Scale-Up Design for Biodegradable Vanillin-Based Polymer Production

(Technical Paper)

Characterization of the Relationship Between Media Technology and Development of the Anti-Vaccination Movement

(STS Paper)

A Thesis Prospectus Submitted to the

Faculty of the School of Engineering and Applied Science
University of Virginia • Charlottesville, Virginia

In Partial Fulfillment of the Requirements of the Degree
Bachelor of Science, School of Engineering

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Fall, 2019

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On my honor as a University Student, I have neither given nor received unauthorized aid on this assignment as defined by the Honor Guidelines for Thesis-Related Assignments

Introduction

The eradication of smallpox in 1980 marked the only triumph of humanity over one of its most devastating pathogenic threats. Forty years later, smallpox is still the sole infectious disease affecting humans that has been officially declared globally eliminated (CDC, n.d). The eradication of the disease was accomplished solely through widespread implementation of the smallpox vaccine, which generally prevents the inoculated from contracting the disease in the future. Vaccines are among the most influential products of the field of preventative medicine due to their efficiency at halting the spread of infectious diseases including polio, tetanus, and tuberculosis. Despite their necessity, vaccine opposition is as old as the vaccines themselves. While various groups have antagonized vaccines since their inception ("Disease Eradication | History of Vaccines," n.d.), the past 21 years have witnessed an exponential rise in vaccine hesitancy and opposition otherwise known as the 'anti-vaccination movement.' Though the movement lacks a centralized administrative body, its devotees have fostered the spread of false information, panic, and preventable diseases across the United States.

While this research aims to characterize the development of the anti-vaccination movement through the lens of Science, Technology and Society (STS) theory, the objective of the technical capstone project is to develop a chemical process for the manufacture of a biological plastic substitute for PET, poly(dihydroferulic acid), from lignin feedstock. The term 'plastic' encompasses thousands of synthetic or semi-synthetic organic polymers that generally consist of a carbon backbone bound to various molecular groups that form "side chains." Formation of the final plastic occurs through crosslinking, in which the functionalized polymer chains fold and react with one another to create a massive, tightly bound polymer. The chemical properties of side chain groups determine the strength of attraction or repulsion between

neighbors, which then determines the properties of the plastic. The vast majority of plastics are manufactured from petrochemicals extracted from ever-dwindling natural reservoirs of crude oil, a process that will be both financially and environmentally unsustainable in the coming decades. Another environmental and financial problem inherent to most plastics is that their synthetic origin prevents them from undergoing biodegradation. They then degrade by UV-induced radical reactions, the process of which can take anywhere from ten to ten thousand years. (EPA). The technical capstone project aims to research scaleup of an environmentally sustainable manufacturing process for a biologically-sourced polymer with properties that make it a suitable substitute for PET plastic.

Technical Topic: Industrial Process Design for Production of a Naturally-Derived Degradable Thermoplastic

Current State of Biopolymer Research and Development

As national media sources intensify the spotlight on plastic pollution and the general public's distaste for non-sustainable materials heightens, the scientific community is expanding its efforts to innovate biologically-based, functionalized materials for polymerization. The fabrication of polymers that are both practically useful and environmentally-friendly is difficult for researchers, even those in groups that prioritize that field of study. Holmberg et al. summarize the primary issues, "Practical bio-based materials that can compete with petroleum-based plastics in both cost and performance are of growing interest yet are challenging to design due to trade-offs between cost, feedstock sustainability, and macromolecular properties" (2016, p. 1286). Kristufek, Wacker, Tsao, Su, and Wooley, researchers from the chemistry and chemical engineering departments at Texas A&M University, contended that recent advances in natural

product synthesis and isolation bolster the development of scalable reaction schemes for bio-derived polymeric materials (2016, p. 433).

A myriad of review articles, exemplified by University of Florida chemist Stephen Miller's 2013 publication, extol the benefits of sustainable polymers supported by laboratory-scale research on the production and degradation of the materials. One such reaction that is gaining particular interest from researchers involves the depolymerization of lignin to obtain aromatic compounds for continued processing (Nicastro, Kloxin, & Epps, 2018, p. 14812; Ganewatta, Lokupitiya & Tang, 2019). Lignin is a natural polymer representing 30% of the world's biomass and is generated as waste in the pulp and paper industry on the scale of millions of tons annually (Ganewatta et al., 2019, p. 2).

