Conversion of Wet Ethanol to Syngas via Filtration Combustion

by

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Approved by
Supervising Committee:

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Dedication

To my family
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Abstract

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In this work, experiments were undertaken to determine if ethanol and wet ethanol could be converted to syngas via filtration combustion. The effect of three parameters, equivalence ratio, inlet velocity, and water fraction, on the conversion was investigated. Experimental results included ethanol to hydrogen conversion efficiency, ethanol to carbon monoxide conversion efficiency, energy conversion efficiency, reaction zone propagation speed, and temperatures. Experimental results were compared to equilibrium calculations, computational modeling, and other studies of the conversion of ethanol to syngas. The system energy flows were analyzed to determine the optimum value of water fraction in terms of system energy inputs and to determine if the process required external energy contributions. Additionally, equilibrium calculations were used to determine the potential of other fuels and mixtures of fuels for syngas production by filtration combustion.
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CHAPTER 1 : INTRODUCTION

1.1 SYNGAS

Figure 1-1 describes the relative versatility of fuel types and the relative efficiency of energy conversion technologies. In this figure, the lines that link the fuels with the conversion technologies indicate which fuels may be used with which conversion technologies. Solid lines indicate that a fuel can easily be used with a particular technology and dashed lines indicate that a fuel can be used with a conversion technology in some cases. Solid fuels are the least versatile, only usable in steam boilers, or as a feedstock to create liquid or gaseous fuels. Liquid fuels are more versatile than solid fuels, but cannot generally be used in gas turbines or fuel cells, both of which are efficient conversion technologies. Gaseous fuels are extremely versatile, able to be used under most circumstances in all energy conversion technologies. As seen in the figure, syngas, a gaseous mixture of hydrogen, carbon monoxide and other species, is very versatile. It can be used directly as a fuel for solid oxide fuel cells and combustion systems, including internal combustion engines and turbines for power generation (Spath and Dayton 2003; Laboratory 2007; Burnette, Kremer et al. 2008). Syngas is also very valuable as a chemical feedstock, and is the principle source of hydrogen (Pruett 1981; Spath and Dayton 2003; Speight 2007). Syngas and syngas-derived hydrogen are critical to the petrochemical industry because they are used for upgrading and processing fossil fuels and for producing synthetic liquid fuels (Speight 2007; Takeshita and Yamaji 2008).
Syngas was originally produced by the gasification of coal and solid biomass, but today syngas is primarily obtained from natural gas by catalytic steam reforming, a process that is very efficient and well-understood (Spath and Dayton 2003). Natural gas, however, is not renewable, has a volatile price, and contributes to atmospheric carbon dioxide concentrations when used. To avoid the use of fossil fuels, researchers have revisited the production of syngas from biological sources, the most common being solid biomass for gasification, which often utilizes catalysts (Reed 1981; Bridgwater 1995; Spath and Dayton 2003). Other research has been conducted on the catalytic conversion of bio-derived liquids to syngas (Adjaye and Bakhshi 1995; Marquevich, Czernik et al. 1999; Takanabe, Aika et al. 2004; Rioche, Kulkarni et al. 2005; Bi, Hong et al. 2007; Haryanto, Fernando et al. 2007; Sanchez-Sanchez, Navarro et al. 2007; Tasaka, Furusawa
et al. 2007; Wang, Ye et al. 2007). These catalytic conversion processes can be very effective, but they also have some drawbacks: catalysts are expensive and fragile, may deactivate from solid carbon deposition (coking) and may be poisoned by fuel impurities, specifically sulfur (Moon, Ryu et al. 2004). Also, catalytic conversion processes often require specific feedstock and operating conditions to work effectively (Czernik, Evans et al. 2007; Dupont, Ross et al. 2007).

1.2 PARTIAL OXIDATION AND WET ETHANOL

To overcome the problems associated with using catalysts for the conversion of biomass to syngas, a noncatalytic process to convert a biologically-derived liquid fuel, ethanol (C$_2$H$_5$OH), to syngas was investigated. This process, partial oxidation, is the reaction of a mixture of fuel and oxidizer that has more than the stoichiometric amount of fuel. The three main steps of the partial oxidation of ethanol can be described by the following simplified global reactions at a rich equivalence ratio ($\varphi=3$):

Fuel Breakdown (balanced for $\varphi=3$)

$$C_2H_5OH + O_2 \leftrightarrow 3H_2 + CO + CO_2 + 226 \frac{\text{joules}}{\text{mole of ethanol}}$$

Steam reforming

$$C_2H_5OH + H_2O \leftrightarrow 4H_2 + 2CO - 299 \frac{\text{joules}}{\text{mole of ethanol}}$$

Water-gas shift

$$CO + H_2O \leftrightarrow H_2 + CO_2 + 41 \frac{\text{joules}}{\text{mole of ethanol}}$$
The chemical equation representing exothermic fuel breakdown is balanced for an equivalence ratio of three. In this reaction there is three times as much fuel per oxygen as there is in the stoichiometric reaction ($\phi = 1$):

$$C_2H_5OH + 3O_2 \leftrightarrow 3H_2O + 2CO_2 + \frac{1226 \text{ joules}}{\text{mole of ethanol}}$$

Although the fuel breakdown equation is a simplification of the chemistry because the products would include water and some other species, it describes how diatomic hydrogen and carbon monoxide are formed through reactions at rich equivalence ratios. In this reaction, some of the hydrogen atoms bond to form diatomic hydrogen because there is insufficient oxygen to form water. Also, some of the carbon atoms form carbon monoxide because there is insufficient oxygen to form carbon dioxide.

According to the simplified reaction model for rich mixtures, water and remaining ethanol react in the endothermic steam reforming reaction to produce carbon monoxide and hydrogen. Then the produced carbon monoxide reacts with water to form hydrogen and carbon dioxide in the slightly exothermic water-gas shift reaction. As long as the mixture can be reacted, water addition should contribute to hydrogen through these reactions and decrease carbon monoxide through the water-gas shift reaction. This decrease in carbon monoxide is an advantage for pure hydrogen production from syngas. To examine of the benefits of water addition, mixtures of ethanol and water were investigated for syngas production.

Ethanol is a promising biofuel because of the existence of a substantial production, storage and transportation infrastructure, and because ethanol can be less
carbon-intensive than fossil fuels. Many have suggested, however, that the energy required to produce ethanol is greater than the energy content of the final product (Pimentel and Patzek 2005). Water removal, which takes place in distillation and dehydration steps, is one of the most significant energy-consuming steps in the production process, and therefore is a prime contributor to the skepticism surrounding ethanol and its energy balance.

Because of the potential energy savings in eliminating, in part or in whole, the distillation and dehydration steps of ethanol production, there has already been some research on the use of wet ethanol, notably in HCCI engines (Mack 2007) and for catalytic conversion to syngas (Deluga, Salge et al. 2004). Figure 1-2 shows the net energy balance for pure ethanol. The full circle represents all of the energy contained in ethanol and its coproducts, and the slices represent the distribution of that energy amongst energy inputs and outputs (net energy gain). As shown in Figure 1-2, 37% of the energy contained in dry ethanol and its coproducts is required for its distillation and dehydration. In contrast, Figure 1-3 (Martinez-Frias, Aceves et al. 2007) shows the energy balance for a mixture of 35% ethanol and 65% water. To create this mixture of water and ethanol, only 3% of the energy contained in the ethanol and its coproducts is required for distillation, and dehydration is eliminated entirely. From this analysis, it is concluded that 34% of the energy in ethanol and its coproducts would be saved by using a mixture such as this in an HCCI engine rather than using dry ethanol (Mack 2007). Similarly, in the present study, experiments with wet ethanol were undertaken to
determine if it is a suitable replacement for dry ethanol as a feedstock for syngas production.

Many groups have investigated the conversion of ethanol, including wet ethanol, to syngas. Much research has been conducted on catalytic processes (Galvita, Semin et al. 2001; Cavallaro, Chiodo et al. 2003; Deluga, Salge et al. 2004; Bi, Hong et al. 2007; Ni, Leung et al. 2007; Sanchez-Sanchez, Navarro et al. 2007; Silva, Barandas et al. 2007), while much less attention has been given to noncatalytic processes (Christensen, Silveston et al. 2004). These studies are discussed in greater detail in section 3.6. Two of the most significant problems, sulfur poisoning and coke formation, with catalytic techniques are strongly dependent on fuel selection. Because ethanol has no sulfur and, in comparison to large hydrocarbons, it has a relatively low tendency to coke (Böhm and Braun-Unkhoff 2008), attempts at catalytic conversion have been successful. However, attempts at converting logistic fuel (JP-8), which has significant sulfur components (Azad and Duran 2007), and heavier bio-derived fuels, such as rapeseed oil (Dupain, Costa et al. 2007), have been less successful. Because of the inherent difficulties with catalytic conversion of these fuels to syngas, the potential for conversion by noncatalytic partial oxidation of some of these fuels was studied through equilibrium calculations. This work is discussed in Chapter 4.
Figure 1-2: Net energy balance for pure ethanol (Mack 2007)

Figure 1-3: Net energy balance for a wet ethanol mixture containing 35% ethanol and 65% water by volume (Mack 2007)
1.3 EXCESS ENTHALPY COMBUSTION

1.3.1 Concept and Designs

In 1971, F.J. Weinberg (Weinberg 1971) proposed controlling combustion temperatures through heat recirculation as a means to optimize intensity and efficiency and to minimize pollution. Figure 1-4 describes a conventional combustion device to be contrasted with Figure 1-5, which describes a combustion device based on his idea.

In the combustion device depicted in Figure 1-4, cold reactants enter a chamber and react, releasing heat. The hot combustion products exit the chamber at the adiabatic equilibrium temperature. Increasing the temperatures in the system requires external heat addition. During steady-state operation of a device like that shown in Figure 1-5, cold reactants enter a chamber and are heated by the hot combustion products in a heat exchanger before reacting. Because of this preheating, superadiabatic temperatures, or temperatures that exceed the adiabatic equilibrium temperature, are reached. The superadiabatic combustion products are then cooled to the adiabatic flame temperature after transferring heat to the incoming cold reactants. Weinberg (Weinberg 1971) proposed that this type of reactor, which creates high reaction temperatures, could be used to burn mixtures that would not react in conventional combustion devices. Hardesty and Weinberg (Hardesty and Weinberg 1974) expanded on Weinberg’s original idea, presenting a more detailed theory and reporting experimental results, including the observation of superadiabatic temperatures for ultra-lean combustion.
In conventional combustion devices, self-supporting flames will occur in mixtures with equivalence ratios between the lean and rich flammability limits. The flammability limits are defined empirically as the lowest and highest equivalence ratios for which a propagating reaction front will be sustained (Law 2006). Flammability limits exist because, when a fuel/oxidizer mixture is too dilute, the heat release is not great enough to
increase the temperature of the surrounding mixture to a point where a sufficient reaction rate is achieved. Given this relationship between reaction rate and temperature (the Arrhenius law), it is clear that increasing the temperature of the bulk mixture allows more dilute mixtures to react. Figure 1-6 shows that the flammability limits of an ethanol/air mixture are broadened when the temperature of the reactants is increased. The lean and rich flammability limits of an ethanol/air mixture at standard temperature and pressure are 0.48 and 2.8, respectively (Law 2006). As the figure shows, increasing the reactant mixture temperature extends the flammability limits, and ultra-rich partial oxidation becomes possible.

