

LSU

College of
Engineering

Department of

Biological & Agricultural Engineering

SPRING 2018 NEWSLETTER





Biological and Agricultural Engineering Introduction

The Department of Biological and Agricultural Engineering (BAE), which offers both a bachelor (accredited by the Accreditation Board for Engineering and Technology) and master of science in biological and agricultural engineering, has requested approval from the Louisiana Board of Regents to add a PhD with a concentration in biological engineering.

BAE brings innovation to a wide range of groups – from biomedical to bioprocessing to bioenvironmental applications – by integrating applied biology into fundamental engineering principles for the purpose of designing processes and systems that influence, control, or utilize biological materials, animals, plants, humans, and other living organisms for the benefit of society.

In 2012, the department transitioned officially from the College of Agriculture to the College of Engineering, better aligning its programs and degrees but maintaining its ties to the LSU AgCenter in research and extension activity. In 2015, BAE initiated a new program between LSU and the Health Sciences Center in New Orleans called “Fast Path.” It provides a compressed format for the BS/MD/PhD track leading to biomedical academia and research. While focusing in the biomedical area, BAE continues research and extension with three AgCenter research stations and associated adjunct faculty.

Below are summaries of a few of our current research projects:

RXHypoxia – Professor Emeritus Louis Thibodeaux and Chair and Professor W. David Constant

There is a thin surface layer of decaying organic matter on the seafloor in the Gulf of Mexico. It is placed there each year as the water column algae grow, die, and settle downward after spring and summer bloom growth. In late summer and early fall, this biomass undergoes a microbial, enzyme-catalyzed, oxidation decay commonly referred to as sediment oxygen demand (SOD). Completely or partially void of molecular oxygen, this bottom surface of the water column provides the “sink” for the downward transport of oxygen from the surface air-water interface, or “source.”

Vertical profiles taken by Rabalais et al. (2002) over many years confirm the areal extent and oxygen gradient in the “dead zone” of hypoxic salt water underlying freshwater discharge from the Mississippi and adjacent rivers. Much has been observed and published regarding the impact of nutrients on this hypoxic layer (Rabalais et al., 2010). However, this theoretical laboratory study is focused on the nature and behavior of the oxygen gradient, as found in shallow shelf waters along the northern Gulf of Mexico, and how that

gradient can be impacted by engineered solutions other than the nutrient source. This is also an excellent opportunity for a better understanding of chemical transport in the upper marine water column. Theoretical behavior patterns in the vertical transport of oxygen can be used to explore the efficacy of water mixing at depth to increase mixing and prevent or minimize the development of low oxygen concentrations below the pycnocline that result in hypoxia.

The term “reaeration” is the natural or engineered oxygen resupply process from the atmosphere to surface waters, both marine and fresh. It occurs naturally as a result of ocean currents and surface winds, which stir or mix the upper layers to enhance absorption and diffusion of oxygen into the mixed layer. The use of mechanical devices or bubble sparging of gas into the water are engineered reaeration processes commonly used in wastewater treatment of ponds and tanks. The theoretical details of these processes as applicable to the shallow waters of the Gulf of Mexico are being investigated via math models and laboratory tank-confirming experiments to project the efficacy of using engineered processes to artificially reduce hypoxia. Preliminary work will be completed in mid 2017, with additional experiments to more accurately simulate the layered system being completed in fall 2017.

Nancy N. Rabalais, R. Eugene Turner, and William J. Wiseman Jr., Gulf of Mexico Hypoxia, a.k.a. ‘The Dead Zone’, *Annual Review of Ecology and Systematics*, Vol. 33 (2002), pp. 235-263.

N. N. Rabalais, R. J. Diaz, L. A. Levin, R. E. Turner, D. Gilbert, and J. Zhang, Dynamics and Distribution of Natural and Human-Caused Hypoxia, *Biogeosciences* (2010), 7, pp. 585–619.

Polymeric Nanoparticle System for Cataract Treatment – Professor Cristina M. Sabliov and Assistant Professor Carlos E. Astete

Age-related cataracts is a leading cause of visual impairment in the United States. The prevalence of age-related cataracts is increasing, with an estimated 30.1 million Americans likely to be affected by 2020.¹ Although cataracts can be successfully removed with surgery, this approach is expensive, and most individuals blinded by severe cataracts in developing countries go untreated. In the United States, a significant proportion of companion animals are also diagnosed with cataracts each year; about 9.79 million dogs and 1.17 million cats have cataracts.² Oral nutritional supplementation with antioxidants is the only cataract treatment other than surgery. These antioxidants, however, are not able to target the inner eye to combat the problem directly when orally delivered. A nanoparticle-delivered antioxidant that could potentially be used in eye drops to reverse cataracts in people and companion animals has been

engineered by a team of scientists in BAE.

The team recently completed an animal study with an eye-drop formulation in rats with chemically induced cataracts. The eye drops, applied daily for seven days, restored transparency to mouse lenses affected by cataracts, as shown below.

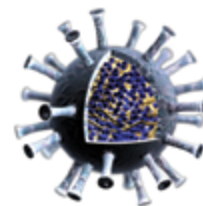


Image by Mathew Faust (lsu.faust@gmail.com)

1. Chew, E. Y., et al. 2013. Lutein/Zeaxanthin for the Treatment of Age-Related Cataract: Areds2randomized Trial Report no. 4. *JAMA Ophthalmology*, 131: 843-50.
2. Robledo, E. Composition and Method for the Treatment of Eye Disease. 7,960,350 B2, April, 2011.

