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Tuning Cellulose Pyrolysis Chemistry: Selective Decarbonylation via Catalyst-Impregnated Pyrolysis

Matthew S. Mettler[†,††,‡], Alex D. Paulsen[††,‡], Dionisios G. Vlachos[†], and Paul J. Dauenhauer[††*]

[†] Department of Chemical Engineering and Catalysis Center for Energy Innovation, University of Delaware, 150 Academy Street, Newark, DE 19716

[††] Department of Chemical Engineering and Catalysis Center for Energy Innovation, University of Massachusetts, 686 North Pleasant Street, Amherst, MA 01003

* To whom correspondence should be addressed. Email: dauenhauer@ecs.umass.edu

[‡] These authors contributed equally to this work

Keywords

Lignocellulosic Biofuels, Biomass Pyrolysis, Catalytic Pyrolysis, Decarbonylation, Deoxygenation, Pyrolysis Oil

Abstract

Widespread adoption of biomass pyrolysis for lignocellulosic biofuels is largely hindered by a lack of economical means to stabilize the bio-oil (or pyrolysis oil) product. In this work, impregnation of supported metal catalysts provides a new approach to selectively decarbonylate primary pyrolysis products within intermediate cellulose liquid to targeted gasoline-like molecules with enhanced energy content and stability. Selective deoxygenation of hydroxymethylfurfural (HMF) and furfural (F) to 88% yield of stable furans occured over carbon-supported Pd, with negligible loss in overall bio-oil yield or furanic content.

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Paper Body

Biomass conversion to transportation fuels and commodity chemicals has become one of the major challenges of the 21st century. The advantages of pyrolysis-based conversion processes over biological methods are significant and have the potential to shift the technology landscape. Benefits include: 10^3-10^5 higher reaction rates which allow for smaller reactors and distributed biomass processing; the ability to convert recalcitrant lignocellulosic material into fuel; the low cost and reliability of inorganic heterogeneous catalysts; and the potential to utilize the existing petroleum refining infrastructure for upgrading.[1] The relatively high temperatures (~400-600 °C) of pyrolytic processing leads to thermolytic depolymerization of lignocellulose, largely achieved through cleavage of ether linkages that connect biomass monomers (e.g., glucose, xylose). Recent work found that during thermolysis, solid biomass is converted first to a high temperature, short-lived intermediate liquid phase from which dozens of different C_1-C_6 oxygenates volatilize.[2] Vapor phase oxygenates are then condensed at room temperature to form pyrolysis oil which can be transported to centralized refineries via pipeline for upgrading to fuels and platform chemicals.

While the benefits of pyrolysis are significant, broad commercialization is hindered by several barriers, the most cited being the instability of the pyrolysis oil (or bio-oil) product.[3] Pyrolysis oil stabilization is commonly accomplished through catalytic hydrodeoxygenation which requires a large amount of hydrogen (relative to petroleum processes) and sacrifices yield to meet fuel quality specifications.[4-6] Technologies capable of reducing the hydrogen requirement, while improving pyrolysis oil stability and maintaining yield, would help bring pyrolytic biofuels to market.

The stability of pyrolysis oils is related to a number of chemical attributes, such as pH, oxygen content, and chemical composition. Furans are a major component of pyrolysis oil (5-20%)[7-11] and, while desirable as fuels (due to high energy density and research octane number)[12] and building block chemicals (due to having both nucleophilic and electrophilic centers),[13] they polymerize readily in the presence of sunlight or acidic substances. Aldehydic furans, such as 5-hydroxymethylfurfural (HMF) and furfural, are thought to be particularly prone to polymerization though acid-catalyzed aldol-condensation reactions.[14] This chemistry should be minimized during (1) primary pyrolysis in the intermediate liquid and (2) transportation and storage of the pyrolysis oil. In the case of biomass-derived furans (e.g., HMF and furfural), the aldehyde group is beta to the ring oxygen and can readily react with other ketones via aldol-condensation or with other nearby unsaturated carbons. This predisposition for polymerization makes aldehydic furans an undesirable product and minimizing their yield in favor of less reactive furans (e.g., furan, methyl furan, dimethyl furan) would produce a more stable (and thus more transportable) pyrolysis oil.

