

CHEMISTRY & SUSTAINABILITY

CHEM5USCHEM

ENERGY & MATERIALS

Accepted Article

Title: Investigation of the Reaction Pathways of Biomass Derived Oxygenate Conversion into Mono-alcohols in Supercritical Methanol with CuMgAl Mixed Metal Oxide.

Authors: Peter H. Galebach, Sean Thompson, Ashley M Wittrig, Scott J. Buchanan, and George W. Huber

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemSusChem 10.1002/cssc.201801816

Link to VoR: http://dx.doi.org/10.1002/cssc.201801816



WILEY-VCH

www.chemsuschem.org

Investigation of the Reaction Pathways of Biomass Derived Oxygenate Conversion into Mono-alcohols in Supercritical Methanol with CuMgAl Mixed Metal Oxide.

Authors: Peter H. Galebach^a, Sean Thompson^a, Ashley M. Wittrig^b, J. Scott Buchanan^b, Prof. George W. Huber^{a*}.

[a] Department of Chemical and Biological Engineering, University of Wisconsin, 1415 Engineering Drive, Madison, Wisconsin 53706, United States.

[b] ExxonMobil Research and Engineering, 3545 Route 22 East Clinton Township, Annandale, NJ 08801, United States.

*Corresponding author: George W. Huber Email: gwhuber@wisc.edu



Table of Contents:

Cellulose is converted to alcohols over $CuMgAlO_x$ catalyst in supercritical methanol. The reaction proceeds through retro-aldol condensation of cellulose to oxygenates, condensation with methanol, and C-C scission reactions to mono-alcohols.

Keywords: Biomass, C-C coupling, Fuels, Hydrodeoxygenation, Supercritical Fluids.

Abstract:

The reaction pathways for conversion of cellulose into C_2 - C_6 mono-alcohols by supercritical methanol depolymerization and hydrodeoxygenation (SCM-DHDO) over a CuMgAl oxide catalyst have been elucidated using a range of model compounds. SCM-DHDO of intermediate oxygenates including glycerol, methyl lactate, and 1,2-ethanediol produces similar products as SCM-DHDO of cellulose. The pathway to C_2 - C_6 mono-alcohols occurs through rapid C-C coupling reactions between methanol and diols followed by C-C scission between vicinal alcohol groups to produce two mono-alcohols. Methyl branched mono-alcohols are produced through a methyl shift in a secondary diol followed by dehydration. Esters are produced by dehydrogenative coupling between an adsorbed methoxy and a primary alcohol. Both dehydrogenation to a ketone and esterification to a methyl ester are in equilibrium with the corresponding alcohol and were reversible. Dehydration of diols is the slowest observed reaction and not a main pathway to mono-alcohols. SCM-DHDO of glucose, dihydroxyacetone, and

Accepted Manuscript

cellulose all produced similar high molecular weight species indicating that condensation of intermediates can produce undesired side products.

Keywords: Cellulose, hydrodeoxygenation, supercritical methanol, alcohols, C-C coupling

Introduction:

In recent years several biomass conversion technologies have been studied as a method to produce renewable fuels and chemicals.^[1-3] A recent approach first proposed by Ford and coworkers involves the supercritical methanol depolymerization and hydrodeoxygenation (SCM-DHDO) of biomass into mono-alcohols and cyclohexyl alcohols with a CuMgAl catalyst.^[4-8] This process has a number of advantages including very high yields (up to 121 wt% due to methanol incorporation and complete conversion of biomass to products) of fuel range alcohols, all reactions occur in a single reactor, and it utilizes all fractions of biomass including the energy rich lignin fraction. The alcohol products could either potentially be used directly as a fuel or upgraded via condensation or oligomerization.^[9-11] Other biomass conversion processes like enzymatic hydrolysis, supercritical water hydrolysis, or aqueous phase hydrodeoxygenation require separate depolymerization and sugar conversion steps that leads to lower yields and higher processing costs.^[12-14] While single stage processes like pyrolysis have the benefit of low processing costs, they suffer from poor fuel quality and often require additional downstream fuel upgrading.^[15, 16] Subsequent studies have shown that SCM-DHDO works with alternate catalysts, solvents, and feedstocks.^[17-19] Wu et al. examined SCM-DHDO of cellulose using CuO-MO/Al₂O₃, where M was a promoting metal either Ce, Mg, Mn, Ni, or Zn, and produced C₄-C₇ alcohols.^[17] Yin et al. demonstrated that SCM-DHDO of sugars from pyrolysis oil produced a similar alcohol mixture to cellulose.^[18] Huang used supercritical ethanol to depolymerize and isolate monomers from soda lignin.^[19] Palkovits and co-workers showed that cellulose produces C₁-C₃ mono-alcohols and diols in water with CuO-ZnO/Al₂O₃ catalyst.^[20] Much of the work on elucidating the chemistry occurring in SCM-DHDO has focused on the lignin fraction while the reaction pathway of cellulose is largely unknown, but is thought to involve hydrodeoxygenation and methanol incorporation reactions.^[8, 17, 19, 21, 22]

We have previously used isotopic labeling and model compounds to show that SCM-DHDO of cellulose occurs through retro-aldol condensation of soluble sugars followed by reactions with methanol to form a mixture of C_2 - C_6 mono-alcohols, diols, esters, and ethers. Isotopic studies showed that methanol is incorporated into all the liquid products. The reaction also produced high molecular weight species that varied between C_7 to C_{25} with 2 to 4 oxygen atoms and 4 to 12 double bond equivalents.^[23] Although our research showed that retro-aldol condensation is an intermediate step during conversion of cellulose, we do not yet understand the subsequent reactions that produce the large number of products from the smaller oxygenates. Retro-aldol condensation of glucose and fructose produces C_2 - C_4 oxygenates like dihydroxyacetone and glyceraldehyde. In this study we used glycerol and other polyols as model compounds to help elucidate the reactions that occur in SCM-DHDO. Glycerol conversion to 1,2-propanediol conversion has been studied extensively with copper and noble metal catalysts.^[24-32] Glycerol conversion occurs primarily through dehydration of glycerol to hydroxyacetone over acid sites followed by hydrogenation over metal sites to 1,2-propanediol.^[31] Copper catalysts have

improved selectivity to 1,2-propanediol due to lower C-C hydrogenolysis activity while noble metal catalysts have high hydrogenation activity after dehydration, but suffer from high selectivity to undesired C-C scission reactions to produce 1,2-ethanediol, CO, or CH₄.^[26, 31] Although this is a widely studied reaction, conversion of glycerol to 1,2-propanediol with copper catalysts has mainly been done with water which eliminates the possible reactions between methanol and reactants that may be occurring during SCM-DHDO. Copper catalysts have also been studied for Guerbet coupling of alcohols and conversion of diols to aldehydes and ketones which includes many of the same reactions likely occurring in SCM-DHDO including C-C coupling, esterification, and dehydrogenation reactions.^[9, 33-36] Despite the abundance of literature on glycerol conversion in water and on coupling of alcohols, to our knowledge no study has examined conversion of polyols in an alcohol solvent. The objective of this paper is to elucidate the chemistry that occurs for SCM-DHDO of cellulose and cellulose derived chemicals by studying the SCM-DHDO of C₂-C₄ oxygenates.

Experimental Setup:

Reactions were run with high pressure batch reactors made from Swagelok unions with a bleed valve for gas analysis.^[23] These reactors are used in similar high pressure biomass conversion processes in the literature and were used in this study to maintain consistency between reaction systems.^[8, 37] During a typical reaction, a reactor is put in a sand bath preheated to 300°C. The reaction time is measured from when the sand bath reheats to 300°C to when the reactor is removed. Liquid samples were taken from opened reactors and filtered using a 0.22 µm syringe filter. Reactions with polyols were run with 10 mg of catalyst for every 100 mg of model compound to keep conversion low. Reactions with mono-alcohols were run with 50 mg of catalyst. Reactions with triol and diol model compounds were run from 0 minutes (just after reheating to 300°C) to 49 minutes depending on the reactivity of the model compound. Catalyst amount and reaction time were varied to achieve approximately 10-50% conversion of each model compound. All reactions with mono-alcohols were run for 1 hour. Model compound reactions to make high MW products were run for 4 hours with 100 mg of catalyst.

