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The use of syngas derived from biomass and waste products to produce ethanol and hydrogen

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Much attention has been placed on finding efficient processes for the production of ethanol and other biofuels. One area that shows promise is the conversion of synthesis gas (syngas) to ethanol and hydrogen by both thermochemical and microbiological methods. Two promising methods for creating syngas are the gasification of plant biomass and the pyrolysis of carbon-based waste products. Overall the process of converting syngas generated from waste products to ethanol and hydrogen can greatly reduce the use of imported petroleum fuels and also reduce the effects of greenhouse gases in the atmosphere.

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Abbreviations
BRI- Bioengineering resources incorporated
CSTBR- Constant stirred tank bioreactor

Introduction

As the amount of fossil fuels available decreases and the cost of petroleum-based fuels increases, there is a greater need for alternative fuel sources [1]. While methods for the production of cleaner, more abundant fuels exist, there is no consensus as to which method holds the maximum promise, resulting in an ongoing debate and also a high demand for more efficient processes to generate clean biofuels [2••]. One promising process for biofuel production involves the formation of synthesis gas which can then be converted to useful compounds.

Synthesis gas (syngas) is formed by a variety of processes with sources ranging from commonly-used fossil fuels to completely renewable organic compounds. The vast array of feedstocks is one promising aspect of the use of syngas to produce fuel. The main components of syngas are carbon monoxide, carbon dioxide, and hydrogen. Each of these components can be converted to valuable products [3••]. While multiple pathways exist for the transformation of these products, most of the conversions are performed by microbial or thermochemical processes.

This paper will identify current methods for syngas production along with the methods used to convert syngas to useful compounds. Also, potential areas for improvement and refinement will be identified leading to an analysis of the current marketability of biofuel production from syngas on a large scale.

Sources of syngas

One advantage of the use of syngas to produce fuels is that syngas can be produced from waste materials that would otherwise need to be discarded. Instead of placing waste products in landfills or the ocean, these waste products can be used to generate a useful, energy rich product [4]. This makes the syngas conversion process both an efficient means of producing energy and an environmentally friendly option for the recycling of waste products.

One waste product that is used to generate syngas is sewage sludge. Domínguez et al. [5•] performed an experiment to determine if syngas could efficiently be produced by the pyrolysis of sewage using both microwave and conventional heating. The source of sewage was a wastewater treatment facility. Prior research had shown the need for a microwave absorber to be mixed with the sewage in order to permit the pyrolysis to occur. In their experiment, char from previous reactions was added to the sewage to serve as the absorber. The char/sewage mixture was placed in a reactor which was then placed in an oven and heated to undergo pyrolysis. During the pyrolysis process, a variety of gases and liquids were formed, the desired product being synthesis gas. When using multi-chambered microwave ovens, the gases produced were 94% syngas. In a similar experiment also carried out by Domínguez et al. [6], it was determined that the calorific values for the produced gases were in the range of 7000 - 9500 kJ/m^3. This is similar to the values obtained for the gasification of coal. Therefore waste sewage could be used as a replacement for commonly-used coal in the gasification process.

Another method for producing syngas is the pyrolysis of glycerol. Glycerol was selected as a potential source of syngas because it is estimated that the rising production of biodiesel will result in increasing amounts of glycerol as a byproduct. Canada alone is expected to produce 55 million liters of glycerol annually. Valliyappan et al. [7•] performed an experiment to analyze the effects of gas flow rate and temperature on syngas production from glycerol. It was observed that gas flow rate had little effect on syngas production while the effects of temperature were very evident. When glycerol was heated to 800 ˚C, syngas compositions of up to 93.5% were observed, more than 20% greater than the compositions of syngas at 700 ˚C.

Possibly the most promising process for the generation of syngas is the gasification of plant biomass. Virtually any carbon-based material can be gasified to produce syngas. The carbon that is stored in the plant material is released as carbon monoxide and carbon dioxide allowing for nearly all the carbon in the biomass to be converted to syngas [2••]. The United States Department of Energy estimates that over 75 million tons of corn stover alone is produced annually [1]. Utilizing the energy stored in these waste products would greatly increase the amount of ethanol and other biofuels produced annually.

