CHEMSYSTEMS
PERP PROGRAM

Report Abstract

Biomass Gasification
PERP06/07S5

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INTRODUCTION

Biomass gasification represents one part of the spectrum of conditions and phenomena involving the rapid, high temperature mass oxidation of biomass. Gasification produces a gaseous mixture of primarily H_2, CO, and CO_2, and water vapor. The relative amount of oxygen provided and other conditions determine if biomass will gasify or "pyrolyze" (convert mainly to a mixture of condensable liquids and gases with a large residue of char). In gasification, with biomass being heated with no oxygen or as little as only about one-third the oxygen needed for efficient complete combustion, it gasifies to a mixture of CO and H_2 - known as synthesis gas or syngas. This is a process that is completely analogous to gasification of coal, heavy oil, and petroleum coke, all commercialized technologies.

Gasification can be used to convert the by-products and residues from other biofuels processes as well as from the agricultural value chain that supplies these processes and agricultural, forest products, and food processing biomass wastes in general. Some such materials that can and have been used, or are currently proposed for gasification include: straw and chaff from various grains or legumes, peanut shells, seed oil expeller residue, DDGS from dry mill grain fermentation, sawdust and wood chips or pellets, prepared corn stover, sugarcane field trash and bagasse, paper pulp mill black liquor, sugar beet pulp, cotton linters, poultry litter, other animal bedding, citrus pulp, lignin and unconverted sugars from cellulosic biomass fermentation, etc.

Second-generation biofuels produced from lignocellulosic feedstocks like straw, grasses and wood have long been seen as the necessary successor to today's first-generation grain ethanol plants, but the costs of implementing the fermentation and/or gasification technologies have been too high for these technologies to be competitive. The capital costs for advanced biochemical and thermochemical biorefineries - which are comparable - may be four to five times as high as comparably sized grain ethanol plants of comparable sizes.

Lignocellulosic biofuels platforms include enzymatic hydrolysis of cellulose to sugars and fermentation of these C_5 and C_6 sugars to either ethanol or butanol (the biochemical platform). It should be noted that the residuals from such fermentation will be lignin plus concentrates of un-digested biomass, unhydrolyzed starches, unfermented sugars, and other residuals. These materials can be utilized for energy production (power and heat) for internal use and/or sale either by anaerobic digestion-plus combustion of biogas or by gasification, or a combination of both.

The thermochemical platform (biomass gasification for syngas production) with no direct biomass fermentation involved can have several potential end products – biodiesel fractions from as Fischer-Tropsch (F-T) synthesis, methanol for sale or conversion to gasoline or olefins, hydrogen, or higher alcohols by modified Fischer–Tropsch (F-T) or other catalytic syntheses.

Drivers for Biomass Gasification

Biomass gasification has a broader applicability and feasibility. It can be employed to make renewable substitutes or blendstocks for both gasoline and diesel engine/distillate heating oil fuels. Various different catalytic systems can be used with the syngas produced. The primary advantages of this approach is its flexibility in contrast to fermentation of various carbohydrate substrates to fuel alcohols or transesterification of natural oils and fats (triglycerides) to biodiesel (fatty acid alkyl esters).

- Both the feedstocks (all the organic components of biomass – carbohydrates, lignin, proteins, and fats) and products (hydrocarbons in most cases, but also higher alcohols in some cases) are more fungible than with fermentation-based alcohols or with triglyceride-based biodiesel (FAME or FAEE).
- Processing technologies are more fungible with thermochemical conversions of other carbonaceous resources, in that materials handling, gasification, syngas treating, and catalytic synthetic fuels production can all be leveraged (i.e., designers and operators can learn from and add to experience with and developments of coal, coke, and heavy oil gasification); and the same feedstocks and front end systems can be used to make either gasoline-range or diesel-range fuels.
- Syngas-based complexes can be used to make power and chemicals as well as biofuels.