The ability to burn mixtures with equivalence ratios outside the conventional flammability limits has been applied to practical devices such as efficient, low-pollution radiant heaters at low equivalence ratios (Howell, Hall et al. 1996) and syngas production at high equivalence ratios (Drayton, Saveliev et al. 1998). These various applications have led to multiple design configurations. Researchers have applied the concept of heat recirculation in reactors that transfer heat through reaction chamber walls (Hardesty and Weinberg 1974; Ronney 2003; Schoegl and Ellzey 2007), while others investigated heat transfer through conducting media, often porous, inserted into a reaction chamber (Zhdanok, Kennedy et al. 1995; P. Bingue, V. Saveliev et al. 2002; Barra and Ellzey 2004; Bingue, Saveliev et al. 2004; Pedersen-Mjaanes, Chan et al. 2005). Heat recirculation has also been used in a spouted bed combustor (Khoshnoodi and Weinberg 1978; Weinberg, Bartleet et al. 1988). Many other designs can be found in a paper by Jones, et al. (Jones, Lloyd et al. 1978).
1.3.2 Filtration Combustion

Filtration combustion is the combustion of a mixture that is flowing through the pores of a porous matrix. In a theoretical study, Takeno and Sato (Takeno and Sato 1979) first proposed this method to accomplish the heat recirculation described by Weinberg. Depending on the composition and velocity of the reactants and the material properties of the solid, the reaction may exhibit various characteristics, including significant variation in the propagation of the reaction zone relative to the reactor. Babkin (Babkin 1993) identified, in terms of reaction zone propagation, five steady-state combustion regimes: the low-velocity regime, the high-velocity regime, the sound-velocity regime, the low-velocity detonation, and the normal detonation with losses. As described by Babkin, there is a transition from the low velocity regime (thermal wave velocity $\approx 10^{-4}$ m/s) to the high velocity regime (thermal wave velocity $\approx 10$ m/s) when the pores are large enough for a combustion wave to propagate through the porous media.
in a stationary gas. In the high velocity regime, the thermal interaction between the solid and the gas has a relatively small effect on the reaction zone propagation. In contrast, there is significant thermal interaction between the solid porous media and the reacting gases in the low velocity regime, resulting in heat recirculation from the hot combustion products to the cold reactants. For the study presented in this thesis, all experiments were conducted in the low-velocity regime, which is typical for filtration combustion in a medium with relatively small pores.

Figure 1-7 describes the heat transfer processes that recirculate heat from the products to the reactants in a porous media reactor. The hot gases downstream of the reaction front heat the porous solid. Then heat is transferred by convection from the hot pellets to the incoming cold mixture until the mixture reacts, releasing heat. Additionally, heat is transferred from the reaction zone upstream through the porous media by radiation and conduction. These heat transfer processes can be further illuminated by Figure 1-8, a plot of gas and solid temperature vs. distance from the filtration reactor base, as calculated by the computational model for a rich mixture of ethanol and air (Leahey 2008). Approximately 5 cm from the reactor entry (distance = 5), the hot solid begins to transfer heat to the cold gas. At approximately 10 cm from the reactor entry, the gas, having reached a sufficient temperature, reacts and releases heat, which raises the temperature of the combustion products above the solid temperature. The hot gas transfers this heat to the solid downstream, reaching thermal equilibrium shortly after the reaction zone.
One of the unique characteristics of filtration combustion is that the reaction may propagate in the same direction as the flow of reactants (co-flowing), in the opposite direction (counter-flowing), or remain steady relative to the reactor depending on the conditions. In the counter-flowing case, the reaction zone propagates into a region that has been cooled by the incoming reactants, resulting in a relatively cool reaction temperature, which is less than the adiabatic equilibrium prediction. In the present study, the reactions occurred in the co-flowing case where the reaction front propagates into a region of the porous media that has been heated by the exhaust gases. This propagation results in pre-heated reactants, which produce superadiabatic local temperatures upon reaction. These high local temperatures are necessary to drive the reactions in the ultra-rich mixtures.
Many groups have studied filtration combustion in the low-velocity regime. Babkin et al. (Babkin, Drobyshevich et al. 1983) performed a theoretical and experimental investigation of filtration combustion with hydrogen and air and reported the fundamental characteristics, such as peak temperature in the reaction zone and the different propagation directions described above. Babkin (Babkin 1993) also published a review of filtration combustion, identifying the four velocity regimes. Researchers at the University of Texas at Austin (UT) published experimental and numerical studies of methane-air filtration combustion, (Hsu, Evans et al. 1993; Hsu, Howell et al. 1993; Hsu and Matthews 1993), and Zhdanok, et al. (Zhdanok, Kennedy et al. 1995), studied...
methane-air filtration combustion obtaining similar results to Babkin. Since Zhdanok’s publication, many studies of low-velocity regime filtration combustion have been published. A review discussing some of the early work in low-velocity regime filtration combustion of hydrocarbons can be found in a paper by Howell et al. (Howell, Hall et al. 1996).

The properties of the porous media strongly affect the characteristics of a combustion wave, therefore the selection of materials and geometries for porous media are important. Additionally, as Weinberg (Weinberg 1971) noted in his original paper, high combustion temperatures caused by heat recirculation may exceed the melting point of materials commonly used to contain combustion processes, making materials selection especially important. Consequently, researchers have used a wide variety of materials and geometries for porous media reactors: Babkin (Babkin, Drobyshevich et al. 1983) used granular Carborundum SiC with 1-1.25 mm grains; Zhdanok et al. (Zhdanok, Kennedy et al. 1995) used 5.6 mm solid alumina spheres, and others used reticulated, porous ceramic foams, many of which are described by Howell et al (Howell, Hall et al. 1996). Fay et al. (Fay, Dhamrat et al. 2005) compared the performance of alumina spheres and reticulated ceramic for syngas production. Although they found that the reticulated ceramic performed better than the alumina spheres for syngas production, they noted that the reaction zone propagated much slower in the bed of alumina spheres. Slow propagation is useful in practice; when the combustion front reaches the end of the reactor the experiment must be restarted. Also, it was found that the reticulated ceramics cracked
under thermal cycling, while the alumina pellets remained unaffected (Elverum, Ellzey et al. 2005).

Figure 1-8: Solid and gas temperature (Leahey 2008)

1.3.3 Filtration Combustion for Syngas Production

As mentioned previously, mixtures with equivalence ratios outside the conventional flammability limits can be reacted in a heat recirculating device such as a porous media reactor for filtration combustion. In fact, it has been shown that there are no theoretical flammability limits (Babkin, Drobyshevich et al. 1983; Aldushin 1993), and it is this reason that filtration combustion has been used for the production of syngas; the partial oxidation of ultra-rich mixtures (mixtures with equivalence ratios greater than the conventional rich flammability limit) is possible. Though early researchers observed
reactions outside the flammability limits, filtration combustion was not initially used for syngas production. A paper by Drayton et al. (Drayton, Saveliev et al. 1998) was an early demonstration of syngas production by filtration combustion (Drayton, Saveliev et al. 1998). They used a reciprocal flow burner to react mixtures of methane and air at pressures of 1, 3 and 5 atm and equivalence ratios between 2 and 8, highlighting that the product composition included significant concentrations of hydrogen and carbon monoxide. More recently, Bingue et al. (Bingue, Saveliev et al. 2002) studied syngas production from methane and hydrogen sulfide, and Kennedy et al. (Kennedy, Saveliev et al. 2002) studied syngas production from methane-air mixtures with oxygen doping. Pederson-Mjaanes et al. (Pedersen-Mjaanes, Chan et al. 2005) used a two-section porous media reactor to produce syngas from air and liquid fuels including, methanol, methane, octane and gasoline. Their study is an early demonstration the conversion of liquid fuels to syngas via filtration combustion. It must be noted that they used a two-section reactor, which is fundamentally different from the filtration reactor used for the present study because the reaction zone does not propagate in a two-section reactor. Around this time, researchers at UT began to publish results of the conversion of methane to syngas in porous media reactors (Dhamrat and Ellzey 2006). Recently they published results of the conversion of n-heptane to syngas by filtration combustion (Dixon, Schoegl et al. 2008).

Researchers at UT have also published experimental and computational results for syngas production by partial oxidation in a parallel channel reactor (Schoegl and Ellzey 2007; Schoegl and Ellzey 2009). Though this reactor is not a filtration reactor, it relies on the same principle of heat recirculation as filtration reactors do. Their reactor consisted of
parallel channels with alternating flow directions. The hot combustion products transferred heat through the containing wall to the incoming reactants, preheating the mixture and allowing superadiabatic combustion temperatures. They experimented with methane at different equivalence ratios and inlet velocities, achieving a peak methane to hydrogen conversion efficiency of 55% (Schoegl and Ellzey 2009), and they experimented with propane, achieving a peak propane to hydrogen conversion efficiency of 50% (Schoegl, Newcomb et al. 2009).

In the present study, filtration combustion was used to react ethanol-air mixtures at various equivalence ratios, including some that are higher than the conventional flammability limit. Also, experiments were conducted with mixtures of ethanol, water and air that are not flammable in traditional combustion devices due to the dilution of the fuel-air mixture with water. Similar to a flammability limit based on how much excess fuel or oxidizer is in a mixture, there is a flammability limit based on how much water is in the reactants. The water acts as a heat sink, decreasing the temperature of reacting mixture. The flammability of mixtures of ethanol, water and air are shown in Figure 1-9 (Shustrov, Korol'chenko et al. 1977). The vertical axis describes the relative amounts of ethanol in the mixture, and the horizontal axis describes the relative amount of water in the system. The lines drawn on the top and right of the figure show the mixture composition in terms of variables (\( \varphi \) and \( \chi \)) used in the present study. Mixtures with compositions lying to the left of the curve are flammable, while mixtures with compositions lying to the right of the curve are not flammable. Figure 1-9 makes clear that significant water addition affects the flammability of mixtures of ethanol and water.
1.4 SCOPE

In contrast to the studies of fossil fuels described above, this research is focused on the conversion of a specific liquid biofuel, ethanol. Ethanol was selected for this study for various reasons. First, it is the most common biofuel, with a substantial production and distribution infrastructure and federal targets for production. Second, the kinetics
mechanisms, which are required for computational modeling, are available. Third, the physical properties of ethanol are similar to n-heptane which was used previously and consequently, the experimental rig could be used without significant redesign. Finally, ethanol and wet ethanol provide an interesting system-level energy aspect for study.

The objectives of this study were to demonstrate the conversion of wet ethanol to syngas through filtration combustion, to determine the relationships between operating conditions and reactor performance, to compare equilibrium calculations and computational results described by Leahey (Leahey 2008) with the experimental results, and to analyze the system energy inputs and outputs. Additionally, as discussed in Chapter 4, other biologically-derived liquid fuels were investigated though an equilibrium study to determine their potential for conversion to syngas through filtration combustion.

