Activities and Engagement 2023

Georgia Tech
Renewable Bioproducts Institute

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Executive Director's Statement

Fiscal year (FY) 2023 was a year of record achievements for the Renewable Bioproducts Institute (RBI), which I am excited to share with you. Thank you for taking a few minutes to peruse this activities and engagement report. But first and foremost, I want to thank and acknowledge the wonderful people who make it all possible. RBI is a community of people who are committed to cutting-edge research, education, and public outreach in renewable bioproducts. This includes our phenomenal staff, expert research scientists and engineers, talented graduate students, and internationally recognized faculty from schools across Georgia Tech.

We started assigning new Ph.D. student fellows to the **13 new student slots** approved in FY2022, and we approved **eight new Ph.D. fellowships** this FY, which will be assigned to students in Fall 2023. This includes new projects in using lignocellulose in batteries, non-thermal drying of paper products, and valorization of wastes and forest residues to carbon neutral fuels and chemicals. In addition, we welcomed **14 new faculty advisors** who have not previously received RBI seed funding, after expanding our support to include faculty and students in the Schools of Industrial and Systems Engineering, Public Policy, and Civil and Environmental Engineering, and the Bioengineering Program. This expansion helps to meet the evolving needs of the bioproducts industry.

RBI launched its new philanthropy goals as part of the Transforming Tomorrow Campaign for Georgia Tech, which include capital improvements to the Paper Tricentennial Building (PTB), expansion of fellowship seed funding support for addressing UN Sustainable Development Goals and adding staff to the Robert C. Williams Museum of Papermaking to bring science-inspired art programming to underserved students in the local Atlanta area.

Carson Meredith
Executive Director,
Renewable Bioproducts Institute

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We are thankful for the support of the Executive Vice President for Research, Chaouki Abdallah, the Vice President for Interdisciplinary Research, Julia Kubanek, Facilities Design and Construction, the College of Engineering, and the Georgia Tech Foundation for enabling us to make important improvements to PTB. Over **1,900 square feet of lab space were renovated** for new faculty hires. We also initiated design and construction of a laboratory to house a next-generation multiphase paper forming line. This facility will **position Georgia Tech as a leader in developing climate and environment friendly production of paper and packaging** products through processes that utilize significantly less energy and water.

The year 2023 was a record-breaking year in interdisciplinary proposal submissions that resulted from RBI seed funding or cost-sharing. RBI-funded investigators submitted **$45.5 million in proposals** to federal and industrial opportunities, at least 20% of which has been funded to date. In addition, based on RBI seed funding and facilities, **44 peer-reviewed papers** were published – the first page of the 44 published papers are presented toward the end of the report.

Finally, I am excited to report that RBI launched a new center in FY2023, **ReWOOD: The Center for a Renewables-Based Economy from Wood**. ReWOOD is based on the belief that the challenges posed by the global competition for finite natural carbon resources can be solved only by a commitment of leaders from academia, government, and business. In particular, the cultivated forests of the Southeastern United States hold transformational answers for a broad portfolio of sustainable industrial chemicals, biodegradable plastics, generic pharmaceuticals, sustainable aviation fuels, and electric vehicle batteries. The key to unlocking the forests' potential lies in **regional collaboration that assembles the best scientific and business minds who share this vision**. ReWOOD is a Georgia Tech-led collaboration among 10 Southeastern Universities in GA, FL, TN, AL, and MS.

Carson Meredith
Executive Director, Renewable Bioproducts Institute

FY 2023 RBI Facts & Figures

1,900 sq.ft.
renovated lab space for new COE faculty

$1.9M
committed to new RBI fellowships

44
peer-reviewed publications from RBI support

$45.5M
interdisciplinary research proposals

30%
increase in core facility testing revenue

$900K
committed to next generation paper forming lab

$1.3M
cost–sharing committed to proposals

Georgia Tech
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Spring Workshop Explores Innovations in the Packaging Industry and the Circular Economy

May 26, 2023 – Atlanta, GA

On Thursday, May 11, the Renewable Bioproducts Institute (RBI) of Georgia Tech hosted a workshop on "Packaging Innovation and the Circular Economy" at the Bill Moore Student Success Center on the Georgia Tech campus. More than 90 attendees from academia, national labs, and industry convened and discussed the cutting-edge research and industry developments happening across the world and got an opportunity to network with leading researchers and peers. This unique workshop featured speakers from the USDA Forest Products Laboratory, WestRock, Stora Enso, Georgia Tech, University of Maine, and many others.

Keynote at the RBI Workshop on Packaging Innovation and the Circular Economy

The workshop started off with an introduction by Carson Meredith, executive director of RBI, who gave a perspective on the institute's goals in promoting bioeconomy technology and innovation. Meredith emphasized RBI's role in "catalyzing a community of researchers who focus on solving challenges in packaging by investing in team building across interdisciplinary boundaries."

Research talks began with a presentation from Tequila Harris, professor in the George W. Woodruff School of Mechanical Engineering. Harris shared her team's research on a continuous coating process of cellulose- and chitin-derived materials to create enhanced packaging barrier films. Meisha Shofner, associate professor and Faculty Fellow in the School of Material Science

and Engineering shared her work on mechanical and thermal properties of single use packaging materials and paths to improving circularity.

Meredith, who also serves as a professor in the School of Chemical & Biomolecular Engineering informed on renewable barriers from carbohydrates as viable alternatives to plastics and the research methods involved to get more promising results for circular functional barrier packaging materials. Joe Bozeman, assistant professor in the School of Civil and Environmental Engineering at Georgia Tech presented the Systemic Equity framework as it relates to circularity.

Mehdi Tajvidi, professor from the University of Maine, discussed his team's research to produce particle board and other packaging materials using nanocellulose and the audience got an opportunity to look and get a feel for his research team's samples.

Discussions from industry experts included material innovations to replace plastics, packaging requirements in the European Union and the United States and how brands drive innovation more than regulations, methods to optimize package size and packing speed for sustainability, paper-based packaging equipment and systems to replace plastics including plastic water bottles, dye choices and the influence of defect detection in waterborne barrier coated papers, and innovations in fiber-based cold chain packaging.

Ken Zwick from the U.S. Forest Products Laboratory discussed managing forests using methods like forest thinning such that the biomass prevents wildfires and what success looks like for his team – less plastic in packaging and less burning of wood. Their Madison building also houses the largest wood library in Wisconsin.

Poster Session at the RBI Workshop on Packaging Innovation and the Circular Economy

Participants had a chance to interact with Georgia Tech students and get to know their research at the student poster presentation. The dinner keynote was presented by researchers Bo Arduengo and Stefan France from the School of Chemistry and Biochemistry at Georgia Tech.

The keynote provided an overview of RBI's newly created ReWOOD research center. Abbreviated from "Renewables-based Economy from WOOD," research at the center focuses on using sustainable plant-based raw materials to develop industrial products ranging from jet fuel to solvents to generic pharmaceutical additives and more. The presentation provided a glimpse on the expansion of ReWOOD since its launch through research affiliations from universities across the world. ReWOOD's partnership list continues to grow as the center focuses on targeted research areas and funding proposals to develop technology and commercial opportunities.

"The workshop turned out to be a huge success with a highly engaged audience of faculty, students, national lab, and industry experts," said Meredith. "RBI will continue to host such events as we are committed to providing thought leadership and be a catalyst of cutting-edge research in the areas of circular materials; bio-industrial manufacturing; and paper, packaging, and tissue."

Participants at the RBI Workshop on Packaging Innovation and the Circular Economy

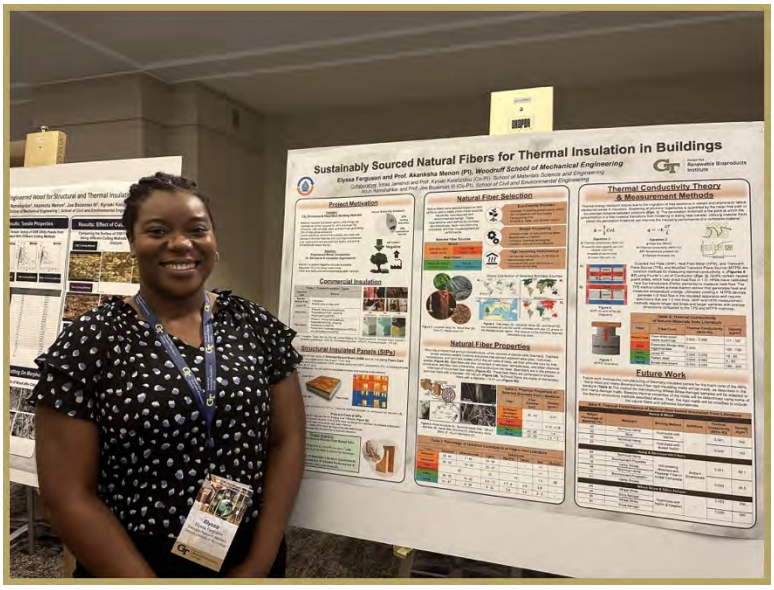
Article Link: https://research.gatech.edu/spring-workshop-explores-innovations-packaging-industry-and-circular-economy

Georgia Tech
Renewable Bioproducts Institute

2023 RBI Spring Workshop Experience from a Student's Perspective

August 1, 2023 – Atlanta, GA

A highlight of the Renewable Bioproducts Institute (RBI) workshops is the student poster session that provides industry interaction for Paper Science and Engineering (PSE) Fellows and an opportunity to communicate the breadth of research supported by RBI to the workshop participants. The session also provides a chance for new students to share their project scope, goals and receive useful feedback. This is the first in a series of Q&As from PSE students who share their experience at the 2023 RBI Spring Workshop on Packaging Innovation and the Circular Economy. Elyssa Ferguson, a mechanical engineering graduate student shares her experience below.



Elyssa Ferguson, RBI Fellow during the Student Poster Session at the 2023 RBI Spring Workshop on Packaging Innovation and the Circular Economy

Tell us about yourself.

My name is Elyssa Ferguson. I earned my B.S. in mechanical engineering at the University of Maryland, Baltimore County (UMBC). I am pursuing my M.S. in mechanical engineering at Georgia Tech. I am an RBI Fellow, GEM Fellow, and Women of Woodruff (WoW) Fellow, and I work in the Water-Energy Research (WERL) Lab, under the direction of Akanksha K. Menon, assistant professor in the School of Mechanical Engineering. My research focuses on developing sustainably sourced natural fibers for thermal insulation in buildings. My project is a part of the Carbon-Negative Building Materials based on Engineered Wood for Structural and Thermal

Insulation Applications project. Menon and I collaborate with Kyriaki Kalaitzidou, Rae S. and Frank H. Neely Professor in the School of Mechanical Engineering and Joe F. Bozeman III, assistant professor in the School of Civil and Environmental Engineering and Public Policy. I also work with graduate students, Elnaz Jamshidi from the School of Materials Science and Engineering and Arjun Thangaraj Ramshankar from the School of Civil and Environmental Engineering on this project.

How was your experience at the RBI workshop?

Attending the RBI workshop was a valuable learning experience. I learned about the variety of exciting work in the renewable packaging realm that is going on at Georgia Tech and other organizations. This work is driving sustainable innovation, yet there are challenges. The discussions regarding the barriers to innovation and areas for growth were very thought-provoking and motivating.

What was your main takeaway from the poster session?

During the poster session, I shared information about my research and had the privilege to talk to many people in the industry. There is much interest in thermally insulating natural fibers for building applications and for other applications like cold-chain packaging and textiles. Speaking with the workshop participants during the poster session broadened my mind to the potential myriad of applications for natural-fiber-based thermal insulation on a global scale. I also learned more about the existing challenges researchers and industrial peers are facing – one being the lack of standardization of nomenclature and methodology. Receiving positive feedback on the design of my poster was also helpful. I deliberately designed a poster that incorporated aesthetics to convey my ongoing research. I plan to apply the helpful information and feedback that I received during the RBI workshop to my future work.

What more would you like to see in future events at the Renewable Bioproducts Institute?

I am very interested in seeing more seminars related to sustainable building materials, especially insulating materials, and textiles, as these topics are closely related to my research project. Fascinating work is happening at other universities and at companies in Georgia and around the world. It would be great if there is a seminar series including these organizations.

Article Link: https://research.gatech.edu/2023-rbi-spring-workshop-experience-students-perspective-part-1

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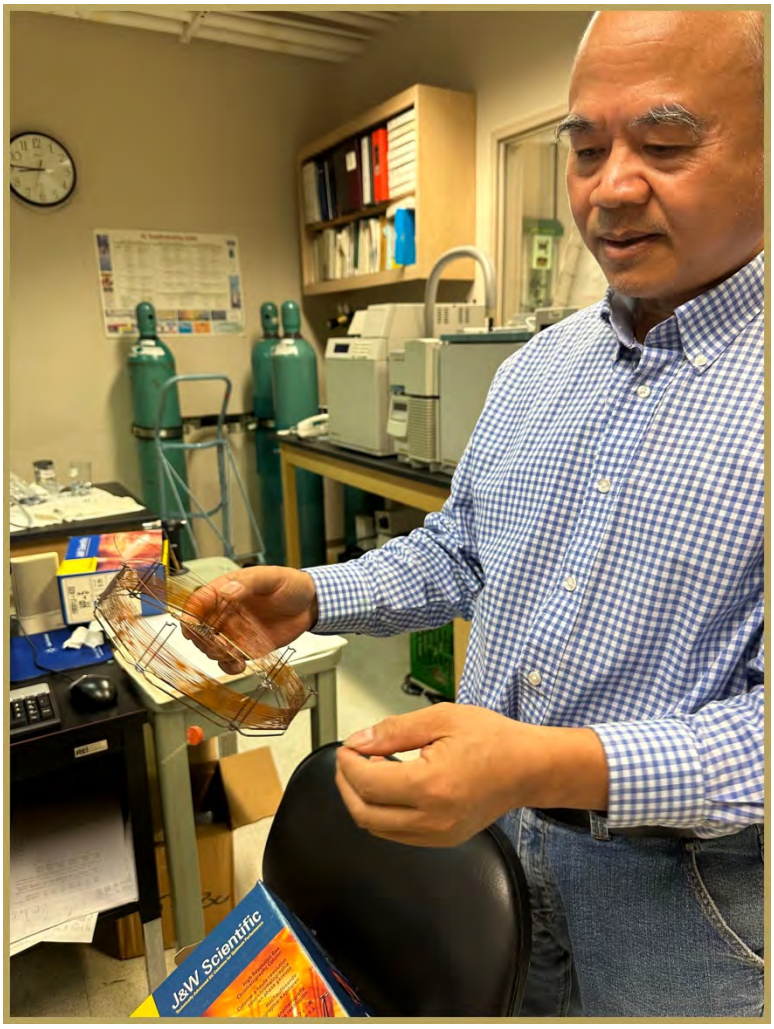
A Day's Work at the RBI Chemical Analysis Lab

November 9, 2023 – Atlanta, GA



Rallming Yang, Senior Research Scientist and head of the Chemical Analysis Lab explains how FTIR Spectrometer works at the RBI Chemical Analysis Lab

Providing research testing services to both internal and external stakeholders is an integral function of the Renewable Bioproducts Institute (RBI). These services include chemical analysis; corrosion; paper, board and box testing; pulp analysis; and pulp recovery analysis. Established over 25 years ago, RBI's testing services are well-known in the industry for their quality and customer service. RBI is one of the ten interdisciplinary research institutes at Georgia Tech that champions innovation in converting biomass into value-added products, developing advanced

chemical and bio-based refining technologies and advancing excellence in manufacturing processes.

The RBI research testing services is a team of professional scientists and engineers who work together to provide information and offer solutions required by a manufacturers and users of biomass products, as well as Georgia Tech faculty and students engaged in research on campus. The multidisciplinary capabilities of the team make them uniquely qualified to address customers' technical needs in the areas of process and product development, and quality control. Where appropriate, the team involves RBI faculty and other staff experts to arrive at the best possible solution for their customers and users.

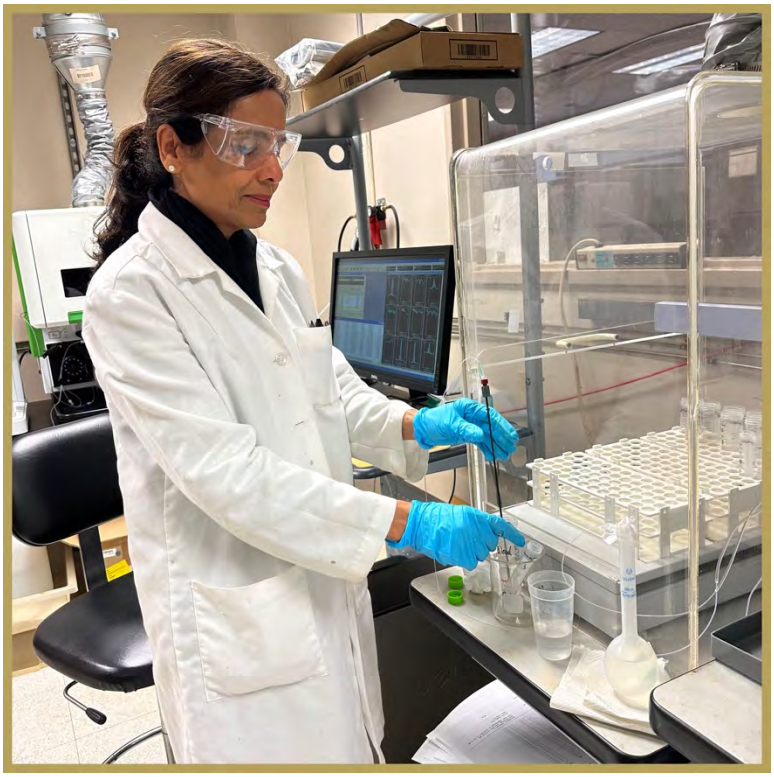
In this article, we will focus on a day's work with the chemical analysis team. Headed by Rallming Yang, senior research scientist at RBI, the team is equipped to follow the Technical Association of the Paper and Pulp industry (TAPPI) standard of testing, which only a small number of labs in the country can do, and has also developed some of its own internal protocols. Yang leads two specific characterization programs within RBI: (1) the pulping and bleaching analysis, paper recycling, and recovery lab, and (2) the chemical analysis lab.

The chemical analysis team is busy year-round with research projects and testing services. In addition, during the Spring semester, the team also provides support to a paper science laboratory course for undergraduate and graduate students. In the recent times, chemical analysis of black liquor from pulp mills has kept the team busy with more than 30 projects completed by the team over three months for various industry customers. Currently, black liquor analysis continues to account for over 50% of the workload of the lab.

Black liquor (BL) is a byproduct of a wood pulping and is released when cellulose fibers are separated from wood chips. BL contains lignin, which is used as a biofuel within the mill, and several other chemicals that are recovered and reused. In most pulp mills, nearly 50-70% of BL is converted into a convenient source of fuel or energy. Due to the important role played by black liquor in a paper mill, it needs to be tested regularly to ensure consistency in composition.

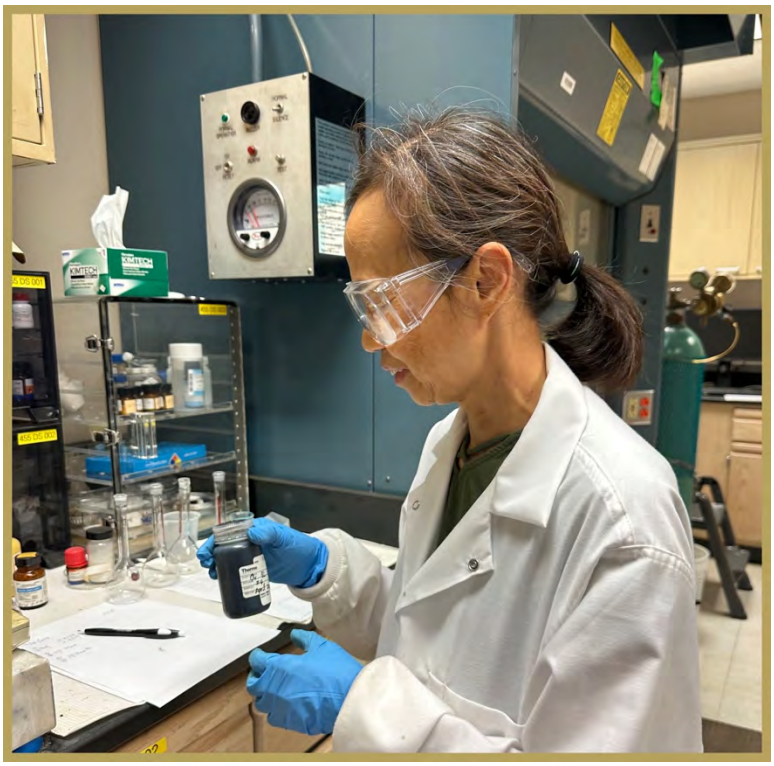
The RBI chemical analysis lab gets BL samples from a pulp mill, who contact the lab by email to get their testing request into the queue. The process involved in the testing is very intense and has multiple steps that need to be carefully administered.

