#### Introduction:

It's not just for the so-called "hippies," the bleeding hearts, or the environmentalists marching and singing about saving the whales. Commonwealth Edison invests in renewable energy futures, British Petroleum has instituted a green technology division, Ford gave its dilapidated Rogue Factory a \$2 million eco-makeover. Environmental sustainability is now extremely profitable to corporations and their shareholders. The "dot-com" era left with the 20<sup>th</sup> century, and in its place companies have started going "green" to get "green". (This was totally preliminary... somewhere in here we need our real objective... I wrote my version of it, below)

Much environmental damage is caused by the extraction and use of fossil fuels (i.e. oil, coal, and natural gas). This IPRO sets out to find an alternative liquid fuel to power automotive vehicles, thus alleviating much of the stress placed on the environment.

Fossil fuels come from the long-term (millions of years) decomposition of plant and animal matter. These fossil fuels are the main source of energy (85%) used by Americans today to generate electricity, heat, and fuel transportation.<sup>1</sup> Another 8% comes from nuclear power and 7% from all other sources, mostly hydroelectric power and wood.<sup>2</sup> Figures 1 and 2 (see appendix) show in greater detail the breakdown of energy resources used as of 1995.<sup>3</sup> It is predicted that the nation's reliance on fossil fuels to power an expanding economy will increase over at least the next two decades even with aggressive development and deployment of new renewable and nuclear technologies. Fossil fuels cannot be replenished on a human time-scale once they are extracted and burned; hence they are a non-renewable resource. Fossil fuel processing plants suffer from high rates of atmospheric pollutant emissions.

In his 2003 State of the Union address, President Bush announced a \$1.2 billion initiative to reverse America's growing dependence on foreign oil by developing the technology for commercially viable hydrogen-powered fuel cells to power cars, trucks, homes, and businesses with no pollution or greenhouse gases.<sup>4</sup> As a consequence of economic, geopolitical and environmental issues, there is significant interest in the generation of transportation fuels and chemicals from renewable feedstocks. As crude oil prices rise, alternative energy technologies become more attractive economically. One exciting option for sustainable energy is the concept of a biorefinery, a process analogous to today's petroleum refineries that produce multiple fuels and products from crude oil. Realization of this vision requires application of engineering fundamentals to a thoroughly modern problem.

The methods for a renewable energy are not very efficient. Wind and solar power are not effective ways to gather energy since specific conditions must be met. Solar power was one of the earlier attempts to find a renewable energy source. There are some limitations associated with this process. The average power of the solar radiation incident on North America lies somewhere between 125 and 375 W/m<sup>2</sup>, between 3 and 9 kWh/m<sup>2</sup>/day.<sup>5</sup> However, this is only the maximum power that the sun produces. At any

<sup>&</sup>lt;sup>1</sup> U.S. Department of Energy, Fossil Energy. http://www.fossil.energy.gov/

<sup>&</sup>lt;sup>2</sup> One thousand links for learning how North America uses fossil fuels. http://www.bydesign.com/fossilfuels/links/

<sup>&</sup>lt;sup>3</sup> Fossil Fuels. http://www.umich.edu/~gs265/society/fossilfuels.htm

<sup>&</sup>lt;sup>4</sup> U.S. Department of Energy, Hydrogen & Other Clean Fuels.

http://www.fe.doe.gov/programs/fuels/index.html

<sup>&</sup>lt;sup>5</sup> Wikipedia. Solar Power. Retrieved April 28, 2006. http://en.wikipedia.org/wiki/Solar\_power

given time and place, the amount of sunlight received is limited. The best collectors today only have an efficiency of approximately 15%. The ability of solar collectors to provide sufficient energy is highly dependent on geographic location. The further from the equator the solar collectors are built, the less intense the sun-rays are and, consequently, the less power that can be extracted. Finally, the ability to gather power from the sun is seasonal dependent. In Iowa, a test was done to see how the seasons affected the collection of solor energy. It was found that, in the summer, the maxium amout of power was 280 Watt/m<sup>2</sup>, and in winter, the maxium was only 90 Watt/ m<sup>2</sup>.<sup>6</sup>

Wind energy also has a fair amount of limitations. Wind turbines can only be effectively used in rural areas. In order to create electricity, the wind must be traveling about twelve to fourteen miles per hour.<sup>7</sup> On a given wind farm, there are from one-hundred to five-hundred wind turbines. These turbines are only producing electricity if the wind is blowing so this is considered intermitted power. When chosing locations, one must pick a place where a region is most likely have strong winds and often. This severly limits where wind farms can be made.

A third type of energy, biomass, is a renewable resource derived from the carbonaceous waste of various human and natural activities. Biomass is pratically unlimited, and can be burned anywhere for fuel. It is not seasonal, and is, therefore, a perpetually available renewable source of energy that is far more reliable than wind or solar power. Unlike solar and wind power, biomass can be turned into liquid fuel when processed through a biorefinery. (this is an important point when comparing solar to wind, to water to biomass—only the latter is a liquid. Make sure you point this out in your presentation. Because really, it is unfair to compare them) Therefore, it is portable and is ideal for use as a transportation fuel. It is hoped that biologically-derived fuels (known as biofuels) can replace the use of petroleum-based gasoline and diesel in automotive vehicles.

The petroleum industry began with the successful drilling of the first commercial oil well in 1859 and the opening of the first refinery two years later.<sup>8</sup> (see table 1) The United States has nearly 150 refineries that can process anywhere between 5,000 and 500,000 barrels of oil per day.<sup>9</sup> Refining is the processing of one complex mixture of hydrocarbons into a number of other complex mixtures of hydrocarbons. Hydrocarbons are chain molecules that contain hydrogen and carbon structures. They come in various lengths from straight chains to branching chains to rings. Hydrocarbons contain a lot of energy and can take on many different forms. The major classes of hydrocarbons in crude oils include paraffins, aromatics, cycloalkanes, alkenes, dienes, and alkynes. The processing of crude oil into flammable gases and liquids at high temperatures and pressures requires considerable knowledge, control, and expertise. Crude oil, or petroleum, is the term for unprocessed oil. Crude oils vary in color from clear to tarblack, and in viscosity from water-like to almost solid. Crude oil is fractioned into liquefied petroleum gas, gasoline, kerosene, diesel oil, industrial fuel oil, lubricating oil,

<sup>&</sup>lt;sup>6</sup> Iowa Energy Center. Solar Energy. Retrieved April 28, 2006.

http://www.energy.iastate.edu/renewable/solar/

<sup>&</sup>lt;sup>7</sup> Colorado Wind Power Campaign. Wind Power Facts. Retrieved April 28, 2006. http://www.cogreenpower.org/Wind.htm

<sup>&</sup>lt;sup>8</sup> OHSA Technical Manual. Section IV: Chapter 2. Petroleum Refining Processes. http://www.osha.gov/dts/osta/otm/otm\_iv/otm\_iv\_2.html

<sup>&</sup>lt;sup>9</sup> U.S. Department of Energy. Efficiency and Renewable Energy.