Rare Contamination Found in Louisiana Drinking Water

Two drinking water systems in Louisiana were found to have *Naegleria fowleri* contamination in 2011 and 2013, resulting in three deaths due to primary amebic meningoencephalitis. While *N. fowleri* is not uncommon in surface waters during the summer months, cases involving drinking water in the United States are very rare, and *N. fowleri* was detected in the drinking water systems in the above three cases. Work by W.D. Constant at LSU suggests that it may be possible for the amoeba to survive disinfection processes while in the sediments commonly found in drinking water storage tanks. Sediment samples were collected from a Louisiana water system storage tank and placed in beds to simulate the exposure of the sediment to overlying water with high levels of chlorine present (5-10 ppm), as one would find in a chlorine “burn.” Chlorine (or chloramine) concentrations were then measured with depth and time for several months in repeated tests. Preliminary results indicate effective diffusivity of chlorine in St. Bernard Parish sediment to be on the order of 0.5×10^{-8} to 5.1×10^{-8} cm²/sec, which is about an order of magnitude less than observed in typical sand. This represents a fairly slow diffusion rate into the sediment, requiring three to 30 years for a 5 mg/l source to yield 0.5 mg/l at 5 cm depth. With the Louisiana Department of Health and Hospitals’ required residual chlorine concentration now being 0.5 ppm throughout drinking water systems, the above results suggest that regular removal of sediments from drinking water storage tanks may improve efforts to control *N. fowleri*.

Biofuel Production From Chinese Tallow Tree Seeds Using Microwave Technology

Mohamad Barekati-Goudarzi,¹ Dorin Boldor¹

¹LSU Agricultural Center, Department of Biological and Agricultural Engineering, Baton Rouge, LA 70803, United States

ACKNOWLEDGEMENTS:

The authors would like to acknowledge the LSU Agricultural Center and LSU Biological & Agricultural Engineering Department for the support of this project. Funding for this research was provided by the Louisiana Board of Regents, Industrial Ties Research Subprogram (ITRS), Award #LEQSP (2007-10)-RD-B-01; US Department of Transportation, Sun Grant Initiative, Award #AB-5-61770.LSU1; and US Department of Agriculture (USDA) National Institute of Food and Agriculture under the Hatch funding mechanism (project LAB #93884 and LAB #94196). Published with the approval of the director of Louisiana Agricultural Experiment Station as Manuscript #2017-.....

ABSTRACT

In situ transesterification (simultaneous extraction and transesterification) of Chinese tallow tree seeds into methyl esters using two microwave systems was investigated in this study.

In the first part, utilizing a batch system, parameters tested were catalyst concentration (1-4 wt.%), solvent ratio (2-6 v/w), reaction time (15-60 min.), and temperature (50-70°C). A high degree of oil extraction and efficient conversion of oil to biodiesel were found in the proposed range. The process was further optimized in terms of product yields and conversion rates using Dohler optimization methodology. Based on the experimental results and statistical analysis, the optimal production yield conditions for this process were determined as – catalyst concentration of 1.74 wt.%, solvent ratio of about 3 (v/w), reaction time of 20 minutes, and temperature of 58.1°C. GC and hydrogen nuclear magnetic resonance (H-NMR) were used to profile the fatty acid methyl esters and reaction conversion, respectively. All methyl esters produced using this method met ASTM biodiesel quality specifications.

For the second part, a continuous in situ transesterification of the seeds using a microwave-assisted continuous stir-tank

reactor (CSTR) system was investigated with determination of kinetic parameters. A high production yield of 90.02% with 97.53% conversion rate was obtained in 24 minutes CSTR residence time at a methanol/hexane/CTT seed ratio of 3:3:1 (v/v/w), a microwave heating power of 290 watts and 14 seconds exposure time, reaction temperature of 60°C, and sodium hydroxide catalyst loading of 4% wt. of oil. The experimental data fits the first-order reaction kinetics. The values of rate constants at different temperatures and the corresponding activation energy were found out to be 0.083-0.087 min⁻¹ and 1,987.82 J/mol, respectively. The thermodynamic parameters values such as Gibbs free energy (ΔG), enthalpy (ΔH), and entropy of activation (ΔS) were also determined. The positive values of ΔG and small negative value of ΔH indicated that the reaction has an unspontaneous/endergonic nature and is slightly exothermic.

1. INTRODUCTION

Energy sustainability and the development of frameworks for an effective application of energy technologies in both local and global settings are still major challenges for all developed and developing countries, mostly due to the continual increase in transportation fuel consumption for economic development. In 2013, total

primary energy consumption increased by 2.3%, while the global oil consumption reached 91.3 million barrels per day, a 1.4% rise compared to previous years. In 2013, it was estimated that a total of only 1,687.9 billion barrels remained in the oil reserves worldwide, sufficient for only 53.3 years of global production (Su et al., 2015). The consequences of the current increase in global energy demand, as well as the negative environmental impacts of fossil fuels, has led to a renewed interest for renewable energy resources. Energy sources can be divided into two main categories – renewable and nonrenewable.

The nonrenewable sources of energy are mainly fossil fuels and nuclear energy, which can be replaced by other renewable sources like solar, wind, modern biomass, geothermal, etc. The reason behind this replacement is the many positive effects of renewables. The local or domestic nature of renewable energy improves the energy supply security by minimizing the risk of energy supply disruptions (Dincer, 2000; Panwar et al., 2011). Besides that, the abundant and wide availability of renewable resources (Suganya et al., 2014) compared to fossil fuels' geographical concentration, cleanness of renewable energies, minimal environmental impacts and reduced waste generation, such as pollutant gas

emissions, are their main advantages. Thus, although fossil fuels are still the major contributor to the world's energy supply chain, the proportion of biofuels is raising rapidly with the development of science and technology.

The US Energy Information Administration (EIA) estimates that renewable energy will comprise 15% of total energy consumption by 2040. Amongst the mentioned alternative sources of energy, biomass-based renewable energy attracted the most attention, as it has been at the top of the renewable energy source list for production of liquid fuels for transportation. In addition to being the world's largest industrial producer and agricultural product supplier, the United States is also the biofuel global developer (Quinn & Davis, 2015). Energy security, reduction of dependence on oil imports, the promotion of a sustainable economy, development of employment opportunities in the agricultural field, and new industrial explorations in order to implement new technologies for development of wide sources of energy are the main driving forces of biomass development in the United States (Su et al., 2015).

