Conversion of Bio-butanol to Syngas via Filtration Combustion

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Abstract
Deriving hydrogen from biomass, which is renewable, domestically-produced and potentially carbon-neutral, is critical if hydrogen-consuming devices are to be used at a large scale while avoiding the negative effects of continued reliance on fossil fuels. Although hydrogen is quite abundant in nature, it is generally bound to other chemical species in larger molecules that must be processed to produce diatomic hydrogen. In this paper, we present experimental results for the conversion of butanol to a hydrogen-rich syngas. In contrast to traditional technologies based on catalysts, which may be poisoned by fuel impurities, we use filtration combustion in a non-catalytic porous media reactor to produce syngas. We compare the results for butanol to our previous results obtained with ethanol. Because the focus of this study is on the production of syngas, our primary results are the hydrogen yield, carbon monoxide yield, and the energy conversion efficiency as functions of equivalence ratio. In addition, we experimented with mixtures of butanol and water, which require less energy to produce than pure butanol. This study is intended to increase the understanding of liquid biofuel filtration combustion for syngas production.
1 Introduction

Syngas, a mixture of hydrogen, carbon monoxide and other gases, is valuable as a fuel and feedstock for chemicals [1]. It is most often produced from natural gas and coal, but it has also been produced from solid biomass and liquid fossil fuels [1]. The conversion of fuels to syngas is most commonly accomplished with the use of catalysts to enhance the reaction rate. These techniques can be very efficient, but catalysts have some significant drawbacks such as high cost and fragility [2]. Noncatalytic partial oxidation is a promising alternative for conversion of both gaseous and liquid hydrocarbons to syngas [3-5] without the limitations of catalysts.

Previous research has shown that filtration combustion is an effective means of converting fuels to syngas [6-11]. Instead of using a catalyst to enhance the reaction rate, heat is transferred to produce locally high temperatures that are sufficient to drive the reactions even for mixtures with equivalence ratios outside the conventional flammability limits [12-14]. In the most common configuration, premixed fuel and air flow through an inert porous solid. Heat is transferred through the solid by conduction and radiation from the hot products to the reactants. Additional heat recirculation can occur if the reaction front propagates downstream into the porous solid that has been heated by combustion products.

Different from previous work, we are using filtration combustion to convert bio-derived liquid fuels to syngas. In earlier work, we presented the conversion of ethanol [8] to syngas, and in this paper we report the results of the conversion of butanol. As described by DuPont and BP, butanol has strong potential as a biofuel because its energy content is similar to gasoline, and it can be mixed with gasoline in high concentrations. In addition, it is adaptable to the existing fuel distribution and storage infrastructure [15]. Since butanol production may become widespread, it has potential for becoming a significant source of syngas if an appropriate conversion process can be developed.

Though both ethanol and butanol have significant potential for widespread use, they require large amounts of energy to produce [16, 17]. For ethanol production, much of this energy input is required to remove water from the water/ethanol mixture that is produced from fermentation
Likewise, the Acetone-Butanol-Ethanol (ABE) fermentation process from which butanol is most-often produced requires multiple energy-intensive distillation steps to separate butanol from ethanol, acetone and water [19]. In our earlier work, we investigated the conversion of “wet” ethanol, which has not been completely distilled and/or dehydrated, and found that amounts of water up to 60% by liquid volume do not significantly inhibit the conversion process [8]. This represents a significant energy savings in comparison to production from the pure fuel. In this work, we conduct a similar study with wet butanol and compare to our results from ethanol.

Specific Objectives:

The objectives of this study are to demonstrate the conversion of butanol to syngas by filtration combustion and to understand how syngas production varies with equivalence ratio and water fraction. An additional goal is to compare the performance of butanol with the performance of ethanol in terms of syngas production.

To achieve these goals, we ran two sets of experiments. In the first set, we held water fraction at 0 and inlet velocity at 20 cm/s while varying the equivalence ratio from 1 to 4.5. In the second set we held the equivalence ratio at 2, the inlet velocity at 20 cm/s, and varied the water fraction from 0% to 22%. The experiments are summarized in Table 1.

2 Experimental Apparatus

The experimental apparatus (Fig. 1) consisted of the reactor, the fuel vaporization system, the reactant delivery system and the data acquisition system.

The reactor was identical to the reactor used for our experiments with ethanol [8]. It was a packed bed of alumina spheres with 3-mm average diameter. The bed, 20 cm-long and 5.59 cm in diameter, was insulated with alumina. A thin section of porous ceramic supported the bed of spheres.
The vaporization system consisted of an air-atomizing nozzle and a quartz chamber for mixing. The atomized fuel droplets, approximately 20 microns in size, were vaporized in a separate heated air stream in the quartz chamber. The separate air stream entered the chamber at an angle that produced a swirl flow to facilitate mixing and vaporization. The base of the chamber, which held the nozzle and air heater, was machined from stainless steel. The outer surface of the quartz chamber was wrapped with resistance band heaters and insulation to prohibit condensation of the fuel. Portions of the band heaters and insulation were removable to allow for observation of the reactants.