1.4.1 Controlling Parameters

In the filtration combustion of wet ethanol, there are three controlling parameters: equivalence ratio ($\phi$), water fraction ($\chi$) and inlet velocity ($\vartheta$), which are defined by the following equations:

$$
equivalence \, ratio \, (\phi) = \frac{\dot{N}_{C_2H_5OH}}{\frac{\dot{N}_{O_2}}{1/3}}$$

where $\dot{N}_{C_2H_5OH}$ and $\dot{N}_{O_2}$ are molar flow rates, and $1/3$ is the stoichiometric ratio of ethanol to diatomic oxygen.
volumetric water fraction \( (\chi) = \frac{\dot{V}_{H_2O}}{\dot{V}_{H_2O} + \dot{V}_{C_2H_5OH}} \)

where \( \dot{V}_{C_2H_5OH} \) and \( \dot{V}_{H_2O} \), are volumetric flow rates in the liquid phase

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

where \( R \) is the universal ideal gas constant, \( T \) is the absolute temperature, \( P \) is the pressure, \( \sum \dot{N} \) is the total molar flow rate of air and ethanol, and \( \text{Area} \) is the cross-sectional area of the reactor. It should be noted that, under this definition, increasing the water fraction has no effect on \( \vartheta \). The inlet velocity was defined this way so that the molar flow rate of ethanol was not varied with water fraction at constant \( \vartheta \).

In this study we performed three independent experimental investigations. Each investigation involved the variation of one of the three controlling parameters while the other two were held constant. The rows in Table 1-1 describe the operating conditions for each of the three investigations.

<table>
<thead>
<tr>
<th>Investigation Parameter</th>
<th>( \varphi )</th>
<th>( \chi ) (%)</th>
<th>( \vartheta ) (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equivalence Ratio ( (\varphi) )</td>
<td>1 to 5</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>Water Fraction ( (\chi) )</td>
<td>2</td>
<td>0 - 60</td>
<td>20</td>
</tr>
<tr>
<td>Inlet Velocity ( (\vartheta) )</td>
<td>2</td>
<td>0</td>
<td>20 - 60</td>
</tr>
</tbody>
</table>

### 1.4.2 Equilibrium Calculations and Computational Modeling

Two numerical models were used to investigate syngas production by filtration combustion of wet ethanol. Equilibrium calculations were used to determine trends in syngas production as a function of \( \varphi \) and \( \chi \). A computational model of the filtration
reactor was used to predict syngas production and combustion characteristics as a function of $\varphi$, $\chi$, and $\theta$.

**Equilibrium Calculations**

Thermodynamic equilibrium calculations were performed using the Cantera software suite (Goodwin 2002-2007). For this study, the desired equilibrium results are the species concentrations and the temperature of various wet ethanol and air mixtures. To simulate the reactor, constant pressure (atmospheric pressure) and constant enthalpy (adiabatic walls) equilibrium calculations were performed.

Equilibrium often cannot be considered an accurate model of a real reacting system because it contains no information about time or reaction pathway. However, these calculations can provide useful information especially if the system being modeled has high reaction rates. Additionally, equilibrium can represent an upper bound on temperature and species conversion in a chemical reactor (Smith and Missen 1980). In the particular physical system being studied, peak temperatures exceed the adiabatic equilibrium temperatures. These temperatures represent a deviation of the system from the equilibrium representation, but create high reaction rates that support the use of equilibrium for modeling. Most importantly, previous research in filtration combustion shows that experimental values, although not identical in magnitude, follow similar trends to equilibrium as a function of $\varphi$ (Pedersen-Mjaanes, Chan et al. 2005; Dhamrat and Ellzey 2006; Dixon, Schoegl et al. 2008).
Computational Modeling

The primary work for this thesis was experimental. Fortunately, another researcher, Daniel Leahey, worked on the detailed computational modeling of the process in parallel. In the results section of the present study, the computational results are compared with experimental results. The following, based on Leahey’s thesis (Leahey 2008), is a brief description of the computational model and a discussion of the kinetics mechanisms that were used for study.

Detailed computational modeling was based on the Henneke and Ellzey filtration combustion model (Henneke and Ellzey 1999). This model was adapted slightly to account for the particular characteristics of the physical system. Details can be found in Leahey (Leahey 2008).

To solve the system of governing equations in the porous media computational model, boundary and initial conditions were implemented. For the gas energy equation, a temperature gradient of zero was specified at the reactor exit, the reactor inlet temperature was set to the ambient temperature of 300 K, and the initial gas temperature throughout the domain was also set to 300 K. For the gas species equation, a concentration gradient of zero was specified at the reactor exit, and gas composition and velocity at the inlet are investigated in this study through the independent variables, $\phi$, $\chi$, and $\theta$. For the solid porous media energy equation, a temperature gradient of zero was applied at the inlet and exit, and the initial solid temperature was set to the axially-constant value of 1500 K to model the experimental preheating procedure. It is important to note that the inlet temperature of the gas and the initial temperature of the solid, though
different from the experimental conditions, did not significantly affect the composition of the exhaust gases in the computational results (Leahey 2008).

The computational results were generated using the Marinov kinetics mechanism (Marinov 1999), and the porous media material properties shown in Table 1-2. More information on the particular characteristics of the computational model can be found in (Henneke 1998) and (Henneke and Ellzey 1999).

Table 1-2: Porous media material properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific heat ([c_s])</td>
<td>1255 J/kg-K</td>
</tr>
<tr>
<td>Conductivity ([k_s])</td>
<td>1.195 W/m-K</td>
</tr>
<tr>
<td>Albedo ([\omega])</td>
<td>0.8</td>
</tr>
<tr>
<td>Extinction Coefficient ([\beta])</td>
<td>100 m(^{-1})</td>
</tr>
<tr>
<td>Density ([\rho_s])</td>
<td>2334 kg/m(^3)</td>
</tr>
<tr>
<td>Pore Diameter</td>
<td>0.003 m</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.4</td>
</tr>
</tbody>
</table>

As noted above, the results of the computational model are included in this study for comparison. As described by Leahey (Leahey 2008), the results of the computational model would be expected to differ from the experimental results for two known reasons: the kinetics mechanism that was used was not developed to model rich or ultra-rich oxidation, and the formation of solid carbon was not modeled. Results from previous work have shown that the computational model deviates from experiments at high values of \(\varphi\) (Dixon, Schoegl et al. 2008). Although this limitation was known, a mechanism that modeled ethanol oxidation under rich conditions was not successfully implemented in the computational model. Leahey showed through equilibrium calculations that solid carbon
formed in significant concentrations at $\varphi > 3.8$. A comparison of equilibrium calculations, one with solid carbon formation allowed and the other with solid carbon formation disallowed, showed that the hydrogen and carbon monoxide mole fractions were significantly different between the two cases. Based on the equilibrium results, it can be expected that the computational model under-predicts hydrogen concentration and over-predicts carbon monoxide concentration at high values of $\varphi$. It should be noted that the $\chi$ investigation and the $\vartheta$ investigation were undertaken with $\varphi$ held constant at two, so the shortcomings of the computational modeling results should be less significant in these studies than results from the $\varphi$ study, which included ultra-rich conditions.
CHAPTER 2 : EXPERIMENTAL APPARATUS AND METHOD

2.1 EXPERIMENTAL APPARATUS

The experimental apparatus, depicted in Figure 2-1, was developed and used by previous researchers (Vogel 2003; Dhamrat 2004; Fay 2004; Dixon 2007), but was modified slightly for the present study. A detailed description of the system can be found in Dixon’s Masters Thesis (Dixon 2007). The apparatus consists of three main parts: the reactor, the data acquisition system, and the flow system.

The reactor was a 20 cm long packed bed of alumina spheres, with properties shown in Table 1-2. The packed bed was surrounded by an insulating sleeve of alumina with a 5.59 cm inside diameter and a 10.16 cm outside diameter. These components were supported by a steel casing. A small section of yttria-stabilized zirconia/alumina (YZA) porous ceramic supported the bed of spheres. A quartz tube was placed on the top of the reactor to flare the combustible exhaust gases about 20 cm away from the top of the reactor. Flaring syngas 20 cm from the top of the reactor prevented the combustion of the exhaust gases from affecting the temperature and exhaust measurements.

The data acquisition system included 11 B-type thermocouples and a Varian, Inc., three-channel micro gas chromatograph (GC). The thermocouples, accurate for 200°C to 1700°C were placed at 1.5 cm intervals along the length of the reactor with the thermocouple junctions at the centerline of the reactor. The 11 thermocouples reported temperatures at 1 second intervals, allowing estimation of the reaction zone location and propagation speed. 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. Exhaust gas samples for GC analysis were taken through a quartz tube placed at the top and centerline of the packed bed. The samples were then routed to the GC through inert Silco treated steel tubing. All GC measurements were reported as dry, carbonless mole fractions because water was filtered out with a Genie membrane separator (model 170) before reaching the GC and because solid carbon deposited in the reactor. Extensive details about the GC operation and calibration can be found in Dixon’s Master’s Thesis (Dixon 2007).
The flow system for ethanol, water and air is shown in Figure 2-2. The ethanol was contained in a tank and pumped through a rotameter for flow control using an automotive fuel pump. Water flow from the Engineering Teaching Center at UT was also
controlled using a rotameter, and then combined with ethanol in a Swagelok T-connector. After flowing through about 1 meter of 0.635 cm OD tubing, the mixture was vaporized in a heated stainless steel tube and mixed with dry laboratory air in a mixing chamber before entering the reactor. The flow system is nearly identical to that used by Dixon (Dixon 2007), except for the water connection and the expanded-diameter stainless steel tube. All external surfaces between the vaporization tube and the reaction chamber were wrapped with heating tape to minimize condensation. Calibrations of the air flow controller and the ethanol and water rotameters were performed, yielding linear calibration curves with coefficients of determination ($R^2$) values greater than 0.98 (Devore 2004). Detailed calibration procedures can be found in (Dixon 2007).

![Figure 2-2: Experimental Flow System](image)

A weakness in the present study is that the inlet temperature of the mixture of vaporized ethanol, water and air was not measured. It is possible that, in the prevaporization process, the mixture of ethanol and water became superheated. The goal
of filtration combustion is to accomplish preheating by recirculating heat from hot combustion products, rather than adding energy to the system from an external source, such as that used to vaporize the ethanol/water mixture. Although it is impossible to know the temperature, and therefore the excess internal energy of the inlet mixture for the experimental results, Leahey found that the inlet temperature did not significantly affect the product species (Leahey 2008). Therefore, it is assumed that any superheating of the inlet ethanol/water mixtures in the experiments was small and did not affect the composition of the exhaust species.

2.1 EXPERIMENTAL METHOD

In the experiments, the bed of packed alumina pellets was preheated to approximately 1200 °C by reacting a methane/air mixture in the bed. Ignition was accomplished by igniting the mixture at the outlet of the reactor and then letting the reaction zone propagate upstream until the most upstream thermocouple began to show a temperature increase. After initial preheating, ethanol, water, and air were controlled to flow into the porous media reactor in mixtures with specific values of $\phi$, $\chi$, and $\theta$ as described by Table 1-1.

Initial experiments were undertaken to determine the behavior and effectiveness of the liquid vaporization system, shown in Figure 2-3, which was used by Dixon (Dixon, Schoegl et al. 2008). The figure shows the vaporization coil and the Bunsen burner used for heating. Attempts were made to operate the reactor at various values of $\phi$, $\chi$ and $\theta$. It was found that the original vaporization system was effective for only a small range of
operating conditions without significant oscillations occurring in the ethanol and water rotameters.