Laboratory Research Basis for Process Design

Mialon et al, researchers at The George and Josephine Butler Laboratory for Polymer Research at the University of Florida, reported a novel, biodegradable, and potentially lignin-derived thermoplastic replacement for polyethylene terephthalate (PET) in 2010. The final product of their reported reaction, poly(dihydroferulic acid) (PHFA), exhibits thermal and mechanical properties comparable to those of PET, the third most common synthetic polymer, accounting for nearly twenty percent of global plastic production (Mialon et al., 2010, p. 1704). The monomer, dihydroferulic acid, is a modified form of vanillin, a product of wood-derived lignin depolymerization. The other reagent, acetic anhydride, can also be derived from wood, resulting in a fully wood-sourced material (Mialon et al., 2010, p. 1704). A patent and trademark (Gatoresin™) for the product followed its discovery, indicating its perceived viability (Mialon & Miller, 2015; Florida Institute for Commercialization of Public Research, 2014). The technology then led to the founding of US Bioplastics, with Miller as the CTO. The company received initial

funding, but never acquired the resources to build a pilot facility for the production of the material (Wayback Machine, 2019). Given the promise of the bioplastic itself, and the recent increase in demand for bioplastics, it is worth considering the development of a new design for industrial scale production of this sustainable material.

Thesis Project Objectives and Methods

The objective of the technical project is to design a fully-operational plant to mass-produce a bioplastic using the vanillin synthetic scheme described by Mialon et al., and the corresponding patent of Mialon and Miller (2010; 2015). A proposed high-level block flow diagram for the process is shown in Figure 1. By transitioning the synthesis from a batch to the continuous process portrayed below and addressing issues of energy efficiency, operational safety, and waste abatement, the design will allow for profitable production of the bioplastic in quantities required for commercial applications. In addition to producing a sustainable product, it is crucial that the process design itself sustainable to ensure that the environmental good of the PHFA polymer is not diminished by the production phase.

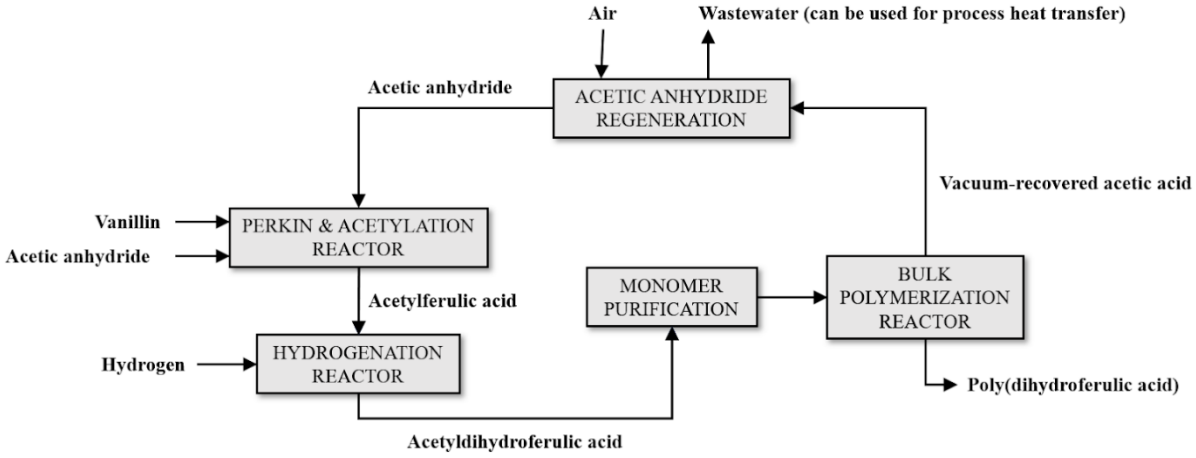

Figure 1. Block Flow Diagram for Proposed Process (Created by Bush, 2019). Presents essential operations, feeds, products, and intermediate flows. Poly(dihydroferulic acid) is the desired thermoplastic product. Vanillin, acetic anhydride, hydrogen, and atmospheric oxygen must be

> continuously supplied, and the regenerated acetic anhydride flow will at best be equal to the rate of fresh acetic anhydride feed.