Product Analysis:

Liquid products were analyzed by gas chromatography using a Shimadzu GC-2010 equipped with a RTX-VMS column and a flame ionization detector and by mass spectroscopy using a Shimadzu GCMS-QP2010 mass spectrometer equipped with a RTX-VMS column. The GC oven was held at 40°C for 5 minutes then ramped to 240°C at 7.5°C min⁻¹ and held for 15 minutes. Products were quantified using calibrations of known standards. Dodecane was used as an internal standard to measure methanol conversion.

Mass spectrometric data were acquired with a Bruker solariX XR Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer with a 15 T actively shielded superconducting magnet. Instrument control, data acquisition and preliminary processing were performed on Bruker Daltonics ftmsControl 2.1.0 and Bruker Compass DataAnalysis 4.5 software. Atmospheric pressure chemical ionization (APCI) was used to investigate each sample. Samples were taken directly from the liquid after reaction. All samples were diluted as needed in LCMS

grade methanol prior to analysis. Flow rates were controlled by the instrument syringe pump at 180-300 μ L h⁻¹. The conditions were set to an APCI temperature of 380-400°C, corona needle current of 1200-1250 nA, dry gas flow of 3.5-4.0 L min⁻¹, and dry gas temperature of 200°C. Nitrogen was used as the drying gas. The data was processed by using the sine-squared apodization method in absorption mode. Each mass spectrum is an average of at least 80 scans. After acquisition, elemental formulas for each peak were assigned by PetroOrg software.^[38]

The selectivity and carbon yield for reactions run for 4 h and with complete conversion is defined by carbon % shown in equations 1 and 2. Our previous study showed that SCM-DHDO of cellulose produces high MW species that are not detectable by GC.^[23] In this study we are only reporting the yield and selectivity of GC detectable products.

Selectivity (C %) =
$$\frac{\text{moles of carbon in the product}}{\sum \text{moles of carbon in all products}}$$
 (1)

Total Carbon Yield (C %) =
$$\frac{\sum \text{moles of carbon in all products}}{\text{moles of carbon in the feed}}$$
 (2)

The reactions with model compounds involve many C-C addition and C-C scission steps which complicate selectivity and yield calculations based on carbon amounts in the products. Instead, the selectivity for low conversion model compound studies is defined as the moles of reactant that were converted to each product as shown in equation 3. In this way incorporation of methanol should not affect the selectivity and if a reaction results in two moles of a product, e.g. 2,3-butanediol to 2 moles of ethanol, the selectivity to the C-C scission product is not double counted. We have also defined the yield in equation 4 by mole % rather than C % to avoid greater than 100% yields due to methanol incorporation.

Selectivity (mole %) =
$$\frac{\text{moles of reactant to the product}}{\sum \text{moles of all products}}$$
 (3)

The rates of different reactions were also compared using space time yield which is defined here as the moles of product from reactant divided by the moles of reactant, the mass of catalyst, and the reaction time, shown in equation 5.

Space time yield (STY) =
$$\frac{\text{mmol of reactant converted to the product}}{\text{mmol of reactant } \cdot \text{g of catalyst} \cdot \text{hours}}$$
 (5)

Space time yield also allows comparison between reactions in which the catalyst mass, feed type, and reaction time are not held constant. Since these reactions were performed in batch reactors and heat up times could not be completely eliminated, the calculated space times in this paper should only be examined qualitatively. Space time yields were only calculated at $\sim 30\%$ conversion as some conversion occurred during the initial heating, preventing an accurate measure of reaction time for low conversion points, and at higher conversions the product mixture becomes too complex to attribute products to specific reaction pathways.

The thermodynamics of each reaction were calculated using values taken from Aspen APVpure32 database which is based on the most recent thermodynamic data from DIPPR.^[39] In cases where the thermodynamics of each reaction were not available in a database we calculated values using Gaussian 09 software (geometry optimization and frequency calculations with B3LYP/6-311+G(2d,p)).^[40]

Catalyst Preparation:

Catalyst was prepared using co-precipitation according to literature.^[7, 23, 41-43] In a typical synthesis a 150 mL solution of DI water containing 0.06 moles of $Mg(NO_3)_2 \cdot 6(H_2O)$, 0.025 moles of $Al(NO_3)_3 \cdot 9(H_2O)$, and 0.015 moles of $Cu(NO_3)_2 \cdot 3(H_2O)$ was added to a 187.5 mL solution of DI water containing 0.025 moles of Na_2CO_3 over the course of 1 hour at 60°C. The pH was kept at 10 by addition of a 250 mL 1 M NaOH solution. The combined solution was aged at 60°C for 24 h then washed and filtered. The filtered catalyst was dried in a 110°C oven overnight. The dried catalyst was calcined by ramping to 460°C at 5°C min⁻¹ then holding at 460°C for 12 hours in an air atmosphere.

The calcined catalyst contains CuO sites rather metallic Cu which is required for hydrogenation reactions.^[44] In typical SCM-DHDO the catalyst is reduced in-situ from hydrogen reformed from methanol. However, in-situ reduction introduces an induction period during which the catalyst will act as a solid base/acid that can catalyze aldol and retro-aldol condensation reactions, but is inactive for hydrogenating alkenes, ketones, or aldehydes. To remove this induction period we reduced the calcined catalyst at 350°C in a flow through cell for 4 hours with a 1°C min⁻¹ temperature ramp using 100 mL min⁻¹ of H₂. The reduced catalyst was cooled to room temperature and then passivated by alternating 100 mL min⁻¹ flows of Ar and 1% O₂/balance Ar over the catalyst 7 times. 1% O₂/balance Ar was then flowed over the catalyst for 1 hour before removing the catalyst from the cell. Reduced and passivated catalysts were used immediately after preparation to reduce oxidation from the atmosphere over time. X-ray diffraction of the reduced and passivated catalyst confirmed that the surface contained well dispersed Cu⁰ sites. XRD was performed with a Bruker D8 Discover diffractometer using a Cu Ka source $(\lambda = 1.54184 \text{ Å})$. Scans were collected via an area detector with 300 s acquisition time to obtain data from 5 to $80^{\circ} 2\theta$ in 3 steps of 25° . Unless noted otherwise, all catalysts in this study were reduced and passivated to keep the Cu oxidation state consistent between reactions.

Results and Discussion:

Conversion of cellulose with pre-reduced catalyst

Table 1 shows the SCM-DHDO of cellulose with a pre-reduced catalyst and a calcined (nonreduced) catalyst. The pre-reduced catalyst had higher overall carbon yield and selectivity to mono-alcohols than the calcined catalyst and better selectivity to GC-FID identifiable products. The carbon yield is defined as moles of carbon in GC detected products divided by the moles of carbon in the cellulose. The carbon yields are above 100% because of methanol incorporation into the products.^[23] The carbon yield to total detectable products increased from 90% to 119% and the selectivity to mono-alcohols increased from 28% to 48% after pre-reducing the catalyst. The selectivity to diols decreases after pre-reduction from 24% to 14% and selectivity to esters and ethers remain essentially constant. Reactions with calcined catalyst after 8 hours reaction time had lower carbon yield and product selectivity than the pre-reduced catalyst.

