

Oxygen Reforming of Tar and Methane in Biomass-Derived Syngas

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Abstract

One important source for renewable energy is the production of transportation fuels from biomass feedstocks. This 'biofuel' can be produced from gasified biomass. However, the gasifier types under consideration produce both tar and methane when biomass is gasified. The tars and methane in the syngas contain a significant portion of the energy in the syngas; converting these to CO and hydrogen increases the overall process yield substantially. In addition, FT catalysts and biological processes are sensitive to the components in the "tars"; clean-up systems have been identified as a significant cost in the biomass to liquid fuels processes. Recent efforts at Praxair have focused on the development of an oxygen-based reforming technology that can effectively reform the methane into syngas and remove tars. These efforts, described in this paper, include both experimental testing in an existing 1 ton/d oxygen blown gasifier and detailed modeling of the reforming process.

Background

An increasing desire for energy independence and reduced carbon emissions has led to increased emphasis on the use of renewable energy. One such use is the conversion of biomass to useful end products, e.g. electricity, liquid fuels such as ethanol and diesel. Biomass being considered includes municipal solid waste (MSW), agricultural residue, e.g. rice hulls, forest residue, wood chips, energy crops such as switchgrass, poplar and willow. Thermochemical and biological processes are being considered for the conversion of biomass into fuels.

The first step of converting biomass to a biofuel, e.g. ethanol thermochemically is gasification in which the biomass is converted to syngas through a partial oxidation reaction. Steam and/or oxygen can be used as the oxidant for the gasification step. The syngas composition is generally a function of:

- Biomass composition,
- Type of gasifier, e.g. fluidized bed, fixed bed, entrained flow, plasma,
- Process conditions in the gasifier, e.g. temperature, pressure, thoroughness of circulation in fluidized bed gasifiers, degree of channeling in fixed bed gasifiers,
- Amount and type of oxidant used.

The syngas, usually produced at temperatures in excess of 800 °F (450 °C), has to be cleaned for removal of impurities such as particulates, alkali metals, sulfur compounds and tar. It is also possible to recover the sensible heat from the hot syngas as steam or power. The clean syngas is then converted to the desired end-product. Conversion processes include biological and catalytic (e.g. Fischer-Tropsch type) processes.

It is expected that the majority of the biomass gasifiers will be of the fluidized bed or fixed bed type. With fluidized bed or fixed bed gasifiers, the syngas is typically at 1500 °F (800 °C) and contains 5 – 15% CH₄ and 1 – 100 g tar/Nm³ syngas. CH₄ will act as an inert in the downstream conversion process, be it catalytic, Fischer-Tropsch or fermentation. Thus, CH₄ formation in the gasifier reduces the overall fraction of carbon in the biomass that is converted to fuel. Tars are generally defined as all organics with a boiling temperature above that of benzene. They are produced by thermal or partial oxidation of any organic material. Conventional syngas cleanup units typically contain a tar scrubbing system. In such cases, the tar is either re-injected into the gasifier or combusted in a boiler.

Recently Praxair developed a process to increase the overall conversion of biomass to syngas by reforming the tar and methane into useful gasification products, CO and H₂. This tar/methane reforming is done through a non-catalytic partial oxidation (POx) process using Praxair's hot oxygen burner (HOB) technology. An illustration of the HOB is provided in Figure 3. An excess of O₂ is mixed with a small amount of fuel (e.g. natural gas, propane, recycled syngas). Combustion of this fuel yields temperatures in excess of 2000°F (1100 °C). The hot gas (combustion products and O₂) accelerates to sonic velocity through a nozzle, forming a turbulent jet. This turbulent jet has an enormous entrainment appetite that enhances mixing between the tar/methane containing syngas and the reactive hot oxygen stream. The combination of high temperature, high O₂ concentration and rapid mixing make the jet extremely reactive. Therefore a HOB-based POx process can provide better syngas (defined as CO and H₂) yields than if ambient temperature oxygen were used. The hot oxygen jet characteristics also allow the HOB system to process difficult to use fuels. In the past, HOB technology has been shown to work well with a diverse range of materials, including sewage sludge, manure, glycerin. It is thus expected that such a system will be more tolerant of particulates, sulfur and other impurities that tend to be present in the syngas.

