WHITEPAPER

Renewable & Synthetic Fuels Production

MODULAR SMALL SCALE GASIFICATION & F-T SYSTEMS FOR RENEWABLE AND SYNTHETIC FUELS PRODUCTION

A Systems Approach for Achieving Domestic Energy Security and Self-sufficiency, Sustainable, Legacy Employment, Robust Economic and Environmental Stewardship Benefits with Integrated BioEconomy Cluster Parks.

CLEAN ENERGY – CLEAN AIR – CLEAN WATER – SAFE FOOD – GOOD JOBS

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Order of Presentation

1.0 Overview

This Whitepaper addresses the manufacture of high value, "renewable" and "synthetic" liquid transportation fuels produced from non-petroleum feedstocks by standard chemical engineering unit operations.

These liquid fuels are more efficient and environmentally responsible than conventional fuels produced from petroleum, and, in the case of fuels produced from biomass including biosolids and manures, biogas, coal seam methane and flared natural gas, are "renewable" as well.

Gasification describes a thermochemical process by which carbohydrate materials, e.g. biomass, and hydrocarbon materials, e.g. petroleum, coal, petroleum coke, are converted to a gas state by high temperatures in substoichiometric oxygen atmospheres by means of partial oxidation reactions with air, oxygen, and/or steam.

Gasification's product gas is a mixture of Carbon Monoxide plus Hydrogen ($CO + H_2$) that is known in the industry as ***synthesis gas*** or ***syngas,*** which is a fuel in its own right that can directly power gas engines, produce hydrogen, methanol and mixed alcohols and converted via the ***Fischer–Tropsch process*** into synthetic diesel and aviation turbine fuels.

Advantages of gasification includes the ability to utilize abundant renewable biomass and waste resources, including forest products, agwastes and municipal solid wastes which are otherwise disposed of as problem biodegradable wastes (Re: **2011 *U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry***) and the ability to utilize syngas and syngas-based fuel products, allowing these energy feedstocks to be utilized in incongruent power generation systems.

The ***Fischer-Tropsch (F-T) process*** was developed by Franz Fischer and Hans Tropsch at the "Kaiser-Wilhelm-Institut für Kohlenforschung" in Mülheim an der Ruhr (Germany) in 1925, fueled Germany's war machine 1939-1945, and today, more than 1 million barrels/day of jet fuel and/or diesel fuel is created using natural gas or synthetic gas derived from coal.

The Fischer-Tropsch process converts syngas Carbon Monoxide and Hydrogen produced by the gasification of coal, natural gas, or biomass into synthetic lubrication oils and fuels. It is a source of high quality, low-sulfur diesel and aviation turbine fuels, expands the supply and can reduce the cost of petroleum-derived hydrocarbons.

1.1 Use of Biomass, Flare Gas and Problem WWTP Biosolids for F-T Fuels

Municipal Wastewater Treatment Plant (WWTP) biosolids are the most expensive solid waste management problem in the U.S. Economy.

WWTP biosolids consist of carbohydrates, clays and sand with problem heavy metals, pharmaceuticals, viruses and bacteria, with biologically contaminated Fats, Oils and Greases (FOG's) from restaurant and household kitchens.

Great Plains Biosciences Group LLC's (GPBG's) modular gasification/F-T systems can utilize most biomass, municipal solid wastes and plastics, agwastes and biogases, WWTP digester biogas and biosolids to generate electrical power or produce diesel/jet fuel or fuel alcohol.

By converting natural gas collected from petroleum drilling sites on the Bakken and Eagle Ford formations where it is currently being flared, GPBG's modular gasification/F-T systems can achieve production rates of 500 BOPD, (7.4 MGPY), 1,000 BOPD (14.7 MGPY), ***and more***, of Diesel and Jet Fuel, depending on available flare gas rates, logistics and site characteristics.

F-T liquid fuels have been approved for procurement by the US Military.

