Title of the project: Renewable Gasoline from Waste Biomass

Focus Area: Energy, climate change, and the environment

Collaborative Team:

United States – Texas A&M University

Great Britain – University of Aberdeen

Brazil – Universidade Federal de Pernambuco (UFPE)

Vision

Global population is growing at a rate of 1.14% per year. The United Nations estimates that we reached 7 billion in 2011 and we will reach 8 billion in 2024, only 13 years later. [1] In addition to a growing population, the global standard of living continues to improve. According to the World Bank, global per capita GDP was $6700 in 2004 and it increased to $10,500 in 2013. [2] Some impacts of these statistics are to increase demand for energy while simultaneously increasing production of wastes.

This project focuses on developing the MixAlco process, which converts biodegradable wastes (e.g., municipal solid waste, sewage sludge, manure, agricultural residues) into "green" gasoline for a selling price of about $2/gallon. [3] Because the feedstock is biological in origin, combustion of "green" gasoline does not accumulate carbon dioxide in the atmosphere; the emitted carbon dioxide is fixed by photosynthesis and is converted to more plant matter. This technology has the potential to benefit the economy (domestic jobs, inexpensive transportation fuels), security (less dependence on foreign oil), and the environment (recycle wastes, reduce global warming).

A promising biofuel technology, the MixAlco process has received the Presidential Green Chemistry Challenge Award (1996) from the president and vice president of the United States, the McGraw-Hill Environmental Champion Award (1997), the Sigma Xi Walston Chubb Award for Innovation (2006), and the Odebrecht Award for Sustainable Development (2014).

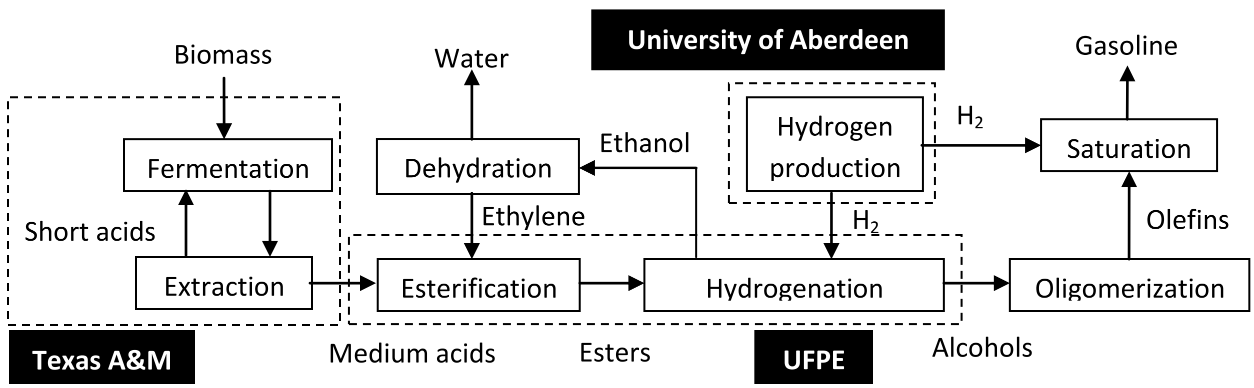

Figure 1. Schematic of MixAlco process.

Process Description

Figure 1 shows a schematic diagram of the MixAlco process. In principle, any biodegradable biomass can be employed. In this case, we will use waste food scraps because their putrid nature makes them a significant disposal problem. On a continuous basis, the biomass is fermented to carboxylic acids ranging from acetic acid (two carbons) to octanoic acid (eight carbons). To prevent conversion of acids to methane – a low-value product – methanogen inhibitors such as iodoform are added periodically. To maintain pH neutrality, a buffer is added to react with the carboxylic acids to form the corresponding salt. The microorganisms in the fermentor are a mixed culture derived from marine soil, so selected because they are well adapted to a salty environment. The fermentation broth is filtered to remove solid debris so the liquid can contact an immiscible extractant that has high affinity of medium-chain carboxylic acids (four to eight carbons) but low affinity for short-chain carboxylic acids (two to three carbons). The short-chain acids are returned to the fermentor where they continue to elongate.

The extracted medium-chain carboxylic acids react with ethylene to make esters, which are subsequently hydrogenated to make primary alcohols. Ethanol is recovered from the alcohol mix and is dehydrated to ethylene, which is recycled. The higher alcohols are oligomerized to olefins using a zeolite catalyst. The olefins are hydrogenated to form gasoline.

