expenses and stay even. By the 1980s the diversified family farm was history in Iowa, and corn was king.

There Goes The Sun

The great turning point in the modern history of corn, which in turn marks a key turning point in the industrialization of our food, can be dated with some precision to the day in 1947 when the huge munitions plant at Muscle Shoals, Alabama, switched over to making chemical fertilizer. After the war the government had found itself with a tremendous surplus of ammonium nitrate, the principal ingredient in the making of explosives. Ammonium nitrate also happens to be and excellent source of nitrogen for plants.

Hybrid corn turned out to be the greatest beneficiary of this conversion[4]. Hybrid corn is the greediest of plants, consuming more fertilizer than any other crop. To keep the land from getting "corn sick" farmers in Nayler's father's day would carefully rotate their crops with legumes (which added nitrogen to the soil), never growing corn more than twice in the same field every five years; they would also recycle nutrients by spreading their cornfields with manure from their livestock. Before synthetic fertilizers the amount of nitrogen in the soil strictly limited the amount of corn an acre of land could support.

The discovery of synthetic nitrogen changed everything - not just for the corn plant and the farm, not just for the food system, but also for the way life on earth is conducted. When humankind acquired the power to fix nitrogen, the basis of soil fertility shifted from a total reliance on the energy of the sun to a new reliance on fossil fuel. Heat and pressure are used to combine nitrogen and hydrogen gases to create the fertilizer. This heat and pressure are supplied by oil, coal, or natural gas - fossil fuels.

On the day in the 50s we first spread ammonium nitrate fertilizer, the ecology of the farm underwent a quiet revolution. What had been a local, sun-driven cycle of fertility, in which legumes fed the corn which fed the livestock which in turn (with their manure) fed the corn, was now broken. Now we could plant corn every year and on as much acreage as we chose.

Fixing nitrogen allowed the food chain to turn from the logic of biology and embrace the logic of industry. Instead of eating exclusively from the sun, humanity began to sip petroleum.

When you add together the natural gas fertilizer to the fossil fuels it takes to make the pesticides, drive the tractors, and harvest, dry, and transport corn, you find that every bushel of industrial corn requires the equivalent of between and quarter and a third of a gallon of oil to grow it - or around fifty gallons of oil per acre of corn. Put another way it takes more than a calorie of fossil fuel energy to produce a calorie of food.

What happens to the one hundred pounds of synthetic nitrogen that corn plants don't take up? Some of it evaporates into the air, where it acidifies the rain and contributes to global warming. Some seeps down to the water table. Some is washed by the rain into drainage ditches that eventually spill into the rivers and finds its way into the water source for the towns around the farm.

[4] Pollan, Omnivore's Dilemma, [Pol06]

A Plague of Cheap Corn

Today the price of a bushel of corn is about a dollar beneath the true cost of growing it which is good for everyone except the corn farmer. Why then if there's so much corn being grown in America today that the market won't pay the cost of producing it would any farmer in his right mind plant another acre of it. The answer is it has something to do with the economics of agriculture, which seem to defy the classic laws of supply and demand. Government farm programs once designed to limit production and support prices (and therefore farmers) were quietly revamped to increase production and drive down prices. Instead of supporting farmers, during the Nixon administration the government began supporting corn at the expense of farmers. Corn already the recipient of biological subsidy in the form of synthetic nitrogen, would now receive an economic subsidy too, ensuring its final triumph over the land and the food system.

In 1933 in the depths of the farm depression the New Deal established a target price for corn based on the cost of production, and whenever the market price dropped below the target, the farmer was given a choice. Instead of dumping grain into a weak market, the farmer would take out a loan from the government - using his crop as collateral - that allowed him to store his grain until prices recovered. This was called the "Ever-Normal Granary" which was the start of the "nonrecourse loan." This system was in place until the 1970s but plans to dismantle the New Deal began in the 1950s.

The Sage of Purdue

Earl "Rusty" Butz, Richard Nixon's second secretary of agriculture, revolutionized American agriculture, helping to shift the food chain onto a foundation of cheap corn. Butz took over during the last period in American history that food prices climbed high enough to generate political heat. By 1973 the inflation for groceries reached an all time high. Farmers were killing chicks because they could not afford to feed them and the price of beef had slipped beyond the reach of middle-class consumers. Some foods became scarce; horse meat began showing up in certain markets. Butz told farmers to plant their fields "fencerow to fencerow" and advised them to "get big or get out." Bigger farms were more productive, he pushed farmers to consolidate ("adapt or die") and to regard themselves not as farmers bus as "agribusinessmen." Butz abolished the Ever-Normal Granary and with the 1973 farm bill, began replacing the New Deal system of loans, with a new system of direct payments to farmers[5].

Paying farmers directly for the shortfall in the price of corn was revolutionary. Instead of keeping corn out of a falling market, like the old loan programs and federal granary had done, the new subsidies encouraged the farmer to sell their corn at any price, since the government would make up the difference. Or, as it turned out, make up some of the difference.

The Naylor Curve

Similar to the Laffer curve, the Naylor curve shows why falling farm prices force farmers to increase production in defiance of all rational behavior. The more bushels each farmer produces, the lower the prices go. So corn farmers persist in measuring their success in bushels per acre, a measurement that improves as the farmer goes broke.

[5] Pollan, Omnivore's Dilemma, [Pol06]

Corn is the most efficient way to produce energy, soybeans the most efficient way to produce protein. What else would a farmer grow? Not broccoli or lettuce. Farmers have a long term investment in corn and soybeans; the elevator is the only buyer in a farming town and the elevator only buys corn or soybeans. The market and the government are telling farmers to grow corn or soybeans, period. The government calculates a farmer's subsidy payments based on his yield of corn.