Table 1. Total carbon yield and selectivity for SCM-DHDO of cellulose with calcined catalyst and pre-reduced catalyst.

| | Calcined ^[a] | Reduced and | | | | |
|--|-------------------------|-------------|--|--|--|--|
| | Calcilleu | passivated | | | | |
| Total carbon yield (%C) ^[b] | 90 (0.5) | 119 (1.7) | | | | |
| Selectivity-%C by carbon number of product (standard error) | | | | | | |
| C ₂ oxygenates | 5 (0.3) | 9 (0.1) | | | | |
| C ₃ oxygenates | 10 (0.0) | 12 (0.0) | | | | |
| C ₄ oxygenates | 26 (0.3) | 28 (0.1) | | | | |
| C ₅ oxygenates | 15 (0.1) | 14 (0.1) | | | | |
| C ₆ oxygenates | 7 (0.1) | 10 (0.0) | | | | |
| Unspecified C ₂ -C ₆ + alcohols, esters, and ethers ³ | 38 (0.7) | 27 (0.0) | | | | |
| Selectivity-%C by product type (standard error) | | | | | | |
| Mono-alcohols | 28 (0.9) | 48 (0.1) | | | | |
| Diols | 24 (0.3) | 14 (1.0) | | | | |
| Ethers | 6 (0.1) | 6 (0.0) | | | | |
| Esters | 4 (0.0) | 5 (0.0) | | | | |
| Unspecified C_2 - C_{6+} alcohols, esters, and ethers ^[c] | 38 (0.7) | 27 (0.0) | | | | |

^[a]calcined data is from 4 h time point during previous study²³

^[b]Total carbon yield = moles C in all detected product/moles C in feed molecule. Total carbon yield is above 100% because methanol is incorporated into the products.

^[c]Unspecified products are observed in the GC-FID, but cannot be identified due to other similar mass spectra or a lack of reference spectra

Higher MW products, which are not detectable by GC, can form by condensation of ketones and aldehydes such as dihydroxyacetone.^[45] We analyzed the liquid products using Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) to evaluate the higher MW products. Products below 100 Da are not seen due to a low MW cutoff in the FT-ICR MS. Because of this, most liquid products observed in the GC are not observed by FT-ICR MS and vice versa. Based on the retention time of products around the low MW cutoff, approximately 13 to 24% of the GC observable products may be observed in the FT-ICR MS while C₁₀₊ polyoxygenates seen in the FT-ICR MS are likely not seen in the GC. The carbon, oxygen, and double bond equivalents of the high MW products from cellulose using calcined and pre-reduced catalyst are shown in Figure 1. The liquid products from the reaction with pre-reduced catalyst (c,d) have much lower oxygen content, carbon number, and double bond equivalents (DBE) than the products with calcined catalyst (a,b). The spectra from the pre-reduced catalyst has a large peak at 7C, 2O, and 1 DBE, but only smaller peaks in the rest of the spectra. The overall intensity of spectra with pre-reduced catalyst was very low due to a lack of observed species. Many of these peaks may be due to background noise. Conversely the spectra from the calcined catalyst (a, b) has two main

peaks centered at 12C, 2O, 4 DBE and 26C, 3O, 9 DBE with a broad distribution of similarly sized products. The DBE increases linearly with increasing carbon size at a ratio of approximately 0.4:1. The high number of DBE and low oxygen content (1-4 oxygen) suggests that these high MW products are primarily 1 to 2 ring aromatics with a small amount of 3+ ring aromatics. The lack of these species in the products using the pre-reduced catalyst suggests that the initial hydrogenation activity of the catalyst is necessary to decrease selectivity to this side reaction.



Figure 1. FT-ICR MS results from 4 hour SCM-DHDO reaction with cellulose using calcined $CuMgAlO_x$ catalyst (a,b) and reduced and passivated $CuMgAlO_x$ catalyst (c,d). Carbon number vs. oxygen (a,c) double bond equivalents (b,d).

Conversion of dihydroxyacetone and glucose with calcined catalyst

SCM-DHDO with dihydroxyacetone and glucose using the calcined catalysts were done to test whether high MW products are produced. The FT-ICR MS spectra of products from SCM-DHDO of dihydroxyacetone and glucose with the unreduced catalyst are shown in Figure 2 a-d. Glucose was used to examine the possibility of oligomerization of soluble sugars after depolymerization. Dihydroxyacetone was used to examine the possibility of condensation of ketones after retro-aldol condensation of glucose. Oligomerization of glucose would be expected to produce distinct peaks centered at C₆, C₁₂, or C₁₈ while condensation of dihydroxyacetone should produce a complicated mixture of aromatics.^[45, 46] The high molecular weight products from glucose and dihydroxyacetone appear to be similar in composition with carbon numbers from 8 to 36, oxygen numbers from 0 to 6, and double bond equivalents (DBE) from 2 to 14. Most products from glucose and dihydroxyacetone are concentrated around 24C, 2O, and 9DBE, although glucose appears to have slightly lower oxygen content and fewer DBE than dihydroxyacetone. The products from dihydroxyacetone and glucose are slightly different than the products from cellulose using the calcined catalyst in Figure 1 which has the high MW products centered at 12C, 2O, and 4DBE. However, the DBE of the products from all 3 feeds appear to increase with carbon number with a similar slope (~0.4 to 0.47 DBE:C) which suggests that the products are similar in functionality. The ratio of DBE to carbon and the low amount of oxygen at high carbon numbers suggest these products are linked aromatic or furanic units.

Glucose is known to produce humins via a reaction pathway through hydroxymethylfurfural (HMF).^[47-49] However, SCM-DHDO of HMF is selective to hexanols and methyl branched tetrahydrofuran which make it doubtful that this is the pathway to high MW products.^[23, 50] Another possible pathway is condensation of ketones which can produce high carbon number aromatic compounds.^[51-54] This pathway is the most likely as it is supported by our observation of high MW products from conversion of hydroxyacetone and is in agreement with previous work on conversion of sugars to oxygenated aromatics.^[45, 46]



Figure 2. FT-ICR MS results (Carbon number vs. oxygen and double bond equivalents) from 4 hour SCM-DHDO reaction with dihydroxyacetone (a-b) and glucose (c-d). Reaction Conditions: 300° C, 100 mg model compound, 100 unreduced CuMgAlO_x, 2.4 g methanol, dodecane tracer.

SCM-DHDO of mono-alcohols

The rate of C-C coupling of mono-alcohols with methanol and C-C scission of mono-alcohols is shown in Figure 3. Products from these reactions were produced by four reactions: 1) C-C coupling between a reactant alcohol and methanol, 2) C-C scission between an alcohol group and a neighboring carbon of the reactant alcohol, 3) dehydrogenation of a secondary alcohol to a ketone, and 4) esterification of a reactant alcohol to a methyl ester. The rates of dehydrogenation and esterification were verified to be near equilibrium by calculating the $Q_{reaction}$ (the mole fraction of products divided by mole fraction of reactants) and dividing this value by the equilibrium constant (K_{equil}). A value of $Q_{reaction}/K_{equil}=1$ indicates the reaction is at equilibrium. The effluent composition from esterification to methyl acetate and propanol esterification to methyl propanoate are 29.5 kJ mol⁻¹ and 35.1 kJ mol⁻¹ respectively. While the standard Gibbs free energy for dehydrogenation of isopropanol to acetone and 2-butanol to butanone are 25.7 kJ mol⁻¹ and 20.2 kJ mol⁻¹ respectively, indicating the equilibrium conversion for dehydrogenation at these conditions is low.

