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Interim Report: Feasibility of Microscale Glucose Reforming for Renewable Hydrogen

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INTERIM REPORT

Feasibility of Microscale Glucose Reforming for Renewable Hydrogen

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Abstract

Micro-scale aqueous steam reforming of glucose is suggested as a novel method of H₂ production for micro fuel cells. Compact fuel cell systems are a viable alternative to batteries as a portable electrical power source. Compared with conventional lithium polymer batteries, hydrocarbon powered fuel cells are smaller, weigh less, and have a much higher energy density. The goal of this project is to develop a hydrocarbon powered microfuel processor capable of driving an existing microfuel cell, and this interim report provides a summary of the engineering information for microscale reforming of carbohydrates and the summarizes the work completed as of September 2006. Work on this program will continue.

Gas analysis of the gas evolved from glucose breakdown using a quadrupole mass spectrometer is now possible due do significant modifications to the vacuum chamber and to the mass spectrometer electronics. Effective adhesion of Pt/Al₂O₃ to 316SS microstructured catalyst plates is still under investigation. Electrophoretic and dip coat methods of catalyst deposition have produced coatings with poor adhesion and limited available Pt surface area.

CONTENTS

INTRODUCTION	7
BACKGROUND	9
Hydrogen Production	9
Hydrogen from Biomass	13
Aqueous Phase Reforming of Hydrocarbons.....	19
Catalysts	21
Microreactors	26
EXPERIMENTAL RESULTS	31
Mass Spectrometer and Vacuum Chamber	31
Catalyst Deposition.....	34
DISTRIBUTION LIST	37

FIGURES

Figure 1.	Cellulosic biomass consists of cellulose surrounded by a hemicellulose and lignin sheath[1].....	14
Figure 2.	Cost of ethanol and glucose from various sources (2005\$).....	18
Figure 3.	Relative rates of C-C bond cleavage (first bar), WGS reaction (second bar), and methanation reaction (black bar)[2].....	23
Figure 4.	Reaction pathways for production of H ₂ aqueous phase reforming of oxygenated hydrocarbons[3]. (Asterisk represents a metal site.)	24
Figure 5.	Catalytic performance of metals for ethylene glycol reforming at 483K and 22 bar[2].....	25
Figure 6.	Competing reactions equations used in mixing evaluation[4].....	28
Figure 7.	Molecular weight distribution of poly(butyl acrylate). Solid line is polymer obtained from microreactor, dashed line is polymer obtained from macroscale batch reactor. Residence time in each reactor was 4 min[5].....	29
Figure 8.	Vacuum chamber, pumping station, and mass filter electronics.	33
Figure 9.	Reforming system setup (To RGA indicates the gas sample outlet to a residual gas analyzer or mass spectrometer).....	33
Figure 10.	316SS sample plate with Pt/Al ₂ O ₃	35
Figure 11.	View of Pt particles supported on Al ₂ O ₃	36
Figure 12.	Pt/Al ₂ O ₃ coating after adhesion test.	36

TABLES

Table 1.	Optimistic estimated hydrogen production cost from various sources[28]. All values are reported in 2005 US dollars using a LHV basis.....	12
Table 2.	Hydrogen density of Ethanol and Glucose.	17
Table 3.	Reactions involved in aqueous phase reforming of ethylene glycol.....	25

INTRODUCTION

Alternative energy has been given much attention lately due to concerns about depletion of fossil fuel reserves and atmospheric pollutants resulting from increased energy consumption. An attractive option is polymer electrolyte membrane (PEM) fuel cells, which efficiently convert chemical energy directly to electrical. PEM fuel cells use oxygen and either hydrogen gas or a hydrogen-containing compound like methanol and produce water and heat. The potential for hydrogen use as an energy carrier is limited by the ability to produce and store hydrogen. Microscale steam reforming of glucose, a biomass derived carbohydrate, is proposed as a novel method of hydrogen production and is the focus of this research.

Current technologies for hydrogen production involve the breakdown of either H₂O or hydrocarbon fuel stocks. The available avenues of water splitting, including electrolytic, photolytic, photobiological and photoelectrochemical based systems, are inefficient and cost prohibitive compared with thermochemical breakdown of hydrocarbons. The problematic production of CO₂ during thermochemical hydrocarbon processing is of major concern given the atmospheric complications of CO₂ emissions and the disruption of the carbon cycle. The utilization of biomass as a hydrocarbon fuel source mitigates this concern as the carbon dioxide produced is consumed for biomass growth leading to a closed carbon loop.

Aqueous steam reforming of biomass-derived hydrocarbons is a promising method of hydrogen production. Of current hydrocarbon reforming methods including partial and preferential oxidation, and autothermal reforming, steam reforming has the highest theoretical efficiency and potential H₂ selectivity[6, 7]. It has been demonstrated that biomass related sugars and alcohols can be converted to hydrogen via steam reforming in bench scale packed bed reactors[3, 8, 9]. It is anticipated that miniaturization of aqueous phase reforming of

biomass related hydrocarbons via the use of microreactors will enable quicker and more cost effective large-scale production of hydrogen. A micro scale fuel converter also may be used for portable power applications when combined with a micro fuel cell for battery replacement[10].

Glucose and ethanol have emerged as the best candidates for biomass derived hydrocarbon processing for hydrogen. Glucose is a major component of biomass[11]; the fermentation of sugars such as glucose produces ethanol which can then be easily reformed. A fuel cost analysis indicates that glucose is a more cost effective fuel from any source.

This research will examine both the scientific and economic feasibility of microscale glucose aqueous phase reforming. Designed experiments will be conducted to determine optimal conditions for glucose processing. Ethylene glycol will be used as a test feed molecule as it contains the same functional groups as glucose and can be processed more expeditiously. The optimal conditions for ethylene glycol reforming will then be used in glucose reforming. Reactor temperature, pressure, flow rate and fuel concentration will be evaluated for glucose reforming. Pt supported on -325 mesh Al_2O_3 will be used as the catalyst. The surface activity of the catalyst will be evaluated by irreversible CO absorption.

BACKGROUND

Hydrogen Production

Alternative energy has been given much attention lately due to concerns about depletion of fossil fuel reserves and atmospheric pollutants resulting from increased energy consumption. An attractive option is fuel cells, which efficiently convert chemical energy directly to electrical energy. Different types of fuel cells, from solid oxide fuel cells, phosphoric acid fuel cells, and polymer electrolyte membrane (PEM) fuel cells, are being considered for applications including transportation, stationary power and portable power. PEM fuel cells operate on hydrogen, which because of its abundance and zero emission characteristics make it a particularly strong candidate compared to conventional fossil fuel energy sources. Energy derived from fossil fuels such as coal, oil and natural gas is harnessed via combustion, a process limited by the loss of energy in converting thermal to mechanical energy. Emissions associated from the processing of conventional fuel sources are another concern. Carbon dioxide, the single largest waste product of modern industrial society, is the largest contributor to global warming[12].

Polymer electrolyte membrane (PEM) fuel cells produce electricity by converting hydrogen electrochemically to water using oxygen. PEM fuel cells are a new potential source of portable power because they operate more efficiently compared to combustion engines in motor vehicles and because the superior energy density of hydrogen fuel makes them an attractive alternative to batteries for small portable power applications. The potential for hydrogen use as an energy carrier is limited currently by the ability to produce and store hydrogen. The use of hydrogen fuel cells in vehicles or in portable power applications must include either light weight hydrogen storage or direct hydrogen reforming. Storage of

hydrogen is a significant problem given its size, flammability, and gaseous state; an “on-board” reformer would require storage of the hydrocarbon H₂ source, a considerably more feasible option.