After a discussion with Dr. Matthew Hall, professor of Mechanical Engineering at UT, a new evaporation system was designed for operation without oscillation. Dr. Hall suggested that the oscillations found when using the original vaporization coil were being caused by pressure variations resulting from evaporation within the small diameter tube. He suggested vaporizing the liquid in a tube with a larger diameter, which would decrease the pressure fluctuations. This design, shown in Figure 2-4, was found satisfactory for vaporizing a wider range of mixtures of ethanol and water than could be vaporized with the original design. Still, the operating conditions were limited; at high flow rates of water and ethanol, liquid could be observed on the walls of the heated mixing chamber, indicating incomplete vaporization. Initial experiments were undertaken to find a set of operating conditions that would be acceptable for the experimental investigation. It was decided that acceptable set would include values of $\varphi$ up to 5 and values of $\chi$ up to 60%. These requirements and the limits of the evaporation system determined that the $\chi$ and $\theta$ investigations could be performed with a maximum $\varphi$ of 2; higher $\varphi$ with large values of $\chi$ or $\theta$ desired for experiments required flow rates of ethanol and water that could not be vaporized. Also, it was determined that the $\varphi$ and $\chi$ investigations could be performed at a maximum $\theta$ of 20 cm/s; higher $\theta$ with large values of $\varphi$ or $\chi$ desired for experiments required flow rates of ethanol and water that could not be vaporized. These limitations were unfortunate because previous research has shown that the most efficient syngas production occurs with higher values of $\varphi$ and $\theta$ (Dhamrat
and Ellzey 2006; Dixon, Schoegl et al. 2008). Future work will include the design and construction of a vaporization system capable of vaporizing mixtures with higher values of $\phi$, $\chi$, and $\theta$.

Figure 2-3: Original vaporization system
At each operating condition, the GC measured the exhaust gas four times, with each measurement taking approximately 150 seconds. The measurements began when the reaction zone location, defined by the approximate location of the maximum temperature gradient, was 5-9 cm from the bottom of the porous ceramic support shown in Figure 2-1. Because the reaction zone propagates at different speeds depending on the operating conditions, the subsequent samples were taken when the reaction zone was at various locations. All reported experimental data are the average values of the last two measurements taken. The first two measurements were discarded because they were taken to clear residual gas in the tube connecting the quartz sampling probe and the GC.

As noted above, the reaction zone propagates to the end of the reactor at high values of $\varphi$, necessitating a reheating of the bed for a new experiment. When the reaction zone reached the end of the reactor the water flow was stopped, $\vartheta$ was decreased and $\varphi$...
was changed to near-stoichiometric so that the reaction zone propagated upstream, reheating the porous media along the way. Under these operating conditions, the temperatures measured in the bed significantly exceeded the peak temperatures found under rich operating conditions. After reheating the bed, the operating conditions were changed to those for a specific experimental condition, which usually lead to a downstream-propagating reaction zone. As the reaction zone propagated downstream, measured temperatures decreased from the preheating temperatures until they reached a relatively stable magnitude. Because the measurements were taken when the temperatures approximately reached their steady-state value, it is assumed that the initial preheating process did not affect the exhaust composition.

The following is a summary of the experimental procedure:

1. Preheat the bed of porous media with lean methane/air mixture.
2. Start ethanol/air/water flows at a specific $\varphi$, $\chi$, $\vartheta$ from Table 1-1 for experimentation.
3. When the reaction zone, defined by maximum temperature gradient, is $\approx 5$ cm from the bottom of the porous ceramic support, start GC measurements.
4. If reaction zone has propagated farther than 5 cm from the base of the porous ceramic support after the last GC measurement has been made, change the operating conditions to $\varphi \approx 0.8$, $\chi = 0\%$, $\vartheta \approx 20$ cm/s for an upstream propagating reaction zone.
5. When the reaction zone is $\approx 5$ cm from the bottom of the porous ceramic support, restart at Step 2.
2.2 Method for Data Analysis

For each of the investigations, product species were reported by the GC and temperatures were reported by thermocouples. With these data and data known from controlled inputs, metrics to describe the performance of the reactor were calculated. The methods to calculate these metrics are described in this section.

To calculate the total mole outflow of gas (moles per second), it was assumed that diatomic nitrogen (N₂) did not react to form other species such as NOₓ. Because NOₓ formation is often a result of high temperatures and excess oxygen, it is greatest on the lean side of stoichiometric (Law 2006). Though high peak temperatures are created in filtration combustion, we experimented with fuel-rich mixtures that yield low combustion temperatures relative to the high temperatures seen in slightly lean combustion. Also, rich conditions indicate a lack of oxygen available for NOₓ formation. The assumption that N₂ did not react yielded the following equation for total mole outflow (dry and carbonless):

\[
\sum \dot{N}_{\text{out}} = \frac{0.78 \times \dot{N}_{\text{air}}}{[N_2]}
\]

The units of \(\sum \dot{N}_{\text{out}}\) and \(\dot{N}_{\text{air}}\) are moles per second and \([N_2]\) is the dry, carbonless mole fraction reported by the GC.

From the total mole outflow, the mole outflow of individual species was calculated with the following representative equation for hydrogen:

\[
\dot{N}_{H_2} = [H_2] \times \sum \dot{N}_{\text{out}}
\]
Where $\sum \dot{N}_{out}$ is the total mole outflow and $[H_2]$ is the dry, carbonless mole fraction reported by the GC.

The ethanol to hydrogen conversion efficiency was calculated for each GC measurement. This metric describes how effectively the reactor converts ethanol-bound hydrogen to diatomic hydrogen. It is important to note that the denominator does not include hydrogen bound in water, which can contribute to hydrogen in the numerator. Therefore the theoretical ethanol to hydrogen conversion efficiency can be greater than 100%.

\[
\text{ethanol to hydrogen conversion efficiency} = 100 \times \frac{2 \times \dot{N}_{H_2}}{6 \times \dot{N}_{C_2H_5OH}}
\]

The units of $\dot{N}_{C_2H_5OH}$ and $\dot{N}_{H_2}$ are moles per second.

We also calculated the ethanol to carbon monoxide conversion efficiency for each measurement.

\[
\text{ethanol to carbon monoxide conversion efficiency} = 100 \times \frac{\dot{N}_{CO}}{2 \times \dot{N}_{C_2H_5OH}}
\]

The units of $\dot{N}_{CO}$ and $\dot{N}_{C_2H_5OH}$ are moles per second.

The ethanol to hydrogen energy conversion efficiency and the ethanol to carbon monoxide energy conversion efficiency were calculated. These metrics describes how much of the chemical energy in ethanol was converted to energy in hydrogen and carbon monoxide, respectively. These energy conversion efficiencies were calculated using the lower heating value (LHV) of the individual species as described by the following representative equation for hydrogen:
ethanol to hydrogen energy conversion efficiency = 100 × \frac{57.8 \times \dot{N}_{H_2}}{326.7 \times \dot{N}_{C_2H_5OH}}

\dot{N}_{H_2} and \dot{N}_{C_2H_5OH} units are moles per second and the values for LHV are in units of kcal per mole.

We also calculated the total (chemical) energy conversion efficiency, which includes the energy of all of the species in the exhaust with a non-zero lower heating value (LHV). The total energy conversion efficiency is a measure of how much energy in ethanol was lost to thermal energy in the process. The total energy conversion efficiency was calculated as follows:

\textit{total energy conversion efficiency} = 100 \times \frac{\sum_i \dot{N}_i \times LHV_i}{326.7 \times \dot{N}_{C_2H_5OH}}

The summation is performed over all energy-containing (LHV > 0) species in the exhaust with non-negligible concentration (concentration > 0.1%). Values for LHV were taken from (Lewis and Von Elbe 1961).

As mentioned, the GC measures the dry, carbonless mole fraction. Because water does not contribute to the denominator in the mole fraction, the mole fractions reported by the GC are different from what they would be if the GC measured water. To calculate the wet mole fraction of the product species, the difference between hydrogen inflow and outflow was calculated according to the following equation:

\dot{N}_h = (6 \times \dot{N}_{C_2H_5OH} + 2 \times \dot{N}_{H_2O}) - (2 \times \dot{N}_{H_2} + 4 \times \dot{N}_{CH_4} + 4 \times \dot{N}_{C_2H_4} + 2 \times \dot{N}_{C_2H_2})

It was assumed that all unmeasured hydrogen was contained in water molecules. This assumption is not entirely valid, because there is no way to prove that other
hydrogen-containing species were not formed. Equilibrium calculations and the computational model do not predict the formation of any hydrocarbons that were not measured by the GC, so it is very likely that water was the primary, if not sole, hydrogen-containing species not measured by the GC. With this assumption, the wet mole fraction of each species was calculated as described by the following representative equation for hydrogen:

$$[H_2](wet) = \frac{\dot{N}_{H_2}}{\sum\dot{N} + 1/2 \times \dot{N}_h}$$

Water was a significant product species, therefore the mole fraction changed appreciably from the dry value reported by the GC to the wet value calculated as described above. This deviation can be seen in Figure 2-5, which shows the mole fraction (dry) reported by the GC and the wet mole fraction as a function of $\phi$. 

38
Figure 2-5: Dry and wet hydrogen concentration as a function of equivalence ratio

The GC also does not measure the amount of solid carbon formed in the reactor, however solid carbon was not used, like water was, for determining an alternate mole fraction because solid carbon is not a component of the exhaust gas. The maximum solid carbon mole fraction, defined as the number of carbon moles divided by the total number of moles, was 2%. The mole outflow of carbon atoms was calculated from the following equation.

$$\dot{N}_c = (2 \times \dot{N}_{C_2H_5OH}) - (\dot{N}_{CH_4} + 2 \times \dot{N}_{C_2H_4} + 2 \times \dot{N}_{C_2H_2} + 2 \times \dot{N}_{CO_2})$$

Uncertainties in $\phi$, $\chi$, and $\theta$ resulted from uncertainty in ethanol, water and air flow rates. Uncertainties in species measurements were calculated using a Student-t distribution (Devore 2004). Uncertainties for all calculations were calculated by
sequential perturbation (Wheeler and Ganji 2004). Details on uncertainty can be found in Appendix A.
CHAPTER 3 : RESULTS AND DISCUSSION

In this chapter results from equilibrium calculations, experimental measurements and computational modeling are presented and discussed. When possible, the results from the three methods of investigation are compared. Equilibrium results are shown in section 3.1 to describe trends in temperature, hydrogen production and carbon monoxide production as a function of $\phi$ and $\chi$. In the next three sections, results from the experiments, equilibrium calculations, and the computational model are presented to describe the conversion of wet ethanol to syngas as a function of the three controlling parameters, $\phi$, $\chi$, and $\theta$. In section 3.5, an analysis of the energy inflows and outflows is presented, and in section 3.6, the results from the present study are compared with other published results.

3.1 EQUILIBRIUM

As mentioned previously, equilibrium calculations generally follow the trends of species production in filtration combustion reactions although the magnitudes of species concentrations do not generally agree with experiments (Dixon, Schoegl et al. 2008). The ethanol to hydrogen conversion efficiency, the ethanol to carbon monoxide conversion efficiency and the adiabatic equilibrium temperature were calculated with equilibrium calculations and shown in Figure 3-1, Figure 3-2, and Figure 3-3.

