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Catalytic Partial Oxidation of Isobutanol for the Production of Hydrogen

by Jeffrey G. St. Clair, Ivan C. Lee, and Adam S. Gamson

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14. ABSTRACT Catalytic partial oxidation of isobutanol was investigated at various contact times, as were equivalence ratios, for the purpose of H ₂ production. The reactor was tested using a γ -Al ₂ O ₃ -coated foam as a catalyst, as well as a similar foam with rhodium (Rh) added. Both catalysts achieved isobutanol conversion greater than 99% at an operating temperature of 500 °C for a contact time of 25 ms. The results show little H ₂ is produced when the Rh is absent, whereas selectivities as high as 62.92% were achieved with the noble metal present. The alumina catalyst also displays no complete combustion regime for fuel lean combustion; instead, olefins, carbon dioxide (CO ₂), and water are the dominant products at all equivalence ratios. With approximately 8.25 W of isobutanol, 3.61 W of H ₂ can be attained with the Rh catalyst for use in small power devices, such as a proton exchange membrane fuel cell.					
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1. Introduction

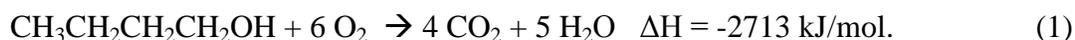
As technology improves, power requirements increase with a decreasing size envelope. Although batteries can provide power for small applications, such as personal electronics or small unmanned aerial vehicles (UAVs), they generally cannot provide it for an extended amount of time. To this end, much research has been invested into alternative sources of power with a longer endurance. One alternative is a fuel cell. Fuel cells employ the high gravimetric energy density of H₂, but this fuel needs to be stored in a manner that does not dampen the effective energy density of the power system. Storing enough gaseous hydrogen (H) for long-duration operation requires a high-pressure, heavy storage tank, increasing system mass to unacceptable levels for small scale applications. Instead, liquid, energy-dense fuels can be reformed to produce H₂, which can then be fed directly to the fuel cell. Therefore, an improvement in H production will lead to the advancement of smaller and smarter technology.

Several fuels are being investigated for fuel processing applications, including alcohols like methanol and ethanol. Salge *et al.* investigated the catalytic partial oxidation of ethanol and ethanol-water mixtures; high H selectivities (above 80%) were achieved using a rhodium (Rh)-ceria (CeO₂) catalyst at short contact times (~10 ms) (7). This catalyst has also been used to reform methanol, 1-propanol, and 2-propanol with similarly promising high H₂ selectivities (8). It was found, however, that without the Ceria coating, the reactor operated at higher temperatures with less successful results. This could mean that the Rh requires certain catalytic reactions to take place before it can produce the desired H₂, and that these reactions occur on the surface of the support coating.

Little work has been done in the catalytic reforming of heavier alcohols, such as butanol. Butanol isomers are an attractive renewable fuel source; the alcohol can be synthesized using yeasts or bacteria, such as *E. coli* (1-4). Butanol has a higher energy density than both methanol and ethanol, and a lower hygroscopicity, easing the issues of storage and transport associated with ethanol. Previous work by Behrens *et al.*, however, reports that ethanol has a higher H₂ selectivity than 1-butanol when using Rh/alumina as a catalyst (5). 2-butanol has been decomposed using a Pt/ZrO₂ catalyst for H production (12). It was found that at temperatures below 275 °C, dehydrogenation is the dominant decomposition pathway; but above this temperature, dehydration occurs to produce water instead of H₂. This change was attributed to carbon build-up on the catalyst surface and the alkenes blocking interfacial sites. Isobutanol has been the preferred fuel to synthesize recently, due to its high yield production (1). Branched-chain alcohols also are known to have higher octane numbers than the straight-chain isomers. Taylor *et al.* formed linear and branched butenes from isobutanol by dehydrating it over gamma-alumina catalysts (6). These butenes could be further used to create other fuels like gasoline and butyl rubber.

In catalytic conversion, the time the reactant has to react with the surface has been shown to play a prominent role in product composition (7–9). The contact time, when considering a monolithic foam, is determined by the volume of the foam, the volume flow rate of the reactants, and the operating temperature of the catalyst foam. With a large enough contact time, the chemistry within the reactor will reach its equilibrium condition. When operating at shorter times, however, intermediate molecules will still be present in the exhaust. The kinetic pathways at these contact times then play a greater role in what is produced.