In this work, we present a process wherein solid biomass is impregnated with decarbonylation catalysts (e.g., palladium on carbon, Pd/C) to convert oxygenated furans (e.g., HMF, furfural) to decarbonylated analogues (e.g., furan, methyl furan) within the intermediate liquid (Scheme 1). By directly impregnating biomass with decarbonylation catalysts, we produce a deoxygenated pyrolysis oil with fewer aldehydic furans that is less prone to polymerization.

Previous work impregnating biomass with inorganic materials has focused largely on understanding naturally occurring materials in biomass, such as metal oxides and silica,[15] with the idea that inorganics, detrimental to pyrolysis oil quality, should selectively be removed. Here, we test the potential benefits for impregnating solid biomass prior to pyrolysis, an approach that has been largely unexamined in the literature.[16] Scale-up issues (difficulty in impregnating solid biomass and concerns about catalyst recovery and regeneration) not-withstanding, our work addresses for the first time whether this approach should be investigated in future research.

Catalyst impregnation experiments were conducted by combining cellulose and catalysts to form a solid mixture that is then pyrolyzed in a short contact time reactor.[7, 8, 17, 18] The cellulose-catalyst powder mixture has a characteristic length of ~2 mm making conversion limited by internal heat transfer.[8] Previous work in our group has utilized thin films to overcome

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heat transfer limitations for study of fundamental thermolysis chemistry. However, in this work, larger samples representative of the length scales of biomass particles used in fast pyrolysis reactors are subjected to catalyst impregnation. This allows oxygenates to interact with catalytic active sites prior to evaporation from the cellulose melt, similar to previous work which showed that secondary melt-phase reactions of levoglucosan were significant at the length scales of real biomass particles.[18]

Figure 1 shows pyrolysis oil yield as a function of percent decarbonylated furans for a number of catalysts. The obvious operational objective of any pyrolysis reactor designed for biofuels production is to maximize pyrolysis oil yield while improving stability and quality (e.g., energy density, C-to-O ratio). Here, our objective is to produce the same or better pyrolysis oil yield as in the non-catalytic case (blue square in Figure 1) while achieving 100% decarbonylated furans in the product mixture. We find that supported palladium catalysts (Pd/C, Pd/SiO_2) largely achieve this goal with Pd/C being the best (at constant metal surface area (0.75 m^2 / g-cellulose). Figure 1 shows that when Pd/C is impregnated within cellulose, the percentage of decarbonylated furans increases from 23% (no catalyst case) up to 88% (1.5 m^2/g-cel.) while pyrolysis oil yield is only slightly reduced from 77 %C (catalyst free case) to 68 %C. Further evidence for decarbonylation chemistry (rather than dehydration) is the sharp increase in CO yield from 1.4 %C to 9.0 %C (0.75 m^2/g-cel.) and then 17.9 %C for the highest catalyst load (1.5 m^2/g-cel.; see Table 1).

In addition to Pd, Pt also showed activity for decarbonylation and was tested on three supports (carbon, Al_2O_3 and SiO_2). Pt/C was found to be the most active for decarbonylation but the least selective (in terms of pyrolysis oil yield). At a constant surface area (0.75 m^2/g-cel.), decarbonylated furans increase from 23% (no catalyst) to 67% when Pt/C is added. However, in addition to being active for decarbonylation, Pt catalysts reduce pyrolysis oil yield (from 77% to 51% for Pt/C) due to increased C-C bond cleavage. This limits the utility of Pt catalyst for

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decarbonylation of pyrolysis products. Ni and Co supported metals were also tested, but they were largely inactive (Figure 1).

Figure 2 shows a detailed breakdown of furan yields for the catalyst-free, C only, Pd/C, and Pt/C cases. Addition of the carbon support increased total furan yield compared to the catalyst-free case (+2.1 %C on total C basis). The slight change in product distribution is statistically significant (90% confidence interval is 0.5 %C) and could be due to the mild acidity of the carbon support or to changes in the temperature profile throughout the cellulose/catalyst mixture when the carbon is added (since the powder experiment is heat transfer limited).[8] When the Pd catalyst is added to the carbon support at 1.5 m^2-Pd / g-cellulose, the total furan yield decreases from 9.9 %C to 7.5 %C. This decrease in total furan yield is near the expected stoichiometric carbon loss for a single decarbonylation of furfural and a double decarbonylation of HMF (-1.8 %C based on the difference in yields between support only and Pd/C experiments). This supports the hypothesis that Pd/C is selectively converting aldehydic furans through decarbonylation chemistry (rather than alkylation or hydrogenation).