So the plague of cheap corn goes on, impoverishing farmers, degrading the land, polluting the water, and bleeding the federal treasury, which now spends **$ 5 billion** a year subsidizing cheap corn. But though the subsidy checks go to the farmer (and represent nearly half of the net farm income today), what the Treasury is really subsidizing are the buyers of all that cheap corn. Agriculture will probably always be organized by the government; the question is, organized for whose benefit? Now it seems to benefit Coca-Cola and Cargill, not the farmer.

Increasing yield with more technology

A neighbor of George Nayler, Billy, is really in debt with his farm. Billy has state of the art equipment and uses all the new technology. He plants Bt corn - corn genetically engineered to produce its own pesticide. Billy gets 220 bushels of corn per acre on that seed.

George on the other hand is getting around 160-180 bushels per acre, however, he is almost certain he is getting more money per acre by growing less corn more cheaply. But in Iowa, bragging rights go to the man with the biggest yield, even if it is bankrupting him.

In a nearby shed Billy has an eighteen-wheeler. He needs this for his hauling side job to pay for his farm equipment. Two hundred and twenty bushels of corn is an astounding accomplishment, yet it didn't do Billy nearly as much good as it did for the bank, John Deer, Monsanto, Pioneer, and Cargill.

2.1.3 The Elevator

In 1856 the Chicago Board of Trade instituted a grading system on produce. Now any number 2 corn was guaranteed to be as good as any other number 2 corn. This system redirected the evolution of Zea Mays[6]. Now the pride in corn has vanished. As long as your corn meets the grade number 2 you get the same amount of money as any other farmer. In one train load we can haul at least 440,000 bushels of corn with no idea of where it came from. With technology, machinery, chemical, hybrid genetics, and skill a farmer can coax five tons of corn from an acre of Iowa soil.

The Iowa Farmers Cooperative writes a check from the elevator yield for the farmer's corn. The farmer gets a second check from the U.S. Department of Agriculture for about twenty-eight cents a bushel no matter what the market price of corn is, and considerably more if the price of corn drops below a certain threshold. If for example the price of a bushel drops to $ 1.45, since the official target price stands at around $ 1.87, the government would then send the farmer another $ 0.42 in "deficiency payments" for a total of $ 0.70 for every bushel of corn they can grow. These federal payments can account for nearly half of the income of the average Iowa corn farmer and represent roughly a quarter of the $ 19 billion U.S. taxpayers spend each year on payments to farmers.

Moving that mountain of cheap corn - finding people and animals to consume it, the cars to

[6] Pollan, Omnivore's Dilemma, [Pol06]

burn it, the new products to absorb it, and the nations to import it - has become the principle task of the industrial food system, since the supply of corn vastly exceeds the demand.

This 10-billion-bushel pile of commodity corn is a vast new stock of biomass to the environment. Ecology teaches us that whenever an excess of organic matter arises anywhere in nature, creatures large and small inevitably step forward to consume it. In this case we have the agribusiness corporations, foreign markets, and whole new industries (like our test subject ethanol), and then there are the food scientists, livestock, and human eaters, as well as the usual array of microorganisms.

What's involved in absorbing all this excess biomass goes a long way toward explaining several seemingly unconnected phenomena, from the rise of factory farms and the industrialization of our food, to the epidemic of obesity and prevalence of food poisoning in America.

Though the companies won't say, it has been estimated that Cargill and ADM together probably buy more than a third of all corn grown in America. They provide pesticide and fertilizer to the farmers; operate most of America's grain elevators; broker and ship most of the exports; perform the wet and dry milling; feed the livestock and then slaughter the corn-fattened animals; distill the ethanol; and manufacture the high-fructose corn syrup. Oh, and they help write many of the rules that govern this industry. These companies are the true beneficiaries of the "farm" subsidies that keep the river of cheap corn flowing. Cagrill is the biggest privately owned corporation in the world!

The bottom line - the place where most of the kernels wind up - about three of every five - is on the American factory farm, a place that could not exist without them. Hundreds of millions of food animals that once lived on family farms and ranches are gathered together in great commissaries, where they consume as much of the mounting pile of surplus corn as they can digest, turning it into meat. Enlisting the cow in this undertaking has required particularly heroic efforts, since the cow is by nature not a corn eater.

2.2 The Feedlot and other Consumers of Corn

2.2.1 Cattle Metropolis

Mills convert America's river of corn into cattle feed twelve hours a day, seven days a week. The cow a herbivore by nature is cajoled into consuming massive amounts of our biomass. About 60 percent of a bushel, some fifty-four thousand kernels goes to feeding livestock, and much of that goes to feeding America's 100 million beef cattle[7].

A new term was coined to describe the new operations feeding corn to cows. Concentrated Animal Feeding Operations, CAFO, now took the place of traditional grazing. Corn itself profited from the urbanization of livestock twice. As the animals left the farm, more of the farm was left for corn. Next the cattle were being engineered to tolerate corn. Not just cows were eating corn, farmed salmon were also being bred to tolerate grain.

In their short history CAFOs have produced more than their fair share of environmental and health problems: polluted water and air, toxic wastes, novel and deathly pathogens. A striking thing animal feedlots do is to take an elegant solution of the ecological loop and divide it into two new problems: a fertility problem on the farm (which must be remedied with chemical fertilizers)

[7] Pollan, Omnivore's Dilemma, [Pol06]

and a pollution problem on the feedlot (which is seldom remedied at all).

2.2.2 Industrial: Garden City, Kansas

At the feed mill of most feedlots three meals a day for thirty-seven thousand animals are designed and mixed by computer. A million pounds of feed pass through the mill every day. In addition to the corn, vats of liquid vitamins and synthetic estrogen and pallets of antibiotics along with alfalfa hay and silage are automatically blended and then piped into the parade of dump trucks which three times a day fan out to keep the Poky feeder's eight and a half miles of trough filled.