In the first step, inorganic elements in BL are identified by digesting it in a precise mixture of acids and filtering the mixture. The filtrate is introduced into an Inductively Coupled Plasma (ICP) Emission Spectrometer that can identify more than 70 different inorganic elements and compounds like sulfur, potassium, sodium, iron, calcium, etc. The next step involves identifying the proportion of anions like sulfate, chloride, and thiosulfate. In this step, BL is diluted to a specific level and analyzed using a method called Capillary Ion Electrophoresis (CIE).



Tabassum Shah, Research Coordinator at RBI, tests black liquor using ICP

The next step involves analyzing BL for organic substances using two methods – gas chromatography mass spectrometry (GC/MS) and Fourier Transform Infrared Spectrometry (FTIR). For organic substances with a lower molecular weight of less than 600 Daltons (Da), GC/MS is employed where the gas chromatography separates the chemical mixture, and the mass spectrometry identifies each of the components.



Xiaoyan Zeng, an RBI Research Scientist prepares black liquor for identifying anions

The final step is to identify organic substances and polymers with higher molecular weights. For example, lignin is one of the main polymers in BL with a molecular weight higher than 600 Da. FTIR is used for testing during this step. Based on vibrations within each molecule, an FTIR spectrum allows identification of molecular groups within lignin. The equipment then uses a computer to identify the substances by comparing the sample spectrum with a built-in library. The RBI team provides detailed lab reports that is used by the pulp mill to adjust their operating parameters for trouble-free operations.

In addition to the chemical analysis of byproducts like black liquor and other chemical compounds, Rallming Yang's team also conducts studies on pulping and bleaching, repulping, and fiber characterizations.

Article Link: https://research.gatech.edu/days-work-rbi-chemical-analysis-lab

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2023 Peer-Review Papers Funded by RBI

The year 2023 was a record-breaking year in interdisciplinary proposal submissions that resulted from RBI seed funding or cost-sharing. RBI-funded investigators submitted $45.5 million in proposals to federal & industrial opportunities, at least 20% of which has been funded to-date. In addition, based on RBI seed funding and facilities, 44 peer-reviewed papers were published. The first page of each publication is presented below.

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Chemically reacting mixing in coaxial miscible liquid jets under variable viscosities and reaction rates

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HIGHLIGHTS

- Multiscalar mixing in a chemically reactive miscible two-fluids system.
- A parametric study by varying the viscosity and reaction rate constant ratios.
- Inverse correlation between undesirable product and the desirable product.
- Reaction fronts for different reaction rate constant and viscosity ratios.
- Optimum reaction route with higher conversion efficiency of the desirable product.

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LES
Turbulent reacting flows
Multiphase flows
Coaxial jets
Miscible liquids
Competitive-consecutive reactions

ABSTRACT

We study the mixing and reactions between two fluids with disparate viscosities in a co-axial flow at high Schmidt number, through numerical simulations. The chemical reactions chosen in this work are competitive-consecutive in nature. Numerical implementation of the reactions proceeds as given by Li and Toor (1986), in a Large-Eddy Simulation (LES) framework. The aim of the present study is to investigate the effect of reaction rate constant ratio on the product and byproduct formations under distinct viscosity ratios between the annular and central jets. Flow features promoting mixing and reactions such as turbulence, engulfment, jet instability, waves and break-up are described. The effect of viscosity difference between the jet and co-flow on the mixing and reactions are also delineated. It is found that selectivities of the undesirable product decrease with reducing viscosity ratio as well as increasing reaction rate constant ratio.

1. Introduction

The chemically reacting turbulent mixing hold a great deal of applications ranging from combustion engines, propulsion systems, to chemical reactive devices. Mixing is ostensibly a process of approaching uniformity from segregated constituents by stretching and folding material surfaces but essentially an intricate dynamic process that may span an enormous range of spatio-temporal scales. Uniformity of the scalar species is best achieved through turbulence, where the energy cascades from large scale eddies to the smallest possible eddies are determined by Kolmogorov length scale (Aref et al., 2017). In the scenario of two fluids with disparate viscosities, the turbulent mixing between the two fluids is able to occur thoroughly or not at all, being contingent on a criterion, which is a function of the input Reynolds number (*Re*) and the viscosity ratio (Campbell and Turner, 1985). Given the ubiquity of the turbulent advection, there arises chaotic advection (Aref, 1984; Aref and Balachandar, 1986), which relies on a fully deterministic Eulerian velocity field to create an actually stochastic Lagrangian response to transport the passive scalar and is a subclass of laminar advection. Chaotic advection creates small-scale structures by its chaotic dynamics without large energy input (Ottino, 1990; Aref et al., 2017). As for industrial applications, turbulent mixing is nevertheless of paramount importance and especially a more realistic and efficient way than chaotic advection to realize large-scale productions.

The quasi two-dimensional planar mixing layer is a simple way to form the shear layer for scalar mixing to occur. The dynamics of the planar mixing layers is governed by the primary Kelvin–Helmholtz (KH) instability mode creating spanwise vortices and the secondary instability mode associated with the streamwise vortical structures (Karasso and Mungal, 1996). Breidenthal (1981) experimentally studied the effect of Schmidt number on planar turbulent

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Coaxial jets with disparate viscosity: mixing and laminarization characteristics

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Mixing of fluids in a coaxial jet is studied under four distinct viscosity ratios, $m = 1$, 10, 20 and 40, using highly resolved large-eddy simulations (LES), particle image velocimetry and planar laser-induced fluorescence. The accuracy of predictions is tested against data obtained by the simultaneous experimental measurements of velocity and concentration fields. For the highest and lowest viscosity ratios, standard RANS models with unclosed terms pertaining to viscosity variations are employed. We show that the standard Reynolds-averaged Navier–Stokes (RANS) approach with no explicit modelling for variable-viscosity terms is not applicable whereas dynamic LES models provide high-quality agreement with the measurements. To identify the underlying mixing physics and sources of discrepancy in RANS predictions, two distinct mixing modes are defined based on the viscosity ratio. Then, for each mode, the evolution of mixing structures, momentum budget analysis with emphasis on variable-viscosity terms, analysis of the turbulent activity and decay of turbulence are investigated using highly resolved LES data. The mixing dynamics is found to be quite distinct in each mixing mode. Variable viscosity manifests multiple effects that are working against each other. Viscosity gradients induce additional instabilities while increasing overall viscosity decreases the effective Reynolds number leading to laminarization of the turbulent jet, explaining the lack of dispersion and turbulent diffusion. Momentum budget analysis reveals that variable-viscosity terms are significant to be neglected. The scaling of the energy spectrum cascade suggests that in the TLL mode the unsteady laminar shedding is responsible for the eddies observed.

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Inline spectroscopic measurements and LES of competitive consecutive reaction in a confined liquid jet in coflow

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HIGHLIGHTS

- Selectivity of competitive consecutive Bourne reaction in jet in coflow mixer.
- Non-intrusive experimental measurements of competitive consecutive Bourne Reaction.
- LES modeling of competitive consecutive Bourne Reaction.

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Turbulent mixing
Bourne Chemistry
Mixing-limited reactions

ABSTRACT

Dynamic inline spectroscopic measurements and Large Eddy Simulation (LES) observe the products of a competitive-consecutive test reaction system within a well-characterized coaxial flow. The test reaction is a competitive consecutive chemistry which produces two spectrophotometrically measurable products. For the first time, these products are measured spatially throughout the reactor. Experimental and computational results map the reaction progress and product distribution. The evolution of this chemical process is explained in terms of the inlet, jet, and pipe flow regimes of the confined jet. The inlet and jet regimes were demonstrated to produce the majority of the desired product, whereas the undesired product is predominantly generated in the pipe regime.

1. Introduction

Many industrial processes rely on chemistries with fast reaction rates. With chemistries that produce finished products on contact, the reaction progress is often limited not by reaction rate, but by the host fluid's ability to transport fresh reactants to each other.

In an effort to intensify such chemical processes, a recent effort has been invested into diagnostic approaches to observe the underlying fluid mechanics. Such approaches include Planar Laser Induced Fluorescence (PLIF) studies which observe the transport of a passive scalar, referred to as ξ, within a planar cross-section. Chornyi and Kornev (2005); Kornev et al. (2008); Tkatchenko et al. (2007); Zhdanov et al. (2004); Zhdanov et al. (2006); Zhdanov and Chornyi (2007); Zhdanov and Chorny (2011); Komori et al. (1991); Dahm and Dimotakis (1987); Dimotakis (1989); Dimotakis (2000); Koochesfahani (1985); Rehab et al. (1997); Rehab et al. (1998); Villermaux and Innocenti (1999); Dimotakis (1990a); Dimotakis (1990b); Lima and Palma (2002); Eltayeb et al. (2021); Rodriguez et al. (2018) Such studies provide critical information for reaction modeling such as the mean concentration field and the concentration variance field of a conserved scalar. However, at typical Reynolds numbers observed in such experiments, the diagnostic is limited by the laser sheet thickness and camera resolution. Accordingly, these statistics often resolve Taylor scale fluctuations, missing physical processes at the Kolmogorov and Batchelor scales. To improve upon such diagnostics new more advanced approaches include simultaneous two-color PLIF with pH insensitive and sensitive indicators within streams of differing pH (Koochesfahani and Dimotakis, 1986; Komori et al., 1993; Kuhn and Jensen, 2012; Ribeiro et al., 2022). The Rhodamine signal is insensitive to changes in pH, while the Sodium Fluorescein while 5-(and 6)-carboxy SNARF-1 and bromothymol blue signals die out at high and low pH. In addition to observing passive scalar transport, these studies provide images of the actual reactive field data based upon molecular scale mixing as seen through the Sodium Fluorescein fluorescence (Koochesfahani and

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Turbulent channel flow of generalized Newtonian fluids at $Re_\tau = 180$

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ARTICLE INFO

Keywords:
Turbulent channel flow
Shear-thinning fluids
Yield stress fluids
Direct numerical simulation
Turbulence anisotropy
OpenFOAM

ABSTRACT

Direct numerical simulations (DNS) of generalized Newtonian fluids in a rectangular channel at a friction velocity of 180 are performed using OpenFOAM. The simulations are performed for a Newtonian fluid, a power-law fluid, and a Herschel-Bulkley (HB) fluid. Two-point correlations of the streamwise velocity reveal that a significant increase in the computational domain size is required to avoid statistical correlation due to the shear-thinning and yield stress. The analogous Kolmogorov scale shows that the dissipative structures may be orders of magnitude larger with these two non-Newtonian behaviors. This is demonstrated to be linked to the significant increase in the viscosity. The mean streamwise velocity field integrates to a larger bulk velocity with increased shear-thinning as compared with the Newtonian fluid flow. The addition of the yield stress does the same with respect to the power-law fluid flow. The difference in the velocity profiles is more pronounced in the outer layer. It, however, is observed that the rheology does not play a significant role in the outer layer for the mean streamwise velocity. It is shown that an HB fluid flow does not necessarily show an increase in the fluctuating streamwise velocity with respect to a power-law fluid flow. It is also shown that low power index and high Hedstrom number lead to strong turbulence anisotropy due to the weakening of turbulence. The turbulent kinetic energy (TKE) budget reveals that the studied non-Newtonian behavior mainly affects the inner layer of the flow. The yield stress is also seen to show small variations in the TKE budget in the outer layer. This is attributed to the weakening turbulence as a result of the increased viscosity near the center. It is also demonstrated that the studied HB fluid flow results can be successfully reproduced by under-resolved DNS.

1. Introduction

Turbulent flows of generalized Newtonian (GN) fluids are often encountered in industrial applications such as paper making [1], drilling of oil wells [2], and food processing [3]. These fluids are described by their strain-rate-dependent viscosity, and different constitutive relationships are available to account for their complex behavior. Herschel-Bulkley constitutive relation is one such widely used GN fluid model that characterizes many time-independent fluids exhibiting yield stress and power-law behavior. Upon the application of a stress τ, the deformation of an HB fluid takes place according to

$$\tau = \tau_y + k\dot{\gamma}^n, \text{ if } \tau > \tau_y \tag{1}$$

$$\dot{\gamma} = 0, \text{ otherwise} \tag{2}$$

where the fluid properties τ_y, k, n, are the yield stress, consistency index, and power index, respectively, and $\dot{\gamma}$ is the effective strain rate.

HB fluids are a general class of Newtonian ($n = 1$, $\tau_y = 0$), power-law ($\tau_y = 0$), and Bingham ($n = 1$) fluids. Therefore, HB fluid flows retain the flow characteristics of its subsets. HB fluids are called shear-thinning if $n < 1$ and shear-thickening if $n > 1$. In this work, only shear-thinning and Newtonian fluids are considered, and the terms power-law and HB fluids implicitly imply shear-thinning. Pulp suspensions [4], aqueous and fiber-laden foams [1,5], slurries [6], and concentrated foods [3] are examples of shear-thinning HB fluids that are transported through channels and pipes every day in large amounts in industrial applications. These are multi-phase or structured fluids, and the experimental analysis of their flows may be difficult or even impossible due to, for example, lack of optical access, toxicity, and limited pumping capability in a laboratory. There are also challenges in the computational analysis of these multi-phase flows in terms of tracking the dispersed phase, resolving interfaces properly, and modeling particle–particle or particle–carrier phase interactions.

The HB constitutive relationship offers a macroscopic deformation of such fluids and makes it feasible to make detailed predictions of the flow field. Therefore, utilizing single-phase shear-thinning HB fluids as a surrogate fluid for complex fluids [4,6–10] has become an active

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Total turnover number prediction of an aggregating biocatalyst: Amino ester hydrolase (AEH)

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Keywords:
Amino ester hydrolase
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ABSTRACT

Amino ester hydrolase (AEH) from *Xanthomonas campestris* is a promising candidate for β-lactam synthesis but suffers from low thermostability and rapid deactivation. Wild-type AEH was found to deactivate with an apparent order that varies with temperature from n = 2 at 30 °C (close to the temperature of optimum activity T_{opt}) to n = 1.5 at 25 °C. AEH features two transitional temperatures: (1) from native 'N' to partially unfolded, inactive intermediate 'I', and (2) from partially unfolded to fully unfolded entity 'U' at the melting temperature T_m. CD and light scattering data suggest aggregation near T_{opt}. To determine the total turnover number *TTN*, AEH was deactivated by imposing a temperature gradient and recording instantaneous rates of cephalexin hydrolysis. The *TTN* increased ~ 5-fold from the wild-type (WT) for the quadruple variant N186D/A275P/E143H/V622I (QVH) at 25 °C and 10 nM AEH but varied significantly with AEH concentration and temperature.

1. Introduction

The current most common route to semi-synthetic beta-lactam antibiotics (Scheme 1) involves kinetically controlled enzymatic coupling between a beta-lactam moiety, 6-aminopenicillanic acid (6-APA) in penicillins and 7-aminocephalosporanic acid (7-ACA) or 7-aminodesacetylcephalosporanic acid (7-ADCA) in cephalosporins, and an ester or amide of the side chain acid constitutes. While penicillin G acylase (PGA) is commonly employed in this route, amino ester hydrolases (AEHs) recently have gathered attention, as their synthetic capabilities can be superior to PGA for the synthesis of ampicillin and cephalexin (but not amoxicillin) leading to higher reaction rates, higher yields, and less sensitivity to hydrolysis (Barends, 2006; Lagerman, 2021).

AEHs, however, are not sufficiently stable for large-scale use and thus their stabilization is a priority. The best characterized wild-type AEH from *Xanthomonas campestris pv. campestris* (WT, ATCC 38835) (Lagerman, 2021; Blum and Bommarius, 2010) features an observed melting point $T_{m,app}$ of 40 °C (CD scan rate of 1 K·min^{-1}), a point of maximum reactivity, T_{opt}, of 25 °C, a temperature at which half the initial activity is left after 30 min, T_{50}^{30}, of 27 ± 2 °C, and a half-life, $\tau_{1/2}$, at 30 °C of 5 min (Blum and Bommarius, 2010). The protein is either not tightly packed or undergoes rapid conformational changes, as is shown by very similar energies of activation (E_a = 56.7 kJ/mol) and deactivation (E_d = -82 kJ/mol) and rapid deactivation after T_{opt} (Blum and Bommarius, 2010).

AEH monomers have been previously shown to associate into a tetrameric structure (Barends, 2003). The low thermostability of AEH may be associated with subunit dissociation that may lead to kinetic inactivation of the protein without degradation of the secondary structure (Vázquez-Figueroa, 2008). Alternatively, the uncooperative, gradual unfolding may lead to small changes around the active site that lead to kinetic inactivation before the majority of the protein unfolds, a concept developed by Daniel *et al.* in the form of the equilibrium model, with T_{eq} as the temperature at which small changes around the active site lead to inactivation (Daniel, 2007). This model was found to hold for a series of enzymes (Daniel, 2007; Rogers et al., 2009). AEH exhibits similar thermostability qualities relevant to the enzymes, including a much higher melting temperature relative to the inactivation temperature, but the details of AEH deactivation remain unclear. Better understanding of the low stability of AEH as well as the mechanism of unfolding can aid in understanding process development around AEH-catalyzed synthesis processes as well as provide better targets for

Abbreviations: AEH, amino ester hydrolase; TTN, total turnover number.

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Data-driven simultaneous process optimization and adsorbent selection for vacuum pressure swing adsorption

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ABSTRACT

Technologies for post-combustion carbon capture are essential for the reduction of greenhouse gas emissions to the atmosphere. However, they are still associated with high costs and energy consumption. Intensified processes for carbon capture have the potential to overcome these challenges due to their higher efficiency, lower capital cost, and increased operational flexibility. This work investigates simultaneous optimization of process conditions and adsorbent selection for a modular Vacuum Pressure-Swing Adsorption system designed for CO_2 capture. Both surrogate-based Nonlinear Programming and Mixed-Integer Nonlinear Programming approaches are applied and compared in terms of computational efficiency and solution accuracy. Moreover, process performance results are examined by applying several data analytics techniques to gain insights into the material-process correlations. Data-driven classifiers and neural networks can accurately predict whether a material is likely to satisfy purity, recovery, and energy constraints when operated at optimal process conditions.

1. Introduction

Emission of CO_2 has been recognized as an important environmental issue and one of the major contributing causes of climate change (Choi et al. 2009, Bhown and Freeman, 2011, Hasan et al. 2014, Hasan et al. 2015, Ben-Mansour et al. 2016, Bui et al. 2018). In 2017, the amount of CO_2 emissions in the U.S. totaled 6457 million metric tons ("U.S. EPA's Inventory of U.S., 2019). Carbon Capture and Storage (CCS) has been proposed to reduce CO_2 emissions but several existing techniques are currently associated with high cost and large energy consumption (Yang, Xu et al. 2008, Hasan et al. 2013, Ben-Mansour et al. 2016, Leperi et al. 2019). One promising technology for post-combustion carbon capture is adsorption using solid sorbents due to its relatively high separation efficiency, low energy cost in comparison to absorption-based technologies, and its potential for modularization (DeWitt et al. 2019).