Figure 3-1 shows that equilibrium predicts the conversion of ethanol to hydrogen at $\phi > 1$, peaking between $\phi = 3$ and $\phi = 4$. Ethanol to hydrogen conversion efficiency increases with increasing water fraction, $\chi$. This trend has added importance because of the energy input for ethanol production. If hydrogen is produced from wet ethanol ($\chi > 0$)
with better, or even equal, efficiency as it can be produced from dry ethanol ($\chi = 0$), the process has a greater overall energy efficiency (in terms of hydrogen produced per unit energy input) because less energy is needed to produce the wet ethanol than is needed to produce dry ethanol. The theoretical ethanol to hydrogen conversion efficiency is greater than 100% at large values of $\chi$ because water-bound hydrogen is not counted in the denominator in our definition of hydrogen conversion.

Figure 3-2 shows that ethanol to carbon monoxide conversion efficiency increases after $\phi = 1$, peaking near $\phi = 3$. Unlike ethanol to hydrogen conversion efficiency, ethanol to carbon monoxide conversion efficiency decreases with increasing $\chi$. These trends suggest that adding water to the reactants would increase the $\text{H}_2/\text{CO}$ ratio for syngas production.

Figure 3-3 shows that, as expected, the temperature is a maximum with $\chi = 0$ at $\phi \approx 1$. The temperature decreases as excess fuel ($\phi > 1$) or water ($\chi > 0$) is added to the system because the heat released under these conditions must be distributed to a greater amount of mass. The values shown in Figure 3-3 will be compared to the temperatures seen in the experimental and computational results to determine if superadiabatic temperatures are achieved.
Figure 3-1: Ethanol to hydrogen conversion efficiency as a function of $\varphi$ and $\chi$

Figure 3-2: Ethanol to carbon monoxide conversion efficiency as a function of $\varphi$ and $\chi$
3.2 EQUIVALENCE RATIO INVESTIGATION

As seen in Figure 3-4, for mixtures of dry ethanol and air at the conventional rich flammability limit of 2.8, peak temperatures exceed the adiabatic equilibrium temperature. For the computations, the reaction zone propagation speed (positive speed means downstream propagation) increases with increasing $\phi$ as seen in Figure 3-5. Since thermocouple measurements were only taken every 1 cm in the experiments, there was insufficient resolution to measure the temperature distribution, and thus the reaction zone propagation speed, accurately. Nonetheless, estimates of the propagation speed were
possible. The reaction zone propagates downstream at $\phi > 2$, but at $\phi = 2$ it propagates upstream.

Figure 3-4: Peak gas temperature as a function of $\phi$ ($\theta = 20$ cm/s, $\chi = 0$)
Figure 3-5: Reaction zone propagation speed as a function of $\phi$ ($\theta = 20$ cm/s, $\chi = 0$). Experimental values are estimates.

Figure 3-6 shows the ethanol to hydrogen and ethanol to carbon monoxide conversion efficiencies as a function of $\phi$. The trends for syngas production were similar to those of previous investigations of methane and n-heptane (Dhamrat and Ellzey 2006; Dixon, Schoeogl et al. 2008). In the experiments, there is a rapid increase in hydrogen and carbon monoxide production from $\phi = 1$ to $\phi = 2$ and a peak near $\phi = 3$ for both species. The computational results show different behavior, diverging from the experimental results for both hydrogen and carbon monoxide at $\phi > 2$. Deviations from experimental values at $\phi > 2$ are not surprising since, in general, kinetics mechanisms are tuned for conditions close to stoichiometric ($\phi = 1$).
Figure 3-7 shows how the energy in ethanol is distributed amongst the syngas product species as a function of $\phi$. Because our computational model assumes adiabatic walls and our reaction chamber is not perfectly insulated, greater total energy efficiency is seen in the computational results. For total energy conversion efficiency, the trend in the computational results matches the trend in the experiments quite closely, but with the expected offset due to the adiabatic assumption in the model. In contrast, the computational and experimental results for hydrogen and carbon monoxide energy conversion efficiency diverge at $\phi > 2$. The trends in energy conversion efficiency for both hydrogen and carbon monoxide are identical to the trends seen in Figure 3-6.

Figure 3-8 shows how the energy in ethanol is distributed amongst the species, excluding hydrogen and carbon monoxide, that contribute to the total energy conversion efficiency. In the experiments, nearly all of the chemical energy in the exhaust is contained in hydrogen and carbon monoxide at $\phi = 2$. At $\phi = 3$, the ethanol to methane ($\text{CH}_4$) energy conversion efficiency is 10% and then rises with $\phi$ to a maximum of 20% at $\phi = 5$. Ethanol to ethylene ($\text{C}_2\text{H}_4$) energy conversion is negligible until it reaches 3% at $\phi = 5$. Compared to the experiments, the computations show a greater overall contribution to the total energy conversion efficiency from species other than hydrogen and carbon monoxide. The computational value for ethanol to methane energy conversion efficiency rises with $\phi$ to a peak of 22% at $\phi = 5$. Differing from the experimental values, the computational values for ethanol to ethylene energy conversion efficiency never exceed 0.2%. Also different from the experiments, in which acetylene concentrations were negligible, the computational values for ethanol to acetylene ($\text{C}_2\text{H}_2$) energy
conversion efficiency are relatively large, reaching a peak of 20% at $\varphi = 4$ and contributing significantly (9%) to the total energy conversion efficiency at $\varphi = 2$. The equilibrium calculations show small values of ethanol to methane energy conversion efficiency at $\varphi > 3$. The conversion of ethanol to species other than hydrogen and carbon monoxide at high values of $\varphi$ indicates that further process optimization is necessary.

Figure 3-6: Ethanol to hydrogen and ethanol to carbon monoxide conversion efficiency as a function of $\varphi$ ($\dot\vartheta = 20$ cm/s, $\chi = 0$)
Figure 3-7: Energy conversion efficiency as a function of $\phi$ ($\theta = 20 \text{ cm/s}, \chi = 0$)

Figure 3-8: Energy conversion efficiency as a function of $\phi$ ($\theta = 20 \text{ cm/s}, \chi = 0$)
3.3 Water Fraction Investigation

Syngas production as a function of $\chi$ was investigated at $\varphi = 2$ and $\vartheta = 20$ cm/s. When analyzing these results, it is important to consider the flammability limits of ethanol/water/air systems shown in Figure 1-9; at $\varphi = 2$, mixtures with $\chi \approx 17\%$ would not be flammable in conventional combustion devices. The experimental values are compared with the computational values, but only up to with $\chi = 30\%$ because computational values could not be obtained with larger values of $\chi$.

Figure 3-9 shows that peak gas temperatures in the experiments and the computational model remain relatively constant as a function of $\chi$, though, according to the equilibrium results, the temperature should decrease with increasing $\chi$. Most likely, the temperature drop predicted by equilibrium calculations is not observed because high gas temperatures are created as a result of the heat recirculation from the hot solid to the gas during downstream propagation seen in the experiments in Figure 3-10. It should also be noted that the peak temperature seen in the experiments exceeds the adiabatic equilibrium temperature at $\chi = 60\%$. 
Figure 3-9: Peak gas temperature as a function of $\chi$ ($\varphi = 2, \theta = 20$ cm/s)

Figure 3-10 Reaction zone propagation speed as a function of $\chi$ ($\varphi = 2, \theta = 20$ cm/s). Experimental values are estimates.
The experimental results in Figure 3-11 show that ethanol to hydrogen conversion efficiency is constant or increases slightly with increasing $\chi$. This trend is predicted by the equilibrium calculations and the computational model, though the equilibrium values are significantly larger than the experimental values and the computational values are slightly lower than the experimental values. In the experiments, the ethanol to carbon monoxide conversion efficiency decreases with increasing $\chi$. This trend is predicted by the equilibrium calculations. Similar to the experiments, the computational model shows almost no change in ethanol to carbon monoxide conversion efficiency up to $\chi = 30\%$. The computational values and equilibrium values exceed the experimental values of ethanol to carbon monoxide conversion efficiency. Figure 3-12 shows that total energy conversion efficiency is a fairly weak function of $\chi$ at $\varphi = 2$ and $\vartheta = 20$. The maximum experimental value for total energy conversion efficiency, 55%, occurs at $\chi = 20\%$. In the experiments at all values of $\chi$, 20% to 30% of the energy in ethanol is converted to chemical energy in hydrogen, and 15% to 25% of the energy in ethanol is converted to chemical energy in carbon monoxide. In the experiments, the ethanol to methane energy conversion efficiency reached a maximum of 2% at $\chi = 30\%$ (not shown). The energy conversion efficiencies for other species were negligible. For the computations, the ethanol to methane energy conversion efficiency was $\approx 3\%$, and the ethanol to acetylene energy conversion efficiency was $\approx 8\%$ at all values of $\chi$ (not shown).

Figure 3-11 and Figure 3-12 show that syngas production is as efficient with wet ethanol as it is with dry ethanol. These results confirm that ethanol can be converted to
syngas with reduced energy costs from the dehydration and distillation process. Another potential benefit of water addition can be seen in Figure 3-13, which shows the ratio of hydrogen to carbon monoxide as a function of $\chi$. The figure shows a greater than 50% increase in hydrogen to carbon monoxide ratio from $\chi = 0\%$ to $60\%$. If pure hydrogen is desired for a particular use, such as for chemical production or for use in a PEM fuel cell, this trend is appealing.

Figure 3-11: Ethanol to hydrogen and ethanol to carbon monoxide conversion efficiency as a function of $\chi$ ($\phi = 2$, $\vartheta = 20$ cm/s)
Figure 3-12: Energy conversion efficiency as a function of $\chi$ ($\varphi = 2, \theta = 20 \text{ cm/s}$)

Figure 3-13: Hydrogen to carbon monoxide ratio as a function of $\chi$ ($\varphi = 2, \theta = 20 \text{ cm/s}$)
3.4 Inlet Velocity Investigation

Syngas production through filtration combustion depends on reaction temperatures, which in turn depend on the inlet velocity, $\vartheta$, of the fuel/air mixture. Figure 3-14 and Figure 3-15 show the peak gas temperature and reaction zone propagation speed, respectively, as a function of $\vartheta$. The peak gas temperatures and propagation speeds predicted by the computational model increase monotonically with increasing $\vartheta$. The experiments show a generally increasing trend up to 50 cm/s, but both the temperature and estimated propagation speed decrease as $\vartheta$ increases from 50 to 60 cm/s.

Figure 3-14: Peak gas temperature as a function of $\vartheta$ ($\varphi = 2$, $\chi = 0$)
Figure 3-15: Reaction zone propagation speed as a function of $\vartheta$ ($\varphi = 2$, $\chi = 0$). Experimental values are estimates.

Consistent with previous research (Henneke and Ellzey 1999; Dhamrat and Ellzey 2006; Dixon, Schoegl et al. 2008), syngas production is a strong function of peak temperature. As shown in Figure 3-16, both ethanol to hydrogen and ethanol to carbon monoxide conversion efficiencies increase with increasing $\vartheta$, and thus increasing peak temperature. The experimental values of ethanol to hydrogen and ethanol to carbon monoxide conversion efficiencies exceeded those predicted by equilibrium when $\vartheta$ was increased to 40 cm/s and beyond.

Figure 3-17 shows that the experimental value for total energy conversion efficiency increases significantly from $\vartheta = 20$ cm/s to $\vartheta = 30$ cm/s then levels off to a magnitude ($\approx 60\%$) similar to that predicted by the computational model and
equilibrium. Hydrogen energy conversion efficiency and carbon monoxide energy conversion efficiency both increase with increasing velocity, which is likely a result of increased peak gas temperatures.