http://www.eere.energy.gov/industry/petroleum\_refining/profile.html

paraffin wax, and asphalt.<sup>10</sup> (see figure 3) Distillation processes, thermal cracking processes, catalytic processes and treatment processes are used to achieve the desired product specifications. Certain refineries also produce feedstocks for the manufacture of lubricating oils and bituments. Other refineries manufacture coke. (this is hysterical, does this mean cocaine or coca cola or what?  $\odot$  ... these two sentences needs to be removed but they make me laugh) (also, this paragraph is just sitting here, can we say something like (at the beginning of the next paragraph), "biomass conversion processes are based on those of petroleum" or "are more efficient than petroleum" "or take at least 4 lines of cocaine before you can even begin to understand what is going on)

TIE IN There are two main methods used to convert biomass into synthetic gas: a thermo-chemical and a biological method. Although the biological route is highly therotical, the thermo-chemical method is coming into practice. Biological methods use bacterium to break down biomass into the necessary components to form ethanol. Most bacterium for basic yeast fermentation cannot yield the desired results or cannot survive in the harsh conditions to create the biofuel. According to the Department of Energy, lignocellulose-derived sugar streams pose significant technical barriers. They contain five sugars, the hexoses glucose, mannose, and galactose, as well as the pentoses D-xylose and L-arabinose.<sup>11</sup> Since some of these sugars contain five carbon structures, it is difficult for the bacterium to metabolize them. In addition, tolerance to harsh environments, including elevated temperatures, high salt, and low pH, will be essential. Currently available strains are severely limited in pentose utilization and exhibit poor hydrolysate tolerance.<sup>12</sup> Researches still have much more work to do in order to create a strain that can survive in the previously stated conditions and can also break down more complex hydrocarbons. Bioprocess engineers from South Korea have identified three possible technologies that will be required. "The biological process of ethanol fuel production utilizing lignocellulose as substrate requires: (1) delignification to liberate cellulose and hemicellulose from their complex with lignin, (2) depolymerization of the carbohydrate polymers (cellulose and hemicellulose) to produce free sugars, and (3) fermentation of mixed hexose and pentose sugars to produce ethanol<sup>13</sup>.

The thermo-chemical technique uses a gasifier in order to take the biomass and create a synthetic gas. "Integrated biomass gasification combined cycles can be used to generate synthesis gas that is primarily a mixture of hydrogen and carbon monoxide with traces of hydrocarbons and other impurities".<sup>14</sup> This gas can then be used to produce electricity or converted into transportation fuel. In order to convert syngas into useable fuel it must be cleaned of impurities before it is mixed with a catalyst. Biofuel type depends on the hydrogen to carbon monoxide ratio. The cyclic nature of the use of biofuels can be examined in figure 5 (um, I don't understand this cycle, how does the waste and byproducts get turned into animals—how do the animals get turned into

<sup>&</sup>lt;sup>10</sup> Wikipedia. The Free Encylopedia. http://en.wikipedia.org/wiki/Oil\_refining

<sup>&</sup>lt;sup>11</sup> US Department of Energy. Energy Efficiency and Renewable Energy. "Biological Conversion".

Retrieved April 27, 2006. http://eereweb.ee.doe.gov/biomass/biological\_conversion.html

<sup>&</sup>lt;sup>12</sup> US Department of Energy. Energy Efficiency and Renewable Energy. "Biological Conversion". Retrieved April 27, 2006. http://eereweb.ee.doe.gov/biomass/biological conversion.html

<sup>&</sup>lt;sup>13</sup> PubMed. Biological conversion of lignocellulosic biomass to ethanol. Retrieved April 28, 2006.

http://www.ncbi.nlm.nih.gov/entrez/query.fcgi?cmd=Retrieve&db=PubMed&list\_uids=9246788&dopt=Ab stract

<sup>&</sup>lt;sup>14</sup> National Renewable Energy Lab. Research Highlights—Thermochemical Conversion of Biomass. Retrieved April 28, 2006. http://mfnl.xjtu.edu.cn/gov-doe-nrel/chemistry\_bioenergy/thermochem.html

plants?... I know that is not what she is saying, but that is what it looks like from the chart). All the carbon dioxide that goes into the air from this process was already in the air, so there is no addition to hazardous greenhouse gases. (adam, you explained this to me once, can we do a better job here?)

The need for a renewable fuel is extremely pressing. The thermo-chemical process is ready to be put into practice, while the biological process is still being refined. Therefore, this IPRO team has chosen to use a thermo-chemical process, because it is more likely to give useable results.

#### **Biomass Selection:**

Biomass resources include primary, secondary, and tertiary sources of biomass. Primary biomass resources are produced directly by photosynthesis and are taken from the land. They include perennial short-rotation woody crops and herbaceous crops, the seeds of oil crops, and residues resulting from the harvesting of agricultural crops and forest trees (e.g. wheat straw, corn, and the tops, limbs and bark from trees). Secondary biomass resources result from the processing of primary biomass resources either physically (e.g. the production of sawdust in mills), chemically (e.g. black liquor from pulping processes) or biologically (e.g. manure production by animals). Tertiary biomass resources are post-consumer residue streams including animal fats and greases, used vegetable oils, packaging wastes, and construction and demolition debris.<sup>15</sup> Biomass can be used to produce transportation fuel, energy, heat, electric power, chemicals, and materials. The advantages and disadvantages of biomass can be found in table 3.

Wood is the largest source of bioenergy from a primary source and has been used to provide heat for thousands of years. With proper reforestation, wood is a renewable resource. Common wood wastes have various applications in industrial and consumer products such as thermal and electrical energy, wood flours, composite wood products, mulch, automotive materials, hog fuel, livestock bedding, house-pet bedding applications, as well as products for the environmental control industry.<sup>16</sup> Black liquor, a secondary biomass, is a recycled byproduct formed during the chemical pulping of wood in the papermaking industry. The U.S. forest paper/pulp manufacturing industry produces 4.6 billion gallons per year of renewable Fischer-Tropsch (FT) diesel, about 10% of the annual U.S. diesel demand.<sup>17</sup> A recent study by the American Forest & Paper Association's (AFPA) "Agenda 2020 Technology Alliance", showed that besides the diesel-range fuels resulting from gasification, another 1.9 billion gallons per year of cellulosic ethanol (for gasoline blending) emerges from the pulp/paper industry.<sup>3</sup> Black liquor gasification (BLG) also has the potential to create "green" renewable electric power, about 12,200 gigawatt-hours exported to the U.S. power grid. This is in addition to the 83,000 gigawatt-hours of avoided electricity consumption, by building Integrated Gasification Combined Cycle (IGCC) plants at pulp/paper mills.<sup>3</sup>

Corn is the most widely produced agricultural crop in the United States setting an all-time production record in 2005 of 11.8 billion bushels with an average yield of 160.4 bushels per acre.<sup>18</sup> Ethanol is a significant market for U.S. corn, consuming more than

<sup>&</sup>lt;sup>15</sup> Bioenergy Feedstock Information Network. <u>http://bioenergy.ornl.gov/main.aspx</u>

<sup>&</sup>lt;sup>16</sup> TechLine, Forest Products Laboratory, Wood Biomass for Energy. http://www.fpl.fs.fed.us

<sup>&</sup>lt;sup>17</sup> World Fuels Today, *Ten Percent U.S. Diesel From Pulp/Paper 'Black Liquor'*. (December 7, 2005) <u>http://www.worldfuels.com</u>

<sup>&</sup>lt;sup>18</sup> Corn Refiners Association Annual Report 2005, Corn Part of Our Daily Lives. <u>http://www.corn.org/CRAR2005.PDF</u>

1.2 billion bushels in 2004.<sup>19</sup> Ethanol production in 2005 approached 4 billion gallons, which translates into 14% of corn use.<sup>4</sup> Corn is also processed into a multitude of food and industrial products including sugars, syrups, chemicals, food oils, and human and animal consumption.<sup>20</sup>

For many centuries, animal manure has been used as a fertilizer in the U.S. for farming since it is rich in nitrogen and other nutrients that facilitate the growth of plants. The dried manure of animals (usually known as dung) has been used as fuel through history. On the Oregon Trail, pioneering families collected large quantities of "buffalo chips" in lieu of scarce firewood. It was used for many purposes, in cooking fires and to combat the cold desert nights.<sup>21</sup> Paper is also made from animal manure, this has been done with dung from elephants where it is a small industry in Africa and Asia.<sup>7</sup> The dung from horses, llamas, and kangaroos is also used to make paper. These animals are not ruminants so they tend to pass plant fibers undigested in their dung.