The two hydrogenation steps must be supplied with hydrogen. In the near term, the hydrogen can be supplied from standard technology (reformed natural gas); however, this process emits carbon dioxide. Eventually, a more sustainable low-carbon source of hydrogen must be found. A promising alternative is thermal water splitting, such as the sulfur-iodine cycle [4], which employs high-temperature heat (>850^{o}C) to split water into hydrogen and oxygen. The high-temperature heat can be derived from a solar furnace or Generation IV nuclear reactors.

Process Advantages

The advantages of the MixAlco process follow:

- *No sterility* – The fermentation employs a mixed culture of microorganisms derived from soil. Literally, dirt is added to the fermentor, so there is no need for sterile operating conditions. This greatly simplifies processing because contamination is not an issue.
- *No enzyme addition* – The mixed culture of microorganisms make their own enzymes, so the addition of expensive enzymes is not required.
- *Versaltile* – The mixed culture of microorganisms can ferment a wide variety of biomass components (e.g., cellulose, hemicellulose, starch, sugar, polysaccharides, gums, lipids, proteins, nucleic acids), so a wide variety of biomass wastes can be employed.
- *Wet processing* – Wet biomass feedstocks can be employed without the need for drying.
- *Scalable* – At small scale, the process is economical when making industrial chemicals, which are more valuable than fuel. This is an essential stepping stone in the path to commercialization.
- *Distributed processing* – The fermentations can be scaled down to process wastes produced by municipalities and farmers' co-ops. The product acids can be shipped to centralized facilities, such as conventional oil refineries, where they are upgraded to gasoline. In essence, the mixed acids are an infinitely renewable "bio-crude."
- *Compatible fuels* – Current transportation fuels employ energy-dense hydrocarbons. Our products are perfectly compatible with the current fuel infrastructure and require no special handling, such as are required by ethanol or hydrogen fuels.

Participating Organizations

As shown in Figure 1, the MixAlco process has the following three key steps: (1) fermentation of biomass to carboxylic acids, (2) production of hydrogen, and (3) reaction of hydrogen with carboxylic acids to produce gasoline. Each university is responsible for one of the steps, so each plays a vital role in the project as described below:

Texas A&M University

Role – Texas A&M will focus on fermenting biomass to carboxylic acids. Using a mixed culture of microorganisms derived from marine sediment, waste food scraps will be fermented to carboxylic acids. The medium-chain acids (four to eight carbons) will be extracted and the short-chain acids (two to three carbons) will be returned to the fermentor to continue being elongated.

Background – Since 1991, Texas A&M University has been developing the MixAlco process. The research program has involved 36 masters students, 30 PhD students, five post-doctoral students, and three faculty totaling over 270 person years. The process is being commercialized by Earth Energy Renewables, which has a demonstration plant in Bryan, TX.

Collaboration – Texas A&M is located 90 miles from Houston, the "Energy Capital of the World." Many of its graduates find employment in the energy industry, so Texas A&M seeks collaborations with universities that have a similar profile.

University of Aberdeen

Role – Currently, industrial hydrogen is produced from natural gas, which forms carbon dioxide as a byproduct that is released into the atmosphere and thereby increases global warming. To overcome this problem, the University of Aberdeen will investigate thermochemical production of hydrogen (i.e., water-splitting) from GEN-IV high-temperature nuclear reactors (HTR). Rather than conduct experiments, the studies will focus on two-folds, evaluating the literature to determine the most-suitable technology (gas-cooled or molten-salt based nuclear reactors or solar radiation power plants) for our application, and initial simulations of heat recovery in hypothetical HTRs.

Background – Since 2001, Dr Gomes has been actively engaged in nuclear research. Most recently, investigations have focused on safety assessment of two GENIV reactor designs: very-high temperature reactor (VHTR) and gas-cooled fast reactor (GFR). Cooling gasses reach temperatures of the order of 1000-1300°C that can be readily extracted in steam-generators. Such temperature range is ideally suited to water-splitting. Advanced thermo-hydraulic models developed by Dr Gomes were used in the reactors' safety assessment and may help in the design of an efficient heat extractor for water-splitting processes.

Collaboration – The University of Aberdeen is located near the North Sea oilfields and is located in the "Energy Capital of Europe." In 2009, Dr. Mark Holtzapple of Texas A&M presented seminars on sustainability at the University of Aberdeen. Recognizing that both institutions graduate students who serve the energy industry, they have negotiated a collaborative agreement that involves both student exchanges and research collaboration.