Products from Syngas

Currently, the most desirable product that can be formed from syngas is ethanol. Ethanol is already in use as a biofuel, but it has only replaced a small percentage of petroleum-based fuels. Ethanol needs to be produced from low-value feedstocks in order to be highly marketable. While promising technologies are currently being developed to convert the cellulosic content of plants to ethanol, these methods are only able to convert about 50% of the plant material to ethanol. However, the gasification of plant biomass results in over 90% of the plant material being converted into syngas [2••].

Ethanol as a fuel shows much promise in helping reduce greenhouse gas effects and lowering domestic dependence on foreign petroleum. While complete replacement of petroleum-based fuels is likely a long ways off, it is estimated that ethanol could replace as much as one-third of the domestic petroleum use in the near future [1].

The use of mesophilic bacteria is one method for converting syngas to ethanol. Henstra et al. [2••] describe the process by which bacteria use the acetyl-CoA pathway to produce ethanol. During the process, hydrogen and carbon monoxide are oxidized while carbon dioxide is reduced multiple times until methyl-tetrahydrofolate is formed. The attached methyl group, along with carbon monoxide formed by the reduction of carbon dioxide and CoA present in the cell, is then converted to acetyl-CoA by acetyl-CoA synthase and carbon monoxide dehydrogenase. Ethanol and a variety of other useful compounds can then be derived from acetyl-CoA.

An experiment performed by Younesi et al. [8] demonstrated the production of ethanol from syngas fermentation using the bacterium *Clostridium ljungdahlii*. Younesi discusses multiple advantages of using microbes rather than pure chemical reactions, the most noteworthy of which are lower energy costs, higher yields, and avoidance of equilibrium reactions. In preparation for the experiment, *Clostridium ljungdahlii* was grown and incubated and placed in serum bottles with nutrients. The culture media containing *Clostridium ljungdahlii* was then placed in bioreactors that were sealed to allow for anaerobic fermentation to occur. The bacteria were then inoculated into the media in reactors and exposed to syngas for 48 hours. Samples were taken from both the gas and liquid phases within the reactor to determine the compositions of each phase. Various syngas pressures were used to determine the optimal pressure at which the bacteria produced ethanol. While acetate production did not vary with pressure, ethanol production was significantly higher at higher syngas pressures. The optimal pressure of 1.8 atm produced ethanol concentrations of 0.6 g/L.

Ethanol can also be produced from syngas using various thermochemical processes. Both carbon monoxide and carbon dioxide can be hydrogenated to form ethanol and water. This process is favorable and can produce large quantities of ethanol, but side reactions must be limited. If methane is allowed to form, it becomes the dominant product and ethanol yields become negligible. In order to produce higher yields of ethanol, catalysts such as rhodium are used. Figure 1 shows the process of forming ethanol by the hydrogenation of carbon monoxide with a rhodium catalyst. After both hydrogen and carbon monoxide bind to the catalyst, some carbon monoxide gets hydrogenated and becomes methanol. The remaining carbon monoxide dissociates and can then be hydrogenated to make a hydrocarbon. Upon further hydrogenation, methane is formed. In order for ethanol to be formed, an undissociated carbon monoxide molecule must bind between the Rh and the hydrocarbon. This creates an enol intermediate that can form either ethanol or higher oxygenates [3••].

While ethanol has much potential as an alternative fuel source, hydrogen has the potential to be even more efficient as a fuel source. Hydrogen introduces no new carbon to the atmosphere and produces no harmful byproducts. The main hindrances to hydrogen use as a fuel are the difficulties in transportation and storage, as hydrogen is highly volatile. While hydrogen seems to be the ideal fuel for the future, more improvements are necessary to make hydrogen more portable and more easily stored. Future research will likely address these issues.