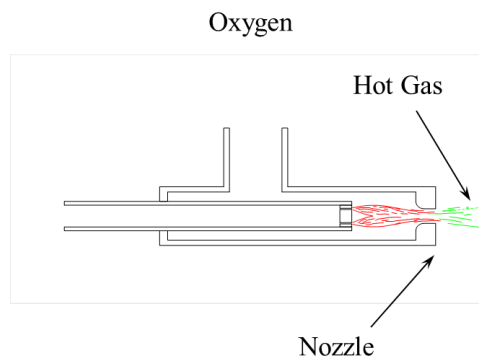


Figure 1. Schematic of hot oxygen burner (HOB)

Experimental results

For this program an existing entrained flow gasifier system was used to generate syngas for testing tar and methane reforming. The entrained flow gasifier, used previously to partially gasify coal to produce powdered activated carbon (PAC), mixes hot oxygen with the solid feedstock to rapidly gasify the feedstock. Typical feedstock flowrates are 1-2 ton/day, depending on feedstock type. Several different feedstocks were used, including specific woody biomass samples supplied by a potential customer. Injection ports were installed in the top of the gasifier to allow the resulting syngas to be ‘doped’ as needed to simulate a given commercial syngas composition. For example, preliminary testing of the reforming concept used coal-derived syngas doped with methane. Other additions include steam and specific hydrocarbon contaminants of interest. The syngas composition could also be modified by changing the hot oxygen to feedstock ratio (gasifier stoichiometric ratio, SR), with lower gasifier SR leading to lower temperatures and higher methane production. Hot (1300 °F, 700 °C) syngas exits the gasifier and flows horizontally into the transition section.

The transition section (shown in Figure 2) has a hot oxygen “lance” mounted at a right angle to the gas flow. Natural gas and oxygen are burned to form the hot oxygen stream which passes through the nozzle. Secondary reagents, such as steam, can be injected in an annulus around the nozzle. Given the rapid mixing between the hot oxygen and the syngas, the bulk of the reforming occurs in the transition section with the vertical reforming section used to provide additional residence time. Thermocouples are installed in both the transition section and reformer to provide time-temperature data. As the syngas leaves the reformer it is quenched by injecting nitrogen to reduce the temperature before it passes into a cyclone for particulate control. Cyclone inlet temperatures are typically 350-500 °F (175-260 °C). The cooled gas leaves the cyclone and passes through a burner to incinerate the syngas. Gas composition and tar measurements are made at the gasifier outlet and the reformer outlet simultaneously. Gas flowrates, feedstock flowrate, temperatures and gas composition measurements are automatically logged with a DAQ system.



Figure 2. 1 ton/d entrained flow gasifier and reformer

In the gasification/reforming experiments a wide range of syngas compositions, including methane concentration, were tested. A relatively narrow range of reformer stoichiometric ratios, defined as the amount of residual oxygen injected through the hot oxygen nozzle over the oxygen required to completely consume the syngas, were tested (~0.15-0.3). Figure 3 shows a summary of the hot oxygen reforming tests when biomass was used as the gasifier feedstock. The conversion efficiency is defined as the ratio of syngas generated ($\text{CO}+\text{H}_2$) compared to that if all the contained methane was converted to CO and H_2 . These data illustrate two key points. First, the higher the original methane concentration the higher the observed conversion efficiency. This is likely due to the fact that some of the syngas is initially consumed in the POx process in order to increase the bulk gas temperature to the critical temperature for reforming reactions to begin. For these experiments the gasifier outlet temperature was relatively constant, therefore the required syngas, and contained methane, consumption to heat the gas is fairly constant. As the methane content in the syngas increases, the relative amount of methane that is consumed just to heat the gas therefore decreases. The data also indicates that HOB-based reforming can more effectively convert methane to CO and H_2 than ambient temperature, or “cold” oxygen. This is due, in part, to increased mixing and reactivity with the hot oxygen. Further, since the hot oxygen has been heated externally using ‘lower value’ (in the case of biofuel production) natural gas, less syngas, including CO and H_2 , is consumed to heat the mixture to the critical temperature. Data with fixed methane concentration show that the conversion efficiency generally is a function of the reformer stoichiometric ratio, which is confirmed by the kinetic modeling shown later. Therefore the scatter in Figure 3 is largely due to the reformer stoichiometric ratio differences at each methane concentration.