As calves progress from grazing to feedlots they move to a daily ration of thirty-two pounds of feed, three-quarters of which is corn - nearly half a bushel a day. Of course this corn-fed meat is less healthy for us, since it contains more saturated fat and less omega-3 fatty acids than the meat of animals fed grass. Unsurprisingly since ruminants or cows are ill adapted to eating corn; humans in turn may be poorly adapted to eating ruminants who eat corn.

Another consideration to feedlots are its waste. The waste or manure from cattle that used to be used as a fertilizer now contains heavy metals and hormone residues, persistent chemicals that end up in the waterways downstream, where scientists have found fish and amphibians exhibiting abnormal characteristics. The CAFOs transform what used to be a precious source of fertility into toxic waste.

The health of feedlot animals is linked to our own. The unnaturally rich diet of corn that undermines a steer's health fattens his flesh in a way that undermines the health of the humans who will eat it. Some 400 steers an hour are slaughtered and processed at the feedlot. These animals have been living in their own waste and it is caked on their hides. Some of that waste is bound to end up in the meat.

Keep going further into the corn chain and we find that the nitrogen runoff from the fertilizer goes all the way down to the Mississippi and into the Gulf of Mexico adding its poison to an eight-thousand-square-mile zone so starved of oxygen nothing but algae can live in it. If you follow the fertilizer further you find it heading all the way to the oil fields of the Persian Gulf.

Bottom Line: Looking at a cow who eats about 25 pounds of corn a day and reaches a weight of twelve hundred pounds, he will have consumed in his lifetime the equivalent of thirty-five gallons of oil or nearly a barrel.

So this is what commodity corn can do to a cow: industrialize the miracle of nature that is the ruminant, taking this sunlight- and prairie grass-powered organism and turn it into the last thing we need: another fossil fuel machine.

2.3 The Processing Plant

2.3.1 Taking the Kernel Apart: The Mill

One truly odd thing about the 10 billion bushels of corn harvested each year is how little of it we eat. We grind some corn to make cornmeal, but most of the corn we eat as corn - whether on the cob, flaked, or baked into muffins or tortillas or chips - comes from varieties other than number 2:

usually sweet corn or white corn[8]. These uses represent a tiny fraction of the harvest - less than a bushel per person per year.

About a fifth of the corn river flowing out of the elevators at the Iowa Farmers Cooperative travels to a wet milling plant, usually by train. The first rough breakdown of all that corn begins with the subdivision of the kernel itself: Its yellow skin will be processed into various vitamins and nutritional supplements; the tiny germ will be crushed for oil; and the biggest part, the endosperm, will be plundered for its rich cache of complex carbohydrates.

This oversized packet of starch is the corn's most important contribution to the industrial food chain: an abundance of carbohydrate molecules in long chains that chemists have learned to break down and then rearrange into hundreds of different organic compounds - acids, sugars, starches, and alcohols. If you look at any processed food the names will be familiar: citric and lactic acid; glucose, fructose, and maltodextrin; ethanol (for alcoholic beverages as well as cars - what a combination!), sorbitol, mannitol, and xanthan gum; modified and unmodified starches; as well as dextrins and cyclodextrins and MSG, to name a few.

Again the two companies who wet mill the most corn are Cargill and ADM. One of their biggest processes is the one we are most interested in; the conversion of corn sugar to ethanol for alcohol we drink and use to fuel our cars. The process is virtually invisible since it takes place inside of a series of sealed vats, pipes, fermentation tanks, and filters.

Wet milling is essentially an industrial version of digestion: A food is broken down through a series of steps that includes the application of physical pressure, acids, and enzymes, The order of the steps is different in the industrial digestion - the acids come before the mechanical chewing, for instance - but the results are the same: A complex food is reduced to simple molecules, mostly sugars.

First the corn is separated into its botanical parts - embryo, endosperm, fiber - and then into its chemical parts. First a shipment of corn is steeped for thirty-six hours in a bath of water containing a small amount of sulphur dioxide. After the soak, the swollen kernels are ground by the mill. The slurry is then run through a centrifuge where the germ floats off. After it is dried it is squeezed for corn oil. Corn oil can be used for cooking or hydrogenated for use in margarine and other processed foods.

Once the germ has been removed and the kernels crushed, what's left is a white mush of protein and starch called "mill starch". The mill starch undergoes a progressively finer series of grindings and filterings and centrifuges to draw off as much protein as possible. The extracted protein, called gluten, is used in animal feed. At each step more fresh water is added - it takes about five gallons to process a bushel of corn, and prodigious amounts of energy. For every calorie of processed food produced it takes about ten calories of fossil fuel.

At this point the process has yielded a white slurry that's poured out onto a stainless steel table and dried to a fine, super-white powder-cornstarch[9]. Since the 1840s we have been refining and redesigning cornstarch for many uses. It started in the laundry business and then cooks and early food processors began adding cornstarch to as many recipes as they could. By 1866, corn refiners had learned how to use acids to break down cornstarch into glucose, and sweeteners quickly became - as they are today - the industry's most important product. Corn syrup became the first domestic substitute for cane sugar. We discovered that an enzyme called glucose isomerase could

[8]Pollan, Omnivore's Dilemma, [Pol06]
[9]Pollan, Omnivore's Dilemma, [Pol06]

transform glucose into the much sweeter sugar molecule called fructose. By the 1970s the process of refining corn to fructose had been perfected, and high-fructose corn syrup-which is a blend of 55 percent fructose and 45 percent glucose that tastes exactly as sweet as sucrose - came onto the market. Today it is the most valuable food product refined from corn, accounting for more than 530 million bushels every year. (A bushel of corn yields thirty-three pounds of fructose.)

