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Systems Analysis and Futuristic Designs of Advanced Biofuel Factory Concepts

James Leathers, Mathias Celina, Russ Chianelli, Steven Thoma, and Vipin Gupta

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Abstract

The U.S. is addicted to petroleum—a dependency that periodically shocks the economy, compromises national security, and adversely affects the environment. If liquid fuels remain the main energy source for U.S. transportation for the foreseeable future, the system solution is the production of new liquid fuels that can directly displace diesel and gasoline. This study focuses on advanced concepts for biofuel factory production, describing three design concepts: biopetroleum, biodiesel, and higher alcohols. A general schematic is illustrated for each concept with technical description and analysis for each factory design. Looking beyond current biofuel pursuits by industry, this study explores unconventional feedstocks (*e.g.*, extremophiles), out-of-favor reaction processes (*e.g.*, radiation-induced catalytic cracking), and production of new fuel sources traditionally deemed undesirable (*e.g.*, fusel oils). These concepts lay the foundation and path for future basic science and applied engineering to displace petroleum as a transportation energy source for good.

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The Problem

The U.S. is addicted to petroleum—a dependency that periodically shocks the economy, compromises national security, and adversely affects the environment.

Oil market disruptions have cost the U.S. economy approximately \$7 trillion over the past 30 years (Greene and Tishchishyna 2000).¹ Major oil price spikes have occurred five times (1973–74, 1979–80, 1990–91, 1999–2000, 2005 to present), with the first four oil price spikes contributing to economic recession in the U.S. (Davis and Diegel 2006).

Transportation is key to petroleum dependency because transportation vehicles account for 68% of U.S. oil consumption and nearly all of the high-value light products that drive the market (Davis and Diegel 2006). In 2005, the petroleum share of the transportation sector in the U.S. was 97.5% (Energy Information Administration 2005a). The lack of alternative transportation fuels and absence of revolutionary advances in vehicle fuel efficiency has made the U.S. unable to rapidly change the transportation fuel economy.

In the U.S., the combination of growing transportation demand and decreasing U.S. petroleum production is resulting in steady increases in foreign oil imports (Gross 2002). Consequently, the U.S. is increasingly dependent upon foreign nations to supply the majority of the petroleum it consumes each day.

In 2004, the twelve leading oil exporting countries each shipped at least 1.34 million barrels per day.² Of these twelve countries, five present immediate concern to future supply stability. Nigeria has been overwhelmed by civil strife and corruption. In 2006, militants declaring war on President Olusegun Obasanjo, forced Shell to halt 455,000 barrels a day of oil production, 19 percent of Nigeria's output (Mahtani 2006). The war in Iraq has reduced Iraq's oil production by 26%.³ Iran is in conflict with the U.S. over nuclear technology development and Venezuela is an outspoken critic of U.S. foreign policy. These conflicts periodically spook the oil markets, resulting in higher oil prices. Lastly, the Saudi Arabian government, the top oil exporter in the world, is besieged by domestic terrorism and extremism, which makes the country vulnerable to overthrow.

In addition to terrorist threats, natural disasters have disrupted petroleum supplies. In 2005, Hurricanes Katrina and Rita destroyed or extensively damaged 212 oil platforms or rigs (Office of Electricity Delivery and Energy Reliability 2005). This decimated two thirds of the total gulf coast oil production for a minimum of ten weeks following the hurricanes (Minerals Management Service 2005). These hurricanes also forced oil refinery shutdowns that resulted in a loss of 367,000 barrels per day for a minimum of three months following the disasters (Energy Information Administration 2005b).

¹Estimates made in present value 1998 dollars.

² The U.S. is the largest crude oil importer in the world at 12.1 million barrels per day.

³ Reduction based on oil production for 1998-2002 compared to oil production for 2003-2005.

Environmental concerns associated with petroleum emissions also mount as petroleum consumption continues to rise. The key global concern is the amount of anthropogenic carbon dioxide emitted into the atmosphere by fossil fuel combustion. These carbon dioxide emissions contribute to global climate change by acting as greenhouse gases (Botkin and Keller 2003). Of the total carbon dioxide emissions from fossil fuel combustion, petroleum is the largest contributor at 33% (Hockstad 2006). Of more local concern, vehicular petroleum emissions represent the largest nationwide contributor to air toxics⁴ and contribute four significant pollutants into urban air pollution: carbon monoxide, hydrocarbons, nitrogen oxides, and particulate matter (United States Environmental Protection Agency 2006 and Baird and Cann 2005).

The System Solution

If the US requires liquid transportation fuels for the foreseeable future, the system solution to this problem is the production of alternative liquid fuels that can directly displace petroleum, diesel, and gasoline. This concept study focuses on advanced concepts for biofuel production—the growth, processing, and distribution of transportation biofuels in North America. This paper describes design concepts for three biofuel producing factories, each of which displaces liquid petroleum fuels: biopetroleum, biodiesel, and longer chain alcohols (referred to as higher alcohols) that can substitute for gasoline⁵. Biopetroleum can take advantage of the petroleum-refining infrastructure already in place. Biodiesel can displace petrodiesel with little effort and encourage the transition to a 30% more energy efficient combustion process compared to gasoline-fueled engines. Higher alcohol is more energy dense than bioethanol and is less susceptible to separation in the presence of water than ethanol/gasoline blends. This allows for the potential use of existing distribution infrastructure in the future. Each biofuel has distinct advantages and disadvantages (See Table 1).

Each concept tackles a fundamental problem faced by the biofuel industry: the production of feedstock that is cost competitive with petroleum.⁶ The design concepts presented in this paper address this through the growth and cultivation of the feedstock using factory efficient processes. The factory concept breaks from conventional food crop agriculture by exploiting benefits provided by a factory: high-density production, automated reaction processes, cost control, quality control, reduced waste, and greater efficiency. The factory concept also avoids competition for land and water resources required for food crops, which already limit and inhibit growth of biofuel production through traditional, open-field farming. Although attempts are being made by the biofuel industry to improve upon production processes and fuel properties, progress is slow and incremental. For example, some of the issues associated with bioethanol

⁴ Air toxics are pollutants known or suspected to cause cancer or other serious health or environmental effects. Significant air toxics resulting from transportation emissions include: benzene, formaldehyde, acetaldehyde, 1,3-butadiene (United States Environmental Protection Agency 2006).

⁵ DuPont and BP have entered a partnership in an effort to produce biobutanol, a longer chain alcohol compared to ethanol, that is reported to be available by the end of 2007 (Biobutanol Fact Sheet 2006).

⁶ “The grand challenge for biomass production is to develop crops with a suite of desirable physical and chemical traits while increasing biomass yields by a factor of 2 or more.” (Ragauskas, Williams, and Davison, *et al.* 2006). “There are many ways to produce fuel quality esters...Lipid feedstock represents the single largest part of production costs.” (Tyson 2005).

are: limitations regarding use with standard gasoline engines, inability to use current distribution pipelines, and reduced energy density as compared to gasoline. To address these issues, DuPont and BP have entered into a partnership to produce biobutanol—a biofuel that is similar to bioethanol with mitigated limitations. Although biobutanol is a step in the right direction, the differences between biobutanol and gasoline are still significant. This incremental improvement approach is the motivation for exploring more risky, advanced concepts that take a direct path to producing a biofuel that is better suited to displace petrofuels.

Table 1. Biofuel Advantages and Disadvantages.