During adsorption, separation units containing solid adsorbent sequester CO_2 from flue gas through a dynamic cyclic operation (Ruthven, 1984, Ebner and Ritter, 2009). During each cycle, CO_2 is captured and separated from the rest of the mixture; the adsorbent is then regenerated, and the cycle is repeated (Ruthven, 1984). Depending on how the adsorbent is regenerated, adsorption-based technology, which is typically carried out in packed-bed adsorbers, can be grouped into three main operational modes: (1) pressure-swing adsorption (PSA), (2) vacuum-swing adsorption (VSA), and (3) temperature-swing adsorption (TSA) (Ruthven, 1984, Ruthven et al. 1994). Significant research efforts have focused on improving these packed-bed adsorbers by overcoming pressure-drop limitations, mitigating adsorption enthalpy, and improving mass transfer to make the operation more cost- and energy-efficient (Samanta et al. 2012, Rezaei et al. 2014, DeWitt et al. 2019, Jang et al. 2019, Sinha and Realff, 2019). Parallel to these

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RESEARCH ARTICLE

Surrogate-based branch-and-bound algorithms for simulation-based black-box optimization

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Abstract
Black-box surrogate-based optimization has received increasing attention due to the growing interest in solving optimization problems with embedded simulation data. The main challenge in surrogate-based optimization is the lack of consistently convergent behavior, due to the variability introduced by initialization, sampling, surrogate model selection, and training procedures. In this work, we build-up on our previously proposed data-driven branch-and-bound algorithm that is driven by adaptive sampling and the bounding of not entirely accurate surrogate models. This work incorporates Kriging and support vector regression surrogates, for which different bounding strategies are proposed. A variety of data-driven branching heuristics are also proposed and compared. The key finding of this work is that by bounding fitted, approximate surrogate models, one can employ a branch-and-bound structure that converges to the same optimum despite different initialization of samples and selection and training of a surrogate model. The performance of the algorithm is tested using box-constrained nonlinear benchmark problems with up to ten variables.

Keywords Black-box optimization · Surrogates · Machine learning · Gaussian process · Support vector regression · Branch-and-bound

List of symbols

General

f^* Global solution to the problem
f^*_{lb} The current best lower bound
f^*_{ub} The current best upper bound
f_{lbk} The lower bound of node k

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ORIGINAL RESEARCH

The influence of electrostatic interactions in polyelectrolyte complexes on water retention values of cellulose nanofiber slurries

Nasreen Khan · Alexis R. Renfroe · Petra von Grey · Heather A. Witherow · Blair K. Brettmann

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Abstract Polyelectrolyte complexes (PECs) are used as drainage and retention aids to improve dewatering of cellulose fibers as they form networks during paper web formation. While the appropriate addition of PECs to standard pulp fibers has shown improved dewatering, more work is needed to understand how they may impact the dewatering of cellulose nanofibers (CNFs). In this fundamental study, we show how the selection of polycations in a PEC system and the electrostatic interactions influence dewatering of CNF and PEC networks, through water retention value (WRV) testing. We examine three readily available polyamines and complex them with the polyanion polyacrylic acid at conditions where the electrostatic interactions between these polymers are tuned by changing the salt concentration or the charge ratio. At low salt concentrations, the presence of PECs can prevent dewatering and formation of a fiber pad, resulting in WRVs higher than a CNF control, but at high-salt concentrations, reduced electrostatic interactions allow for improved WRVs, below the CNF only control. By understanding how polycation selection and PEC phase behavior influences WRVs of CNF-PEC networks in the context of tuning electrostatic interactions, we provide scientific insights that may be applied to improve dewatering during fiber mat formation.

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Superhydrophobic elastomer with leaf-spring microstructure made from natural wood without any modification chemicals

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ABSTRACT

Herein, we report a superhydrophobic elastomer which was made directly from natural wood with a simple chemicothermal treatment without adding any modification chemicals. One of the most important findings is that the unique micro-nano structure in original wood was well maintained in the final wood elastomer, which result in many unique physical–chemical properties. The chemicothermal process tailors the nano-microstructure of wood by deteriorating polysaccharides into cellulose nanoarrays, and simultaneously, removes the hydrophilic groups in lignin which then re-assembles to cellulose nanoarrays to form a superhydrophobic surface with a contact angle up to 152°. Retained lignin aromatic skeleton also results in significant self-photothermal effect. Meanwhile, ray tissues in natural wood are hollowed to leave leaf-spring-like microstructure, which leads to great elasticity of wood elastomer with 97% stress retention at 60% strain after 10^3 compression cycles. Thanks to the microstructure and functions arising from wood itself, the elastomer shows many potential applications such as in solar-assisted crude oil recovery as well as water/oily liquids separation.

1. Introduction

Wood is one of the most abundant sustainable biomaterials on Earth. It has evolved unique hierarchical micro-nano structure and lignocellulosic compositions, which provide opportunities for preparing wood-based advanced materials for various applications [1]. The unique micro- and nanostructures make woods strong and flexible [2,3], and they are also the critical for water and nutrition transportation within wood body. For example, at microscale, the transpiration process occurred in cellular tracheids inspired the ingenious design of efficient multiphase fluidics transport system [4,5]. Submicron-pore sized pits in a natural wood are served as a physical sieve in xylem, which could make wood as a biodegradable filter to capture particulate contaminants in water [6,7]. At nanoscale, nano or sub-nano channels between cellulose nanofibrils in wood membrane/hydrogel can efficiently regulate ion flux [8,9].

To obtain the extraordinary properties that wood process, various wood-inspired elastic materials with wood-like micro-nano structures were prepared. 1D nanowire/nanofiber, 2D nanosheets, nanoplates, polymer chains, and biomacromolecules have been widely assembled into elastic aerogel/sponge via directional freeze-drying [10]. In harness with superhydrophobicity induced by chemical modification and/or surface etching, the elastic aerogels/sponges show wider function scope from compressive sensor, piezoelectric generator, thermal insulator to absorbent, etc. [11,12]. However, above elastic materials suffered from complex preparation process which would be limitations for scalable application.

In recent works, many efforts have been dedicated to turn the natural

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PERSPECTIVE

Energy Demand of Nitrogen and Phosphorus Based Fertilizers and Approaches to Circularity

Damilola A. Daramola* and Marta C. Hatzell

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ABSTRACT: The climate-related concerns associated with the manufacturing of synthetic fertilizers are largely traced back to energy and carbon emissions during the chemical manufacturing of ammonia. However, synthetic fertilizers are made up of several macronutrients (nitrogen, phosphorus and potassium), each with different energy intensities and environmental impacts. With the movement toward resource circularity, there is a need to create a more holistic view regarding the process energy associated with synthetic inorganic fertilizers, including nitrogen and phosphorus. Here, we first describe the growing production and consumption of inorganic (synthetic) and organic (animal waste) nutrients in agriculture as well as the process energy associated with the production of granular phosphorus and nitrogen-based fertilizers. Next, we present projected global demand of nitrogen and phosphorus nutrients based on various sustainability and societal equity scenarios to make an argument for nutrient recovery as a viable approach to meet this demand. Finally, we discuss the characteristics and challenges of emerging technologies for nutrient recovery along with baseline performance and costs of current operational recovery facilities.

Improving crop yield through the application of synthetic fertilizers is of increasing importance as the global population continues to increase. Seventeen nutrients are known to regulate agricultural yield, and nitrogen (N), phosphorus (P) and potassium (K) are the three main macronutrients. For this reason, most fertilizers come with the label "NPK" followed by three numbers indicating the mass fraction of each of the primary macronutrients. The raw feedstocks used to chemically manufacture NPK fertilizers are air (N), phosphate rock (P) and potassium salts/potash (K). However, because air is inert, the nitrogen in air is further refined to ammonia and nitric acid prior to fertilizer manufacturing. Some common fertilizer formulations with the "NPK" designations are ammonia (82%N), urea (46%N), ammonium salts (∼27%N), superphosphates (20−46%P_2O_5) and ammonium phosphates (∼11−20%N/%P_2O_5), with P typically represented as P_2O_5: 2.29 kg P_2O_5 is equivalent to 1 kg P. Ammonia synthesis is widely recognized as an energy-intensive process and is currently the fourth largest energy consumer in the chemical manufacturing sector in the United States.[1] Ammonia is also the second largest energy consumer worldwide, with estimates suggesting the energy consumption to be 30 × 10^6 GJ/t (t, used throughout this Perspective, represents metric tonnes). Most of this energy consumption is related to a steam generation process that is required to produce hydrogen.

Phosphate rock is mined in multiple regions of the world, yet 70% of global availability is in Morocco and the Sahara region.[2] Production of phosphate rock mainly consists of mining, beneficiation and drying, resulting in 1.18 GJ/t.[3] Although the energy consumption for processing phosphate rock is several orders of magnitude lower than the energy consumption associated with processing nitrogen (ammonia), the energetics are relevant due to the high volume. In 2019, 227 million t of phosphate rock was mined globally,[2] i.e., 2.7 × 10^8 GJ/year spent for phosphate rock generation as a raw material. Land use concerns, excess waste produced during mining, the significantly slow rate of natural phosphate fixation and the unequal distribution of phosphate rock reserves worldwide raise several potential supply chain issues.

The associated risks with both N and P nutrient supply are more stark today because of the 2022 Russian invasion of Ukraine and the accompanying sanctions, which have disrupted global energy supply and increased global energy costs.[4] This impact on energy has further led to an increase in global food prices due to both the associated energy demand for fertilizer synthesis and the associated transportation costs for food and fertilizer delivery.[4] These risks may be mitigated by lowering the dependence of N availability and delivery on

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Article

Influence of Highly Stable Ni^{2+} Species in Ni Phyllosilicate Catalysts on Selective Hydrogenation of Furfural to Furfuryl Alcohol

Sasithorn Kuhaudomlap, Okorn Mekasuwandumrong, Piyasan Praserthdam, Kiat Moon Lee, Christopher W. Jones,* and Joongjai Panpranot*

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ABSTRACT: Enhancing the catalytic performance of non-noble Ni catalysts in the selective hydrogenation of furfural to furfuryl alcohol (FA) in terms of furfural conversion, selectivity, and good recyclability is challenging. Here, spherical nickel phyllosilicate catalysts (Ni_PS) with fibrous-like structures are prepared via a modified sol−gel method with Ni loadings of 2−30 wt %. Upon exposure to air, all the reduced Ni_PS catalysts exhibit more than 80% $Ni^0/Ni_{phyllosilicate}$ species on the surface, whereas a large portion of Ni oxide species (>55%) is presented on the impregnated catalyst. The Ni^{2+} species in nickel phyllosilicate catalysts are active and highly stable during reduction, reaction, and regeneration, yielding stable catalytic performance for multiple recycle tests in furfural hydrogenation to FA. Furfural conversion over the Ni_PS catalysts increased monotonically with increasing Ni loading without an FA selectivity drop. The presence of both metallic Ni^0 and $Ni_{phyllosilicate}$ also produces a synergistic promotional effect for FA formation.

INTRODUCTION

Nickel is one of the most frequently used metals in a wide variety of industrial manufacturing. Silica-supported nickel catalysts (Ni/SiO_2) are used extensively in catalytic reactions due to their low cost, high specific surface area, easy functionalization, and controllable morphology/adjustable pore structures.[1−3] However, Ni/SiO_2 usually suffers from a weak interaction between nickel species and silica supports, which is a significant drawback that can cause leaching of nickel species during a liquid phase reaction as well as agglomeration and sintering of nickel under a high thermal treatment and reaction process, leading to low catalytic activity, deactivation of catalyst, and poor stability. Several efficient strategies have been reported to improve nickel dispersion and enhance the metal−support interaction such as the addition of various promoters such as La_2O_3[4] and V_2O_5,[5] the formation perovskite and hydrotalcite structures,[6,7] the modification of the support and developed preparation methods to enhance the metal−support interaction and inhibit the catalyst agglomeration such as molecular layer deposition,[8] and the construction of nickel-based catalysts with a confinement effect like mesostructured cellular foam.[6] However, there are still some limitations for these methods such as high cost, complicated procedures, and requirement for multiple steps and unique instruments for preparation.

Metal phyllosilicates have received considerable attention in recent catalysis research because of their unique layered structure that can offer outstanding properties such as a strong metal−support interaction, small metal domain size and high dispersion of active metal species, rich porous structures, excellent adsorption properties, high thermal stability, and simple preparation procedures. Ni phyllosilicates typically possess a lamellar structure, consisting of tetrahedral layers of SiO_4 (Si-O-Si) and octahedral layers of Ni(II) (Ni coordinated to oxygen atoms or hydroxyl groups, Si-O-Ni-O(OH)).[9] It has been reported that metallic nickel derived from the reduction of nickel phyllosilicate can provide nickel particles with fine sizes at a high nickel content and high dispersion. Ni phyllosilicates show good performances in a number of reactions including CO_2 and CO methanation,[10] hydrogenation of levulinic acid to γ-valerolactone,[11] xylose hydrogenation to xylitol,[12] hydrogenation of maleic anhydride,[13] hydrogenation of polycyclic aromatic hydrocarbons,[14] and carbon dioxide reforming of methane.[15]

Generally, nickel phyllosilicates with different crystal structures can be synthesized via various methods including hydrothermal methods,[1,16−18] ammonia evaporation meth-

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Research Article

Selective Conversion of Malononitrile and Unprotected Carbohydrates to Bicyclic Polyhydroxyalkyl Dihydrofurans Using Magnesium Oxide as a Recyclable Catalyst

Nima Ronaghi, Elizabeth V. Jones, Hyun June Moon, Sang Jae Park, Christopher W. Jones,* and Stefan France*

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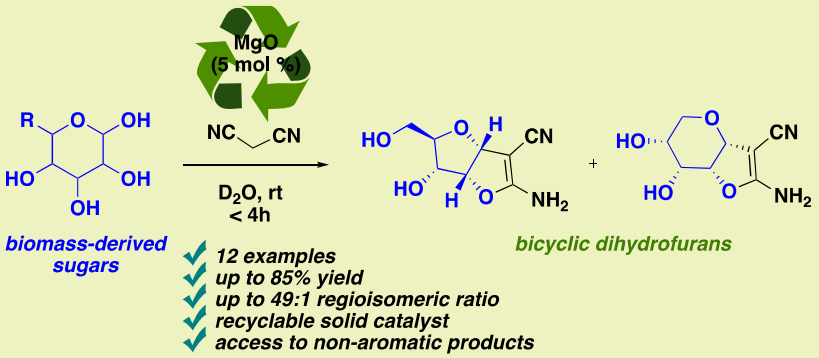

ABSTRACT: Using renewable feedstocks to access highly functionalized molecules in a concise manner is a promising approach to sustainable syntheses. Previous studies used malononitrile to convert simple sugars to polyhydroxylalkyl aminofurans in the presence of various catalysts. Herein, a chemodivergent method is disclosed for the reaction of the same unprotected sugars with malononitrile to instead form bicyclic 2,3-dihydrofuran products in yields up to 85% with good regioselectivities. Kinetic, NMR, and computational studies support a proposed mechanism for the formation of dihydrofuran products. By employing a mild set of reaction conditions (aqueous solvent, at room temperature, in under 4 h) and a recyclable heterogeneous MgO catalyst, this method serves as a powerful tool for carbohydrate upcycling that offers useful and interesting nonaromatic products.

KEYWORDS: *solid base catalysis, biomass conversion, sugars, heterogeneous catalysis, cascade reactions*

■ INTRODUCTION

The conversion of biomass to useful intermediates and products provides a renewable alternative to synthesis, starting from traditional fossil feedstocks.[1] Carbohydrates, the most abundant category of biomass, are cheap, readily available starting materials for synthesizing many value-added products.[2] Several synthetically accessible compounds such as hydroxymethylfurfural[3−5] and levulinic acid[6−8] have been previously established as platform molecules in biomass conversion processes, but there is much room for expansion to more diverse and complex biomass-derived molecules. Currently, most processes to synthesize densely functionalized molecules from carbohydrates require multiple reactions, purifications, and isolations and often have varying and noncompatible reaction conditions between steps. Thus, more efficient and direct approaches to versatile products from simple carbohydrates are highly desired.

Our groups recently reported success in the synthesis of polyhydroxyalkyl and *C*-glycosyl furans from simple carbohydrates and a 1,3-dicarbonyl through the Garcia Gonzalez reaction,[9−25,32] which gives products with great promise as precursors for platform chemicals, value-added chemicals, pharmaceutical intermediates, and materials.[26−31] First, using $ZrCl_4$ as an efficient homogeneous Lewis acid catalyst,[32] we followed that report with the subsequent development of zirconium terephthalate-based metal−organic frameworks (MOFs) as heterogeneous catalysts for the same transformation.[33]

We were interested in expanding our studies using heterogeneous catalysts to include the related reactions of malononitrile for the upcycling of simple carbohydrates. The prior literature on the reaction of malononitrile with simple sugars demonstrated that aminofurans could be readily formed

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Zr-Catalyzed Synthesis of Tetrasubstituted 1,3-Diacylpyrroles from *N*-Acyl *α*-Aminoaldehydes and 1,3-Dicarbonyls

Caria Evans, William J. Berkey, Christopher W. Jones,* and Stefan France*

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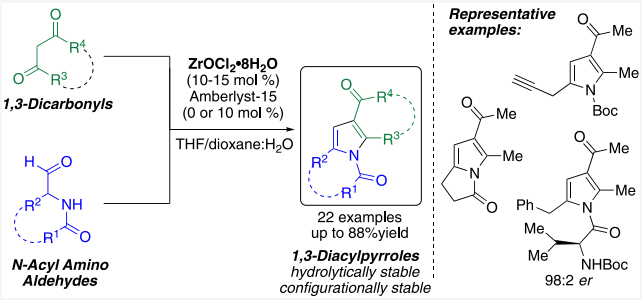
ABSTRACT: A Zr-catalyzed synthesis of tetrasubstituted 1,3-diacylpyrroles is reported that employs the direct use of *N*-acyl *α*-aminoaldehydes with 1,3-dicarbonyl compounds. The products were formed in up to 88% yield and shown to be hydrolytically and configurationally stable under the reaction conditions (THF/1,4-dioxane and H_2O). The *N*-acyl *α*-aminoaldehydes were readily prepared from the corresponding *α*-amino acids. The reaction tolerates a wide array of substrate types including alkyl-, aryl-, heteroaryl-, and heteroatom-containing groups on the aminoaldehyde side chain. A variety of 1,3-dicarbonyls proved amenable to the reaction along with an aldehyde derived from a L,L-dipeptide, an aldehyde generated *in situ*, and an *N*-acylated glucosamine.



■ INTRODUCTION

Pyrroles constitute an important heterocyclic framework that is heavily represented in biology, natural products, pharmaceuticals, and materials science.[1] In particular, the 3-acylpyrrole motif is one of the most studied classes of pyrroles and appears in a number of drug molecules and other biologically active derivatives, such as piquindone, atorvastatin, and sunitinib (Figure 1). Based on its therapeutic potential, the 3-acylpyrrole framework has garnered a lot of attention from the synthetic community.[2] Many approaches have been reported toward their synthesis, including classical ones like the Hantzsch, Knorr, and Paal−Knorr reactions.[3] Most methods for 3-acylpyrroles involve the use of *β*-ketocarbonyl compounds, *β*-enaminones, *α*-aminoketones, propargylamines, allenamides, and/or *α*-haloketones.[4] Despite the wealth of approaches, there is no one size fits all solution as each method comes with its own limitations. Many of these methods require high reaction temperatures (>80 °C) and the use of strong Lewis or Brønsted acids (often in stoichiometric amounts) as well as offer limited scope and functional group compatibility. These caveats necessitate the development of new, milder methods for the synthesis of functionalized 3-acylpyrroles.

