Fuels From Biomass via Sub- and Supercritical Fluid Processes

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Introduction

Biomass, whether deliberately cultivated energy crops, residues from agriculture or the forest products industry, or food processing waste is a renewable source of energy. The developed world is accustomed to the use of liquid and gaseous fuels as energy carriers, so biomass conversion to these fuels is an integral part of a sustainable energy future. Supercritical fluid processes, which involve the simultaneous action of a solvent, elevated temperature, and elevated pressure, are one type of thermochemical process that can do this necessary conversion. In this article, we report on the use of supercritical water and alcohols for converting biomass to gaseous and liquid fuels. In both cases, the fluid (water or ethanol) serves not only as the solvent but also as a key reactant in the process.

It has been known since the 1970s that biomass can be gasified in supercritical water [1] and that the water suppressed or even eliminated char formation. This area of research has become popular again in recent years and several review articles have recently appeared. Some of the basic research needs in this field include obtaining a clear understanding of the effects of the relevant process variables for both catalyzed and uncatalyzed gasification of different materials and a clear understanding of the governing reaction pathways. We have explored the supercritical water gasification (SCWG) of biomass in quartz mini-reactors so that the influence of catalysis by metals can be removed completely. These are among the first systematic studies of truly homogeneous SCWG. We have also done experiments with metal wires inserted into the reactors to study catalyzed SCWG. Finally, we have developed the first kinetics model for SCWG that uses the underlying reaction pathways as the basis for calculating and predicting the yields of the different gaseous products. The first portion of this article summarizes our recent work in SCWG.

The second portion describes recent work on supercritical fluid processing to obtain liquid fuels. Plant oils are a source of renewable liquid fuels. The naturally occurring oils are not suitable for use in modern diesel engines, so they are typically converted to alkyl esters in a chemical reaction process. These esters can then be blended with petroleum-based diesel fuel to make biodiesel. The main routes for biodiesel synthesis require catalysts (either acid or base). These routes are effective for pure feedstocks, but they have disadvantages when processing used oils that may contain free fatty acids and/or water. For these materials, a catalyst-free process would be of interest, and we recently published an assessment of non-catalytic biodiesel synthesis [2]. Transesterification and esterification can be done without catalyst in supercritical alcohols. But, using supercritical conditions drives up the processing cost. Therefore, there is interest in developing a catalyst-free process that operates at milder conditions. To this end, we have examined the esterification of oleic acid in ethanol in nominally liquid, gaseous, and supercritical fluid phases. Being able to use liquid or gas-phase processes (rather than supercritical) would likely reduce the processing cost.

Experimental

All chemicals were obtained commercially and used as received. SCWG experiments were done as described previously [3,4]. Briefly, we load a quartz tube (about 6 mm od, 2 mm id) sealed at one end with the compound to be gasified and with water. In some experiments we also added a metal wire that ran the entire length of the reactor. We then flame seal the open end of the reactor and place it in a preheated sand bath or tube furnace at the desired gasification temperature for the desired reaction time. The reactor is then opened, products are recovered, and analyses are done by gas chromatography.

Esterification experiments in ethanol are done in a similar manner. Oleic acid and ethanol are loaded into the quartz tube such that a certain fraction (f) of the total volume was occupied by the reactants. Altering the value of f (filling fraction) provides a means to explore the reaction at different pressures and in different phases. After loading, the reactor was flame sealed and placed in the sand bath for isothermal reaction. After the reaction, we recovered the products and analyzed them by HPLC.

Results and Discussion.

In this section we first present results from biomass SCWG and then results from oleic acid esterification.