Figure 2 also shows that the most abundant aldehydic furan molecules are HMF and furfural whereas the dominant decarbonylated furans are methyl furan and furan. This is also consistent with decarbonylation stoichiometry of aldehydic furans since methyl furan and furan are the products of HMF and furfural decarbonylation, respectively. In the catalyst-free reference case, the methyl furan-to-HMF ratio is 0.05, whereas for the Pd/C high catalyst load case (1.5 m^2-Pd / g-cel.) the ratio is 5.5, a 100-fold increase. Pd does not only act as an excellent decarbonylation catalyst but is also capable of hydrodeoxygenating side groups of furans to saturation. Interestingly, the ratio of furan methanol (another product of HMF decarbonylation) to HMF changes less with the addition of Pd/C (from 0.1 to 1.1) indicating that the C_6 CH_2OH group of HMF does not undergo decarbonylation to the same extent as the C_1=O group since decarbonylation (C-C bond scission) is promoted upon dehydrogenation of a species.[19] It is

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important to note that since no external hydrogen is provided, hydrogenation occurs through hydrogen-transfer between liquid-phase species (with char being the likely by-product for the species losing the hydrogen).

Figure 3 shows the effect of catalyst loading (in the form of metal surface area) on furan yields for Pd/C and Pt/C. Pd/C and Pt/C have very different functionalities with increasing surface area. The yield of decarbonylated furans (blue bars; furan, methyl furan, dimethyl furan, and furan methanol) increases with increasing surface area for both Pt/C and Pd/C. However, the catalysts exhibit different total furan yield with increasing surface area. Total furan yield is constant with increasing surface area for Pt/C while total furan yield is parabolic for Pd/C. Interestingly, Pd/C has a minimum total furan yield at intermediate catalyst loading. This indicates that at higher surface areas, Pd/C not only selectively decarbonylates furans but also promotes furan ring formation. This indicates that furan decarbonylation catalysts can potentially increase decarbonylated furans yield higher than the total furan yield of the catalyst-free case.

In summary, our work shows that decarbonylation catalysts can effect condensed-phase pyrolysis chemistry (Scheme 1) and reduce aldehydic furan production to improve pyrolysis oil quality while maintaining pyrolysis oil yield. Additionally, we find that palladium catalysts, especially Pd/C, are selective towards decarbonylation of aldehydic furans within the pyrolytic intermediate liquid. Future work will focus on identifying other, less expensive heterogeneous catalysts of similar or higher decarbonylation activity and selectivity to help improve the economics of next-generation pyrolytic biofuels production processes.

Experimental

Catalytic pyrolysis experiments were conducted by pyrolyzing solid mixtures of cellulose and supports or supported metal catalysts with 20 wt % support + metal and 80 wt % cellulose. For most experiments, the metal surface area to cellulose (m^2-metal / g-cellulose) was constant at 0.75 m^2-metal / g-cellulose in order to distinguish the difference between different metals. Solid mixtures of catalyst and cellulose were pyrolyzed in a batch micropyrolysis reactor (Frontier 2020 micropyrolyzer) under a helium atmosphere (total pressure of 3 bar) and a typical pyrolysis reaction temperature (500 °C). The reactor is capable of matching the heating rates seen in fast pyrolysis.[8] Catalytic and non-catalytic pyrolysis experiments produced very similar product species, albeit in different amounts. Permanent gases (CO and CO_2) and volatile oxygenates were characterized in a gas chromatograph-mass spectrometer (GC-MS), as reported in previous work by the authors.[7, 8, 18] Solid char was quantified using a post-reaction burn off step wherein oxygen was injected into the reactor and CO and CO_2 were measured by GC-TCD. Catalyst metal surface areas were determined by hydrogen (Pt catalysts) or CO (Pd, Ni, Co catalysts) chemisorption.

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Table 1. Yields from catalytic pyrolysis of cellulose at 500 °C. Samples were pyrolyzed as solid mixtures with a cellulose-to-catalyst ratio of 80:20 (mass basis). All experiments were run in triplicate and generally 90% confidence intervals were <20% of the values reported below. Metal surface areas were measured using H_2 or CO chemisorption. Carbon balance is pyrolysis oil components [8], CO, CO_2 and char (quantified via burn off).