Though various methods are reported toward 3-acylpyrroles, to the best of our knowledge, *α*-aminoaldehydes[5] as synthetic precursors have never been directly employed for their synthesis.[6] This is largely due to their instability and propensity to polymerize or undergo a variety of degradation pathways. For 3-acylpyrrole synthesis, the closest example of the use of an *α*-aminoaldehyde with a 1,3-dicarbonyl comes from the Garcia Gonzalez reaction[7] using glucosamine,[8] which resembles a Knorr pyrrole[9] synthesis (Scheme 1). As an aldose, glucosamine exists in an equilibrium between its cyclic hemiacetal and acyclic *α*-aminoaldehyde forms. We recently reported the enhancement of the Garcia Gonzalez reaction with unprotected sugars using Zr(IV)-based Lewis acid catalysis and demonstrated the compatibility of glucosamine to this process.[10] In the presence of a catalytic $ZrCl_4$, a cascade reaction occurs to form a 2-(polyhydroxyalkyl)-substituted 3-acylpyrrole **I** (65%) and a *C*-glycosyl 3-acylpyrrole **II** (3% yield).

Encouraged by this success, we sought to explore the direct reactions of *α*-aminoaldehydes in the reactions with 1,3-dicarbonyls. Given the instability of unprotected *α*-aminoaldehydes, we looked to employ bench-stable *N*-acyl derivatives instead. The resulting reactions with 1,3-dicarbonyls would form tetrasubstituted 1,3-diacylpyrroles, which have been identified as potent inhibitors of MEK kinase for the treatment of various cancers.[11] Thus, herein, we report the first successful synthesis of functionalized 1,3-diacylpyrroles from the direct use of stable *α*-aminoaldehyde precursors (Scheme 1B).

N-Acyl *α*-aminoaldehydes **1** were mainly prepared from the corresponding *N*-acyl *α*-amino acids using the one-pot CDI/DIBAL-H method reported by Breinbauer and co-workers.[12] At the outset, we selected *N*-Boc-phenylalaninal (**1a**, *N*-Boc-Phe-H) as the model system due to its high yield and purity

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First-order Policy Optimization for Robust Markov Decision Process *

Yan Li † Guanghui Lan ‡ Tuo Zhao §

Abstract

We consider the problem of solving robust Markov decision process (MDP), which involves a set of discounted, finite state, finite action space MDPs with uncertain transition kernels. The goal of planning is to find a robust policy that optimizes the worst-case values against the transition uncertainties, and thus encompasses the standard MDP planning as a special case. For $(\mathbf{s}, \mathbf{a})$-rectangular uncertainty sets, we establish several structural observations on the robust objective, which facilitates the development of a policy-based first-order method, namely the robust policy mirror descent (RPMD). An $\mathcal{O}(\log(1/\epsilon))$ iteration complexity for finding an ϵ-optimal policy is established with linearly increasing stepsizes. We further develop a stochastic variant of the robust policy mirror descent method, named SRPMD, when the first-order information is only available through online interactions with the nominal environment. We show that the optimality gap converges linearly up to the noise level, and consequently establish an $\widetilde{\mathcal{O}}(1/\epsilon^2)$ sample complexity by developing a temporal difference learning method for policy evaluation. Both iteration and sample complexities are also discussed for RPMD with a constant stepsize. To the best of our knowledge, all the aforementioned results appear to be new for policy-based first-order methods applied to the robust MDP problem.

1 Introduction

We consider the problem of solving the robust Markov decision process (MDP) where the transition kernel is uncertain, and one seeks to learn a policy that behaves robustly against such uncertainties. Specifically, a robust MDP $\mathcal{M}_{\mathcal{U}} := \{\mathcal{M}_u = (\mathcal{S}, \mathcal{A}, c, \mathbb{P}_u, \gamma) : u \in \mathcal{U}\}$ consists of a set of MDPs, where $\mathcal{S}$ and $\mathcal{A}$ denote the state and action space, respectively; $\mathbb{P}_u : \mathcal{S} \times \mathcal{A} \to [0, 1]$ denotes the transition kernel, indexed by $u \in \mathcal{U}$; $c : \mathcal{S} \times \mathcal{A} \to \mathbb{R}$ denotes the cost function, which we assume with loss of generality that $0 < c(s, a) \leq 1$ for all (s, a); γ denotes the discount factor. The set of MDPs differ from each other only in their respective transition kernels. The standard value function $V_u^\pi : \mathcal{S} \to \mathbb{R}$ of a policy π with respect to MDP $\mathcal{M}_u$, is defined as

$$V_u^\pi(s) = \mathbb{E}\left[\sum_{t=0}^\infty \gamma^t c(s_t, a_t) \middle| s_0 = s, a_t \sim \pi(\cdot|s_t), s_{t+1} \sim \mathbb{P}_u(\cdot|s_t, a_t)\right], \quad \forall s \in \mathcal{S}.$$

Our end goal is to learn a policy π^* that is the solution of the following problem

$$\min\left\{V_r^\pi(s) := \max_{u\in\mathcal{U}} V_u^\pi(s) : \ \pi \in \Pi\right\}, \tag{1.1}$$

where Π denotes the set of all stationary and randomized policies. That is, (1.1) aims to learn a policy that minimizes the worst-case value simultaneously for every state. Clearly, when $\mathcal{U}$ is a singleton, the problem of finding robust policy (1.1) reduces to solving a standard MDP planning problem.

Before any technical discussions, we first construct a simple example motivating our study of finding a robust policy in the sense of (1.1), when facing transition uncertainty. Specifically, we will construct a

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Article

Effect of Shear on Pumped Capillary Foams

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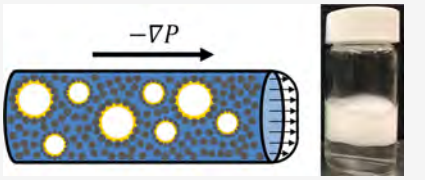
Read Online

ABSTRACT: Foam flow in many applications, like firefighting and oil recovery, requires stable foams that can withstand the stress and aging that result from both shear and thermodynamic instability. Events of drainage and coarsening drive the collapse of foams and greatly affect foam efficacy in processes relying on foam transport. Recently, it was discovered that foams can be stabilized by the synergistic action of colloidal particles and a small amount of a water-immiscible liquid that mediates capillary forces. The so-called capillary foams contain gas bubbles that are coated by a thin oil-particle film and integrated in a network of oil-bridged particles; the present study explores how this unique architecture impacts the foams' flow dynamics. We pumped capillary foams through millimeter-sized tubing (ID: 790 μm) at different flow rates and analyzed the influence of stress and aging on capillary foam stability. We find that the foams remain stable when pumped at higher flow rates but undergo phase separation when pumped at low flow rates. Our observations further show that the particle network is responsible for the observed stability in capillary foams and that network strength and stability of an existing foam can be increased by shearing.



1. INTRODUCTION

Liquid foams are gas−liquid mixtures found throughout products and processes in various industries. These multiphasic materials are versatile because their geometrical and rheological properties provide benefits such as high specific surface area, high viscosity, and finite yield stress.[1] These benefits can be observed in applications such as froth flotation, where hydrophobic particles are separated from slurries through particle adsorption at the interface of rising bubbles; in firefighting, where foams are used to suppress combustion; in oil recovery where foams help to displace oil trapped in reservoirs; and in household/cosmetic products where foams are used as a delivery vehicle for active ingredients.[1,2] In many of these processes, foams are pumped and experience shear stress; if the stress is below the yield stress, the foam can flow in a plug via slip at the wall. However, if the applied stress is above the yield stress, steady shear flow sets in, causing bubbles to slide past each other and liquid to be displaced from the Plateau borders and thin films.[3,4] Foam performance in applications is determined by the stabilization mechanism as well as the interdependent dynamic processes of coarsening and drainage that govern the liquid fraction and bubbles sizes, which, in turn, affect the properties of the foam during use.[5] A fundamental understanding of foam dynamics can therefore help in effectively engineering foam properties for different applications.[6]

Foams undergo changes from formation to complete collapse.[7] Aqueous foams are formed by generating metastable gas bubbles in a continuous water phase; this process is governed by interfacial and chemical properties of the applied foaming agent and the technique used in foam generation.[8−11] Once the foam is generated, the foam structure and composition evolve over time through the action of gravity that leads to liquid loss, surface tension that minimizes the gas−liquid interfacial area, and Laplace pressure differentials that drive diffusive coarsening, and inertial and viscous forces that can deform interfaces and hasten foam collapse.[12−14] Coarsening and drainage are strongly coupled aging processes that induce internal dynamics affecting the rheological properties of foams.[12,15] Drainage refers to the flow of liquid out of foams. In high-quality foams, where the gas volume fraction (ϕ) is above 70%, the liquid exists in the Plateau borders and thin films between the polyhedral-shaped gas bubbles of the foam. Drainage occurs under the influence of gravity and causes thinning of films separating bubbles, thus giving way to coalescence or bursting of bubbles. Capillary action counteracts drainage in foams and prevents complete loss of liquid from the foam. Diffusive coarsening is another means through which foams age; here bubble sizes evolve through a net diffusive flux of dissolved gas molecules across the liquid separating bubbles of different sizes. This flux causes larger bubbles to grow at the expense of smaller bubbles, which have higher Laplace pressure, leading to an increase in the average bubble size in the foam over time.[16]

The rates of coarsening and drainage can be slowed when films between bubbles are thick and when particles accumulate in the Plateau borders, respectively.[13] The high free energy of the gas−liquid interface can be reduced by surfactants that adsorb at the air−water interface, slowing down thinning and

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ACS APPLIED POLYMER MATERIALS

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Multilayer Chitin–Chitosan–Cellulose Barrier Coatings on Poly(ethylene terephthalate)

Zeyang Yu, Yue Ji, and J. Carson Meredith*

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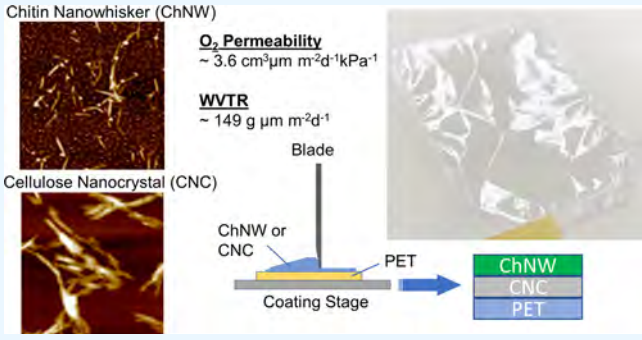
ABSTRACT: Currently, effective barrier properties over a wide range of humidity are achieved by layering multiple plastics, resulting in structures that are nearly impossible to recycle through current systems. There is strong interest in developing barriers that are recyclable, biodegradable, or compostable. Chitin and cellulose nanomaterials are promising alternatives because of their high crystallinity, renewable sourcing, strong electrostatic interactions, and potential for biodegradation or composting. In this paper, we explore the potential to create multilayer materials with effective oxygen and water vapor barrier properties at elevated humidity by combining recyclable poly(ethylene terephthalate) (PET) films with single-layer and bilayer coatings of chitin nanowhiskers (ChNWs), chitosan (CS), and cellulose nanocrystals (CNCs). The addition of CS to the ChNW suspension improved the gas barrier properties of ChNW coatings, likely by filling voids, and short ChNWs (SChNW, 114 nm) performed better than long ChNWs (LChNW, 230 nm). At the optimal mass ratio of 1:1 SChNW/CS, the oxygen permeability (OP) of SChNW/CS-coated PET films was 5.1 cm^3 μm m^{-2} day^{-1} kPa^{-1} versus 15.9 cm^3 μm m^{-2} day^{-1} kPa^{-1} for neat PET. To take advantage of electrostatic attraction and hydrogen bonding, CNC was first coated on the PET, followed by coating with ChNW/CS, resulting in an OP as low as 3.6 cm^3 μm m^{-2} day^{-1} kPa^{-1} at 50% relative humidity (RH), and 6.4 cm^3 μm m^{-2} day^{-1} kPa^{-1} at 80% RH. Moreover, after thermal treatment (120 °C, 2.5 h), the OP dropped to 2.2 cm^3 μm m^{-2} day^{-1} kPa^{-1} (50% RH) and 4.8 cm^3 μm m^{-2} day^{-1} kPa^{-1} (80% RH). The ChNW/CS and CNC coating can be efficiently removed with alkali treatment enabling possible recycling of the coated PET films.



KEYWORDS: *chitin, chitosan, cellulose, blade coating, sustainable packaging*

1. INTRODUCTION

Sustainability, industrial ecology, eco-efficiency, and green chemistry are guiding the development of the next generation of packaging materials and their production processes. There is intense interest in biodegradable and biobased polymers from renewable biomass feedstocks for sustainable packaging products that can serve as alternatives to single-use packaging, most of which is currently landfilled at end of life.[1] Poly(ethylene terephthalate) (PET) is widely used in current packaging due to its low cost and film-forming characteristics. While PET is a good water vapor barrier and is recyclable or depolymerizable, PET is often layered with other materials to improve its oxygen barrier properties, such as poly(ethylene-*co*-vinyl alcohol) (EVOH), poly(vinylidene chloride) (PVDC), metal, or metal oxides. However, the addition of these nonrenewable components also gives rise to environmental concerns and makes the multilayer difficult to recycle in the current infrastructure. Combining a renewable oxygen barrier layer with PET would create a hybrid multilayer of a recyclable petroleum-derived polymer with a biodegradable and/or renewable alternative material. Because many renewably sourced oxygen barriers are sensitive to humidity, hybrid products with PET could both mitigate the humidity dependence and potentially enable the recycling of PET and biodegradation/recycling of the bioderived layers if they can be separated at the end of life.

Cellulose and chitin are the first and second most abundant naturally occurring biopolymers, which have an annual production estimated to be 10^{10}–10^{12} tons per year.[2,3] Cellulose is a polymer consisting of D-glucopyranose units linked together through 1,4-β glycoside bonds. The intermolecular hydrogen bonds and oxygens of the adjoining ring molecules stabilize the linkage and lead to a linear, stereoregular configuration.[4,5] Cellulose is most abundantly located in plant cell walls, but it is also available from bacteria and

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Materials Advances

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Optimization of spray-coated nanochitin/nanocellulose films as renewable oxygen barrier layers *via* thermal treatment†

Yue Ji,[a] D. Eric Shen,[bc] Elizabeth K. Young,[d] Callie L. Goins,[b] John R. Reynolds,[bcd] Meisha L. Shofner[de] and J. Carson Meredith *[ae]

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The demand for food and pharmaceutical packaging materials is increasing, but the most common materials used are non-renewable, non-biodegradable petroleum-based plastics, which has resulted in many end-of-life problems. Cellulose nanocrystals (CNCs) and chitin nanowhiskers (ChNWs) have high strength and low oxygen permeability (OP), providing a renewable alternative. In this work, we spray coated ChNWs and CNCs on cellulose acetate (CA) film and tuned the film properties by adjusting the spray coating temperature (T_{spray}) and the post thermal treatment temperature ($T_{thermal}$). Importantly, by increasing T_{spray} (from 40 to 100 °C) and $T_{thermal}$ (from 40 to 140 °C), the OP decreased 48% and 62%, respectively. The optimal OP (*i.e.*, 11.5 cm^3 μm m^{-2} day^{-1} kPa^{-1}) is comparable to that of commercial oriented poly(ethylene terephthalate). Film transmittance and haze were dependent on both temperatures, with higher T_{spray} and $T_{thermal}$ giving rise to coated films with lower haze and higher transmittance values approaching those of bare CA. The mechanical properties and water vapor barrier properties of the coated films were on average 20% and 11% enhanced compared to neat CA, without being significantly influenced by the temperatures. These properties support the use of the polysaccharide-based film as a renewable substitute in packaging applications.

Introduction

Barrier packaging materials, which are used to protect food and pharmaceuticals from deterioration, contamination, and damage, are playing an increasingly significant role in modern life.[1] These materials often require low gas permeabilities, especially for oxygen and moisture, mechanical integrity, and in some cases high optical transparency for customers to clearly see the product.[2]

Common materials for barrier packaging include layers consisting of metal films, plastics, and paper materials.[1] Among them, plastics are the most used materials for food and beverage packaging, and ~50% of Europe's food is packed in layered plastics, consisting often of poly(ethylene terephthalate) (PET), polyolefins, poly(vinyl chloride) (PVC), polyamide, and ethylene vinyl alcohol (EVOH), *etc.*[3] However, these are petroleum-based materials, which are non-renewable, non-biodegradable and are not recycled. It takes decades to thousands of years for them to degrade, which has resulted in widescale pollution in the ocean and soil.[4] Though some PET and polyolefins are synthesized from renewable sources, the end-of-life problems caused by their non-biodegradability still exist.[5] Only limited types of bio-based, biodegradable materials have been commercialized as gas barriers in food packaging, such as starch, cellophane, poly(lactic acid) (PLA), and poly(hydroxyalkanoates) (PHAs).[1]

Cellulose and chitin, as the first and second most abundant polysaccharides in nature, have gained attention for packaging applications.[6] Cellulose is a homopolymer of D-glucose, and chitin consists of *N*-acetyl-D-glucosamine units. Because of strong intermolecular hydrogen bonding, cellulose and chitin have high crystallinity, and their nanomaterials have high modulus and strength as well as low oxygen permeabilities (OP).[7,8] These nanomaterials include cellulose nanofibrils (CNFs),[9] cellulose nanocrystals (CNCs),[10] chitin nanofibers (ChNFs),[10,11] chitin nanocrystals,[12] and chitin nanowhiskers (ChNWs).[13]

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Research Article

Roll-to-Roll, Dual-Layer Slot Die Coating of Chitin and Cellulose Oxygen Barrier Films for Renewable Packaging

Kwangjun Jung, Yue Ji, Tae-Joong Jeong, Peter N. Ciesielski, J. Carson Meredith, and Tequila A. L. Harris*

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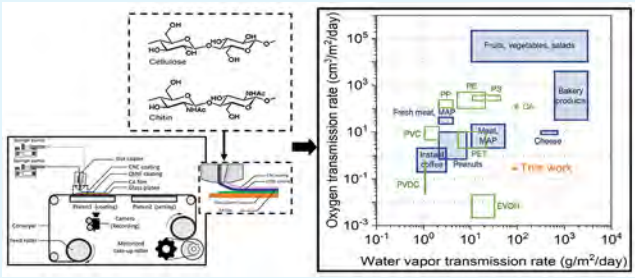
ABSTRACT: Cellulose and chitin are the two most abundant naturally produced biopolymers and are being extensively studied as candidates for renewable oxygen barrier films used in packaging. It has been shown that bilayers formed from cellulose nanocrystals (CNCs) and chitin nanofibers (ChNFs) exhibit oxygen barrier properties similar to polyethylene terephthalate (PET). However, this prior work explored only coating each layer individually in sequence through techniques such as spray coating. Here, we demonstrate the viability of dual-layer slot die coating of CNC/ChNF bilayers onto cellulose acetate (CA) substrates. The dual-layer slot die method enables significantly lower oxygen permeability versus spray coating while using a roll-to-roll system that applies the bilayer in a single pass. This work discusses suspension properties, wetting, and drying conditions required to achieve well-controlled ChNF/CNC bilayers. Spray-coated bilayer films were on average 25% thinner than the dual-layer bilayer film; however, the thickness-normalized oxygen permeability (OP) of the dual-layer-coated ChNF/CNC bilayer film on CA was 20 times better than that of the spray-coated bilayers. It has been shown that ChNF contributes to the wetting and barrier properties. Values of OP for the slot die-coated bilayers under optimized drying conditions were as low as 1.2 $cm^3 \cdot \mu m \cdot m^{-2} \cdot d^{-1} \cdot kPa^{-1}$, corresponding to a normalized oxygen transmission rate of 0.32 $cm^3 \cdot m^{-2} \cdot d^{-1}$ at 23 °C and 50% relative humidity. It is also noted that the adhesive properties of the dual-layer coating are also improved when films are air-dried and that ChNF contributes to the wetting and barrier properties.