Biomass SCWG. We have gasified cellulose [3], lignin [4], and simpler biomass model compounds [5-7] in supercritical water. The experimental objectives were to determine the effects of the process variables (time, temperature, biomass loading, and water density) and catalysts on the gas composition and yields. This section provides some representative results from experiments with lignin and cellulose. Note that these results may differ from those we reported previously because we have continuously improved the experimental methods to make them more accurate and more reproducible.
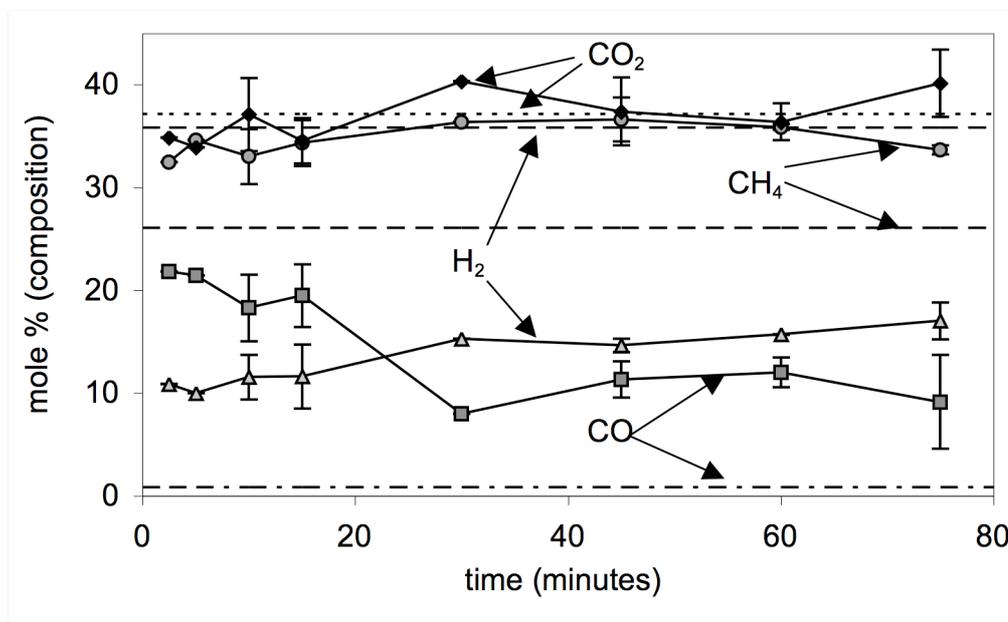
Figure 1: Temporal variation of the dry gas composition from noncatalytic lignin SCWG at 600 °C (9 wt% lignin loading, water density 0.08 g/cm^3)