C-C coupling reactions were observed between the mono-alcohols and methanol. The chemistry that is occurring during C-C coupling appears to be similar to Guerbet chemistry of ethanol conversion into higher alcohols.^[55-57] The rate of C-C coupling to the mono-alcohols is similar to the rate of Guerbet coupling of ethanol with copper catalysts in the literature.^[33] The first step involves dehydrogenation of the reactant alcohol to an aldehyde or ketone followed by keto-enol tautomerization to the enol.^[58] Since methanol cannot form an enol, formaldehyde is always the electrophile during condensation. C-C coupling is also only observed at the α carbon which is consistent with Guerbet chemistry. C-C coupling of methanol with primary alcohols appears to be slower than C-C coupling of methanol with secondary alcohols (0.34-0.71 STY for primary alcohols vs. 0.77-1.81 STY of secondary alcohols). The difference in rates may be due to the relative concentration of the ketone compared to the aldehyde. The ketone is always present in thermodynamic equilibrium with the alcohol, but aldehydes are not observed. The absence of aldehydes appears to be due to a more favorable dehydrogenative coupling pathway methanol with the feed alcohol to form a methyl ester rather than the aldehyde. Dehydrogenative coupling of alcohols to esters is catalyzed by Cu and is reversible through hydrogenation of the ester over Cu.^[59, 60] The absence of the aldehyde in solution could account for the lower rate of C-C coupling with primary alcohols. The Gibbs free energy for C-C coupling of ethanol with methanol to form propanol and water is -60.6 kJ mol⁻¹ indicating that C-C coupling is thermodynamically favorable.

We observed C-C scission of the secondary alcohols to an alcohol and an alkane. C-C scission of the primary alcohols also likely takes place. However, scission of the primary alcohols would produce methanol which cannot be quantified and an alkane which is in the gas phase which was not analyzed. C-C scission appears to take place through C-C hydrogenolysis although the specific reaction mechanism is not known. C-C scission always takes place between the hydroxyl carbon and either of the α carbons. C-C scission is never observed between C-C bonds two bonds away from the C-O. For example, C-C scission of 2-butanol only produces 1-propanol and ethanol and never produces isopropanol. The Gibbs free energy of C-C scission of ethanol to methanol and methane is -51.4 kJ mol⁻¹ indicating that C-C scission is also thermodynamically favorable. Dehydration of the mono-alcohols was not quantified as the gas phase was not analyzed. The Gibbs free energy of dehydration and hydrogenation of ethanol to ethane is -102.7 kJ mol⁻¹ which is also thermodynamically favorable.

We also performed reactions with select aldehydes, ketones, and methyl esters to demonstrate that dehydrogenation to aldehydes and ketones and dehydrogenative coupling to esters are reversible. The results from these reactions are included in the supplemental information in Table S1 and S2. The results show that aldehydes are rapidly converted to alcohols and methyl esters or condense with methanol to form higher alcohols. Ketones are converted to secondary alcohols or condense with methanol to form higher alcohols. Methyl esters are hydrogenated to alcohols although this reaction is slower than hydrogenation of aldehydes and ketones.



Figure 3. Space time yields for SCM-DHDO of mono-alcohols. Space time yields are limited to C-C addition and C-C scission products since dehydration cannot be accurately quantified and dehydrogenative reactions are in equilibrium. Reaction Conditions: 300°C, 1 hour, 100 mg model compound, 50 mg reduced and passivated CuMgAlO_x, 2.4 g methanol, dodecane tracer.

SCM-DHDO of polyols

Our previous study of SCM-DHDO of dihydroxyacetone showed that C_3 oxygenates produce a similar product distribution as SCM-DHDO of cellulose.^[23] In this paper we started with glycerol as a model compound for cellulose rather than dihydroxyacetone. Glycerol was found to produce a similar product distribution as dihydroxyacetone and cellulose. During conversion of glycerol we observed a number of intermediates including 1,2-ethanediol and methyl lactate that when converted on their own produced a similar product distribution to glycerol as shown in Table 2. The primary products are C₄ alcohols including isobutanol (6.9% to 19.3% carbon yield), 2-butanol (6.1% to 8.1% carbon yield), and 2,3-butanediol (3.3% to 6.5% carbon yield). Monoalcohols are the most abundant product type (57% to 97% carbon yield) and contain a mixture of linear and methyl branched primary and secondary alcohols. The highest carbon yield is

obtained with 1,2-ethanediol as the reactant demonstrating that this feed has the largest amount of methanol incorporation. SCM-DHDO of these four reactants produce a similar product distribution suggesting that there exists a common reaction pathway between them. A possible common intermediate is 1,2-propanediol. This molecule can be produced from dehydration and hydrogenation of glycerol, dehydrogenation of 1,2-ethanediol followed by aldol condensation with methanol, or hydrogenation of methyl lactate.^[60] In order for these reactants to give similar products, the dehydration of glycerol, C-C coupling with 1,2-ethanediol, and hydrogenation of methyl lactate must be rapid.

| Table 2. SCM-DHDO carbon yield from cellulose, glycerol, 1,2-ethanediol, and methyl lactate. |
|--|
| Reaction conditions. 300°C, 4 hours, 100 mg feed compound, 100 mg CuMgAlOx pre-reduced, |
| 2.4 g methanol, dodecane tracer. |

| Feed | Cellulose | Glycerol | 1,2-ethanediol | Methyl lactate | | |
|---|---|----------|----------------|----------------|--|--|
| Total carbon yield (%C) ^[a] | 119 | 139 | 155 | 140 | | |
| | Selectivity-%C by carbon number of product (standard error) | | | | | |
| C ₂ | 9.2 | 10.7 | 16.3 | 12.4 | | |
| C ₃ | 12.3 | 13.1 | 18.1 | 15.6 | | |
| C4 | 27.8 | 41.0 | 38.2 | 38.9 | | |
| C ₅ | 13.7 | 16.7 | 13.2 | 13.6 | | |
| C_6 | 10.4 | 3.2 | 2.2 | 3.5 | | |
| Unspecified C ₂ -C ₆₊ alcohols, | | | | | | |
| esters, and ethers | 26.6 | 15.3 | 12.2 | 16.0 | | |
| | Selectivity-%C by product type (standard error) | | | | | |
| Mono-alcohols (%C) | 48.2 | 61.4 | 59.6 | 63.4 | | |
| Diols (%C) | 13.7 | 18.1 | 17.2 | 8.4 | | |
| Esters (%C) | 6.1 | 2.7 | 4.8 | 2.0 | | |
| Ethers (%C) | 5.0 | 2.2 | 6.3 | 8.7 | | |
| Ketones (%C) | 0.5 | 0.4 | 0.0 | 1.6 | | |
| | | | | | | |
| Most abundant products | | | | | | |
| Primary alcohols | | | | | | |
| Ethanol (%C) | 9.2 | 10.2 | 16.3 | 12.1 | | |
| 1-propanol (%C) | 4.6 | 6.3 | 6.2 | 7.0 | | |
| 1-butanol (%C) | 3.3 | 1.7 | 2.5 | 2.7 | | |
| 1-pentanol (%C) | 2.1 | 0.8 | 1.4 | 0.7 | | |
| 1-hexanol (%C) | 2.7 | 0.3 | 0.2 | 0.3 | | |
| Secondary alcohols | | | | | | |
| 2-butanol (%C) | 6.1 | 7.4 | 8.0 | 8.1 | | |
| 2-pentanol (%C) | 3.0 | 4.0 | 3.1 | 3.8 | | |
| 3-hexanol (%C) | 2.3 | 1.1 | 0.8 | 1.1 | | |
| 2-hexanol (%C) | 1.8 | 0.4 | 0.4 | 0.4 | | |
| Methyl branched alcohols | | | | | | |
| Isobutanol (%C) | 6.9 | 19.3 | 14.2 | 17.5 | | |
| 2-methyl-butanol (%C) | 2.7 | 6.3 | 4.1 | 6.3 | | |
| 2-methyl-pentanol (%C) | 1.7 | 1.4 | 0.8 | 1.7 | | |
| Diols | | | | | | |
| 2-methyl-1,2-propanediol (%C) | 1.2 | 4.0 | 4.4 | 1.7 | | |
| 2,3-butanediol (%C) | 6.1 | 6.5 | 6.4 | 3.3 | | |
| 1,2-butanediol (%C) | 1.8 | 0.7 | 0.9 | 0.3 | | |
| 2,3-pentanediol (%C) | 3.3 | 5.5 | 3.8 | 2.8 | | |
| Sum of abundant products (%C) | 59.0 | 76.1 | 73.4 | 69.9 | | |

^[a]Total carbon yield = moles C in all detected product/moles C in feed molecule. Total carbon yield is above 100% because methanol is incorporated into the products.