	Advantages	Disadvantages
Biopetroleum	<ul style="list-style-type: none"> ▪ Compatible with existing petroleum distribution infrastructure ▪ Can feed directly into petroleum refineries ▪ Can produce gasoline, diesel, kerosene, and jet fuel products 	<ul style="list-style-type: none"> ▪ Unknown energy requirements for biomass conversion ▪ Vulnerable to more favorable economics associated with synthetic petroleum processes (e.g., tar sands, heavy feeds, etc.) ▪ Rate limited by disruptions in refining operations caused by nature (e.g., hurricanes), terrorism, and industrial accidents
Biodiesel	<ul style="list-style-type: none"> ▪ High energy content ▪ Compatible with diesel vehicles ▪ Can motivate consumers to purchase clean diesel vehicles which are 30% more fuel efficient compared to gasoline powered vehicles ▪ Can be blended with petrodiesel 	<ul style="list-style-type: none"> ▪ NO_x emissions (solutions in the works) ▪ Conventional feedstock supply is limited (e.g., soy oil, canola oil, waste vegetable oil) ▪ May be corrosive to rubber fuel system components ▪ Cloud point higher than that of low sulfur diesel or diesel #2
Higher Alcohol	<ul style="list-style-type: none"> ▪ Easily added to conventional gasoline ▪ Energy content close to that of gasoline ▪ Compatible with current vehicle and engine technologies ▪ Can be distributed in multipurpose pipelines ▪ Synergy with bioethanol (e.g. cost effective conversion of production plant, similar or same feedstock) 	<ul style="list-style-type: none"> ▪ Increased higher alcohol yield from fermentation process is unknown ▪ Fuel-flow increases may be necessary to match gasoline engine combustion characteristics ▪ May not be compatible with some fuel system components ▪ Requires amino acids for bioconversion pathway, which adds to feedstock cost

Biopetroleum Factory

The biopetroleum factory concept illustrated in Figure 1 needs to produce biomass that is many times greater than conventional agricultural crops. As shown in Table 2, at least a seven-fold gain is achieved using photoautotrophic microalgae when compared to corn or soybeans, with the potential for greater feedstock yield using heterotrophic algae. Candidate organisms make use of their extremophilic nature (high temperature, high or low pH, high salt content, etc.) to out-compete predator species that might contaminate the culture environment. This is important since culture stability has been shown to be problematic for large-scale high lipid producing algae in the past through contamination by invasive species (Sheehan and Dunahay *et al.* 1998). Given that the environment outside the culture does not provide favorable extremophilic conditions that allow the algal strains to thrive, the threat to the environment is also mitigated.

The first stage in Figure 1 is biomass growth. The candidate feedstock is an extremophilic microorganism. Once the feedstock has matured, it exits the harvest stage in Figure 1. Next the conversion of the biomass to biopetroleum occurs. There are two approaches to this conversion. The first is the application of conventional petroleum upgrading approaches that have been studied and continue to be improved. These include hydro-conversion (hydrogen pressure and high temperature > 350°C), pyrolysis (high temperature > 350°C) and hydrothermal liquefaction (water pressure and high temperature > 350°C). This would be the quickest way to introduce biomass into the fuel supply. The approach would be to add a small amount of biomass (5 -10%) to existing fuel processing reactors thus increasing the sustainable portion of the fuel supply. However, this approach is clearly limited in that it is not currently known how much biomass can be added without disrupting these processes (*e.g.*, adding too much water).

The second approach is to learn from natural geological processes—particularly diagenesis. Diagenesis is the initial process that occurs in the burial of biomass that results in the production of kerogen, the dispersed organic matter of ancient sediments insoluble in the usual organic solvents (Vandenbroucke and Largeau 2007). Catagenesis is a naturally occurring process that occurs over the course of millions of years in which kerogen is converted to petroleum. Catagenesis transforms kerogen into hydrocarbons through molecule cracking. This conversion process is driven by increasing temperatures and pressures that result from extended periods of layered deposition and sedimentation. Additionally, the radioactive environment surrounding petroleum deposits may contribute to the conversion of organic matter to petroleum (Thompson 2006; Morse and Zinke 1995). It has been observed that concentrated uranium alters the reaction path of kerogen during diagenesis and catagenesis via radiolysis (Landais 1996). Some observed reaction mechanisms responsible for alternative reaction paths in the presence of uranium are: enhanced oxidation, decrease in the average length of aliphatic components, and an increase in C=C and C=O bonds and a decrease in C-H bonds (Willingham and Nagy *et al.* 1985).

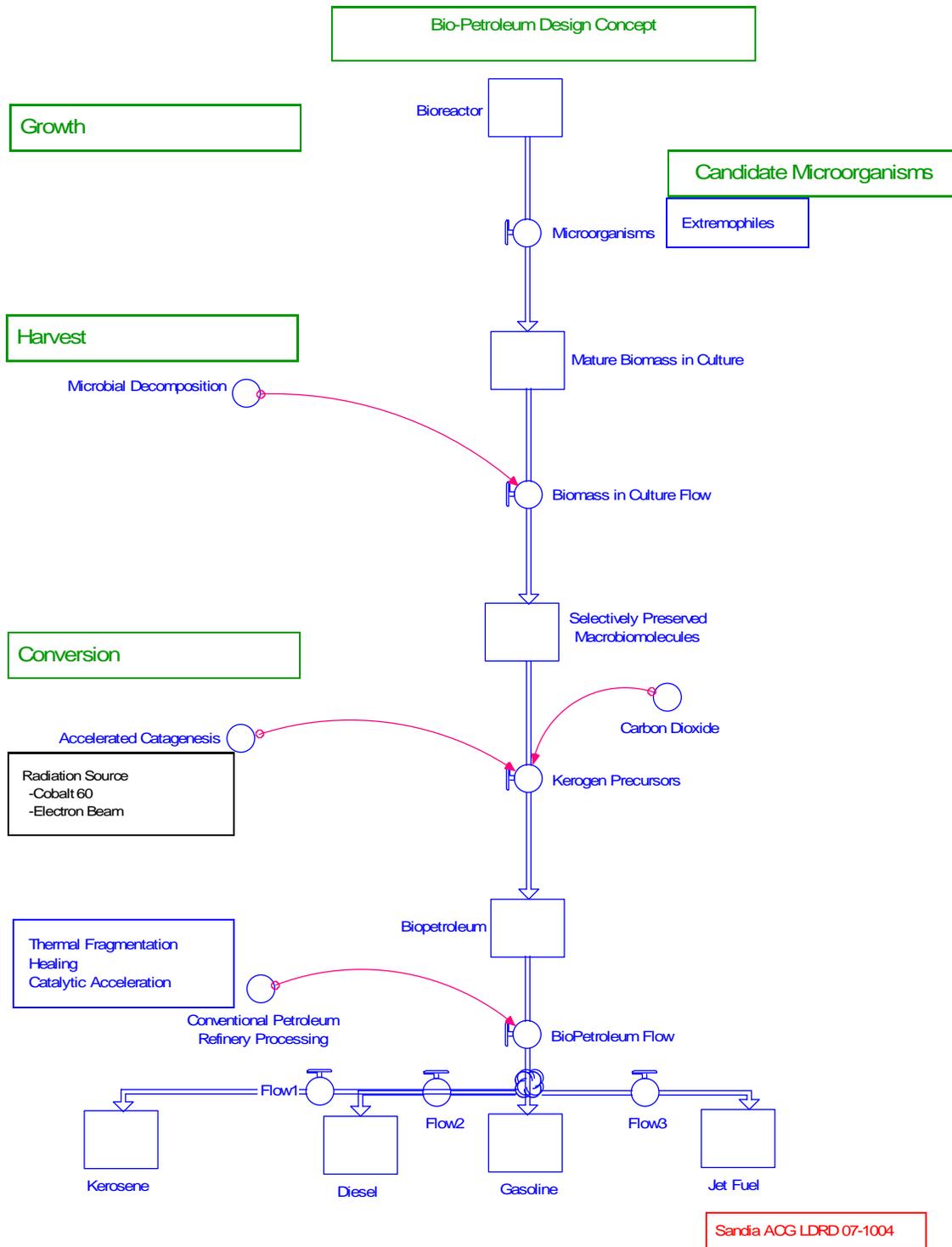


Figure 1. Biopetroleum Factory System Diagram.

Table 2. Comparison of Feedstock Yield and Lipid Content.