Figure 1 shows the temporal variation of the gas composition from lignin during uncatalyzed gasification. The discrete points are the experimental measurements and the dashed lines are the compositions expected at equilibrium. We used the RGIBBS block in ASPEN Plus to perform the equilibrium calculations. The uncertainties shown represent the standard deviation in the measurements, as determined from performing replicate experiments. CO_2 is almost always the most abundant gas, and its mole fraction is always near the expected equilibrium value. Methane is the next most abundant, and its mole fraction exceeded that expected at equilibrium. For lignin, methane could possibly be formed via pyrolytic cleavage of methyl substituents within the lignin macromolecular structure. At short times, CO is the next most abundant gas, but its mole fraction decreases with time. At equilibrium, very little CO is expected to be present. It is likely the action of the water gas shift reaction ($CO + H_2O = CO_2 + H_2$) that is responsible for the decline in the CO mole fraction with time. Hydrogen is present in the lowest percentage at short times, but its percentage of the total dry gas increases with time. Even at the longest time used in this experiment, H_2 is still well below the level expected at equilibrium. The hydrogen mole fraction will increase as the methane mole fraction decreases (because of steam reforming reactions) and the CO mole fraction decreases (because of the water gas shift reaction).
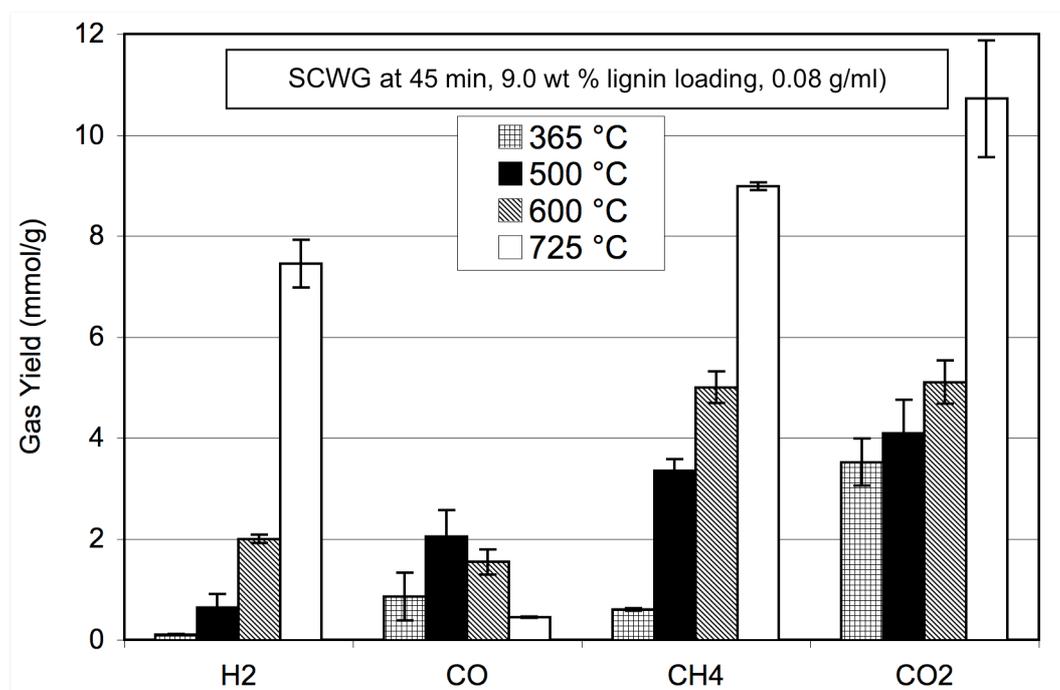
Figure 2: Gas yields from lignin SCWG at different temperatures

Figure 2 shows the yields of the individual gaseous species from lignin SCWG at different temperatures. The precise conditions used in the experiments are indicated on the figure itself. The yields of all gases are low at the one subcritical temperature tested. The effect of temperature is similar for all species except CO. The molar yields of H_2, CH_4 and CO_2 increase with temperature, and there is a large jump from 600°C to 725°C. The species most strongly affected by temperature is H_2. It is barely produced at 365°C (only 0.1 mmol/g), but it is produced in amounts 75 times larger at 725°C (7.5 mmol/g). The absolute increase in H_2 yield (5.5 mmol/g) from 600°C to 725°C is very close to the absolute increase in CO_2 yield

(5.6 mmol/g). This outcome is consistent with both H_2 and CO_2 formation being accelerated mainly by an increase in the rate of water-gas shift. The change in the CO yields is smaller, though, which suggest that the CO yields are influenced by reactions in addition to water-gas shift. The CH_4 yield is also strongly affected by temperature, most likely because of its production from pyrolysis of lignin or its fragments. CH_4 yields increase from 0.6 mmol/g to 8.9 mmol/g as the temperature increases from 365°C to 725°C.