Fuel cells powered by hydrocarbons like glucose or methanol have a higher energy density giving them an advantage over other power sources for remote or portable power applications[10]. Compressed PEM fuel cell systems coupled with advanced metal hydride storage systems have energy densities as high as 0.5 kW_e hr/kg, while current lithium polymer batteries have energy densities less than 0.3 kW_e hr/kg (the subscript e denotes electrical energy). The energy storage densities of hydrocarbon-based fuels such as diesel fuel and methanol are 13.2 and 5.6 kW_t hr/kg (t denotes thermal energy). Even at low system efficiency, a hydrocarbon based fuel system has a higher energy density than a lithium polymer battery or a metal hydride powered PEM fuel cell.

A major concern in fuel reforming is the generation of undesirable byproducts. PEM fuel cells employ Pt or Pt alloy catalysts as they are effectively reactive in bonding and releasing H₂ and O₂ intermediates. The effluent from glucose reforming is comprised of H₂, CO₂, CO, C_nH_n and H₂O. The small concentration of alkanes isn't a concern. Carbon dioxide is inert with respect to Pt and Pt alloys and can exist in the H₂ fuel stream without any notable effects other than dilution. The major product of concern in hydrocarbon reforming is CO. Typical PEM fuel cells can tolerate only 10-20 ppm CO in the fuel stream, and most reforming methods produce about 10-15mol % CO[13]. Fuel cleanup steps include a water gas shift (WGS) reactor treatment followed by H₂ extraction[7]. The water-gas-shift reaction is an equilibrium between H₂ + CO₂ and H₂O + CO. A WGS reactor pushes the equilibrium to H₂ and CO₂.

Most of the available hydrogen on the planet is stored in the form of hydrocarbons or water. Approximately 95% of the hydrogen produced today comes from nonrenewable fossil fuels in the form of gasification of coal and steam reforming of natural gas[14]. Hydrogen is also produced by electrolysis of water[15]. There are numerous avenues of hydrogen production being pursued. The most promising methods fall in one of three categories: thermochemical, electrolytic, and photolytic hydrogen production. Thermochemical production of hydrogen utilizes heat and chemical reaction methods (often combustion) to break down various hydrocarbon fuel stocks. Examples include methane steam reforming[16-18], methane partial oxidation[19], and pyrolysis or direct gasification of biomass[20, 21]. Electrolytic hydrogen production involves the splitting of water into hydrogen and oxygen using electrical current[22]. Commercially available water electrolyzers are used for high purity H₂ production. Wind power can be used to generate the current required for water splitting[23]. Fuel cells operating in reverse are also being investigated as possible electrolyzers. Photolytic hydrogen production harnesses sunlight to split water into hydrogen and oxygen[24-26]. Newer technologies use photobiological and photoelectrochemical systems for direct water splitting. Light energy is harnessed metabolically by certain hydrogen producing photosynthetic microbes[27]. Green algae (*Chlamydomonas reinhardtii*) can be cycled using sulfur deprivation between hydrogen production and photosynthetic growth[28, 29].

The cost of hydrogen production from different sources varies widely given unique capital equipment costs, feedstock cost, availability and transport, and technology maturity. A hydrogen production economics survey summarized the results of numerous studies on the estimated cost for hydrogen production, storage and transportation technologies near

commercialization[28]. Table 1 includes the most optimistic projected cost of hydrogen production for each method.

Table 1. Optimistic estimated hydrogen production cost from various sources[28]. All values are reported in 2005 US dollars using a LHV basis.

Category	Method	\$/GJ	\$/kg
Thermochemical Production	Steam Methane Reforming	6.45	0.78
	Coal Gasification	11.71	1.41
	Hydrocarbon Partial Oxidation	8.23	0.99
	Biomass Gasification	10.31	1.24
	Biomass Pyrolysis	10.51	1.26
Electrolytic Production	Electrolysis	23.96	2.88
Photolytic Production	Solar Electrolysis	35.75	4.29
	Photobiological Production	31.36	3.77

Ongoing research in the hydrogen production field is aimed at reducing hydrogen cost; the US Department of Energy has cost targets for each individual technology. Certain technologies, such as water electrolysis, can be produced on site eliminating storage and transportation costs; the higher capital cost of water electrolysis is therefore permissible. With the exception of methane reforming, coal gasification, and partial oxidation of residual hydrocarbons (all nonrenewable resources), current hydrogen production methods are cost prohibitive. Novel hydrogen production technologies and efficiency improvements in current technologies are still needed.

Concerns regarding the atmospheric complications of CO₂ emissions and disruption of the carbon cycle lead to interest in sustainable sources of hydrogen. Biomass is a particularly attractive source of hydrogen; biomass is considered to be nearly CO₂ neutral as the carbon dioxide produced is consumed for biomass growth leading to a closed carbon loop. Biomass is the largest U.S. renewable resource and the only renewable energy source that can be converted readily to a liquid fuel capable of displacing petroleum products and reducing

greenhouse gas emissions.[30] While fossil fuels account for approximately 84% of US energy consumption, renewable energy is used for only 5-6% with biomass being just under 3%. Currently biomass is used in the form of wood waste (~74%), biowaste (20%) and alcohol fuels (6%) in the form of ethanol from corn. Over 70% of biomass is used for thermal energy; the remaining is used to produce electricity.

Current biomass reforming technologies for hydrogen are biomass pyrolysis and gasification[31, 32]. However, the bio-oil produced from pyrolysis is of poor quality, and gasification is both extremely complex and is not energetically favorable. A viable alternative is steam reforming of biomass-derived hydrocarbons, a comparatively simple process that is thermodynamically favorable and efficient. Of the various biomass derived hydrocarbons available, glucose and ethanol have shown promise in bench scale reactor designs.

Hydrogen from Biomass

Two biomass derived hydrocarbons, glucose and ethanol, have been successfully converted to hydrogen using aqueous phase reforming[9, 33]. Both are abundant, renewable and carbon cycle neutral biomass components and are an excellent alternative fuel candidates. The bulk of sugar found in biomass is stored in the form of starch and cellulose, both of which are copolymers of glucose[11]. Ethanol can be manufactured from a variety of feedstocks including corn, sugar cane, wheat, barley, or potatoes. The majority of ethanol produced in the United States is synthesized from the starch contained in corn[34]. Bench scale glucose steam reforming has been demonstrated to remove ~%60 H₂ from the fuel stream, while ethanol reforming yields 96% H₂. Ethanol is a more attractive fuel from an efficiency standpoint, yet cost may be a consideration as it is not a direct product of biomass.

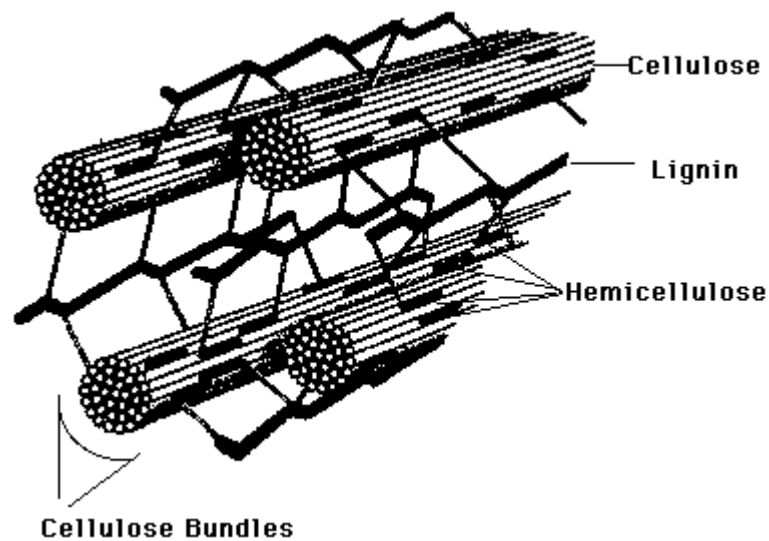


Figure 1. Cellulosic biomass consists of cellulose surrounded by a hemicellulose and lignin sheath[1].