Identification of Reaction Pathway for SCM-DHDO of diols

We measured the product selectivity for SCM-DHDO of 1,2-ethanediol (1,2-EDO), 1,2propanediol (1,2-PDO), 1,2-butanediol (1,2-BDO), 2,3-butanediol (2,3-BDO), and glycerol (Gly) at 10%, 30%, and 50% conversion to further investigate the reaction pathway. The products from the reaction at 30% conversion are shown in Table S3 and the yield of products to the different reaction pathways at 10%-50% conversion are shown in Figure S1. The main products from the diols are formed from C-C coupling of the diol with methanol resulting in products such as 2,3butanediol or 2,3 pentanediol. Large amounts of ketones (hydroxyacetone) and esters (methyl lactate) are also produced from the diols by dehydrogenation and esterification pathways respectively. The yield of products towards the dehydrogenation pathway decreases as conversion increases from 10% to 50% showing that dehydrogenation is reversible as more methanol is reformed. The yield of products towards esterification increases from 10 to 30% conversion, but either remains constant or decreases from 10% to 50% indicating esterification of the feed alcohols is near equilibrium. The major products from glycerol include hydroxyacetone > methyl-lactate >1,2-propanediol. Mono-alcohols are produced in small quantities from C-C scission or dehydration. The reactions observed with diols are the same as the mono-alcohols. We only studied vicinal diols since these were the only diols observed during SCM-DHDO of cellulose. Since the diols are vicinal, C-C scission cannot take place via retroaldol condensation which requires a β -hydroxy ketone. Thermodynamic properties of large oxygenates such as 2,3-pentanediol, 3-methyl-1,2-butanediol, 1-hydroxy-butanone, and 2hydroxy-methyl butyrate are not available in the Aspen database so the thermodynamics of the reactions with these compounds were calculated using Gaussian 09 software. Calculations of compound energies in Gaussian assume a vacuum so the contribution of pressure was not accounted for. The thermodynamics of all studied reactions are included in Table S4 in the supplemental information.

Using the data from Table S1 we have put together a reaction pathway for SCM-DHDO of glycerol shown in Figure 4. Figure 4 assumes that the catalyst has been reduced before reaction. Without pre-treatment the conversion of glycerol would still occur through the same pathway, but reactions that occur over Cu sites would not be catalyzed the copper oxide had been reduced to Cu metal by hydrogen generated from methanol reforming. Glycerol undergoes two possible reactions, either dehydration to hydroxyacetone (ΔG =-65.4 kJ mol⁻¹) or C-C scission to 1,2-ethanediol (ΔG =-18.2 kJ mol⁻¹). 1,2-ethanediol is dehydrated and hydrogenated to ethanol (ΔG =-106.1 kJ mol⁻¹) or undergoes C-C coupling with methanol to produce 1,2-propanediol. Hydroxyacetone also produces 1,2-propanediol via hydrogenation (ΔG =-19.5 kJ mol⁻¹). 1,2-propanediol can dehydrogenate back to hydroxyacetone or esterify to methyl lactate via dehydrogenative coupling although the ΔG for both of these reactions is greater than 0 (ΔG =-19.5 and 20.8 kJ mol⁻¹) and undergoes C-C scission to form ethanol and methanol (ΔG =-100.0 kJ mol⁻¹) and undergoes C-C scission to form ethanol and methanol (ΔG =-39.4 kJ mol⁻¹) or 1,2-ethanediol and methane (ΔG =-57.4 kJ mol⁻¹). 1,2-propanediol produces 2,3-butanediol through C-C coupling at the first position (ΔG =-103.9 kJ mol⁻¹) or 1,2-butanediol

Accepted Manuscript

 $(\Delta G = -74.3 \text{ kJ mol}^{-1})$ by C-C coupling at the third position. No C-C coupling is observed at the tertiary carbon due to the lack of the hydrogen atoms necessary for facile coupling.^[61] 1,2butanediol and 2,3-butanediol undergo dehydrogenation (ΔG =-38.2 kJ mol⁻¹ and ΔG =51.4 kJ mol⁻¹ respectively) to produce 1-hydroxy-butanone or 3-hydroxy-butanone. 1,2-butanediol undergoes esterification (ΔG =-29.9 kJ mol⁻¹) to produce 2-hydroxy-methyl butyrate. 1,2butanediol forms 1-butanol via dehydration (ΔG =-83.6 kJ mol⁻¹) or 1-propanol and methanol via C-C scission between the first and second positions (ΔG =-25.7 kJ mol⁻¹). 1,2-butanediol also produces 1,2-ethanediol and ethane from C-C scission between the second and third positions $(\Delta G=-34.5 \text{ kJ mol}^{-1})$. No products from scission between the third and fourth positions of 1,2butanediol are observed which is consistent with the observation from the mono-alcohols that the mechanism of C-C scission requires scission adjacent to a C-O. 1,2-butanediol also undergoes C-C coupling at the first position to produce 2,3-pentanediol (ΔG =-50.8 kJ mol⁻¹) or C-C coupling at the third position to 3-methyl-1,2-butanediol (ΔG =-28.7 kJ mol⁻¹). 2,3-butanediol undergoes C-C coupling at the first or fourth positions to produce 2,3-pentanediol (ΔG =-37.1 kJ mol⁻¹). Diols larger than 2,3-pentanediol cannot be differentiated using the GCMS method used in this paper so the products after C-C coupling to 2,3-pentanediol and 3-methyl-1,2-butanediol are not known. 2,3-butanediol is converted to 2-methyl-1,2-propanediol via a methyl shift (ΔG=28.8 kJ mol⁻¹). No methyl shift was observed in the other model compounds. 2-methyl-1,2-propanediol is dehydrated to isobutanol (ΔG =-54.0 kJ mol⁻¹) and 2.3-butanediol is dehydrated to 2-butanol $(\Delta G=-68.1 \text{ kJ mol}^{-1})$. Ethanol is produced from C-C scission of 2,3-butanediol between the second and third positions (ΔG =-8.3 kJ mol⁻¹) while 1,2-propanediol is produced from C-C scission of 2,3-butanediol between the first and second positions (ΔG =-20.3 kJ mol⁻¹). As larger alcohols are produced more C-C scission products are possible. 2,3-pentanediol can undergo C-C scission at 3 positions to produce either 1,2-butanediol and methane, 1,2-propanediol and ethane, or 1-propanol and ethanol. Figure 4 is not comprehensive as the mono-alcohols can undergo C-C coupling, C-C scission, dehydrogenation, esterification, and dehydration reactions.



Figure 4. Reaction pathway from glycerol to mixture of mono-alcohols, diols, and esters with the Gibbs free energy of reaction at standard conditions shown.