The equivalence ratio (ϕ), which compares the actual fuel-to-air ratio of the reactor to the stoichiometric fuel-to-air ratio, also plays an important role in fuel reforming. A ϕ -value of unity signifies a stoichiometric feed of fuel and air, which, for butanol, is given as



The ϕ -value can be controlled by adjusting the amount of fuel and/or oxygen (O_2) fed to the reactor. A condition where the ϕ -value is greater than unity is considered “fuel rich,” and incomplete combustion occurs because not enough O is present to combust the entire amount of fuel; the incomplete combustion process is also known as partial oxidation. Running slightly fuel rich ($1 < \phi < 3$) is usually the optimum condition for H_2 production. Low ϕ -values (between zero and one) indicate a “fuel lean” environment that has more than enough O to oxidize all the fuel into its stoichiometric combustion products.

This work investigates isobutanol reforming in an adiabatic, catalytic reactor to form H_2 suitable for applications such as fuel cells. The effect of adding Rh to the γ -alumina monolith foam for improved performance is also a subject of interest. Using each catalyst, a wide range of equivalence ratios including both fuel lean and fuel rich regimes, at multiple contact times, is investigated.

2. Experimental

Figure 1 is a schematic of the cylindrical quartz reactor. Nitrogen (N) and O gases were premixed and introduced near the top of the reactor; the flowrates of the gases were controlled using mass flow controllers. Liquid fuel entered the reactor via a stainless steel tube with outer and inner diameters of 1.70 mm and 1.20 mm, respectively. The fuel is electrically conductive enough that it can be injected using low power electro spray techniques (10). Electro spray of the fuel in cone-jet mode was employed by creating a voltage difference between the droplet source and a neutral grounded mesh (~3300 V). When operated in cone-jet mode, charged liquid particles are emitted with a narrow droplet size distribution, which allows for a steady state evaporation rate to be established. The grounded tantalum mesh was placed a distance of 1 cm below the fuel inlet. An inert foam mixer was placed directly under the grounded mesh to aid in mixing the fuel vapor with the incoming N and O gases. This foam also aided in providing gas

flow uniformity. The mixing foam was 1 cm in thickness. The inner diameter of the reactor was 2 cm.

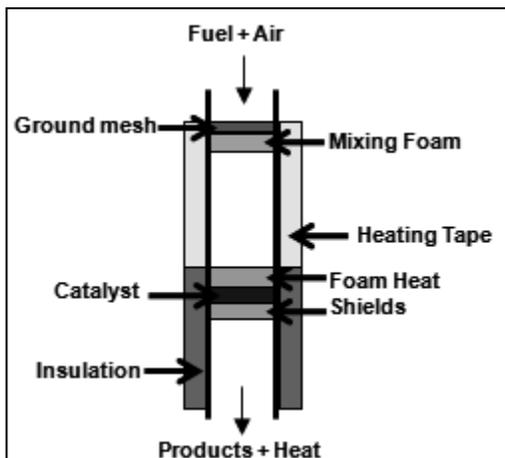


Figure 1. Schematic of adiabatic reactor (not to scale).

The catalyst was located 12.5 cm below the grounded mesh. Blank alumina foams (45 ppi) with a thickness of 1 cm were placed above and below the catalyst. The foams primarily acted as heat shields but also as another mixing layer to ensure uniformity of the fuel vapor over the entire catalyst surface. Two types of catalysts were tested. Both were built using an alumina monolith foam (Vesuvius, 80 ppi, 17 mm diameter, 1 cm thick), which was coated with γ -alumina to roughen the foam surface and to increase the surface area. The foams were calcined in a box furnace at 700 °C for 15 h. One of the foams was set aside at this point, and will be referred to as the alumina catalyst. An aqueous $\text{Rh}(\text{NO}_3)_3$ solution was added to the other foam, and the resultant foam was again calcined in the box furnace at 700 °C for another 15 h. This foam will be referred to as the Rh catalyst. The foam contained 0.07353 g of Rh and was prepared in the manner detailed in the literature (11).

Sufficient heat was supplied via heating tape to the grounded mesh and mixing foam (generally a few degrees above the boiling point of the fuel) to ensure complete vaporization and catalytic ignition. Typical catalyst ignition temperature was approximately 240 °C. Below the heating tape, insulation was wrapped around the reactor—including the catalyst portion—to impose adiabatic conditions. Temperatures were observed at the nozzle, ground mesh, and catalyst, and were used just as a reference. The effluent gas exits the reactor, where it is sent through an Agilent four-channel micro gas chromatograph (GC).