Most literature reports show a significant increase in renewable energy supplies. In 2013, biofuel productions increased by 71,782 million L from 2006 and reached 117,715 million L in 2013 (Koizumi, 2015). Of the total biofuel production, 75% was allocated to bioethanol in 2013, and the remaining was attributed to biodiesel. Bioethanol production increased to 83,353 million L in 2012, in comparison to 39,187 million L in 2006. The United States (as the world's largest producer) and Brazil (the second producer) produced 50,397 million L and 25,530 million L, respectively, in 2013. These two countries accounted for 86% of worldwide bioethanol production, followed by China, France, and Canada. Biodiesel

production, as the second renewable energy source, increased from 6,746 million L in 2006 to 29,545 million L in 2013. The European Union is the largest producer of biodiesel by production rate of 12,103 million L in 2013, followed by the United States, Argentina, Brazil, and Indonesia.

The direct combustion of vegetable oils as fuel in diesel engines proved to be impractical due to high acid content, high free fatty acid composition, and gum formation due to oxidation and polymerization. Carbon sedimentation and thickening of lubricating oil are the other obvious problems (Fukuda et al., 2001). In order to overcome these issues, researchers have developed methods to convert oil into more environmentally and technically suitable fuel. Microemulsion, thermal cracking, and transesterification are the most established methods. Amongst them, transesterification is the most popular and preferred (Ma & Hanna, 1999). Transesterification is the reaction of oil with an alcohol to form methyl esters and glycerol. The reaction accelerates by catalyst in presence of primary or secondary monohydric aliphatic alcohols (having one to eight carbon atoms) (Demirbas, 2005). An excess amount of alcohol can shift this equilibrium reaction to the right side to produce more methyl esters, with methanol and ethanol being most commercially used. Even though ethanol is more renewable and biologically friendly and can be produced from agricultural crops, methanol is preferable due to economical, physical, and chemical advantages (Wen et al., 2009). The reaction is catalyzed by alkali and acid catalyst, as well as enzymes (Fukuda et al., 2001; Wang et al., 2011). The use of both batch and continuous process has been reported. However, the high cost of investment to build large volume reactors to run batch systems is the main challenge and makes continuous process preferable (Maçaira et al., 2011).

Transesterification occurs either with homogeneous or heterogeneous catalysts. In homogeneous form, the use of catalyst is in liquid/dissolved form, and it is mainly acid or alkali catalysts. The protonation of the carbonyl group in triglycerides is the basic factor in the acid catalysis, where the alcohol attacks the protonated carbon to create a tetrahedral intermediate. However, creating nucleophilic alkoxide from the alcohol to attack the electrophilic part of the carbonyl group of the triglycerides is the important factor in a homogeneous-base catalyzed reaction (Schuchardt et al., 1998). The first conventional method applied in the biodiesel production industry was the use of homogeneous catalysts. Even though its industrial application has been decidedly proven, recent investigations are focusing on the application of heterogeneous catalysis with a view to improve productivity. The application of heterogeneous catalysts, which are solid in form, in biodiesel production lessens the issues contributed to homogeneous catalysis. The catalyst can be recycled and reused for several times with better separation of final product due to high productivity and reduced cost of operation and production. This method is proven to be environmental friendly and can be utilized in both batch and continuous process without any further purification steps (Endalew et al., 2011; Yan et al., 2010). The first objective in this work is to develop an in situ method for direct production of biodiesel from Chinese tallow tree seeds through a homogeneously catalyzed reaction. In order to facilitate the reaction pace, the application of microwave technology as a fast source of heat was investigated. Doehlert optimization methodology was used to optimize the process in terms of reaction operation factors like catalyst concentration, reaction time and temperature, and solvent ratio. The second objective was to apply the optimized condition in a continuous process and study the kinetics of the reaction, as well as the thermodynamic parameters, with im-

portant impacts on the process.

2. MATERIALS AND METHODS

2.1. MATERIALS

Lab grade methanol alcohol and reagent grade ACS (99.5%) hexane used in the reactions were purchased from Fisher Scientific (Pittsburg, Pennsylvania) and Mallinckrodt Chemical Inc. (St. Louis, Missouri), respectively. The catalyst sodium hydroxide was supplied by Pharmco-AAPER (Brookfield, Connecticut). The seeds used in this study were manually collected from near Baton Rouge, Louisiana between October-November 2012 (30°23'22.3"N 91°11'57.2"W), dried at 103°C in a conventional hot air oven for 24 hours, ground using a blade-type coffee grinder, and stored in sealed plastic bags in the freezer at -4°C to avoid moisture gain until further use.

2.2. METHODS

2.2.1. DETERMINATION OF MOISTURE CONTENT

In order to measure the moisture content, three samples of 10 g CTT seeds were weighed and placed in the oven for 72 hours. The samples' weight were periodically measured and, using the following formula, the moisture content was calculated, where X_1 is the initial weight of samples and X_2 is the weight at the end:

$$\text{Moisture Content: } \frac{X_1 - X_2}{X_1} \times 100 \quad [\text{Eq. 1}]$$

2.2.2. DETERMINATION OF OIL CONTENT

The theoretical maximum oil yield in the seeds was measured using a Soxhlet extraction (ASTM D5369-93(2008)e1) apparatus, where 20 g of ground CTT seed was used for three samples. An equivalent mixture of hexane and methanol was used as extraction solvent for 15 hours. The solvent was removed eventually using a Rotavapor (Buchi R-124), and the remaining oil was dried in a vacuum dryer (Isotemp Vacuum Oven Model 285A) for another 15 hours to

measure the final oil weight. The following formula was used to calculate the oil content:

$$\text{Oil Content: } \frac{\text{Extracted oil weight (g)}}{\text{Biomass weight (g)}} \times 100 \quad [\text{Eq. 2}]$$

2.2.3. BATCH IN SITU

TRANSESTERIFICATION

Batch in situ transesterification was performed in an Ethos E batch microwave system (Milestone Inc., Monroe, Connecticut) with a maximum power output of 1.6 kW and 270 mL of sealed high-pressurized TFM (tetrafluoromethane) vessels equipped with magnetic stirrers. The temperature was monitored with a built-in optical fiber temperature sensor. Twenty grams of ground CTT seeds were mixed with methanol, hexane, and sodium hydroxide as catalyst and heated to a set temperature for a certain amount of time. The sample was finally collected and used for final separation stage.