KEYWORDS: *Roll-to-roll dual-layer slot die coating, renewable packaging, cellulose nanocrystal, chitin nanofiber, oxygen permeability*

1. INTRODUCTION

Cellulose and chitin nanomaterials have been studied extensively as alternative packaging materials because their crystallinity results in high modulus and tensile strength and low gas permeability.[1,2] Cellulose and chitin are the two most abundant natural biopolymers produced in nature in quantities of ∼10^{10}−10^{12} tons per year.[3,4] Cellulose is obtained from plants but can also be obtained from bacteria and tunicates. Chitin is a structural polysaccharide found in crustaceans (e.g., food processing waste streams), insects, and fungi.[5] The properties deriving from the nanocrystalline or nanofibrous forms of these biopolymers, including cellulose nanocrystals (CNCs) and chitin nanofibers (ChNFs), have made them promising candidates for renewable, biodegradable materials for applications including primary barrier packaging for food, electronics, and pharmaceutical/medical products.[6] Unfortunately, the challenge in melt-processing cellulose and chitin as neat materials limits their manufacturability by packaging converters. However, the ease of suspending cellulose and chitin nanomaterials in water suggests their application as coatings to produce barrier films.[6]

Various methods for fabricating CNC and ChNF films have been presented in the literature. CNC film fabrication from suspension has utilized batch techniques such as spin coating[7] and continuous processes such as slot die[8] and gravure[9] coating. Methods such as spray coating,[6] regeneration from the gel,[10] and layer-by-layer deposition[11] have been used for coating ChNF suspensions (or chitin nanowhiskers) for biomedical,[12] optical,[11] and barrier applications.[6,13−16] Gravure and spray coatings often require multiple applications to achieve a desired, uniform thickness and can be challenging for suspensions with relatively high viscosity.[6] Spin coating is not suitable to produce films continuously with a large area.[7] However, roll-to-roll (R2R) manufacturing utilizing slot die coating offers solutions to these problems as it is a scalable, inexpensive, and relatively fast continuous process.[17] Slot die

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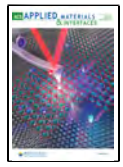

Cellulose (2022) 29:5575–5591
https://doi.org/10.1007/s10570-022-04626-2

ORIGINAL RESEARCH

Dewatering of cellulose nanofibrils using ultrasound

Udita Ringania · Joseph Harrison · Robert J. Moon · M. Saad Bhamla

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Abstract Although cellulose nanomaterials have promising properties and performance in a wide application space, one hinderance to their wide scale industrial application has been associated with their economics of dewatering and drying and the ability to redisperse them back into suspension without introducing agglomerates or lose of yield. The present work investigates the dewatering of aqueous suspensions of cellulose nanofibrils (CNFs) using ultrasound as a potentially low-cost, non-thermal, and scalable alternative to traditional heat-based drying methods such as spray drying. Specifically, we use vibrating mesh transducers to develop a direct-contact mode ultrasonic dewatering platform to remove water from CNF suspensions in a continuous manner. We demonstrate that the degree of dewatering is modulated by the number of transducers, their spatial configuration, and the flow rate of the CNF suspension. Water removal of up to 72 wt.% is achieved, corresponding to a final CNF concentration of 11 wt.% in 30 min using a two-transducer configuration. To evaluate the redispersibility of the dewatered CNF material, we use a microscopic analysis to quantify the morphology of the redispersed CNF suspension. By developing a custom software pipeline to automate image analysis, we compare the histograms of the dimensions of the redispersed dewatered fibrils with the original CNF samples and observe no significant difference, suggesting that no agglomeration is induced due to ultrasonic dewatering. We also perform SEM analysis to evaluate the nanoscale morphology of these fibrils showing a width range of 20 nm–4 um. We estimate that this ultrasound dewatering technique is also energy-efficient, consuming up to 36% less energy than the enthalpy of evaporation per kilogram of water. Together with the inexpensive cost of transducers (< $1), the potential for scaling up in parallel flow configurations, and excellent redispersion of the dewatered CNFs, our work offers a proof-of-concept of a sustainable CNF dewatering system, that addresses the shortcomings of existing techniques.

Keywords Dewatering · Ultrasonic dewatering · Cellulose nanofibrils · Energy-efficient · Continuous platform

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10570-022-04626-2.

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Introduction

Cellulose nanofibrils (CNFs) are nanosized cellulose particles (20–100 nm in diameter, microns in length)

Article

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Lightweight polyester composites *via* nanoreinforced syntactic foams

Edward DiLoreto[1], Arielle Berman[2], Robert J Moon[3] and Kyriaki Kalaitzidou[1,2]

Abstract

Syntactic foams and their reinforcement with cellulose nanocrystals (CNC) in a thermosetting polyester resin (PR) matrix were studied in order to provide a pathway for lightweight composites for automotive applications with enhanced performance including thermomechanical properties and water uptake. A novel method for coating hollow glass spheres (HGS) with CNC was developed. Various combinations of functionalized CNC and surface modified HGS were studied to determine interactions between the two materials. Surface analysis techniques indicated that CNC were successfully deposited onto the HGS surface and remained at the surface after compounding with PR. Dynamic mechanical analysis of composites samples indicated a 30% increase in high temperature storage modulus between CNC coated HGS samples and uncoated HGS samples. Shifts in tan(δ) peak intensity and beta-relaxation temperature also indicated an increase in interphase volume around CNC coated HGS as compared to uncoated HGS samples. Coating HGS with CNC reduced the maximum water adsorption by as much as 40% indicating the potential for this material system in high moisture environments.

Keywords

composites, nanocellulose, syntactic foams, environmental conditioning

Introduction

Lightweighting, the reduction in density of materials without sacrificing performance using scalable techniques, has been a continuing objective for the field of materials science as it can lead to enhanced fuel efficiency in the transportation sector and thus reduction in greenhouse gas emissions, and increased payload in structural materials. In addition to lightweighting, reduction of the carbon footprint can be achieved by using sustainable or renewable materials. According to theoretical calculations, use of renewable nanomaterials as reinforcements can lead to both lightweighting and sustainable products.[1] However, when it comes to practice the inevitable formation of agglomerates no matter what processing techniques are used limits translation of nanoscale properties to macroscopic structures.[2,3] Furthermore, overall sustainability (i.e. the environmental impact or carbon footprint) of the material system and the resulting product is of growing concern. A common approach to achieving these goals is twofold: reducing the part's mass and incorporating an increased amount of renewable materials.

Cellulose nanomaterials (CNM) are cellulose based nano particles extracted from bulk cellulose materials (e.g. plants, trees, agricultural waste streams, recycled paper, etc.) and can provide mechanical reinforcement to a wide variety of polymers if properly used (e.g. fine-scale dispersion, compatibilizing surface chemistry, etc.). Although CNM mechanical properties are not notably better than other nanomaterials, the biogenic, renewability, biodegradability, low toxicity, and high-volume production potential of these materials makes them particularly appealing.[1,4,5] Additionally, with a density of ~1.59 g/cm^3 the addition of CNM has only a slight effect on the overall composite density. Cellulose nanocrystals (CNC) are one type of CNM and are spindle-shaped particles comprised of highly crystalline cellulose domains. This study will examine the effects of CNC additions to polyester resin (PR) composites. Prior studies demonstrated increased mechanical properties by

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ORIGINAL RESEARCH

Transmission electron microscopy image analysis effects on cellulose nanocrystal particle size measurements

Sezen Yucel · Robert J. Moon · Linda J. Johnston · Douglas M. Fox · Byong Chon Park · E. Johan Foster · Surya R. Kalidindi

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Abstract A semi-automatic image analysis program, SMART, was used to analyze transmission electron microscopy (TEM) images from four laboratories that participated in an interlaboratory comparison study by Meija et al. on CNC particle size measurement by TEM using conventional manual image analysis approaches. Detailed image-to-image comparisons found that the percentage of "correctly" identified CNCs by SMART was 58% to 78%, while manual was 70% to 87%, depending on TEM image quality from a given laboratory. SMART was able to parameterize image quality, and it was found that SMART had difficulties in CNC identification for images with a combination of higher noise, lower contrast, and higher CNC density. Overall, the SMART image analysis was consistent with the manual approach. SMART showed lower laboratory-laboratory variation as compared to manual, suggesting that the variability of analyst bias of manual approach was removed and demonstrates an opportunity with SMART to improve the standardization of CNC size characterization. An approach to estimate the likelihood of reaching a representative measurement for CNC particle size was developed. SMART area analysis found that less than 10% of CNCs were used in morphology characterization; to assess more CNC material, SMART was used to analyze CNC agglomerates as a proof-of-concept demonstration. The total SMART image analysis time for each laboratory, having between 115 and 244 images, was less than 15 min, after selection of appropriate parameters. The SMART code is now available for the public to use for free at Github™.

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Research Article

Recovery and Enrichment of Organic Acids from Kraft Black Liquor by an Adsorption-Based Process

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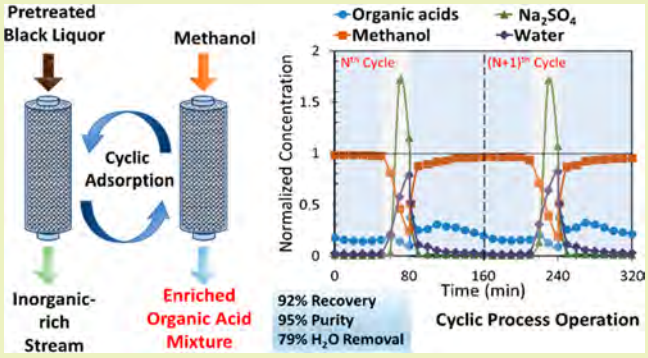
ABSTRACT: Kraft black liquor (BL) is a complex multicomponent byproduct from wood pulping processes. After lignin, carbohydrate-derived carboxylic acids are the second most abundant class of organics in kraft BL and comprise a potential biomass-derived feedstock of more than 50 million tons/year globally. These acids can be valorized in biofuels and biobased chemicals production or further fractionated to produce specific high-value carboxylic acids from the mixture. However, both of these routes require a viable process to separate carboxylic acids from BL. In this work, an adsorption-based process was developed to address this challenging issue. The kraft BL stream was first pretreated to remove most of the lignin by membrane nanofiltration (NF) combined with lignin-selective adsorption. To separate organic acids from this pretreated BL, organophilic/hydrophobic granulated activated carbon (GAC) was identified as a promising adsorbent with excellent organic/inorganic selectivity and adsorption capacity (>100 mg/g GAC). We present comprehensive adsorption measurements and analysis to characterize the adsorbent and develop a viable cyclic operation scheme for the adsorption process. The GAC adsorbents show robust separation performance over 20+ cycles. We have successfully obtained concentrated aqueous organic acid mixtures with ∼95% purity from kraft BL. We propose a modified kraft process with energy-efficient BL dewatering by NF and organic acids recovery for valorization.



KEYWORDS: *Biorefinery, Black liquor, Organic acids, Cyclic adsorption, Activated carbon*

INTRODUCTION

Kraft black liquor (BL) is a high-volume byproduct of the kraft pulping process, with more than 1 billion metric tons (BMT) of BL being generated annually in kraft mills. BL is a complex stream containing a variety of organic and inorganic fractions.[1] After lignin, carbohydrate-derived aliphatic acids are the second most abundant organic fractions of BL.[2] Globally, kraft BL contains more than 50 million metric tons (MMT) of organic acids including hydroxy acids (HAs) as well as conventional carboxylic acids (mainly formic and acetic acids).[3,4] HAs are aliphatic carboxylic acids substituted with one or several hydroxyl groups. Overall, this C_1−C_6 organic acids fraction could be valorized as a large-scale bioderived feedstock for conversion to biofuels and biobased chemicals.[5−7] Additionally, it could be further fractionated to recover specific high-value acids (such as lactic acid, glycolic acid, and gluco-isosaccharinic acid) that can be used in the production of cosmetics, bioplastics, metal chelating agents, food additives, and scaffolds for bone repair.[8−12]

Separation and enrichment of the organic acid fraction from kraft BL is an important requirement for the success of future valorization efforts. Moreover, compatibility of such separation processes with the overall kraft process is a key requirement since the remaining components of BL (water, inorganics, lignin) must be returned to the kraft process. Proposed separation processes to recover HA mixtures from BL[4,13−22] mostly involve BL pretreatment for lignin removal to clarify the BL and facilitate further processing. Acid precipitation and membrane filtration are the two main methods to separate lignin,[14,22,23] with adsorption also possible for removing lower concentrations of lignin.[24] In the alkaline conditions of BL, the organic acids are in the form of sodium salts. However, they must be recovered as acids to enable valorization, for which the addition of a strong inorganic acid (e.g., sulfuric acid) or ion exchange with a cationic resin is the typical process.[15,19] Subsequently, different combinations of methods such as distillation,[13] crystallization,[14] electrodialysis,[17] liquid−liquid extraction,[20,22] esterification of organic acids followed with distillation,[18] ion exclusion,[25] and ion exchange[21] have been

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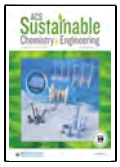

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Scalable aqueous-phase fabrication of reduced graphene oxide nanofiltration membranes by an integrated roll-to-roll (R2R) process

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ABSTRACT

Economic fractionation of multicomponent biomass-derived streams is a key challenge in biobased fuels and chemicals production. Kraft black liquor (BL) is generated at ~1 billion tons/yr globally from biomass pulping and contains ~15 wt% total solids including lignin, hemicellulose fragments, and inorganics. Membrane-based BL concentration is attractive but challenged by low solute rejections and poor stability in BL, which combines alkaline pH (~13), high dissolved solids content (15+ wt%) and high temperature (70–85 °C). Here we discuss the scaled fabrication and characterization of reduced graphene oxide (rGO) nanofiltration membranes by slot die coating on a roll-to-roll (R2R) with integrated vacuum filtration. We obtain high-quality 90 × 30 cm rGO membranes (referred to as "R2R-rGO membranes" in this work) with ~100 nm average thickness supported on porous poly(ethersulfone) (PES) sheets, and an effective area of 2700 cm^2. We present characterizations of their microstructure and uniformity as mapped over large areas by scanning electron microscopy (SEM), ellipsometry, adhesion test and X-ray photoelectron spectroscopy (XPS). The constructed ellipsometry model for the rGO membrane/PES substrate composite was successfully applied to 48 different locations of the R2R-rGO membranes. The R2R-rGO membranes showed >98% lignin rejection with a steady state flux of ~12 LMH at 50 bar in a 15.7 wt% total solids (TS) kraft BL stream at 72 °C and 2–3 gal/min crossflow rates. Slot die coating on a R2R platform with integrated vacuum filtration can enable rapid fabrication of high-quality GO membranes at scale without organic solvents or volatile organic compounds.

1. Introduction

There is an increasing demand in many industrial sectors for large-scale separation of complex aqueous streams to produce useable water, simultaneously recover/concentrate valuable resources (such as biomass components, salts, metals), and save energy relative to conventional separation processes such as distillation or liquid extraction [1–4]. Nanofiltration (NF) membranes are considered a key technological element in such processes. While polymeric membranes have so far dominated NF applications, there are many emerging separation problems in which polymeric membranes cannot provide the desired combination of performance and stability. Such problems typically involve elevated temperatures, pH extremes, and high dissolved solids content [5,6]. A particular example is in the conversion of forest biomass by the kraft process [7]. For every ton of cellulose pulp produced, about 6 tons of black liquor (BL) byproduct is generated. BL is generated at about 1 billion tons/year in pulp and paper mills, and is a complex stream at high alkaline pH (~13) [8,9], high temperature (70–95 °C) [10,11], and high dissolved solids content (15 wt% total solids, including lignin, other organics, and inorganic salts) [12,13]. In current kraft processes, BL is dewatered to 75–80 wt% solids by multi-effect evaporators [14], which is a highly energy intensive process. Using NF membranes to concentrate BL from 15 wt% to about 30 wt% solids can allow the removal of more than 50% water from BL without the use of evaporation [15]. While polymeric membranes cannot provide the required performance and stability in this demanding application, recent work on reduced graphene oxide (rGO) NF membranes supported on polyethersulfone (PES) has shown favorable performance in terms of their lignin rejection, flux, and stability in BL conditions [15–17]. These performance parameters allow integration of rGO NF membranes into modified kraft process designs, in which membranes can concentrate BL and produce process-quality (i.e., reusable in the kraft process) water in an economical manner [15].

To enable the eventual deployment of GO membranes, scalable

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RESEARCH ARTICLE

Separations: Materials, Devices and Processes

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Transport properties of graphene oxide nanofiltration membranes: Electrokinetic modeling and experimental validation

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Abstract

There is a need for developing reliable models for water and solute transport in graphene oxide (GO) membranes for advancing their emerging industrial water processing applications. In this direction, we develop predictive transport models for GO and reduced-GO (rGO) membranes over a wide solute concentration range (0.01–0.5 M) and compositions, based on the extended Nernst–Planck transport equations, Donnan equilibrium condition, and solute adsorption models. Some model parameters are obtained by fitting experimental permeation data for water and unary (single-component) aqueous solutions. The model is validated by predicting experimental permeation behavior in binary solutions, which display very different characteristics. Sensitivity analysis of salt rejections as a function of membrane design parameters (pore size and membrane charge density) allows us to infer design targets to achieve high salt rejections. Such models will be useful in accelerating structure-separation property relationships of GO membranes and for separation process design and optimization.

KEYWORDS

desalination, Donnan, graphene oxide, separation membranes, transport model

1 | INTRODUCTION

There is intense interest in energy-efficient and versatile membrane separation processes for water treatment.[1–10] Conventional polymeric thin-film composite (TFC) membranes have had good commercial success in some desalination and resource recovery applications. Process design using these membranes has been considerably aided by membrane transport models incorporating meaningful physicochemical parameters such as solute size, pore size, diffusion activation energy, interaction free-energies, and others.[11,12] Examples include the solution-diffusion model for reverse osmosis (RO) membranes[13–15] and the model based on the extended Nernst–Planck (ENP) equation and Donnan equilibrium partitioning for nanofiltration (NF) membranes,[16–23] which provided mechanistic insights into the structural-property relationships of polymeric TFC membranes.[24–27] Parametrization and validation of these models with experimental data allows them to be used for predictive purposes,[21] thereby significantly reducing the need for experimentation.[19] and enabling process simulations,[28,29] intensification/optimization,[30,31] and technoeconomic analysis (TEA).[32,33]

Graphene oxide (GO) membranes are rapidly emerging as a next-generation nanofiltration membrane separation platform[8,9,34–41] with high water permeability,[8,39,42] selectivity,[8,37] and fouling resistance,[43] due to their unique physical and chemical properties.[44] Recent work has also pioneered the development of GO membranes for demanding applications such as processing of kraft black liquor, wherein GO membranes provide robust stability and NF characteristics for rejection of lignin, other organics, and inorganics.[32,40,45,46] Given the present stage of GO membrane science and technology,[47,48] there is a significant need to develop appropriate models for describing separation in GO membranes, which have distinctive transport mechanisms.

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Physics-based Penalization for Hyperparameter Estimation in Gaussian Process Regression

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ABSTRACT

In Gaussian Process Regression (GPR), hyperparameters are often estimated by maximizing the marginal likelihood function. However, this data-dominant hyperparameter estimation process can lead to poor extrapolation performance and often violates known physics, especially in sparse data scenarios. In this paper, we embed physics-based knowledge through penalization of the marginal likelihood objective function and study the effect of this new objective on consistency of optimal hyperparameters and quality of GPR fit. Three case studies are presented, where physics-based knowledge is available in the form of linear Partial Differential Equations (PDEs), while initial or boundary conditions are not known so direct forward simulation of the model is challenging. The results reveal that the new hyperparameter set obtained from the augmented marginal likelihood function can improve the prediction performance of GPR, reduce the violation of the underlying physics, and mitigate overfitting problems.