The Aspen Plus software suite will be used to simulate the unit operations required of the process (AspenTech, 2019). Other computer programs, including MATLAB, will supplement the modeling done in Aspen Plus (MathWorks, 2019). Specifically, since Aspen Plus excels in thermodynamic calculations but lacks in its reaction kinetics modeling, MATLAB will be used to design the reactors essential to the process.

The technical project will last the entirety of the 2019-2020 academic year, in a two-semester senior design sequence directed by Professor Eric W. Anderson. The design group is comprised of fourth-year chemical engineering students Christopher Brodie, Ethan Bush, Jillian Dane, Gavin Restifo, and Rebecca Richardson. By the end of the fall semester, the initial plans for a plant will be detailed in a design basis memorandum. This document will include a description of feedstocks and final products and a high-level overview of the material and energy balances and purification techniques relevant to the process. Additionally, an economic appraisal will be included as a proof-of-concept for financial feasibility. At the end of the spring semester, a technical report will be authored, fully defining the bioplastic production process.

Role of Deliverable in the Future of Sustainable Materials

This project will contribute to the progress of chemical industries: biomass-derived plastic is valuable not only for its lower environmental impact compared to fossil-fuel-derived equivalents, but as an element of cross-industry sustainability. As the transition to renewable resources is driven by the rapid consumption of nonrenewable oil and gas, future material feedstocks could be made in biorefineries that utilize biologically-generated molecules in real time, rather than millions of years after the fact. Lignin would be one component of this system.

Biofuels from Algae, which details the algal component of a biorefinery vision, points out, "[E]conomic analyses have consistently indicated that algal-based biofuel feasibility hinges on the possibility of production coproducts with a market value from the spent biomass" (Guedes, Amaro, Sousa-Pinto, & Malcata, 2014, p. 206). In this context, failing to scale bioplastic production will not only result in continued issues with conventional plastics, but will obstruct the future of sustainability in all other chemical industries currently based on fossil fuel inputs.

STS Topic: Characterization of the Relationship Between Media Technology and Development of the Anti-Vaccination Movement

In 1998, Andrew Wakefield's now-infamous paper 'Ileal-lymphoid-nodular hyperplasia, non-specific colitis, and pervasive developmental disorder in children' was published by widely respected British medical journal, *The Lancet*. The Wakefield paper's central conclusion was a connection between the measles, mumps & rubella (MMR) vaccine and development of autism in young children based off of a study Wakefield conducted using deeply flawed and unethical scientific practices. While the paper was redacted six years later, and Wakefield stripped of his medical license, the fact that it was published at all catalyzed a tidal wave of science denialism and conspiracy ideation that blossomed into what is now known as the anti-vaccination movement. Colloquially known as 'anti-vaxxers,' followers generally believe vaccines are the artifacts of a nebulous conspiracy between medical professionals, pharmaceutical companies, and governments to extract revenue from an unwitting general public. Based off of multiple studies on rhetorical claims and reasoning posted by anti-vaccination websites, common assertions include that vaccines cause illness, that they are ineffective, that they are tools of a government, medical or pharmaceutical conspiracy, and that… A 2010 study of all anti-vaccine websites within the first 50 Google results for vaccine-related search terms found that every site

claimed that vaccines contained poisonous materials such as antifreeze, mercury, ether, and formaldehyde (Kata 2010).

The motivation driving this research is simple. People are suffering and dying from preventable diseases directly because of underimmunization spurred by the spread of anti-vaccine rhetoric and falsehoods. The American Academy of Pediatrics reported that over 70% of all pediatric flu deaths between 2010 and 2014 were unvaccinated children (AAP 2017). Between January 1 and October 3 of 2019, the CDC reported 1,250 cases of measles in the United States, the largest number of reported measles cases within a year since 1992. Over 70% of the incidents occurred in unvaccinated people, while over 98% of the affected individuals were U.S. residents. The vast majority of outbreaks occurred in underimmunized communities, especially within large cities such as New York (CDC 2019).