Potential sources for biomass-derived hydrocarbons include crop residues, biowaste[33], corn stalks and cobs, sawdust and wood chips[35], and “energy crops” such as switch grass and fast growing hybrid poplar trees[36]. Most plant material is composed of cellulose (38-50%), hemicellulose (23-32%) and lignin (15-25%)[37]. Cellulose is a glucose ($C_6H_{12}O_6$) polymer. In most plant structures, cellulose is wrapped in a protective sheath of hemicellulose and lignin (Figure 1). Dilute acid hydrolysis, a thermochemical pretreatment, can hydrolyze the sugars in hemicellulose, effectively breaking down the structure and removing the outer protective hemicellulose/lignin layer. Cellulose then is converted to glucose via either acid or enzymatic hydrolysis. The glucose syrup can be fermented to ethanol. Another possible source of glucose or ethanol is the starch, another biopolymer of glucose commonly found in corn. The process of breaking down starch is nearly identical to that of cellulose. Dilute acid hydrolysis or enzymatic saccharification breaks down the starch into glucose; the sugar can then be fermented to produce ethanol.

Both glucose and ethanol can be produced from corn starch. Over 30 years of research have been invested in reducing the cost and increasing the efficiency of ethanol production from corn as a renewable replacement for gasoline. The cost and energy involved in ethanol production from corn starch has undergone considerable debate; a wide variety of studies over the years have yielded very different interpretations of the cost effectiveness of the process. Generally, the energy required to grow and convert corn into ethanol is compared with the energy produced under combustion as a gasoline additive. Past studies have suggested both positive[38] and negative energy balances[39]. The differences are often related to methods of estimating energy costs such as those for fertilizer production and ethanol plant efficiency. Current studies indicate it is marginally practical to produce ethanol from an energetic standpoint. Recent estimates of the energy used to convert corn to ethanol have been reported by a U.S. industry survey conducted by BBI International[40]. Estimates were constructed for both dry and wet milled corn. Dry mill facilities are used primarily for generating ethanol, while wet mill facilities or “corn refineries” also produce high fructose corn syrup and glucose syrup. Corn starch from the milling processes is hydrolyzed using dilute acid hydrolysis, fermented and distilled to yield ethanol. A net energy value, or NEV, is calculated that compares the energy content (standard heat of combustion) to the fossil energy required to produce it. When considering the energy expenditure of corn production and transportation and ethanol conversion and distribution, the net energy value is 1.17 kJ/gal for dry mill ethanol and 1.10 kJ/gal for wet mill ethanol. The weighted average considering the quantity of ethanol produced by either mill process is 1.14 kJ/gal. While costs have fluctuated, the cost of ethanol over the last ten years is approximately \$1.20/gallon[41].

Corn starch is also a viable source of glucose. Recent figures from the USDA report the wholesale price of glucose at 16 cents/lb (dry weight)[42]. Currently glucose is

manufactured from corn, beets and sugar cane with corn starch being the primary source. Corn starch is composed of alpha-linked glucose polymers that are easily reduced[43]. Corn derived glucose is produced from either dry or wet milling. In the dry milling process the corn kernel is broken down, typically in a hammer mill, to a flour-like consistency[44]. Wet milling involves steeping the kernels in water, then milling and filtering. The corn starch is hydrolyzed using glucoamylase to produce glucose.

Producing ethanol or glucose from more generic biomass sources is a more flexible alternative. A recent study analyzed the process economics of producing ethanol from cellulosic biomass[45]. The analysis adds information on process design, cost of critical equipment, up to date enzyme costs for saccharification, vendor testing, and corn stover handling to a previous process design and economic model[46]. Aden *et al.* suggest corn stover (stalks, leaves, husk, and cobs) as a suitable source of cellulosic material for conversion to ethanol. The process utilizes dilute acid prehydrolysis as a pretreatment to liberate the hemicellulose and other sugars, followed by enzymatic saccharification with co-fermentation[46]. An ethanol price of \$1.18/gal with a minimum of \$1.08/gallon was projected for the year 2010. Novozymes (Bagsvaerd, Denmark) in partnership with the National Renewable Energy Laboratory (NREL) (Golden, CO) has recently announced technological advances in enzyme activity, fermentation yield and reduced production costs of enzymes for conversion of cellulosic biomass to sugars[47]. They report this will reduce the cost of ethanol to below \$0.30 per gallon.

Aden *et al.* also reported the cost of the intermediate sugar stream. All processes related to subsequent ethanol production (fermentation, distillation, etc.) were removed from the model, and a necessary process was added to remove lignin from the saccharified mixture. Sugar (of which the majority is glucose) is projected to cost 6.7cents/lb. Selling the separated

lignin reduces the glucose cost to 5.4 cents/lb. The lignin stream can be sold to a production plant to convert it to higher value byproducts. The lignin byproduct could also be sold to a biomass fueled power plant that would either burn lignin directly to produce steam and power or produce gasified lignin for use in a gas/steam turbine combination to generate power.

The hydrogen density of most saturated hydrocarbons is very similar (Table 1). Equal volumes of liquid ethanol and anhydrous glucose have hydrogen densities of 102.8 and 102.6 mol H/L respectively. While a saturated glucose solution contains only 60.6 mol H/L, identical concentrations of ethanol or glucose in a fuel stream will have the same amount of available hydrogen because of their similar hydrogen density.

Table 2. Hydrogen density of Ethanol and Glucose.

	Hydrogen Mass Fraction	Density (g/mL)	Hydrogen Density (mol H/kg) (mol H/L)	
Glucose	0.07	1.54	66.6	102.6
Ethanol	0.13	0.789	130.3	102.8

Ethanol from any source costs more to produce than does glucose (Figure 2). The cost of ethanol from corn starch at \$5.89/L[42] is an order of magnitude more than that of glucose (\$0.36/L). From recent advances in enzyme research and current projected costs it is estimated that ethanol cost from cellulosic biomass will be almost identical to the current price while glucose cost is expected to drop to \$0.11/L[46]. Recent advances in enzyme research are also projected to reduce the cost of ethanol from corn starch from \$5.89/L (\$1.20/gal) to \$1.48/L (\$0.30/gal)[47]. Data on a reduction in sugar price isn't available, but given that the enzymatic saccharification process in both glucose and ethanol processes is identical it can be assumed that the glucose price will also decrease. While these costs are projected for the year 2010, it should be noted that at minimum they are not out of range of

current costs. Given that the projections of recent economic studies are realistic, even further reduction in cost can be anticipated for such a new technology.

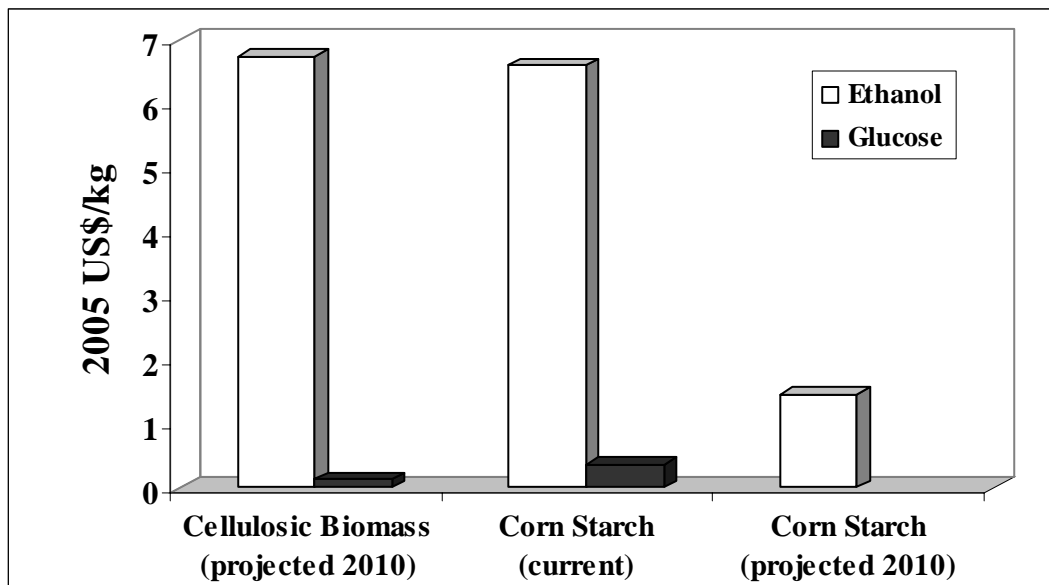


Figure 2. Cost of ethanol and glucose from various sources (2005\$).