The experimental values for ethanol to methane energy conversion efficiency never exceeded 3.5%, and the energy conversion efficiencies for other species were negligible. The computational values for ethanol to acetylene energy conversion efficiency decreased nearly linearly with increasing $\dot{\vartheta}$ from 9% at $\dot{\vartheta} = 20$ cm/s to 1.4% at $\dot{\vartheta} = 60$ cm/s. The ethanol to methane energy conversion efficiency also decreased linearly with increasing $\dot{\vartheta}$ from 3.2% at $\dot{\vartheta} = 20$ cm/s to 1.1% at $\dot{\vartheta} = 60$ cm/s.

![Figure 3-16: Ethanol to hydrogen and ethanol to carbon monoxide conversion efficiency as a function of $\dot{\vartheta}$ ($\varphi = 2$, $\chi = 0$)](image-url)
In this work, wet ethanol was examined because it requires less energy to produce than dry ethanol. To determine if there is a real energy benefit to using wet ethanol for syngas production by filtration combustion, an analysis of the energy inflows and outflows of the conversion process was conducted.

The energy and mass inflows and outflows relevant to converting wet ethanol to syngas via filtration combustion are shown in Figure 3-18. The red ovals represent energy flows, and the gray ovals represent mass flows. The green ovals show the starting and finishing states of the system, and the blue boxes represent processes. The inflows of energy include the energy required for distillation and dehydration, and the energy required for heating and vaporization. The energy outflows include the sensible enthalpy...
in syngas and the enthalpy in water outflows. According to Figure 1-2, 42% of the energy contained in ethanol and its coproducts is required to produce the wet ethanol mixture ($\chi = 88\%$). This energy input, which includes corn growth, corn transportation, mashing and cooking, and ethanol distribution, was not considered in the following analysis because it is not variable. To convert wet ethanol ($\chi = 88\%$) to dry ethanol ($\chi = 0\%$), distillation and dehydration require 23% and 14%, respectively, of the energy contained in ethanol and its coproducts (Martinez-Frias, Aceves et al. 2007). At the filtration reactor, there is an energy inflow for heating and vaporizing wet ethanol and an outflow of sensible enthalpy in syngas.

There are two parts to this energy analysis. First, the energy inflows are analyzed to determine if there is a wet ethanol mixture that is optimal, in terms of energy input, for syngas production by filtration combustion. Second, the sensible enthalpy available in the exhaust stream is compared to the input energy requirements to determine if the system requires an external energy source for heating and vaporization.
In Figure 3-18, the three energy inputs are energy for distillation, energy for dehydration and energy for heating and vaporization. Typically, in ethanol processing a mixture of 88% water and 12% ethanol ($\chi = 88\%$) is the result of fermentation. Distillation is then used to remove water until a mixture of 95% ethanol and 5% water ($\chi = 5\%$) is left. Finally, dehydration is used to remove the last 5% of water (Martinez-Frias, Aceves et al. 2007). In the experiments described in this thesis, a source of heat was required to heat and vaporize the wet ethanol mixture. To find the total energy input to the system, from post-fermentation to pre-reaction, the energy required for heating and vaporization was added to the energy required for distillation. It will be shown that
mixtures with less than 5% water by volume (χ < 5%) are not optimal for syngas production, so the energy input for dehydration is not included in the following analysis.

The energy input for heating and vaporization was found from the following equation:

\[
\text{energy required for heating and vaporization} = (m_{eth} \times c_{p,eth} \times \Delta T) + (m_{wat} \times c_{p,wat} \times \Delta T) + (m_{eth} \times h_{f,eth}) + (m_{wat} \times h_{f,wat}) + (m_{air} \times c_{p,air} \times \Delta T)
\]

The terms in the equation above are: the energy required to heat liquid ethanol \( (m_{eth} \times c_{p,eth} \times \Delta T) \), the energy required to heat liquid water \( (m_{wat} \times c_{p,wat} \times \Delta T) \), the energy required to vaporize ethanol \( (m_{eth} \times h_{f,eth}) \), the energy required to vaporize water \( (m_{wat} \times h_{f,wat}) \), and the energy required to heat air \( (m_{air} \times c_{p,air} \times \Delta T) \). The change in temperature, \( \Delta T \), was 80 degrees, which corresponded to raising the fluids from room temperature, 293 K, to the saturation temperature, 373 K, of water. The relevant values for thermodynamic properties are given in Table 3-1.

Table 3-1: Fluid thermodynamic properties

<table>
<thead>
<tr>
<th></th>
<th>Ethanol</th>
<th>Water</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>(c_p) (kJ/kg °C)</td>
<td>2.84</td>
<td>4.23</td>
<td>1.005</td>
</tr>
<tr>
<td>(h_{fg}) (kJ/kg)</td>
<td>855</td>
<td>2257</td>
<td>NA</td>
</tr>
</tbody>
</table>
The mass of ethanol was 1 kg, the mass of air was 0.94 kg, as required for \( \varphi = 2 \), and the mass of water was found from the following equation:

\[
m_{wat} = \frac{m_{eth}}{\rho_{eth}} \times \frac{1}{1 - \chi} \times \rho_{wat}
\]

where \( \rho_{eth} = 783 \text{ kg/m}^3 \), \( \rho_{wat} = 1000 \text{ kg/m}^3 \), and \( \chi \) is the water fraction.

Figure 3-19 shows the ratio of the energy required for distillation to the lower heating value of ethanol as a function the fraction of ethanol by volume (1-\( \chi \)) (Martinez-Frias, Aceves et al. 2007). The energy required to remove water from a mixture starting at 12% ethanol by volume (\( \chi = 88\% \)) is a linear function of water fraction until a mixture of approximately 80% ethanol, 20% water (\( \chi = 20\% \)) is reached. To remove more water, a significantly increasing amount of energy is required. The nonlinearity of the curve in Figure 3-19 suggests that retaining even small fractions of water in wet ethanol could have a significant impact on energy requirements and that an optimum value for \( \chi \) is likely to be found.

The data from Figure 3-19 were used along with the energy required for heating and vaporization to produce Figure 3-20, which shows the total energy required to produce a vaporized mixture of wet ethanol. In Figure 3-20, the dotted curve is a reproduction of the data shown in Figure 3-19, the solid curve is the energy required for heating and vaporization, and the dash-dot curve is the sum of the values shown in the other two curves, representing the total energy input required for water removal, heating and vaporization. Figure 3-20 shows that mixtures with very high values of \( \chi \) require large
amounts of energy to vaporize the water and mixtures with very low values of $\chi$ require large amounts of energy for distillation. The sum of the energies shows that the minimum, of $\approx 25\%$ of the LHV of ethanol is required for distillation and heating and vaporization of wet ethanol at $\chi \approx 30\%$. This analysis was performed for $\varphi = 2$, but is approximately valid for all values of $\varphi$ because a change in $\varphi$ only alters the energy required for air heating, which is small relative to the other energy inputs.

![Figure 3-19: Energy required for water removal by distillation as a function of ethanol fraction (Ladisch and Dyck 1979; Martinez-Frias, Aceves et al. 2007)](image)

Figure 3-19: Energy required for water removal by distillation as a function of ethanol fraction (Ladisch and Dyck 1979; Martinez-Frias, Aceves et al. 2007)
To determine whether external energy is required for the heating and vaporization of wet ethanol, the sensible enthalpy in the products is compared to the energy required for heating and vaporization for a range of operating conditions. Equilibrium calculations performed with Cantera were used to find the sensible enthalpy of the products, and analytical calculations were used to find the energy required for vaporization. To find the sensible enthalpy in the products, the following procedure was implemented in Cantera:

1. Specify a mixture of ethanol, water and air for particular values of $\phi$ and $\chi$ at 373 K and 1 atm.

2. Determine the equilibrium composition for the mixture at constant pressure and constant enthalpy.
3. Find the enthalpy of the equilibrium mixture determined in step 2.

4. Using the equilibrium product composition determined in step 2, determine the enthalpy of that mixture at 373 K and 1 atm.

5. Subtract the enthalpy found in step 4 from the enthalpy found in step 3. This enthalpy difference is the sensible enthalpy of the mixture of the equilibrium products.

Figure 3-21 shows the sensible enthalpy in the combustion products and the energy required for heating and vaporizing given mixtures of ethanol, air, and water. The energy required for heating and vaporization was determined for 1 kg of ethanol and the mass of air and water corresponding to the values of $\phi$ and $\chi$ specified in the figure. As Figure 3-21 shows, there is enough sensible enthalpy in the products to heat and vaporize the incoming mixture for all values of $\phi$ with $\chi = 0\%$ and $\chi = 40\%$, though there is insufficient sensible enthalpy in the products to heat and vaporize a mixture with $\chi > 80\%$ and $\phi > 4.5$.

Figure 3-20 shows that wet ethanol with $20\% < \chi < 40\%$ is optimal, in terms of energy inputs, for syngas production by filtration combustion. Figure 3-21 shows that there is sufficient sensible enthalpy in the product stream, syngas, to heat and vaporize a reactant mixture of air and wet ethanol with $20\% < \chi < 40\%$. Because the energy required to heat and vaporize wet ethanol can be obtained from available sensible enthalpy in the exhaust, the results shown in Figure 3-20 show that wet ethanol is a better feedstock than dry ethanol for syngas production by filtration combustion in terms of minimizing energy.
inputs. These conclusions are valid for this equilibrium analysis, but experiments or more detailed analysis that accounts for system energy losses and heat exchanger efficiency are required to determine if the enthalpy difference between what is required for heating and vaporization and what is available in the products is sufficient for practical application.

![Figure 3-21: Enthalpy of vaporization compared with sensible enthalpy in combustion products as a function of equivalence ratio](image)

3.6 COMPARISON WITH PUBLISHED RESULTS

Another demonstration of noncatalytic conversion of ethanol to syngas was done by Christensen et al. (Christensen, Silveston et al. 2004). Their reactor was an externally heated quartz tube, rather than a porous media reactor. In their experiments, they varied reactor temperatures, residence times and values of $\varphi$. In the experiments, the reactor
temperature was set at 600, 700 or 800 °C; the residence time was 2 or 4 seconds; and the oxygen to ethanol ratio was 0.5 or 1, which translates to \( \varphi = 6 \) and \( \varphi = 3 \), respectively. At \( \varphi = 6 \), they observed a maximum hydrogen mole fraction of \( \approx 14\% \) and a maximum carbon monoxide mole fraction of \( \approx 21\% \) with a 2 second residence time, and an 800 °C reactor temperature. At \( \varphi = 3 \), they observed a maximum hydrogen mole fraction of \( \approx 9\% \) with a 2 second residence time and a maximum carbon monoxide mole fraction of \( \approx 17\% \) with a 4 second residence time, both at 800 °C reactor temperature. With these results they concluded that noncatalytic partial oxidation of ethanol is not an attractive method for hydrogen production.

