MinnesotaCorn RESEARCH & PROMOTION COUNCIL

2024 FINAL REPORT (project ongoing)

PROJECT TITLE: **Direct Conversion of Corn-Derived Carbohydrates to Ether-Based Clean Fuels**
PROJECT NUMBER: 6136-24DD
PRINCIPAL INVESTIGATOR AND CO-INVESTIGATOR(S): Paul J. Dauenhauer

ABSTRACT
Provide a project summary describing an overview of the project including principle findings. Include a statement on how the project was of benefit to corn farmers.

The proposed one-year research study assessed the potential of a chemical process to convert corn to methanol and/or dimethyl-ether (DME), a chemical feedstock for the production of sustainable aviation fuels (SAF) and materials such as polymers. The process utilized a hydrogenolysis catalyst to break apart the carbon-carbon bonds of corn-derived carbohydrates, ultimately yielding methanol which can be readily dehydrated to dimethyl ether. Research evaluated two general strategies for catalyst design including discrete catalyst compositions and a continuously tunable catalyst surface. Finally, experimental data was used to determine the potential of a future corn-to-methanol and ether process and the path forward for a future multi-year project to design and patent the entire process technology.

INTRODUCTION
Provide background information related to the project including such item as the problem statement, knowledge gaps, and relevant previous work completed on this issue.

The utilization of corn for ethanol fuel enables biorenewable gasoline alternatives or an oxygenate supply for petroleum-derived combustion engines.[1] Expanding corn use to the production of methanol requires new molecular product structures that exhibit the properties required of existing jet fuels or materials precursors.[2] Carbohydrates of corn could potentially be turned into alkanes that are chemically identical jet fuels and existing materials monomers,[3] but this first requires the synthesis of methanol from the sugars of corn.

In this work, we focused on the core engineering required for converting carbohydrates (starch and glucose from corn) into methanol and dimethyl ether (DME) and eventually into larger molecules for jet engines or smaller molecules such as DME.[4] These molecules lack C-C bonds that dehydrogenate, aromatize, and polymerize to form soot; instead, the combustion of C1-based ethers burn cleanly to CO_2 (constituting net zero carbon emissions).[5] Additionally, C1-based ethers are readily condensable for high energy density; DME in particular has physical properties

comparable to propane.[6] Larger ethers such as oxymethylene ethers (OME) with structure $CH_3O(CH_2O)_nCH_3$ and *n* of 3-to-5 also have properties comparable to fuel while retaining their cleaning burning characteristics.

Corn-derived ethers for jet fuel also match the scale of agriculture in the United States. In 2022, the USA produced about ~14 billion bushels of corn (~360 million tonnes of corn, source: USDA). In the same year of 2022, the USA consumed about ~145 million tonnes of diesel fuel (source: EIA). Using about half of the annually produced corn would provide the renewable carbon required to manufacture all of the country's current jet fuel consumption. This transition could occur piecewise, with current fuels being converted over to switch from conventional petro-fuel to bioderived fuel (e.g., DME or methanol-derived jet fuel) in different timescales. For example, school buses that generate dirty exhaust in the presence of children could be among the first applications to switch to clean burning DME fuel derived from corn. The industry could then grow in new sectors as fleets of jets and engines are converted over for transportation, agriculture, and industrial applications.

The challenge of manufacturing methanol and fuel ethers from biomass has historically been challenged by *conventional* production methods. In a technology that has existed for almost a century, biomass can be gasified to synthesis gas ($CO + H_2$), which is then cleaned and modified to remove oxygenates (undesired impurities) and to shift the ratio of H_2/CO.[7,8] The gases are then compressed to high pressure and reacted over Cu/ZnO catalysts to synthesize methanol.[9,10] In the final step, methanol is dehydrated to form dimethyl ether and water.[11] This approach has historically only been economically viable at large scale (millions of tonnes) using reduced hydrocarbons such as natural gas or petroleum. Moreover, it is a major capital investment comprised of significant volume of gas handling equipment that operates at high temperature. For these reasons, this synthetic approach to converting biomass to alcohols has failed many times, including most recently by the heavily invested 'Range Fuels' startup company. A new approach to synthesizing ethers from biomass, corn and carbohydrates is required.