The starch itself is capable of being modified into spherical, crystalline, or highly branched molecules, each suitable for a different use: adhesives, coatings, sizings, and plastics for industry; stabilizers, thickeners, gels, and "Viscosity-Control agents" for food.

What remains from the slurry is "saccharified" - treated with enzymes that turn it into dextrose syrup. A portion of this syrup is syphoned off for use as corn syrup; other fractions are recruited to become sugars like maltodextrin and maltose. The largest portion of the corn syrup steam is piped into a tank where it is exposed to glucose isomerase enzymes then passed through ion exchange filters, emerging eventually as fructose. What is left is pumped into a fermentation tank, where yeasts or amino acids go to work eating the sugars, in several hours yielding an alcoholic brew. This itself is fractioned into various alcohols, ethanol chief among them, our gas tanks being the ultimate destination of a tenth of the corn crop. The fermented brew can also be refined into a dozen different organic and amino acids for use in food processing or the manufacturing of plastic.

And that is about it: There's no corn left, and not much of any thing else either except for some dirty water.

Stepping back a moment one can behold the great, intricately piped stainless steel beast; This is the supremely adapted creature that has evolved to help eat the vast surplus of biomass coming off America's farms, efficiently digesting the millions of bushels of corn feed to it each day by trainload. Go around back of this beast and you will see a hundred different spigots, large and small, filling tanker cars of the other trains with HFCS, ethanol, syrups, starches, the alcohol and acids, emulsifiers and a stabilizers and viscosity-control agents. It takes a certain type of eater, an industrial eater, to consume these fractions of corn, and we are, or have evolved into, that supremely adapted creature; the eater of the food process.

2.4 The Consumer - Us

In the early years of the nineteenth century, Americans began drinking more than they ever had before or since, embarking on a collective bender that confronted the young republic with its first major public health crisis - the obesity epidemic of its day. Corn whiskey, suddenly superabundant and cheap, became the drink of choice, and in 1820 the typical American was putting away half a pint of the stuff every day. That comes to more than five gallons of spirits a year for every man, woman, and child in America[10]. Today it is less than one - what is worse obesity or drunkenness?

As it is today, the clever thing to do with all the cheap corn was to process it - specifically, to distill it into alcohol. The appalachian range made it difficult and expensive to transport surplus corn from the lightly settled Ohio River Valley to the more populous markets of the East, so farmers turned their corn into whiskey - a more compact and portable, and less perishable, value-added commodity. Before long the price of whiskey plummeted to the point that people could afford to drink it by the pint. Which is exactly what they did - what a fun way to consume a biomass!

[10] Pollan, Omnivore's Dilemma, [Pol06]

The Alcoholic Republic has long since given way to the Republic of Fat; we're eating today much the way we drank then, and for the same reasons. According to the surgeon general, obesity today is officially an epidemic.

Since the Nixon administration, farmers in the United States have managed to produce 500 additional calories per person every day (up from 3,300, already substantially more than we need); each of us is heroically, managing to put away 200 of those surplus calories at the end of their trip up the food chain. Presumably the other 300 are being dumped overseas, or turned (once again!) into ethyl alcohol: ethanol for our cars.

The parallels with the alcoholic republic of two hundred years ago are hard to miss. In the 1820s you could turn your corn into pork or alcohol. Today there are hundreds of things a processor can do with corn, yet the human desire for sweetness surpasses even our desire for intoxication. So the cleverest thing to do with a bushel of corn is to refine it into thirty-three pounds of high-fructose corn syrup. That is what we are doing with 530 million bushels of the annual corn harvest - turning it into 17.5 billion pounds of high-fructose corn syrup. Corn sweetener is to the republic of fat what corn whiskey was to the alcoholic republic.

On average an American consumes sixty-six pounds of high-fructose corn syrup each year. It is in soft drinks that we consume most of the sixty-six pounds. In 1980 corn first became an ingredient in Coca-Cola. By 1984, Coca-Cola and Pepsi had switched over entirely from sugar to high-fructose corn syrup. HFCS was a few cents cheaper than sugar and consumers didn't seem to notice the substitution. Now corn is not the only source of cheap energy at the supermarket - much of the fat added to processed foods comes from soybeans - but corn is by far the most important. A quarter of a century of farm policies designed to encourage the overproduction of this crop and hardly any other has drastically changed the way we eat. Very simply, we subsidize high-fructose corn syrup in this country, but not carrots. While the surgeon general is raising alarms over the epidemic of obesity, the government is signing farm bills designed to keep the river of cheap corn flowing, guaranteeing that the cheapest calories in the supermarket will continue to be the unhealthiest.

2.5 The Meal - Fast Food

A typical trip to a fast food restaurant will use corn in almost every portion of the meal including the car ride with the fuel having ethanol in it. Even though the ethanol additive promises to diminish air quality in California, new federal mandates pushed by the corn processors require refineries in the state to help eat the corn surplus by diluting their gasoline with 10 percent ethanol[11].

It would be impossible to calculate exactly how much corn a typical family would consume at one visit to a fast food restaurant. A 4-ounce burger represents nearly 2 pounds of corn (based on a cow's feed conversion rate of 7 pounds of corn for every pound of gain, half of which is edible meat). Chicken nuggets are hard to determine because there is no telling how much chicken actually goes into the nugget; but if 6 nuggets contain a quarter pound of meat, that would have taken a chicken half a pound of feed corn to grow. A 32-ounce soda contains 86 grams of high-fructose corn syrup (as does a double thick shake), which can be refined from a third of a pound of corn; so 3 drinks use another pound of corn so far we are at about 6 pounds of corn. Adding up all the parts in the packaging, sweeteners in salad dressing, ketchup, corn oil the fries are cooked in, all the chemicals

[11] Pollan, Omnivore's Dilemma, [Pol06]

used to process and fortify the food gets even more complicated. Finally if you took the fact that it takes a bushel of corn to produce 2.5 gallons of ethanol and a 25 gallon tank would have 2.5 gallons it it your amount of corn is getting rather large. This compact fast food meal in loose corn could probably fill up a SUV from the driver's seats to the trunk.