Feedstock	Biomass Yield (per volume, per area respectively if available)	Lipid Content	Source
Microalga: heterotrophic <i>C. protothecoides</i>	2 gram /liter/day Dry weight yield not specified	55%	Xu and Miao <i>et al.</i> 2006
Microalga: photoautotrophic <i>P. tricornutum</i>	0.14 gram/ liter /day 21 gram/m ² /day Dry weight yield with culture depth approximated to be 15 cm	20–22 %	Sheehan and Dunahay <i>et al.</i> 1998
Microalga: photoautotrophic <i>T. sueica</i>	0.12 gram/ liter /day 19 gram/m ² /day Dry weight yield with culture depth approximated to be 15 cm	15–23 %	Sheehan and Dunahay <i>et al.</i> 1998
Microalga: photoautotrophic <i>D. primolecia</i>	0.09 gram/ liter /day 14 gram/m ² /day Dry weight yield with culture depth approximated to be 15 cm	23 %	Sheehan and Dunahay <i>et al.</i> 1998
Microalga: photoautotrophic <i>M. salina</i>	0.08 gram/ liter /day 12 gram/m ² /day Dry weight yield with culture depth approximated to be 15 cm	21–22 %	Sheehan and Dunahay <i>et al.</i> 1998
Microalga: photoautotrophic <i>Isochrysis sp.</i>	0.08 gram/ liter /day 12 gram/m ² /day Dry weight yield with culture depth approximated to be 15 cm	28–33 %	Sheehan and Dunahay <i>et al.</i> 1998
Microalga: photoautotrophic <i>B. braunii</i>	0.02 gram/ liter /day 3 gram/m ² /day Dry weight yield with culture depth approximated to be 15 cm	29 %	Sheehan and Dunahay <i>et al.</i> 1998
short-rotation woody crops	2.73 gram/m ² /day	Unknown	Ragauskas and Williams <i>et al.</i> 2006
Corn for grain	2.73 gram/m ² /day	Unknown	United States Department of Agriculture 2004
Soybeans	0.8 gram/m ² /day	Unknown	United States Department of Agriculture 2004

This second approach is a valuable path to pursue to generate understanding and to discover hidden pathways to a practical process. A benefit to this approach is that it addresses difficulties in isolation and extraction of specific biomass components that are necessary for some conventional biofuel processes. To emulate this process, biomass undergoes an accelerated catagenesis process using a radiation source that can provide the energy needed for biomass transformation.

In general, radiation treatments by simply irradiating biomass and expecting formation of specific products are not a viable option (Appendix A). Radiation induced scission and bond reforming always compete, and the required doses from an energetic perspective appear to be prohibitive.

However, radiation facilitated breakdown of materials and the coupling of catalysts with radiation sources may represent novel directions that require fundamentally different approaches and ground breaking innovation. Radiation energy transformation must be geared towards well defined reactions and should be coupled with increased efficiency and yield targets, *e.g.*, radiation induced chain reactions. Possible approaches are:

- Explore the use of radiation processing to reduce molecular weight, process, or chemically modify otherwise non-digestible raw materials for fermentation and other biological fuel production processes. Similarly, consider if radiation treatments could also be applied to industrial processing of otherwise unattractive carbon sources.
- Explore if radiation energy deposition could be used more efficiently when coupled with novel high-efficiency catalysts, *e.g.* nano-particles. Design processes in which small molecules such as methane and CO₂ could be used as precursors for new chemical synthesis avenues.
- Explore if irradiation of small molecules in their liquid state or under pressure could be fundamentally different to the established reactions of ‘radiation chemistry’ currently described in the literature.

Although little is known about radiation induced biomass transformation, the radiochemistry of hydrocarbons has been studied for decades (Lucchesi and Baeder *et al.* 1960; Mirkin and Zaykina *et al.* 2003; National Energy Technology Laboratory 2006). The motivation has been to achieve refinery processes that are less expensive and more energy efficient for refining heavy petroleum fractions.

General observations regarding hydrocarbon radiochemistry include:

- Radiolysis does not create different species than thermally promoted reactions in similar systems.
- Exposure of hydrocarbons to ionizing radiation promotes organic dehydrogenation with or without oxidation.
- The general trend of creating larger molecules from smaller molecules occur
- G values for C-C bond scission are typically less than 10 (G = molecules reacted per 100 MeV of absorbed energy).

As such, one might dismiss radiolysis for chemical processing, yet depending on reactor design there may be reasons to consider radiolysis in combination with catalyst systems or concentrated solar energy in these processes.

1. Temperature—reactions may be performed at lower temperatures under radiolytic conditions.
2. Penetration—a more uniform penetration and absorption of high energy radiation
3. Relative excitation—the difference in absorption coefficients between the catalyst and CO₂/hydrocarbon is greater under radiolytic conditions.

These differences may have an impact on total conversion/selectivity.

Effective application of radiolysis depends greatly on the efficiency of energy absorption. Absorption of 1 MeV radiation by hydrocarbons and CO₂ is quite low, but this can be mitigated by use of a highly absorbing catalyst that is activated by the absorbed radiation. Uranium compounds have been studied for use as both thermal and photo-active catalysts for a variety of industrial reactions (*e.g.*, U.S. Patents 6483005, 4451343). A photo-active uranium compound could be similarly radiation-activated. Uranium also has an exceptionally high absorption cross section for high-energy radiation. Figure 2 demonstrates the relative stopping power of CO₂ gas, liquid CO₂, and 30 wt% MoS₂ or UO₂ catalyst in liquid CO₂ at 25 °C.

There is a theoretical process that combines the potential of UO₂ to activate CO₂ with the known properties of zeolitic cracking catalysts that reduce molecular weight. Thus, while the zeolite is reducing the large biomolecules to smaller fuel range molecular weights, the UO₂ is activating CO₂ and adding the products to the cracked biomolecules. Such hybrid dual reaction schemes are worthy of exploration to produce sustainable fuel supplies.

Zeolites are catalysts used industrially to crack heavy petroleum fractions to light fractions. These are typically alumino-silicates and hence relatively weak gamma radiation absorbers. Conceivably, due to the different physical and chemical nature of the catalysts, a reactor could be designed to combine large molecule cracking and CO₂ activation in one system. For example, it may be possible to line the flow path with uranium based radiation-activated catalyst and adjust the liquid CO₂-catalyst contact time and mixing by appropriate surface roughness, flow path tortuosity, and volumetric rate. Reactor design, however, depends entirely upon such factors as measured rates of reaction under static conditions and rates of radical generation and lifetime.

The feasibility of this process can be determined by studying the photo- and radiation-activated reaction of carbon dioxide and methane. Methane (CH₄) is the ‘simplest’ hydrocarbon molecule and is an abundant resource from natural, industrial, and agricultural sources (United States Environmental Protection Agency 2007).

In order to react these chemical species, they must be catalytically activated. In the case of CO₂, activation is reduction to CO₂⁻. A variety of catalysts have been used for electrochemical and photochemical reductions (Ayers 1988). Methane is activated typically by thermally cleaving a C-H bond, often promoted by molecular adsorption on the (110) face of W or Ni.

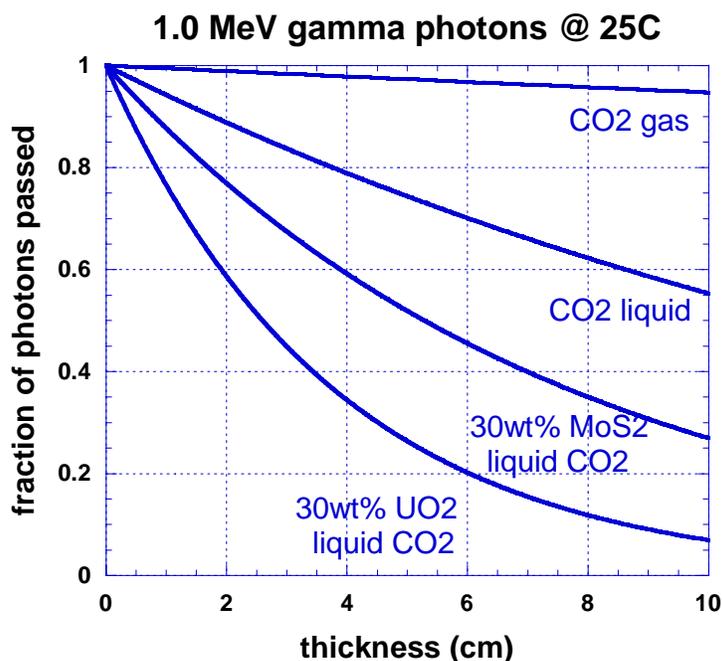


Figure 2. Relative Gamma Absorption by CO₂ with and without Catalyst.

Observed reactions using CO₂ as a feedstock are (Leitner 1999 and Ochiai 2005):

1. CO₂ + H₂ → HCOOH (formic acid) noble metal catalyst, supercritical CO₂, amine needed to shift equilibrium toward desired products.
2. Oxidation of cycloalkenes, then polymerization to polycarbonates.
3. Co-polymerization of propylene oxide and CO₂.

This demonstrates that CO₂ can be catalytically reacted with oxygenated alkenes (ether, epoxide, oxirane group and C=C bond), both of which occur via irradiation of saturated hydrocarbons in the presence of oxygen. Kudo *et al.* have reported in the literature other reaction pathways that use CO₂ to create hydrocarbons without the use of H₂ (Kudo 1997 and Kudo 1999).