2.2.4. CONTINUOUS IN SITU

TRANSESTERIFICATION

The continuous system was comprised of a 6 kW microwave system operating at 2,450 MHz generously donated by Sairem LLC in France. The reactor was a 7/8-inch tube placed at the center of a resonant cavity. The temperature was measured with a Raytek® MI3 infrared temperature sensor, which was coupled to a National Instrument Data Acquisition Board in order to monitor the temperature and control the power of the generator using LabVIEW 8.6 (National Instruments Corporation, Texas). After being pumped through the microwave, the mixture was transferred into an insulated continuous stir tank reactor (CSTR) in order to maintain the reaction temperature to reaction completion.

2.2.5. SEPARATION OF BY-PRODUCTS

The separation process started with centrifugation of product samples at 3,600 rpm for 10 minutes in order to separate

suspended solid biomass from the liquid mixture. The obtained liquid phase was transferred into a separating funnel where more hexane and distilled water were added to accelerate separation of phases. The upper phase was decanted and washed a few times to remove the impurities. The solvents were finally recovered, and products were dried overnight.

2.2.6. ANALYTICAL AND STATISTICAL ANALYSIS METHODS

Nuclear magnetic resonance spectroscopy and gas chromatography (GC) were used as analytical methods for biodiesel analysis (quantification of major/minor components and monitoring the transesterification reaction) due to their high accuracy.

In order to study the effects of experimental conditions, four factors were chosen – catalyst concentration, solvent ratio, reaction time, and temperature – and they ranged from 1-4 wt.%, 2-6 v/w, 15-60 minutes, and 50-70°C, respectively. A set of 25 experimental runs were designed using the Doehlert method to find the effects of these factors. The results of the experiments were used to fit the data for the following second order polynomial equation in order to optimize the reaction conditions:

$$Y = b_0 + \sum_{i=1}^k b_i x_i + \sum_{i=1}^k b_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j>i}^k b_{ij} x_i x_j \quad [\text{Eq. 3}]$$

Where b_0 , b_i , b_{ii} and b_{ij} are model coefficients for intercept, linear, quadratic and interaction terms, respectively, and x_i and x_j are coded independent variables.

2.2.7. KINETIC MODEL OF

TRANSESTERIFICATION

The overall transesterification reaction takes place in the CSTR following the microwave exposure, according to the following expression:



Assuming a first-order reaction rate equation for the transesterification reaction is

$$r = k C_{-FAME} ; \quad [\text{Eq. 5}]$$

where k is the rate constant, a mathematical model was developed in the following form:

$$\ln C_{FAME} \cdot t = k \cdot t \quad [\text{Eq. 6}]$$

3. RESULTS AND DISCUSSION

3.1. MODELING AND OPTIMIZATIONS OF THE BATCH PROCESS

3.1.1. PRODUCT YIELD AND REACTION CONVERSION

The experimental factors, experimental (Y_{exp}) and theoretical product yields (Y_{mod}), as well as experimental (C_{exp}) and theoretical reaction conversions (C_{mod}) under different

treatment conditions are presented in Table 1. The model coefficients for the polynomial equations and P-values for both “product yields” are given in Table 2. (The tables and figures in this manuscript were reproduced with permission from the master’s thesis entitled Biofuel Production from Chinese Tallow Tree Seeds Using Microwave Technology by Mohamad Berekati-Gourdazi at LSU in Baton Rouge, Louisiana).

The calculated P-value was less than 0.05 for the linear effect of temperature, quadratic effect of time, and interaction effects of catalyst concentration and solvent ratio, catalyst concentration and temperature, and solvent ratio and time, showing that they have significant effects

on the model for their study. Different significant factors were defined in other studies compared to the one presented here. These contradictions could be due to the effects of the microwave on oil extraction and transesterification efficiency in comparison to conventional methods. Since, the microwave interacts directly with the bio-oil trapped in the biomass matrix as previously described (Balasubramanian et al., 2011; Terigar et al., 2010), as well as the nature of the vegetable material (*Jatropha curcas* in their case and the CTT seeds in this work), better efficiency and different influential factors were obtained in this study.

Regression coefficient and average RSEE calculated for product yield were 0.980

Table 1 Coded and un-coded values for Doehlert experimental design, experimental and theoretical product yields and reaction conversion

