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Syngas Fermentation is one in a series of papers published by Advanced Biofuels USA exploring the technologies, products and policies related to the development, deployment and use of advanced biofuels. Thanks to Coskata for their work on this project.

SYNGAS FERMENTATION

The Third Pathway for Cellulosic Ethanol

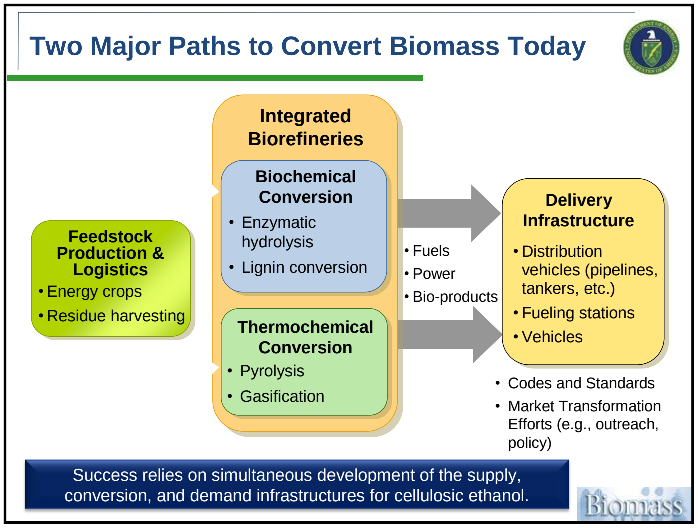
I. Introduction

Historically there have only been two major pathways recognized by the U.S. Government for producing cellulosic ethanol: biochemical and thermochemical. For years, these two pathways have received the majority of DOE research funding for producing renewable transportation fuels. However, in recent years technological advances have given rise to a third pathway – called **syngas fermentation** – which enjoys unique efficiencies compared to other pathways, and should receive universal recognition as one of the major pathways for producing cellulosic ethanol, as well as other fuels and chemicals. This paper will outline the mechanics behind the syngas fermentation pathway, and the benefits that three of the leading companies in cellulosic ethanol industry enjoy, as they commercialize technologies based on this pathway.

II. New Cellulosic Ethanol Production Techniques

Technologies that tap into the vast global resources of non-food and cellulosic materials – forestry residues, agricultural residues, new energy crops and municipal and industrial wastes – can make a significant contribution to displacing gasoline and reducing our dependency on foreign oil. Cellulosic ethanol also has tremendous potential to dramatically decrease greenhouse gas emissions over gasoline (DOE's estimate is up to an 86% reduction).

The U.S. Department of Energy (DOE) has defined two primary pathways for producing cellulosic biofuels – the **biochemical** and **thermochemical** approaches – detailed in the schematic below:



Two Major Paths to Convert Biomass Today

Integrated Biorefineries

Feedstock Production & Logistics
- Energy crops
- Residue harvesting

Biochemical Conversion
- Enzymatic hydrolysis
- Lignin conversion

Thermochemical Conversion
- Pyrolysis
- Gasification

- Fuels
- Power
- Bio-products

Delivery Infrastructure
- Distribution vehicles (pipelines, tankers, etc.)
- Fueling stations
- Vehicles

- Codes and Standards
- Market Transformation Efforts (e.g., outreach, policy)

Success relies on simultaneous development of the supply, conversion, and demand infrastructures for cellulosic ethanol.

Figure 1 - U.S. Department of Energy characterization of the two pathways for producing cellulosic ethanol

- The biochemical process uses water and enzymes to convert pretreated lignocellulosic biomass materials into sugars which can then be fermented into ethanol and carbon dioxide.
- The thermochemical process is a two-step process where a biomass feedstock is gasified to produce syngas (carbon monoxide and hydrogen) which is then converted to a biofuel by a chemical reaction utilizing chemical catalysis.

The Hybrid Process

However, there is a third, hybrid process which combines both biochemical and thermochemical elements, capturing the benefits of each pathway while mitigating some of their deficiencies. This process, called syngas fermentation, is a process where a biomass feedstock is gasified to produce syngas. The syngas is then fermented into the desired biofuel or chemical, without other byproducts. Finally, the fuel or chemical is then separated from water through standard distillation and dehydration to recover the final product.