2.0 GPBG's *Systems Approach* for Production of Renewable & Synthetic Fuels

GPBG's AgraPlex® corporate objective is to create petroleum-replacement transportation motor fuels for spark-ignition (SI) and compression-ignition internal combustion engines from abundant non-food terrestrial and aquatic microalgae resources. Algae have been proven to be an ideal biofuels feedstock resource; ***these fuel products are significantly more environmentally responsible than fossil fuels and achieve sustainable domestic employment, as well as economic and national security benefits.***

GPBG has developed a ***Systems Approach*** which elegantly and efficiently can simultaneously provide solutions for national energy, air quality, water quality, waste management and unemployment problems.

GPBGs' ***Systems Approach*** achieves process efficiencies capable of yielding biofuels and other organic chemical products at the lowest available production costs.

2.1 GPBG's Renewable Synthetic Fuels Programs

Phase I Program	**Phase II a. Program**	**Phase II b. Program**
BioGasoline	Phase I Products, plus	Phase I & II a. Products, plus
BioDiesel	Synthetic Natural Gas	Aviation Turbine Fuel
Oxygen	Methanol	FT Synthetic Diesel & Gasoline
Clean Water	Catalytic Ethanol	Ammonia
	Butanol	Thermal and Electrical Power

2.2 Renewable and Alternative Fuels

BioGasoline
BioDiesel
BioEthanol and Catalytic Ethanol
Butanol
Dimethy-ether (DME)
Furfural
Methanol
Gasoline, diesel and Aviation turbine fuel via Gas-to Liquid (GTL), Coal-to-Liquid (CTL) and Biomass-to-Liquid (BTL) Fischer-Tropsch synthesis, and
Ammonia, NH_3, for the U.S. agricultural market and mining industries.

2.3 GPBG Program Benefits

1.) FlexFuels production facilities yielding cost-effective petroleum-replacement motor fuels via an integrated system of optimized discrete process loops,

2.) carbon dioxide, CO_2 mitigation,

3.) beneficial utilization and extinguishment of problem biologically active agricultural and animal metabolic waste streams, including municipal wastewater effluents, and

4.) significant, sustainable employment.

3.0 Gasification

Gasification describes a thermochemical process by which carbohydrate materials, e.g. biomass, and hydrocarbon materials, e.g. petroleum, coal, petroleum coke, are converted to a gas state by high temperatures in substoichiometric oxygen atmospheres by means of partial oxidation reactions with air, oxygen, and/or steam.

3.1 Basic Gasification Thermochemical Reactions

Gasification is accomplished with heat, pressure and water. The process operates in a heated, oxygen starved environment (known as **pyrolysis**) which drives off moisture and volatile gases contained in the feedstock. Gasification is not a combustion process.

Pyrolysis produces carbon char and ash which converts the solid carbon molecule into a gas.

A third process is accomplished with the injection of ionized water in a process known as **steam reformation**, creating a **water shift reaction** to yield Synthesis Gas.

The basic chemical reaction used in this process is

$$\mathbf{C + H_2O = CO + H_2.}$$

Conventional gasification processes requires the injection of oxygen for the reaction:

$$\mathbf{2C + O_2 + H_2O = CO + H_2 + CO_2}$$

Conventional gasification plants produce high amounts of carbon dioxide in their process heated by combustion which is represented by:

$$\mathbf{C + O_2 = CO_2.}$$

An advanced gasification process actually reduces CO_2 through the reaction:

$\mathbf{CO_2 + C = 2CO}$ (and does not produce combustion by products)

3.2 Gasification Technology Development

The development of the thermochemical technology process family today categorized as ***gasification*** dates to the mid-eighteenth century, contemporaneous with James Watt's development of the first successful steam engine.

America's first gasification technology-based commercial installation dates to 1816 at Sparrows Point, Baltimore Maryland, off-shore from which the British Navy's rocketry barges and frigates fired on Fort McHenry, September 13-14, 1814. Gasification systems produced "town gas" for lighting and cooking from the early 1800's to the 1960's first using wood then coal feedstocks. Electricity and natural gas later replaced town gas for these applications, but the gasification process has been utilized for the production of synthetic chemicals and fuels since the 1920s.