To further develop the biopetroleum design concept, there are two areas in need of further research. First is the identification of biomolecules that have the greatest potential for hydrocarbon conversion following catagenesis. Once the target biomolecules are identified, characterization of the microbial decomposition for various biomass feedstocks is needed. Since microbial decomposition is responsible for the biopetroleum precursors, it is necessary to know about the community of organisms that can produce the target biomolecules and optimize their production. Following the production of target biomolecules via microbial decomposition, further research is required for the conversion of the biomolecules to hydrocarbons using radiation to drive the catagenesis process. Research in the area of radiation chemistry is needed to manipulate and alter the biomolecules using radiation energy as the source for conversion to hydrocarbons.

Biodiesel Factory

Production of biodiesel from algae involves four key steps: growth of algae, maximization of lipid content, separation, and chemical conversion of lipid molecules to biodiesel. The separation and chemical conversion and other potential improvements are described below.

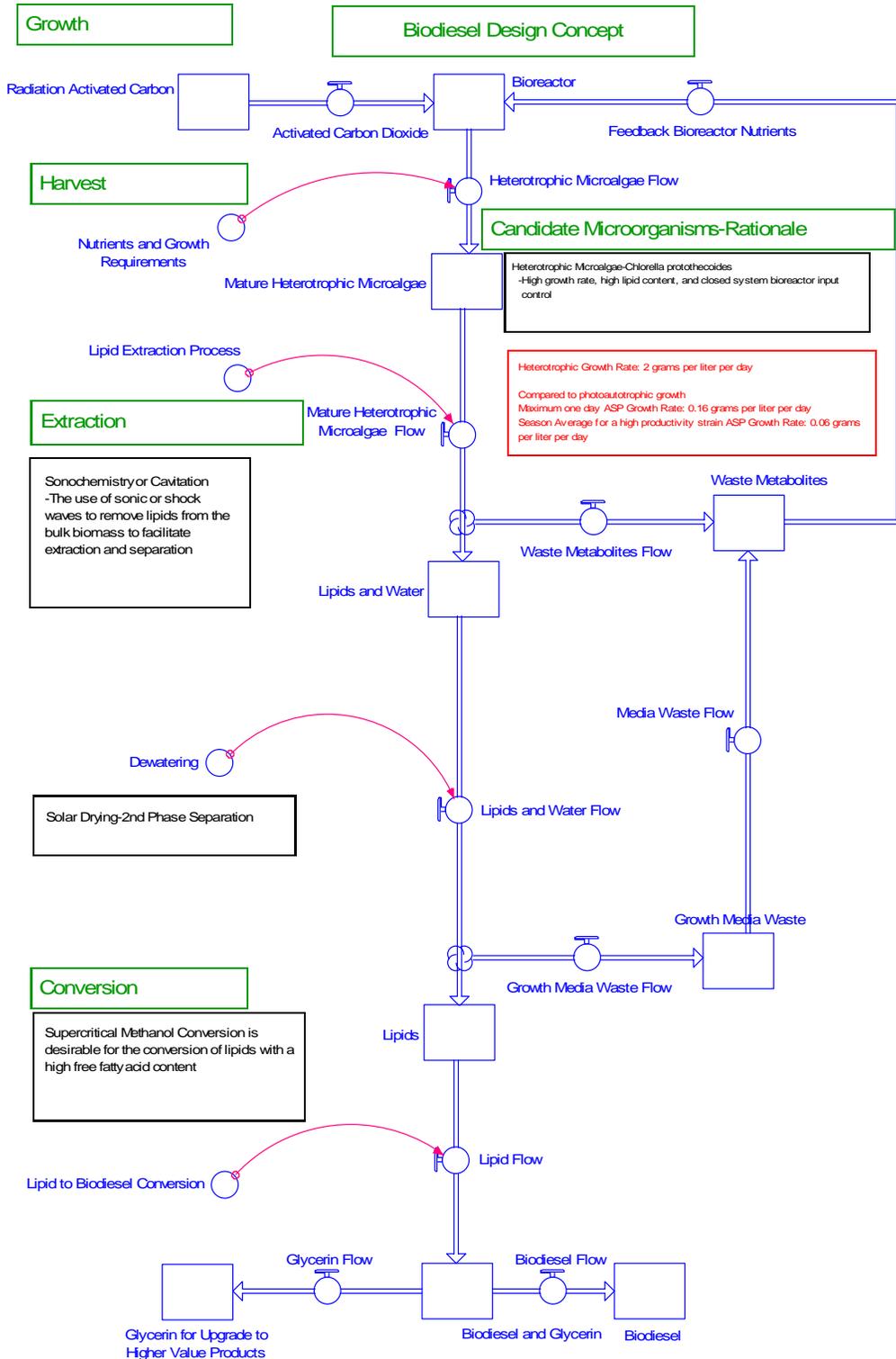
The key to biodiesel from algae is the microbiology of the algae. An analogy can be made to the history of corn production as a source of food. Ancient peoples hand picked corn kernels that were larger than average and replanted them. Over hundreds of years larger kernel species came to predominate. In the twentieth century hybrids appeared that had higher yields and quicker maturation times creating the “green revolution” of the latter half of the twentieth century. Today, there are genetically modified corn species that have high resistance to weed killers and diseases, again increasing productivity. Seed companies that produce these products control the industry by implanting suicide genes to insure that the product must be purchased each year. In an analogous way, lipid producing algae evolve with the help of molecular geneticists to be higher lipid producers, have shorter growth times and resistance to invasive species. Thus, companies and organizations that develop the new strains of algae dominate the field.

The necessary components for biodiesel production are captured in the biodiesel factory concept shown in Figure 3 starting with the growth and cultivation of heterotrophic⁷ microalgae. One advantage of using heterotrophic microalgae is the increased lipid production needed for biodiesel production (See Table 2). Since heterotrophic growth can occur in closed system bioreactors, weather is insignificant. This also eliminates the cultivation system’s need for direct solar irradiation. Uniform illumination and photo-inhibition are problems faced by open and closed system photoautotrophic configurations—conditions that are difficult to control. Furthermore, UV is damaging to some of the internal microalgal structures vital for biomass production.

The benefits of heterotrophic growth must be evaluated considering the heterotrophic growth requirement of an organic carbon source. Therefore, it would be of great value if heterotrophic cultivation could create economic products from abundant low-value organic feedstock and carbon dioxide.

A general scheme would be to decompose biomass waste material using either concentrated solar energy or radiation-activated catalysis to break chemical bonds. This source material would be combined with liquid carbon dioxide (CO₂) and radiation-sensitive catalysts suitable for generating CO₂ radicals. If the *a priori* intimacy of the two species with catalysts or their rate of mixing following catalysis is sufficient to favor CO₂-biomass fragment combination, then one could expect to generate carboxylic acids which may be an inexpensive and sustainable feedstock for heterotrophic algal biomass production. A flowchart of this scheme is given below in Figure 4.

⁷ Photoautotrophs are capable of living on inorganic materials, water, and sunlight. This is in contrast to heterotrophs, organisms that require preformed organic molecules as food.



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Figure 3. Biodiesel Factory System Diagram.

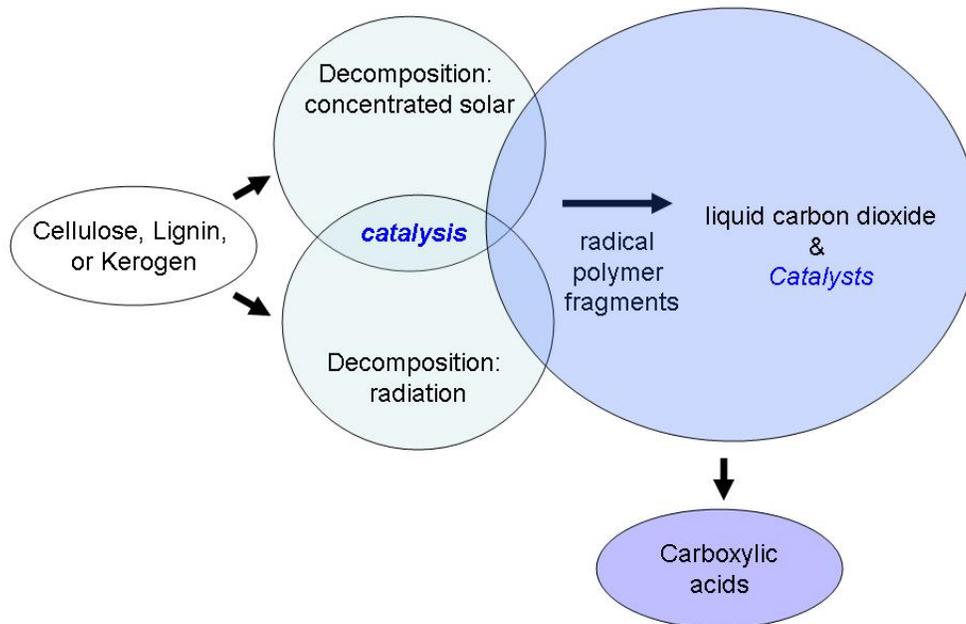


Figure 4. Schematic Flowchart for Heterotrophic Algal Feedstock Generation.