Figure 3 shows results from SCWG of cellulose at 500 °C, at times in the presence of Ni wires as a catalyst. The Ni surface area/cellulose ratio is 80 mm²/mg for one wire, 160 mm²/mg for two wires, and 240 mm²/mg for 3 wires. The non-catalytic H_2 yield is 0.7 mmol/g, and one nickel wire increases it to 8.3 mmol/g. With 2 wires, the H_2 yield increases to 15.5 mmol/g, and 3 wires increase it to 23.5 mmol/g. This is the highest H_2 yield from all the conditions studied in this work. Interestingly, the H_2 yield increases linearly with the catalyst surface area available. The CO yield remains at about 3 mmol/g at most cases, except with 3 wires, where it nearly vanishes. The CO_2 yield increases from 7 mmol/g non-catalytic to 11 mmol/g with 1 wire, and about 20 mmol/g with 2 or 3 wires. The CH_4 yield stays around 2.5 mmol/g with 2 or 3 wires. At 240 mm²/mg (3 wires), there are great improvements in the H_2 yield and nearly a CO-free gas, with the CH_4 yield remaining largely unaffected.
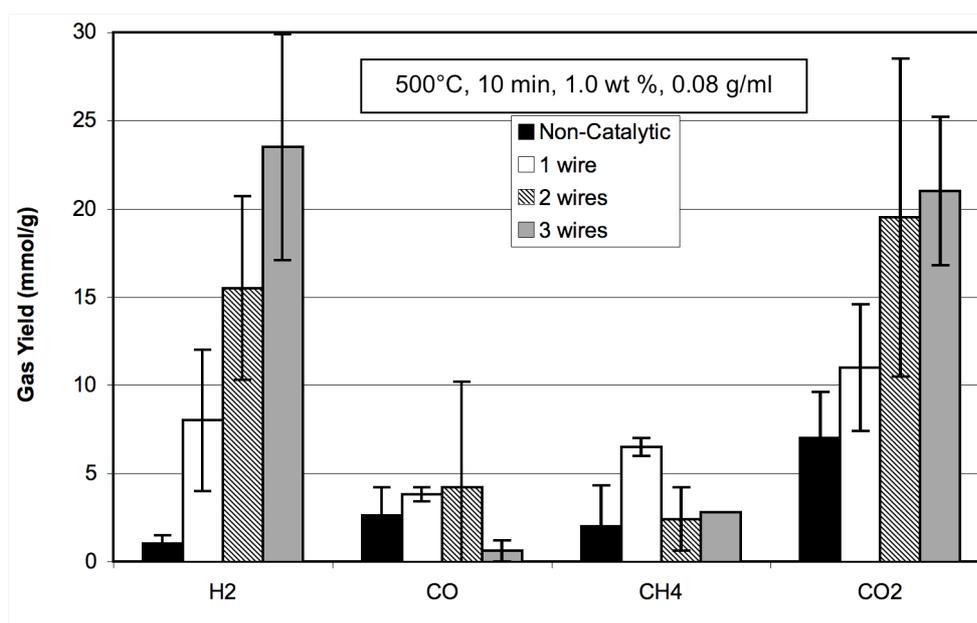
Figure 3: Gas yields from cellulose SCWG with 0, 1, 2, and 3 nickel wires in the reactor

Oleic Acid Esterification. We examined the esterification of oleic acid with ethanol, where ethanol also served as the solvent. Since most of the previous work [8,9] on uncatalyzed esterification used supercritical conditions, we sought to determine whether appreciable rates could be obtained at temperatures and/or pressures below the critical values for ethanol (240.9 °C, 61.4 bar). We conducted experiments at 250 and 320 °C with f = 0.04, which leads to pressures of approximately 11 and 15 atm, respectively. These values are well below the critical pressure of ethanol, and these experiments tested the feasibility of esterification at subcritical pressures, primarily in the vapor phase. An experiment at 250 °C with f = 0.26 led to a pressure of 49 atm. We estimate that the reactor contained roughly 60%

vapor and 40% liquid (by volume) at these conditions. We also did experiments at 230 °C with f = 0.56. We calculated the pressure in the reactor to be about 44 atm. At these subcritical conditions, two phases existed, and the liquid phase occupied about 70% of the total reactor volume.