Universidade Federal de Pernambuco (UFPE)

Role – Mixed-acid samples produced in the demonstration plant of Earth Energy Renewables will be sent to the Universidade Federal de Pernambuco where they will be chemically processed into esters, alcohols, olefins, and gasoline using the chemical steps described in Figure 1. In this project, the focus will be the optimization of the first two steps: esterification and hydrogenation using heterogeneous catalysts. Experiments will be performed initially with reagent-grade carboxylic acid as a model compound representative of the acid extract. After optimization, the reactions will be performed with the acid extracts provided by Earth Energy Renewables, our commercialization partner.

Background – Since 1990, the Universidade Federal de Pernambuco (UFPE) has been actively engaged in chemical engineering research related to the production of chemicals by hydrogenating sugars. Since 2004, UFPE has done research on biofuel production from the conversion of biomass residues, lignocellulose, and vegetable oil with support from Petrobras. Jose Pacheco (UFPE) and Rafael Holanda (TAMU) have researched the energy integration of crude oil refining.

Collaboration – In 2012, Texas A&M created an alliance with Brazilian universities that share common goals and serve similar student bodies.

Project Management

Texas A&M is the lead institution and will be responsible for all reporting and fiduciary requirements of the grant. Texas A&M has a well-developed management infrastructure that manages about $800 million in research annually. The three universities will be in constant contact via e-mail. On a monthly basis, conference calls will be held via Skype. On an annual basis, the researchers will meet at an international conference to present the results of their research and to discuss the project face-to-face.

As shown in Figure 1, the research responsibilities are clearly delineated by the steps each university is investigating. The break points were selected to manage the project in a rational manner. Texas A&M will focus on the biological steps, UFPE will focus on chemical transformation of the acids to create esters and alcohols (key intermediates to form gasoline), and the University of Aberdeen will focus on hydrogen production. Within each domain, faculty members will manage the activities of their students, which is a natural line of authority.

Program Activities

Texas A&M

The fermentations will be conducted in plastic centrifuge bottles that are incubated at 40^{o}C, a temperature that is known to favor the formation of medium-chain carboxylic acids. The fermentations will be conducted in a countercurrent train employing a series of fermentors, typically four per train. Biomass is added to Fermentor 1 (F1) and water is added to Fermentor 4 (F4). Every second day, the contents of each bottle are centrifuged. The excess liquid is passed from F4 to F3, and so on. Excess solids are passed from F1 to F2, and so on. A buffer (e.g., sodium bicarbonate) is added periodically to maintain near-neutral pH. The liquid exiting F4 has concentrated carboxylic acids and their salts.

The product will be recovered by contacting with ion exchange resins, which are convenient to use at the laboratory scale. We have already performed preliminary batch fermentations using ion exchange resins, which in some cases have proven to double product yields compared to no-resin batch fermentations. Further, ion exchange resins have proven to selectively remove medium-chain carboxylic acids, which allows the short-chain acids to recycle to the ferment and elongate. In an industrial setting, the solid ion exchange resins will be replaced with liquid extractants that have similar abilities to selectively remove medium-chain carboxylic acids.

The ultimate objective of the research is to study operational parameters (e.g., solid feed rate, liquid feed rate, product concentration) on fermentation rates, yields, and product spectrums. These data are essential to perform economic evaluations.

University of Aberdeen

Thermal water splitting involves the use of chemicals that react with water at low temperature. When the chemicals are heated to high temperatures, hydrogen and oxygen evolve, thus regenerating the chemicals so they can be recycled and used again. The most famous example is the sodium-iodine cycle [4]; however, other cycles have been explored as well. For example, the University of Colorado has recently developed a process to use solar energy to thermally split water using ZnO. [5]

The focus of this study is to evaluate the water splitting literature to determine which technologies are most suitable for our application. A major goal is to determine if solar or nuclear energy is the best option. Further, to perform economic assessments, the cost of the hydrogen must be estimated so it can be compared to conventional technology (steam reforming of methane).

Universidade Federal de Pernambuco (UFPE)

UFPE has well-equipped laboratories that include Parr reactors and gas chromatographs. All the chemical processing steps shown in Figure 1 can be performed using existing equipment. Appropriate catalysts and operating conditions are selected for each reaction performed in the Parr reactors. Appropriate columns and operating conditions are selected to measure the product spectrum produced in the reaction.