Development of a glucose-based micro reforming system is a cost effective way to produce hydrogen for renewable energy. While both ethanol and glucose are promising fuel sources for hydrogen production, glucose will always be a significantly less expensive fuel to produce regardless of source. Glucose is a more energetically stable fuel than ethanol, which has a low flash point of 54°C and is reactive with oxidizing and alkali metals. Using bio-based sugars that can be obtained from tree sap or sugar cane (or in the case of a bio-embeddable device, glucose in blood) also eliminates the necessity of fuel storage, effectively increasing the overall efficiency of the fuel reforming system. The development of an efficient glucose fuel reforming system is anticipated to be a competitive method of harnessing biomass for renewable energy.

Aqueous Phase Reforming of Hydrocarbons

Current fuel reforming technologies for processing hydrocarbons include partial oxidation, autothermal reforming and steam reforming[6, 7]. An external combustor (vaporizer) is used to heat the fuel solution which is then transported to a reactor; room temperature fuel can also be fed directly into a heated reactor. In partial oxidation systems, heat is generated by partial combustion of the hydrocarbon fuel with O_2 [48]. Autothermal reforming is a thermally neutral hybrid of steam reforming and partial oxidation. While partial oxidation and autothermal reforming do not require an external heat source, both systems required an expensive and complex O_2 removal system. The preferred process for hydrogen generation is steam reforming[49].

Recently, it has been demonstrated that hydrogen can be produced from glucose by steam reforming over Pt/Al_2O_3 [3]. A glucose/water solution was fed directly into a pressurized reactor chamber containing the catalyst. The temperature of the reactor was optimized to 533K. Using a low concentration of glucose in water (1 wt%) a hydrogen selectivity of 50% was obtained. However, processing dilute concentrations is not economically practical. Higher hydrogen selectivities at greater concentrations (10 wt%) were found for other more reduced compounds such as sorbitol and glycerol, but while these compounds can be derived from renewable feedstocks[50] they aren't as immediately available as sugars. The higher selectivity at higher concentrations for these compounds was attributed to fewer undesirable competing reactions. The hydrogen selectivity of glucose can be increased to 63% at a 10 wt% concentration by using a dual reactor system that first converts glucose ($C_6O_6H_{12}$) to sorbitol ($C_6O_6H_{14}$) via hydrogenation[8]. Glucose and H_2 are fed directly into the first reactor where glucose is converted to sorbitol. Either Pt or Ni-Sn alloys can be used as catalysts in this conversion reactor. The sorbitol is then fed into a

second reactor where it is converted to H_2 and CO_2 over Pt. While this arrangement increases the number of reforming steps, the increase in H_2 selectivity and fuel concentration is more desirable. Steam reforming of glucose has been found to be energetically neutral. A fraction of the glucose in the reactor is converted to alkanes via an exothermic pathway, meaning the additional energy required for the aqueous reforming of glucose can be produced internally.

Another biomass-derived fuel under consideration is ethanol. Ethanol is produced from the starch (a biopolymer of glucose) contained in corn[7]. It has been demonstrated that ethanol can be converted to H_2 via autothermal reforming [51], but it also has the potential to be produced via a similar steam reforming process to glucose [9] utilizing Ni/ La_2O_3 supported on Al_2O_3 as a catalyst. Steam reforming of ethanol is feasible from a thermodynamic standpoint[52] - [53]. The selectivity of H_2 in both steam and autothermal reforming is 96%, which is higher than the H_2 selectivity achieved with glucose. Ethanol reforming is more attractive from an efficiency standpoint as it is reformed using a single step reactor system and has greater hydrogen selectivity. However, ethanol is not a raw component of biomass but rather a product of glucose fermentation[11]. This fermentation process increases the cost of ethanol as a fuel, and ethanol fuel from any biomass source costs ten times that of glucose. Utilizing glucose directly as a fuel removes this processing step and is the preferred hydrocarbon fuel.

Bench scale reactors convert hydrocarbon fuel to H_2 at different efficiencies. Steam reforming of ethanol above $600^\circ C$ over Al_2O_3 supported Ni/ La_2O_3 yields a hydrogen selectivity of ~95%[9, 51]. Practical steam reforming of glucose using Pt/ Al_2O_3 has maximum selectivities of 50 – 62% depending on the complexity of the setup[3, 8]. Hydrogen selectivity is the number of H_2 molecules produced divided by C atoms in the reformer effluent gas as related to the reforming ratio of the molecule.

$$\% \text{H}_2 \text{ selectivity} = \left(\frac{1}{\text{RR}} \right) \left(\frac{\text{molecules H}_2 \text{ produced}}{\text{C atoms in gas phase product}} \right) \times 100\%$$

The reforming ratio (RR) is the H₂/CO₂ reforming ratio for a particular hydrocarbon assuming complete conversion. Davda *et al.* reported that a low weight hourly space velocity (WHSV) was required to produce the high H₂ selectivities for glucose conversion[8]. The highest hydrogen selectivity of 62% was achieved at a WHSV of 0.065 g g⁻¹ h⁻¹ (grams of reactant per gram of catalyst per hour). Fatsikostas *et al.* reported 95% H₂ selectivity at a WHSV of 1.90×10⁴ g g⁻¹ h⁻¹ (converted units)[9]. On a molar basis, the ethanol process achieves H₂ conversion at 2.06×10² mol EtOH g⁻¹ h⁻¹ while the glucose process produces H₂ at 3.61×10⁻⁴ mol glucose g⁻¹ h⁻¹. While considerations such as catalyst surface area/mass ratio and reactor design must be taken into account, the ethanol process is clearly more efficient. It is unknown how these efficiencies will scale with development of micro reforming processes.

Catalysts

Catalyst usage has been one of the most challenging aspects of hydrocarbon steam reforming from the standpoint of practicality. To date, platinum, an expensive and rare precious metal, has been found to be the most successful catalyst in breaking apart hydrocarbons. Surveys of various catalysts and supports have indicated Pt supported on Al₂O₃ to be the most promising combination for successful conversion of oxygenated hydrocarbons to component gases. Non-precious metal catalysts are of interest due to cost and limited availability of Pt. A tin-promoted Raney-nickel catalyst has been shown to produce similar H₂ selectivities to those produced using Pt[54]. However, these results were obtained using low concentrations of hydrocarbon fuel, effectively limiting the practicality of Raney-nickel catalysts. While efforts

have been made in the arena of non-precious metal catalysts, the discovery of an affordable catalyst has remained elusive.

The main technical requirements for catalysts used in steam reforming are C-C bond cleavage ability, water-gas-shift (WGS) preferetiation, and high H₂ selectivity. Steam reforming of light oxygenated hydrocarbons like methanol to produce hydrogen has been successfully conducted using copper based catalysts[14, 55]. Copper based catalysts, however, show low activity for C-C bond cleavage and so are unsuited to steam reforming of heavier oxygenated hydrocarbons. Catalysts that have shown better activity for C-C bond cleavage are Group VIII metals[56],[57]. The relative rates of C-C bond cleavage of different metals during ethane hydrogenolysis are shown in Figure. While Pt has reasonable bond breaking ability, Ru, Ni, Ir and Rh all demonstrate higher activity for C-C bond cleavage. An effective catalyst must also be active for the water-gas-shift reaction: at the reaction temperature and pressure it must prefer the H₂ side of the WGS reaction and also release CO from the metal surface. WGS activities have been reported for different metals supported on alumina[58]; these are also shown in Figure 3. Cu, which shows no activity for C-C bond breaking in heavier oxygenated hydrocarbons, has the highest WGS rate. Finally, maintaining a high H₂ selectivity of hydrogen requires minimizing or eliminating hydrogen consuming side reactions, e.g. methanation of CO and Fisher-Tropsch synthesis. The relative methanation rates for different metals supported on silica have been reported[59] and are shown in Figure 3. Metals that show high activity for the undesirable methanation reaction are Ru, Ni and Rh; Pt, Ir, and Pd all have low catalytic activity for the methanation reaction. Comparing the metals based on these three reactions in Figure 3, Pt and Pd emerge as having suitable activity for oxygenated hydrocarbon reforming.