One way to obtain hydrogen from syngas is through the use of the bacterium *Rhodospirillum rubrum. R. rubrum* is a photosynthetic *proteo*-bacterium that converts syngas to hydrogen through a process known as the Water Gas Shift reaction in which carbon

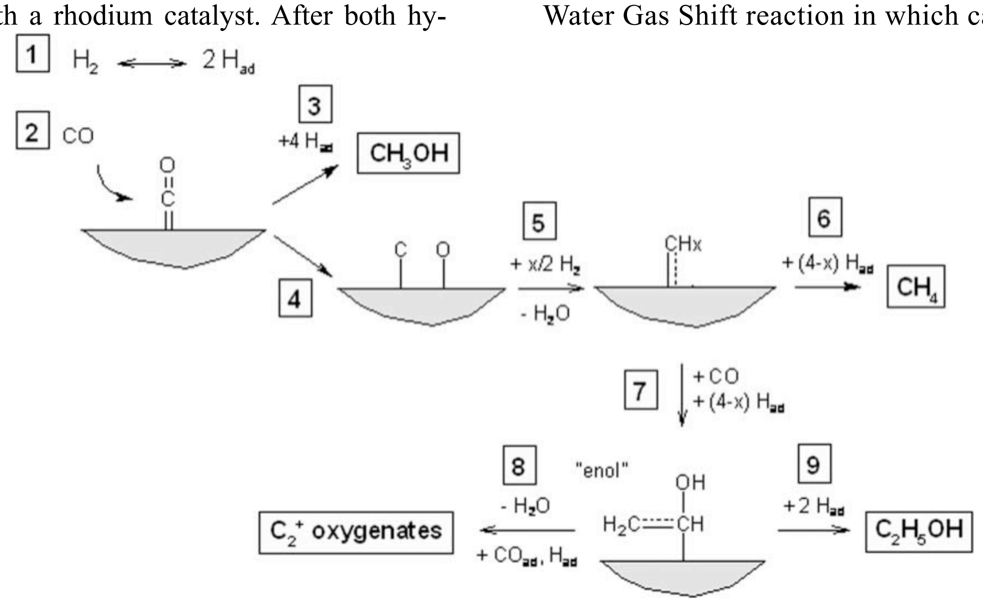

Figure 1 The process by which hydrogen and carbon monoxide (syngas components) are converted using a Rhodium catalyst (the gray semicircle) into methanol (Step 3), methane (Step 6), ethanol (Step 9), and other oxygenates (Step 8). From Spivey JJ, et al. *Chemical Society Reviews* 2007, **36**:1518.

monoxide and water are converted to carbon dioxide and hydrogen. Najafpour et al. [9,10•] have performed multiple experiments to test the ability of *R. rubrum* to convert carbon monoxide to hydrogen while analyzing the effects of substrate concentrations in the culture media and the effects of using various bioreactors.

In one experiment performed by Najafpour et al. [9] *R. rubrum* was grown in a serum bottle with various acetate concentrations in the media. After being exposed to syngas, *R. rubrum* converted carbon monoxide into hydrogen through the Water Gas Shift reaction. After being incubated for 120 hours, samples were taken to determine the cell dry weight, acetate concentrations, and carbon monoxide concentrations present in the reactor. At acetate concentration of 1.5 g/L and initial carbon monoxide pressure of 0.53 atm, 2.35 mmoles of hydrogen were produced resulting in a 98% yield of hydrogen.

One company that makes use of multiple processes discussed here is Bioengineering Resources Incorporated. BRI takes in waste products and uses gasification to convert the various feedstocks into syngas. Then, the bacterium *Clostridium ljungdahlii* is exposed to syngas and performs fermentation producing ethanol in the process. The ethanol is then extracted by distillation of the mixture. An overview of this process can be seen in Figure 2. In addition to producing ethanol, BRI plants also generate electricity. Before the *Clostridium ljungdahlii* can utilize syngas for growth, the syngas must be cooled. The heat released during cooling is used to generate electricity. BRI claims that its process converts up to 85 gallons of ethanol for every ton of biomass it takes in and up to 150 gallons for every ton of hydrocarbon-rich material. BRI also states that its process takes 7 minutes to complete. This allows one reactor to generate 7 million gallons of ethanol annually. BRI states that a mid-sized plant would contain 7 reactors converting 700,000 tons of waste to 49 million gallons of ethanol annually [2••].