As stated above, there are many uses for wood waste/black liquor and corn in the U.S. but limited uses for animal manure (the only exception being fertilizer). Reaserch has indicated that as few as 6 counties in a farming state like Wisconsin could generate enough fuel from biomass to supply the IPRO's refinery with 500 tons of wet manure.<sup>22</sup> The maps shown in figures 6-11 display the number of tons of manure per animal unit (AU). An AU is calculated by multiplying the number of animals by an animal unit factor for the specific type of animal per county for 1997. Determination of the biorefinery location involved comparing the maps and locating areas of high animal density. Because it is easier to gasify manure of similar make up, and from the data it is clear that cows are the most prevalent livestock in the U.S., the swine and poultry data were eliminated from consideration (figures 9-10). Cows also produce the most manure per animal unit of any significant livestock population. Observation of figures 6-8 indicate that areas of high animal density are South Western Wisconson, Southwest Arizona, Western New Mexico, Southern California, South Eastern Oregon, Central Washington, and Western South Dakota. In an effort to keep the biorefinery applicable to Illinois, the biorefinery was modeled using Wisconson data. According to these maps, the summation of available manure (see table 3) implies a minimum of 717 tons for one county-far exceeding the minimum processing requirements for the model biorefinery.

Human feces was also explored as a possible biomass feedstock. In the United States, there are no practical uses for this material. The use of human excrement in agriculture as fertilizer is practiced in Eastern and Southern Asia.<sup>23</sup> People in these regions use human excrement as a fertilizer as opposed to animal manure. They use human excrement to control and eliminate diseases that had developed over time by using animal manure. In the U.S. human excrement is discarded into sewers and septic

<sup>&</sup>lt;sup>19</sup> National Corn Growers Association. <u>http://www.ncga.com/ethanol/main/index.asp</u>

<sup>&</sup>lt;sup>20</sup> Inglett, G.E. (ed.) 1970. *Corn: Culture, Processing, Products*. Avi Publishing Co., Westport, CN.

<sup>&</sup>lt;sup>21</sup> Wikipedia, The Free Encyclopedia. <u>http://en.wikipedia.org/wiki/Manure</u>

<sup>&</sup>lt;sup>22</sup> United States Department of Agriculture, *Manure Nutrients Relative to the Capacity of Cropland and* 

Pastureland to Assimilate Nutrients: Spatial and Temporal Trends for the United States <a href="http://www.nrcs.usda.gov/technical/land/pubs/manntr.pdf">http://www.nrcs.usda.gov/technical/land/pubs/manntr.pdf</a>

<sup>&</sup>lt;sup>23</sup> MacFarlane, Alan, *The use of Human Excrement in Agriculture* <u>http://www.alanmacfarlane.com/savage/dung.html</u>

systems.<sup>24</sup> Much of the discarded human excrement finds its final resting place in a landfill. Every time we flush the toilet, 3.3 gallons of drinkable water are degraded.<sup>25</sup> At 5.2 flushes per day (average), each of us presently degrades 6260 gallons of drinking water each year to flush away our 1300 pounds of excrement—that is 1.6 trillion gallons of water per year in the U.S.<sup>10</sup> Human feces, when kept out of the sewers, collected as a resource material, and properly processed (composted), makes a fine agricultural resource suitable for food crops.<sup>26</sup> Scientists in Thailand have produced a reactor that transforms human excrement into high quality fuel. At present, it costs twice as much to produce as petroleum-based diesel fuel.<sup>27</sup> The advantage is that, unlike the oil made in the Earth, the supply of ingredients for this people-derived fuel will never dry up.

According to the Chicago Water Reclamation Department, about 3.2 billion gallons of human excrement is processed per day in the city of Chicago. They produce about 180,000 dry tons per year which is about 500 dry tons per day. Research is still being conducted on human excrement especially on finding the chemical composition. The composition of human excrement is important in order to compare it to the composition of cow manure and see if the two can be combined for gasification purposes. **Gasification: the following is red because you should have the final version of this.** 

The process of gasification is where a fuel such as biomass, wood or coal is burned with limited oxygen at high temperatures. When the fuel goes under complete combustion the main products are water and carbon dioxide. During gasification the fuel does not under go complete combustion, so the main products are now carbon monoxide, hydrogen, carbon dioxide and water. <sup>28</sup> The gas that is produced is referred to as syn-gas and can be used for either combustion to produce electricity or fed into a FT reactor where larger hydrocarbons are formed. In this project the syn-gas will be fed into a FT reactor to produce the larger hydrocarbons for bio-gasoline and bio-diesel.

**Types of Gasification:** 

For coal the most common process uses lump coal in a vertical retort. The coal is fed through the top of the reactor with the air as the steam is fed through the bottom. The gas, air and steam rise up and react with the coal and convert it to a gas. The ash falls to the bottom where it is removed. The Winkler process uses a fluidized bed where finely powdered coal is agitated with the gases. There is also the Koppers-Totzek operates at a much higher temperature, and the powdered coal is reacted while it is entrained in the gases passing through the reactor. The ash is removed as a molten slag at the bottom of the reactor. Both of these processes are

<sup>&</sup>lt;sup>24</sup> History of Biosolids

http://biosolids.org/docs/history%20of%20biosolids.pdf

<sup>&</sup>lt;sup>25</sup> Rachel's Environment & Health Weekly #644, *Excrement Happens*. (April 1, 1999) <u>http://www.purewatergazette.net/excrementhappens.htm</u>

<sup>&</sup>lt;sup>26</sup> The Human Nutrient Cycle

http://weblife.org/humanure/chapter2\_1.html

<sup>&</sup>lt;sup>27</sup> BBC News, Fuel From Human Waste. <u>http://news.bbc.co.uk/1/hi/sci/tech/768672.stm</u>

<sup>&</sup>lt;sup>28</sup> Clark, E.L. "Trouble Times, Coal Gasification" 25 March 2006, http://www.zetatalk.com/energy/tengy11a.htm

being used for fuel gas production and in the generation of gases for chemical and fertilizer production. <sup>29</sup>