The relative youth of the anti-vax movement and internet as we know them today curtail the availability of comprehensive research and quantitative data pertaining to the interactions between them. Previous literature on the history of anti-vaccine activism jumps directly from the first anti-vaccination protests in nineteenth-century Britain to online protests after 2015, dancing around the 15-year period during which rapid technological advances changed how people communicate and disseminate information (many). There is no comprehensive research that fully and explicitly explores the progression of interactions between vaccine skeptics, medical professionals, pharmaceutical companies, media organizations, communication technologies, and lawmakers between the Wakefield paper of 1998 and today. Thus, the objective of the STS research is to fill this void.

Due to the transient nature of the technological and societal forces at hand, the primary STS theories implemented in the research will be Paradigm Shift Theory and Actor Network

Theory. Paradigm Shift Theory will be used as a lens through which to characterize the transition of Internet users from content consumers to content producers, as well as the change in the patient-doctor relationship with the ubiquity of health-related information on the Internet. Actor Network Theory was chosen for its versatility and focus on the specific interactions that are so often 'black-boxed' in previous literature. Online anti-vaccine communities are veritable microcosms of the rest of society operating as if in a separate reality. Devotees of anti-vaccine rhetoric have their own "research," their own "facts," and their own "experts." Anti-vaxxers themselves are the primary actors, the sociologist-engineers of this sprawling web of false truths. Research will be conducted throughout the remainder of the fall and spring semesters, culminating in the STS Thesis at the end of the spring term.

This research aims to answer the following question: How did anti-vaccine rhetoric suddenly become so prevalent in America? What is the degree of responsibility held by media organizations in verifying the accuracy of the information they disseminate? Are people entitled to make health decisions that may jeopardize the health of others? How have American policymakers navigated the boundary between protecting public health and overstepping individual freedoms? The specific technological systems observed include network television, the Internet, and social media (specifically, Facebook and Twitter). The research question will be investigated through the lens of STS using Paradigm Shift Theory to describe shifts in the American doctor-patient relationship and Actor-Network Theory to characterize the social groups formed by anti-vaxxers. Paradigm Shift Theory was created by Thomas Kuhn in order to describe fundamental changes in the basic concepts of a scientific field, but is commonly extended to describe significant changes in non-scientific contexts. Actor-Network Theory is a framework useful for producing micro-level studies of interactions between human or nonhuman

actors in the context of scientific and technological development. Though Actor-Network Theory has been criticized for its inclusion of nonhumans as participants in networks, vaccines themselves are critical inanimate actors around which the movement is centered. Major research methodologies will include documentary research, historical case studies, policy analysis, discourse analysis, network analysis, and wicked problem framing. Specific case studies analyzed will be Jenny McCarthy's appearance on the Oprah Show and New York State's 2019 passage of a law barring unvaccinated children from attending public schools. Additionally, Actor-Network Theory-based research on the anti-vax community will be conducted by identifying as many anti-vaccination websites as possible and analyzing the similarities between their rhetoric, 'scientific references,' and interactions with other anti-vaccination sites. Social-media based research will be conducted using data collected from studies of anti-vaccination Facebook groups (Smith, 2019; Schmidt, 2018) and tweets (Mitra, 2016), as well as independently examining the content and communication between members of anti-vaccination Facebook pages.

Conclusion

The technical capstone project aims to research scaleup of an environmentally sustainable manufacturing process for a biologically-sourced polymer with properties that make it a suitable substitute for PET plastic. The technical deliverable will be a design of a fully-functional, scaled-up industrial process for the synthesis of Poly(dihydroferulic acid) from vanillin feedstock. In order to reduce reliance on environmentally harmful petrochemical-derived plastics, ensuring that the bioplastic manufacturing process is both energetically and economically viable is critical.

While the STS research project does not investigate plastics, its analysis will be vital for curtailing the spread of dangerous misinformation and falsehoods and hopefully preventing

future deaths from preventable illnesses. The STS research aims to characterize the relationships between media technology and the anti-vaccination movement between the publication of the Wakefield paper in 1998 and present day. The STS deliverable will be a Thesis detailing the nature of this phenomenon and the proposal of a potential solution determined using STS theory.

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