Gasification has been used commercially worldwide for more than 50 years by the chemical, refining, and fertilizer industries and for more than 35 years by the electric power industry. Currently over 40% of South African motor fuel is derived from coal gasification, as well as 100% of their aviation fuel. There are more than 420 gasifiers currently in use in some 140 facilities worldwide, with 19 plants operating in the United States.

The major suppliers of gasification technology are Sasol Lurgi, GE, Conoco-Phillips, and Shell Oil with dozens of large, expensive plants operating worldwide. In the U.S. a large gasification plant is producing synthetic natural gas in North Dakota; integrated gasification combined cycle (IGCC) demonstration plants in Florida and Indiana are generating electricity.

Eastman Chemical's coal gasification plant located in Tennessee once produced all Kodak film for the photography industry has operated successfully for over 25 years and continues to produce methanol, plastics, and other products for the chemical industry.

3.3 Synthesis Gas from Gasification

In standard industrial gasification thermochemical process reactions, carbohydrate (biomass) and hydrocarbon (petroleum, coal and natural gas) materials are converted to **synthesis gas:** $H_2 + CO$ and typically includes trace methane, carbon dioxide and water. It is a medium Btu-value gas in range 475-515 Btu/SCF which is appropriate for powering electrical power generator sets, chemicals and fuel alcohol production.

GPBG's Systems reduce the organic feedstock volume by at least 90 percent, and will consume and extinguish municipal solid and agricultural carbohydrate wastes, and produce electrical power, petroleum replacement generator set, transportation fuel and aviation fuel.

GPBG can utilize **gasification** technology to extinguish the residual algal material left from the production of biodiesel. Gasification of carbohydrate–biomass or hydrocarbon feedstocks produces clean, high Btu fuel gas for use in thermal or electrical power systems and for synthesis of chemicals.

Gasification of carbohydrate (biomass) and hydrocarbon (petroleum and coal) materials results in material volume reductions of 90 to 97 %. Syngas produced from residual algal biomass and other carbohydrate feedstocks is available for the concurrent catalytic production of additional fuel alcohols and other products in Biomass-to-Liquids, BTL, standard chemical engineering processes.

The synthesis gas can be used as a clean energy source for industrial processes, the generation of electrical power, or as a raw feedstock material for chemical synthesis processes. The mineral ash may be disposed in a landfill, used as a soil amendment, or mixed with concrete as filler for construction.

Syngas combustion produces 36% less CO_2 vs. Natural Gas and 66% less CO_2 vs. wood.

Great Plains Biosciences' gasification technology's syngas fuel product can be upgraded to pipeline quality gas–1,000 Btu/SCF HHV. Residual ash is between 2-15 % by weight; ash from residual algal biomass is typically in the range 2-3%.

Other valuable chemicals; ammonia, urea, DME, methanol, acetic acid, vinyl acetate, acetic esters, etc., can be produced at the biorefinery utilizing these feedstocks.

3.4 GPBG's Biomass Gasification Energy Program

Management of solid wastes is an increasingly compelling issue for urban areas, smaller communities and all facets of agriculture and food processing. GPBG addresses theses serious environmental problems by providing an efficient and environmentally responsible method for the elimination of problem organic wastes, including municipal solid wastes, by means of an Integrated Gasification Combined Cycle ("IGCC") biomass gasification power plant.

Approximately 15-to-20 percent of the solid waste stream from municipalities is made up either of metals, glass, and plastics that can be recovered and recycled, or non-recyclable demolition wastes such as concrete, wallboard, etc. However, about 80 to 85 percent of the Municipal Solid Waste – MSW - is mixed organic materials, Non-Recyclable Organic Solid Wastes – NROSW - "just garbage".

GPBG's renewable energy program utilizes primarily waste materials including MSW/NROSW, Residential Green Yard Waste and Agricultural Waste as its IGCC system feedstock. "Tipping fees" are charged for disposal of these feedstocks creating an additional revenue stream.

It is important to secure long term contracts with adjoining counties, municipalities, national haulers such as Waste Management, Inc. etc., and large agricultural operators for feedstocks.