These GC measurements are vital in determining how much H is being produced and what other byproducts may also be present. The amounts of H, O, N, carbon monoxide (CO), CO_2 , and methane, ethylene, ethane, acetylene, propane, propylene, 2-butyne, butane, isobutane, 1-butene, t-2 butene, c-2 butene, isobutylene, 1,2-butadiene, 1,3-butadiene, pentane, ethyl acetylene, 1-pentene, t-2 pentene, c-2 pentene, hexane, 1-hexene, t-2 hexene, and c-2 hexene were monitored using the four-channel micro-GC. Before each experiment, N was passed through the reactor to

clear out any lingering gases and to ensure no leaks in the system. Heating tape was activated to provide heat to the region between the fuel atomizer and the catalyst. Then the appropriate N and O flow rates were set to give the equivalence ratio and contact time desired. Once the temperatures reached a steady state, the voltage differential between the ground mesh and the stainless steel tube was established to electrospray, and fuel flow was initiated. Voltages were then adjusted to maintain electrospray stability in cone-jet mode as needed. The temperatures were again allowed to reach a steady state operating condition, and the GC recorded the effluent gas composition during this time.

Equivalence ratio and contact time are the two operating parameters that were varied while investigating the alumina and Rh catalysts. The equivalence ratios tested ranged from very fuel lean ($\phi = 0.17$) to fuel rich values up to $\phi = 6.34$. The equivalence ratio set the total O flow rate, using a set fuel flow rate, which was generally 1 mL h^{-1} . At higher ϕ values, the O flow rate would dip below 5 mL min^{-1} , which was too low for the flow controllers; at these ratios, the fuel would be increased, instead, to keep the O flow rate at acceptable levels for the flow controllers. The nitrogen flow rate was adjusted for each O flow rate to ensure the total volumetric flow rate of gas remained the same. This guaranteed that the contact time inside the reactor remained the same, within 5 ms, while the equivalence ratio was varied. The contact times are calculated at the catalyst backface temperature.

Fuel conversion was observed using syringe samples of the effluent gas in a separate GC with an Innowax column, a flame ionization detector (FID) (Agilent 6890). The column was set to detect acetaldehyde, acetone, methanol, 2-butanone, 1 or 2 butanol, and isobutanol. Water was not detected using GC, but calculated using an O species balance of the compounds detected that contain O:

$$O_{water} = O_{in} - O_{microGC} - O_{FIDGC} \quad (2)$$

Conversion was defined as the amount of isobutanol in the effluent gas compared to the initial amount entering the reactor. Thus, if no peak appeared at the retention time of isobutanol for a GC sample that was taken, the conversion was considered 100%. Species selectivity can be used as a metric of how complete the combustion process is, meaning how much CO_2 and H_2O are formed compared to the stoichiometric amounts. Carbon selectivity was defined as the number of carbon atoms in a particular species, divided by the total number of carbon atoms in the product gas as shown:

$$C \text{ atom Selectivity} = \frac{\# C \text{ in Species } X}{\sum C \text{ in product}} \quad (3)$$

Thus, if the carbon selectivity of CO_2 is 100%, complete combustion has occurred. Similarly, H selectivity was defined as the number of H atoms in a particular species divided by the total number of H atoms in the product gas. This represents the percentage of converted H atoms in each of the species studied and is analogous to equation 3 if H is substituted for carbon.

3. Results

Catalytic partial oxidation of isobutanol was studied using the catalyst that did not contain Rh. The reactor was operated at three contact times—25, 56, and 125 ms—at ignition backface temperatures of 460, 420, and 290 °C, respectively. The results using the alumina catalyst are shown in figure 2. For all three contact times, the vast majority of products were olefins and water. H is formed, but at small amounts. The largest selectivity value using the alumina catalyst was at a contact time of 125 ms and a $\phi = 6.3377$, with a value of 1.59%.

The H selectivity using the Rh catalyst at each contact time is given in figure 3, with similar ignition backface temperatures as previously stated. For all contact times, fuel lean conditions exhibit complete combustion when using a Rh catalyst. Fuel rich conditions cause syngas (H_2 and CO) and residual hydrocarbons to appear in the exhaust gas. H_2 selectivity has a maximum point in each contact time, whereas olefin production increases with increasing equivalence ratio. The major product within the olefin category was isobutylene. Trace amounts of paraffins are found in all cases, usually in the form of methane and propane. For the 25 ms contact time, the maximum selectivity to H_2 was at $\phi = 3.501$ with a value of 52.15%. At the other two times, 56 and 125 ms, the maximums were observed at $\phi = 1.4248$, with values of 62.92% and 24.65%, respectively. The production of H as a ratio of fuel input at all contact times and equivalence ratios tested using the Rh catalyst is provided in figure 4. The maximum is 995 sccm H_2 per sccm of isobutanol.