Using chicken litter as the biomass the basic operation is of a fixed bed reactor where the airflow is maintained constant and the fuel feed is adjusted to keep the height constant. The temperature reaches about 1500 °F. The syn-gas produced depends on the operating conditions, such as temperature, air flow rate and the condition of the biomass. The condition of the biomass is referring to the amount of surface area. Adding Na or K to the feed promotes agglomeration in the fuel bed which helps in the gasifying process. The composition of the syn-gas does not vary very much based on the different type of feed. The range of concentration for carbon monoxide varies between 23% and 30%, for hydrogen 4% to 7%, for carbon dioxide 3% to 9% and methane .3% to 1.4%. The gasification yields a low Btu gas. A main concern with chicken litter is the amount of ash produced during gasification. The ash needs to be removed from the syn-gas and then needs to be disposed of. This ash can not be used as land fill or fertilizer but needs to be treated because of the amount of K and P.<sup>30</sup>

Steam reforming gasification process uses steam instead of open air in order to produce a syn-gas composition with higher hydrogen content.<sup>31</sup> When animal waste is inserted into the gasifier, it is mixed with a sand-like bed in order to facilitate heat transfer. This mixture is then subjected to super heated steam. This will keep the bed fluidized, and break down the organic compounds in the animal waste into gases. The bed temperature is held at a temperature of about 1500 °F. This temperature is high enough to kill all pathogens, but is low enough to prevent the formation of dioxins. <sup>32</sup> The left over ash stays mixed with the bed material while the gas particles rise up to a separate chamber where it is cooled and eventually cleaned of contaminates. Steam, as opposed to open air, will keep the syn-gas from obtaining high nitrogen content. The H<sub>2</sub> to CO ratio is about 2.1. The complete break down of the syn-gas is: 41% H<sub>2</sub>, 20% CO, 21% CO<sub>2</sub>, 8% C<sub>2</sub>H<sub>2</sub>, 4% CH<sub>4</sub>, and 6% other. <sup>33</sup> This is the syn-gas composition after gas clean up. The syn-gas has an average energy value of 350 - 500 Btu per cubic foot.<sup>34</sup> One negative, as it relates to

<sup>&</sup>lt;sup>29</sup> Clark, E.L. "Trouble Times, Coal Gasification" 25 March 2006, http://www.zetatalk.com/energy/tengy11a.htm

<sup>&</sup>lt;sup>30</sup> Annamalai, K. Holtzapple, M.T. Mukhtar, S. Priyadarsan, S. Sweeten, J.M. "Fixed-Bed Gasification of Feedlot Manure and Poultry Litter Biomass" American Society of Agricultural Engineers, copyright 2004, Vol 47(5) pages 1689-1696 22 February 2006

<sup>&</sup>lt;sup>31</sup> Annamalai, K. Holtzapple, M.T. Mukhtar, S. Priyadarsan, S. Sweeten, J.M. "Fixed-Bed Gasification of Feedlot Manure and Poultry Litter Biomass" American Society of Agricultural Engineers, copyright 2004, Vol 47(5) pages 1689-1696 22 February 2006

<sup>&</sup>lt;sup>32</sup> Theo van Kempen. <u>Re-Cycle: A Profitable Swine Production System with Zero Waste</u>. 5 March 2006 <u>http://www.banffpork.ca/proc/2003pdf/17avanKempen.pdf</u>

<sup>&</sup>lt;sup>33</sup> J.B. Koger, G.A. Wossink, B.A. Kaspers, and T.A. van Kempen Department of Animal Science, NCSU, Raleigh, NC Department of Agricultural and Resource Economics, NCSU, Raleigh, NC. "BELT MANURE REMOVAL AND GASIFICATION SYSTEM TO CONVERT MANURE TO FUEL: THE "RE-CYCLE" SYSTEM". <u>North Carolina Pork Confrence</u>. 5 March 2006

<sup>&</sup>lt;sup>34</sup> J.B. Koger, G.A. Wossink, B.A. Kaspers, and T.A. van Kempen Department of Animal Science, NCSU, Raleigh, NC Department of Agricultural and Resource Economics, NCSU, Raleigh, NC. "BELT MANURE REMOVAL AND GASIFICATION SYSTEM TO CONVERT MANURE TO FUEL: THE "RE-CYCLE" SYSTEM". North Carolina Pork Confrence. 5 March 2006

the "green" aspect of the steam gasification process, is the ash resulting from the process is contaminated by the bed material. A magnesium bed was used in most of the trials done with steam reforming gasification, and the ash had a high concentration of magnesium. Therefore, in order for the ash to be a useable byproduct, it must be cleaned or an alternative bed material must be used.

For this project the fuel was chosen as biomass. After much consideration the biomass was narrowed down to cow manure. There are two different types of gasification of the cow manure that we considered. There is slagging and nonslagging, the difference is in the operating conditions and the phase of the ash. With the slagging, the syn-gas flows through a pebble bed filter, which is several layers of alumina spheres. The temperature is kept at about 1350-1400°C. At this temperature the ash is melted or softened and is collected in a sludge form through a slit and is quenched. The syn-gas molar composition is 26.9% carbon monoxide, 6.1% carbon dioxide, 17.1% hydrogen and 49.9% nitrogen. Has a heat value of 5.09x10^6 J/kg. There is a gross and net conversion efficiency of 83.5 and 66.1%. <sup>35</sup>

The non-slagging gasification which will be the one used for this IPRO has a temperature range of 800-900 °C, at this temperature the ash is kept dry in particle form. The fuel gas goes through a solid particulate removal device, known as an aerodynamic module. The syn-gas consists of 30.2% molar carbon monoxide, 5.5% carbon dioxide, 25.7% hydrogen and 38.6% nitrogen. Has a heat value of 7.14x10^6 J/kg. There is a gross and net conversion efficiency of 96.7 and 84.2%. The ash produced from this process can be used as land fill, fertilizer, and foam insulation and made into tiles.<sup>36</sup>

The animal biomass which contains a lot of moisture needs to be dried before it is fed into the gasifier. The cow manure is dried using a press to about 70% moisture, in which the liquid is separated from the solids. This type if drying prevents a large loss of volatile compounds. The liquid portion can then be used as fertilizer. The solid portion is then stored in a slurry tank. Then before the manure is fed into the gasifier it needs to be dried to about 5 to 10% moisture using heat recovered from the product-gas stream. <sup>37</sup> The manure is transported via ram pumps, pipes and conveyer belts depending on the moisture percentage. This is a basic flow sheet of the gasification process:

<sup>&</sup>lt;sup>35</sup> Lincoln Young, Carlson C.P. Pian "High-temperature, air-blown gasification of dairy-farm wastes for energy production" Elsevier Science Lst., Copyright 2003, Energy 28(2003) pages 655-672, 22 February 2006

<sup>&</sup>lt;sup>36</sup> Lincoln Young, Carlson C.P. Pian "High-temperature, air-blown gasification of dairy-farm wastes for energy production" Elsevier Science Lst., Copyright 2003, Energy 28(2003) pages 655-672, 22 February 2006

<sup>&</sup>lt;sup>37</sup> Lincoln Young, Carlson C.P. Pian "High-temperature, air-blown gasification of dairy-farm wastes for energy production" Elsevier Science Lst., Copyright 2003, Energy 28(2003) pages 655-672, 22 February 2006



Manure:	Carbon (wt %)	44.65
	Hydrogen	5.85
	Oxygen	38.18
	Nitrogen	2.05
	Sulfur	.31
	Ash	8.96
Ash:	Al <sub>2</sub> O <sub>3</sub> (wt %)	1.51
	CaO	32.13
	Fe <sub>2</sub> O <sub>3</sub>	.93
	MgO	9.84
	MnO	.17
	$P_2O_5$	13.04
	K <sub>2</sub> O	9.41
	SiO <sub>2</sub>	19.83
	Na <sub>2</sub> O	5.95
	SO <sub>3</sub>	5.57
	TiO <sub>2</sub>	.11
This gives a	alaan een gag aamn	esition of 20.20/ molor corbon monovide

This gives a clean syn-gas composition of 30.2% molar carbon monoxide, 5.5% carbon dioxide, 25.7% hydrogen and 38.6% nitrogen. <sup>38</sup> The operating conditions and the physical design are the next steps for our group.