3.4.1 Operation of the GPBG Gasification System

- RDF, a carbohydrate-hydrocarbon feedstock mixture, is fed into GPBG's IGCC systems' high - temperature reactor(s) containing limited oxygen for further reaction kinetics.
- Under these substoichiometric, limited, oxygen "reducing" conditions and the reactors' elevated temperatures and pressures, the feedstock's carbon chemical bonds are disrupted and the vaporized feedstocks' carbon, hydrogen and oxygen free radical elements preferentially recombine in a gaseous state consisting of mixtures of hydrogen and carbon monoxide. Chemists and Industry refers to this product as ***synthesis gas*** or ***"syngas."***
- The syngas is then cleansed using commercially available, proven systems that remove particulates, vaporized trace metals such as sodium and mercury, and sulfur compounds.
- Synthesis gas' hydrogen-carbon monoxide ratios typically range around 50%-50%. This varies with reactor technology, temperature, pressure, process conditions, feedstock moisture and composition, steam state and injection rate, control loops, and other factors.
- Synthesis gas can be directly fired in lean-burn heat engine generators for electrical power production, fired in boilers for steam, upgraded by methanation to yield "Synthetic Natural Gas" (methane), upgraded to yield ***methanol***, a 1-carbon alcohol, CH_3OH, a valuable chemical, fuel and solvent, and a vast list of organic chemicals and products.
- Synthesis gas can be further synthesized to yield synthetic gasoline, diesel and aviation turbine fuels by standard chemical engineering unit operations including the pre-WW2 German ***Fischer-Tropsch*** process.
- Synthesis gas is modern societies' basic hydrocarbon chemical building block ***"…for production of everything from Chanel Number 5 to Aviation Turbine Fuels."***

3.4.2 Organic Materials Accepted by GPBG's Biomass IGCC/F-T station

- Plastics, tires, automotive and industrial rubber belts, hoses, lubricants, oils and greases
- Forest Industry and Agricultural Biomass including animal CAFO metabolic wastes
- Food wastes and Non-recyclable Organic Solid Wastes – NROSW, MSW, RDF and SRF
- Biological Wastewater Treatment Plant Sludge -"Sewage Biosolids," and medical wastes
- Scrap lumber, tree trimming/yard green wastes, other carbohydrates and hydrocarbons

4.0 Fischer-Tropsch (F-T) fuels

The term used for F-T systems producing "drop-in" diesel and kerosene – class liquid motor fuels is "XTL technologies" – for projects which synthesize methane, coal and biomass feedstocks, eg: gas-to-liquids (GTL), coal-to-liquids (CTL), or biomass-to-liquids (BTL).

The typical F-T reactions produce alkanes which are valuable as diesel fuel substitutes:

$$(2n + 1)\ H_2 + n\ CO \rightarrow C_nH_{(2n+2)} + n\ H_2O$$

F-T chemical reactions produce a variety of hydrocarbon products and intermediates. In addition to ***alkanes***, F-T catalysts produce ***alkenes***, ***alcohols*** and other ***oxygenated hydrocarbons***.

"Synthetic diesel fuel's" H+O+C chain is constructed by catalytically stacking hydrogen atoms on carbon and oxygen atoms in the F-T process until the desired chemical product is achieved; converting CO and H_2 into "synthetic diesel fuel" products is a multi-step reaction with several intermediates.

4.1 Diesel Fuel from Modular Gasification/F-T Fuel Production Systems

GPBG's team has the technology for small scale ASTM grade F-T diesel fuel production systems utilizing gasified biomass and biogas, pipeline or stranded natural gas (flare gas). By converting natural gas collected from petroleum drilling sites where it is currently being flared, GPBG's modular systems can achieve production rates of 500 BOPD, (7.4 MGPY), 1,000 BOPD (14.7 MGPY), ***and more***, of Diesel D2, JP8 and JetA1, depending on available flare gas rates, logistics and site characteristics.

Municipal Wastewater Treatment Plant (WWTP) biosolids are the most expensive solid waste management problem in the U.S. Economy. WWTP biosolids consist of carbohydrates, clays and sand with problem heavy metals, pharmaceuticals, viruses and bacteria, with contaminated Fats, Oils and Greases (FOG) from restaurant and household kitchens.