As seen in Figure 3-22, the maximum hydrogen concentration found in the present experiments was 22\%, and the maximum carbon monoxide concentration was 19\%, both at \( \varphi = 5 \). The hydrogen value exceeds that found in the work of Christensen et al. (Christensen, Silveston et al. 2004) even though the inlet velocity was not optimal. As noted earlier, the value of \( \vartheta \) for the \( \varphi \) investigation was very likely not optimal; previous researchers found increased conversion efficiency with higher inlet velocities (\( \vartheta > 20 \) cm/s) (Dixon, Schoegl et al. 2008). Figure 3-23 shows an increase in hydrogen concentration from 10.3\% at 20 cm/s to 16.1\% at 50 cm/s. Though \( \varphi \) was 2 for the \( \vartheta \) study, rather than 5, where the peak hydrogen and carbon monoxide concentrations are seen in Figure 3-22, the upwards trend in hydrogen concentration as a function of \( \vartheta \) would likely be observed at higher values of \( \varphi \), producing a maximum hydrogen concentration greater than the 22\% seen in the present study. The contrast between the
present work and that of Christensen et al. shows the benefit of using filtration combustion for noncatalytic syngas production.

Ni et al. (Ni, Leung et al. 2007) published a review of catalytic ethanol to hydrogen conversion processes. The study presented the results of various catalytic steam reforming studies and a few autothermal reforming studies. The results of catalytic steam reforming studies included hydrogen selectivity (identical to ethanol to hydrogen conversion efficiency) up to 95% using noble metal catalysts and up to 96% using non-noble metal catalysts. The results from studies of autothermal reforming, which is partial oxidation over a catalyst with heat provided by fuel oxidation rather than by an external source, included hydrogen selectivity up to 98%. Their review included a discussion of a recent study by Deluga et al. (Deluga, Salge et al. 2004), who produced hydrogen from wet ethanol by autothermal reforming. Deluga et al. (Deluga, Salge et al. 2004) report an output stream of approximately 50% hydrogen from a mixture of 25% ethanol, 75% water (on a mole basis). This product stream corresponded to an ethanol to hydrogen conversion efficiency of 130%, which indicates that steam contributed significantly to the hydrogen production. Their study included a discussion of the energy benefits of using wet ethanol.

The results of the studies discussed by Ni et al. (Ni, Leung et al. 2007) show that ethanol can be very efficiently converted to syngas by catalytic steam reforming and autothermal reforming. These methods have weaknesses, though. Catalytic steam reforming requires significant energy input to the system, which is not required for syngas production by filtration combustion under most operating conditions. Although
autothermal reforming does not require external energy input, this technique, like catalytic steam reforming, suffers from the general problems with catalysts noted in the introduction such as fuel inflexibility and susceptibility to catalyst deactivation.

Dobrego et al. (Dobrego, Gnezdilov et al. 2008) performed a numerical study of syngas production by filtration combustion of methane and water mixtures. Because they varied water concentration in the reactant stream, it provides some comparison to the present study in terms of water addition. They found, interestingly, that hydrogen mole fraction peaks with about 5% concentration of water in the input gas (water mole fraction) at $\varphi = 2.5$ and peaks with 10% water mole fraction at $\varphi \geq 3$. In both cases, the hydrogen mole fraction decreased rather rapidly with increasing water mole fraction. The experimental results for hydrogen mole fraction from the present study are shown in Figure 3-24 as a function of water mole fraction rather than $\chi$. Though the experimental uncertainty is large, it appears that, similar to the results of Dobrego et al. (Dobrego, Gnezdilov et al. 2008), hydrogen mole fraction peaks with a relatively small water mole fraction and decreases with increasing water mole fraction. A similar trend was also found in the computational results of Leahey (Leahey 2008). Further experiments are necessary to understand the complex effects of water addition on hydrogen production.
Figure 3-22: Concentration as a function of $\phi$ ($\chi = 0, \vartheta = 20 \text{ cm/s}$)

Figure 3-23: Concentration as a function of $\vartheta$ ($\phi = 2, \chi = 0$)
Figure 3-24: Hydrogen concentration as a function of water mole fraction ($\phi = 2$, $\theta = 0$)
CHAPTER 4 : CONSIDERATION OF OTHER FUELS

As noted in the introduction, the noncatalytic partial oxidation process described in this thesis has some advantages over catalytic conversion processes. These advantages are not fully realized when converting ethanol to syngas because catalytic processes can also efficiently produce syngas from ethanol as described in Chapter 3. Future research will include experimenting with other biologically-derived fuels, some of which would pose difficulties for catalytic conversion processes because of their varied composition and tendency to coke. To help determine which fuels are most suitable for syngas production, calculations were performed to determine the adiabatic equilibrium temperature and the fuel to hydrogen and fuel to carbon monoxide conversion efficiency for various fuels and fuel mixtures.

The selection of fuels for study was based on the following considerations:

1. Fuels with available thermodynamic were selected
2. Fuels with potential for large scale production were selected
3. Fuels that offer the potential of utilizing waste streams as feedstock were selected
4. A strength of the porous media reactor is that it can accept relatively unprocessed fuels, so fuels that require processing steps that may be reduced or eliminated were selected
5. A strength of the filtration reactor is that it can accept a variety of feedstocks and feedstock mixtures, so fuels with variable compositions
were selected

Based on these considerations, the following fuels were selected for study: cottonseed oil, rapeseed oil, sunflower seed oil, soybean oil, algae oil, pyrolysis oil, ethanol, and heptane. A short description of each fuel and the reasons for its selection follows.

**Ethanol**

Ethanol was selected as a reference fuel for comparison and because mixtures of ethanol and oil have lower viscosities than pure oil (Resa, González et al. 2002). High-viscosity fluids, such as pure oils, are inherently difficult for flow systems and require greater energy input for pumping than do low-viscosity fluids, so it may be practical to mix two fuels to create mixtures with lower viscosities.

**Heptane**

Solvents such as hexane and heptane are often used to extract oil from oil-producing plants and seeds (Conkerton, Wan et al. 1995; Wan, Hron et al. 1995; Wan, Pakarinen et al. 1995). Since the production of pure vegetable oil from an oil and solvent mixture requires the energy-intensive distillation of a solvent, directly converting a mixture of solvent and oil to syngas could present an energy savings over using pure oil. This idea, analogous to using wet ethanol, might be practical for the oilseeds and algae, depending on the processing methods and cost of solvent.

**Cottonseed oil**

Cottonseed oil was selected because it is the third most produced oilseed (45.86 million metric tons of cottonseeds were produced globally in 2007 (USDA 2009), but
also because the seed and its oil may be considered a waste stream. Unlike the other major oilseeds, cotton is not grown primarily for the oilseed; it is grown primarily for the fiber. The utilization of waste streams is profitable because the feedstock is free, but it is also is an important way to conserve energy (Demirbas 2003).

Soybean oil / Rapeseed oil / Sunflower seed oil

Soybean oil, rapeseed oil and sunflower seed oil were all selected for the same reasons. They are the first, second and fifth most produced oilseeds in the world (USDA 2009), and thermodynamic data are readily available for each. Along with cottonseed oil, each of these fuels is a combination of fatty acids. The compositions of these oils and cottonseed oil are given below (Demirbas 2003; Sadrameli, Seames et al. 2008).

Table 4-1: Oilseed composition (Demirbas 2003; Sadrameli, Seames et al. 2008)

<table>
<thead>
<tr>
<th>Fatty Acid</th>
<th>Cottonseed oil</th>
<th>Rapeseed oil</th>
<th>Sunflower seed oil</th>
<th>Soybean oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic acid</td>
<td>28.7</td>
<td>3.5</td>
<td>6.4</td>
<td>13.9</td>
</tr>
<tr>
<td>(C_{16}H_{32}O_{2})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stearic acid</td>
<td>0.9</td>
<td>0.9</td>
<td>2.9</td>
<td>2.1</td>
</tr>
<tr>
<td>(C_{18}H_{36}O_{2})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oleic acid</td>
<td>13</td>
<td>64.1</td>
<td>17.7</td>
<td>23.2</td>
</tr>
<tr>
<td>(C_{18}H_{32}O_{2})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linoleic acid</td>
<td>57.4</td>
<td>22.3</td>
<td>72.9</td>
<td>56.2</td>
</tr>
<tr>
<td>(C_{18}H_{32}O_{2})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linolenic acid</td>
<td>0</td>
<td>8.2</td>
<td>0</td>
<td>4.3</td>
</tr>
<tr>
<td>(C_{18}H_{30}O_{2})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

NOTES:
- All values are percents
- Fractions of fatty acids less than 0.5% were omitted

Algae oil

Algae oil, although in its developmental infancy, has the potential to dwarf the oilseeds in oil production capacity and does not compete for land with food crops (NREL
Algae oil can also take advantage of the strengths of our reactor. For example, it has a widely varying composition and must go through many steps of processing, presenting the opportunity to save energy by converting less processed forms of algae. Because algae oil can have a widely varying composition, no single combination of chemical compounds can be used to model it. However, the composition of algae oil is often similar to the oil of the major oilseeds (NREL 1998), thus the equilibrium results for the oils of oilseeds should be representative of the results expected from a study of algae oil. In all cases, cottonseed oil was used as a surrogate for algae oil.

Extraction and separation of valuable products from algae cultures is a significant research area. Two significant problems in this realm of research are separating water from algae and extracting oil from algal biomass, both of which are energy intensive processes. Avoiding these steps would be advantageous in terms of total energy requirements. Mixtures of algae oil and water were investigated in this equilibrium study to determine the effect of retaining significant fractions of water in an algae oil and water mixture. Similarly, mixtures of algae oil and solvent (heptane) were investigated to determine the effect of retaining significant fractions of solvent. In both cases, energy savings may be realized if the energy input for water removal or solvent removal were decreased or eliminated entirely.

**Pyrolysis oil / Acetic acid**

Pyrolysis oil was selected because it can be produced from waste streams like Municipal Solid Waste (MSW) and various biomass sources (Demirbas 2003) and because, with its highly variable composition, it takes advantage of the strengths of the
reactor. In this study, acetic acid was used as a surrogate for pyrolysis oil as many others have done because acetic acid is often a significant component of pyrolysis oil (Marquevich, Czernik et al. 1999; Takanabe, Aika et al. 2004; Rioche, Kulkarni et al. 2005).

**Results**

Experiments have shown that syngas production by partial oxidation is most efficient, in terms of fuel to hydrogen conversion efficiency, from $\phi = 2$ to $\phi = 3$ with methane (Zhdanok, Kennedy et al. 1995; Kennedy, Saveliev et al. 2002; P. Bingue, V. Saveliev et al. 2002; Dhamrat and Ellzey 2006; Hull 2007), from $\phi = 2.5$ to $\phi = 3.5$ with n-heptane (Dixon, Schoegl et al. 2008), and at approximately $\phi = 3$ with ethanol. The syngas production characteristics of the fuels listed above are not known, so an attempt was made to study a wide range ($\phi = 1$ to 5) of equivalence ratios. Unfortunately, insurmountable convergence errors due to problems with the available thermodynamic data limited the investigation to mixtures with $\phi \leq 3$. The convergence errors occurred because solid carbon formation, which begins to form at $\phi > 3$, could not be modeled with the available thermodynamic data. It was possible to compute the equilibrium composition of mixtures with $\phi > 3$, but the production of syngas would have been misrepresented because solid carbon is known to form in partial oxidation reactions with high values of $\phi$ (Leahey 2008). Though the full range of $\phi$ was not studied, a comparison of fuels and fuel mixtures was possible.