Following the cultivation process, mature biomass is separated from the culture media. The separated biomass then undergoes lipid extraction to harvest the lipid content of the biomass, shown in Figure 3 as Lipids and Water. Extraction potentially could be accomplished using sonochemistry or cavitation, where sonic waves or shock waves remove lipids from the biomass bulk.

The lipids then undergo a conversion process that results in biodiesel, the output of the lipid flow in Figure 3. The conventional conversion process involves the transesterification of lipids in the presence of a base catalyst, resulting in fatty acid methyl esters (FAME) and glycerol as a co product. This process typically occurs at atmospheric pressure at a temperature of 60° C with a reaction time of approximately two hours. The problem with this conversion is that the base catalyst introduces a competing reaction, saponification, in the presence of free fatty acids. Therefore, the conventional process requires the feedstock to have little to no free fatty acid content. This requirement limits the ability to use good candidate feedstock without front end refining, such as algal oil that can contain 40% to 60% free fatty acid content (Crooker and Wu 2006).

A solution to this problem is the conversion of lipids and free fatty acids using a supercritical methanol reaction. This conversion process requires no chemical catalyst, and occurs at approximately 350° C at 1,000 psig for less than 5 min (Crooker and Wu 2006). This conversion process offers flexibility in feedstock selection, which is crucial in identifying the best biomass solution for petroleum displacement.

Supercritical methanol transesterification (SCMT) may allow for the direct processing of algal biomass, eliminating the need for separation and extraction mentioned above. Although separation and extraction techniques are available for conventional biodiesel production feedstock, industry is struggling to adapt these techniques to advanced feedstock. Therefore, the direct processing of algal biomass is an advanced concept for biodiesel production. For direct processing to be a viable option, SCMT reaction inhibition must be tested and eliminated. After direct processing has been proven, water removal and algal cell lysis need to be optimized. Solar drying can reduce the heating costs resulting from the elevated temperatures required for the SCMT reaction. Cell lysis is necessary for the SCMT reaction, and is assumed to occur during pumping and mixing. In the event that the assumed cell lysis is less efficient than desired, sonochemistry could be used to increase cell lysis efficiency.

In a working paper authored by Peter Merkle of Sandia National Laboratories/New Mexico, experiments in the following three areas are outlined: pilot scale cultivation of heterotrophic *Chlorella protothecoides*, SCMT process yields, and process design integration and economic study estimate (Merkle 2007).

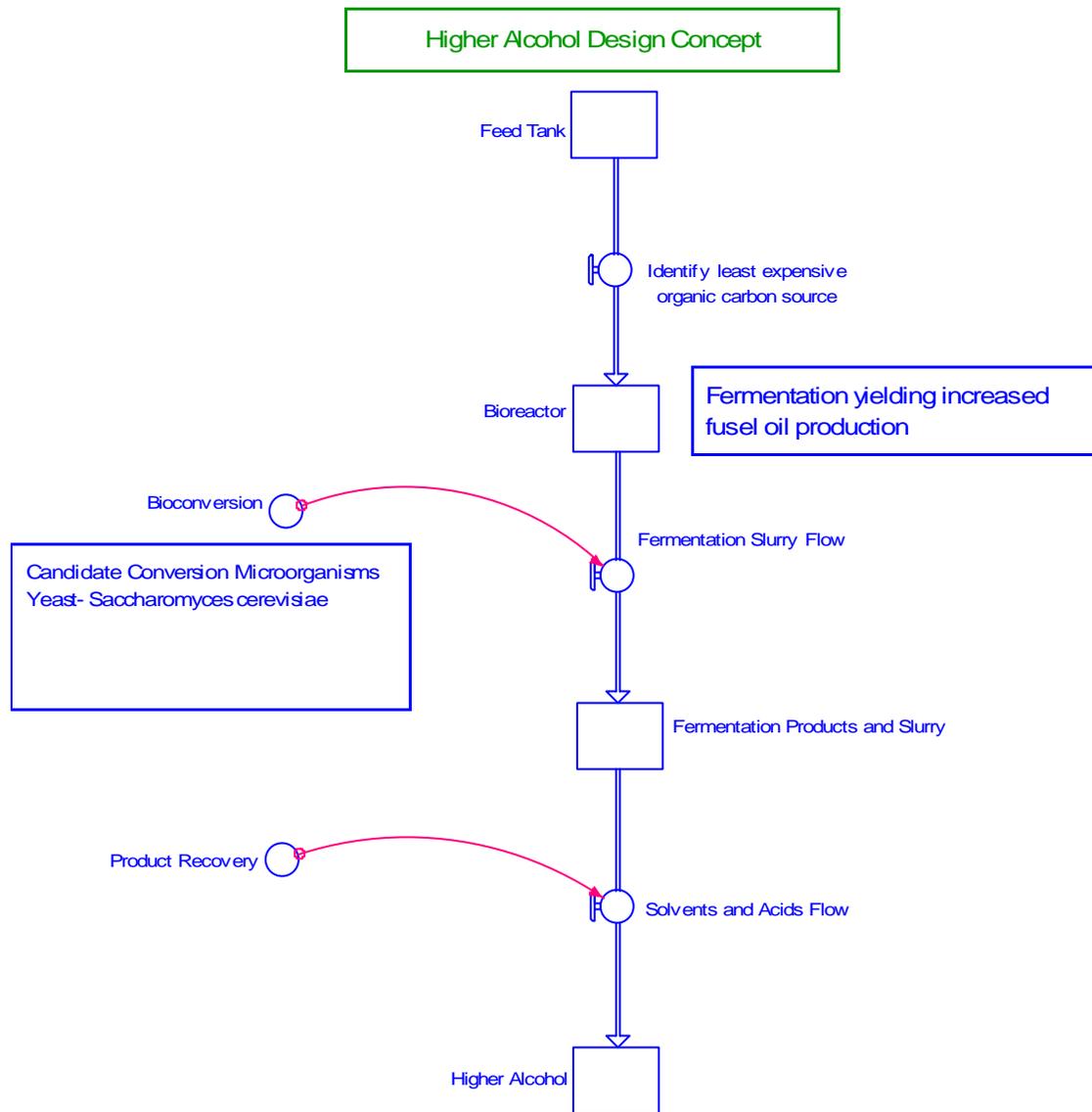
Higher Alcohol Factory

One of the largest drawbacks to bioethanol is the decrease in energy density compared to gasoline. For this reason, there are efforts to displace gasoline with biobutanol, a 4-carbon alcohol with superior energy density. Our higher alcohol factory concept follows this progression to produce higher order mixed alcohols (targeted C₅ and C₆) that offer greater energy density compared to bioethanol and biobutanol.

It is well known in the beer brewing industry that it is possible to achieve higher mixed alcohols through common fermentation processes. In fact, although normally present in very low concentrations, these higher mixed alcohols are so common that they have come to be known as fusel oil. Fusel oil is a varying composition mixture of propanols, butanols, pentanols, hexanols, and phenols that are deleterious to beer quality when present in higher than normal concentrations (Hardwick 1995). Fusel oil reduces foam quality and beer stability. Furthermore, fusel oil can cause sensory abnormalities and can induce headaches in susceptible consumers (Hardwick 1995). For these reasons, a good amount is known about how to limit fusel oil production, but much less is known about increasing fusel oil yield.

Some typical bioreactor parameters that can be adjusted to limit fusel oil production are: fermentation feedstock, yeast strain, temperature, inoculum size, degree of agitation, level of oxygen, and pH. It may be possible to adjust these parameters to increase fusel oil production in the same way they are used to limit production. This coupled with biological advances in the fermentation process pathway could lead to fusel oil yields that could rival ethanol production.