Exp't No	Experimental matrix				Responses					
	X1 (wt.%)	X2 (v/w)	X3 (min)	X4 (°C)	Yexp (%)	Ymod (%)	RSEE	Cexp (%)	Cmod (%)	RSEE
1	4	4	37.5	60	76.88	77.27	0.50	94.52*	92.05*	eliminated
2	1	4	37.5	60	82.35	81.96	0.47	4.42	4.42	1.42e-5
3	3.25	6	37.5	60	74.89	75.64	0.99	94.37	96.89	2.66
4	1.75	2	37.5	60	86.38	85.64	0.86	86.91	84.39	2.88
5	3.25	2	37.5	60	81.87	82.95	1.32	94.44	97.33	3.06
6	1.75	6	37.5	60	78.72	77.64	1.37	94.08	91.19	3.07
7	3.25	4.67	60	60	75.85	76.80	1.25	95.85	98.15	2.40
8	1.75	3.33	15	60	83.99	83.04	1.13	90.44	88.13	2.54
9	3.25	3.33	15	60	87.55	88.66	1.27	93.97	96.96	3.18
10	2.5	5.33	15	60	75.44	75.13	0.41	94.47	93.84	0.66
11	1.75	4.67	60	60	88.23	87.12	1.26	91.34	88.34	3.27
12	2.5	2.67	60	60	78.59	78.90	0.39	90.74	91.37	0.69
13	3.25	4.67	43.13	70	78.79	76.70	2.64	94.95	90.14	5.06
14	1.75	3.33	31.88	50	79.61	81.70	2.62	75.21	80.02	6.39
15	3.25	3.33	31.88	50	84.81	82.23	3.04	94.36	88.48	6.23
16	2.5	5.33	31.88	50	77.56	78.20	0.83	94.65	95.65	1.06
17	2.5	4	54.38	50	78.31	78.16	0.18	94.42	94.49	0.06
18	1.75	4.67	43.13	70	79.34	81.92	3.25	74.09	79.97	7.93
19	2.5	2.67	43.13	70	83.85	83.21	0.76	94.29	93.28	1.06
20	2.5	4	20.63	70	79.25	79.40	0.18	94.66	94.59	0.06
21	2.5	4	37.5	60	83.25	84.4077	1.38	94.58	94.58	8.75e-6
22	2.5	4	37.5	60	85.35	84.4077	1.10			
23	2.5	4	37.5	60	84.90	84.4077	0.58			
24	2.5	4	37.5	60	83.44	84.4077	1.15			
25	2.5	4	37.5	60	85.07	84.4077	0.78			

X₁: Catalyst Concentration, X₂: Solvent Ratio, X₃: Reaction Time X₄: Reaction Temperature, Y_{exp}: Experimental Product Yield, Y_{mod}: Predicted Product yield, C_{exp}: Experimental Reaction Conversion, C_{mod}: Predicted Reaction Conversion, RSE: relative standard error of the estimate, * data were eliminated

Table 2 Model constants and P values for product yield and reaction conversion

	Product Yield		Reaction Conversion	
	Coefficient	P-value	Coefficient	P-value
b0	84.41	0.000	94.59	0.000
b1	-2.35	0.019	9.32	0.042
b2	-4.42	0.000	1.83	0.520
b3	-0.82	0.352	-0.22	0.937
b4	0.15	0.861	-0.11	0.970
b11	-4.79	0.012	-80.84	0.000
b22	-3.65	0.042	24.11	0.023
b33	-2.09	0.186	11.51	0.167
b44	-4.63	0.008	1.03	0.887
b12	0.39	0.859	-4.18	0.568
b13	-9.91	0.002	2.08	0.797
b14	-1.22	0.637	2.07	0.805
b23	10.16	0.002	37.53	0.006
b24	-2.30	0.381	14.28	0.142
b34	4.01	0.141	10.33	0.258

and 2.62%, respectively. According to the P-values obtained, catalyst concentration (X_1), quadratic effects of both catalyst concentration (X_1^2) and solvent ratio (X_1^3), and the interaction of solvent ratio and reaction time ($X_2 \times X_3$) (P-value < 0.05) were the significant factors affecting reaction conversion. A direct comparison with other studies cannot be done on conversion rate, as most of the other studies considered completely different experimental factors, setup, and feedstock.

3.1.2. OPTIMIZATION

The mathematical optimum values obtained by finding the extremum points on the calculated mathematical model were $X_1 = 1.74$ (% catalyst), $X_2 = 2.98$ (v/w methanol per seed mass), $X_3 = 43$ (min), and $X_4 = 58.1$ (°C). Since one of the main points of this study is to minimize the reaction time, a shorter reaction time of 20 minutes was chosen and fed to the mathematical model to

find the theoretical yield and conversion. The result was very close to 43 minutes, thus, the experiment was repeated at the optimum point with 20 minutes and 43 minutes reaction time to ensure the validity of the model. Even though a lower product yield was expected at a shorter reaction time, 89.19% yield was obtained with more than 95% conversion rate. This shows that the experimental production yield at 20 minutes was not only higher than that for 43 minutes, but the energy used at 43 minutes increased by 36 W (corresponding to 49680 J). This conflict could be attributed to the reliability of the model in prediction as there is always a margin of error for each mathematical model, as well as the reverse transesterification reaction from 20 to 43 minutes. Another possibility could be due to the soap formation as a result of longer extraction time, leading to higher water extracted from the biomass matrix (Eevera et al., 2009).

3.2. Parametric Study of Reaction Factors on Product Yield and Reaction Conversion

The results of main effect plots for each factor affecting the product yield and reaction conversion, as well as the significant interaction effect of factors on product yield in the form of 3D surface curves, were shown in Figures 1 and 2.

As catalyst concentration increases, the product yield starts to improve (very slightly by almost 2%) until it reaches a maximum. However, overloading the system with catalyst decreases product yield (final product weight). According to Figure 1, there is no negative for reaction conversion in correspondence to the catalyst concentration, as increasing the catalyst amount would improve the reaction conversion. In the case of product yield, catalyst concentration can worsen the soap formation and convert some of the extracted oil to the un-