Potential Improvements

While the process of converting waste products to useful fuels is at a marketable stage, there is still room for improvement. One process that could potentially be performed more efficiently is the process in which the syngas is cooled after the gasification stage. While a portion of the excess heat can be converted into electricity, some of the heat is also lost to the surroundings. The discovery or genetic engineering of thermophilic bacteria that are capable of converting carbon monoxide to ethanol would eliminate the need to cool the syngas before it can be converted to ethanol. This would greatly reduce the amount of heat that is lost in the process [2••].

Another area of potential improvement is the reactor design and function. Younesi et al. [10•] performed an experiment very similar to the one performed by Najafpour et al. [9], using various reactor types to determine the optimal conditions for syngas conversion. In order to maximize syngas conversion, the mass transfer rate must be optimized. In the experiment by Younesi et al., a microsparger was used to minimize the size of the gas bubbles, and the reactor used was a constant stirred tank bioreactor. Both these factors increased the mass transfer rate. In the experiment, *R. rubrum* was placed in a 2-liter bioreactor and exposed to syngas for a period of 2 months. The agitation speed and gas flow rates were varied in order to determine their effects on the mass transfer rate. At low agitation speeds, little carbon monoxide was converted due to the low mixing of reactants. However, when agitation speeds were raised above 500 rpm, the nutrients became toxic due to foaming of the mixture. Low gas flow rates did not provide significant amounts of carbon monoxide to be converted to hydrogen. However, when high gas rates were used, some of the carbon monoxide passed through the reactor too quickly and was not converted. For the experiment by Younesi et al., it was determined that the conversion of syngas to hydrogen occurred best with a gas flow rate of 14 mL/minute and an agitation speed of 500 rpm [10•].

Marketability

The use of waste products to produce syngas

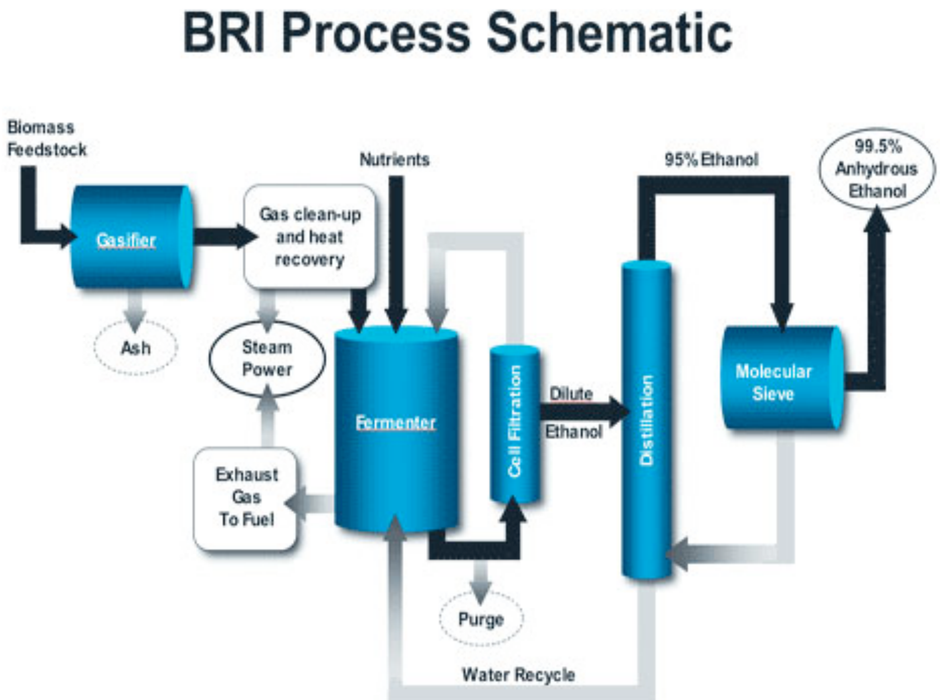

Figure 2. The process used by BRI by which syngas generated from the gasification of biomass is converted into ethanol. From Henstra AM, et al. *Current Opinion in Biotechnology* 2007, **18**:201.

that can be converted into ethanol and hydrogen is currently being used by BRI. Though the process is efficient, BRI has not yet opened any commercial plants. While the plans exist to build two plants that will convert municipal solid wastes and coal into ethanol, BRI is waiting for federal loan guarantees until it starts building these plants [2••]. There have been no plans to develop large plants. One of the strengths of the plant design is that it is small and can be modified rather easily. This gives the advantage of being able to set up plants in any given location to take care of a specific waste product or produce a specific fuel.