The higher alcohol factory concept illustrated in Figure 5 uses the well known brewing yeast, *saccharomyces cerevisiae*, for the fermentation. This yeast is chosen for its known production of fusel alcohols. The concept focuses on the sequencing and isolation of the enzyme that catalyzes the production of ethanol and fusel alcohols. Once these enzymes are sequenced and isolated, the



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Figure 5. Higher Alcohol Factory System Diagram.

enzyme responsible for ethanol formation would be suppressed while the enzyme responsible for fusel alcohol formation would be cloned and overexpressed. It is vital to determine if the appropriate substrate molecules can be made available for this newly overexpressed pathway in such a way that is energetically feasible.

Saccharomyces cerevisiae is also being engineered to metabolize xylose, a major contributor to lignocellulose. This allows the yeast to utilize the least expensive feedstocks known to be readily available. The problem with this genetic transformation is that the most efficient enzyme for xylose metabolism is found in the yeast *Pichia stipitis*, living in the bellies of beetles. This yeast metabolizes xylose and regulates ethanol production as a response to oxygen limitation (Jeffries and Grigoriev *et al.* 2007). However, *Saccharomyces cerevisiae* regulates ethanol production by sensing the presence of glucose (Jeffries and Grigoriev *et al.* 2007). This disconnect leads to low ethanol production rates for *Saccharomyces cerevisiae*.

To further develop the higher alcohol factory concept, two approaches can be followed. The first is to continue with genetic modifications that will allow the yeast, *Saccharomyces cerevisiae*, to metabolize lignocellulose. The genetic manipulation should focus on increasing naturally occurring fusel oil through a modified fermentation pathway. The other approach should focus on the production of increased amino acid composition in fermentation feedstock. Although the details are unclear concerning the sequencing of biochemical reactions involved in the formation of fusel oil, the predominant theory envisages an aminotransferase reaction resulting in products that are reduced to fusel oil. Therefore, since the amino acid content in the fermentation feedstock is the limiting reactant to the aminotransferase reaction, more amino acids are needed to increase fusel oil production. The challenge will be to identify a waste stream that can provide the necessary amino acids or to develop a cost effective process that can produce amino acids to supplement a lignocellulose based feedstock.

Observations and Conclusions

While startups, investors, and the petroleum industry are all in hot pursuit of new biotechnologies for cost-competitive biofuel production, there are novel R&D ideas on the fringes of this biofuel movement that may hold the key to the elusive breakthrough that everyone seeks. This project's exploration of biofuel factory concepts—in marked contrast with the open-field agricultural paradigm for biofuels that dominate today—looked beyond current biofuel avenues and delved into unconventional feedstocks (*e.g.*, extremophiles), out-of-favor reaction processes (*e.g.*, radiation chemistry), and production of new fuel types traditionally deemed undesirable (*e.g.*, fusel oils). In each of the three biofuel factory concepts developed in this paper, there is much science and engineering to do to advance these concepts and reduce the technical risk to a point that private industry would be willing and able to commercialize ideas with basic and applied R&D results behind it.

For the biopetroleum factory concept, the principal science and engineering area is not only the selection of a suitable extremophilic species and optimal growth of that microorganism, but also the development of radiation-induced catalytic cracking technology. This paper documents specific ideas in this arena worthy of experimentation, particularly the combined use of uranium

compounds and zeolites. It's these approaches that may be able to overcome the inherent limitations associated with simply irradiating biomass (as detailed in Appendix A), resulting in self-propagating reactions initiated by novel coupling of radiation sources and catalysts.

The biodiesel factory concept also includes a radiation component for overcoming the dominant issue of feedstock cost. Utilizing heterotrophic algae in a closed factory setting instead of photoautotrophic algae species favored by farmers and photobioreactor advocates, this concept requires an organic carbon source that attempts to overcome the feedstock cost obstacle that plagues virtually all current biofuel ventures. If radiation processing can reduce molecular weight, process, or chemically alter otherwise non-digestible, cheap feedstocks (*e.g.*, lignocellulose) that could subsequently be an organic carbon source for heterotrophic algae with high lipid content, existing and developing technologies (as described and referenced in this paper) could then be utilized for the separation, extraction, and conversion of these lipids to biodiesel.

In the search for a direct gasoline substitute or complement, the key idea behind the higher alcohol factory is to take advantage of the research, development, and experience in the brewing industry to maximize production of a by-product that has typically been minimized and not desired—fusel oil. This will require science to understand how to overexpress fusel oil production in fermentation and bioengineering to do so on a scale at least two orders of magnitude larger than the brewing industry. Since this novel approach is believed to begin with an aminotransferase reaction, supplementing conventional lignocellulosic feedstocks with amino acids could be the path to follow. However, production of low-cost amino acids or identification of amino acids from waste streams is a challenge that also requires breakthroughs in biology and bioengineering.

In 1978, the US Department of Energy initiated the Aquatic Species Program to conduct basic science and applied engineering to the concept of producing biodiesel from microalgae lipids. Decades ahead of its time, it was a fringe idea that became a mainstream pursuit shortly after the year 2002. Biofuel factory concepts—like the ones described in this paper—likely fall into the same fringe category today. While not viable now or in the next few years, the concept lays the foundation and path for the scientific experiments and technological breakthroughs necessary to displace petroleum as a transportation energy source for good.

Beyond Bio: Other Advanced Concepts Worthy of Exploration

Methane and Carbon Dioxide

Traditional and novel approaches to biofuel production require a carbon feedstock and a hydrogen source to initiate and sustain the biochemical processes for producing liquid transportation fuels. An alternative concept for doing this would be to take an abundant point source of carbon such as CO₂ and a simple, producible, or harvestable hydrogen source such as CH₄ and then devise synthetic chemical processes with unconventional energy inputs (*e.g.*, radiation, concentrated solar UV) to produce specific liquid transportation fuels. Through this

approach, the complexity of growth biology as well as the industrial challenges associated with separation and extraction processes can be greatly simplified or avoided altogether.

Methane and carbon dioxide are abundant resources available as dispersed sources from a variety of natural phenomenon (*e.g.*, methanogens) and point sources from human activity (*e.g.*, flaring). Methods of reacting carbon dioxide and methane together represent an enormous opportunity for both reduction of greenhouse gases and capturing large amounts of wasted energy. These methods have been studied extensively, but are presently deemed uneconomical because of the high-energy input required.

Carbon Dioxide Reforming

A recent American Chemical Society (ACS) symposium focused on the conversion and utilization of CO₂. The proceedings emphasize the opportunity for research and development of new catalytic technology for converting carbon dioxide to useful products including fuels and chemicals. Some of the important reactions are:

- CO₂ + CH₄ → 2CO + 2H₂ (synthesis gas reaction)
- CO₂ + CH₄ → CH=CH and CH₂CH₂
- CH₄ → C (high surface area) + 2H₂

Many other reactions and various conditions are reported including plasma reactions and reactions in critical CO₂. The first reaction to produce 1:1 has received considerable attention as being desirable in producing a syngas stream that leads to useful products. The thermodynamics have been studied in detail with the interesting result that temperature increases the conversion but pressure decreases the conversion. Catalyst deactivation with carbon coating the catalyst is a major problem. To date, no current commercialized processes have been discovered. However, a process was recently patented for the conversion of agricultural bio-waste containing carbon dioxide and methane to syngas. The final liquid product is methanol in this process.

Novel Methods for Research in Utilization of CO₂ and CH₄

One area that has not been extensively investigated is the use of radioactivity to provide the energy required for reaction. Radioactive reactions of CO₂ have had only limited study. The primary ionic form of irradiated CO₂ is CO₂⁺. In addition it seems that the liquid or supercritical route might enable better reaction specificity. Irradiation of hydrocarbons tends to lead to C-H bond scission. Irradiated mixtures of CO₂ and alkanes yield carboxylic acids (at room temperature or in liquid CO₂). Methane plus CO₂ is also known to yield acetic acid (an important large volume intermediate) or short chain acid mixes. Ethylene plus CO₂, at low temperature is a possible route to making acrylic acid, CH₂=CHCOOH, a major paint additive. Current processes use ethylene and CO plus H₂O and catalyst/pressure. The number of reactions of this type is potentially very large and might make a large impact on the petrochemical industry.