Syngas fermentation has been researched since before 1983, when Dr. Rathin Datta at Exxon and Dr. Greg Zeikus at the University of Wisconsin, Madison worked together to write a paper on “Anaerobic conversion of One-carbon compounds”. Over the last 30 years, the technology has progressed to the point where today anaerobic bacteria that produce only the desired fuel are being demonstrated at a semi-commercial scale and are ready for commercial scale production.

Syngas fermentation compares favorably to the biochemical and thermochemical processes and presents a promising additional pathway toward meeting the nation’s biofuels goals.

III. Syngas Fermentation – The Third Pathway

Depending on the process, the most common elements of the Syngas Fermentation approach are gasification, syngas cooling and cleaning, biological fermentation, and product separation. Gasification has been around for more than 100 years, with some of the first commercial deployments included producing “town gas” for street lamps and heating. The gasification process simply decomposes the incoming carbon based material in the absence of oxygen into its core gas components of carbon monoxide and hydrogen, called syngas. Another approach takes waste gasses from steel mills or anaerobic digesters, to be reformed into syngas. After the syngas is cleaned and cooled, it is sent to a proprietary “bioreactor” where anaerobic microorganisms consume it as a food source and produce the desired biofuel.

Microorganisms – the “biological catalyst”

Microorganisms do what syngas conversion via chemical catalysis cannot, which is produce predominately only one fuel under low temperature and pressure. Microorganisms can extract the energy value available in the incoming syngas stream, producing some of the industry’s leading yields.

There are several microorganisms which can produce fuels and chemicals by syngas utilization. These microorganisms are mostly contained within the Clostridium family of anaerobic bacteria.

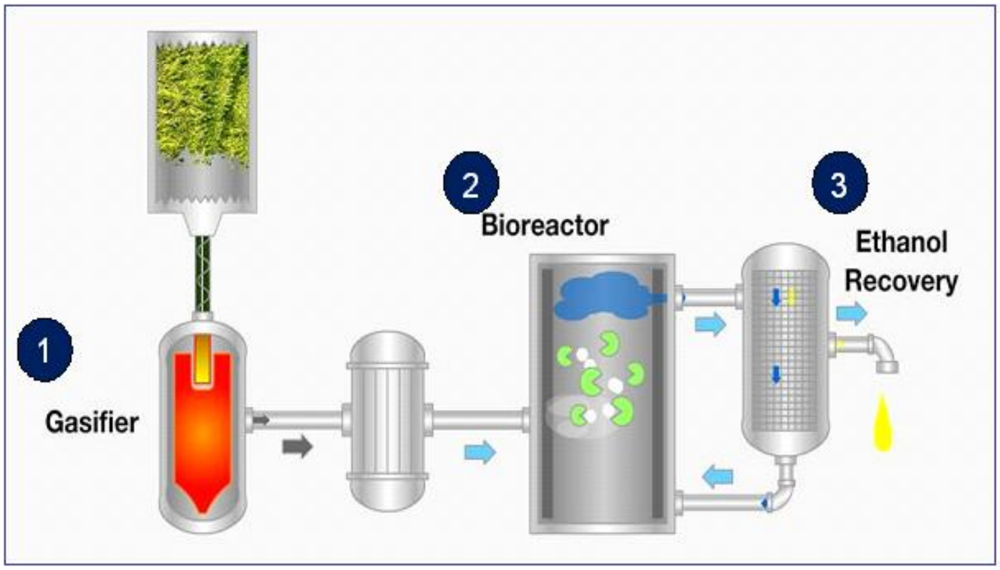


Figure 2 - Process schematic of Coskata Inc's syngas fermentation process

The organisms are extremely hard to find in nature, but companies such as Coskata in the US, and LanzaTech in New Zealand have successfully found unique organisms for the conversion of syngas into ethanol. Most of the organisms follow a standard *wood ljundahl* pathway (shown to the right in Figure 3).

The balanced net chemical reactions performed by the bacteria are seen below. A proprietary mixture of trace minerals, metals and vitamins are used to direct and optimize the energy flow within the pathway, maximizing the production of ethanol.