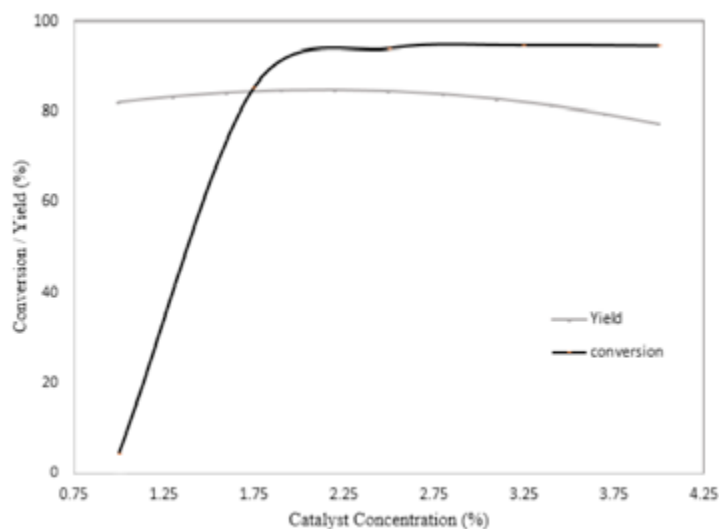


Figure 1) Catalyst concentration main effect plots of reaction conversion and product yield

desired products. This is due to the fact that water moisture in the biomass can significantly reduce the effectiveness of catalyst by saponification (Canakci & Van Gerpen, 1999). Saponification is the dominant side reaction in biodiesel production using sodium hydroxide. The water molecules in the solution can be substituted by the methyl groups and form a water-soluble ester chain (soap), which would remain in the aqueous solution and consequently lower the product yield (Komers et al., 2002).

The same behaviour for effect of solvent ratio, reaction time, and temperature was observed as they all initially improved the product yield. By increasing them to higher values, however, they applied a negative effect. In the case of methanol ratio, it can be seen that a higher amount of methanol than the optimum point would result in higher microwave absorption and therefore, limit the extraction process. Methanol, due to

its high polarity (large dielectric constant), is an effective solvent in terms of microwave radiation absorption. The other possible reason is the lesser hexane (co-solvent) and sodium hydroxide (catalyst) contact with the biomass and extracted oil as a result of higher methanol amount in the solution. This can reduce the extraction process to some extent.

As shown in Figure 2b, reaction time does not significantly affect the production yield. According to our previous work on CTT seed oil extraction only, microwave exposure can effectively decrease the extraction time to as little as 20 minutes (Boldor et al., 2010). Thus, due to such an improvement in extraction and, consequently, transesterification, there is no need for a longer reaction time than 20 minutes. In other words, the efficiency of the system in terms of time is considerably high.

Similar to trends observed with reaction time, the variation of product yield with reaction temperature was not significant as they varied only between 81.5% and 84.5%. The role of temperature is much more crucial in working with microwaves. On one hand, increasing the temperature would apply more power and irradiation to the biomass, which increases the extraction. On the other hand, not only does it increase the solvent evaporation, but it also favors the saponification reaction. Therefore, these three phenomenon would cancel each other's effects and result in insignificant effects of higher temperature.

Figure 3 demonstrates the interactive effects of catalyst concentration and reaction time on product yield. By gradually increasing catalyst concentration, maximum product yield of the reaction started to move toward lower reaction time. This could be due to the higher catalyst concentration effect on

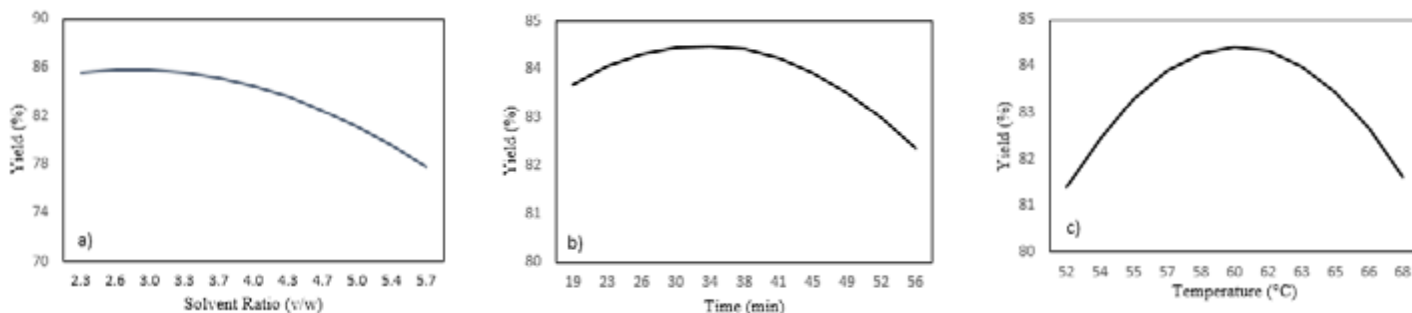


Figure 2) Product yields as mainly affected by a) Solvent ratio; b) Reaction time; and c) Reaction temperature

reaction kinetics of both saponification and transesterification. At lower temperatures, the product yield decreases with reaction time as expected (under the used reaction conditions). As the temperature increased, the yield increased to an optimum value then decreased again at temperatures above the boiling points of the methanol and cosolvent, presumably due to reduced contact with the biomass resulting from evaporation and soap formation elevation as earlier described. The same behavior was observed for palm oil transesterification (Abdullah et al., 2009). Even though it is contrary to the fact that higher temperatures favor saponification reaction velocity (higher

temperature increases saponification so that product yield must decrease by increasing time and temperature), in this case, the negative effect of evaporation on solvent and cosolvent contact with a biomass is dominant and slows down the extraction and esterification.

3.3. FATTY ACID METHYL ESTERS COMPOSITION AND BIODIESEL PROPERTIES

The principal fatty acid methyl esters (FAME) composition for CTT oil by in situ transesterification using microwaves presented in Table 3 shows that palmitic and

linoleic acids are the major components – as expected – from waxy layer and kernel, respectively, which is similar to our earlier study (Picou & Boldor, 2012). The properties of FAME produced at optimum operating reaction conditions (1.74 wt.% catalyst, 2.98:1 methanol to seed ratio, 20 and 43 minute reaction time, and 58.1°C temperature) indicate that biodiesel produced by in situ transesterification of Chinese tallow tree seeds met the ASTM standard specification for biodiesel fuel (Table 4).