A laboratory can identify how much carbon in a meal comes from corn by looking at a mass spectrometer[12]. In order of corniness this is how the laboratory measured a fast food meal: soda(100 percent corn), milk shake (78 percent), salad dressing (65 percent), chicken nuggets (56 percent), cheeseburger (52 percent), French Fries (23 percent). So what looks like a diverse meal turns out to be basically all corn.

We also consume a lot of petroleum in this meal. Not just in the car but to grow and process 4,510 food calories took at least ten times as many calories of fossil energy, the equivalent of 1.3 gallons of oil.

[12]Pollan, Omnivore's Dilemma, [Pol06]

Chapter 3

Finding Our Way Through the Maize Maze!

Now we should ask ourselves a few questions as we embark on using more and more ethanol in our vehicles. Next time we eat a meal we should think about how much corn, soybeans, and fossil fuel are in the meal.

Happy Dinning!

3.1 National Geographic - Green Dreams

Access the National Geographic Web Site and read the Green Dreams story.

The Web Site is:

`http://magma.nationalgeographic.com/ngm/2007-10/biofuels/biofuels.html`

3.2 Questions to Ponder Regarding Ethanol

1. Should we keep subsidizing corn farmers?
2. Is corn based ethanol an efficient fuel source?
3. How much corn is required to make a gallon of ethanol and how much fossil fuel is used to distill it?
4. Can we maximize efficiency of ethanol production without hurting other corn product use?
5. How will an increase in ethanol effect fossil fuel consumption?
6. Can we effect our addiction to oil by using corn?
7. Should we increase or decrease our research on alternate fuels?
8. Can we change the automobile industry to accept ethanol fuel and rebuild internal combustion engines?

9. Can we maximize ethanol production enough to offset the cost of distillation and transportation?

10. What is our reliance on corn doing to our economy and our world?

Chapter 4

Bioreactor Math

In biosynthesis, the cells, also referred to as the biomass, consume nutrient to grow and produce more cells and important products.

The mathematical formulas and ideas for this chapter come from [Fog92]

In general, the growth of an aerobic organism follows the equation:

$$[\text{cells}] + [\text{carbon source}] + [\text{nitrogen source}] + [\text{oxygen source}] + [\text{phosphate source}] \tag{4.1}$$

$$+ ... \longrightarrow [\text{more cells}] + [\text{Products}] + [H_2O] + [CO_2] \tag{4.2}$$

A more abbreviated model

The stick figure version of Bioreactors:

$$\text{Cells} + \text{Substrate} \longrightarrow \text{More Cells} + \text{Product} \tag{4.3}$$

4.1 Phases of bacteria growth:

I. Lag II. Exponential III. Stationary IV. Death

4.2 Rate Laws

Monod growth rate law:

$$r_g = \mu C_c \tag{4.4}$$

where r_g = cell growth rate
C_c = cell concentration
μ = specific growth rate [1]

[1] Fogler, Elements of Chemical Reaction Engineering, [Fog92]

The specific growth rate can be expressed as

$$\mu = \mu_{\text{max}} \frac{C_s}{K_s + C_s} \tag{4.5}$$

where μ_{max} = a maximum specific growth reaction rate
K_s = a parameter based on the rate constants of the reaction
C_s = Substrate concentration

Most of the time K_s is very small leaving us with:

$$r_g = \mu_{\text{max}} C_c \tag{4.6}$$

If we combine the equations we get:

$$r_g = \mu_{\text{max}} \frac{C_c C_s}{K_s + C_s} \tag{4.7}$$

In many systems the product inhibits the rate of growth. As in wine-making, beer-making, and ethanol-making. This happens when the fermentation of glucose to produce ethanol is inhibited by the product ethanol. A more robust yeast is needed to continue the process. This rate law looks like:

$$r_g = k_{\text{obs}} \frac{\mu_{\text{max}} C_s C_c}{K_s + C_s} \tag{4.8}$$

where

$$k_{\text{obs}} = (1 - \frac{C_p}{C_p^*})^n \tag{4.9}$$

with
C_p = concentration of product in the reaction
C_p^* = product concentration at which all metabolism ceases
n = empirical constant[2]

For the glucose to ethanol fermentation typical inhibition parameters are

$$n = 0.5 \quad \text{and} \quad C_p^* = 93$$

4.3 Stoichiometry

In general we have:

$$\text{Cells} + \text{Substrate} \longrightarrow \text{More Cells} + \text{Product} \tag{4.10}$$

[2]Fogler, Elements of Chemical Reaction Engineering, [Fog92]

$$\text{S} \quad \underrightarrow{cells} \quad Y_{c/s}C + Y_{p/s}P \tag{4.11}$$

where S = substrate
$cells$ = cells of the bioreactor
C = cells of the bioreactor produced in the reaction
P = product produced in the reaction

The yield coefficients are

$$Y_{c/s} = \frac{\text{mass of new cells formed}}{\text{substrate consumed to produce new cells}}$$

with

$$Y_{c/s} = \frac{1}{Y_{s/c}}$$

The stoichiometric yield coefficient that relates the amount of product formed per mass of substrate consumed is:

$$Y_{p/s} = \frac{\text{mass of product formed}}{\text{substrate consumed to produce product}}$$