Just as syngas mixes and reacts more readily with oxygen for combustion, it is also more readily reactive with chemical catalysts than are solid fuels, greatly enhancing its ability to be converted to other valuable fuels, chemicals and materials. The Fischer-Tropsch process converts syngas to liquid transportation fuels. The water-gas shift process can convert syngas to more concentrated hydrogen for fuel cells. A variety of other catalytic processes can turn syngas into a myriad of substitute gasoline, diesel, chemicals, or other potential fuels or products.

Other drivers of biomass gasification briefly discussed in the report include:

- Peak Oil
- Global Warming
- Other factors (Environmental Drivers, Rural Development, National Balance of Payments, Sustainable Economics, Corporate/NGO Initiatives).

Biofuels Limits – Biomass Abundance

Nexant believes and details in this report that utilization of total biowaste, without using any on-purpose new energy crops or biological products, such as switchgrass, energy cane, or algae, could alone potentially supply nearly the total current gasoline demand in the United States, and also globally, depending on the much less certain annual inventory outside the United States.

The following topics are also briefly discussed in the introduction of this report:

- Co-generation of Chemicals, Electricity, and Heat
- Leveraging Coal Gasification and Syngas Technologies
- Role of Pyrolysis – Preparing Biomass for Logistics and Process

BIOMASS GASIFICATION TECHNOLOGIES

Several different approaches can be used to convert solid fuels, including biomass, to liquid fuels of various types and qualities.

Biomass Pyrolysis

Pyrolysis is thermal decomposition occurring in the absence of oxygen. It is also always the first step in processes for combustion and gasification of solid materials, followed by total or partial oxidation of the primary products. Lower process temperature and longer vapor residence times favor the production of char (charcoal). Higher temperatures and longer residence times increase biomass conversion to gas.

Biomass pyrolysis liquids differ greatly from petroleum-based fuels in both their physical properties and their chemical compositions. Pyrolysis liquids generally contain more water and have problems of overall chemical instability, susceptibility to aging, acidity, corrosivity, high viscosity, relatively low calorific value, and are they are especially unstable when heated in air. Pyrolysis liquids need to gasified or upgraded or otherwise stabilized soon after they are produced to avoid formation of polymers, gums, and gels.

Various pyrolysis technologies briefly discussed in this report include:

- Fast Pyrolysis - occurs in a few seconds or less, therefore chemical reaction kinetics play a role along with heat and mass transfer and phase transition phenomena
- Slow pyrolysis - another version of the thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen
- Torrefaction - airless, mild pyrolysis of biomass materials.

Choren Carbo-V – Staged Gasification

Carbo-V gasification is described as a dry-feed, three phase biomass gasification system. (The name of the company is derived from the components of the words **C**arbon, **H**ydrogen, **O**xygen and **Ren**ewable). The Carbo-V process is designed to handle variability in biomass properties, low heating value, and other issues to produce syngas.

Pearson Technologies Inc.

Pearson Technologies, Inc. ("PTI"), Aberdeen, MS, is a private corporation with a mission to research, develop, optimize and commercialize their process for ethanol production, described as a proprietary "reformer" that gasifies biomass in an oxygen-starved environment to produce syngas, which is reacted with a proprietary catalyst in a Fischer-Tropsch synthesis under conditions that produce ethanol with a conversion of greater than 98 percent with recycle.

Indirect Gasification

There are several versions of indirect gasification in which heat can be transferred from a source burning biomass derived fuel to a process step which converts biomass or fractions such as char, bio-oil, or gases to syngas, generally in the presence of steam. Heat may be transferred by using a circulated heated, fluidized particulate medium, such as sand, in arrangements that resemble FCC units, or indirectly in enhanced versions of tubular heat exchangers. With the application of steam to the gasification regime, the system is often called “biomass steam reforming”.

- The BCT-TRI development is described in the report as a salient example of this approach.

Syngas Fermentation

Although most corporate efforts and the vast majority of U.S. federal resources have gone towards developing enzymatic conversion, there also has been some good work done on biosyngas fermentation in the United States and elsewhere.