The temperature of the catalyst, more specifically, its backface in the flow field, was recorded for each test. Figure 5 presents the final catalyst backface temperatures as a function of the equivalence ratio, for the contact time of 25 ms. The other two contact times show a similar trend. The alumina catalyst fluctuates little in temperature, whereas the Rh catalyst operates at higher temperatures in fuel lean conditions. The fuel rich temperatures for both catalysts generally do not show an increase from the baseline temperature, which is the temperature before the fuel is initiated.

The conversion of isobutanol to other compounds is also shown in figure 5. With a Rh catalyst, no remaining isobutanol was detected at lower equivalence ratios. Increasing amounts of isobutanol were observed at higher ϕ values. The alumina catalyst does not show a particular trend; however, isobutanol was detected at all equivalence ratios tested. With both catalysts, the conversion of isobutanol to some other product appears to be high (above 99%).

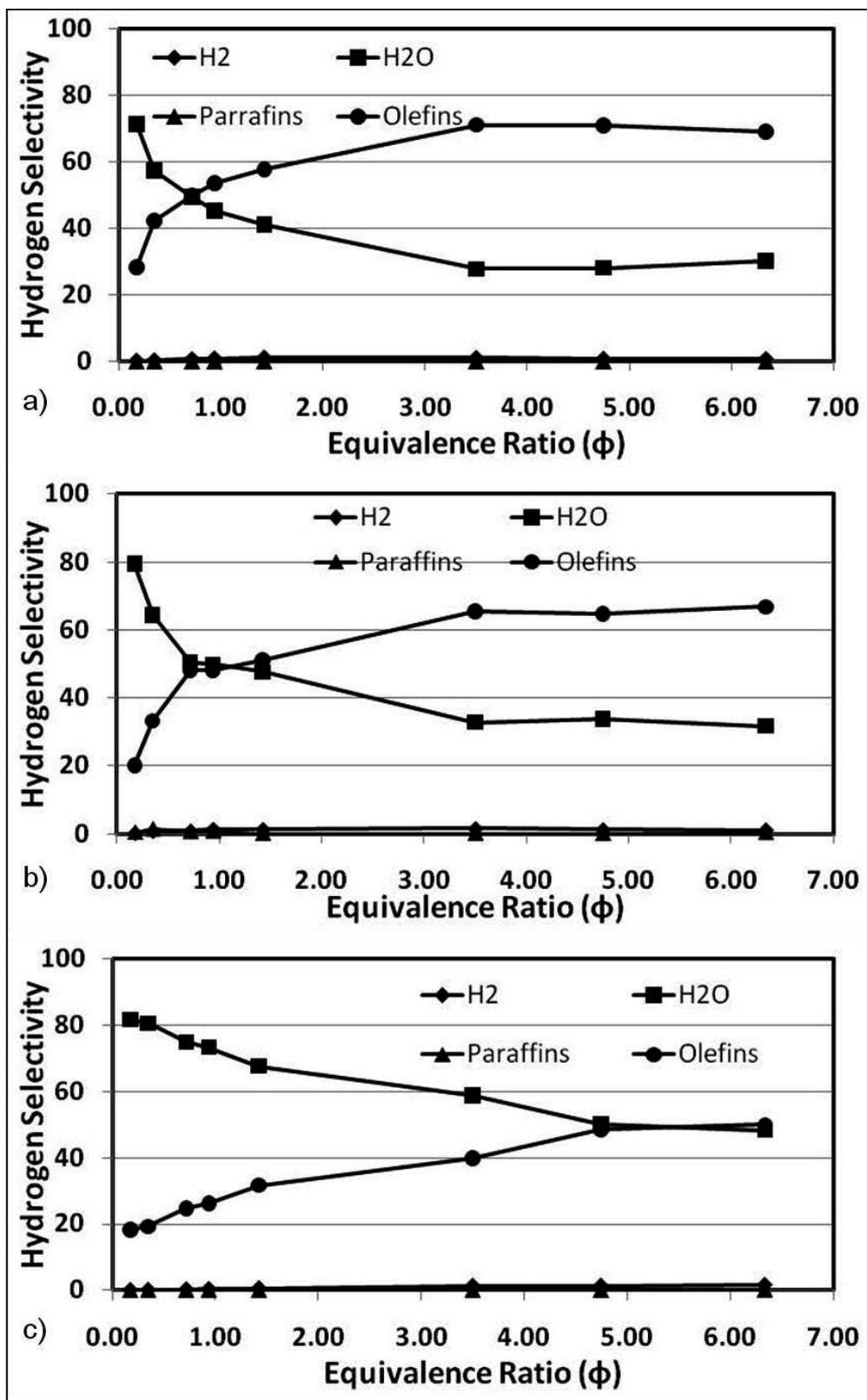


Figure 2. Hydrogen selectivity of the reactor products for a contact time of (a) 70, (b) 135, and (c) 270 ms using the alumina catalyst (i.e., without rhodium).

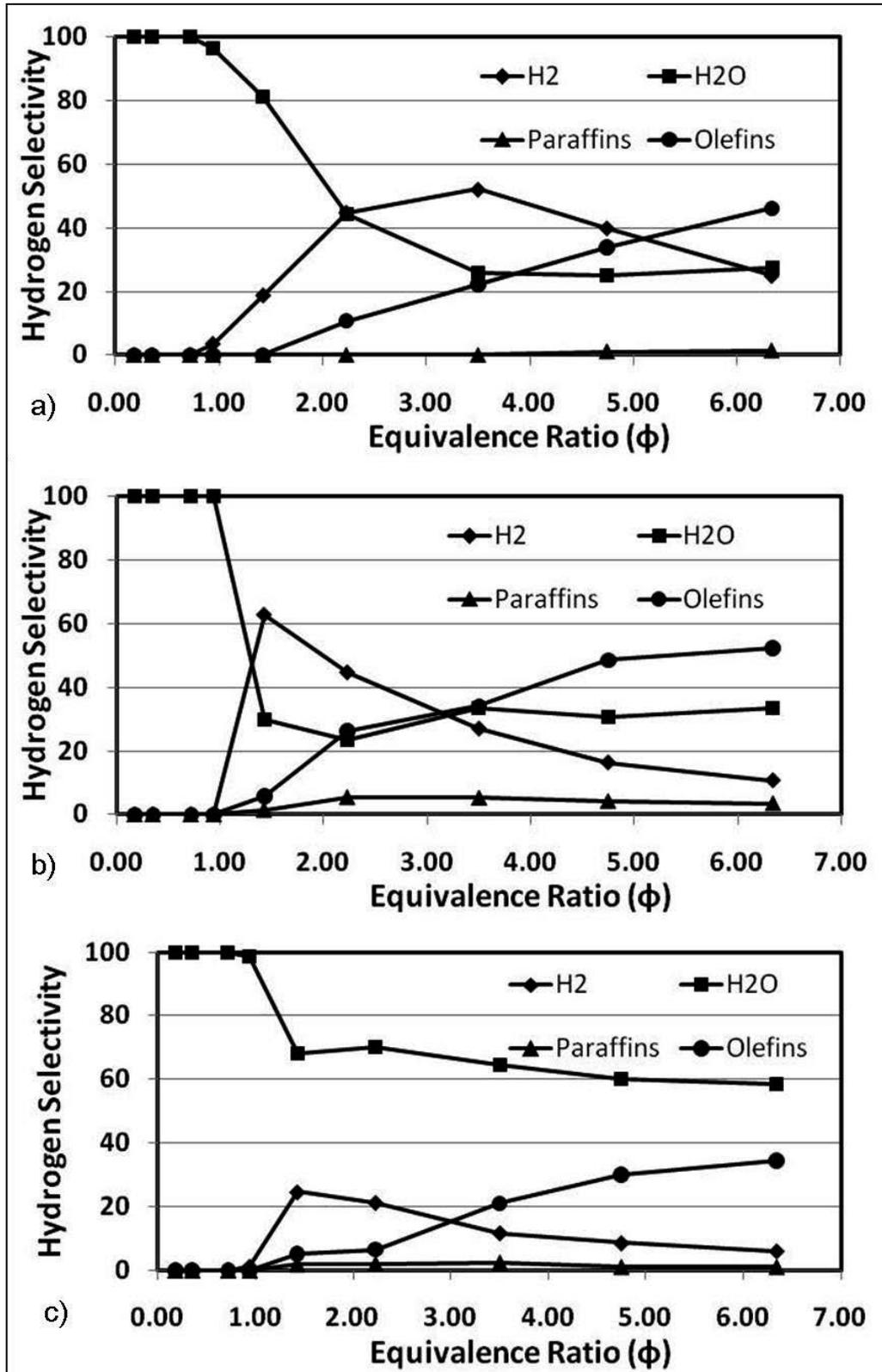


Figure 3. Hydrogen selectivity of the reactor products for a contact time of (a) 70, (b) 135, and (c) 270 ms using the rhodium catalyst.