Figure 4 shows the experimental results. Complete conversion occurred at 320 °C, f = 0.04 while about 85% conversion was achieved for 250 °C, f = 0.04 at long times. A similar long-time conversion was obtained at the same temperature (250 °C) for a higher loading of f = 0.26. These results indicate that the conversion increases as temperature increases and that the reaction does not require high pressure to reach completion (higher loading will give higher pressure). In addition, conversions up to 70% were obtained at the subcritical temperature for reaction at 80 minutes. The results in Figure 4 show that supercritical conditions are not required for the noncatalytic esterification of oleic acid. Milder, and hence less costly, reaction conditions might be suitable.
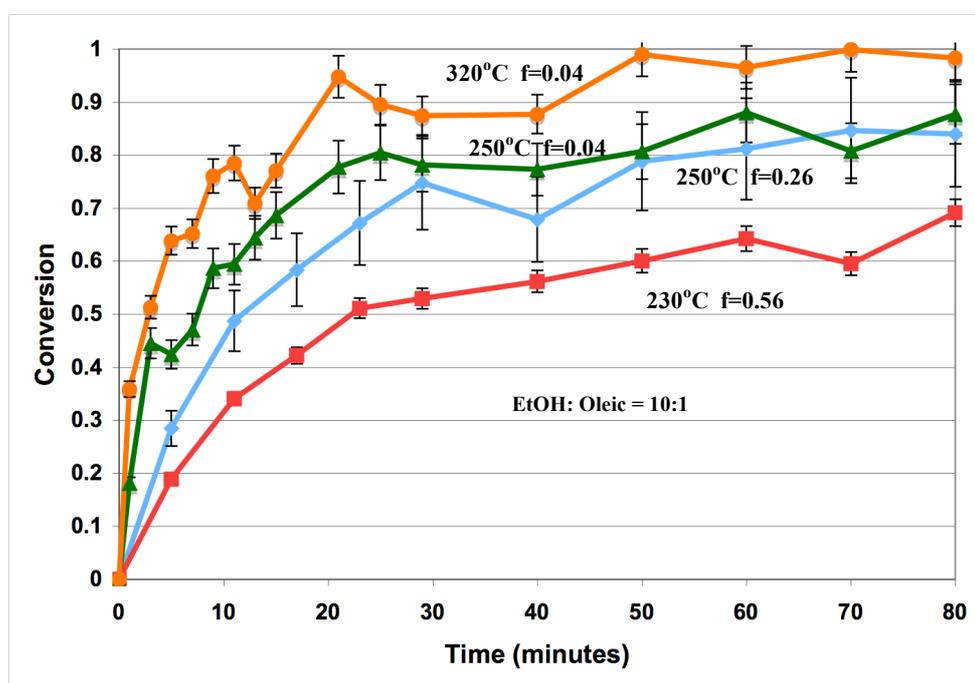
Figure 4: Temporal variation of oleic acid conversion at four different reaction conditions (230 °C f = 0.56, 250 °C f = 0.26, 250 °C and 320 °C, f = 0.04) with a molar ratio of ethanol to oleic acid of 10:1

The molar ratio of alcohol to fatty acid is another important variable in the esterification reaction. Since the reaction is reversible, more alcohol will drive the reaction to produce more product. In the supercritical esterification experiments done in the past [8,9], very large alcohol to acid ratios were used. For a commercial process, one desires as low a ratio as possible, so that excess alcohol is minimized. Therefore, we performed experiments to determine the effect of the alcohol to acid molar ratio on the esterification conversion. Figure 5 shows the results from experiments at three different conditions, and these correspond to the same reaction conditions used in Figure 4