Gas Clean-up: edited by me but no one changed it. So I left my questions in here.

The syngas produced by gasification of the biomass feedstock contains some unwanted constituents, in addition to the main products (Carbon Monoxide, Hydrogen, Carbon Dioxide and Water). Typical contaminants are: dust particles, organic compounds (e.g. Benzene, Toluene, Xylene, CH<sub>4</sub>, other light hydrocarbons), tars, ammonia, hydrogen sulfide (H<sub>2</sub>S), ash, and alkalis. These contaminants must be removed before the syngas is sent into the Fischer-Tropsch reactor to form bio-diesel.

<sup>&</sup>lt;sup>38</sup> Lincoln Young, Carlson C.P. Pian "High-temperature, air-blown gasification of dairy-farm wastes for energy production" Elsevier Science Lst., Copyright 2003, Energy 28(2003) pages 655-672, 22 February 2006

Tar is a mixture of numerous condensable hydrocarbons. Removal of this (corrosive, clog-forming?) substance is the first stage in the gas clean-up process. The tars are typically removed by either thermal or catalytic cracking, which involves breaking up the hydrocarbons. With catalytic cracking, the gas is passed through a chamber containing a Nickel (Ni) catalyst. This breaks down the hydrocarbons to a mixture of Hydrogen (H<sub>2</sub>) and carbon monoxide (CO). There are a number of crackers designed for this purpose; the most efficient of them is the Reverse Flow Catalytic Tar Converter (RFCTC). The gas enters the chamber at about  $350^{\circ}$ C –  $650^{\circ}$ C, and the entrance of the chamber is heated to about 900°C to  $950^{\circ}$ C (temperatures favorable for cracking).<sup>39</sup> In the mid-section of the converter, the gas is exposed to the Nickel catalyst, and steam reforming reactions take place. This is a highly endothermic (i.e. heat absorbing---is that correct? I added it.) process in which almost all of the ammonia is removed. To counter temperature drop during the reactions, a stream of air, which is roughly 5% of the flow of the product gas, is fed into the reactor. The general formula for the steam reforming process is as follows:

 $C_nH_m + nH_20 \rightarrow nCO + (1/2 m + n)H_2^{40}$ 

Another efficient tar removal process utilizes the OLGA, a gas cleaning unit designed for the removal of tars from syngas. With the OLGA technology, the gas is scrubbed with a special liquid to remove both heavy and light tars. The tar-laden liquid is then passed through a gas which strips the tar from the liquid. The stripper gas is then routed back into the gasifier for thermal destruction of the tar. Figures from the Energy Research Center of the Netherlands (ECN) show that 90% phenol, ~50% Benzene, 99% Xylenes (are these types of tars?) are removed from biomass syngas streams.<sup>41</sup>

Next, alkaline metal oxides and dust and ash particles are removed. The metal oxides are condensed at 550°C which causes them to stick to dust and other particulate impurities present.<sup>42</sup> They are then removed with these particles. Different approaches are taken to accomplish this depending on particle size and type.

A cyclone separator removes large particles. In a typical cyclone separator, the gas enters the top of the cylindrical chamber tangentially. This causes a downward spiral flow. The conical shape at the top of the vessel causes the radius of the spiral to reduce until the gas spins up the center and through an outlet at the top. While spinning, the centrifugal force generated, throws the particles to the outer walls of the chamber and they move down to a receptacle at the bottom of the separator. This is only effective in removing particles 50 microns or larger in diameter.<sup>43</sup>

Bag filters are used to remove even smaller particles ( $\leq 0.1$  microns). The 'dusty' syngas enters the chamber where particles stick to the filtration elements in the bags. A reverse pulse-jet (what is a pulse-jet? Do you mean a reverse-pulse jet?) of air is

<sup>&</sup>lt;sup>39</sup> Biomass Technology Group (BTG) http://www.btgworld.com/technologies/tar-removal.html

<sup>&</sup>lt;sup>40</sup> Biomass Technology Group (BTG)

http://www.btgworld.com/technologies/tar-removal.html

<sup>&</sup>lt;sup>41</sup> Energy Research Center of the Netherlands (ECN)

http://www.ecn.nl/en/bkm/products-services/experimental-facilities/olga/

<sup>&</sup>lt;sup>42</sup> Dr Adrej Stergarsek, Institute Ljubljana, Slovenia. <u>Cleaning of Syngas Derived From Waste and Biomass</u> <u>Gasification/Pyrolysis for Storage or Direct Use for Electricity Production</u> 11 October 2004

http://prewin.jrc.nl/kosice2004/pres/Monday/Andrej%20Stergarsek.pdf

<sup>&</sup>lt;sup>43</sup> 3L Filters LTD

www.3lfilters.com

sent through the bags intermittently to extricate the accumulated particles. A pump pulls the gas out of the chamber.

Particles not removed by the cyclone separator or the bag filter are removed by either wet or dry scrubbing. Wet scrubbers remove primarily particulate impurities but can also reduce gaseous contaminants. Conversely, dry scrubbing removes unwanted gaseous compounds only. In each case, there is a reagent that removes specific contaminants by absorbing, adsorbing, or dissolving them.

Using dry scrubbing with adsorption, the reagent is ground into very fine particles. It is then fluidized in the adsorption chamber where it flows in opposite direction to the gas stream. The syngas is forced through a nozzle to increase the speed of the syngas and increase the probability of gas-reagent contact<sup>44</sup>. After the adsorption, the gas is passed through bag filters to remove the reagent particles entrained in the stream.

In a dry spray absorber, the reagent is made into slurry and atomized (divided into small droplets). It is then allowed to fall through the absorption chamber containing the syngas. The impurities are absorbed by the reagent as it falls. It is imperative that the residence time in the chamber is long enough for reagent to evaporate so the slurry does not stick to the vessel walls.

A wet spray tower is fitted with spray nozzles. The dirty syngas is directed up the tower while the reagent liquid is sprayed into it. The contaminants are then absorbed by the liquid droplets as the gas flows through. Cleaned gas exits the chamber with little or no static pressure drop from inlet to outlet.<sup>45</sup> So, are all of these processes used in our model? If not, which ones were used?