In Figure 5 we report the measured space time yields (STY) of each reaction pathway (measured at 30% conversion). The STY of dehydrogenation and esterification are not shown due to the reactions being near equilibrium. Glycerol can undergo either dehydration (251 STY) or C-C scission (27 STY). Dehydration of glycerol is the fastest observed reaction. C-C coupling of 1,2-ethanediol with methanol to produce 1,2-propanediol (58 STY) is fast compared to dehydration/hydrogenation of 1,2-ethanediol to ethanol (4.4 STY). 1,2-propanediol undergoes fast C-C coupling at the first position to 2,3-butanediol (69 STY) or slower C-C coupling at the third position to produce 1,2-butanediol (15 STY). C-C scission of 1,2-propanediol occurs between either the first and second positions to produce ethanol (23 STY) or between the second and third positions to produce 1,2-ethanediol (8.8 STY). Dehydration/hydrogenation of 1,2-propanediol 1,2-propanediol to 1-propanol (5.3 STY) is the slowest observed reaction from 1,2-propanediol. 1,2-propanediol to 1-propanol (5.3 STY) is the slowest observed reaction from 1,2-propanediol. 1,2-butanediol also undergoes fast C-C coupling at the first position to 2,3-pentanediol (98 STY) or slower C-C scission of 1,2-propanediol. 1,2-butanediol also undergoes fast C-C coupling at the first position to 2,3-pentanediol (98 STY) or slower C-C scission of 1,2-propanediol. 1,2-butanediol also undergoes fast C-C coupling at the first position to 2,3-pentanediol (98 STY) or slower C-C scission of 1,2-propanediol. 1,2-butanediol also undergoes fast C-C coupling at the first position to 2,3-pentanediol (18 STY). C-C scission of slower C-C scission of 1,2-propanediol. 1,2-butanediol also undergoes fast C-C coupling at the first position to 2,3-pentanediol (98 STY) or slower C-C coupling at the third position to 3-methyl-1,2-butanediol (18 STY). C-C scission of

1,2-butanediol occurs either between the first and second positions to produce 1-propanol (27 STY) or between the second and third positions to produce 1,2-ethanediol (11 STY). 1,2butanediol can also dehydrate to 1-butanol (3.3 STY). 2,3-butanediol undergoes C-C coupling at either the first or fourth positions to produce 2,3-pentanediol (14 STY). 2,3-butanediol undergoes C-C scission between the first and second positions to produce 1,2-propanediol (13 STY) or between the second and third positions to produce ethanol (22 STY). 2,3-butanediol undergoes a methyl shift to produce 2-methyl-1,2-propanediol (89 STY). 2,3-butanediol can also dehydrate to produce 2-butanol (5.5 STY).

The analysis of STY of the model compounds shows that SCM-DHDO of a poly-ol occurs through multiple reactions. Dehydration of glycerol is the fastest observed reaction, but dehydration of the resulting diols is slow (3.3-5.5 STY). C-C coupling is the next fastest reaction and occurs primarily at the first position of a primary diol (58-98 STY) or secondarily at a methyl carbon at the α position of a primary or secondary diol (14-18 STY). C-C coupling at the first position of a primary diol is consistently 4-5 times faster than C-C coupling at the methyl carbon. The difference in rate could be due to an electronic effect where the carbanion that performs nucleophilic attack of the formaldehyde during C-C coupling is stabilized by the hydroxyl group.^[41, 58] The methyl shift on 2,3-butanediol is the next fastest reaction (89 STY). By comparing the rate of the methyl shift to the rate of C-C coupling to 1-propanol in Figure 3 (0.71 STY) it is clear that methyl branching is primarily due to a methyl shift in the secondary diol rather than condensation of methanol and a mono-alcohol. C-C scission only occurs between carbons adjacent to an alcohol group and is faster between vicinal alcohol groups (22-27 STY) than a methyl and a hydroxyl carbon (8.8-13 STY). Analysis of STY shows that C-C scission of diols is the primary route to mono-alcohols rather than dehydration. Comparing the STY in Figure 5 to the STY in Figure 3 shows that the rate of C-C coupling and C-C scission of diols is 1 to 2 orders of magnitude faster than to mono-alcohols.



Figure 5. Reaction network and space time yields $(\text{mmol}_{\text{product}} \text{ mmol}_{\text{reactant}}^{-1} \text{ g}_{\text{catalyst}}^{-1} \text{ h}^{-1})$ for SCM-DHDO of C₂-C₄ oxygenates. The width of each arrow is proportional to the rate of reaction. ΔG° is in kJ mol⁻¹. **Reaction Conditions**: 300°C, 100 mg model compound, 10 mg reduced and passivated CuMgAlO_x, 2.4 g methanol, dodecane tracer.

The results from measuring the rates of each model compound elucidate many interesting insights about the SCM-DHDO chemistry. A downside of many hydrodeoxygenation reactions is that the reactions produce lower value alkanes rather than alcohols.^[62-64] In SCM-DHDO dehydration/hydrogenation is the slowest observed reaction and mono-alcohols are primarily produced from C-C scission of a diol rather than dehydration which makes mono-alcohols relatively stable end products. The reaction rates explain why conversion in SCM-DHDO is so rapid at early reaction times but the products are stable at long reaction times. Initially the products are more highly oxygenated which leads to the rapid dehydration observed in glycerol. The resulting primary diols such as 1,2-ethanediol, 1,2-propanediol, and 1,2-butanediol undergo C-C coupling which produces the less reactive secondary diols which eventually undergo C-C scission to mono-alcohols which are the least reactive species.

Conclusion

This study elucidated some of the key chemistry occurring during SCM-DHDO of biomass. Prereducing the catalyst increases carbon yield to identifiable products by approximately 35% and decreases selectivity to side reactions that produce high MW products by increasing the hydrogenation activity of the catalyst during early reactions times. High MW products are likely produced from rapid condensation of intermediate oxygenates at short reaction times to produce recalcitrant cyclic aromatics. The reaction pathway for SCM-DHDO of cellulose occurs through C-C cleaving retro-aldol condensation reactions to produce intermediate C₃ oxygenates like dihydroxyacetone and glycerol followed by either condensation of these intermediates to high MW species or dehydration to diols. These diols then undergo C-C coupling with methanol into C₄-C₆ diols which undergo C-C scission reactions to mono-alcohols. The high amount of methanol incorporation observed during conversion of biomass is due to C-C coupling of methanol with diols. The rate of condensation of methanol with diols is approximately 10-100 times faster than methanol coupling with other mono-alcohols. Mono-alcohols are primarily produced via C-C scission between vicinal diol groups and not by dehydration. The rate of C-C scission of diols is approximately 10 times faster than dehydration/hydrogenation of the diols. Methyl branched alcohols are produced from a methyl shift in a secondary diol followed by dehydration. Thermodynamic and kinetic data show that both dehydrogenation and esterification of diols and mono-alcohols are reversible under the reaction conditions. The rate of conversion of mono-alcohols is 10-100 times slower than the other steps indicating that mono-alcohols can be produced in high selectivities with SCM-DHDO reactions.

Acknowledgements

This work was supported by ExxonMobil. We would like to acknowledge Michael P. Lanci from ExxonMobil for his helpful discussion during this study. Calculations using Gaussian were performed by Nathaniel Eagan in the George Huber group. The authors gratefully acknowledge use of facilities and instrumentation supported by NSF through the University of Wisconsin Materials Research Science and Engineering Center (DMR-1121288).

Supporting Information

Product selectivities and conversions from model compound studies of C_3 oxygenates. Selectivity to reaction pathways at 10-50% conversion. Thermodynamics of reactions with C_2 - C_4 oxygenates and single alcohols.