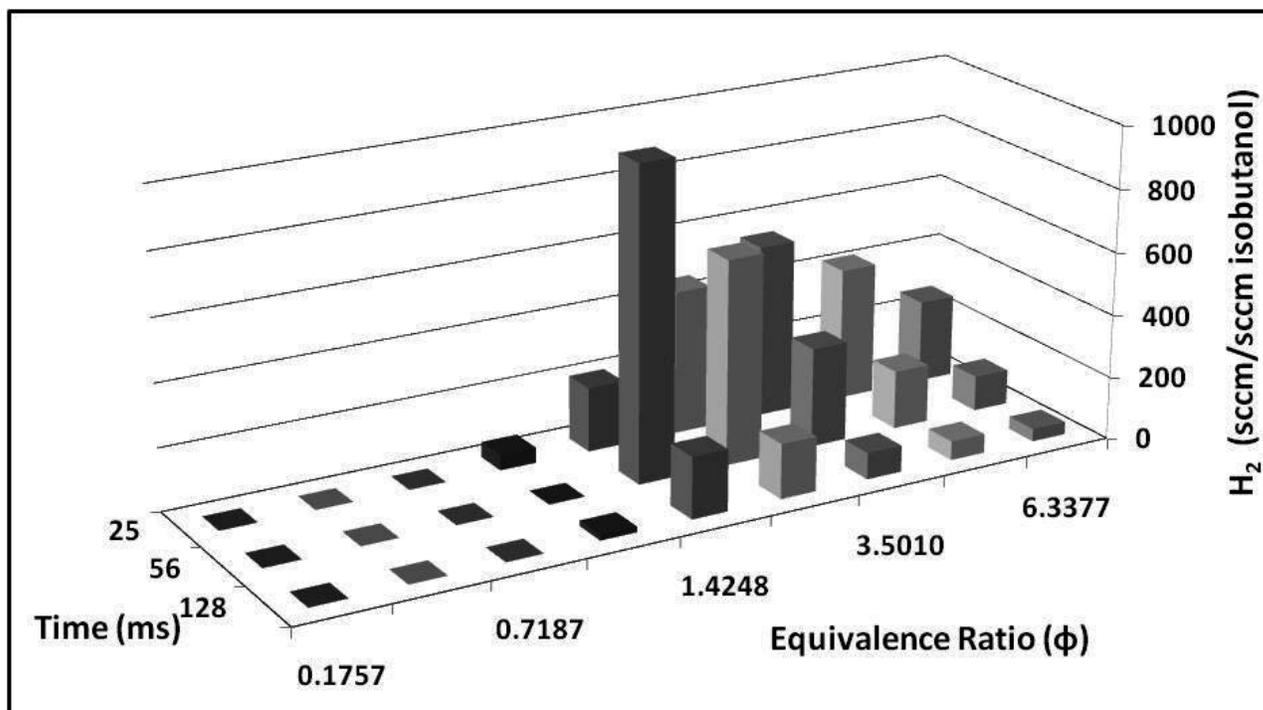


Figure 4. A H₂ produced per amount of isobutanol at various contact times and equivalence ratios.