Contaminant	Scrubbing reagent
HCl + H2S	NaOH
NH3 + HCN	H2SO4 or Sulfinol D
H2S + COS	Sulfinol D

Table showing contaminants and scrubbing reagents.<sup>46</sup>

Fischer-Tropsch section:

Conversion of the syngas into the final products occurs in the Fischer-Tropsch (FT) reactor. Syngas, in the form of carbon monoxide, hydrogen gas, and various impurities, reacts in the presence of a catalyst to form chains of hydrocarbons. The hydrocarbon chain lengths are measured by the number of carbons in the chain. The hydrocarbons produced in FT reactors range in length from CH4, which is methane, to C50 (i.e. a fifty carbon chain). These hydrocarbons are transformed into useful products

<sup>46</sup> Dr Adrej Stergarsek, Institute Ljubljana, Slovenia. <u>Cleaning of Syngas Derived From Waste and Biomass</u> <u>Gasification/Pyrolysis for Storage or Direct Use for Electricity Production</u> 11 October 2004 <u>http://prewin.jrc.nl/kosice2004/pres/Monday/Andrej%20Stergarsek.pdf</u>

<sup>&</sup>lt;sup>44</sup> U.S. Environmental Protection Agency. <u>Introduction to Baseline Source Inspection Techniques</u>. <u>http://yosemite1.epa.gov/oaqps/eogtrain.nsf/DisplayView/SI\_445\_0-5?OpenDocument</u>

<sup>&</sup>lt;sup>45</sup> U.S. Environmental Protection Agency. <u>Introduction to Baseline Source Inspection Techniques</u>. <u>http://yosemite1.epa.gov/oaqps/eogtrain.nsf/DisplayView/SI\_445\_0-5?OpenDocument</u>

which are intended to compete with hydrocarbons formed from crude oil. Therefore, the economic viability of the project is highly dependent on the price of crude oil.<sup>47</sup>

Biodiesel, formed from these hydrocarbons, is a relatively environmentally benign liquid fuel option. This is because the diesel produced via an FT reaction does not contain all of the pollutants of typical crude-derived diesel. Also, the diesel derived from an FT reaction has a high cetane number<sup>48</sup>. The cetane number is a measure of the fuel's combustion quality.<sup>49</sup> Generally speaking, the higher the cetane number, the better the fuels combustion quality. Diesel fuels must meet a minimum cetane number to be used in an engine, depending on engine type. As a result, diesel fuels with low cetane numbers are not very marketable. FT diesel created in a biorefinery can be blended with low cetane diesel derived from crude oil, making this product more marketable, although not as environmentally friendly as pure biodiesel. It is also worth noting that having excessively very high cetane number does not provide much benefit, as long as it is above the minimum.

In addition to diesel, other products are produced via an FT reaction. This occurs because the exact length and shape of the hydrocarbon chain cannot be controlled. This results in the production of a large number of extraneous hydrocarbon chains. Hydrocarbons that can be used to produce commercially viable products will be separated out and sold. Any other hydrocarbons that cannot be sold will either be recycled to change the chain length or they will be burned to produce heat for electricity.

There are currently four different types of FT reactors in commercial use. These are the Sasol Circulating Fluidized Bed Reactor, the Sasol Advanced Synthol Reactor, the Tubular Fixed Bed reactor, and the Sasol Slurry Phase Distillate Reactor.<sup>50</sup> The first two reactors are operated at high temperatures (320 °C -350°C) and are thus called HTFT reactors. The latter two are operated at lower temperatures (220 °C -250°C) and are called LTFT reactors. The Tubular Fixed Bed reactor was chosen based on the availability of kinetics for the model.

The FT reactors depend on catalysts which vary according to the model, products desired, and syngas purity. The only metals with sufficient activities for use in an FT reaction are iron, cobolt, nickle and ruthenium.<sup>51</sup> Ruthenium can be eliminated immediately as a potential catalyst based on price and availability. Nickel is also undesirable as it produces too much methane, which lowers the yield of the FT reaction. This leaves cobalt and iron as the only two catalyst options. Cobalt has a high activity and consequently has a higher per pass yield. However, cobalt is significantly more expensive than iron and as such it is more costly to replace should the catalyst become poisoned or fouled. After investigating the benefits of both Cobalt and Iron catalyst in the FT reactor, it was concluded that the higher yield of the Cobalt catalyst did not compensate for the higher yield it produced and hence, Iron is the better choice.

With the reactor type and the catalyst chosen, a full model of the reactor was modeled in MATLAB which is easily converted into either C++ or Fortran. The raw

<sup>&</sup>lt;sup>47</sup> Fischer-Tropsch Technology, Steynberg, A.J. and Dry, Mark. Elsevier BV, Amsterdam, Netherlands. 2004. pg3

<sup>&</sup>lt;sup>48</sup> Ibid. pg3

<sup>&</sup>lt;sup>49</sup> <u>http://www.answers.com/topic/cetane-number</u>, April 3, 2006

<sup>&</sup>lt;sup>50</sup> Fischer-Tropsch Technology, Steynberg, A.J. and Dry, Mark. Elsevier BV, Amsterdam, Netherlands. 2004., pg 65

<sup>&</sup>lt;sup>51</sup> Ibid pg 533.

code was then put into the chemical engineering program HYSYS. The FT reactor was then optimized and connected to the rest of the project and the final product separated.

## Appendix A: Figures



Figure 1



Figure 2



Figure 3



Figure 4 Refinery process chart<sup>8</sup>



Figure 5



Figure 6 Map 10: Animal units for confined fattened cattle, 1997<sup>52</sup>



<sup>&</sup>lt;sup>52</sup> United States Department of Agriculture, *Manure Nutrients Relative to the Capacity of Cropland and* 

Pastureland to Assimilate Nutrients: Spatial and Temporal Trends for the United States http://www.nrcs.usda.gov/technical/land/pubs/manntr.pdf



Figure 7 Map 12: Animal units for confined milk cows, 1997<sup>52</sup>

Figure 8 Map 14: Animal units for confined other beef and dairy cattle, 1997<sup>52</sup>



Figure 9 Map 16: Animal units for confined swine, 1997<sup>52</sup>



Figure 10 Map 18: Animal units confined poultry, 1997<sup>52</sup>



Figure 11 Map 7: Animal units for confined livestock, 1997<sup>52</sup>

Year	Process name	Purpose	By-products, etc.
1862	Atmospheric distillation	Produce kerosene	Naphtha, tar, etc.
1870	Vacuum distillation	Lubricants (original) Cracking feedstocks (1930's)	Asphalt, residual coker feedstocks
1913	Thermal cracking	Increase gasoline	Residual, bunker fuel
1916	Sweetening	reduce sulfur & odor	Sulfur
1930	Thermal reforming	Improve octane number	Residual
1932	Hydrogenation	Remove sulfur	Sulfur
1932	Coking	Produce gasoline basestocks	Coke
1933	Solvent extraction	Improve lubricant viscosity index	Aromatics
1935	Solvent dewaxing	Improve pour point	Waxes
1935	Cat. polymerization	Improve gasoline yield & octane number	Petrochemical feedstocks
1937	Catalytic cracking	Higher octane gasoline	Petrochemical feedstocks
1939	Visbreaking	reduce viscosity	Increased distillate,tar
1940	Alkylation	Increase gasoline octane & yield	High-octane aviation gasoline
1940	Isomerization	Produce alkylation feedstock	Naphtha
1942	Fluid catalytic cracking	Increase gasoline yield & octane	Petrochemical feedstocks
1950	Deasphalting	Increase cracking feedstock	Asphalt
1952	Catalytic reforming	Convert low-quality naphtha	Aromatics
1954	Hydrodesulfurization	Remove sulfur	Sulfur
1956	Inhibitor sweetening	Remove mercaptan	Disulfides
1957	Catalytic isomerization	Convert to molecules with high octane number	Alkylation feedstocks
1960	Hydrocracking	Improve quality and reduce sulfur	Alkylation feedstocks
1974	Catalytic dewaxing	Improve pour point	Wax
1975	Residual hydrocracking	Increase gasoline yield from residual	Heavy residuals