The basic chemistry of bacterial fermentation of CO, CO_2 and H_2 to ethanol is shown below.

$$6CO + 3H_2O \longrightarrow C_2H_5OH + 4CO_2$$
$$6H_2 + 2CO_2 \longrightarrow C_2H_5OH + 3H_2O$$

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In fermentation, co-production of acetic acid leads to a decreased pH, which inhibits the organisms. To avoid further inhibition the organisms switch to ethanol production.

This type of technology, while still unproven, may enable higher yields than fermentation through conversion of non-carbohydrate (e.g., lignin) and/or hemicellulosic fractions to syngas. The process is described in more detail in the report.

Air Separation - Oxygen for Gasification

Many of the direct gasification technologies under development, if aimed at syngas production for fuel or chemicals synthesis, must use oxygen-enriched or essentially pure oxygen atmospheres to accomplish biomass conversion by partial oxidation. Under this section, the leading technologies for preparing high oxygen atmospheres for this purpose are briefly outlined:

- Conventional Cryogenic Processes
- Conventional Cryogenic Processes
- Ion Transport Membrane (ITM)

Status of Technology Development – Other Initiatives

Some of the leading commercial development initiatives for biomass gasification and production of chemical and fuel syngas derivatives are discussed under the section headings above, as they represent various aspects of development in this field. Under this section heading, some of the other leading developments are summarized:

- GreenField Ethanol and Enerkem - a commercial partnership to develop gasification of lignocellulosic substrates to make ethanol
- Range Fuels, Inc. - gasification-based process for producing ethanol from cellulosic biomass
- Energy Quest, Inc. - Syngas Energy Corp. - fluidized bed gasifier
- Syntec Biofuel – technology parallels the low-pressure catalytic methanol synthesis process
- R&D in Sweden on gasification of biomass and waste to produce a number of different biofuels from syngas
- Coskata – ethanol production from a wide range of feedstocks utilising gasification and fermentation of syngas to ethanol/

Liquid Biofuels - Mixed Higher Alcohols Synthesis (HAS)

Because there were hardly any incentives for development and significant technical and business risks related to mixed alcohols processes, little commercial development occurred in the late 1990s and to date. Developers who were early investigators of this technology in the mid-1980s have since abandoned it. New catalysts, new project developers, and a desire to find alternatives for petroleum based-fuels and fuel oxygenates have encouraged renewed interest in mixed alcohols. Much of the renewed interest is from developers of technologies and projects based on exploitation of coal and stranded gas resources through syngas made in coal gasification and/or natural gas reforming processes, but these developments are completely applicable to syngas made from biomass as well.

Much of the discussion in this section is based on work performed by Nexant for NREL in "Task 9: Mixed Alcohols from Syngas: State of Technology", as part of a larger study, "Equipment Design and Cost Estimation for Small Modular Biomass Systems, Synthesis Gas Cleanup and Oxygen Separation Equipment, Nexant, NREL/ACO-5-44027", which supplements previously reported NREL work in the mixed alcohols section of its 2003 technical report, "Preliminary Screening - Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas, P.L. Spath and D.C. Dayton, December 2003, NREL/TP-510-34929".

The following topics are briefly discussed in this section:

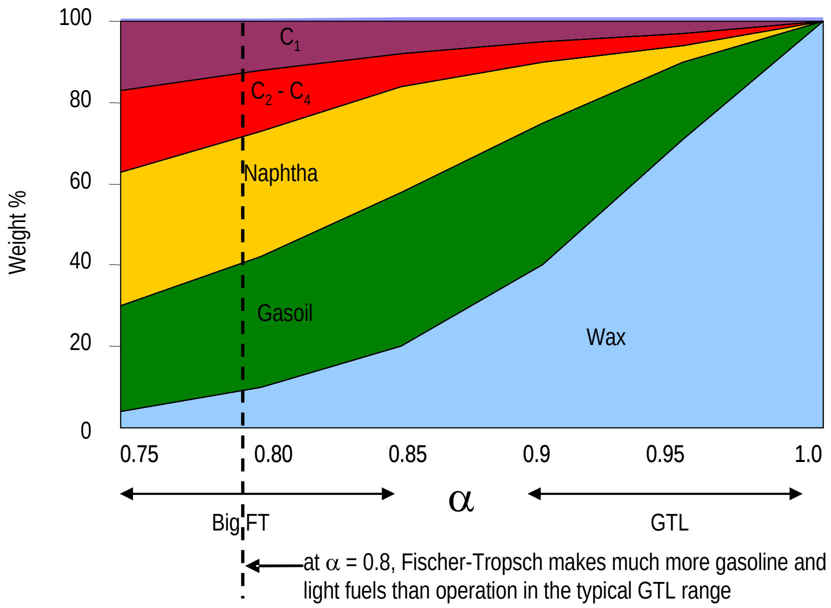
- Catalyst Technology Overview
- Modified High Pressure Methanol Synthesis Catalysts
- Modified Low Pressure Methanol Synthesis Catalysts