1. Introduction

Gaussian Process Regression (GPR) is a powerful interpolation technique to construct a predictive model with a finite set of observation points available in a system (Rasmussen, 2003). Due to its flexibility to approximate arbitrary continuous functions, and to provide an accompanying measure of the uncertainty of prediction, GPR is extensively used in various areas such as time-series analysis (Roberts et al., 2013), Bayesian optimization (Gustafsson et al., 2020; J. Kim & Choi, 2019; M. Kim et al., 2022; Pahari et al., 2021; Paulson & Lu, 2022), model calibration (Bradley et al., 2022; Dai et al., 2022; Eugene et al., 2020; Kennedy & O'Hagan, 2001), experimental design (W. Chen et al., 2008; Olofsson et al., 2018; Olofsson et al., 2021; Petsagkourakis & Galvanin, 2021), feasibility analysis (Boukouvala & Ierapetritou, 2012), prediction (Grbić et al., 2013; Kong et al., 2018), process modeling (Ahmad & Karimi, 2021; Alves et al., 2022), optimization (Davis & Ierapetritou, 2007; Quirante et al., 2015; Schweidtmann et al., 2021; Wiebe et al., 2022) and control (Berkenkamp & Schoellig, 2015; Bonzanini et al., 2021; Jain et al., 2018; Kocijan et al., 2003). Its Bayesian interpretation based on simple parameterization makes GPR a competing candidate among many other Machine Learning (ML) models such as Support Vector Regression (SVR) and Neural Networks (NN). In recent years, GPR has been actively improved and extended under different contexts, including efficient optimization (Cao et al., 2013), improved learning of the data (Damianou & Lawrence, 2013; Mattos & Barreto, 2019), generalizable kernels (Damianou & Lawrence, 2013; Duvenaud et al., 2011; Wilson & Adams, 2013), and integration with physics-based laws (Constantinescu & Anitescu, 2013; Jidling et al., 2017b; Nevin et al., 2021; Paulson & Lu, 2022; Raissi & Karniadakis, 2018; Raissi et al., 2017; X. Yang et al., 2018).

GPR is a nonparametric kernel-based method fully characterized by the mean and kernel functions (Rasmussen, 2003). Therefore, the choice of functional forms of the mean and kernel functions and their hyperparameters play a critical role in GPR performance (Fischer et al., 2016; Rasmussen, 2003). In practice, modelers often use a zero-prior mean and choose a kernel depending on the belief (e.g., smoothness, periodicity) of the system. In this case, hyperparameters of the kernel become a primary interest to modelers since model performance is highly determined by its hyperparameters.

Hyperparameters in GPR are estimated via two popular methods: (a) Maximum (marginal) Likelihood Estimation (MLE) (Blum & Riedmiller, 2013) and (b) Markov Chain Monte Carlo (MCMC) sampling (Titsias et al., 2008). MLE is a point estimation method that produces a single set of hyperparameters by maximizing the (marginal) likelihood function.

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A hybrid additive manufacturing process for production of functional fiber-reinforced polymer composite structures

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Abstract

Fiber reinforced polymer composites (FRPCs) are valued for their high strength and lightweight and have found applications from aerospace to renewable energy. Additive manufacturing (AM, or 3D printing) of FRPCs is of great interest in recent years due to the manufacturing flexibility offered by AM. Direct ink write (DIW) 3D printing is a popular choice for FRPC 3D printing due to its low cost and open framework for broad material choices. However, previously explored techniques for AM of FRPCs are hindered by heavy reliance on fiber orientation dictated by extrusion toolpath and often require specialized hardware to print FRPCs with low viscosity and long cure time thermoset epoxy matrices. In this paper, we introduce a single-stream hybrid DIW AM technique for the creation of mechanically robust FRPC functional structures where the matrix is DIW 3D printed, and pre-epoxy impregnated (prepreg) woven carbon fiber (CF) fabrics are robotically placed. Additionally, functional components, such as conductive elements, can be readily integrated. We investigated the impact of prepreg woven CF reinforcement on a two-stage photo-thermal thermoset resin matrix on the mechanical characteristics of manufactured FRPCs. We also combined these efforts to fabricate functional structures, including strain sensors for in-situ deformation monitoring, heating elements, and embedded light sensors. This study found that the proposed single-stream hybrid DIW AM process could be a facile approach to fabricate high-strength FRPC functional structures.

Keywords

Fiber reinforced polymer composites, multifunctional composites, additive manufacturing, hybrid 3D printing

Introduction

Extrusion-based additive manufacturing (AM, or 3D printing) techniques, including fused filament fabrication (FFF) and direct ink writing (DIW), are layer-by-layer fabrication methods compatible with a vast breadth of materials. In recent years, researchers have employed this material versatility to print a myriad of complex multi-material structures with distinct mechanical, thermal, and electrical characteristics.[1–6] Previous studies have leveraged this material availability to create functional structures such as soft robots, embedded electronics, and stimuli-responsive 4D printing.[7–13] Furthermore, researchers have also utilized this material versatility to create high-strength, lightweight, complex fiber reinforced polymer composite (FRPC) parts.[14–17]

Fiber reinforced polymer composites are valued for their high strength to weight ratio and have found applications from aerospace to renewable energy.[18–20] Conventional FRPC manufacturing techniques for complex three-dimensional parts are limited by high costs, slow production times, and low levels of automation.[21] Thus, AM of FRPCs is of great interest due to its manufacturing flexibility.[22] Extrusion-based AM of FRPCs has been explored,

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Enabling direct ink write edible 3D printing of food purees with cellulose nanocrystals

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ABSTRACT

Additive manufacturing using edible feedstock – known as "edible three-dimensional (3D) printing" – offers a unique method of producing visually appealing meals with customizable nutrition profiles. Direct ink write (DIW) 3D printing is a popular choice for edible 3D printing due to its low cost and open framework for broad material choices. However, the breadth of food suitable for DIW 3D printing is hindered due to the unsuitably low viscosity of many potential edible feedstocks such as food purees. In this paper, we present cellulose nanocrystals (CNCs) as a safe and renewable rheological modifier capable of enabling DIW 3D printing of a variety of foodstuffs, specifically spinach puree, tomato puree, and applesauce, and using freeze-dry to obtain final solid structures. We first analyzed the rheological characterization of foodstuffs combined with varying volume fractions of CNCs to produce shear-thinning, printable inks. The print quality of different inks was then analyzed *via* image processing techniques. Finally, we demonstrated the capability of CNC-laden inks by printing a variety of structures, including multi-material structures with integrated packaging. This study found that CNCs are an effective rheological additive which promoted shear-thinning, viscous behavior in the studied edible feedstocks necessary for DIW 3D printing of self-supporting edible structures.

1. Introduction

Additive manufacturing (AM), also known as "three-dimensional (3D) printing", is a layer-by-layer fabrication technique that allows the creation of custom parts with highly complex geometries. In recent years, researchers have leveraged AM for food production known as "edible 3D printing" by forming edible feedstock using extrusion-based methods such as fused filament fabrication (FFF) (Mantihal et al., 2017; Hao et al., 2010; Lanaro et al., 2017) or direct ink writing (DIW) (Sun et al.; Wegrzyn et al., 2012; Godoi et al., 2016; Sun et al., 2015) as well as sintering and adhesive jetting methods (Diaz, 2017; Holland et al., 2018). Edible 3D printing has the potential to provide access to appealing meals (Zampollo et al., 2012) with personalized nutrition profiles (Sun et al., 2018). As a result, AM techniques that are compatible with a vast assortment of materials (Vorndran et al., 2015; Roach et al., 2019a; Compton and Lewis, 2014; Armstrong et al., 2021) such as DIW are preferred. One critical challenge for edible printing is the availability of "printable" foodstuffs, foods which exhibit highly viscous and/or shear thinning properties such as mashed potatoes or dough (Liu et al., 2018; Yang et al., 2018a; Hamilton and Alici M. in het Panhuis, 2018; Le Tohic et al., 2018). Thus, to create nutrient and flavor diverse edible structures, strategies which modify the rheological properties of foodstuffs to create printable inks are required.

Due to shear thinning (thixotropic) inks being an integral aspect of DIW, there has been great interest in edible rheological modifiers. Edible DIW inks have been created by combining foodstuff with an edible rheological modifier to thicken any food paste so that it can be extruded and hold its shape. Examples of these additives include collagen derivatives and potato starch (Wang et al., 2018; Yang et al., 2018b, 2019; Lille et al., 2018; Vancauwenberghe et al., 2018). However, these additives may alter the nutritional characteristics of the printed foodstuff, such as added carbohydrates from potato starch or proteins from gelatin. Finally, such additions risk altering the flavor of the foodstuff and could complicate personalization of nutrition. As a result, an alternative rheological modifier for edible 3D printing could be advantageous. In this work we propose the use of cellulose nanocrystals (CNCs) as this novel alternative rheological modifier to facilitate edible DIW 3D printing, and subsequently using freeze-dry post-processing to create

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4D Printing of Freestanding Liquid Crystal Elastomers via Hybrid Additive Manufacturing

Xirui Peng, Shuai Wu, Xiaohao Sun, Liang Yue, S. Macrae Montgomery, Frédéric Demoly, Kun Zhou, Ruike Renee Zhao, and H. Jerry Qi**

Liquid crystal elastomers (LCE) are appealing candidates among active materials for 4D printing, due to their reversible, programmable and rapid actuation capabilities. Recent progress has been made on direct ink writing (DIW) or Digital Light Processing (DLP) to print LCEs with certain actuation. However, it remains a challenge to achieve complicated structures, such as spatial lattices with large actuation, due to the limitation of printing LCEs on the build platform or the previous layer. Herein, a novel method to 4D print freestanding LCEs on-the-fly by using laser-assisted DIW with an actuation strain up to −40% is proposed. This process is further hybridized with the DLP method for optional structural or removable supports to create active 3D architectures in a one-step additive process. Various objects, including hybrid active lattices, active tensegrity, an actuator with tunable stability, and 3D spatial LCE lattices, can be additively fabricated. The combination of DIW-printed functionally freestanding LCEs with the DLP-printed supporting structures thus provides new design freedom and fabrication capability for applications including soft robotics, smart structures, active metamaterials, and smart wearable devices.

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1. Introduction

The recent decades have witnessed the booming of additive manufacturing (AM), or 3D printing, not only in conventional areas, such as aviation,[1] automobile[2] and construction,[3] but also in various emerging fields, such as electronics,[4] biomedical engineering[5] and soft robotics.[6] The reason is the growing capability of AM to fabricate complex structures, which are challenging to be realized by traditional machining methods. In this advancement, the material library of 3D printing is no longer limited to static materials for structural construction and has expanded to active materials or stimuli-responsive materials, such as shape memory polymers,[7] hydrogels,[8] magnetic soft materials[9] and liquid crystal elastomers (LCEs),[10] driven by the growing need for soft robots,[10h,11] biomedical devices,[5,8a] smart wearable devices,[12] etc. The active nature of stimuli-responsive materials adds the dimension of time to 3D printing and leads to the emerging 4D printing.[8a,13]

Among active materials for 4D printing, LCEs are appealing candidates due to their large, reversible and rapid actuation through a nematic–isotropic phase transition upon external stimuli, such as heat,[14] light,[10a,b,15] humidity[16] and electric fields.[17] LCEs are a class of soft active materials that inherit both the entropic elasticity of elastomers and the molecular anisotropy of liquid crystals (or mesogens). The actuation relies on the mesogen alignment,[18] which can be achieved by mechanical stretching,[19] surface shearing[10g] or external fields.[20]

3D/4D printing methods have been developed to fabricate LCE-based structures and align the mesogens. Direct ink writing (DIW) has been explored for printing LCEs.[11,15,21] In DIW, mesogens are aligned along the printing path when the LCE ink is extruded out of the syringe through the nozzle. Different inks have been developed for both high-temperature printing[10c,21a,c] and room-temperature printing.[21d,22] In addition, functionally graded LCEs were achieved by varying printing parameters,[10d,21c,g,23] such as printing temperature, printing speed and nozzle size. Although 3D structures, such as pinecone and saddle-shaped structures,[21c] can be achieved by 2D structures via different actuation strains between layers, the layer-by-layer manner of material deposition in DIW makes LCEs to be printed on the build platform or the previous layers.

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Introduction to biomass materials

Meisha L. Shofner *[ab] and Andrew G. Tennyson *[cd]

Biomass is an abundant, renewable feedstock of biological matter that humans first harnessed – as a source of fuels, tools, textiles, materials, and chemicals – long before the earliest human civilizations appeared. The fabrication and wearing of clothing, for example, predates the domestications of dogs and crops by tens of thousands of years. During the Industrial Revolution, biomass fuels were replaced by coal and, later, petroleum, with the attendant consequences that biomass-derived chemicals and materials were phased out in favor of those derived from coal and petroleum.

Tree- and plant-derived biomass was used to make the earliest synthetic polymers, such as cellulose nitrate and vulcanized natural rubber, but materials prepared from biomass feedstocks were largely supplanted by materials prepared from fossil resources. With a growing understanding of the harmful impacts fossil-derived polymers have on the health of the planet and its ecosystems, the science and engineering community has recognized the urgent need to return to biomass feedstocks as precursors for commodity and high performance materials.

Replacement of fossil-derived fuels for transportation and energy with those derived from biomass has been an objective of environmental-protection policies, but pursuit of this objective inherently requires contemporaneous and radical transformations of modern chemical and materials industries. To produce chemicals and materials from biomass instead of fossil resources, interdisciplinary research is needed, spanning a fundamental understanding of synthesis and properties to translational studies for targeted applications.

Because biomolecules and biomaterials naturally occur in highly-heterogeneous, complex mixtures of structurally- and functionally-diverse molecules and macromolecules, obtaining a specific, desired compound or material requires one or more chemical interventions to separate it from the

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RESEARCH ARTICLE

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Tricomponent polymer aerogels containing cellulose nanocrystals and chitin nanofibers and their use in aerogel/hydrogel hybrids as fibrocartilage replacements

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Abstract

Considering the design of structures and materials for use as replacements for biological structures, polymer nanocomposites are desirable materials of construction since they have a large design space, allowing property customization. Biobased nanofibers are particularly suited for these applications since they have high specific mechanical properties and cytocompatibility. Motivated by these attributes, this work examines nanocomposite aerogels and an aerogel/hydrogel hybrid structure designed to mimic an intervertebral disc (IVD), with the aerogel and hydrogel serving as analogs for the annulus fibrosus and the nucleus pulposus, respectively. The aerogels and aerogel/hydrogel hybrid structure contain a mixture of biobased nanofibers, cellulose nanocrystals (CNCs) and chitin nanofibers (ChNFs), and a polyvinyl alcohol (PVA) matrix. Characterization of the structure and properties shows that the nanocomposite aerogels containing CNC/ChNF mixtures have larger pores and decreased mechanical properties as compared to aerogels containing only CNCs or only ChNFs. Building on these results, a hybrid comprised of a CNC/PVA aerogel and a CNC/ChNF/PVA hydrogel is constructed with mechanical properties similar to natural IVDs, providing initial validation of the hybrid concept for IVD replacements and pathways to customization through changing material composition in the aerogel and hydrogel and changing the aerogel and hydrogel fractions in the hybrid structure.

KEYWORDS

aerogel, composites, nanocellulose, nanochitin, poly(vinyl alcohol)

1 | INTRODUCTION

Back pain is a common modern day ailment that has been reported in 80% of the world's population with 75% of cases being attributed to degenerated intervertebral discs (IVDs).[1] The IVD is a relatively simple structure composed of two major components: (1) an outer fibrous set of lamellar rings called the annulus fibrosus (AF) and (2) a gel-like material at the center called the nucleus pulposus (NP). The stiffer AF takes the bulk of the load in most situations, while the NP acts as a shock absorber for instant-impact forces. The NP sits at the center of the disc

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Mechanocatalytic hydrogenolysis of benzyl phenyl ether over supported nickel catalysts†

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Mechanocatalysis is a promising approach for green, solvent-free biomass deconstruction and valorization. Here, the hydrogenolysis of benzyl phenyl ether (BPE), a model lignin ether, *via* ball milling is demonstrated over supported nickel catalysts at nominally room temperature and atmospheric hydrogen pressure. The hydrogenolysis reaction network closely follows that of solution-based reactions, with the primary products being toluene, phenol, and cyclohexanol. The mechanical energy during milling not only drives the chemical reactions but also activates the nickel by exposing fresh metallic surfaces from passivated particles, which replaces a thermal activation step. The hydrogenolysis rate is shown to be largely insensitive to the final nickel particle size, but reactivity of the oxide support can be enhanced during milling which contributes to carbon deposition. This work demonstrates the underlying chemistry necessary for mild lignin depolymerization using reductive mechanocatalysis.

Sustainability spotlight

The production of commodity chemicals and materials from alternative feedstocks is necessary to successfully transition from a fossil-based, linear economy to a sustainable, circular economy. The deconstruction and valorization of biomass, and lignin in particular, is a promising pathway to utilize renewable carbon. However, most conventional approaches rely on the use of organic solvents, which contribute a significant portion of the process-energy and can also have adverse effects on the environment. The current research demonstrates the feasibility of the underlying chemistry necessary to depolymerize lignin under solvent-free and ambient conditions. This work aligns with US SDG #12 (responsible consumption and production) by advancing an approach to utilize renewable resources while minimizing process waste production.

Introduction

As society shifts away from fossil-based fuels and chemicals, the necessity for complete utilization of biomass becomes ever more pressing. Lignin, a primary component of woody biomass, is an abundant renewable resource but is practically unutilized as a feedstock for chemicals and materials. Of the 60 million tonnes of lignin isolated annually, less than 2% is used for value-added products, while the rest is burned as a low value fuel.[1] Lignin is a heterogeneous, amorphous polymer that is primarily comprised of three propyl-phenolic monolignols (*p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol) linked together randomly by various C–O (β-O-4, α-O-4, 4-O-5) and C–C (β–β, β–5, 5–5) bonds.[2] However, the fractionation of lignin from the lignocellulosic matrix typically changes the structure of the polymer and increases the abundance of condensed (C–C) linkages.[3] As the largest natural source of aromatic carbon, lignin is a promising, sustainable alternative starting point for historically benzene–toluene–xylene (BTX) derived chemicals if the polymer can be selectively depolymerized to mono-aromatics.

Two of the most promising approaches to depolymerize lignin utilize hydrogen as either a cleaving or stabilizing reagent: hydroprocessing and reductive catalytic fraction (RCF).[4] Hydroprocessing, generally performed with isolated lignin, combines hydrogenolysis of the linkages to produce monomers and hydrodeoxygenation (HDO) to upgrade monomers simultaneously.[5] These reactions tend to produce monomer yields between 10 and 20 wt%, with harsher reaction conditions increasing monomer yields at the expense of product selectivity.[4] RCF starts with complete lignocellulose and combines the isolation and depolymerization of lignin, where solvolysis formed monomers are stabilized before repolymerization can occur.[6] Most reported monomer yields from RCF studies range from 10 to 30 wt% for softwood and from 30 to 60 wt% for hardwood feedstocks with very high selectivities of phenolics. Both hydroprocessing and RFC reactions employed

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Article

Differences in solvation thermodynamics of oxygenates at Pt/Al_2O_3 perimeter versus Pt(111) terrace sites

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SUMMARY

A prominent role of water in aqueous-phase heterogeneous catalysis is to modify free energies; however, intuition about how is based largely on pure metal surfaces or even homogeneous solutions. Using multiscale modeling with explicit liquid water molecules, we show that the influence of water on the free energies of adsorbates at metal/support interfaces is different than that on pure metal surfaces. We specifically compute free energies of solvation for methanol and its constituents on a Pt/Al_2O_3 catalyst and compare the results to analogous values calculated on a pure Pt catalyst. We find that the more hydrophilic Pt/Al_2O_3 interface leads to smaller (more positive) free energies of solvation due to an increased entropy penalty resulting from the additional work necessary to disrupt the interfacial water structure and accommodate the interfacial species. The results will be of interest in other fields, including adsorption and proteins.