### Appendix B: Tables

			OF PETROLEUM R		
Process name	Action	Method	Purpose	Feedstock(s)	Product(s)
FRACTIONATION I	PROCESSES				
Atmospheric distillation	Separation	Thermal	Separate fractions	Desalted crude oil	Gas, gas oil, distillate, residual
Vacuum distillation	Separation	Thermal	Separate w/o cracking	Atmospheric tower residual	Gas oil, lube stock, residual
CONVERSION PRO	CESSEDDEC	OMPOSITIC	N		
Catalytic cracking	Alteration	Catalytic	Upgrade gasoline	Gas oil, coke distillate	Gasoline, petrochemical feedstock
Coking	Polymerize	Thermal	Convert vacuum residuals	Gas oil, coke distillate	Gasoline, petrochemical feedstock
Hydro-cracking	Hydrogenate	Catalytic	Convert to lighter HC's	Gas oil, cracked oil, residual	Lighter, higher- quality products
*Hydrogen steam reforming	Decompose	Thermal/ catalytic	Produce hydrogen	Desulfurized gas, O <sub>2</sub> , steam	Hydrogen, CO, CO <sub>2</sub>
*Steam cracking	Decompose	Thermal	Crack large molecules	Atm tower hvy fuel/ distillate	Cracked naphtha, coke, residual
Visbreaking	Decompose	Thermal	reduce viscosity	Atmospheric tower residual	Distillate, tar
CONVERSION PRO	CESSESUNIF	FICATION			
Alkylation	Combining	Catalytic	Unite olefins & isoparaffins	Tower isobutane/ cracker olefin	Iso-octane (alkylate)
Grease compounding	Combining	Thermal	Combine soaps & oils	Lube oil, fatty acid, alky metal	Lubricating grease
Polymerizing	Polymerize	Catalytic	Unite 2 or more olefins	Cracker olefins	High-octane naphtha, petrochemical stocks
CONVERSION PRO	CESSESALTI	ERATION O	R REARRANGEMEN	NT	
Catalytic reforming	Alteration/ dehydration	Catalytic	Upgrade low-octane naphtha	Coker/ hydro- cracker naphtha	High oct. Reformate/ aromatic
Isomerization	Rearrange	Catalytic	Convert straight chain to branch	Butane, pentane, hexane	Isobutane/ pentane/ hexane
TREATMENT PROC	CESSES				
*Amine treating	Treatment	Absorption	Remove acidic contaminants	Sour gas, HCs w/CO <sub>2</sub> & H <sub>2</sub> S	Acid free gases & liquid HCs
Desalting	Dehydration	Absorption	Remove contaminants	Crude oil	Desalted crude oil

Drying & sweetening	Treatment	Abspt/ therm	Remove H <sub>2</sub> O & sulfur cmpds	Liq Hcs, LPG, alky feedstk	Sweet & dry hydrocarbons
*Furfural extraction	Solvent extr.	Absorption	Upgrade mid distillate & lubes	Cycle oils & lube feed-stocks	High quality diesel & lube oil
Hydrodesulfurization	Treatment	Catalytic	Remove sulfur, contaminants	High-sulfur residual/ gas oil	Desulfurized olefins
Hydrotreating	Hydrogenation	Catalytic	Remove impurities, saturate HC's	Residuals, cracked HC's	Cracker feed, distillate, lube
*Phenol extraction	Solvent extr.	Abspt/ therm	Improve visc. index, color	Lube oil base stocks	High quality lube oils
Solvent deasphalting	Treatment	Absorption	Remove asphalt	Vac. tower residual, propane	Heavy lube oil, asphalt
Solvent dewaxing	Treatment	Cool/ filter	Remove wax from lube stocks	Vac. tower lube oils	Dewaxed lube basestock
Solvent extraction	Solvent extr.	Abspt/ precip.	Separate unsat. oils	Gas oil, reformate, distillate	High-octane gasoline
Sweetening	Treatment	Catalytic	Remv H <sub>2</sub> S, convert mercaptan	Untreated distillate/gasoline	High-quality distillate/gasoline

 Table 2 Overview of petroleum refining processes<sup>8</sup> \* Note: These processes are notdepicted in the refinery process flow chart.

Advantages	Disadvantages
Renewable	Land use
Solid, gaseous or liquid	Low energy density
	Water and fertilizers
Indiginous fuels and technology	required
	Complex management
Zero atmospheric addition	systems
Creates jobs	Bulk transportation
Residue usage	Pest/weather vulnerability
	Technical and resource
Financial benefit	variability
Low sulfur dioxide, nitrogen oxide, and carbon	
emissions	Residue handling
Minimal amounts of sulfur and metals	
Minimal ash	
Available throughout the world	
	53.54

 Table 3 Advantages and disadvantages of biomass<sup>53,54</sup>

 <sup>&</sup>lt;sup>53</sup> TechLine, Forest Products Laboratory, *Wood Biomass for Energy*. <u>http://www.fpl.fs.fed.us</u>
 <sup>54</sup> <u>http://www.netcentral.co.uk/eclectic/eecoenv/lecture2.html</u>

# Table 2B Table 8: Parameters used to calculate the quantity of manure and manure nutrients for the 16 livestock categories<sup>55</sup>

Livestock category	Tons of manure per animal unit per year as excreted	Pounds of ni of man As excreted	trogen per ton 1re* After losses	Pounds of per ton of As excreted	
Fattened cattle	10.59	10.98	4.39	3.37	2.86
Milk cows	15.24	10.69	4.30	1.92	1.65
Other beef and dairy					
Beef calves, from calving to about 500 pounds	11.32	8.52	2.56	2.33	1.98
Beef heifers for replacement herds	12.05	6.06	1.82	1.30	1.10
Beef breeding herds (cows and bulls)	11.50	10.95	3.30	3.79	3.23
Beef stockers and grass fed beef	11.32	8.52	2.56	2.33	1.98
Dairy calves, from calving to about 500 pounds	s 12.05	6.06	1.82	1.30	1.10
Dairy heifers for replacement herds	12.05	6.06	1.82	1.30	1.10
Dairy stockers and grass fed animals marketed as beef	l 12.05	6.06	1.82	1.30	1.10
Swine					
Breeding hogs	6.11	13.26	3.32	4.28	3.62
Hogs for slaughter	14.69	11.30	2.82	3.29	2.80
Poultry					
Chickens, layers	11.45	26.93	18.46	9.98	8.50
Chickens, pullets	8.32	27.20	13.60	10.53	8.95
Chickens, broilers	14.97	26.83	16.10	7.80	6.61
Turkeys for breeding	9.12	22.41	11.20	13.21	11.23
Turkeys for slaughter	8.18	30.36	16.18	11.83	10.06

Includes nitrogen and phosphorus in urine.
 Note: Values in this table are the same as those previously published by Lander, Moffitt, and Alt (1998).