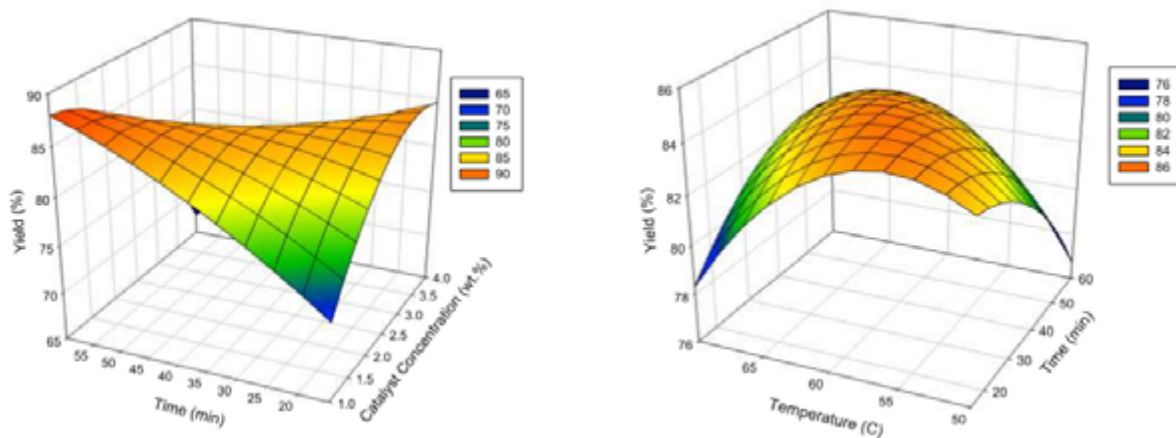


Figure 3a) Surface plots of the product yield as affected by reaction time and catalyst concentration 3b) the product yield as affected by reaction time and temperature

3.4. EFFECT OF OPERATION TEMPERATURE ON YIELD AND CONVERSION IN THE CONTINUOUS SYSTEM

The results of the production yield (in percentage of maximum achievable) and the reaction conversion with error bars are

presented in Figure 4. The results show that using a CSTR in the current study improved the production of biodiesel with the same conversion rates and yields in a continuous mode with lower amount of alcohol and catalyst. A dramatic increase in the reaction conversion was observed as it reached

above 88% in only two minutes. The trend on these two graphs indicates a significantly higher pace of transesterification reaction in comparison to oil extraction from biomass matrix. Therefore, extraction is the rate-limiting step in this process. Similar high-conversion-rate results of 99.93% after

Table 3 Fatty acid composition of Chinese Tallow Tree seeds

Methyl Esters	Fatty acid	Molecular formula	Composition (%)
Methyl butyrate	Butyric acid	C4H8O2	0.001
Methyl hexanoate	Hexanoic acid	C6H12O2	0.002
Methyl octanoate	Caprylic acid	C8H16O2	0.005
Methyl decanoate	Decanoic acid	C10H20O2	0.001
Methyl tetradecanoate	Myristic acid	C14H28O2	0.005
Methyl pentadecanoate	Pentadecanoic acid	C15H30O2	0.002
Methyl cis-9-hexadecenoate	Palmitoleic acid	C16H30O2	0.01
Methyl hexadecanoate	Palmitic acid	C16H32O2	55.789
Methyl cis,cis,cis-9,12,15-octadecatrienoate	Linolenic acid	C18H30O2	28.553
Methyl cis,cis-9,12-octadecadienoate	Linoleic acid	C18H32O2	9.135
Methyl cis-9-octadecenoate	Oleic acid	C18H34O2	5.923
Methyl octadecanoate	Stearic acid	C18H36O2	0.547
Methyl cis-11-eicosenoate	11-Eicosenoic acid	C20H38O2	0.028

Table 4 Properties of fatty acid methyl esters from in situ transesterification of CTT seeds

Property	Units	FAME value		Required by ASTM
		CCT at 20 min	CTT at 43 min	
Kinetic viscosity at 40°C	mm ² s ⁻¹	2.02 ± 0.004	1.72 ± 0.001	D 445 (1.9 – 6.0)
Density at 40°C	g cm ⁻³	0.88 ± 0.001	0.87 ± 0.001	0.850–0.890
Acid value	mgKOH g ⁻¹	0.34±0.006	0.34±0.008	D 664 (Max. 0.5)
Cetane number	---	62.73 ± 0.001	62.75 ± 0.002	D 613 (47 minimum)
Water content	Wt.%	0.06 ± 0.001	0.14 ± 0.002	D 2709 (0.050%)
Cloud point	°C	8-9	9-10	D6751 (-3 – 12)
Pour point	°C	2	2	D6751 (-15 – 10)

one-minute residence time with 0.18 wt.% catalyst concentration for transesterification of soybean oil with ethanol was reported by our previous study.

Due to the different operational conditions and feedstock used in this method, it is difficult to conduct a comparison with other studies. However, the obtained results indicate the efficiency of employing CSTR in terms of energy consumption, as the operational temperature is considerably low. The increasing trend on both graphs indicates that both oil extraction and

transesterification reaction are happening not only during the microwave-exposure period but also while they are under continuous mixing in the CSTR. The new feedstock entering CSTR is carrying heat energy, and therefore, both extraction and reaction are taking place even after microwave exposure.

3.5. TRANSESTERIFICATION KINETIC MODEL

The experimental data of FAME production yield were fitted to the obtained kinetic

model for all of the tested temperatures. The reaction rate constants were calculated and presented in Table 5. The model appropriately fits with all of the experimental data with high accuracy for all temperatures. The correlation shows a first-order reaction kinetic for the system, as well as a linear relationship between the reaction rate and production yield of methyl esters.