The reactant delivery system included a tank and a pump for butanol, rotameters for the fuel and water flows, and flow regulators for compressed, dry laboratory air. The fuel and water flows were independently metered and then mixed using a T-junction before entering the air-atomizing nozzle. The air entering the nozzle and the air entering the inline air heater were controlled with separate flow regulators.

Measurements included temperatures and exhaust species. The temperatures in the bed were measured with 11 B-type thermocouples. The thermocouples were spaced at 1.5 cm intervals with the junctions at the centerline of the reactor. Additionally, the temperature of the reactant mixture was measured with a K-type thermocouple just before entry to the reactor. The exhaust species were measured by a Varian, Inc. gas chromatograph (GC). The GC was calibrated to measure the following species: hydrogen, oxygen, nitrogen, methane, carbon dioxide, carbon monoxide, ethylene, ethane, acetylene, propane, iso-butane, n-butane, iso-pentane, n-pentane and n-hexane.

### 3 Experimental Method

In the experiments, butanol, water, and air were controlled to flow into the reactor in mixtures with specific equivalence ratios, water fractions, and inlet velocities. During the experiments, the vaporization chamber was frequently monitored for condensation. If condensation was observed, the measurements were discarded and the temperature of the heated air stream was increased.
The temperature of the inlet mixture never exceeded 200 °C as measured by the thermocouple placed before entry to the reactor. The water fraction and inlet velocity are defined as:

\[
\text{water fraction } (\chi) = \frac{\dot{V}_{H_2O}}{\dot{V}_{H_2O} + \dot{V}_{C_4H_9OH}}
\]

where \( \dot{V}_{H_2O}, \dot{V}_{C_4H_9OH} \) are volumetric flow rates

\[
\text{inlet velocity } (V) = \frac{R \times T \times \sum \dot{N}}{P}
\]

where R is the universal ideal gas constant, T is the thermodynamic temperature, P is the pressure, and \( \sum \dot{N} \) is the total molar flow rate of air and butanol.

At each operating condition, the GC sampled the exhaust gas for measurement five times. All presented experimental data are the average values of the last three measurements taken, however multiple sets of measurements were taken for some operating conditions. Uncertainty in species measurements was calculated using a Student-t distribution. Uncertainties for all calculations were based on sequential perturbation.

To calculate conversion efficiencies (yields), the total mole outflow of gas (moles per second) was needed. In order to find this value, we assumed that diatomic nitrogen (N\(_2\)) did not react:

\[
mole \text{ outflow (dry \& carbonless)} = \frac{0.78 \times \dot{N}_{air}}{[N_2]}
\]

The unit of \( \dot{N}_{air} \) is moles per second and [N\(_2\)] is the dry, carbonless mole fraction.

Important metrics for syngas production are the hydrogen yield and the carbon monoxide yield. These metrics describe how effectively the reactor converts butanol-bound hydrogen to diatomic hydrogen and butanol-bound carbon to carbon monoxide. The theoretical hydrogen yield can be
greater than 100% for reactant mixtures that include water because the denominator does not include hydrogen bound in water.

\[
\text{hydrogen yield} = 100 \times \frac{2 \times \dot{N}_{H_2}}{10 \times \dot{N}_{C_4H_9OH}}
\]

\[
\text{carbon monoxide yield} = 100 \times \frac{\dot{N}_{CO}}{4 \times \dot{N}_{C_4H_9OH}}
\]

The units of \(\dot{N}_{C_4H_9OH}\), \(\dot{N}_{H_2}\) and \(\dot{N}_{CO}\) are moles per second.

We also calculated values for the chemical energy conversion efficiency. These metrics describe what fraction of chemical energy in butanol was converted to chemical energy in the various exhaust species. The energy conversion efficiencies were calculated using the LHV of the individual species as described by the following representative equation for hydrogen:

\[
\text{hydrogen energy conversion efficiency} = 100 \times \frac{57.8 \times \dot{N}_{H_2}}{638.1 \times \dot{N}_{C_4H_9OH}}
\]

\(\dot{N}_{H_2}\) and \(\dot{N}_{C_4H_9OH}\) units are moles per second and the LHV values are in units of kcal per mole.

We also calculated the total energy conversion efficiency, a measure of how much energy in butanol was lost to thermal energy in the process. The total energy conversion efficiency was calculated as follows:

\[
\text{total energy conversion efficiency} = 100 \times \frac{\sum_i \dot{N}_i \times LHV_i}{638.1 \times \dot{N}_{C_4H_9OH}}
\]

The summation is performed over all species in the exhaust with positive LHV and with concentration > 0.1%. LHV data were taken from Lewis and von Elbe [20].
4 Results and Discussion

Experimental measurements in terms of hydrogen yield, carbon monoxide yield and energy conversion efficiency are shown in the following sections. For comparison, equilibrium values calculated for a constant pressure, isenthalpic process using the Cantera software suite [21] are also presented. Previous work [6, 8] has shown that equilibrium calculations are a decent predictor of trends in exhaust species as a function of reactant composition.