<sup>&</sup>lt;sup>55</sup> United States Department of Agriculture, Manure Nutrients Relative to the Capacity of Cropland and

Pastureland to Assimilate Nutrients: Spatial and Temporal Trends for the United States http://www.nrcs.usda.gov/technical/land/pubs/manntr.pdf

	Animal Units (AU) per	Manure	tons Manure per County	Dried Manure per County	Availability per Day Assuming
Cattle	County	per AU	per Year	per Year	260 days
Confined					
Fattened	-	10 50			
Cattle	5000	10.59	52950	6354	24.4
Confined Milk	-		-		
Cows	5000	15.24	76200	9144	35.2
Other Beef					
and Dairy	-			60.00	
Cattle	5000	11.5	57500	6900	26.5
Totals	15000	37.33	186650	22398	86.1
			1	-	1
Other Sources					
Confined					
Swine	5000	14.69	73450	8814	33.9
Confined					
Poultry	5000	10	50000	6000	23.1
Totals	10000	24.69	123450	14814	57.0
			1		1
	We need				
	to use				
	COW				
	manure				
Conclusion	from	6	Counties		
				7	
			Using	1	
			Mixed		
OR		3	Manure		

 Table 3B Worst Case Scenario Manure Data for South Western Wisconsin<sup>15</sup>



Figure 1



Figure 2



Figure 3



Figure 4 Refinery process chart<sup>8</sup>





Table 1 History of Refining

TABLE IV: 2-1. HISTORY OF REFINING						
Year	Process name	Purpose	By-products, etc.			
1862	Atmospheric distillation	Produce kerosene	Naphtha, tar, etc.			
1870	Vacuum distillation	Lubricants (original) Cracking feedstocks (1930's)	Asphalt, residual coker feedstocks			
1913	Thermal cracking	Increase gasoline	Residual, bunker fuel			
1916	Sweetening	reduce sulfur & odor	Sulfur			
1930	Thermal reforming	Improve octane number	Residual			
1932	Hydrogenation	Remove sulfur	Sulfur			
1932	Coking	Produce gasoline basestocks	Coke			
1933	Solvent extraction	Improve lubricant viscosity index	Aromatics			
1935	Solvent dewaxing	Improve pour point	Waxes			

T.				
	1935	Cat. polymerization	Improve gasoline yield & octane number	Petrochemical feedstocks
	1937	Catalytic cracking	Higher octane gasoline	Petrochemical feedstocks
	1939	Visbreaking	reduce viscosity	Increased distillate,tar
	1940	Alkylation	Increase gasoline octane & yield	High-octane aviation gasoline
	1940	Isomerization	Produce alkylation feedstock	Naphtha
	1942	Fluid catalytic cracking	Increase gasoline yield & octane	Petrochemical feedstocks
	1950	Deasphalting	Increase cracking feedstock	Asphalt
	1952	Catalytic reforming	Convert low-quality naphtha	Aromatics
	1954	Hydrodesulfurization	Remove sulfur	Sulfur
	1956	Inhibitor sweetening	Remove mercaptan	Disulfides
	1957	Catalytic isomerization	Convert to molecules with high octane number	Alkylation feedstocks
	1960	Hydrocracking	Improve quality and reduce sulfur	Alkylation feedstocks
	1974	Catalytic dewaxing	Improve pour point	Wax
	1975	Residual hydrocracking	Increase gasoline yield from residual	Heavy residuals
-				

Table 2 Overview of petroleum refining processes<sup>8</sup>

TABLE IV:2-3. OVERVIEW OF PETROLEUM REFINING PROCESSES.

Process name	Action	Method	Purpose	Feedstock(s)	Product(s)
FRACTIONATION F	PROCESSES				
Atmospheric distillation	Separation	Thermal	Separate fractions	Desalted crude oil	Gas, gas oil, distillate, residual
Vacuum distillation	Separation	Thermal	Separate w/o cracking	Atmospheric tower residual	Gas oil, lube stock, residual
CONVERSION PRO	CESSEDDEC	OMPOSITIC	N		
Catalytic cracking	Alteration	Catalytic	Upgrade gasoline	Gas oil, coke distillate	Gasoline, petrochemical feedstock
Coking	Polymerize	Thermal	Convert vacuum residuals	Gas oil, coke distillate	Gasoline, petrochemical feedstock
Hydro-cracking	Hydrogenate	Catalytic	Convert to lighter HC's	Gas oil, cracked oil, residual	Lighter, higher- quality products
*Hydrogen steam reforming	Decompose	Thermal/ catalytic	Produce hydrogen	Desulfurized gas, O <sub>2</sub> , steam	Hydrogen, CO, CO <sub>2</sub>
*Steam cracking	Decompose	Thermal	Crack large molecules	Atm tower hvy fuel/ distillate	Cracked naphtha, coke, residual
Visbreaking	Decompose	Thermal	reduce viscosity	Atmospheric tower residual	Distillate, tar
CONVERSION PRO	CESSESUNIF	ICATION			
Alkylation	Combining	Catalytic	Unite olefins & isoparaffins	Tower isobutane/ cracker olefin	Iso-octane (alkylate)
Grease compounding	Combining	Thermal	Combine soaps & oils	Lube oil, fatty acid, alky metal	Lubricating grease
Polymerizing	Polymerize	Catalytic	Unite 2 or more olefins	Cracker olefins	High-octane naphtha, petrochemical stocks
CONVERSION PRO	CESSESALTE	RATION O	R REARRANGEMEN	NT	
Catalytic reforming	Alteration/ dehydration	Catalytic	Upgrade low-octane naphtha	Coker/ hydro- cracker naphtha	High oct. Reformate/ aromatic
Isomerization	Rearrange	Catalytic	Convert straight chain to branch	Butane, pentane, hexane	Isobutane/ pentane/ hexane
TREATMENT PROC	CESSES				
*Amine treating	Treatment	Absorption	Remove acidic contaminants	Sour gas, HCs w/CO <sub>2</sub> & H <sub>2</sub> S	Acid free gases & liquid HCs
Desalting	Dehydration	Absorption	Remove contaminants	Crude oil	Desalted crude oil
Drying &	Treatment	Abspt/	Remove H <sub>2</sub> O &	Liq Hcs, LPG, alky	Sweet & dry

sweetening		therm	sulfur cmpds	feedstk	hydrocarbons
*Furfural extraction	Solvent extr.	Absorption	Upgrade mid distillate & lubes	Cycle oils & lube feed-stocks	High quality diesel & lube oil
Hydrodesulfurization	Treatment	Catalytic	Remove sulfur, contaminants	High-sulfur residual/ gas oil	Desulfurized olefins
Hydrotreating	Hydrogenation	Catalytic	Remove impurities, saturate HC's	Residuals, cracked HC's	Cracker feed, distillate, lube
*Phenol extraction	Solvent extr.	Abspt/ therm	Improve visc. index, color	Lube oil base stocks	High quality lube oils
Solvent deasphalting	Treatment	Absorption	Remove asphalt	Vac. tower residual, propane	Heavy lube oil, asphalt
Solvent dewaxing	Treatment	Cool/ filter	Remove wax from lube stocks	Vac. tower lube oils	Dewaxed lube basestock
Solvent extraction	Solvent extr.	Abspt/ precip.	Separate unsat. oils	Gas oil, reformate, distillate	High-octane gasoline
Sweetening	Treatment	Catalytic	Remv H <sub>2</sub> S, convert mercaptan	Untreated distillate/gasoline	High-quality distillate/gasoline

\* Note: These processes are not depicted in the refinery process flow chart.