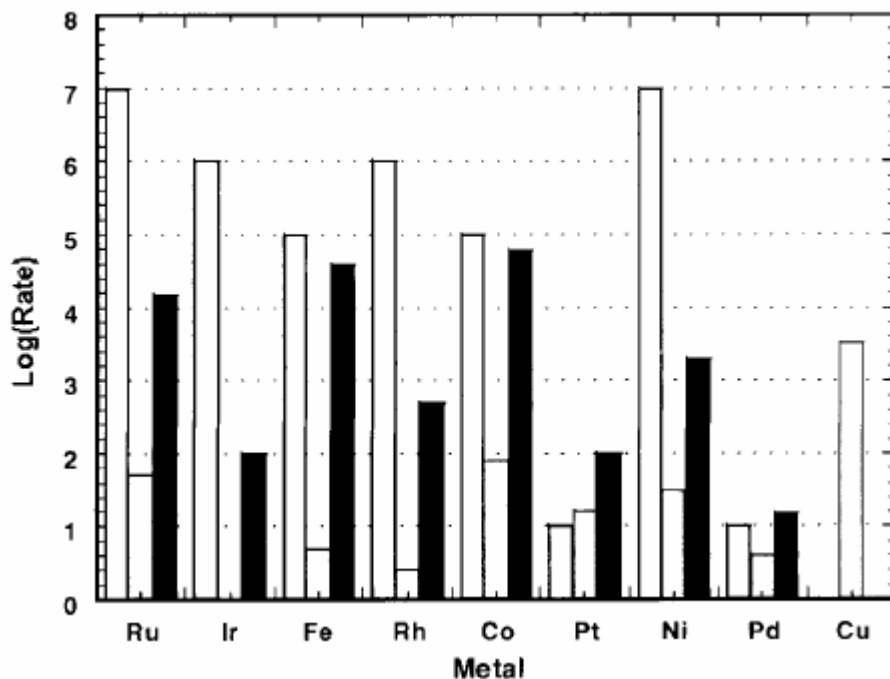


Figure 3. Relative rates of C-C bond cleavage (first bar), WGS reaction (second bar), and methanation reaction (black bar)[2].

While little information is available on alternative catalysts for glucose reforming, relevant catalyst screening experiments have been reported for aqueous phase reforming of ethylene glycol over various catalysts supported on SiO₂. Ethylene glycol (HOCH₂CH₂OH) is a molecule relevant to glucose aqueous-phase reforming because it contains the same functional groups as all larger polyols, including C-C, C-O, C-H, O-H and OH groups on adjacent carbon atoms. Figure 4 is a schematic of the possible reaction pathways of biomass-derived hydrocarbon reforming. The reactions involved in breaking down ethylene glycol are listed in Table 3. All the reactions involved in biomass derived hydrocarbon processing are present in ethylene glycol as well. Therefore, ethylene glycol aqueous phase reforming can be used to model the reactions that occur for direct production of H₂ from biomass-derived polyols like glucose.

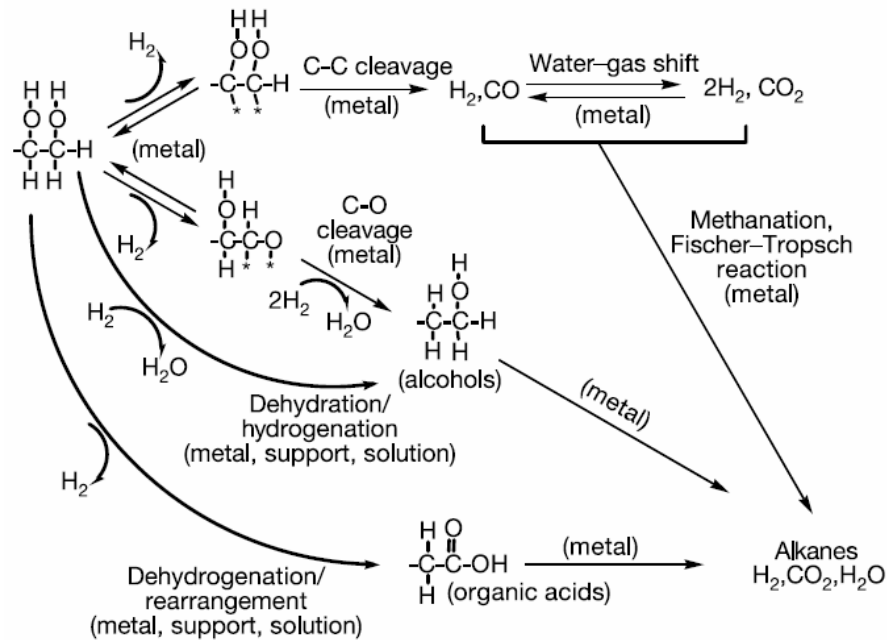


Figure 4. Reaction pathways for production of H₂ aqueous phase reforming of oxygenated hydrocarbons[3]. (Asterisk represents a metal site.)

Figure 5 summarizes the catalytic performance of metals for aqueous phase reforming of ethylene glycol. The rate of ethylene glycol reforming is measured by rate of CO₂ formation as a function of time in the reactor stream. The rate is expressed as TOF (turnover frequencies) and was determined using the number of experimentally determined active catalyst sites using CO adsorption/desorption. Platinum and nickel exhibit the highest reforming rate. Rhodium, ruthenium and nickel have low selectivity for H₂ and high selectivity for alkanes. Platinum and palladium show relatively low selectivity for alkanes and high selectivity for H₂. Comparing catalytic activity of the various metals, it appears that Pt and Pd are both promising catalysts for H₂ selectivity on ethylene glycol. By association Pt and Pd are promising materials for hydrogen production from biomass-derived hydrocarbons.

Table 3. Reactions involved in aqueous phase reforming of ethylene glycol.

	Process	Reaction
1	C-C cleavage leading to CO and H ₂	$C_2H_6O_2 \leftrightarrow 2CO + 3H_2$
2	Water-gas shift	$CO + H_2O \leftrightarrow CO_2 + H_2$
3	Dehydrogenation	$C_2H_6O_2 \leftrightarrow C_2H_{6-x}O_2 + \frac{x}{2}H_2$
4	Dehydration/hydrogenation	$C_2H_6O_2 + H_2 \leftrightarrow C_2H_5OH + H_2O$
5	Methanation	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$