In addition to consuming substrate to produce new cells, part of the substrate must be used just to maintain a cell's daily activities. The corresponding maintenance utilization term is:

$$m = \frac{\text{mass of substrate consumed for maintenance}}{\text{mass of cells * time}}$$

A typical value is : $m = 0.05 \frac{\text{g substrate}}{\text{g dry weight}} \frac{1}{\text{hour}} = 0.05\text{hour}^{-1}$

The rate of substrate consumption for maintenance whether or not the cells are growing is:

$$r_{sm} = mC_c \tag{4.12}$$

The yield coefficient $Y'_{c/s}$ accounts for the substrate consumption for maintenance.

$$Y'c/s = \frac{\text{mass of new cells formed}}{\text{mass of substrate consumed}}$$

Product formation can take place during different phases of cell growth. When the product is only produced during the growth phase then we can write:

$$r_p = Y_{p/c} r_g$$

However, when product is produced during the stationary phase, then we can relate product formation to substrate consumption by[3]:

[3] Fogler, Elements of Chemical Reaction Engineering, [Fog92]

$$r_p = Y_{p/s}(-r_s)$$

We now have to look at the complicated relationship between rate of nutrient consumption, $-r_s$ and the rates of cell growth r_g, product generation r_p, and cell maintenance mC_c. This in words looks like:

[Rate of Substrate used] = [Rate used by cells]
+ [Rate used to make product] + [Rate used for maintenance]

or the formula:

$$-r_s = Y_{s/c}r_g + Y_{s/p}r_p + mC_c \tag{4.13}$$

4.4 Mass Balances

There are two ways we could account for the growth of microorganisms. One is to account for the number of living cells and the other is to account for the mass of living cells. We will use the second. A mass balance would look like:

[Rate of Accumulation of cells] = [Rate of Cells Entering]
- [Rate of Cells Leaving] + [Net Rate of Generation of Live Cells]

The Formula is:

$$V\frac{dC_c}{dt} = v_0C_{c0} - vC_c + (r_g - r_d)V \tag{4.14}$$

The corresponding substrate balance in words is:

[Rate of Accumulation of Substrate] = [Rate of Substrate Entering]
- [Rate of Substrate Leaving] + [Rate of Substrate Generation]

The Formula is:

$$V\frac{dC_s}{dt} = v_0C_{s0} - vC_s + (r_s)V \tag{4.15}$$

Bioreactor systems usually start by having a concentration of the microorganism C_{c0} at zero. For a batch system the mass balances become[4]

4.4.1 *Cell*

$$V\frac{dC_c}{dt} = r_gV - r_dV \tag{4.16}$$

Dividing by the reactor volume **V** gives

$$\frac{dC_c}{dt} = r_g - r_d \tag{4.17}$$

[4]Fogler, Elements of Chemical Reaction Engineering, [Fog92]

4.4.2 *Substrate / Nutrient*

The rate of disappearance of the nutrient (in our case glucose), $-r_s$, results from the nutrient used for cell growth and nutrient used for cell maintenance,

$$V\frac{dC_s}{dt} = -r_s V = Y_{s/c}(-r_g) - mC_c V \tag{4.18}$$

Dividing by V yields

$$\frac{dC_s}{dt} = Y_{s/c}(-r_g) - mC_c \tag{4.19}$$

For cells in the stationary phase, where there is no growth, cell maintenance and product formation are the only reactions to consume the nutrient. Under these conditions the nutrient balance reduces to

$$V\frac{dC_s}{dt} = -mC_c V + Y_{s/p}(-r_p)V \tag{4.20}$$

4.4.3 *Product*

The rate of product formation, r_p, can be related to the rate of substrate consumption through the following balance:

$$V\frac{dC_p}{dt} = r_p V = Y_{p/s}(-r_s)V \tag{4.21}$$

During the growth phase we could also relate the rate of formation product r_p, to cell growth rate r_g. This balance is valid for both the stationary and growth phase of the cells.

4.5 Ethanol Bioreactor Model

In our case the glucose to ethanol fermentation is to be carried out in a batch reactor using an organism such as *Saccharomyces cerevisiae*.

So looking back at our previous model development we get[5]:

1. **Mass Balances:**

   - Cells: Similar to Equation (4.16)

$$V\frac{dC_c}{dt} = (r_g - r_d)V \tag{4.22}$$

   - Substrate: Similar to Equation (4.18)

$$V\frac{dC_s}{dt} = Y_{s/c}(-r_g)V - r_{sm}V \tag{4.23}$$

[5] Fogler, Elements of Chemical Reaction Engineering, [Fog92]

- Product: Similar to Equation (4.20)

$$V\frac{dC_p}{dt} = Y_{p/c}(r_g V) \tag{4.24}$$

2. **Rate Laws:**

   - Growth Rate: Combining Equations (4.9) and (4.10)

$$r_g = \mu_{max}\left(1 - \frac{C_p}{C_p^*}\right)^{0.52} \frac{C_c C_s}{K_s + C_s} \tag{4.25}$$

   - Death Rate:

$$r_d = k_d C_c \tag{4.26}$$

   - Rate of Substrate Consumption: Equation (4.13)

$$r_{sm} = mC_c \tag{4.27}$$

3. **Stoichiometry:**

$$r_p = Y_{p/c} r_g \tag{4.28}$$

4. **Combining the equations and giving some initial data yields**

   We have an initial cell concentration of $1.0g/dm^3$ the initial substrate (glucose) concentration is $250g/dm^3$ and the initial product (ethanol) concentration is 0.