Catalyst	Metal Catalyst Load [m^2 / g-cel.]	Metal Surface Area [m^2 / g-cat.]	Yield, Total Furans [%C]	Decarbonylated Furans [% of total furans]	Yield, Pyrolysis Oil [%C]	Yield, CO [%C]	Carbon Balance [%C]
No Catalyst	-	-	7.8	23.0	77.3	1.4	89.7
C	-	-	9.9	26.4	80.0	1.8	83.7
SiO_2	-	-	8.4	28.6	71.8	2.8	85.2
Al_2O_3	-	-	13.5	17.0	69.0	2.1	76.7
Pd / C	0.28	6.19	6.6	46.6	72	4.2	78.6
Pd / C	0.75	6.19	6.1	71.8	74.4	9	85.1
Pd / C	1.5	6.19	8.0	88.4	69.6	17.9	89.4
Pt / C	0.28	5.16	5.2	57.1	75.9	7.6	85.8
Pt / C	0.75	5.16	5.1	66.8	51.5	29.2	84.4
Pt / C	1.5	5.16	4.9	76.5	37	41.8	83.4
Pd / SiO_2	0.75	1.95	5.3	57.8	78.7	6.7	90.4
Pt / SiO_2	0.75	1.27	5.3	50.3	68	6.3	84.9
Pd / Al_2O_3	0.75	6.24	12.3	30.8	68.3	6	82.3
Pt / Al_2O_3	0.75	2.7	11.2	22.4	72.8	4.9	83.5
Ni / Al_2O_3	0.75	2.51	11.4	19.7	74	3.7	86.2
Co / Al_2O_3	0.75	1.11	14.4	17.3	73.6	3.2	83.1

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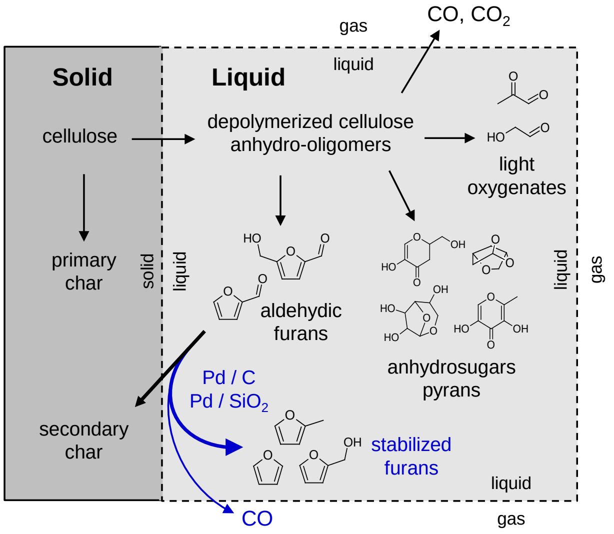

Scheme 1. Solid- and liquid-phase cellulose pyrolysis chemistry. Decarbonylation catalysts can redirect liquid phase chemistry to improve pyrolysis oil quality while maintaining yield.

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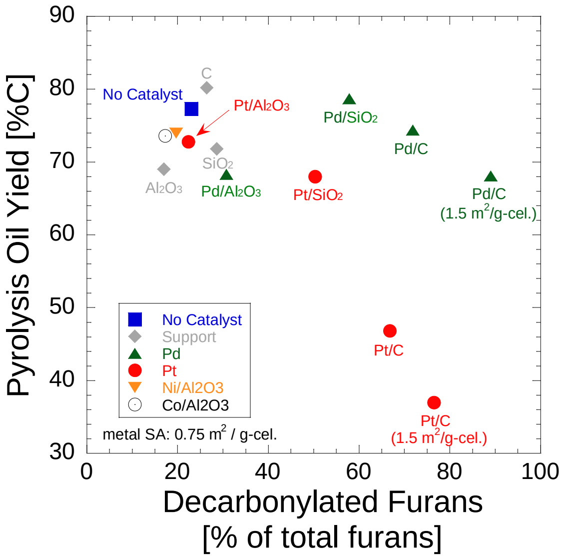

Figure 1. Pyrolysis oil yield versus decarbonylation selectivity for various supported metal catalysts. Supports and supported metal catalysts were co-pyrolyzed with cellulose powder at 500°C. Solid mixtures were 80 wt% cellulose and 20 wt% catalyst (support + metal). Metal surface area was constant at 0.75 m^2-metal / g-cellulose, except as indicated in parentheses.