The problem with many photochemical / electrochemical reactions is the competing reverse reaction. This is also true with radiochemistry. However, if we combine methane with CO₂ reverse reactions may be reduced via reaction of reduced CO₂ with readily available fragments from the methane. Additionally, catalysts may be activated by the radiation, rather than relying on absorbing the radioactive dose in the organic component. If a flow system incorporating a fluidized methane degradation catalyst and supported (immobilized) CO₂ reduction catalyst and flowing liquid CO₂ are combined, then 'product' could be removed before it itself becomes catalyzed into something else.

Photoelectrochemical reduction of CO₂ on p-type semiconductor electrodes has been reported (Ayers 1988). If the incident radiation had energies within the semiconductor bandgap (*i.e.*, radiation would activate semiconductor) reduction of the CO₂ in liquid state and at low temperature may occur and increase the G value of radiolytic CO₂ reactions. Chemistry can be done with CO₂ if the dose is large enough to create sufficient radicals. Radiolysis of carbon dioxide and methane has been reported (Kim and Getoff *et al.* 2006; Yanbing and Baosheng 2007). Radiolysis of CO₂ has been studied extensively by Nikola Getoff (Getoff and Fjodorov 1983; Getoff 1994; Getoff 2003; Getoff 2006). However, the radiolysis of CO₂ and CH₄ is a promising area of research for the future.

Further Thoughts on the Utilization of CO₂ and CH₄

The future of energy particularly sustainable liquid transportation fuels and chemicals now produced from petroleum will likely focus on converting abundant greenhouse gases CO₂ and CH₄ to useful products. In a sense the problem of converting these molecules is very similar to the current efforts in chemistry to understand the "Origins of Life." This problem currently reduces to how can simple and abundant molecules assemble into simple molecules that later can become starting materials for molecules that can assemble in larger molecules necessary for life. These processes are thought to have first occurred in the dark depths of the ocean under high pressure and low temperatures utilizing the most basic materials available from the Earth. Perhaps our experience with modern energy industries has limited our thinking to conditions and reactions that are familiar and compatible with these industries and we need to think more about conditions and molecules outside of this "comfort zone." In the future we need to explore conditions that exist in extreme environments, *e.g.*, high pressure (100 atm) and moderate temperatures (< 250°C), conditions that may exist on other planets, and reactions in liquid methane.

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Appendix A

The Use of Energetic Radiation to Facilitate Novel Biofuel Production Pathways
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Radiation types and radiation chemistry

Energetic radiation types, which can induce chemical or physical reactions in materials, include photons (UV, X-rays and γ -rays) and particulate radiation (alpha, beta-electrons, E-beams and neutrons). Many textbooks provide an overview on the principles of radiation sources, the physics of energy absorption processes and the resulting radiation effects in organic materials and polymers where the reactions are often referred to as ‘radiation chemistry’, *i.e.*, the chemical changes and reactions induced by the deposition of radiation energy (Chapiro 1962; Dole 1972; Dole 1973; Makhliis 1975; Woods 1994; Clegg 1991; Clough 1991; Clough 1996). While photon irradiation can result in nuclear activation (physical) processes when extreme energies are involved (*i.e.*, 20MeV gamma-activation achieved with accelerators), any irradiation process involving neutrons has the potential to more easily involve nuclear reactions and hence induce subsequent radioactive processes. From a practical perspective, electron (e-beam) and gamma irradiation with moderate energies are therefore the most commonly available radiation types used in industrial processing. E-beam generators have the additional advantage of the turning on/off feature, while the classic ^{60}Co gamma source may be available as a cheap radiation source but requires considerable radiation protection efforts. Both ^{60}Co and e-beam sources are used to induce radiative changes in materials. While metals and inorganic substances simply absorb energy, undergo some fatigue processes or display defect formation, organic materials in comparison undergo specific radiation chemical reactions, (*i.e.*, the breaking and reforming of chemical bonds). The “radiation chemistry” in organic materials (polymers and small molecules) depends on individual bond sensitivities and the chemical make-up of the material. In general, radiation chemistry involves bond cleavage (scission, leading to smaller fragments) and bond formation (cross-linking, leading to larger molecules). The outcome of energetic radiation induced damage in organic materials often depends on the balance between individual scission and cross-linking reactions, specifically what constitutes the nature of the more dominant free radical reactions. Radiation induced reactions in organic materials involve a broad spectrum of processes, to name a few: Detrimental and long-term polymer degradation processes (*i.e.* aging of materials in nuclear power plant environments), controlled e-beam initiated curing of reactive resins, polymer modifications via radiation induced grafting reactions, surface modifications of biomaterials, radiation induced depolymerization which is positive when degradation and low molecular weights are required (*i.e.* recycling) and negative when uncontrollable materials degradation occurs, sterilization of implant materials, oxidation and rapid breakdown of organic contaminants (*i.e.* water purification), organic waste processing (scission and breakdown of molecules in sludge and solution), and many others (Clough 2001).

Cross-linking and scission

Bond cleavage and reforming depends on individual bond sensitivities, the stability of the resulting radicals and their preferred follow-on processes. Both processes normally occur in

parallel or competing reactions. Many textbooks on radiation chemistry and radiation induced degradation of organic materials describe the basic principles (Dole 1972; Clegg 1991; Clough 1996). Most importantly, radiation breaks C-C and C-H bonds, which in the presence of oxygen is more likely to result in oxidized fragments; while under inert conditions (nitrogen or vacuum) cross-linking is more commonly observed. The presence of unsaturation encourages cross-linking reactions (*e.g.*, elastomers based on polybutadiene and isoprene crosslink very easily) (Clough 1991; Clough 1996; Clough and Gillen 1991). Polymers like polypropylene, polyamides, polyesters or polyurethanes with non-reactive building blocks have a higher tendency for cleavage and hence loss in molecular weight. It is important to realize that only a few radiation induced cleavage events are required to significantly reduce molecular weight in polymers and affect physical properties. In contrast, using radiation to simply build molecules with higher molecular weight is difficult, unless radiation initiates a high yield propagation reaction, for example in e-beam cured, UV or gamma -initiated polymerization. Deposited doses in this case are low and the radiation only initiates intended polymerization chemistry, often based on free radical polymerization of unsaturated compounds. While irradiation of methane breaks C-H bonds, produces free radicals, and results in detectable quantities of higher molecular weight compounds, such as ethane, propane etc, the yields are overall very low, because larger molecules statistically become more vulnerable to radiation induced fragmentation and essentially the reverse reaction (Chapiro 1962). Simple high yield processes producing high molecular weight by irradiating common molecules (*i.e.*, methane, acetic acid, acetone, etc.) are unknown. To develop such processes based on radiation fundamentally different concepts would need to be applied.

In summary, while cross-linking and hence increases in molecular weight do occur during irradiation of organic materials, they depend on specific chemistries, hydrogen transfer reactions, unsaturation etc, and unfortunately such reactions cannot be applied easily to many small molecules. In contrast, bond cleavage in polymers via irradiation is common and can quickly lead to a measurable reduction in molecular weight and loss of physical properties. Individual radiation yields and preferred reactions also depend on the state of the material (gas, liquid, solid), temperature (mobility of free radicals), and the presence of other agents (oxygen atmosphere) (Celina 1996; Celina 1998). Scission is normally more favored at lower temperatures and under non-oxidative conditions. Polymers can be classified in terms of their preferential behavior when being irradiated.

Basic Terminology

Table 1. Units and Equivalences

Radiation sources: Gamma, e-beam, x-ray synchrotron, strong UV	
Energy [J]	1eV=1.602x10 ⁻¹⁹ J or 6.242x10 ¹⁸ eV=1J
Dose [Gy] = [J/kg]	1rad =0.01Gy
Dose rate [Gy/s] = [100rad/s]	
Linear energy transfer (LET): [J/m]	1keV/μm=1.602x10 ⁻¹⁰ J/m
Radiation chemical yields G: [mol/J]	molecules/100eV=1.04x10 ⁻⁷ mol/J

When discussing the use of radiation and its interaction with organic materials, it is important to consider the following:

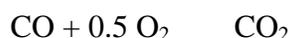
When discussing the use of radiation and its interaction with organic materials, it is important to consider the following:

1. The amount of required energy that results in a specific chemical reaction.
2. The type of radiation as it affects penetration depth, energy transfer, and deposition behavior.
3. The overall radiation dose and applied dose rate.