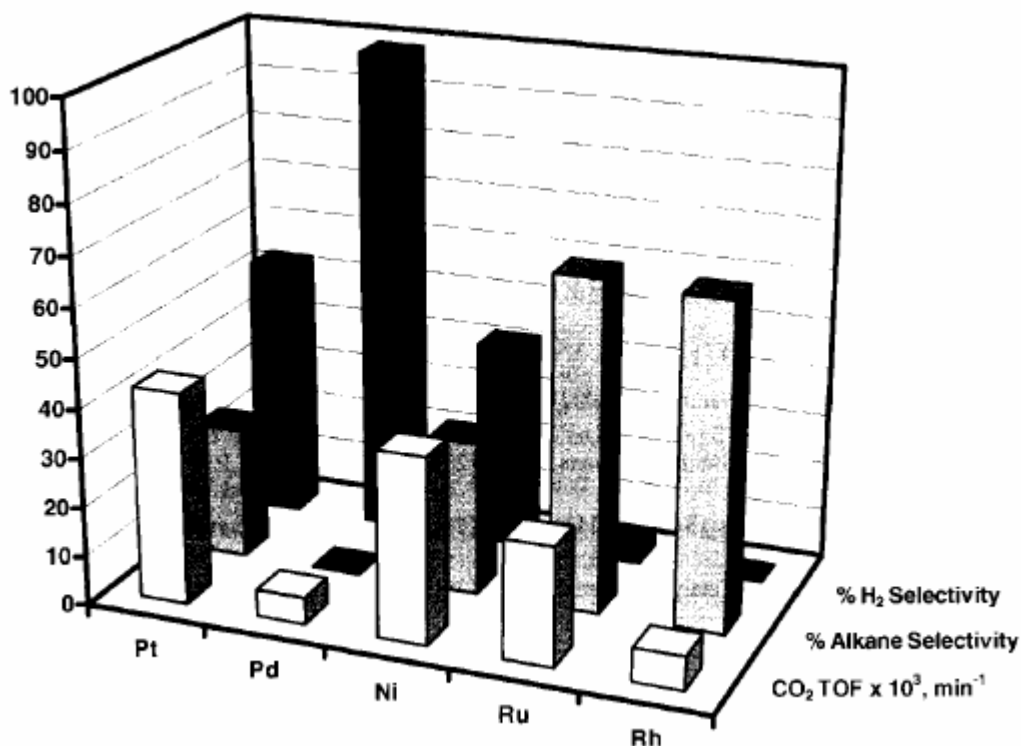


Figure 5. Catalytic performance of metals for ethylene glycol reforming at 483K and 22 bar[2].

The method by which the catalyst is supported is known to affect its activity and selectivity in aqueous phase reforming. There is little published data on Pt catalyst supports for glucose aqueous phase reforming, but catalyst support screening experiments have been reported for aqueous phase reforming of ethylene glycol[54]. Reforming of 10 wt% ethylene

glycol was investigated over Pt black and Pt supported on TiO₂, Al₂O₃, carbon, SiO₂, SiO₂-Al₂O₃, ZrO₂, CeO₂, and ZnO. Platinum supported on TiO₂ was found to be the most active catalyst for hydrogen production, followed closely by Al₂O₃, carbon and Pt-black; the H₂ formation rate ranges from 8-15 min⁻¹. The supported catalysts can be ranked in the following order of decreasing hydrogen production:

TiO₂ > Al₂O₃; carbon; Pt-black > SiO₂-Al₂O₃; ZrO₂ > CeO₂; ZnO; SiO₂

All of the catalysts produced gaseous alkanes and liquid phase alcohols, organic acids and aldehydes in addition to H₂ and CO₂. These undesirable alcohols, organic acids and aldehydes are precursors to gaseous alkane formation as they cannot be reformed to H₂ and CO₂ with high selectivity(<50%)[3]. Pt supported on carbon, TiO₂, SiO₂-Al₂O₃ and Pt-black showed the highest formation of undesirable alkanes and alkane precursors at rates ranging from 1 to 3 min⁻¹. Platinum supported on alumina, and to a lesser extent Pt supported on ZrO₂ and TiO₂, are the most active and selective catalysts for production of hydrogen from ethylene glycol.

Microreactors

There are advantages and disadvantages with converting large scale or bench top devices to the microscale. Microreactors are defined as devices with microstructures for chemical reactions. The reactor casing may be of any size; the internal microstructure is its defining feature. Usual microstructure dimensions range from 10 mm to 500 mm[60]. Microchemical reactors have an advantage over macroscale fuel reformers in that they minimize heat and mass transfer loss[61]. Thermal conduction and mass transfer distances are reduced from millimeters to microns. These reductions are enabled by high surface to volume ratios in the reactors and by short transfer distances. Compared to large-scale reactors, microreforming

systems are more susceptible to thermal losses by conduction from connected instruments and tubing[48]. Input and effluent piping and connected instruments are relatively small compared to large-scale reformers, but their bulk is significant when the reactor component is scaled down. The successful integration of these components into a microreactor system will be necessary to overcome this dilemma.

Microreactors have numerous advantages over typical batch reactors. Practical advantages include safety, “easy modulation”, and numbering up instead of scale-up. Heterogeneous reactions can be carried out efficiently due to short diffusion paths and high surface to volume ratios. There are also features that may enable more selective control over chemical synthesis. Reactions run in macro-scale batch reactors are usually slow (reaction times of minutes to hours) as fast reactions are difficult to control. The superior mixing and heat and mass transfer in microreactors give the control necessary to carry out fast reactions (reaction times from microseconds to seconds), leading to huge increases in production efficiency.

Heat transfer is one of the more important elements of chemical reaction kinetics. Efficient heat transfer is particularly desirable for fast highly exothermic reactions. The heat generated by a chemical reaction is proportional to the volume of reagents used, and hence the volume of the reactor. Conversely heat removal capability decreases with increase in reactor size. Heat produced by the reaction is often removed through the reactor wall, and so the ratio of wall surface area to reactor volume is crucial to efficient heat dissipation. The conduction of heat from highly exothermic reactions and extremely fast reactions in macro-scale batch reactors often leads to heat removal as the limiting factor. The high surface area to volume ratio in micro reactors eliminates this problem.

A large number of reactions have been carried out using micro reactors, among them many famous and industrially relevant organic reactions. Micro reactor technology has advanced from feasibility studies in many cases to more in depth studies and industrial piloting[62]. Each chemical process has unique specifications, so it is difficult to draw generalized conclusions. In general, the use of micro reactors decreases reaction time compared to batch reactors. In some cases increased selectivity is observed, but as data are not reported where an increase is not demonstrated the general effectiveness of microreactors is not fully understood.

Control over product selectivity in chemical reactions is essential in processes with competing reaction pathways. Microreactors can enhance chemical selective for reactions that are extremely fast and highly exothermic due to fast mixing, more precise residence time control, and efficient heat exchange. Microreactors with efficient micromixing have been used to control reactor output with competing parallel reactions in the case where one reaction is very fast[4]. An experiment developed for characterization of mixing in continuously stirred batch reactors was used[63]. The experiment has two potential reaction pathways (Figure 6), one fast and one ultrafast.

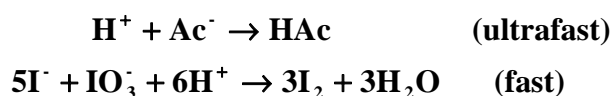


Figure 6. Competing reactions equations used in mixing evaluation[4].

In this scheme, the formation of acetic acid (HAc) is ultrafast, while I₂ formation is fast. As long as there is no local excess of H⁺, HAc formation will always take precedence over I₂ formation. A local excess of H⁺ will significantly enhance the otherwise slow formation of iodine. Imperfect mixing produces local areas of non-uniform concentration

leading to more formation of I_2 . The amount of undesirable I_2 in the product stream can be determined by UV-visible absorption. In this manner the mixing effectiveness can be characterized. A multilaminar mixing technique was used where the substrate and reagent inlets split the fluids into homogeneous ultrathin sheets that are then combined. The resulting ultrafast mixing led to trapping of H^+ by Ac^- , which is the kinetically based prediction. Formation of I_2 was greatly diminished. The use of a conventional T-shaped mixer and batch reactor (with stirring) resulted in significant I_2 production, an outcome attributed to ineffective mixing. These experiments demonstrate the effectiveness of micromixing in controlling fast competitive reaction pathways.

Free radical polymerization is a method of controlling polymer architecture[64]. The molecular weight distribution of polymer batch can be quantified by its polydispersity index, or PDI, which is the weight average molecular weight divided by the number average molecular weight. A high PDI is indicative of a large (and consequently undesirable) weight distribution and a low PDI means a smaller distribution of unique molecules.