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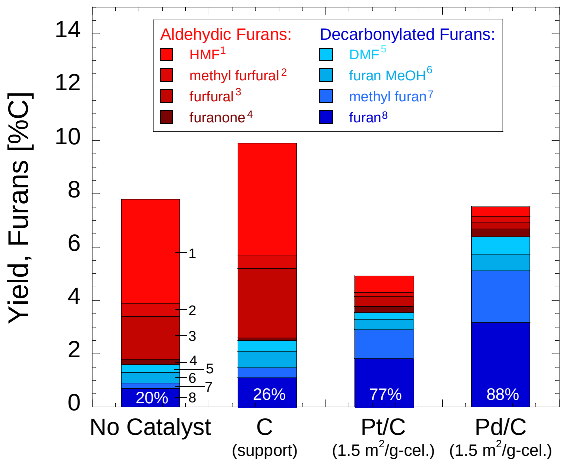

Figure 2. Furan yields for Pt/C and Pd/C catalysts. Supports and supported metal catalysts were co-pyrolyzed with cellulose powder at 500°C. Metal surface area per gram cellulose is indicated in parentheses. Superscripts in the legend correspond to numbers on leftmost bar. Percent decarbonylated furans (out of total furans) is shown in white text at the bottom of each bar.

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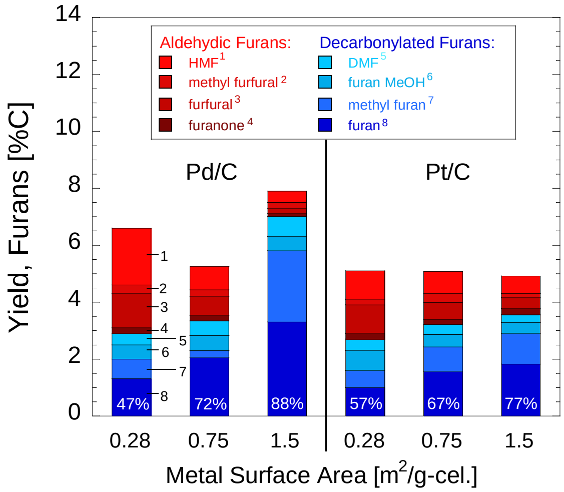

Figure 3. Furan yields as a function of surface area for Pd/C and Pt/C catalysts. Cellulose was co-pyrolyzed with catalyst at 500 °C. Superscripts in the legend correspond to numbers on leftmost bar. Percent decarbonylated furans (out of total furans) is shown in white text at the bottom of each bar.

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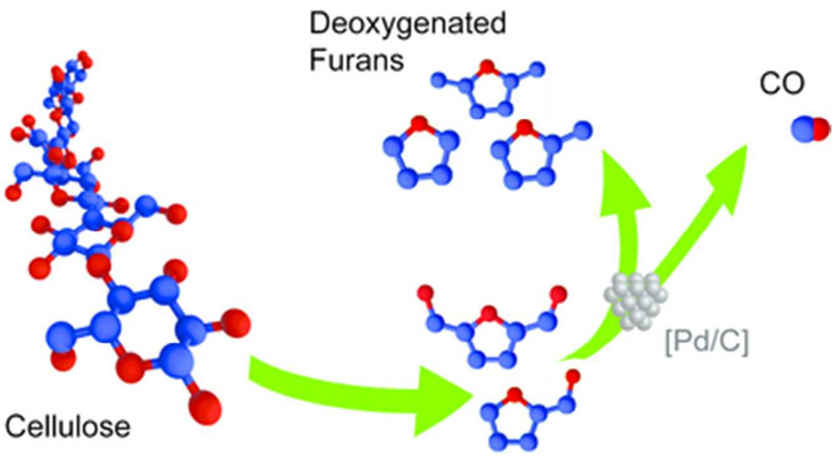

Improving bio-oil stability through aldehydic furan decarbonylation by impregnating cellulose with supported palladium catalysts.
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