Here, we are pursuing a new approach of 'direct-methanol' synthesis from corn starch depicted in **Figure 1**. The initial step utilizes the current production of glucose using acid or enzymes. Thereafter, there exist three possible reaction pathways to produce methanol in the liquid phase; these could happen in a single pot (sequentially) or be divided into multiple sequential reactors. Pathway 1. Glucose can be hydrogenated to sorbitol on supported metal catalysts, after which hydrogenolysis yields ethylene glycol. Hydrogenolysis on Ni/Al_2O_3 and Ni/SiO_2 catalysts (230 °C, 60 bar) then yields high selectivity (~60%) to methanol.[12] Loss of carbon by this method can lead to methane byproduct, or other C2 oxygenated depending on the selected catalyst and conditions. Pathway 2. A single catalyst or mixed bed of active sites can potentially convert glucose directly to methanol, possibly including C2 intermediates or by single C1 species breaking off the glucose chain. This pathway will be evaluated based on insight gained from pathway 1. Pathway 3. This third alternative approach aims to use a hydrogen-free C-C bond breaking reaction to convert carbohydrates to formaldehyde, which is then readily hydrogenated to methanol.

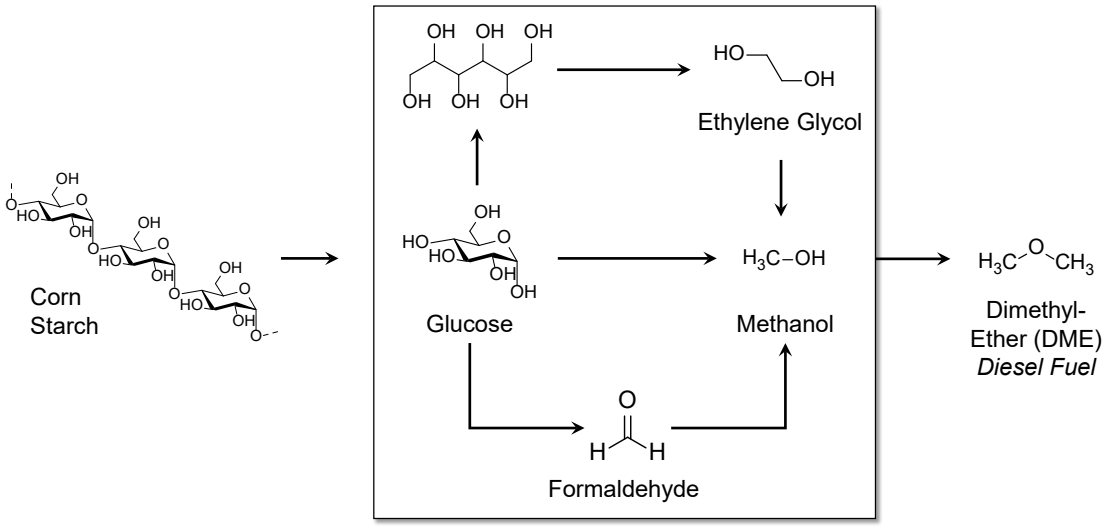
OBJECTIVE AND GOAL STATEMENTS

This research pursued parallel objectives that evaluate catalytic performance towards converting polyols (carbohydrate surrogates) to methanol with varying catalyst properties. The potential of this process will be assessed by the yield of of processing corn to dimethyl ether based on the performance of the catalyst and a reasonable prediction of future catalyst selectivity based on

comparable catalyst improvements. The work will pursue objectives that evaluate the creation of a reactor and conversion of ethylene glycol, the tunability of catalyst and reactor conditions, and the broad economic potential of this process.

Objective 1. Hydrogenolysis of Ethylene Glycol using Heterogeneous Catalysts.