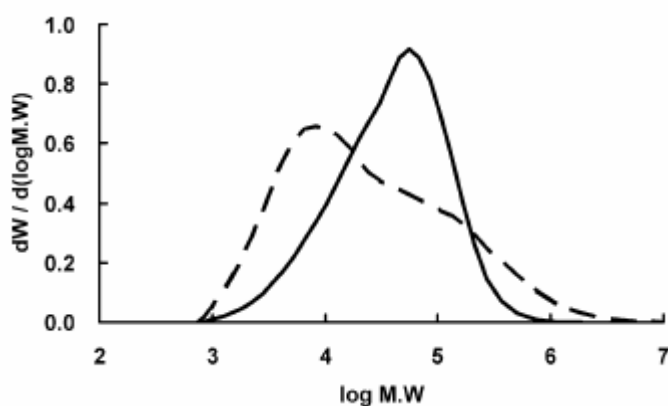


Figure 7. Molecular weight distribution of poly(butyl acrylate). Solid line is polymer obtained from microreactor, dashed line is polymer obtained from macroscale batch reactor. Residence time in each reactor was 4 min[5].

The polymerization of butyl acrylate was carried out in both a microreactor and a batch reactor under otherwise identical processing conditions. As shown in Figure 7, the butyl acrylate obtained using the microreactor had a much smaller PDI than the polymer produced in the batch reactor. This result was attributed to higher heat removal efficiency of the microreactor. Vinyl benzoate and styrene synthesis were also conducted in microreactors and macroscale batch reactors and no difference in PDI was obtained. Vinyl benzoate and styrene synthesis reactions are less exothermic than that of butyl acrylate. Successful drop in PDI by switching to microreactor technology was also reported for benzylmethacrylate and methyl methacrylate, both also formed from highly exothermic reactions. This series of experiments demonstrates that microreactors are effective in molecular weight distribution control for highly exothermic free radical polymerizations.

EXPERIMENTAL RESULTS

At the time of this writing experimental work was just beginning. This initial work focused primarily on set-up and initial characterization of the experimental equipment. As such, the experimental work described in the next few pages should be viewed as preliminary in nature, with the understanding that additional work will be done. In fact, work on this program is expected to continue until a sufficient body of information is available to complete an assessment of the practical utility of micro-scale reforming of carbohydrates for generation of fuel.

Mass Spectrometer and Vacuum Chamber

The mass spectrometer used for analysis of gas evolved from the breakdown of glucose is a Balzers QMA 120 (Balzers-now Pfeiffer Vacuum, Nashua, NH) with a QME 112 mass filter electronics module and a QMS 112 main control module. The mass filter electronics module consists of an RF generator, an ion source supply unit, and an electronic preamplifier control unit. Electronic malfunctions with circuit boards in both the main control unit and in the mass filter electronics unit have been repaired. While the main control unit can be used to sweep across the desired mass range and displays the output current corresponding with the quantity of ions detected at a particular mass, it has no method for computer control, data display or data storage. A 24bit data acquisition module with analog-digital digital-analog conversion capability (Emant300 DAQ USB module) was used in connection with a circuit board to convert all analog output from the control unit to digital format. The DAQ module can be controlled using a variety of software languages; a C# program already written for this application was used. The programmed software allows for control of the emission current and signal amplification. The sweep rate and sweep range are

set using the original control box. The amplified signal height plotted versus mass/charge ratio is obtained and the data can be copied and transferred to any plotting program. The mass spectrometer is now capable of acquiring data.

The vacuum chamber consists of a four-way cross fitting (Varian Inc., Palo Alto, CA). Low and high vacuum sensors are attached to the chamber for pressure monitoring. The chamber is attached to a pumping station that consists of a turbomolecular pump (TPU 050, Pfeiffer Vacuum, Nashua, NH), a roughing pump (DUO 1.5A, Pfeiffer Vacuum, Nashua, NH), and pumping station control box (TCP121, Pfeiffer Vacuum, Nashua, NH). A Swagelok fitting attached to a vacuum flange was used to connect the vacuum chamber to the reactor plumbing. A fine metering valve (Swagelok, Solon, OH) was used to produce a slow leak, though the leak rate was in excess of too fast for the turbo pump to handle (50 L/s). Leak testing this system configuration resulted in a chamber pressure of 1×10^{-6} Torr. To reduce signal/data noise, the mass spectrometer must be used at 1×10^{-7} Torr. Reduction of the pressure inside the vacuum chamber was achieved by replacing several vacuum hardware parts to shorten and widen the attachment of the turbo pump to the chamber. This has reduced the background pressure of the vacuum chamber to 5×10^{-8} Torr. The acquisition of a variable leak valve (Precision Leak Valve 951-5100, Varian Inc, Palo Alto, CA) has eliminated the leak associated with the attached Swagelok fittings at the sample inlet port and has enabled precision control of the gas leak inlet into the chamber. Figure 7 shows the vacuum chamber, pumping station and mass filter electronics for the quadrupole analyzer. Figure 8 shows the microreactor (circled in yellow) and the auxiliary system components that enable product transfer to the vacuum chamber for analysis.

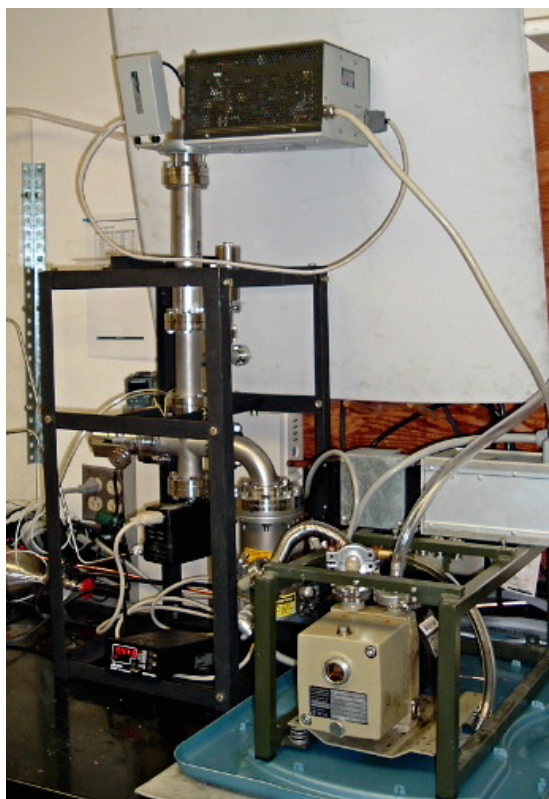


Figure 8. Vacuum chamber, pumping station, and mass filter electronics.

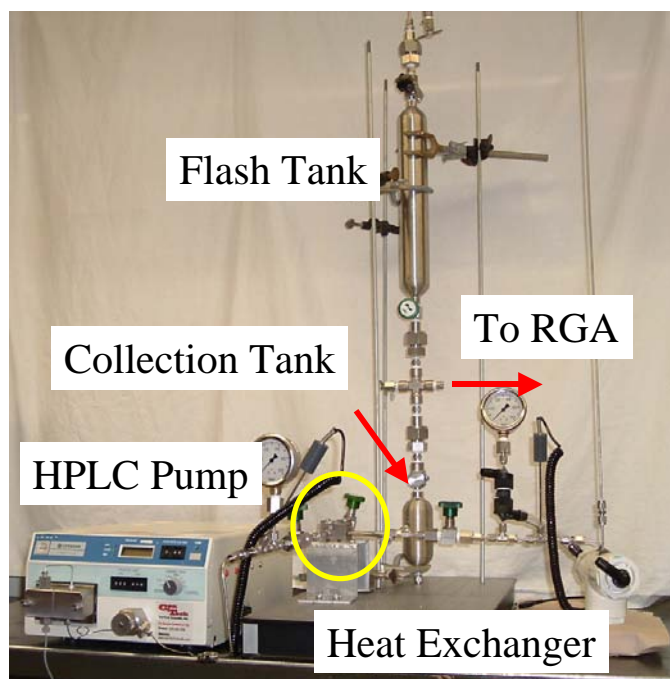


Figure 9. Reforming system setup (To RGA indicates the gas sample outlet to a residual gas analyzer or mass spectrometer).