The first series of experiments will be performed with reagent-grade carboxylic acid as a model compound. The second series of experiments will be performed with liter quantities of industrial-quality mixed acids provided by Earth Energy Renewables, our commercialization partner. The acids will be processed sequentially according to the steps shown in Figure 1. Each step requires separate optimization of operating conditions.

Program Evaluation

Texas A&M

The fermentations are evaluated based on the following criteria: yield (g acids produced/g dry biomass fed), conversion (g biomass digested/g dry biomass fed), selectivity (g acids produced/g biomass digested), product concentration (g/L), and product spectrum (wt % of each acid). The fermentor operating conditions – solid loading rate (g/(L·d), liquid residence time (d) – will be explored to determine their impact on the above criteria.

University of Aberdeen

The literature will be evaluated to select the most promising thermal water-splitting technologies. The following criteria will be used to evaluate the various options: required temperature (^{o}C), materials of construction, chemical make-up requirements, safety, operability, market readiness, and suitability for solar or nuclear heat source. Ultimately, the appropriate technology will be selected based on the cost of hydrogen ($/kg).

Universidade Federal de Pernambuco (UFPE)

The chemical conversions will be based on the following criteria: reaction rates (g product/(L reactor volume·day)), conversion (g reacted/g fed), yield (g product/g fed), and selectivity (g product/g reacted). The reactor operating conditions – temperature (^{o}C), pressure (kPa), and catalyst type – will be explored to determine their impact on the above criteria.

Measures of Sustainability

Expected Outcomes

The process described in Figure 1 is the latest embodiment of the MixAlco process and is different than previous versions. In earlier versions, we recovered short-chain carboxylic acids, which were converted to secondary alcohols (e.g., isopropanol). Via oligomerization, the alcohols were converted to gasoline using zeolite catalysts at fairly aggressive operating conditions that can coke the catalyst. The impact is loss of product and reactor downtime, both of which negatively impact process economics. Even so, our economic evaluations indicated that gasoline could be sold for about $2/gal. [3] The new embodiment shown in Figure 1 employs more gentle operation conditions, which should eliminate coking. Further, the use of primary alcohols results in significantly higher product yields.

A further benefit of the latest embodiment is that products are extracted from the fermentors, which allows for low product concentrations and thereby reduces product inhibition. The impact is that the fermentors should be able to operate with more throughput, which will lower costs.

Previous economic evaluations were performed using hydrogen produced from undigested biomass residues. This required gasification and gas clean-up, all of which were expensive causing the hydrogen to cost about $3/kg. Should thermal water splitting produce hydrogen at a lower cost, process economics will be improved further.

The combined impact of improved performance of the biological and chemical processing steps is to lower operating costs, which should reduce the required selling price of the gasoline product, potentially below $2/gal.

Expected Benefits to Research Capacity

Until now, the primary focus of MixAlco development has been in the United States; however, the technology can be applied globally. Gasoline is required everywhere and wastes are produced everywhere. This proposed project will allow US researchers to collaborate with international researchers and thereby help diffuse the technology around the world.

Great Britain is an example of a developed nation with high population density. The biomass wastes will primarily be municipal solid waste and sewage sludge. Brazil is an example of a developing nation that has a high population density in urban areas, but also has abundant agricultural waste such as sugarcane bagasse. Introducing MixAlco technology to researchers in these nations will allow for a more diverse and sustainable funding base, including both public and private funding.

Anticipated Knowledge Transfer

Since 1991, various versions of the MixAlco process have been explored and documented in the literature. The MixAlco process is not a static technology; rather, it evolves as knowledge improves. By directly involving researchers from other nations, it will "stir" the technology allowing for cross-fertilization of ideas.

Broader Institutional Collaboration

Once the benefits of the MixAlco technology are realized by direct collaboration with international researchers, it is anticipated that the relationships will continue. As new research solicitations are released in each country, the team that has already formed will be well-prepared to respond to the solicitations and hence perpetuate the relationships.

Conclusions

The MixAlco process can transform any biodegradable waste biomass into gasoline at a selling price of about $2/gallon, and therefore is an economical solution to both energy and waste problems. The proposed research project has the potential to lower processing costs. This collaborative effort involves researchers in North America, South America, and Europe, which will enhance technical exchanges and thereby enhance the rate of commercial implementation.

References

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