Objective 2. Tunable Hydrogenolysis Catalyst for DME**.**



Scheme 1. New Process for Jet Fuel Precursors (Methanol & DME) Production from Corn. Reaction pathways for efficient, low-cost production of methanol and dimethyl ether (DME) fuel from corn starch. Upon formation of glucose by existing methods, hydrogenolysis can yield methanol by through possible routes: (1) hydrogenation to sorbitol, cracking to ethylene glycol, and then hydrogenolysis to methanol, (2) direct hydrogenolysis to methanol, or (3) cracking to formaldehyde followed by hydrogenation to methanol. Subsequent dehydration forms DME by existing commercial methods.

MATERIALS AND METHODS

As appropriate, describe the site(s), experimental design, and other relevant methodology used in completing the project.

Initial research tasks focused on designing, building, and validating the design of a catalytic reactor that can safely and accurately convert aqueous solutions of carbohydrates and gaseous H_2 to smaller molecules. As depicted in the design in **Figure 1**, the flow reactor utilizes a pressure regulator and controller to modulate conditions and residence time to explore the catalytic performance to break carbohydrate C-C bonds. The reactor was constructed to operate at pressures up to 150 atm of H_2 pressure with liquid co-feed deliverable with a piston feed of liquid. Pressure was maintained with a back pressure regulator after a gas/liquid separator that permitted online liquid collection. Gases are vented where they can be sampled separately. The system is designed with multiple safety features including a rupture disk and overpressure relief valve.

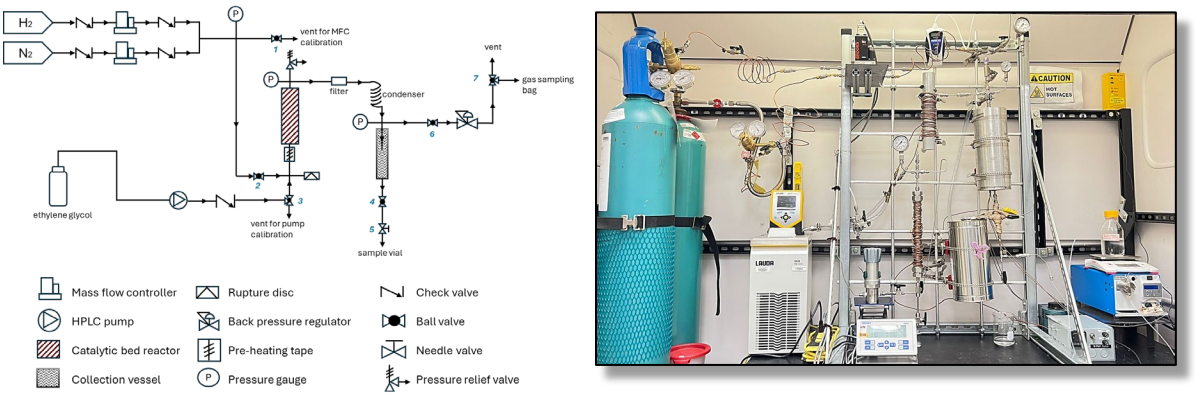


Figure 1. Continuous flow reactor for catalytic testing of ethylene glycol hydrogenolysis to methanol with variable pressure, temperature, and feed composition.

RESULTS AND DISCUSSION

Results evaluated the validation of the continuous flow reactor of Figure 1, identifying the conditions of reactor flow, temperature, and pressure control for varying conditions to evaluate catalyst performance. In parallel, evaluation of the online analytical system to assess both gases and liquids indicated good separation of carbohydrate scission molecules and proportionality between the analyzed molecules and detector response.