INTRODUCTION

Tuning the reaction environment surrounding a catalyst active site is the heart of catalysis design, with use of solvents being a common strategy.[1] Hence, a grand challenge in catalysis research is understanding the specific ways that solvents influence catalytic chemistry.[2] For example, solvents can alter active site chemistries[3,4] and coverages,[5,6] modify reaction energetics,[7–10] stabilize intermediate species[11–13] and transition state[14] structures, promote certain reaction paths[15] and mechanisms,[16,17] and ultimately influence catalytic outcomes.[15] While significant research has been performed to elucidate these roles of solvent, intuition about how solvents will influence any particular catalytic system remains unknown. This is because solvent effects vary greatly depending on the catalytic interface.[18,19]

The dependence of interfacial properties becomes particularly important for reactions that utilize different types of active sites. An example of such a reaction is aqueous phase reforming (APR), which is a process that can produce hydrogen from derivatives of biomass under liquid water solvent.[20,21] APR is generally carried out on metal nanoparticles anchored to metal oxide supports,[20,22] and both sites on the metal components (terrace sites) and at the metal/support interface (perimeter sites) have been shown to be relevant to the observed chemistry.[23–25] However, the ways that these two types of sites promote the APR mechanism are different, even in the absence of solvent. For example, molecules tend to bind more strongly at perimeter sites than at terrace sites,[26,27] due to the presence of undercoordinated metal atoms at perimeter sites. Furthermore, metals in the support at perimeter sites can provide additional anchoring sites,[28] hence providing a richer active site environment.[29]

Solvents interact differently with these two types of sites as well. Specifically, metal sites are relatively hydrophobic,[30] whereas metal oxide supports generally comprise ions which are more attractive to solvent molecules.[31–33] The more attractive interface leads to differences in molecular and structural solvent phenomena. For example, H_2O molecules adsorb more strongly to more hydrophilic interfaces than to more hydrophobic interfaces, which leads to larger water densities near the interfaces of more hydrophilic surfaces.[33–35] These larger densities result in reduced mobilities for interfacial H_2O molecules,[36,37] which influence the free energies[38] of interfacial processes such as catalysis. Indeed, the kinetics of APR has been observed to be different at perimeter sites compared with terrace sites, with these differences being

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CO2 Capture

Insights into the Oxidative Degradation Mechanism of Solid Amine Sorbents for CO_2 Capture from Air: Roles of Atmospheric Water

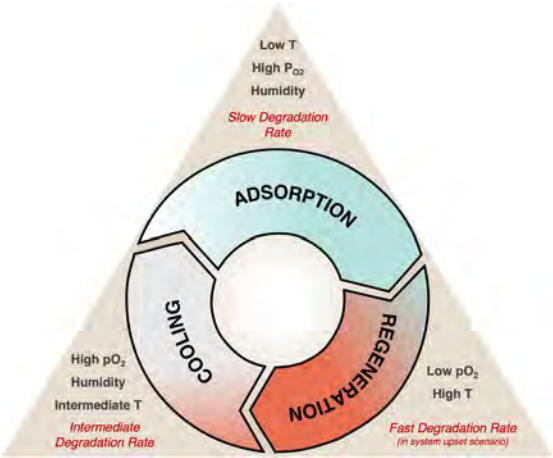
*Juliana S. A. Carneiro, Giada Innocenti, Hyun June Moon, Yoseph Guta, Laura Proaño, Carsten Sievers, Miles A. Sakwa-Novak, Eric W. Ping, and Christopher W. Jones**

Abstract: Direct air capture (DAC) processes for extraction of CO_2 from ambient air are unique among chemical processes in that they operate outdoors with minimal feed pretreatments. Here, the impact of humidity on the oxidative degradation of a prototypical solid supported amine sorbent, poly(ethylenimine) (PEI) supported on Al_2O_3, is explored in detail. By combining CO_2 adsorption measurements, oxidative degradation rates, elemental analyses, solid-state NMR and in situ IR spectroscopic analysis in conjunction with ^{18}O labeling of water, a comprehensive picture of sorbent oxidation is achieved under accelerated conditions. We demonstrated that the presence of water vapor can play an important role in accelerating the degradation reactions. From the study we inferred the identity and kinetics of formation of the major oxidative products, and the role(s) of humidity. Our data are consistent with a radical mediated autooxidative degradation mechanism.

Introduction

The scale of anthropogenic CO_2 emission for the past 100+years has created a global scale problem that requires global scale solutions. Annually, ≈40 Gt of CO_2 are emitted, with ≈3200 Gt of CO_2 currently accumulated in the atmosphere.[1] To limit the consequential increase of the average global surface temperature to below 2 °C (*w.r.t.* pre-industrial levels) by the end of this century, technology for atmospheric CO_2 removal at the gigaton level (≈10 Gt/year by mid-century) must be deployed together with other mitigation technologies.[1,2] To meet the more strict 1.5 °C target by 2100, the deployment of negative emissions technologies (NETs) is required to accelerate the removal of excess atmospheric CO_2. In this context, the development of adsorptive materials for CO_2 capture from ambient air (Direct Air Capture, DAC) is one promising approach from the scientific community aiming to create a robust portfolio of NETs.[3] Nonetheless, the deployment of DAC is still hindered by the nascency of the technology, and concerted R&D is targeted towards technology maturation and cost reduction. For DAC technologies based on solid adsorbents, with supported amine materials representing some of the most promising approaches, the chemical stability of the sorbents can have a large impact on the material and process costs.[4] In addition, concerns are also raised regarding the possible environmental impacts of the formed degradation products, which may represent liquid, gaseous and/or solid chemical residues.

The stability of amine-based solid adsorbents depends on the material composition, chemical structure, as well as process parameters such as temperature, pressure, and gas composition.[5] The oxidative stability of amine-based sorbents is a critical parameter in DAC processes, owing to the potential of sorbent deactivation in an O_2-rich atmosphere (21 % O_2 in air) and the subjection of the sorbent to temperature swings required to remove bound CO_2 during the regeneration cycle. For temperature swing adsorption processes, three particular sources of potential vulnerability must be understood (Scheme 1). First, exposure of the sorbent, during extended operation, to the unconditioned ambient air may lead to slow degradation of the sorbent materials (high P_{O_2}, low T, extended operational time). It is



Scheme 1. Schematic of the general DAC process cycles and corresponding sources of sorbent vulnerability to oxidative degradation.

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Letter

Mechanocatalytic Oxidative Cracking of Poly(ethylene) Via a Heterogeneous Fenton Process

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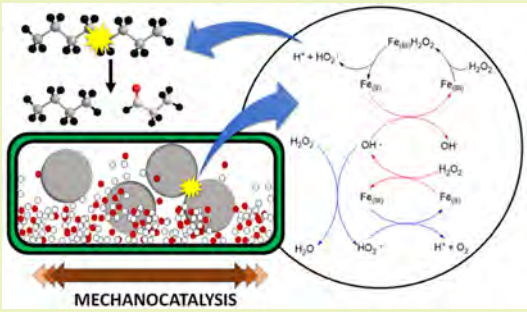
ABSTRACT: In this work, mechanocatalytic oxidative cracking is used to overcome the chemical inertness of poly(ethylene) (PE) and the difficulties associated with processing this solid feedstock. An Fe_2O_3-based Fenton system is applied to introduce oxygen-based functional groups to the PE backbone with hydrogen peroxide as the oxidant. Once an oxygen-based functional group is introduced, the polymer chain can be cleaved to achieve cracking effectivity, with only CO, CO_2, O_2, and H_2O as byproducts. The resulting fragments can be used as intermediates to produce fuels and sustainable chemicals.



KEYWORDS: *Plastics, Chemical recycling, Upcycling, Depolymerization, Ball mill, Mechanochemistry, Iron oxide*

■ INTRODUCTION

Global production of synthetic plastics has increased continuously since its invention in the early 20th century from 2 million tons in 1950 to 459 million tons in 2019.[1,2] Among all plastics produced, polyethylene (PE) has the highest proportion on the global market, accounting for approximately 28.5% of total plastic production.[1] Currently, high-density polyethylene (HDPE) is recyclable to a limited extent, while low-density polyethylene (LDPE) remains unrecyclable.[1,3] This has resulted in landfill accumulation and leakage into the environment, including uncontrollable oceanic pollution.[1,3] While PE can be converted by catalytic or thermal pyrolysis and gasification, these processes are energy-intensive and yield low-value products.[4−10] Other approaches to chemical recycling require the dissolution of PE in toxic organic solvents, expensive catalysts, and/or high temperature and pressure,[11,12] which limits industrial applicability.

Mechanochemistry has the potential to transform our ability to process recalcitrant solid feedstocks in a solvent-free environment and was therefore chosen by the International Union of Pure and Applied Chemistry (IUPAC) as one of "Ten chemistry innovations that will change the world".[13] Thus, typical environmental impacts of traditional PE conversion or disposal are mitigated.[14−16] Mechanochemical processes use mechanical collisions in a ball mill or a similar device to drive chemical reactions and can shear solids against each other in absence of or with limited use of solvents so that the conversion of a solid reactant over a solid catalyst becomes viable.[17] The collisions can create transient sites on the surface of solid catalysts[18] and hot spots that are characterized by rapid local temperature rises, followed by dissipation of heat throughout the feedstock and catalyst within the vessel.[19] Mechanochemical processes for depolymerization of biomass, most notably cellulose and lignin,[20−24] and plastics such as polystyrene (PS) and poly(ethylene terephthalate) (PET)[25−27] have been reported.

In the case of PE, high ceiling temperature (i.e., 883 K),[28] intrinsic chemical inertness of the backbone, and resistance to abrasion and impacts[29] pose general challenges for recycling processes and require a combination of depolymerization/cracking with other reactions (e.g., hydrogenation, oxidation, aromatization of intermediates) to create a thermodynamic driving force. Oxidative Fenton processes, which often include an iron salt as catalyst and an aqueous hydrogen peroxide solution as an oxidant, have been demonstrated for oxidizing numerous organic molecules.[30−32] Meanwhile, PE plastic chains are known to be ruptured photo-oxidatively in a natural environment.[33−35] This is caused by the formation of carbonyl groups on the PE backbone, which can undergo photochemically-induced homolytic cleavage or generate intramolecular hydrogen abstraction. Therefore, Fenton processes are expected to be able to functionalize the recalcitrant PE backbone, forming oxygen-based functional groups that promote subsequent chain cleavage.

This study demonstrates a novel approach to cracking medium-density polyethylene (MDPE) by combining the

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Net Zero Transition: Possible Implications for Catalysis

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ABSTRACT: This Viewpoint discusses the implications of the net zero energy transition on traditional chemical feedstocks and catalytic elements. While the full impact of the upcoming changes is difficult to assess, some trends from scenarios already underway can be mapped. For example, a steady growth in electric passenger vehicles will diminish transportation-related petroleum refining output, which could then create chemical feedstock gaps and changes in the supply/demand dynamics of certain critical metals. These impacts could present unexpected opportunities for emerging feedstocks such as biomass, sequestered CO_2, and recycled carbon to bridge the supply gaps, even within the next decade. Further, catalytic metals such as Pd, Rh, and Pt will be displaced from petroleum refining and automotive exhaust catalytic converter applications and potentially become more available for producing chemicals and aviation fuels from emerging feedstocks. At the same time, metals such as Co and Ni, which are currently considered to be earth abundant, will face increasing demand in energy storage applications and thus could become less attractive for catalytic applications. The availability of carbon-free hydrogen and oxygen will facilitate the march toward decarbonization of the chemical industry. Finally, the enormity of displaced petroleum refining assets offers the possibility of repurposing some of them to process emerging feedstocks. These disruptions will have profound implications in future catalysis research and must be considered for a well-guided transition toward industrial sustainability.

1. INTRODUCTION

While catalysis is a mature discipline, the energy transition coupled with industrial decarbonization will result in disruptive changes to the petrochemical and energy industries that will create new challenges and opportunities. However, many current catalytic studies tend to be directed toward previous paradigms and have not fully considered the implications of these industrial shifts.

Recent reports from the National Academies of Sciences, Engineering, and Medicine (NASEM) highlight the importance of this energy transition and recommend the importance of preparing for new challenges and opportunities (Figure 1).[1,2] One of these reports[1] on the future of chemical engineering dissects some of the important research areas that are needed in order to work toward decarbonization, including exploration of catalysis with different metals due to their shifting availability. The second report[2] focuses on the future of chemical research and its impact on the U.S. economy, noting that future chemical research faces a shifting paradigm caused by the changing feedstock and energy landscapes. Such a shift will challenge some of the current underlying assumptions in the field. This includes a change in demand of traditional metals used in industrial catalysis accompanied by a significant increase in metals demand for renewable energy applications and, in particular, the increasing availability of renewable electricity at a competitive price.[3] Another expected shift will be caused by the steadily decreasing demand for gasoline and diesel combined with increasing demand for aviation fuels that will require current petroleum refining assets, such as catalytic reforming and cracking units, to be repurposed to accommodate emerging circular feedstocks and associated catalytic technologies that promote sustainability.[2]

Figure 1. Drivers for transformations of catalytic processes in chemical manufacturing.

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Reaction Mechanism of Tetrahydrofurfuryl Alcohol Hydrogenolysis on Ru/SiO_2 Studied by In-Situ FTIR Spectroscopy

Giada Innocenti,[a, b] Stefan Emig,[c] Lars Meyer,[c] Matthias Mueller,[b] Schirin Hanf,[b] Stephan A. Schunk,[b] Alois M. Kindler,[c] and Carsten Sievers*[a]

In situ infrared spectroscopy is used to gain a deep understanding of the surface reactions during the hydrogenolysis of tetrahydrofurfuryl alcohol vapor on Ru/SiO_2 and SiO_2 and to identify intermediates that lead to catalyst deactivation. Time-resolved in situ infrared spectroscopy experiments elucidate the formation and consumption of different surface species. Hydroxy valeraldehyde is the key intermediate and can undergo hydrogenation or the Tishchenko reaction. Both reactions yield 1,5-pentanediol, but the latter also produces hydroxy valeric acid, which can polymerize on the catalyst surface. Finally, hydroxy-valeraldehyde can also participate in fouling by means of aldol condensation. The same reaction intermediates are found both on Ru/SiO_2 and SiO_2 suggesting that the support plays a role in retaining the molecules on the surface and favoring the multi-step reaction mechanism on the surface rather than the direct ring opening mechanism.

Introduction

In the last decades, concerns regarding environmentally and socially sustainable alternative to oil-based processes have generated significant interest in the utilization of renewable resources. Biomass is a renewable carbon-based feedstock that is suitable green alternatives to produce chemicals and fuels. The platform molecules derived from biomass, including furanes, are richer in oxygen than the oil-derived building blocks. Therefore, they require additional modification to functionalize or remove some of the C–O bonds. Two of the building blocks, that are the most investigated are, hydroxymethylfurfural (HMF) and furfural, which can be easily converted to tetrahydrofurfuryl alcohol (THFA) as a more stable intermediate.[1,2] THFA, in particular, has gained interest because it can be converted in value-added chemicals, such as pentanediols by ring-opening reactions (hydrogenolysis).[3]

THFA conversion into 1,5 pentanediol (1,5 PDO) was reported for the first time in a pioneering work by Schniepp et al. with a yield of 70%.[4] This yield was achieved by using a three-step procedure that involved THFA dehydration over Al_2O_3 in the gas phase to produce 3,4-dihydro-2H-pyran (DHP) with a yield of 90%. A yield of 78% hydroxy-valeraldehyde (HVAL) was obtained by hydrolyzation of DHP in a 0.05 N HCl solution. Finally, HVAL was quantitatively hydrogenated to 1,5 PDO over copper chromite in an EtOH solution. Recently, this three step process was improved by Dumesic et al., and a 1,5 PDO yield of 87% was reached.[5,6]

However, the idea of producing 1,5 PDO from THFA in a one-pot reaction is appealing since it would reduce the number of separation steps required. For this reason, a lot of effort has been made to study this reaction in the liquid phase.[3,7–12] Koso et al. studied the kinetics and reaction mechanism of THFA hydrogenolysis over Rh–Re/SiO_2, and they reported that the direct scission of C–O bond is mediated by a hydride attack in the liquid phase.[13] The 3-step reaction mechanism reported by Schniepp et al.[4] was discarded since the addition of H_2SO_4 to the reaction medium did not influence the activity or the product distribution. The hydride mediated reaction mechanism was also supported by experiments carried out feeding D_2 instead of H_2 in D_2O by evaluating the exchange rate between H and D on the C1 and C2 of 1,5 PDO.[14] Finally, water was found to be a more effective solvent than alkanes to obtain both high selectivity and conversion over Ir-ReO_x/SiO_2, but the role of water remains unclear.[14] In contrast, the one-pot process in the gas phase is unexplored. It is generally accepted that the chemoselective production of 1,5 PDO requires a noble metal, such as Ir, Rh or Pt, along with an oxophilic element, such as Mo, Re, V or W.[7–10,15–17] The most commonly used supports are SiO_2, activated carbon and ZrO_2.[7,10,15] In contrast Guan et al. reported a hydrogen transfer-ring opening mecha-

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Reduced deactivation of mechanochemically delaminated hierarchical zeolite MCM-22 catalysts during 4-propylphenol cracking

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ABSTRACT

The delamination of MCM-22 using shear forces in a vibratory ball mill, rather than chemical surfactants and sonication, is illustrated. The resulting material has comparable or improved physical properties compared to chemically delaminated MCM-22 without a significant loss of acid sites. The mechanical treatment affected the initial rate of 4-propylphenol cracking to phenol and propylene, a model reaction for lignin-derived aromatics, much less than chemical delamination. It also shows improved deactivation resistance for this reaction known to experience fast deactivation by pore blockage.

1. Introduction

As most abundant source of renewable aromatics, lignin has received significant attention as raw material for bio-refineries [1–3]. In particular, chemical funneling of lignin into phenol is a promising approach to produce considerable quantities of a commodity chemical with a well-established market [3–4]. A key step in this process is the removal of alkyl side chains from the aromatic ring, which can be achieved in a zeolite-catalyzed cracking reaction [5]. Zeolites are well known for their unique microporous structures with a high-density of active sites that allow for shape-selective catalysis [6–10]. However, phenolic reactants and intermediates tend to strongly adsorb on zeolites during this reaction leading to deactivation of the catalyst [11–12]. This phenomenon can be partially reversed by hydrolysis of the deposits with by co-fed water [5,13], but deactivation due to deposits remains an issue [12]. Since zeolitic micropores are comparable in size to small aromatic molecules, carbonaceous deposits readily form diffusional barriers that lead to low utilization of interior micropore volume and deactivation [14–16].

This can be overcome in hierarchical materials that include mesopores to shorten the diffusive path length and significantly increase transport in and out of the microporous domains of the catalyst particles [17]. The mesopores can be created in various ways, including templating, desilication, dealumination, and delamination [18–19]. However, most of these synthesis techniques involve either costly reagents, extended growth/reaction times, harsh chemicals, or some combination thereof. To improve catalyst production at scale, it would be beneficial to develop easier and less costly methods for preparing hierarchical zeolites.

One exciting candidate is the hierarchical delaminated zeolite ITQ-2 [18]. This zeolite is traditionally prepared by synthesizing a layered precursor of the MCM-22 zeolite (MCM-22P - MWW structure), which is then swollen using a surfactant and alkylammonium hydroxide, kept under reflux for several hours and sonicated in a pH-monitored solution [20]. It results in thin sheets that are only a few unit cells thick, randomly stacked against each other, creating mesopores in the delaminated ITQ-2 zeolite. There are alternative methods to perform the delamination of the MWW structure [21–22]. Roth et al. demonstrated that a well dispersed colloid of these monolayer sheets can be smoothly deposited into

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Surface Chemistry of Ketones and Diketones on Lewis Acidic γ-Al_2O_3 Probed by Infrared Spectroscopy

Bryan J. Hare, Ricardo A. Garcia Carcamo, Rachel B. Getman, and Carsten Sievers*

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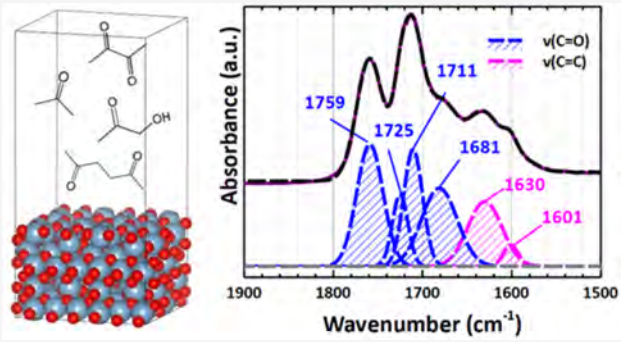
ABSTRACT: To advance the understanding of surface reactions of biomass-derived oxygenates, adsorption and conversion of ketones and diketones on Lewis acidic γ-Al_2O_3 are studied. The model compounds include ketones with hydroxyl groups (di/hydroxyacetone) as well as diketones with different distances between the two carbonyl groups (2,3-butanedione and 3,4-hexanedione, 2,4-pentanedione, and 2,5-hexanedione as α-, β-, γ-diketones, respectively). In situ infrared (IR) spectroscopy is utilized to experimentally observe the surface species. The deconvoluted IR spectra acquired between 50 and 250 °C suggest that intermolecular aldol condensation is the most common reaction path for the studied di/ketone reagents. This reaction path consists of sequential enolization, dimerization, and dehydration to form conjugated products with lower ν(C═O) and ν(C═C) frequencies. Exceptions included intramolecular aldol condensation of 2,5-hexanedione and isomerization and dehydration of dihydroxyacetone. Density functional theory calculations suggest that diketones bind as monodentate surface species provided their stability on γ-Al_2O_3. This study provides insight on di/ketone chemistry on Lewis acidic γ-Al_2O_3 that will be relevant for many fields including prebiotic and industrial chemistry.