   Additional data:

$$\begin{array}{cc} C_p^* = 93g/dm^3 & Y_{c/s} = 0.08g/g \\ n = 0.52 & Y_{p/s} = 0.45g/g \\ \mu_{max} = 0.331/hr & Y_{p/c} = 5.66g/g \\ K_s = 1.7g/dm^3 & k_d = 0.011/hr \end{array}$$

$$m = 0.33\ (g \text{ of substrate})/(g \text{ of cells } \cdot hr)$$

   - **Cells**

$$\frac{dC_c}{dt} = r_g - k_d C_c \tag{4.29}$$

   - **Substrate**

$$\frac{dC_s}{dt} = -Y_{s/c} r_g - mC_c \tag{4.30}$$

   - **Product**

$$\frac{dC_p}{dt} = Y_{p/c} r_g \tag{4.31}$$

We can now change parameters to maximize or minimize the system!

4.6 The Problem

Task 1:

Using (Equations 4.29, 4.30, and 4.31) plot the solutions on the same graph.

Task 2:

Plot the rates of (Equations 4.25, 4.26, 4.27, and 4.28) on the same graph.

Task 3:

In this reaction there are only three things that can be feasibly changed. At the distillery you can change how much time the reaction is allowed to act, the amount of substrate (Corn) initially put into the reaction $C_s[0]$, and the amount of cells (yeast) initially put into the reaction$C_c[0]$. As you may observe at a certain point the product begins to kill off the yeast cells. So we cannot just add more sugar to get more product.

Manipulate these three variables to maximize product and minimize cost. Remember both yeast and corn cost money and each batch reaction has a set up cost. In your manipulation start with $0 \leq C_c[0] \leq 4$, $0 \leq C_s[0] \leq 1000$, and $0 \leq t \leq 12$. After observing the behavior you can go outside of these parameters if you think you have found a better solution.

Research cost of yeast, corn, and batch reaction to validate your model.

Task 4:

Research how much corn is required to make ethanol. Research how much fossil fuel is used to distill ethanol once the corn is at the distillery.

Task5:

Prepare an out-brief detailing your model and your considerations for an ethanol production plant given what you know about the math above and the information you know about the use of corn[6]. Answer the questions posed in Chapter 3.2.

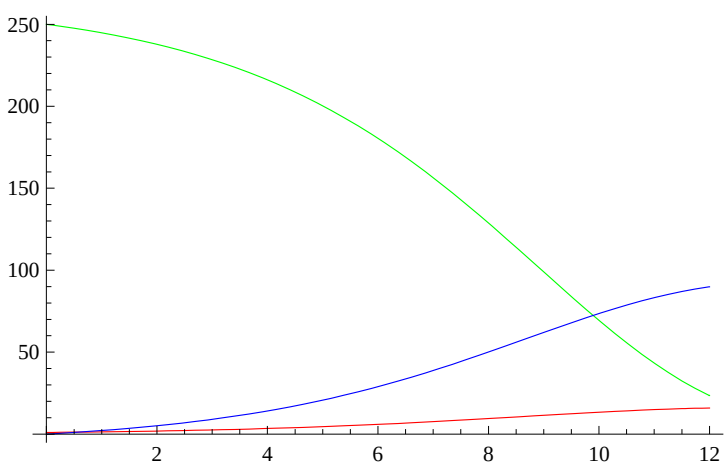
[6]Bowman, GO ARMY! BEAT TERRORISM!

4.7 Sample Solution

Task 1:

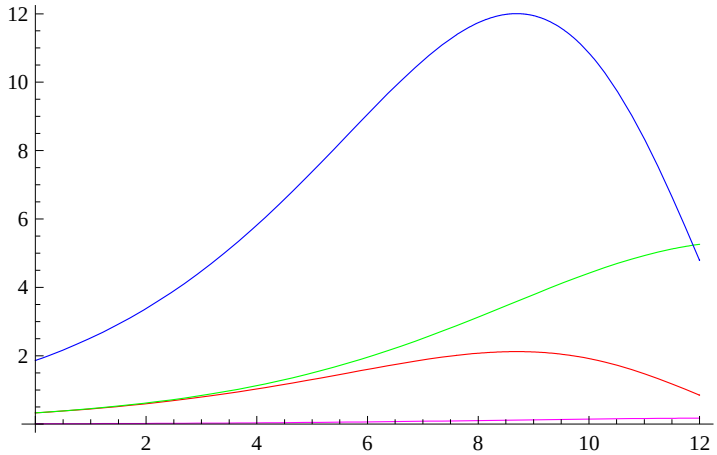
Using (Equations 4.29, 4.30, and 4.31) plot the solutions on the same graph.

```
Clear[Cc, Cs, Cp]
Cpstar = 93.; Ycs = 0.08; Ysc = 1 / Ycs; n = 0.52; Yps = 0.45; μmax = 0.331;
Ypc = 5.66; Ks = 1.7; kd = 0.011; m = 0.33; hours = 12.; Cc0 = 1.0; Cs0 = 250; Cp0 = 0;
kobs[t_] = (1 - Cp[t]/Cpstar)^n;
rg[t_] = μmax * kobs[t] (Cc[t] * Cs[t]/(Ks + Cs[t]));
rd[t_] = kd * Cc[t];
rsm[t_] = m * Cc[t];
Manipulate[
 sol = NDSolve[{Cc'[t] == rg[t] - rd[t], Cs'[t] == -1 * Ysc * rg[t] - rsm[t], Cp'[t] == Ypc * rg[t],
    Cc[0] == Cc0, Cs[0] == Cs0, Cp[0] == Cp0}, {Cc, Cs, Cp}, {t, 0, hour}],
 {Cc0, 0, 4}, {Cs0, 0, 1000}, {hour, 0, hours}]
Cells[t_] = Cc[t] /. sol; Substrate[t_] = Cs[t] /. sol; Prod[t_] = Cp[t] /. sol;
Rateg[t_] = μmax * (1 - Prod[t]/Cpstar)^n * (Cells[t] * Substrate[t]/(Ks + Substrate[t]));
Rated[t_] = kd * Cells[t];
Ratesm[t_] = m * Cells[t];
Ratep[t_] = Ypc * Rateg[t];
Plot[{Cells[t], Substrate[t], Prod[t]}, {t, 0, hours},
 PlotStyle → {RGBColor[1, 0, 0], RGBColor[0, 1, 0], RGBColor[0, 0, 1]}]
(*  Red = Cell fuction, Green = Substrate function, Blue = Product function  *)
Plot[{Rateg[t], Ratesm[t], Ratep[t], Rated[t]}, {t, 0, hours},
 PlotStyle → {RGBColor[1, 0, 0], RGBColor[0, 1, 0], RGBColor[0, 0, 1], RGBColor[1, 0, 1]}]
(*  Red = Growth Rate, Green = Substrate Consumption Rate,
Blue = Rate of Product, Purple = Rate of death*)
```