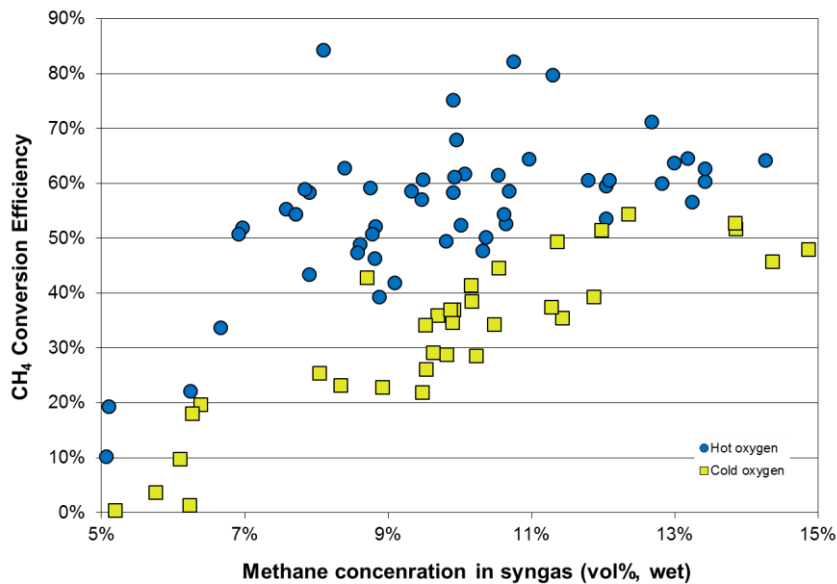


Figure 3. Summary of incremental syngas from gasification tests with HOB reforming

For many applications destruction of the tar contained in the syngas is a requirement for a successful reforming technology. In fact, for some applications tar destruction is the primary driver for the technology. During the experimental program tar concentration measurements were made for select conditions using a standard protocol developed for sampling tar from syngas¹. In this process hot syngas

was drawn through a filter for particulate removal and then passed through a series of impingers containing washing fluids. Figure 4 shows two impingers after tar sampling from the gasifier (G) and from the reformer (R). As can be seen from the figure, oxygen injection provided significant tar destruction. This reforming was found to be based on the peak temperature. At peak temperatures above approximately 2300 °F (1250 °C) greater than 98% tar destruction was achieved (Figure 5). These data compare well with data from the Houben².