The latter is defined as the radiation chemical yield (G-value) and can be assigned to individual reaction, for example a polymer during irradiation may produce 2 molecules of CO₂ and 1 molecule of H₂ per 100eV deposited. Knowing G-values (chemical yield constants) of specific reactions and assuming certain energy depositions (doses) allows one to predict and calculate chemical conversions (yields) and other changes in a material. For example, G-values are also available for scission, cross-linking and overall gas yields for many polymers without defining the exact underlying reactions. In simple terms, a G-value is the expected amount of 'chemistry' per deposited energy (dose) (Chapiro 1962; Woods 1994).

Example of energy deposition via radiation

Irradiation of materials is a simple way of depositing energy into a system, which initially may lead to bond cleavage, ionization, delocalized electrons, free radicals and their follow-up processes, but ultimately is deposited as thermal energy. Strong e-beam irradiation of materials requires cooling, similarly strong gamma dose rates lead to heating of the targets. Hence irradiation competes with thermal energy, the most commonly applied process of inducing chemical reactions. The thermodynamics of chemical reactions provides some guidance on the radiation doses that would be required to induce similar reactions. Chemical reactions proceed under exothermic or endothermic conditions with energies produced or required often on the order of hundreds of KJ/mol. For example, the reaction of



is exothermic with -283 KJ/mol.

Chemical reactions to be conducted by irradiation as the energy source may require overall energy input to produce new molecules. Unless the expected reactions are exothermic and radiation may only act as the catalyst or initiator, many chemical reactions consume energy. Specific thermodynamic calculations would need to be conducted to establish if intended reactions are energetically feasible. As a brief example, for an endothermic reaction requiring 100KJ/mol, and assuming a density of 1 and M_w (molecular weight) of 100 grams/mol (*i.e.* 10 mol/kg), it would require approximately 100KJ/0.1kg = 1MGy or 100Mrad of radiation energy. This shows that very high radiation doses are required when energy is to be deposited purely by the radiation source. In comparison, it also shows how efficiently chemical reactions can be

conducted with a thermal energy supply. In the above example, the same energy could have been produced by the burning of about 10 grams of CO into CO₂.

Example for gas yields

Whenever organic materials are being irradiated, gaseous volatiles are being produced as degradation products. Yet interestingly, the yields of gaseous molecules as a function of deposited radiation energy are normally low, ultimately the G-values (chemical yields per energy) provides guidance. This is another example that shows that major doses are required to induce significant chemical reactions in a system.

Let's assume we irradiate HDPE with 10 Mrad or 0.1MJ/kg. This dose normally results in mechanical property changes, cross-linking, and molecular weight distribution changes in what we call radiative polymer degradation. The total deposited energy in this scenario would be 6.242×10^{23} eV/kg. With an approximate hydrogen yield of 3 molecules/100eV a total of 1.873×10^{22} hydrogen molecules/kg would have been produced. This yield would equate to a conversion of $1.87 \times 10^{22} / 35.7 \text{ mol} \times 6.023 \times 10^{23} \text{ mol}^{-1}$ or only 0.087 mol%. Mass yield would be 0.062 gram H₂/kg HDPE, a very low yield indeed. Hence, massive radiation doses would be required to obtain much larger yields of chemical degradation or volatiles via basic radiation-induced reactions. Similar scenarios would apply to the irradiation of short chain molecules to form larger molecules and the intended liberation of CO or NH₃ or other fragments from polymeric substances.

Polymer	G (gas) [100 eV ⁻¹]
PI	0.0024
PS	0.03
PTFE	0.098
PET	~0.25
PC	0.87
PMMA	1.3
CTA	1.3
PP	2.34 (H ₂)
HDPE	3

Examples of gas yields from (Celina 1998).

Energy supplied from radiation sources

It is apparent that high intensity radiation sources would be required if significant energy deposition is needed. The discussion above demonstrates that many hundreds of Mrads may be needed for certain reactions, and knowing the dose rate of known sources places the magnitude of the required energies into perspective:

- Highest rate of ^{60}Co at SNL is $\sim 29\text{kGy/h}$ (2.9Mrad/h)
- E-beams in industry may operate up to 10MGy/h (needs water cooling).
- SNL pulsed power e-beam, $4 \times 10^{10}\text{Gy/s}$, pulses for 60ns, 15 seconds between pulses, 2.5kGy/pulse or 0.57MGy/h actual dose rate.

Hence, many hours of irradiation with the strongest sources available may only deliver moderate energy levels for chemical reactions where high conversions are required.

Irradiation of methane CH_4 , building larger molecules?

Irradiated methane produces some hydrogen, but also forms some ethane and traces of higher alkanes (Chapiro 1962). The G-value for hydrogen is 5.7, for ethane 2.1 and propane 0.14 (Chapiro 1962).

100 Mrad or 1MGy ($6.242 \times 10^{24}\text{eV/kg}$) hence produce $5.7 \times 6.24 \times 10^{22}$ H_2 molecules/kg or 0.59 mols H_2 per 62.5 mols of methane, a molar conversion of only 0.94%. The ethane yield would be $2.1/5.7 = 0.37$ times less. The yields of higher alkanes are proportionally lower.

1kg methane equals 62.5×4 mols of C-H bonds (bond energies are 338KJ/mol or 3.5eV per bond). To break all C-H bonds at minimum would require 84500KJ/kg , or $5.27 \times 10^{26}\text{eV/kg}$ or 84.5MGy . Obviously, any exothermic follow-on processes may recover some of that deposited energy, but this theoretical calculation demonstrates the magnitude of the problem when chemical energy should be delivered by radiation. Therefore, from a purely chemical perspective radiation sources do not appear to be an attractive choice for significant energy deposition into a chemical system, *unless the intended reactions self-propagate and the radiation source may only have to act as an initiator or catalyst for follow-up reactions.*

Radiation induced degradation of macromolecules

While novel chemical syntheses using radiation based on the discussions above may be challenging, radiation damage to macromolecules is an effective process and actually the basis for the research field of polymer radiation degradation (Clegg 1991; Clough 1996). The underlying reason is that only a few scission events or rearrangements in macromolecules (polymers) can have significant impact on physical and chemical properties. In fact, even the low dose radiation sterilization of UHMWPE implant materials lead to unwanted and difficult to control property degradation. Similarly, radiation processing of polymers for recycling, breakdown, or reduction of molecular weight are attractive possibilities (Clough 2001). Waste irradiation and radiation facilitated breakdown for bio-remediation are other industrial processes of interest. Considering that some food sources or raw materials for ethanol or other bio-fuel synthesis may currently be difficult to process or digest, any radiation treatment, selective breakdown, oxidation etc. that may facilitate a modification of these precursors may present attractive avenues to pursue. Biodegradation of polymers in the environment is often difficult due to initially high molecular weight. Once molecular weight reduction has occurred, follow-up processes can be quite efficient. For example, one season agricultural films in Australia, that should 'bio-degrade' quickly and become mulchable are pretreated with strong UV illumination that facilitates initial photo-catalytic degradation. If radiation processing should be further

explored to assist in energy applications and fuel production, radiation facilitated breakdown of materials may be more attractive than radiation dependent synthesis. At the same time, coupling of catalysts with radiation sources may also represent novel directions and should be considered.

Summary and options for future strategies

Radiation treatments by simply irradiating materials or fuel precursors, and expecting the formation of some specific products, are not an attractive option. Radiation induced scission and bond reforming always compete and the required total doses from an energetic perspective appear to be prohibitive to push the system into a preferred reaction pathway. Using radiation treatments in the development of novel processes would require fundamentally different approaches and groundbreaking innovation. Radiation energy deposition can be attractive but must be geared towards well-defined reactions, and should be coupled with increased efficiency and other approaches to increase yields. Current options that should be considered are:

- The use of radiation processing to reduce the molecular weight, process, or chemically modify otherwise non-digestible raw materials for bio-fermentation and other biological fuel production processes. Similarly, consider if radiation treatments could also be applied to industrial processing of otherwise un-attractive carbon sources.
- Explore if radiation (energy deposition) could be used more efficiently when coupled with novel high-efficient catalysts (nano-particles?) and G-values (yields) could be enhanced (Societe Belge de l'Azote et des Produits Chimiques du Marly 1961). Design processes in which small molecules such as methane and CO₂ could be used as precursors for new chemical synthesis routes (Hearne 1969; Kurbanov 1977).
- Explore if irradiation and subsequent reactions of small molecules in their liquid state or under pressure could be fundamentally different to the established reactions of 'radiation chemistry' currently described in the literature (Davies 1964).

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