Task 2:

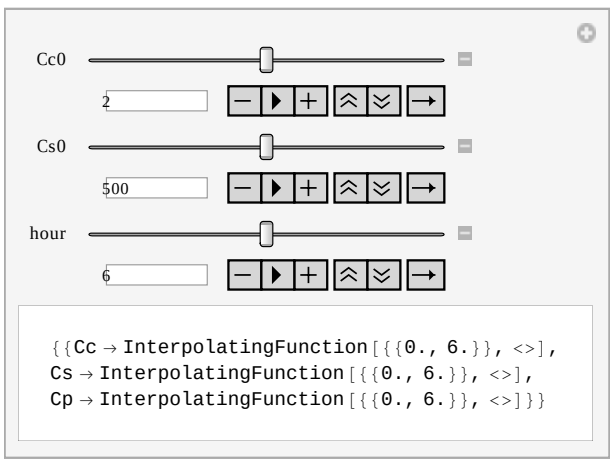
Plot the rates of (Equations 4.25, 4.26, 4.27, and 4.28) on the same graph.



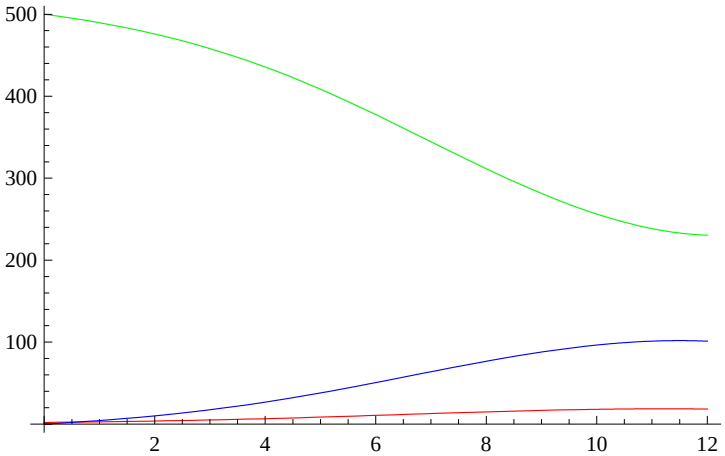
Task 3:

Manipulate these three variables to maximize product and minimize cost. Remember both yeast and corn cost money and each batch reaction has a set up cost.

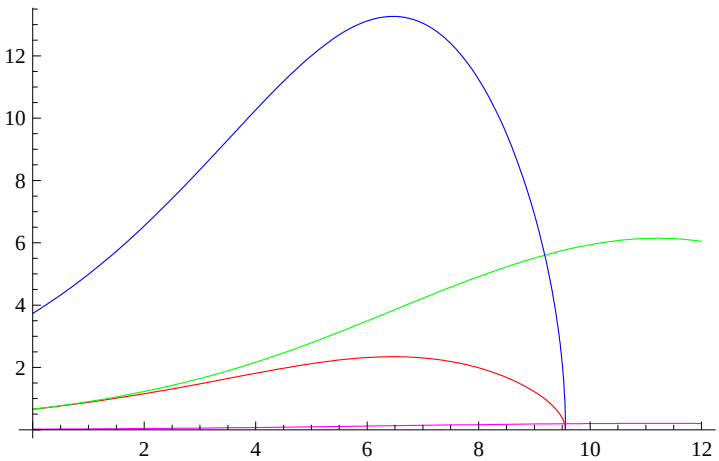
Out[7]=



Out[13]=



Out[14]=



Research cost of yeast, corn, and batch reaction to validate your model.

Task 4:

Research how much corn is required to make ethanol. Research how much fossil fuel is used to distill ethanol once the corn is at the distillery.

Task5:

Prepare an out-brief detailing your model and your considerations for an ethanol production plant given what you know about the math above and the information you know about the use of corn[7]. Answer the questions posed in Chapter 3.2.

[7]Bowman, GO ARMY! BEAT TERRORISM!

Time Line

Date	Ethanol Conversion
4 Dec 07, Tuesday, Day 1	Ben Cole Talk
5 Dec 07, Wednesday, Day	Introduction to Basic Model
6 Dec 07, Thursday, Day3	Model Development
7 Dec 07, Friday, Day 4	Interdisciplinary Day
10 Dec 07, Monday, Day 5	Model and Discipline Integration
11 Dec 07, Tuesday, Day 6	Model and Discipline Integration
12 Dec 07, Wednesday, Day 7	Presentation

Bibliography

[Fog92] Scott H. Fogler. *Elements of Chemical Reaction Engineering.* Prentice Hall, New Jersey, second edition, 1992.

[Pol06] Michael Pollan. *The Omnivoure's Dilema.* Penguin Press, New York, 2006.