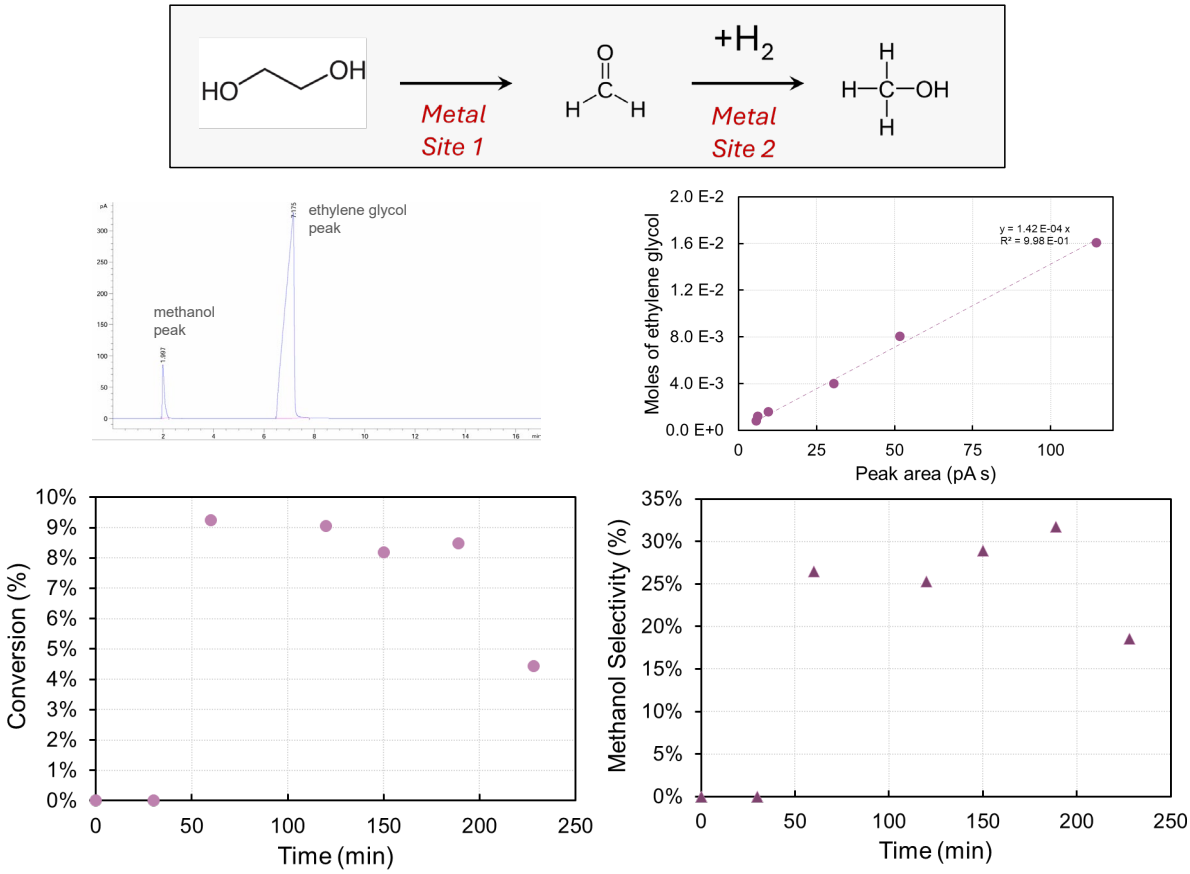


Figure 2. Catalytic conversion of ethylene glycol to methanol on copper-based heterogeneous catalyst.

Experiments evaluated the continuous flow scission of ethylene glycol to methanol, other oxygenates and gases over supported metal catalysts in flowing hydrogen gas and liquid feed in the upflow three-phase reactor. As depicted in Figure 2, catalysts were evaluated for more than three continuous hours of time on stream, providing details on the catalyst activity, selectivity and stability. As shown in Figure 2, copper based catalysts achieved ~25% selectivity to methanol as the major product.