Regardless of the reaction conditions, the lowest conversion was always obtained at the lowest ratio we explored (stoichiometric ratio (1:1)). We obtained about 50% conversion for all conditions at this stoichiometric ratio. For 230 °C, the conversion was highest at a 3:1 ratio and then it decreased as the molar ratio increased. At 250 °C, the conversion increased

to about 80% when the molar ratio increased to 5:1 at both f = 0.26 and f = 0.04. Adding more ethanol beyond this 5:1 ratio did not have any significant impact on the conversion. These results show that high alcohol to fatty acid ratios are not needed for non-catalytic esterification. A ratio that has the alcohol in modest excess is sufficient for the reaction.
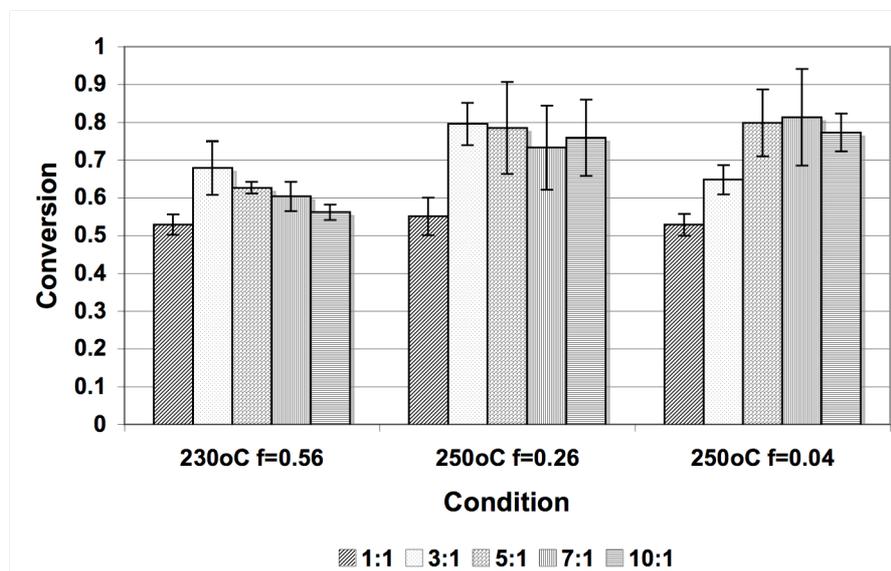
Figure 5: The effect of ethanol to oleic acid molar ratio on oleic acid conversion at 40 minutes and different reaction conditions

Summary

Supercritical fluid processing can be used to advantage for the production of fuels from biomass. SCWG is especially well suited economically and energetically for gasifying wet (> 40 wt % moisture) biomass. Gas yields, especially hydrogen, can be increased, and the gas composition can be manipulated by use of an appropriate metal catalyst and altering the process variables.

Fatty acid esterification proceeds in ethanol in the absence of catalysts even at subcritical temperatures or pressures. Therefore, it may be possible to do solvothermal non-catalytic biodiesel synthesis at pressures lower than the critical pressure. This possibility suggests that a route to lower cost biodiesel synthesis may be available.

References

[1] WALDNER, M. H., VOGEL, F. Ind. Eng. Chem. Res., Vol. 44, **2005**, p. 4543.

[2] PINNARAT, T., SAVAGE, P. E. Ind. Eng. Chem. Res. Vol 47, **2008**, p. 6801.

[3] RESENDE, F. L. P.; NEFF, M. E.; SAVAGE, P. E. Energy & Fuels Vol. 21, **2007**, p. 3637.

[4] RESENDE,. F. L. P. FRALEY, S., BERGER, M. J., SAVAGE, P. E. Energy & Fuels *Vol.* 22, **2008**, p. 1328.

[5] DiLEO, G. J., KIM, S., NEFF, M. E., SAVAGE, P. E Energy & Fuels Vol. 22, **2008**, p. 871.

[6] DiLEO, G. J.; NEFF, M. E.; SAVAGE, P. E. Energy & Fuels Vol. 21, **2007**, *21*, p. 2340.

[7] DiLEO, G. J., SAVAGE, P. E. J. Supercritical Fluids Vol. 39, **2006**, p. 228.

[8] SAKA, S., KUSDIANA, D. Fuel Vol. 80, **2001**, p.225

[9] KUSDIANA, D., SAKA S. Applied Biochemistry and Biotechnology, Vol. 113-116, **2004**, p.781.