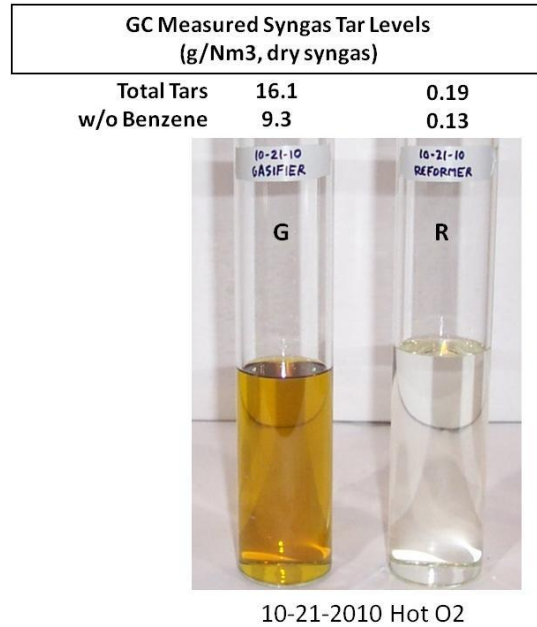


Figure 4. Tar sampling results from hot oxygen reforming

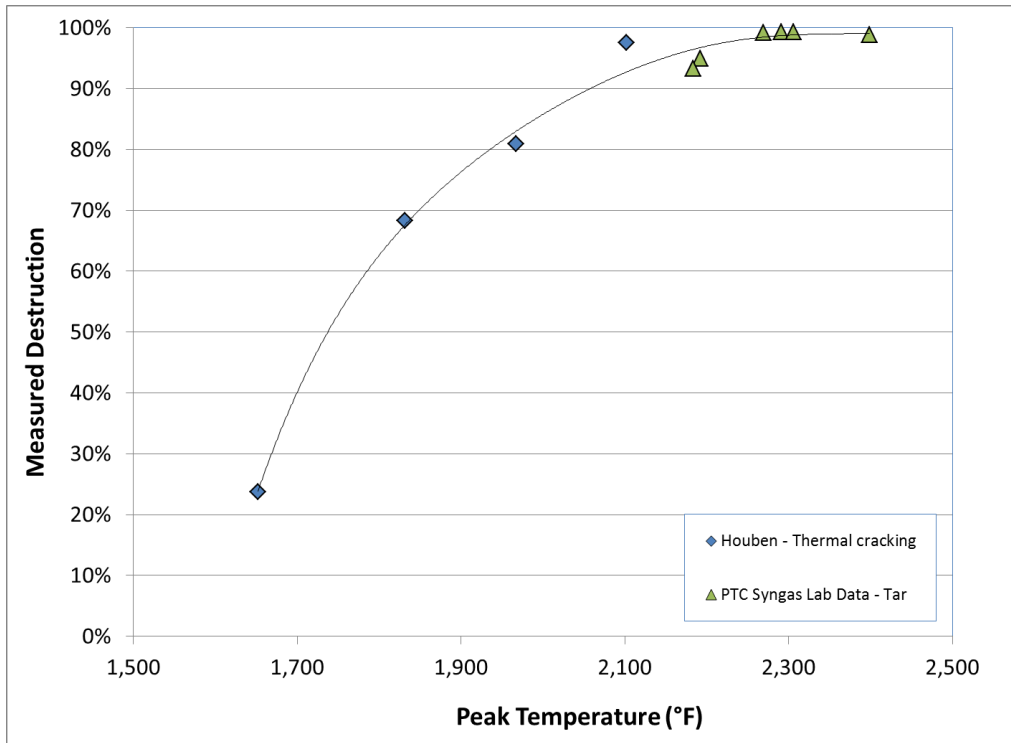


Figure 5. Comparison of measured tar destruction with literature

Modeling results

In order to estimate the performance of an HOB reformer system for different syngas compositions, a proprietary kinetic model of the process was developed. Mixing and heat transfer in the model are imposed as part of the model configuration, with typical literature correlations used to define the mixing rates. This model was used to predict performance of the Praxair Texas City POx unit and was found to agree within 1% (absolute) for H₂, H₂O, CO, CO₂ and CH₄ and 100°F (55 °C) for the exit temperature. The model was also used to predict performance of the pilot system, and matched the general trends described above. However, simplifications of the heat transfer in the model made it difficult to account for the large heat losses experienced at the pilot scale. Generally, CO, H₂, CO₂ and H₂O were predicted to within +/- 20% (relative) of the measured values.

The data in Figure 6 show estimates of incremental syngas yield for reforming with a typical syngas composition from an oxygen-blown CFB gasifier. In general these estimates are similar to the data from the pilot plant, with hot oxygen providing a better increase in syngas for a given reformer SR than ‘cold’ oxygen. The data also show there is a clear optimum reformer stoichiometric ratio that provides a maximum in the syngas yield. Below this optimal stoichiometric ratio only a portion of the incoming methane is actually reacted. At the maximum yield nearly all the methane has reacted, but the syngas is

still fuel rich enough to provide CO + H₂. Above the optimal stoichiometric ratio more of the methane and syngas is converted to CO₂ and H₂O.