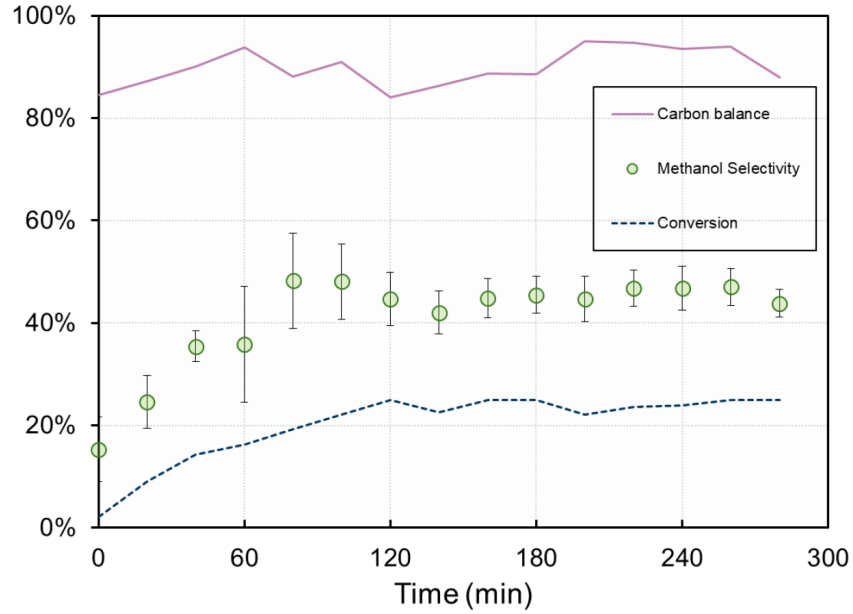


Figure 3. Conversion, carbon balance, ands electivity of MeOH as a function of time with Raney Ni catalyst.

A Raney Ni catalyst was evaluated in Figure 3. In a standard experiment, 0.08 grams of activated Raney Ni was mixed with equal parts of 30-50 microns Si glass beads and packed inside the reactor tube with deactivated quartz wool on both ends of the packing. Prior to the reaction, nitrogen gas was used to purge the reactor for 1 minute to remove oxygen. The catalyst was reduced at 300 °C at 10 °C min^{-1} ramp rate and a one-hour hold in 100 mL min^{-1} 10 v/v% H_2 in nitrogen and then returned to the desired reaction temperature.

To start the reaction, the reactor was pressurized to 60 bar with the relevant feed gas composition. The liquid feed solution (60 wt.% ethylene glycol in water) was then pumped into the reactor at a 0.25 mL min^{-1} flow rate. The gas flow controller flow rate was also set to the desired gas flow rate for a GHSV of 1060 h^{-1} and LHSV of 3 h^{-1}.

The reaction was run three times where the carbon balance was between 80 and 100%, and selectivity to methanol remained between 40 and 50% at steady state (Figure 3). This is consistent with some literature reports, though selectivity as low as 10% have also been reported. The steady conversion over 5 hours is an indicator of catalyst stability. This data set shows that initial catalytic performance results agree with literature benchmarks, validating the experimental approach and setup.

As the water content decreases in glycol/water mixtures, the solubility of hydrogen decreases as shown in Table 1. The resulting decrease in effective H_2 concentration may be limiting the over-hydrogenation of methanol to methane. This can be seen as the MeOH selectivity increases, the methane selectivity diminishes. It has been suggested that converting EG to methanol using activated Raney Ni may involve the competitive adsorption of EG and hydrogen on catalytic sites. In low water content solutions, EG molecules have greater access to the catalyst's active sites, leading to more effective hydrogenolysis and improved methanol formation. The competition between EG and hydrogen for adsorption sites may influence methanol selectivity by site blocking H_2. This helps prevent over-

hydrogenation of intermediates and redirects the reaction pathway towards methanol formation. The effect of ethylene glycol concentration variation provides valuable insight into the mechanisms governing product distribution in catalytic reactions involving EG/water mixtures.

Table 1. Product distribution of ethylene glycol hydrogenolysis over Raney Ni.

	Product Selectivity		
	20 wt.% EG	40 wt.% EG	60 wt.% EG
Methanol	41.7	46.1	59.0
CO_2	3.6	2.9	1.5
Ethanol	9.3	11.4	8.0
1,2-propanediol	>0.1	>0.1	>0.1
Methane	53.4	39.5	31.4

CONCLUSIONS

A three-phase flow reactor demonstrated continuous and moderately efficient hydrogenolysis of ethylene glycol to methanol under varying conditions of temperature, pressure, reactant feed concentration, and reactor space velocity. Maximum methanol selectivity was achieved of 59% to methanol. These results indicate the significant potential for synthesizing methanol from carbohydrates.

EDUCATION, OUTREACH, AND PUBLICATIONS

Identify conferences, workshops, field days etc. at which project results were presented. Include number of farmers estimated to be present. List articles and/or manuscripts in which project results were published.

None

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