4.1 Butanol Results

Yields of both hydrogen and carbon monoxide increase significantly between from $\phi = 1$ to $\phi = 2$ and the peak values are near $\phi = 2.5$. Both yields follow the trend of the equilibrium calculations across all values of $\phi$. At $\phi > 2.5$, both hydrogen and carbon monoxide yields have magnitudes similar to the equilibrium values, but at higher values of $\phi$, the magnitudes differ significantly. The magnitude of the hydrogen yield has an especially pronounced divergence from equilibrium at values of $\phi > 2.5$.

An important metric for conversion of a fuel to syngas is the energy conversion efficiency. When limited to a single species, such as hydrogen, this metric describes how much of the chemical energy in the original fuel was converted to energy in hydrogen. When the total energy content of the products is compared to the heating value of the fuel (total energy conversion efficiency), it is a measure of the overall efficiency of the process. The total energy conversion efficiency and the energy conversion efficiency for hydrogen and carbon monoxide are shown in Figure 3. The trends for hydrogen and carbon monoxide are identical to those seen in the species conversion (Fig. 2). The conversion of energy from butanol to hydrogen reaches about 15% at maximum, while the conversion to carbon monoxide reaches about 20%. The total energy yield, which rises monotonically with $\phi$, reaches a maximum value of more than 40% at $\phi \approx 4.5$. This means that approximately 60% of the energy in butanol is lost to thermal energy during the conversion. Equilibrium calculations show a conversion efficiency of 65% for an adiabatic process at this value of $\phi$. The difference between the total energy conversion efficiency and the
sum of the energy for hydrogen and carbon monoxide is accounted for by other energy-containing products that are not shown in this figure. This point will be discussed further in the comparison of these data with ethanol data.

It has been shown that distillation and dehydration require a significant energy input for the production of ethanol [8]. In the production of butanol, energy input is required for similar processes. We experimented with wet butanol to determine the effect of water addition on the conversion to syngas because, as for ethanol, wet butanol requires less energy to produce than pure butanol. Figure 4 shows the hydrogen yield and carbon monoxide yield as a function of water fraction, $\chi$. The values for both hydrogen yield and carbon monoxide yield remain relatively constant with increasing $\chi$. This trend shows that syngas can be made more efficiently, in terms of system-level energy inputs, from wet butanol than from dry butanol.

4.2 Comparison with Ethanol

One of our research goals is to understand the potential of biofuels to be converted to syngas by filtration combustion. It is, therefore, important to compare the relative abilities of fuels to undergo this conversion. The hydrogen yield is shown in Figure 5 for a comparison between butanol and ethanol. From $\phi = 1$ to $\phi = 3$, the two fuels behave almost identically in terms of hydrogen production. At higher values of $\phi$, however, the yields diverge, with ethanol maintaining a higher hydrogen yield. Figure 6 shows a comparison between the carbon monoxide conversion yields of butanol and ethanol. The carbon monoxide yields compare similarly to the hydrogen conversion efficiencies; at high values of $\phi$, ethanol converts more readily to carbon monoxide than butanol does.

The energy leaving the reactor that is not contained in carbon monoxide and hydrogen and not lost to heat must be contained in other species. Three species, methane, ethylene and acetylene, contain nearly all of the chemical energy not accounted for by carbon monoxide and hydrogen in syngas production from both butanol and ethanol. The energy yield for these three species for both ethanol and butanol is shown in Figure 7. Both fuels show significant conversion to methane at $\phi > 3$. However at $\phi > 4$, the conversion of fuel energy to energy in ethylene and
acetylene is much more significant for butanol than it is for ethanol. The significance of ethylene and acetylene explains the drastic decrease in butanol conversion to hydrogen and carbon monoxide at high values of φ.

A comparison between butanol and ethanol hydrogen yield as a function of χ is shown in Figure 8, and the carbon monoxide yield is shown in Figure 9. In this range of χ, the yields for both hydrogen and carbon monoxide do not vary appreciably for either species.

**Conclusions**

With this work we have demonstrated the conversion of butanol and wet butanol to syngas via noncatalytic filtration combustion. The conversion of butanol is one of the few demonstrations of the conversion of a liquid fuel to syngas by filtration combustion. In addition, the conversion of wet butanol with efficiency equal to the conversion of pure butanol represents a system-level energy savings as wet butanol requires less energy to produce than dry butanol. The experimental results show that butanol behaves similarly to ethanol at equivalence ratios less than 3, but at higher equivalence ratios butanol converts to hydrogen and carbon monoxide less efficiently than ethanol does. At these high equivalence ratios significant levels of methane are found for both ethanol and butanol, but ethylene and acetylene are found at much higher levels in butanol conversion than in ethanol conversion.

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Figure 1: Experimental Apparatus
Table 1: Experimental Operating Conditions

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<th>Investigation Parameter</th>
<th>φ</th>
<th>χ (%)</th>
<th>V (cm/s)</th>
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<tbody>
<tr>
<td>Equivalence Ratio (φ)</td>
<td>1 to 4.5</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>Water Fraction (χ)</td>
<td>2</td>
<td>0 - 22</td>
<td>20</td>
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