References

G. W. Huber, S. Iborra, A. Corma, Synthesis of Transportation Fuels from Biomass: [1] Chemistry, Catalysts, and Engineering. Chem. Rev. 2006, 106 (9), 4044-4098. L. Wu, T. Moteki, A. A. Gokhale, D. W. Flaherty, F. D. Toste, Production of Fuels and [2] Chemicals from Biomass: Condensation Reactions and Beyond. Chem 2016, 1 (1), 32-58. [3] Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu, J. A. Dumesic, Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates. *Nature* **2007**, *447* (7147), 982-985. S. Van Den Bosch, W. Schutyser, R. Vanholme, T. Driessen, S. F. Koelewijn, T. [4] Renders, B. De Meester, W. J. J. Huijgen, W. Dehaen, C. M. Courtin, B. Lagrain, W. Boerjan, B. F. Sels, Reductive lignocellulose fractionation into soluble lignin-derived phenolic monomers and dimers and processable carbohydrate pulps. *Energy Environ. Sci.* **2015**, *8*, 1748-1763. E. M. Anderson, M. L. Stone, R. Katahira, M. Reed, G. T. Beckham, Y. Roman-Leshkov, [5] Flowthrough Reductive Catalytic Fractionation of Biomass. Joule 2017, 1 (3), 613-622. A. B. Barrett, Y. Gao, C. M. Bernt, M. Chui, A. T. Tran, M. B. Foston, P. C. Ford, [6] Enhancing Aromatic Production from Reductive Lignin Disassembly: in Situ O-Methylation of Phenolic Intermediates. ACS Sustain. Chem. Eng. 2016, 4 (12), 6877-6886. K. Barta, T. D. Matson, M. L. Fettig, S. L. Scott, A. V. Iretskii, P. C. Ford, Catalytic [7] disassembly of an organosolv lignin via hydrogen transfer from supercritical methanol. Green Chem. 2010, 12 (9), 1640-1647. T. D. Matson, K. Barta, A. V. Iretskii, P. C. Ford, One-Pot Catalytic Conversion of [8] Cellulose and of Woody Biomass Solids to Liquid Fuels. J. Am. Chem. Soc. 2011, 133 (35), 14090-14097. [9] J. T. Kozlowski, R. J. Davis, Heterogeneous Catalysts for the Guerbet Coupling of Alcohols. ACS Catal. 2013, 3 (7), 1588-1600. [10] R. M. West, E. L. Kunkes, D. A. Simonetti, J. A. Dumesic, Catalytic conversion of biomass-derived carbohydrates to fuels and chemicals by formation and upgrading of monofunctional hydrocarbon intermediates. Catal. Today 2009, 147 (2), 115-125. [11] W. C. Wang, L. Tao, J. Markham, Y. Zhang, E. Tan, L. Batan, E. Warner, M. Biddy, *Review of Biojet Fuel Conversion Technologies*; National Renewable Energy Laboratory: Golden, CO, 2016. [12] S. Kilambi, K. L. Kadam, Production of Fermentable Sugars and Lignin from Biomass Using Supercritical Fluids. U.S. Patent 8968479B2 Mar 3, 2015. D. Humbird, R. Davis, L. Tao, C. Kinchin, D. Hsu, A. Aden, Process Design and [13] Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol: Dilute-Acid Pretreatment and Enzymatic Hydrolysis of Corn Stover; National Renewable Energy Laboratory: 2011. [14] R. Davis, L. Tao, C. Scarlata, E. C. D. Tan, J. Ross, J. Lukas, D. Sexton, Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbons: Dilute-Acid and Enzymatic Deconstruction of Biomass to Sugars and Catalytic Conversion of Sugars to Hydrocarbons; National Renewable Energy Laboratory: Golden, CO, 2015. T. R. Carlson, G. A. Tompsett, W. C. Conner, G. W. Huber, Aromatic Production from [15] Catalytic Fast Pyrolysis of Biomass-Derived Feedstocks. Top. Catal. 2009, 52, 241. A. V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading. *Biomass* [16] Bioenergy 2012, 38, 68-94.

[17] Y. Wu, F. Gu, G. Xu, Z. Zhong, F. Su, Hydrogenolysis of cellulose to C4–C7 alcohols over bi-functional CuO–MO/Al2O3 (M = Ce, Mg, Mn, Ni, Zn) catalysts coupled with methanol reforming reaction. *Bioresour. Technol.* **2013**, *137*, 311-317.

[18] W. Yin, R. H. Venderbosch, G. Bottari, K. K. Krawzcyk, K. Barta, H. J. Heeres, Catalytic upgrading of sugar fractions from pyrolysis oils in supercritical mono-alcohols over Cu doped porous metal oxide. *Appl. Catal., B* **2015**, *166-167*, 56-65.

[19] X. Huang, T. I. Koranyi, M. D. Boot, E. J. M. Hensen, Catalytic Depolymerization of Lignin in Supercritical Ethanol. *ChemSusChem* **2014**, *7* (8), 2276-2288.

[20] K. Tajvidi, K. Pupovac, M. Kukrek, R. Palkovits, Copper-Based Catalysts for Efficient Valorization of Cellulose. *ChemSusChem* **2012**, *5* (11), 2139-2142.

[21] K. Barta, G. R. Warner, E. S. Beach, P. T. Anastas, Depolymerization of organosolv lignin to aromatic compounds over Cu-doped porous metal oxides. *Green Chem.* **2014**, *16*, 191-196.

[22] G. S. Macala, T. D. Matson, C. L. Johnson, R. S. Lewis, A. V. Iretskii, P. C. Ford, Hydrogen Transfer from Supercritical Methanol over a Solid Base Catalyst: A Model for Lignin Depolymerization. *ChemSusChem* **2009**, *2* (3), 215-217.

[23] P. H. Galebach, D. J. McClelland, N. M. Eagan, A. M. Wittrig, J. S. Buchanan, J. A. Dumesic, G. W. Huber, Production of Alcohols from Cellulose by Supercritical Methanol Depolymerization and Hydrodeoxygenation. *ACS Sustain. Chem. Eng.* **2018**.

[24] C. Montassier, D. Giraud, J. Barbier, Polyol Conversion by Liquid Phase Heterogeneous Catalysis Over Metals. *Stud. Surf. Sci. Catal.* **1988**, *41*, 165-170.

[25] J. Chaminand, L. Djakovitch, P. Gallezot, P. Marion, P. Pinel, C. Rosier, Glycerol hydrogenolysis on heterogeneous catalysts. *Green Chem.* **2004**, *6* (8), 359-361.

[26] Z. Yuan, J. Want, L. Wang, W. Xie, P. Chen, Z. Hou, X. Zheng, Biodiesel derived glycerol hydrogenolysis to 1,2-propanediol on Cu/MgO catalysts. *Bioresour. Technol.* **2010**, *101* (18), 7088-7092.

[27] S. Sato, M. Akiyama, R. Takahashi, T. Hara, K. Inui, M. Yokota, Vapor-phase reaction of polyols over copper catalysts. *Appl. Catal.*, A **2008**, *347* (2), 186-191.

[28] M. L. Dieuzeide, M. Jobbagy, N. Amadeo, Vapor-Phase Hydrogenolysis of Glycerol to 1,2-Propanediol over Cu/Al2O3 Catalyst at Ambient Hydrogen Pressure. *Ind. Eng. Chem. Res.* **2016**, *55* (9), 2527-2533.

[29] G. Y. Yang, Y. H. Ke, H. F. Ren, C. L. Liu, R. Z. Yang, W. S. Dong, The conversion of glycerol to lactic acid catalyzed by ZrO2-supported CuO catalysts. *Chem. Eng. J.* **2016**, *283*, 759-767.

[30] M. Checa, F. Auneau, J. Hidalgo-Carrillo, A. Marinas, J. M. Marinas, C. Pinel, F. J. Urbano, Catalytic transformation of glycerol on several metal systems supported on ZnO. *Catal. Today* **2012**, *196* (1), 91-100.

[31] T. Miyazawa, Y. Kusunoki, K. Kunimori, K. Tomishige, Glycerol conversion in the aqueous solution under hydrogen over Ru/C + an ion-exchange resin and its reaction mechanism. *J. Catal.* **2006**, *240* (2), 213-221.

[32] S. Qianhui, W. Shuai, L. Haichao, Selective Hydrogenolysis of Glycerol to Propylene Glycol on Supported Pd Catalysts: Promoting Effects of ZnO and Mechanistic Assessment of Active PdZn Alloy Surfaces. *ACS Catal.* **2017**, *7* (7), 4265-4275.