Catalyst Deposition

Effective adhesion of the Pt/ Al₂O₃ catalyst (Pt on -325 mesh Al₂O₃, Sigma-Aldrich Corp., St. Louis, MO) to the 316 stainless steel microstructured catalyst plates is still under investigation. Sufficient binding of the catalyst is essential given the sheer stress associated with flowing liquid phase reactant across the coatings at a pressure of 30-50 barr. Resistance of the catalyst coating to tape adhesion and removal has been used to gauge binding effectiveness.

Both electrophoretic deposition and dip coating methods exhibit poor adhesion. Catalyst particles were suspended in an aqueous solution using the following: 4 wt% Pt/ Al₂O₃, 1.8 wt% binder (Methocel F4M, Dow Chemical, Midland, MI), and 2 vol% dispersant (Darvan 821A, RT Vanderbilt, Norwalk, CT). Samples of 33 μm Al₂O₃ were also used to gauge the effectiveness of the suspensions. A solvent clean consisting of acetone followed by ethanol was used to reduce residual organics remaining on the surface of the sample plates used. Electrophoretic deposition is carried out using a Pt-Ru electrode and a stainless steel plate holder with a fixed distance between the two. A potential of 9V applied across the electrodes drives the catalyst to the stainless steel plate in the holder. A dip coat method was also employed for catalyst coating. The dip coater consists of a motor attached to a sample holder; the sample is lowered or raised into the suspension at a rate of 1mm/minute. Each sample plate remained in the suspension for 1 minute before being removed. After electrophoretic or dip coat deposition of the catalyst suspension, each sample plate was heat treated at 800°C for 2 hours.

A 316SS sample plate dip coated with Pt/Al₂O₃ is shown in Figure 8. The smaller particles deposited on this plate indicate only the smaller particles from the -325 mesh powder are being suspended using the current method. Figure 9 shows the distribution of the Pt particles on the Al₂O₃ support. Very little active Pt surface area can be achieved with the dispersion as shown post coating. The Pt/Al₂O₃ coating after an adhesion test is shown in Figure 10. A significant quantity of the coating has been removed which indicates unacceptable adhesion has been obtained using the current deposition method. Similar results were also obtained using the electrophoretically deposited coatings. Sputter deposition of Pt on oxidized stainless steel is anticipated to produce a sufficiently bonded catalyst coating and experiments in this area are ongoing.

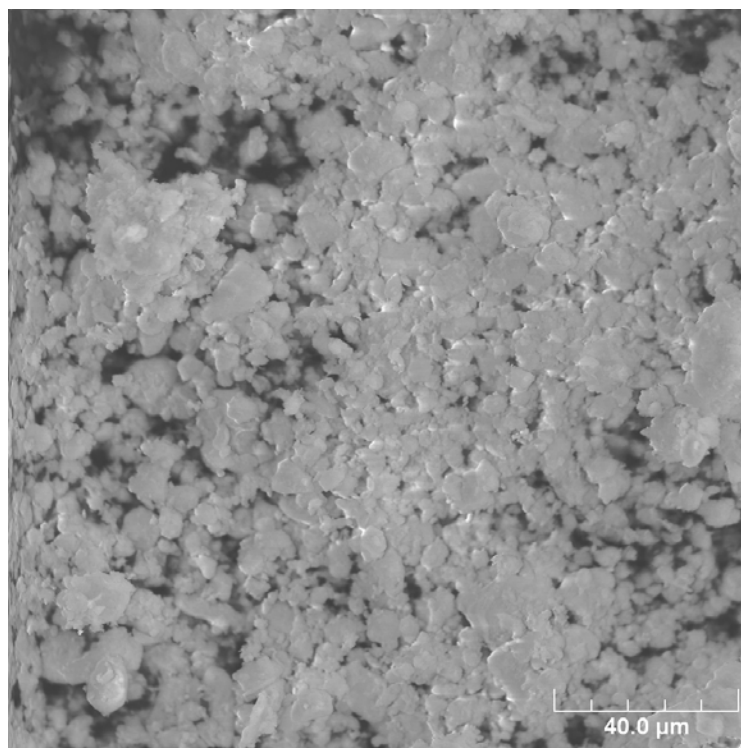


Figure 10. 316SS sample plate with Pt/Al₂O₃.

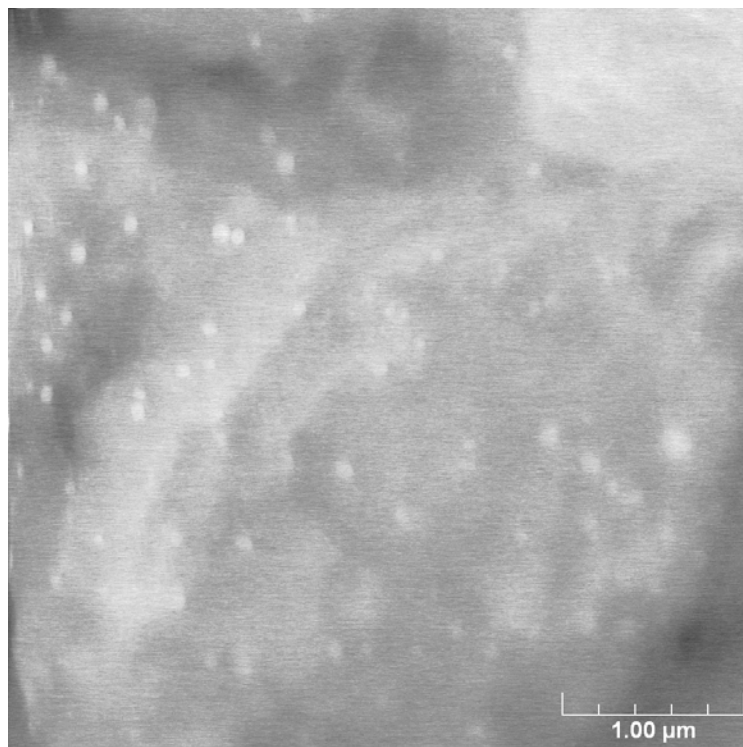


Figure 11. View of Pt particles supported on Al₂O₃.

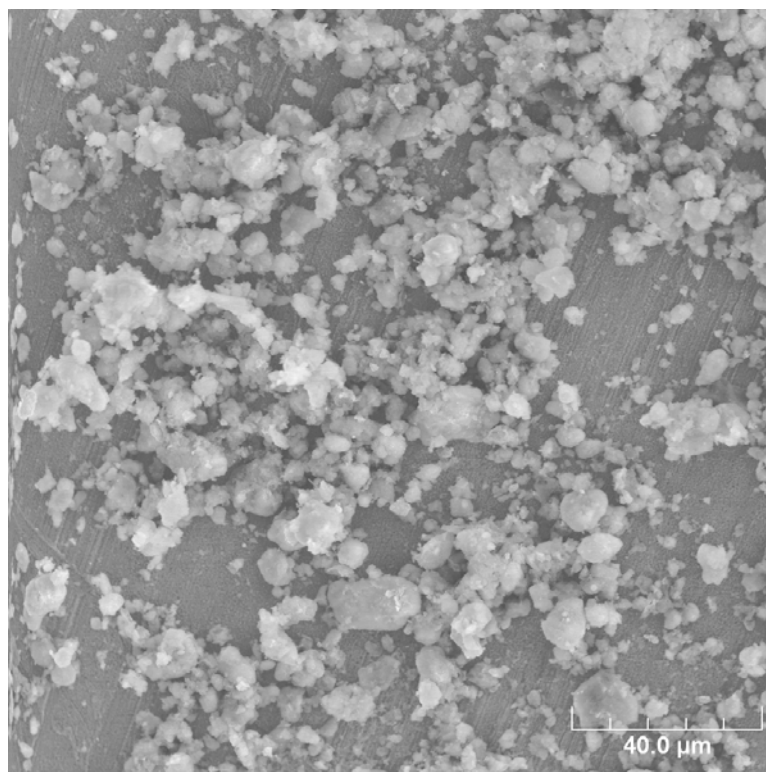


Figure 12. Pt/Al₂O₃ coating after adhesion test.

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