- Modified Low Pressure Methanol Synthesis Catalysts
- Alkali-Doped Sulfides, Mainly MoS_2
- Molybdenum-Sulfide Catalysts
- Pre-Reduced Molybdenum-Based Catalysts
- Other Sulfide Based Catalysts, ZrO_2 Catalysts
- Reactors – multiple slurry
- Technology Developers - Snamprogetti (or SEHT – Snamprogetti, Enichem, and Haldor Topsoe), Dow Chemical, Lurgi, Institut Francais du Petrole (IFP), PEFI - Ecalene™, Pearson Technologies

Fischer-Tropsch Biogasoline

Many energy companies, technology developers, government sponsors, investors and others are interested in stranded gas–to-liquid (GTL) technology because it can provide a clean fuel alternative (though not sustainable) and serve as an alternative to LNG or methanol. The product mix of an F-T design is determined by a set of reaction conditions expressed as the parameter "α", which ranges for practical conditions from about 0.75 to 1.0, describing the range between producing a mix of relatively light products and practically no wax, to 100 percent wax. Naphtha is a chemical feedstock, and gasoil is a diesel blendstock. The figure below illustrates the relationship of α to likely hydrocarbon product mix.

F-T Designed to Maximize Gasoline Production



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In the vicinity of α = 0.8, Fischer-Tropsch makes much more gasoline and light fuels than operation in the typical natural gas GTL range. Mostly, wax needs to be hydro-cracked to produce mainly additional gasoil.

BIOMASS FEEDSTOCKS

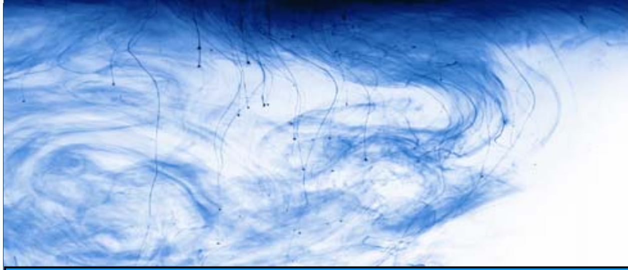
A brief discussion of biomass feedstocks in terms of biomass types (carbohydrates, lignin, oils and animal fats, proteins), food versus fuel competition, and availability of biomass supplies is given in this section.

Switchgrass is highlighted for its prospects as an energy crop demonstrating the potential role of genetic engineering in improving agronomic traits such as yield, mowing ease, and phased maturation (since storage against single-season harvesting is a major challenge of bio-based industry development). Unlike corn, soybeans, and other grains, switchgrass prices are not determined by trading on any commodity exchange, so the costs of supply must be estimated based on fundamentals. Nexant has modelled the economics of growing and supplying switchgrass.

ECONOMIC ANALYSIS

Cost of production estimates for the following processes have been developed:

- *n*-butanol via thermochemical biomass gasification followed by mixed alcohol synthesis with recycle
- *n*-butanol is produced via convention propylene oxo process utilizing the Davy and Dow LP Oxo SELECTOR 30 Technology with rhodium organo-phosphite catalysts
- A brief outline of making chemicals from bio-syngas (background, renewable products purchasing preferences, and bio-olefins production from alcohols) is given.



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