[33] Z. Sun, A. C. Vasconcelos, G. Bottari, M. C. A. Stuart, G. Bonura, C. Cannilla, F. Frusteri, K. Barta, Efficient Catalytic Conversion of Ethanol to 1-Butanol via the Guerbet

Reaction over Copper- and Nickel-Doped Porous. ACS Sustain. Chem. Eng. 2016, 5 (2), 1738-1746.

[34] D. Gabriels, W. Y. Hernandez, B. Sels, P. Van Der Voort, A. Verberckmoes, Review of catalytic systems and thermodynamics for the Guerbet condensation reaction and challenges for biomass valorization. *Catal. Sci. Technol.* **2015**, *5*, 3876-3902.

[35] J. J. Bravo-Suarez, B. Subramaniam, R. V. Chaudhari, Vapor-phase methanol and ethanol coupling reactions on CuMgAl mixed metal oxides. *Appl. Catal., A* 2013, 455, 234-246.
[36] P. A. Torresi, V. K. Díez, P. J. Luggren, J. I. Di Cosimo, Conversion of diols by dehydrogenation and dehydration reactions on silica-supported copper catalysts. *Appl. Catal., A* 2013, 458, 119-129.

[37] J. E. Miller, L. Evans, A. Littlewolf, D. E. Trudell, Batch microreactor studies of lignin and lignin model compound depolymerization by bases in alcohol solvents. *Fuel* **1999**, *78* (11), 1363-1366.

[38] Y. E. Corilo, *PetroOrg Software*, Florida State University: Tallahassee, FL, 2014.

[39] Aspen Plus. Aspen Plus Technology Inc,: Burlington, MA.

[40] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, *Gaussian 09*, Gaussian, Inc.: Wallingford, CT, 2016.

[41] J. I. Di Cosimo, V. K. Diez, M. Xu, E. Iglesia, C. R. Apesteguia, Structure and Surface and Catalytic Properties of Mg-Al Basic Oxides. *J. Catal.* **1998**, *178* (2), 499-510.

[42] W. T. Reichle, Synthesis of anionic clay minerals (mixed metal hydroxides, hydrotalcite). *Solid State Ionics* **1986**, 22 (1), 135-141.

[43] G. S. Macala, A. W. Robertson, C. L. Johnson, Z. B. Day, R. S. Lewis, M. G. White, A. V. Iretskii, P. C. Ford, Transesterification Catalysts from Iron Doped Hydrotalcite-like Precursors: Solid Bases for Biodiesel Production. *Catal. Lett.* **2008**, *122* (3), 205-209.

[44] M. V. Twigg, M. S. Spencer, Deactivation of supported copper metal catalysts for hydrogenation reactions. *Appl. Catal.*, A **2001**, *212* (1-2), 161-174.

[45] T. Popoff, O. Theander, E. Westerlund, Formation of Aromatic Compounds from Carbohydrates. VI. Reaction of Dihydroxyacetone in Slightly Acidic, Aqueous Solution. *Acta Chem. Scand.* **1978**, *32*, 1-7.

[46] C. D. Gutsche, D. Redmore, R. S. Buriks, K. Nowotny, H. Grassner, C. W. Armbruster, Base-Catalyzed Triose Condensations. *J. Am. Chem. Soc.* **1967**, *89* (5), 1235-1245.

[47] P. E. Shaw, J. H. Tatum, R. E. Berry, Acid-catalyzed degradation of d-fructose. *Carbohydr. Res.* **1967**, *5* (3), 266-273.

[48] S. Patil, C. Lund, Formation and Growth of Humins via Aldol Addition and Condensation during Acid-Catalyzed Conversion of 5-Hydroxymethylfurfural. *Energy Fuels* **2011**, *25* (10), 4745-4755.

[49] S. J. Dee, A. T. Bell, A Study of the Acid-Catalyzed Hydrolysis of Cellulose Dissolved in Ionic Liquids and the Factors Influencing the Dehydration of Glucose and the Formation of Humins. *ChemSusChem* **2011**, *4* (8), 1166-1173.

[50] K. Barta, P. C. Ford, Catalytic Conversion of Nonfood Woody Biomass Solids to Organic Liquids. *Acc. Chem. Res.* **2014**, *47* (5), 1503-1512.

[51] J. I. Di Cosimo, V. K. Díez, C. R. Apesteguía, Base catalysis for the synthesis of α , β unsaturated ketones from the vapor-phase aldol condensation of acetone. *Appl. Catal.*, A **1996**, *137* (1), 149-166.

[52] R. M. West, Z. Y. Liu, M. Peter, C. A. Gartner, J. A. Dumesic, Carbon–carbon bond formation for biomass-derived furfurals and ketones by aldol condensation in a biphasic system. *J. Mol. Catal. A: Chem.* **2008**, *296* (1-2), 18-27.

[53] L. Faba, E. Díaz, S. Ordóñez, Gas phase acetone self-condensation over unsupported and supported Mg–Zr mixed-oxides catalysts. *Appl. Catal., B* **2013**, *142-143*, 387-395.

[54] G. S. Salvapati, K. V. Ramanamurty, M. Janardanarao, Selective catalytic self-condensation of acetone. *J. Mol. Catal.* **1989**, *54* (1), 9-30.

[55] M. León, E. Díaz, S. Ordóñez, Ethanol catalytic condensation over Mg–Al mixed oxides derived from hydrotalcites. *Catal. Today* **2011**, *164* (1), 436-442.

[56] C. Carlini, M. M., M. Noviello, A. M. R. Galletti, G. Sbrana, F. Basile, A. Vaccari, Guerbet condensation of methanol with n-propanol to isobutyl alcohol over heterogeneous bifunctional catalysts based on Mg–Al mixed oxides partially substituted by different metal components. *J. Mol. Catal. A: Chem.* **2005**, *232* (1-2), 13-20.

[57] W. Ueda, T. O., T. Kuwabara, Y. Morikawa, Condensation of alcohol over solid-base catalyst to form higher alcohols. *Catal. Lett.* **1992**, *12* (1-3), 97-104.

[58] F. Lin, Y. Chin, Mechanism of intra- and inter-molecular CC bond formation of propanal on Brønsted acid sites contained within MFI zeolites. *Journal of Catalysis* 2014, *311*, 244-256.
[59] K. Inui, T. Kurabayashi, S. Sato, Direct Synthesis of Ethyl Acetate from Ethanol Carried

Out under Pressure. J. of Catal. **2002**, 212 (2), 207-215.

[60] H. Adkins, K. Folkers, The Catalytic Hydrogenation of Esters to Alcohols. J. Am. Chem. Soc. **1931**, *53* (3), 1095-1097.

[61] M. Xu, M. J. L. Gines, A. M. Hilmen, B. L. Stephens, E. Iglesia, Isobutanol and Methanol Synthesis on Copper Catalysts Supported on Modified Magnesium Oxide. *J. Catal.* **1997**, *171* (1), 130-147.

[62] B. O. D. Beeck, M. Dusselier, J. Geboers, J. Holsbeek, E. Morré, S. Oswald, L. Giebeler, B. F. Sels, Direct catalytic conversion of cellulose to liquid straight-chain alkanes. *Energy Environ. Sci.* **2015**, *8* (1), 230-240.

[63] S. Liu, Y. Okuyama, M. Tamura, Y. Nakagawa, A. Imai, K. Tomishige, Production of Renewable Hexanols from Mechanocatalytically Depolymerized Cellulose by Using Ir-ReOx/SiO2 catalyst. *ChemSusChem* **2014**, *8* (4), 628-635.

[64] G. W. Huber, J. N. Chheda, C. J. Barrett, J. A. Dumesic, Production of Liquid Alkanes by Aqueous-Phase Processing of Biomass-Derived Carbohydrates. *Science* **2005**, *308* (5727), 1446-1450.