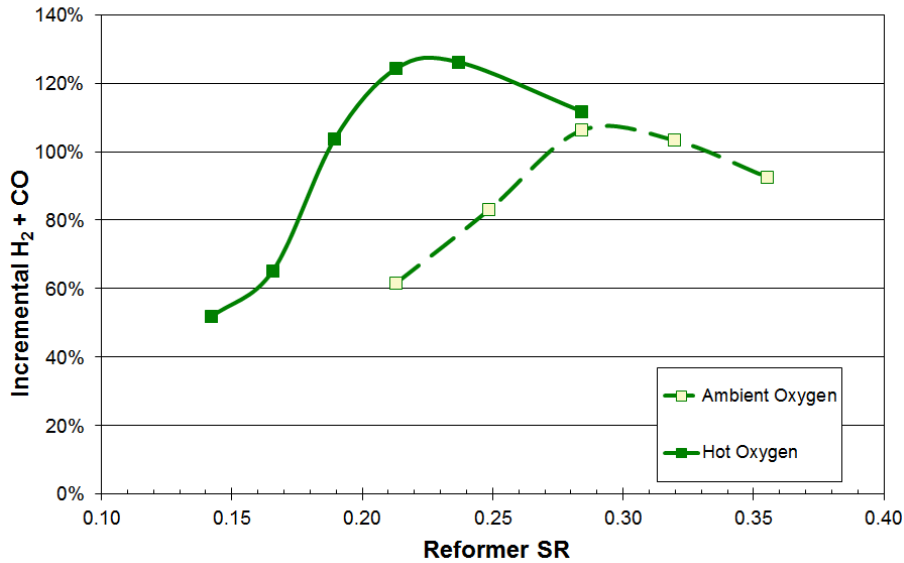


Figure 6. Incremental syngas yields from kinetic model

Although the proprietary kinetic model is a good tool for estimating the reforming performance for different syngas streams, there are several assumptions required to run the model. To get a more ‘realistic’ estimate a CFD model was developed by Reaction Engineering International (REI) for a proposed commercial-scale system. Key factors in the modeling were the behavior of the hot oxygen jet in the reformer (ie, does not impinge on wall or overheat wall), mixing of the jet with the syngas, and overall conversion rates. Figure 7 shows a typical temperature field from the upper portion of the CFD model. The figure shows that the hot oxygen jet stays near the center of the duct, and flame impingement is not likely a problem. Further, predicted wall temperatures (not shown) were within those estimated for this design. Figure 8 illustrates how quickly the hot oxygen jet mixes and reacts with the incoming syngas. After only a few duct diameters all the syngas has been entrained into the hot oxygen jet and the concentration profile is very uniform. The uniform concentration profile persists through the rest of the reformer (not shown) – suggesting there is very little opportunity for unreacted methane to ‘slip’ through the reformer. Methane conversion data predicted by the CFD were typically within ~6% (relative) of that predicted by the kinetic model.

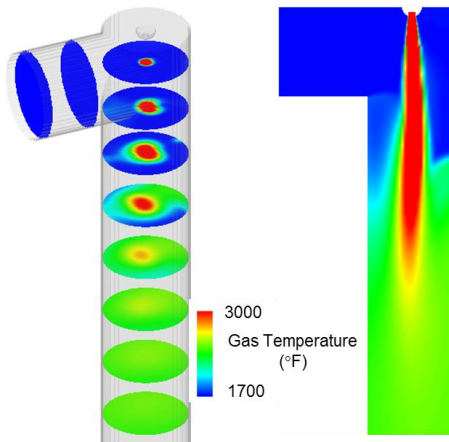


Figure 7. Predicted gas temperature profile for commercial design – only top portion of reformer shown

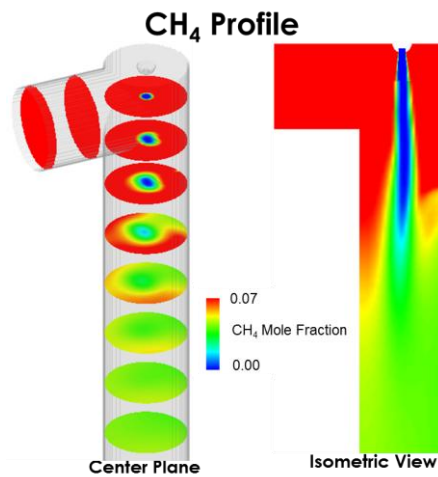


Figure 8. Predicted CH₄ profile for commercial design – only top portion of the reformer shown

Summary

The pilot data and modeling results to date have suggested that using hot oxygen is an effective method to both destroy tars in syngas, and reform the residual methane to desired syngas species. The experimental data suggest the peak temperature needs to be at least 2300 °F (1250 °C) to achieve tar destruction, with a minimum 0.5 sec residence time in the reformer. Kinetic modeling also predicts significant methane reforming, particularly at the higher oxygen injection rates. CFD modeling suggests the hot oxygen jet rapidly mixes with the incoming syngas and provides good reforming.

References

1. “Sampling of tar and particles in biomass producer gases”, Venum, L.G., et al., Report prepared under CEN BT/TF 143 “Organic contaminants in biomass producer gases”, July 2005
2. Houben, M.P. (2004): Analysis of Tar Removal in a Partial Oxidation Burner. Ph.D. thesis, Technische Universiteit Eindhoven