- $6CO + 3H2O \rightarrow C2H5OH + 4CO2$
- $6H2 + 2CO2 \rightarrow C2H5OH + 3H2O$

IV. Commercial Advantages of Syngas Fermentation

The syngas fermentation into fuels or other chemicals is considered by some to be more attractive than the biochemical and thermochemical pathways due to several inherent commercial advantages such as 1) higher yields, 2) lower operating costs, 3) a tolerance to impurities and 4) feedstock flexibility.

1) **Superior yields** - Biomass-to-ethanol via syngas fermentation has natural efficiencies because the process best utilizes the oxygen in the biomass and results in product specificity. Using gasification allows for a greater utilization of biomass because it is able to convert all of the organic biomass material into energy, leaving only a small percentage of the inorganic biomass material as either nutrient rich ash or a vitrified slag that could be used for road material. Even the lignin, which can be a byproduct in a biochemical process, is utilized in the hybrid pathway. On the back end, fermentation allows for greater specificity of results meaning the primary product that is produced is only the desired fuel. Put simply, syngas fermentation is able to utilize more biomass and produce more of the product you want than the traditional pathways.

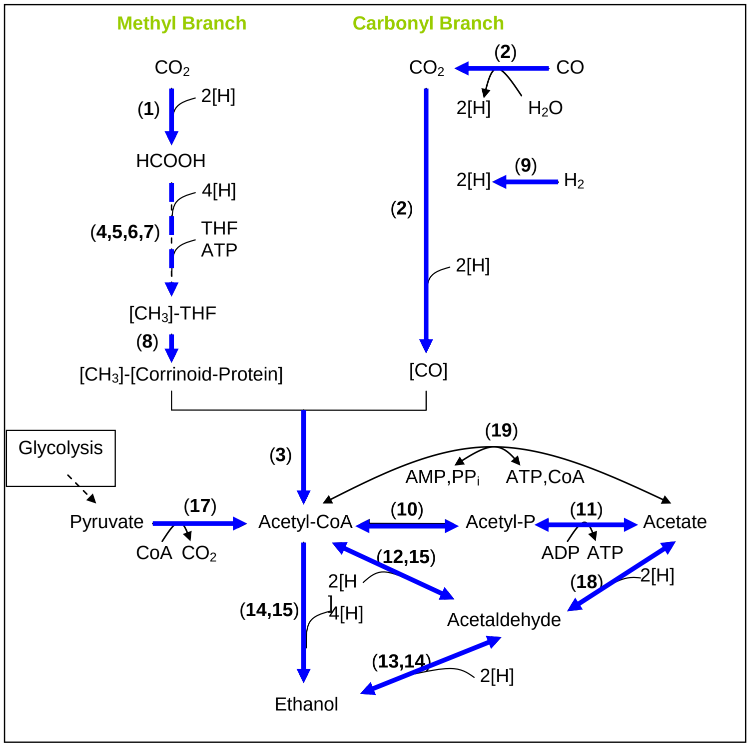


Figure 3 - Wood Ljundahl Pathway

2) **Lower Operating Costs** – Due to the high yields, syngas fermentation has lower production costs, even when paying as much as $60 per ton for biomass, compared to the traditional pathways. In addition to yields, syngas fermentation requires a lower temperature and pressure compared to chemical catalysis which allows for advantages in syngas cleanup, compression and heat recovery. Plus, the process doesn't require expensive enzymes or extensive pretreatment to operate. All these factors combine to give syngas fermentation one of the lowest operating costs among current renewable fuel options.

3) **Tolerance to Impurities** -- Because the organism is a "living catalyst" it has a high tolerance to impurities and can take a much wider range of CO:H2 ratios than the thermochemical process. This saves costs associated with potentially poisoning a catalyst that would then have to be entirely replaced. Not needing to do a "water-gas" shift is also a major strategic advantage, and allows a wider range of gasification technologies to be utilized.