■ INTRODUCTION

Ketones are an important class of organic reactants that are essential to the chemical industry. They serve as important precursors for the manufacturing of synthetic polymers,[1,2] enantiopure alcohols,[3] imines/amines,[4] and more. Diketones have also been utilized to synthesize specific compounds with high regio, diastereo, and enantioselectivity.[5,6] While ketones and diketones may be acquired through a variety of sources and synthesis processes, it is likely that heterogeneous acid−base catalysts, typically metal oxides, are involved in some stage of their production or conversion. Therefore, it is important to understand the surface reactions of di/ketones on metal oxides and how the exact structure of the reactant affects reactivity and the final products.

Many metal oxide catalysts exhibit Lewis acidity, which allows these materials to chemically adsorb both gas- and liquid-phase reactants. Lewis acidic γ-Al_2O_3, in particular, has been extensively studied in regards to its microstructure, surface behavior, and role as a catalyst or support.[7,8] It is commonly utilized as a support for metal particles for a number of reactions in refineries and more sustainable chemical processes, including the Fischer−Tropsch process[9] and aqueous-phase reforming.[10] γ-Al_2O_3 is also used as an acid catalyst for some processes including alcohol dehydration and the Claus process for desulfurization of natural gas.[11,12] Because these reactions are strongly tied to the petrochemical and biorefinery industries, of which many di/ketones originate, a better understanding of the interactions between di/ketones and γ-Al_2O_3 is essential.

Acetone is the simplest of ketones and is historically the most commonly used ketone for deciphering how molecules with carbonyl groups bind and react on different surfaces including those of metallic single crystals and various metal oxide materials.[13−18] It is activated on Lewis acidic oxides, such as γ-Al_2O_3, to produce mesityl oxide through sequential enolization, aldol self-condensation, and dehydration reactions.[19] However, the reactivity trends and surface phenomena of ketones, and certainly diketones, of varying characteristics (size, types of functional groups, distance between functional groups, etc.) have yet to be rationalized in a single study.

Several types of spectroscopy have been employed to probe the adsorption and surface chemistry of ketones, particularly acetone, on surfaces. For instance, infrared (IR) spectroscopy was used by Hanson et al. to observe the Lewis acid-catalyzed transformation of adsorbed acetone into its enol tautomer on γ-Al_2O_3.[20] It was also deduced in the same study that the enol

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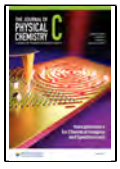

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Surface Interactions of Erythrose on Assorted Metal Oxides: A Solid-State NMR Study

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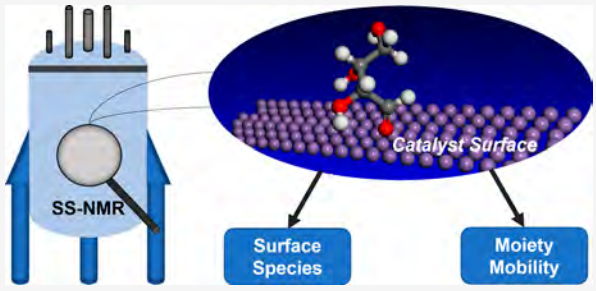
ABSTRACT: The interactions of the C4 sugar, erythrose, with various metal oxides (γ-Al_2O_3, CeO_2, Nb_2O_5, SiO_2, SnO_2, TiO_2, and ZrO_2) were investigated using solid-state nuclear magnetic resonance (SS-NMR) spectroscopy. The surface species created by the impregnation of erythrose onto these oxides reveal a major shift in the equilibrium between cyclic, linear, and hydrated erythrose relative to the confirmations present in solution. Surface species on SnO_2, TiO_2, and ZrO_2 were most significantly affected by the increase in temperature from 25 to 50 °C, while on γ-Al_2O_3, CeO_2, Nb_2O_5, and SiO_2, the effect was minimal. This work reports the first application of NMR relaxometry to study the interactions of erythrose with metal oxides. This was done by measuring the rotating frame relaxation time for each moiety at 25 to 50 °C revealing whether these groups interact strongly or weakly with the oxide surfaces. The Lewis and Brønsted acidity of the materials was characterized using pyridine adsorption followed by FTIR spectroscopy. Various surface reaction pathways are proposed based on the diverse array of surface species that formed. The results provide insights into the trends in surface chemistry of sugars on Lewis acidic, Brønsted acidic, redox active, and inert metal oxide surfaces.



1. INTRODUCTION

The rising need for sustainable alternatives to fossil fuels has prompted significant research into the area of biomass valorization and transformation.[1] Plant biomass has three main constituents: cellulose, hemicellulose, and lignin. Cellulose is a linear polymer of glucose, whereas hemicellulose consists of different C_5 and C_6 sugars. Sugars can be used as platform chemicals that are upgraded to commodity chemicals using heterogeneous catalysts. One major challenge for developing such processes is understanding how the complex sugar molecules interact with the surfaces of potential catalysts.[2,3] Simpler, smaller compounds with similar functionality, such as the C_4 sugar erythrose, can be used in the place of C_5 and C_6 sugars to better understand how sugars interact with catalytic surfaces.[4]

Processes using heterogeneous catalysts, such as metal oxides, account for a large portion of the global GDP and involved in production of 80% of industrially relevant chemicals.[5] An important property of many metal oxides is their Lewis acidity. Lewis acidic (LA) catalysts can promote many important sugar reactions, such as isomerization, retro-aldol condensation, and the Cannizzaro reaction.[6−8] Despite this, a systematic understanding of the factors that promote these reactions occur is missing. Different LA metal oxides will catalyze different reactions and more specific surface-based investigations are needed to rationalize findings. Some important factors of the catalyst that can affect the overall reaction pathway are reducibility, Lewis acidity, Brønsted acidity, and basicity.

The importance of sugars on the surface metal oxides is relevant not only to the heterogeneous catalysis community but also to those who study prebiotic chemistry, sensors, and soil chemistry.[9−11] For example, several glucose biosensors employ metal oxides to detect concentrations because metal oxides are more stable than enzymes.[12] This provides motivation into further expanding the knowledge basis of how sugars interact with metal oxides.

The investigation of catalytic surfaces and how they interact with organic compounds has been heavily studied through various in situ spectroscopic and other relevant techniques,[13] but there has been little to no investigation of the surface interactions of erythrose with various types of metal oxides. One technique that can be utilized for elucidating surface species/interactions is solid-state nuclear magnetic resonance (SS-NMR) spectroscopy, usually including magic angle spinning (MAS).[14−17] Direct polarization (DP) is one specific pulse sequence that can be used to identify surface species

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Introduction to Polymer Upcycling

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Plastics are ubiquitous in our daily life, yet drastic amounts of plastics have found their way into landfills and the environment. In 2015 alone, the global waste generated by plastic packaging was around 6300 metric tons, and global production of waste is anticipated to increase to 12 000 metric tons by 2050.[1] The elimination or reduction of the use of plastics on the consumer side is not foreseeable in the near future. Hence, methods for the disposal of new and existing waste in ways that do not negatively impact the environment, human health, and climate change is imperative. The United Nation's Sustainable Development Goals (SDGs) emphasize the need to reduce single-use plastics to ensure sustainable consumption and production patterns.[2] As part of reaching these goals, approaches to produce high value products from plastic waste, referred to as polymer upcycling, are particularly attractive.

A multi-pronged approach is needed to rapidly develop capabilities for polymer upcycling, including new polymer molecules that are more readily upcycled, new catalysis approaches for transformation of polymer-based waste to new materials and improved understanding of the complex waste streams and products of the depolymerizing and degrading polymers. In this themed collection, we include outstanding contributions in these areas, highlighting the multiple ways that we as a field must approach

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Marco A. Fraga graduated with a DSc degree in Chemical Engineering in Heterogeneous Catalysis at State University of Campinas/UNICAMP in Brazil. He joined the National Institute of Technology (INT, Rio de Janeiro) in 2000 where he is presently a senior scientist. Since 2013, he has also been engaged in high-level teaching in the Master's and Doctoral Program in Chemistry at the Military Institute of Engineering (IME, Rio de Janeiro). His research interests are in heterogeneous catalysis, green chemistry, sustainable catalysis, biomass conversion, CO_2 capture and conversion, and polymer upcycling.

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Chapter Two - Functional naturally derived materials to improve the environment: Chemical structures, modifications, applications, and future perspectives

Geng-Sheng Lin †, Wenbo Peng †, Ji Gao, Abigael Wahlen, Zhaohui Tong

Show more

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Abstract

Naturally derived polymers have recently gained interest worldwide due to concerns about increasing greenhouse gas emissions and depletion of fossil resources. Naturally derived polymers, such as polysaccharides, protein, lipids, fatty acids, and lignin, are produced from renewable resources and abundant in nature, and provide a negative carbon footprint. Naturally derived polymers have played a pivotal role in producing high-performance functional materials in environmental applications. However, the use of naturally derived polymers is largely limited by their cost of collection and separation, hydrophilicity, and mechanical properties. New modification and functionalization methods are urgently needed to satisfy the versatile market needs on material properties and performance. Thus, this chapter reviews (1) the types of naturally derived materials and their molecular structures; (2) various modification and functionalization methods; and (3) their applications in wastewater remediation, environmental sensors, food safety, and smart fertilizers. Finally, we address the existing barriers and challenges faced by bio-based materials and their future perspectives.

Keywords

Bio-based; Natural polymers; Chemical modification; Functionalization; Environmental remediation; Naturally derived polymers; Modification; Environmental applications

1. Introduction

Over millions of years, nature has provided an incredible source of energy and materials for the improvement of human lives, while preserving natural ecosystems. Naturally derived materials are defined as materials created from animals and plants. They have been widely used in architecture, textiles, and medicine since archaic times. For example, during the Neolithic period (10,000 to 2000 BC), Europeans started building houses with thatched roofs (Johns et al., 2014). Hemp has been cultivated in Northern China since 10,000 BC. Due to its fibrous nature, it was used for a variety of things including clothes, rope, paper, and fishing nets (Brand and Zhao, 2017); Ancient Egyptians used coconut shells to repair injured skulls. And wood or ivory worked as false teeth as early as 3000 BCs (Zimmerman and Veith, 1993).

In the 19th century, due to rapid industrialization, fossil-derived materials (from petrochemicals) were greatly developed and occupied a large portion of the market. Until now, petroleum-based materials still play a major role in modern society. In 2020, synthetic fibers

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Synchronous degradation and decolorization of colored poly(ethylene terephthalate) fabrics for the synthesis of high purity terephthalic acid

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ABSTRACT

The grand challenge in chemical recycling of colored poly(ethylene terephthalate) (PET) wastes is to achieve cost-effective decolorization and purification of products. In the present work, an effective method combining hydrolysis, reactive processing and decoloration was developed to convert colored PET fabrics into high purity terephthalic acid (TPA_{ca}). Identification of intermediates and quantification of products were carried out by a range of characterizations, including SEM, EDS, TGA, FTIR, XRD, NMR and GPC. The color removal efficiency and selectivity and yield of the synthesized TPA_{ca} were calculated with the assistance of UV–vis, K/S values and chromaticity diagram to evaluate the viability of the method. It is found that disperse dyes with different structures (azo and anthraquinone) can be decolorized simultaneously with PET degradation under the joint effects of sublimation, pyrolysis and hydrolysis. In the process, calcium terephthalate (CaTP) acts as an essential medium to store and protect the synthesized TPA_{ca}. Overall, the purity of the obtained TPA_{ca} is comparable to that of commercial TPA. The monomer yield (88.51%) and decolorization rate (94.22–97.65%) are higher than TPA_{na} produced from traditional hydrolysis. Along with future development towards sustainability, we anticipate that this method could be utilized as a basis for recycling and upcycling of complex colored PET wastes at an industrial level.

1. Introduction

Poly(ethylene terephthalate) (PET), a semi-aromatic polyester, has a diverse array of end uses in fiber manufacturing and textile industry due to its excellent physical, thermal, optical and mechanical properties (Laldinpuii et al., 2021; Singh et al., 2021). The annually manufactured PET inflicted to a huge increasing tendency of almost 70 million tons in the world (Tournier et al., 2020; Zhang et al., 2021). With a large consumption of non-renewable petroleum in PET production coupled with its biodegradable resistance, PET derived wastes present a serious threat to the global ecosystem (Rubio Arias and Thielemans, 2021; Tian et al., 2021).

According to published data, over 60% of PET is utilized in synthetic fiber/textile products, while bottle grade PET accounts for about 30% (Li-Na, 2013; Ketema and Worku, 2020; Poulikakos et al., 2017). Theoretically, fiber grade PET has lower intrinsic viscosity (0.4–0.75 dL/g) as compared to bottle grade PET (0.95 dL/g) (Cosimbescu et al., 2021), and is considered to be more suitable to be a feedstock in chemical recycling by depolymerization. However, most of the existing chemical recycling attempts have been made on clean, high purity, pigment-free, bottle grade PET (Chen et al., 2015; Wang et al., 2012). Rarely have degradation pathways been proposed using colored PET fabrics with different disperse dyes. On the other hand, if mechanical recycling is used instead, recycling of complex PET wastes requires efficient sorting, separation and cleaning, suggesting a lower economic incentive (Leal Filho et al., 2019). Moreover, colors and auxiliaries will accelerate the quality loss of the end products during re-melting, resulting in down-cycling products. Therefore, most complex PET textiles will ultimately be landfilled or incinerated at the end of their service life (Ellis et al., 2021).

In view of sustainability, decolorization of dyes is becoming one of the biggest bottlenecks in recycling and upcycling of colored PET textiles (Huang et al., 2021; Mu and Yang, 2022). In general, non-ionic disperse dyes are required in the dyeing of PET due to the lack of water

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William J Berkey	CHEM	Unprotected Carbohydrate Derived Furans for the Synthesis of Value-Added Chemicals	Stefan France, Chris Jones
Danae A Chipoco Haro	MSE	Electrochemical Base-Catalyzed Depolymerization of Lignin	Marta Hatzell, Faisal Alamgir
Woosung Choi	MSE	Recyclable, Degradable Random Copolymer with Barrier Properties for Next-Generation Packaging	Zhiqun Lin, Sankar Nair, Mohan Srinivasarao
Caria Evans	CHEM	Development of Aminoethyl o-Nitrophenyl Dimers as Photocleavable Linkers for Recycling of Paper Towels	Stefan France, Chris Jones
Yacine Feliachi	ChBE	Membrane Separation for Crude Tall Oil and Crude Sulfate Turpentines	Ryan Lively, M.G. Finn
Elyssa Ferguson	ME	Sustainably Sourced Natural Fibers for Thermal Insulation in Buildings	Akanksha K. Menon
Qiang Fu	ChBE	Separation of Complex Multicomponent Organic Mixtures: Addressing a Critical Gap in Biorefining and Chemical Recovery from Pulping Processes	Sankar Nair, Scott Sinquefield
Tanner J Hickman	ChBE	Design of polysaccharide-based materials systems for applications in high humidity	Carson Meredith, Natalie Stingelin
Elnaz Jamshidi	MSE	Carbon-Negative Building Materials based on Engineered Wood for Structural and Thermal Insulation Applications project	Asha Menon, Joe Bozeman, Kyriaki Kalaitzidou
Hsiang-Ju (James) Kai	ChBE	Unraveling the physical chemistry of polyolefin-cellulose interfaces	Natalie Stingelin
Dogukan T Karahan	ME	Dynamics of Fiber Motion in Complex Flows	Cyrus Aidun, Devesh Ranjan
Jinhyeun Kim	ChBE	Development of Physics-informed Machine Learning Framework with Gaussian Process Regression & its Application to Paper Production Systems	Fani Boukouvala, Kamran Paynabar, Chris Luettgen
Jungin E Kim	ME	Biodegradable Polymer Design with Quantum Optimization	Yan Wang, Karl Jacob
Akanksha Lakra	ChBE	Advances in refining for better product quality at lower energy consumption in MP forming	Julene Tong, Cyrus Aidun, Chris Luettgen
Geng-Sheng Lin	ChBE	Cellulose-based triboelectric membrane sensor for heavy metal removal and detection	Julene Tong, George Lan
Opeyemi A Ojelade	ChBE	Catalytic Processing of Enriched Hydroxy Acids from Kraft Black Liquor	Sankar Nair, Chris Jones

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Renewable Bioproducts Institute

Listing of RBI Ph.D. Fellow Students

Name	School	Project	Advisors
Jimin Park	ChBE	Renewable Synthesis of Paracetamol from Lignin-derived Phenol.	Andreas Bommarius, Carsten Sievers, Marta Hatzell
Kim Anh Pham	ME	The Effect of Slot Die Coated CNC on Glass Fiber Fabric Reinforced Composites	Kyriaki Kalaitzidou, Karl Jacob, Tequila Harris
Erin V Phillips	CHEM	Mechanocatalytic Depolymerization of Lignin and Lignin Model Compounds	Carsten Sievers, Marta Hatzell
Arjun Thangaraj Ramshankar	CEE	Sustainably sourced natural fibers for Thermal Insulation in Buildings – A holistic life cycle perspective	Akanksha K. Menon, Joe Bozeman, Kyriaki Kalaitzidou
Michael Rettstatt	ChBE	Mechanism of Aqueous Phase Reforming of Organics over Bimetallic Catalysts	Carsten Sievers, Sankar Nair
Javaz Rolle	ChBE	Adhesion and durability effects on bio-based barrier coatings	Carson Meredith, Natalie Stingelin
Fariha Rubaiya	MSE	Understanding Electromechanical Coupling in Cellulose for Single Component Auxetic-Piezoelectric Energy Harvesters	Meisha Shofner, Lauren Garten
Lilly Schroer	MSE	Engineering Damage-Tolerant Packing Materials by Controlling Steady-State Damage Accumulation in Fiber Networks	Chris Muhlstein
Talia Thomas	ME	Functionalized Cellulose Matrices for Battery Applications	Matthew McDowell
Quyen (Peter) Tran	ChBE	Separations and Process Engineering for Aqueous Phase Reforming of Hydroxy Acids	Natalie Stingelin, Thomas Gartner
Preksha Vichare	MSE	Improving dewatering in the press section of paper making industry	Victor Breedveld, Chris Luettgen, Valerie Thomas, Blair Brettmann
David Witdorchic	ChBE	Oxygen containing intermediates from renewable woody biomass	Andy Bommarius
Andrew K Wu	ChBE	Designing tunable chemistries targeted for recyclable multilayer packaging	Natalie Stingelin, Kyriaki Kalaitzidou, Karl Jacob
Kaung Su Khin Zaw	ChBE	Engineering Microstructure of Graphene Oxide for Concentrating & Fractionating of Black Liquor in Kraft Process	Sankar Nair, Meisha Shofner, Scott Sinquefield
Li Zhang	MSE	Controlled Durability and Degradation using ALD in Cellulosic Products	Mark Losego, Todd Sulchek

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