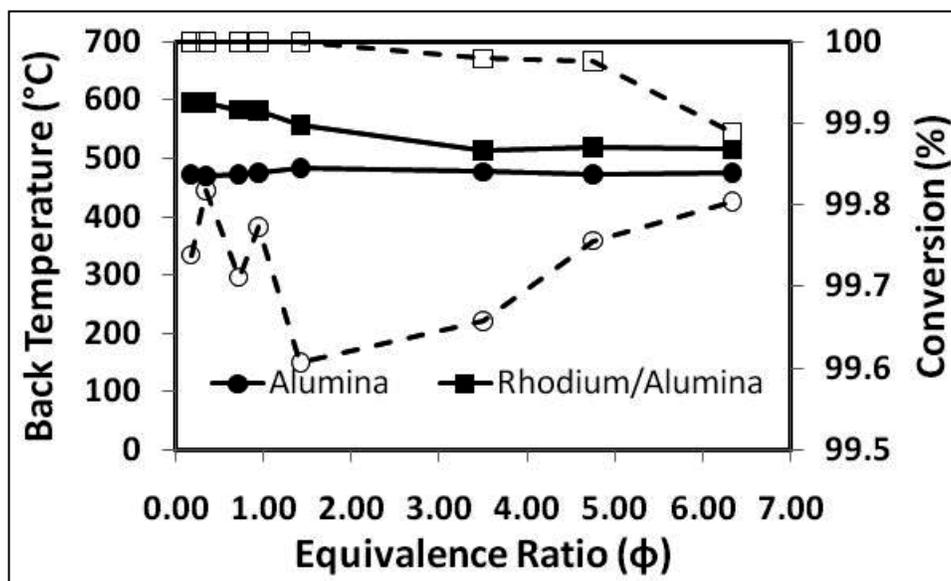


Figure 5. Temperatures recorded at the backface of the catalyst are given with solid lines. Dashed lines represent isobutanol conversion to other species. Contact time: 70 ms.

4. Discussion

4.1 Reaction Pathway

Figures 2 and 3 offer excellent insight into the reaction pathway taken in isobutanol catalytic combustion. Although other pathways may be present, the following proposed pathway is consistent with the experimental results. The first step is known as dehydration of the isobutanol, forming olefins and water:



This reaction is consistent with the study of 2-butanol decomposition (12), because the operating temperatures were always above 275 °C. The following steps are taken to complete combustion and require O to do so.

Partial oxidation of olefins:



Oxidation of H₂:



Oxidation of CO:



Consider the selectivities of catalytic partial oxidation of isobutanol using the alumina catalyst (figure 2) in the fuel lean region ($\phi < 1$). The selectivity of water is higher than olefins, implying that much of the fuel is completely combusted. Some olefins remain, however, meaning that not all the olefins are partially oxidized. As the equivalence ratio increases to the mid range region ($\phi = 1.4248$), the longer contact time is required to progress to combustion. The shorter two contact times (25 ms, 56 ms) limit the reactions in equations 5–7. In the higher ϕ range, even the longest contact time (125 ms) is not slow enough, such that only half the H atoms are converted to water, while the other half are in the form of olefins due to dehydration from the reaction in equation 4. The trend of decreasing water selectivity with equivalence ratio is in part due to the decrease in O relative to the fuel, making the oxidation reactions harder to achieve; O was found, however, in the product gas in all cases using the alumina catalyst. H and CO were found in trace amounts (<1%) at operating condition. This strengthens the argument that catalytic combustion of isobutanol on the γ -alumina surface proceeds through the proposed pathway. Another pathway could be dehydrogenation of isobutanol:



However, because little, if any, H was observed using the alumina catalyst, dehydrogenation does not appear to have taken place. The alumina results also indicate that the reactions of equations 4, 6, and 7 occur quickly relative to the reaction in equation 5; when olefins are partially oxidized, the syngas is quickly converted to water and CO₂.

From figure 3, fuel lean conditions show only water and CO₂ as products when Rh is added to the catalyst foam. At lean conditions, decomposition of isobutanol and oxidation of the intermediate species (equations 4–7) occur on both the alumina and Rh surfaces, converting the fuel into its complete combustion products. It can be assumed that isobutanol decomposition also occurs on the Rh surface, as figure 5 shows that Rh gives a slightly higher conversion of isobutanol (meaning more is dehydrated in addition to the amount converted by alumina). Since the difference in conversion values is very small, most of the dehydration of isobutanol can be attributed to the alumina. This coincides with the recent literature study on 2-butanol decomposition (12), in which the authors concluded that the active sites were on the zirconia support of the Pt/ZrO₂ catalyst for dehydration.

While the higher temperatures may cause deactivation for decomposition, Rh does not show decreased performance in oxidation. The Rh expedites the conversion process so that complete combustion does occur for fuel lean conditions at all three contact times. The olefins blocking the sites may be attributed to the change, since they would be in a favorable position for catalytic oxidation with the Rh. Moving to a higher equivalence ratio of $\phi = 1.4248$ produces H₂ for all contact times. The decrease in O when increasing the ratio means that the syngas oxidation reactions (equation 6 and 7) have less O to use, and cannot fully convert the CO and H₂ into CO₂ and water, respectively. These steps suffer because the preliminary reaction, partial oxidation of the olefins on both surfaces, consumes most if not all the O.