GPBG's modular gasification/F-T systems can utilize WWTP digester biogas, extinguish the WWTP biosolids on-site and produce diesel fuel.

4.2 Methanol Fuel from Modular Gasification/F-T Fuel Production Systems

Methanol is methyl alcohol, CH_3OH, a one-carbon alcohol, the simplest of all alcohols. Methanol is commonly referred to as wood alcohol as it was first produced as a minor byproduct of charcoal manufacturing. Methanol is the simplest, safest and easiest way to store and transport liquid oxygenated hydrocarbon. Methanol is a valuable industrial chemical intermediate and solvent. It is an excellent fuel with an octane number of 100 and it can be blended with gasoline as an excellent oxygenated additive.

Methanol, "wood alcohol" was produced during the both World Wars by acid hydrolysis of cellulose feedstock, fueling German, Japanese, Russian and U.S. war machines. The Acid Hydrolysis process is commercially proven and available today.

Currently, methanol is manufactured almost exclusively from synthesis gas produced from natural gas and coal. Like ethanol, methanol can be produced by fermentation of biomass, as well as the reductive hydrogenative conversion of CO_2. Like ethanol, it can be used directly in current automotive spark ignition (SI) engines with only minor modifications, and is a valuable fuel in stationary power and automotive Direct Methanol Fuel Cells (DMFS).

5.0 Materials Recovery Facility (MRF), RDF and SRF

The IREP Biomass IGCC station has the capability to accept and extinguish a wide range of organic solid wastes, including NROSW, plus other carbohydrate and hydrocarbon materials. The IGCC station's RDF feedstock is prepared by an advanced Materials Recovery Facility (MRF) which separates valuable recyclable materials, inerts, rocks/dirt from the feedstock waste streams, cleans and sizes the feedstock for the gasification system.

Refuse-derived fuel (RDF) or solid recovered fuel / specified recovered fuel (SRF) is a solid fuel product produced by shredding and dehydrating NROSW/MSW by means of a MRF. RDF consists of the dehydrated biodegradable wastes and plastic components of NROSW/MSW. Non-combustible materials such as glass and metals are removed during the post-treatment processing cycle with mechanical separation processing. Valuable copper, aluminum, steel, and clean plastics, cardboard and paper are separated, bailed and sold to their respective markets.

6.0 Carbon Dioxide Sequestration and Recycling

A North Carolina firm announced that it has developed a low-cost method for the extraction and purification of flue gas CO_2 for use in algae farms and other ventures that require CO_2.

The company said that it had reduced the recovery cost for CO_2 to \$5 per ton. 2.1 pounds of CO_2 are generally required per pound of algae produced, providing a CO_2 feedstock cost of \$0.04 per gallon for algal fuel production. The process is reported to achieve 98 percent capture efficiency for CO_2, SO_2, NO_2, NO_3, nitrous oxide (N_20), haloflurocarbons, CH_4, HO (hydroxide), H_2S, Aldehit (H-CHO), Mercury (Hg), Hydrogen Florid (HF), Trifluoromethane (HFC-$_{23}$), phosphor (P), lead, SnO_2 micro crystals, (C_{l2}), Vinyl Chloride (C_2H_3Cl) volatile organic compounds (VOC), sulphur hexafluoride (SF_6), and particulate matter.

Carbon dioxide sequestration is the capture and locking-up or the reutilization of CO_2; Hydrogen produced in GPBG program's gasification system is available for catalytic production of fuel alcohols and more complex hydrocarbon compounds in standard chemical engineering processes.

6.1 Reacting CO_2 from ethanol plants, electrical power stations and cement plants with H_2

a) CO_2 to Methanol: $CO_2 + 3\,H_2 \rightarrow CH_3OH + H_2O$

b) CO_2 to Ethanol: $CO_2 + H_2 \rightarrow CO + H_2O$
$CO + 2\,H_2 \rightarrow \frac{1}{2}\,C_2H_5OH$

c) CO_2 to Gasoline: $CO_2 + 3\,H_2 \rightarrow CH_3OH + H_2O$
$CH_3OH \rightarrow (-CH_2-) + H_2O$ **Mobil Process**