From previous research in porous media fuel reforming (Dhamrat and Ellzey 2006; Dixon, Schoegl et al. 2008) it is evident that reaction temperature is a critical
parameter. As seen in Figure 4-1, all of the fuels have similar adiabatic equilibrium temperatures and trends as a function of $\varphi$, with a maximum difference of 100 degrees at $\varphi = 3$.

The fuel to hydrogen and fuel to carbon monoxide conversion efficiencies as a function of $\varphi$ are shown in Figure 4-2 and Figure 4-3. The fuels have a similar trend in fuel to hydrogen conversion efficiency as a function of $\varphi$. At $\varphi = 3$, where all of the fuels have peak fuel to hydrogen conversion efficiencies, cottonseed oil has the greatest efficiency, 96%, while acetic acid has the lowest efficiency, 89%. The fuels also have a similar trend in fuel to carbon monoxide conversion efficiency as a function of $\varphi$. Cottonseed oil has the greatest efficiency, while sunflowerseed oil has the lowest, but the range of efficiencies is small ($\approx 6\%$). The significant conclusion to be drawn from these data is that the decision to reform oils should be based on economic or practical concerns because all of the fuels have similar potential for syngas production.
Figure 4-1: Adiabatic equilibrium temperature as a function of equivalence ratio

Figure 4-2: Fuel to hydrogen conversion efficiency as a function of equivalence ratio
As described above, the system-level energy efficiency of converting fuels to syngas may be increased by using less processed forms of fuel inputs. This concept may have significant application for algae oil because it must undergo water removal and oil extraction, both of which are often energy-intensive steps.

Figure 4-4, Figure 4-5, and Figure 4-6 show the temperature, fuel to hydrogen conversion efficiency, and the fuel to carbon monoxide conversion efficiency, respectively, as a function of equivalence ratio for mixtures of cottonseed oil, water, ethanol and heptane. In all cases, the amount of cottonseed oil remained constant and the additional fuel (ethanol or heptanes) was balanced with the amount of oxidizer required to maintain the specified equivalence ratio.
There is no appreciable change in temperature, fuel to hydrogen conversion efficiency, or fuel to carbon monoxide conversion efficiency with the addition of water or alcohol solvents. Because syngas (H₂ and CO) is produced as effectively with mixtures of water or heptane and oil (within the range of mixture compositions studied) as it is with pure oil, it may be more energy efficient to use these mixtures for syngas production than to use pure oil. Additionally, these results show that ethanol and oil may be mixed without effect on syngas production, allowing some flexibility in viscosity selection.

Figure 4-4: Adiabatic equilibrium temperature as a function of equivalence ratio
Figure 4-5: Fuel to hydrogen conversion efficiency as a function of equivalence ratio

Figure 4-6: Fuel to CO conversion efficiency as a function of equivalence ratio
CHAPTER 5 : CONCLUSIONS

In this work, experiments were undertaken to determine if ethanol and wet ethanol could be converted to syngas via filtration combustion. The effect of three parameters, equivalence ratio ($\varphi$), inlet velocity ($\theta$), and water fraction ($\chi$), on the conversion process was investigated. Results of experiments included ethanol to hydrogen conversion efficiency, ethanol to carbon monoxide conversion efficiency, energy conversion efficiency, reaction zone propagation, and peak temperatures. These results were compared to those from computational modeling and equilibrium calculations. The system energy flows were analyzed to determine an optimum value of $\chi$ in terms of system energy inputs and to determine if the sensible enthalpy in the syngas was sufficient to heat and vaporize the incoming liquid flows of ethanol and water. Additionally, equilibrium calculations were used to determine the potential of other fuels and mixtures of fuels for syngas production by filtration combustion.

This work has shown that ethanol and wet ethanol can be effectively converted to syngas in a filtration reactor. Experiments showed that trends in hydrogen and carbon monoxide production as a function of $\varphi$ were similar to trends found in previous work with methane and n-heptane. The peak ethanol to hydrogen conversion efficiency was 48% at $\varphi = 4$. Experiments showed that hydrogen conversion efficiency was a relatively weak function of $\chi$, indicating that it is better to use wet ethanol than dry ethanol for syngas production because less energy is required to produce wet ethanol than to produce dry ethanol. Additionally, it was shown that the hydrogen to carbon monoxide ratio increases with increasing water fraction. It was shown that conversion to both hydrogen
and carbon monoxide increased with increasing inlet velocity. This result is consistent with previous results for methane and n-heptane.

The experimental results were compared to equilibrium calculations and the results of a computational modeling study performed by Leahey (Leahey 2008). The experimental values for temperature exceed the adiabatic equilibrium temperature, showing the effect of heat recirculation through the porous media. The values of conversion efficiency for hydrogen, carbon monoxide, and energy remained below those in equilibrium calculations in almost all cases. Because the experiments were done at sub-optimal inlet velocity, it was not expected that experimental values would approach equilibrium values. The results from the computational model diverged at high values of $\varphi$, but predicted well the experimental trends in syngas production as a function of $\chi$ and $\vartheta$.

The results were compared with other techniques to convert ethanol to syngas. It was shown that filtration combustion compares favorably with another demonstration of the noncatalytic partial oxidation of ethanol to syngas, and this difference is attributed to the beneficial effect of superadiabatic temperatures created by heat recirculation in the porous media. The results of catalytic studies were also presented, showing very efficient conversion to ethanol.

An energy analysis of the system was also undertaken. In the first part of this analysis, the energy inputs to the system between ethanol fermentation and conversion in the filtration reactor were quantified. With these data, it was shown that wet ethanol with $\chi \approx 30\%$ requires the minimum amount of energy for distillation, heating, and
vaporization. Second, the sensible enthalpy available in the exhaust products (syngas) was compared to the energy necessary for heating and vaporization, and it was shown that at nearly all operating conditions, sufficient sensible enthalpy is available in the exhaust products for heating and vaporization.

An equilibrium analysis was performed to determine the potential of syngas production by filtration combustion of five different fuels: ethanol, cottonseed oil, sunflower seed oil, rapeseed oil, acetic acid (as surrogate for pyrolysis oil). This analysis showed that fuel selection for syngas production by partial oxidation should be based on economic and practical concerns because syngas production potential was nearly equal for all tested fuels. Also significant are the results for mixtures of an algae oil surrogate, cottonseed oil, with heptane, a solvent used for oil extraction, water, and ethanol. It was shown that mixtures of these compounds with cottonseed oil produce syngas as efficiently as does pure cottonseed oil. This result shows that energy savings may be accomplished by avoiding, in part or in whole, algae processing steps, and that ethanol may be added to oil for the practical purpose of lowering viscosity.
Appendix A: Uncertainty Analysis

Uncertainty analysis relied upon the use of a Student-t distribution and sequential perturbation. The values of concentration reported by the GC were averaged, and the uncertainty was calculated by use of the student-t distribution (Devore 2004):

\[ P_x = \pm t \times \frac{S_x}{\sqrt{n}} \]

Where \( P_x \) is the uncertainty of the mean value, \( t \) is the tabulated value of the Student-t distribution, \( S_x \) is the standard deviation of the samples and \( n \) is the sample size. The distribution parameter, \( t \) is a function of the number of samples, \( n \), and a confidence interval.

The implementation of this equation in Matlab for a sample size of 2 is given by the following Matlab expression:

```matlab
conf = .95;
n = 2;
dof = n-1;
h2Unc = h2StdDev.*tinv(conf,dof)./sqrt(n);
```

where \( h2Unc \) is the one-sided uncertainty bound, \( h2StdDev \) is the standard deviation of the concentration measurements for hydrogen, and \( tinv \) is the Matlab function that computes the value of \( t \) for the given confidence interval, \( conf \), and degrees of freedom, \( dof \). Degrees of freedom is defined as \( n-1 \).

Systematic uncertainty included uncertainty in the GC calibration and the uncertainty in the calibration gas. The total uncertainty for each measurement was found from the following equation:
\[ \delta_{y_i} = \sqrt{\delta_{y_i,\text{meas}}^2 + \delta_{y_i,\text{GC \text{cal}}}^2 + \delta_{y_i,\text{GC \text{gas}}}^2} \]

\( \delta_{y_i} \) is the uncertainty in the measurement of the concentration of species, i. \( \delta_{y_i,\text{meas}} \) is the uncertainty based on the Student-t distribution as described above. \( \delta_{y_i,\text{GC \text{cal}}} \) is the uncertainty in the GC calibration, which is 1% of the calibrated range, and \( \delta_{y_i,\text{GC \text{gas}}} \) is the uncertainty in concentration of the calibration gas. The value of \( \delta_{y_i,\text{GC \text{gas}}} \) was 1% of the specified value for H\(_2\), CO, CH\(_4\), CO\(_2\), N\(_2\), C\(_2\)H\(_4\) and C\(_2\)H\(_2\) and was 5% of the specified value for all other species.

Uncertainties in flow rates resulted from uncertainties in the flow equipment. The air flow controllers are accurate to +/- 1% of full scale, the rotameters are accurate to 2% full scale and the rotometer indicator could be kept at a desired reading ± one tick. These errors combined to yield errors in equivalence ratio, inlet velocity and water fraction by the following representative equations for the mole flow rate of water:

\[
\text{moles per minute uncertainty} = \sqrt{SS} \\
SS = (\text{moles/}min_{\text{set}} - \text{moles/}min_{\text{set+}\Delta})^2 + (0.02 \times \text{moles/}min_{\text{full scale}})^2
\]

where \( \text{moles/}min_{\text{set}} \) is the desired value of moles per minute based on the specified rotameter setting, \( \text{moles/}min_{\text{set+}\Delta} \) is the value of moles per minute that results from the rotameter indicating one tick higher than the specified setting, and \( \text{moles/}min_{\text{full scale}} \) is the maximum flow rate of the rotameter.

The errors in flow rates and GC measurements were combined by sequential perturbation. The following set of equations describes how the uncertainty was found for
an arbitrary variable, $Q$, that is a function of 3 variables, each of which has its own uncertainty, $\Delta$.

$$Q = Q(x, y, z)$$

$$\delta Q_x = Q(x + \Delta_x, y, z) - Q(x, y, z)$$

$$\delta Q_y = Q(x, y + \Delta_y, z) - Q(x, y, z)$$

$$\delta Q_z = Q(x, y, z + \Delta_z) - Q(x, y, z)$$

$$\Delta Q = \sqrt{\delta Q_x^2 + \delta Q_y^2 + \delta Q_z^2}$$

The above procedure was used to find the uncertainty for all quantities, such as ethanol to hydrogen conversion efficiency, and water fraction, that were derived from other quantities with uncertainties.
References


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Vita

Colin Healey Smith was born on December 15th, 1981 in Stoneham, Massachusetts. He is the first child of Robert Smith and Virginia Healey. He has one sister, Kerri and two half brothers, Robert Pereira and Christopher Pereira. He graduated from Central Catholic High School in Lawrence, Massachusetts in 2000 and then attended Rose-Hulman Institute of Technology for one year. He transferred to Cornell University and graduated with a Bachelor of Science in Mechanical Engineering in 2004. After graduating from Cornell, he moved to Boston, Massachusetts to work on the Ballistic Missile Defense System for the Raytheon Company. In the fall of 2007, he moved to Austin, Texas to pursue a Master of Science in Mechanical Engineering at the University of Texas at Austin.

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