While ethanol production from syngas seems to be marketable in the very near future, hydrogen production may be further off. There is still a lot of work being done to determine the most efficient bacteria, reactors, substrate levels, and flow rates. Also, because of the large economic focus on ethanol use, hydrogen is not yet considered to be an ideal fuel by many. Until the market demand for hydrogen surpasses the demand for ethanol, it is unlikely that much funding will be available for that research.

Even though the production of hydrogen from syngas may be a few years off, the fact that both ethanol and hydrogen can be produced from syngas means that syngas conversion is a process that can be used both in the near future as well as in a number of years, when the market shifts from ethanol to hydrogen as a fuel source. This means that the use of syngas to create fuels will likely be one option which will be considered for many years to come.

References and recommended reading

Papers of special significance that have been published within the period of review have been highlighted as follows:
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•• of special significance

1. •R. D. Perlack et al., **Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply**. (DOE/GO-102005-2135, Oak Ridge National Laboratory, Oak Ridge, TN, 2005).

2. ••Henstra AM, Sipma J, Rinzema A, Stams AJM: **Microbiology of synthesis gas fermentation for biofuel production.** *Current Opinion in Biotechnology* 2007, **18**:200-206.

This article provided a critical review of many different factors affecting ethanol production from syngas. It compared the ability of various microorganisms to produce ethanol and also a pathway describing the formation of ethanol. It also contained a link to BRI, which provided useful information on performing the large-scale conversion of biomass to ethanol.

3. ••Spivey JJ, Egbebi A: **Heterogeneous catalytic synthesis of ethanol from biomass-derived syngas.** *Chemical Society Reviews* 2007, **36**:1514-1528.

This article provided Figure 1. Also it showed the effects of a wide variety of catalysts and their effects on many of the reactions that occured during ethanol synthesis.

4. Filippis PD, Borgianni C, Paolucci M, Pochetti F: **Prediction of syngas quality for two-stage gasification of selected waste feedstocks.** *Waste Management* 2004, **24**: 633-639.

5. •Domínguez A, Fernández Y, Fidalgo B, Pís JJ, Menéndez JA: **Bio-syngas production with low concentrations of $C0_2$ and CH_4 from microwave-induced pyrolysis of wet and dried sewage sludge.** *Chemosphere* 2008, **70**: 397-403

This article examined many different factors affecting syngas production from sewage. It also examined how syngas production could be increased.

6. Domínguez A, Menéndez JA, Inguanzo M, Pís JJ**: Production of bio-fuels by high temperature pyrolysis of sewage sludge using conventional and microwave heating**. *Bioreseource Technology* 2006, **96**:1185-1193

7. •Valliyappan T, Bakhshi NN, Dalai AK: **Pyrolysis of glycerol for the production of hydrogen or syn gas.** *Bioresource Technology* 2007, doi:10.1016/j.biotech. 2007.08.069

This article appears to be novel in discussing the possibility of glycerol as a source of syngas. It gave economic reasoning for its use as well.

8. Younesi H, Najafpour G, Mohamed AR: **Ethanol and acetate production from synthesis gas via fermentation process using anaerobic bacterium, *Clostridium ljungdahlii***. *Biochemical Engineering Journal* 2005, **27**:110-119.

9. Najafpour G, Younesi H, Mohamed AR: **Effect of organic substrate on hydrogen production from synthesis gas using *Rhodospirillum rubrum*, in batch culture.** *Biochemical Engineering Journal* 2004, **21**:123-130.

10. •Younesi H, Najafpour G, Ismail KSK, Mohamed AR, Kamaruddin AH: **Biohydrogen production in a continuous stirred tank bioreactor from synthesis gas by anaerobic photosynthetic bacterium: *Rhodospirillum rubrum.*** *Bioresource Technology* 2007, doi:10.1016/ j.biortech.2007.04.059

This article listed many different ways to improve the hydrogen yield. It also discussed a variety of reactor designs that affected the syngas conversion rates.