The differences in magnitude of the H₂ selectivities in the presence of Rh for the three contact times explain the distribution of O, as well. First, it should be noted that unlike the alumina catalyst, no O was observed in the effluent gas. From the alumina catalyst, it is found that oxidation on the alumina surface is more favorable with a longer contact time, and that oxidation of H₂ (or CO) will happen if the olefins are partially oxidized, regardless of the equivalence ratio, leaving only a small amount of H₂. Since the H₂ value in figure 3b is higher than that of figure 3a, it is reasonable to assume that partial oxidation of olefins on the Rh surface also occurs more frequently with longer contact times. Because more O is being used in the partial oxidation of olefins, less O is available for the oxidation of syngas on the Rh surface. Thus, at a contact time of 56 ms, less of the H₂ produced from partial oxidation on the Rh surface is further converted than with the shorter contact time. This would also be the case with the longer time (125 ms), except that now the alumina in the catalyst is in the combustion dominant regime. At this higher contact time, oxidation on the alumina surface takes a more dominant role in converting the olefins to water and CO₂.

Figure 3a shows a different trend in H₂ selectivity than the figures 3b and 3c. The maximum is attained at an equivalence ratio of 3.501. With the decrease in O to the new ratio, partial oxidation of the olefins on the Rh surface is still occurring, perhaps at the same rate, while reactions on the alumina surface and syngas oxidation on the Rh surface are less frequent. At the other contact times, the H₂ selectivity has decreased, meaning that the Rh surface reaction of equation 5 has been reduced with the others. This scenario implies that the Rh at smaller contact times is more effective than alumina at activating O₂ for surface reactions with olefins, but also that this characteristic diminishes with increasing contact time. The rest of the data past this equivalence ratio provides the following insight: as the equivalence ratio increases, less O is available, lowering the rates of oxidation on both alumina and Rh surfaces. This means that only dehydration will occur at even larger ϕ values. Only alumina surface reactions increase in occurrence at high ϕ values when the contact time is increased. Contact times larger than those investigated here could potentially render the Rh useless; however, such contact times would not yield H for fuel cell applications.

4.2 Hydrogen Production

From figure 4, it is clear that for maximum yield a contact time of 56 ms with an equivalence ratio around 1.4248 is desirable. At the fuel flow rate used for experimentation, 1.012 mL/hr (about 8.25 W thermal), the reactor provided at this operating condition the equivalent of 3.61 W of H₂. This translates to a reformer efficiency of approximately 44%. Even the next higher equivalence ratio achieves a higher H yield than the highest peak of the 25 ms contact time, being 651 and 550 sccm H₂/sccm isobutanol, respectively. This implies there is an optimal contact time for H production with this catalyst, not just an optimal equivalence ratio. The optimal contact time and equivalence ratio associated with it will be the topic of future research.

4.3 Temperature Profile

The temperature profiles portrayed in figure 5 concur with the reaction products of the reactor. Because the reactor is adiabatic, all energy entering the system with the reactants also leaves the system with the products. In this scenario, the enthalpy released when combusting the fuel is distributed through the products, which is observed in the form of a temperature increase. A combustion process that sees more than the complete products, CO₂ and H₂O, is using energy to form and sustain those byproducts. Thus, less of a temperature increase will be observed. This is the case with the alumina catalyst at all equivalence ratios tested, and the Rh catalyst at fuel rich conditions.

5. Conclusions

The energy-dense, renewable alcohol isobutanol can be reformed using catalytic combustion to produce H₂ for use in small power applications such as PEM fuel cells. H₂ production requires Rh when using a monolith foam coated with γ -Alumina. This is because the Rh accelerates the process that decomposes olefins into H₂ and CO. The highest H₂ selectivity observed was 62.92% at an equivalence ratio of 1.4248 and a contact time of 56 ms. This operating condition provided 3.61 W of H₂, achieving an approximate reformer efficiency of 44%. Conversion of isobutanol to other species was found to be above 99%.

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8 HCS 1 ELEC	US ARMY RSRCH LAB ATTN IMNE ALC HRR MAIL & RECORDS MGMT ATTN RDRL CIO LL TECHL LIB ATTN RDRL CIO MT TECHL PUB ATTN RDRL SED E A GAMSON ATTN RDRL SED E I LEE (3 HC AND 1 ELEC) ATTN RDRL SED P J ST CLAIR ADELPHI MD 20783-1197
TOTAL:	15 (12 HCS, 1 CD, 2 ELEC)