4) **Feedstock flexibility -** The third pathway can convert virtually any carbon-containing material into syngas, including energy crops such as switchgrass and miscanthus; wood chips, forestry products, corn stover, bagasse and other typical agricultural wastes; as well as municipal and industrial organic waste. What's more, a joint 2005 DOE/USDA study and Sandia National Labs study in 2009 both found that there is over 1 billion tons of sustainable biomass in the US, which could create approximately 90 billion gallons of ethanol and replace more than one third of the petroleum that we use in the United States each year, by 2030.

   This minimizes the food versus fuel debate, will allow companies to hedge against commodity price fluctuations, and allows for geographic flexibility on where plants are built.

V. Advantages Over Traditional Pathways

Advantages over Biochemical Pathway

The biochemical process uses hydrolysis of pretreated lignocellulosic biomass materials to yield sugars which can then be fermented into ethanol and carbon dioxide or serve as a biocrude for other conversion processes. This approach is largely *enzyme-based*, although acid may be used in place of, or in combination with, the enzymes for hydrolysis of the lignocellulosic materials. Lignocellulose comprises cellulose, hemi-cellulose, lignin and pectin, each of which has different chemical and structural compositions and therefore must be treated separately to maximize sugar yield. As lignin has no sugar component, it is separated altogether before hydrolysis and typically burned for its thermal value. The cellulose and hemicellulose components are initially pretreated to expose the sugar polymers to the enzymes or acid to facilitate efficient hydrolysis, producing fermentable sugars. Because the respective sugars contained in the cellulosic and hemicellulosic fractions are different, currently, the two are usually hydrolyzed separately, with the respective sugars fermented separately. In addition, the enzymes are an input into the process and need to be produced independently, generally at large scale.

By contrast, the hybrid, thermo-biological approach does not use enzymes to extract the sugar, or conduct expensive pre-treatment processes involving "slurries" of biomass in large tanks. Syngas fermentation is also able to use the entire value of the incoming material, including the cellulose, hemicellulose, and lignin. As a consequence, this process can yield more gallons of ethanol per ton of material than more traditional approaches. By moving away from the enzymatic process and into the thermal platform, the syngas fermentation allows more input materials to be turned into fuel. The use of the entire feedstock also eliminates the bulky by-products involved in typical enzymatic approaches.

The hybrid process is also similar in many ways to the biochemical pathway in that it gains tremendous efficiency from a fermentation process, which selectively produces ethanol.

Advantages over Thermochemical Pathway

Thermochemical conversion utilizes a two-step process: gasification followed by catalytic conversion of syngas into a range of chemicals and fuels. To get ethanol in this process, the syngas passes over a catalyst at very specific CO:H2 ratio, high pressure and temperature to produce a mixture of alcohols. The mixture of alcohol products must undergo an energy intensive separation process in order for each of the various products to be sold into its own market, or the alcohol products must go through additional processing to produce pure ethanol.

Although the hybrid "syngas fermentation" pathway may utilize a front-end gasification system, similar to the thermochemical process, there are two main differences. The first difference is that the synthesis gas does not need to be pressurized to push across the catalyst. Some estimates put the costs of pressurization required to push the gas through a catalyst at $0.30 to $0.40 per gallon. Since a specific carbon monoxide to hydrogen ratio is not required for the hybrid process, it is also able to eliminate energy intensive water shift reactions and gas clean up steps. The second major difference is that the hybrid process only produces the desired product of ethanol, versus a mixture of alcohols out of the thermochemical process. This saves on fuel separation costs and yields more gallons of ethanol, or the desired product, per ton of input material.

VI. Conclusions

Biofuel production from lignocellulosic biomass feedstocks has been identified as a sustainable alternative for growing energy demands and has several advantages such as a higher availability of biomass, no competition with food and low feedstock cost.

To date, most conversations around producing advanced forms of cellulosic ethanol have focused on two pathways – the biochemical and thermochemical approaches. However, the syngas fermentation pathway represents an additional, hybrid approach which has significant advantages over the biochemical and thermochemical pathways including higher yields, lower operating costs, higher tolerance to impurities and feedstock flexibility.

As governments and investors play a larger role in the funding and deployment of second generation technologies, it is important to recognize syngas fermentation as a separate and distinct pathway to be supported for commercial production.

**Thanks to Coskata, Inc. for their contributions to this paper.*