The Arrhenius equation was used to calculate the activation energy for the reaction to take place. The activation energy and pre-exponential factor were found to be 2,057.382 J·mol⁻¹ and 5.47 min⁻¹, respec-

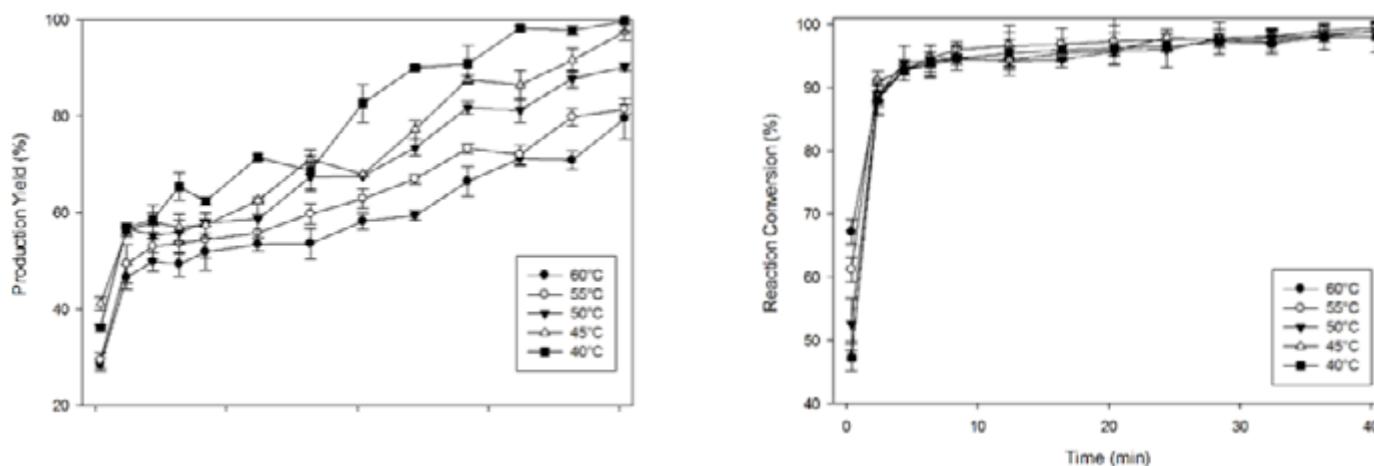


Figure 4) Rate of change in production yield and reaction conversion at all operating temperatures

tively. The activation energy value is lower than those published in literature, while the pre-exponential factor, indicating the degree of molecular agitation, is much higher. The efficiency of microwaves for providing heat to the system can be defined in the lower activation energy calculated for this study. The physical explanation for the efficiency of microwaves is the dipolar rotation and ionic movement. Both of these phenomenon are the effects of microwave irradiation, representing the higher probability of molecular collisions in the system.

CONCLUSIONS

For both batch and continuous microwave-assisted extraction and transesterification of Chinese tallow seeds, microwaves showed higher efficiency compared to the other methods. The microwave in situ transesterification process, followed by a fully isolated CSTR, proved to be an efficient and economical method to produce biodiesel compared to the conventional path. The single-step extractive transesterification process has the potential to be used for

biodiesel production from inedible biomass if the optimal conditions for lowering the soap formation and maximizing oil extraction applied. The first-order kinetic model was a good fit for the overall simplified in situ transesterification reaction. Based on these results, further research studies could focus on the process scale-up for pilot scale and commercialization.

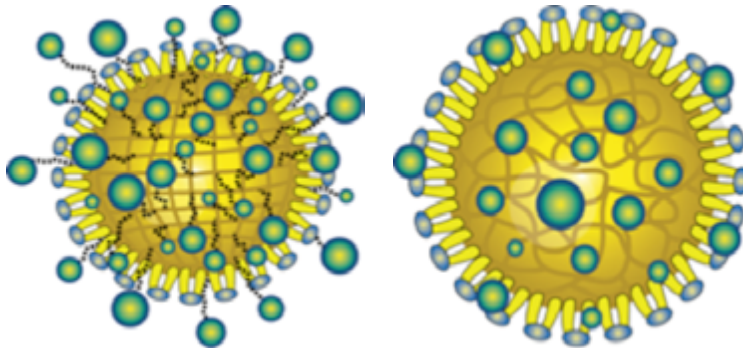
Table 5 Kinetic reaction rate constant and regression coefficient

Temperature (°C)	Rate Constant (min ⁻¹)	Regression Coefficient
60	0.0846	0.9079
55	0.0839	0.9254
50	0.0824	0.9269
45	0.0816	0.9169
40	0.0809	0.9221

REFERENCES

- Abdullah, A.Z., Razali, N., Lee, K.T. 2009. Optimization of mesoporous K/SBA-15 catalyzed transesterification of palm oil using response surface methodology. *Fuel Processing Technology*, 90, 958-964.
- Balasubramanian, S., Allen, J.D., Kanitkar, A., Boldor, D. 2011. Oil extraction from *Scenedesmus obliquus* using a continuous microwave system - design, optimization, and quality characterization. *Bioresource Technology*, 102, 3396-3403.
- Boldor, D., Kanitkar, A., Terigar, B.G., Leonardi, C., Lima, M., Breitenbeck, G.A. 2010. Microwave Assisted Extraction of Biodiesel Feedstock from the Seeds of Invasive Chinese Tallow Tree. *Environmental Science & Technology*, 44, 4019-4025.
- Canakci, M., Van Gerpen, J. 1999. Biodiesel production via acid catalysis. *Transactions of the American Society of Agricultural Engineers*, 42, 1203-1210.
- Demirbas, A. 2005. Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods. *Progress in Energy and Combustion Science*, 31, 466-487.
- Dincer, I. 2000. Renewable energy and sustainable development: a crucial review. *Renewable and Sustainable Energy Reviews*, 4, 157-175.
- Eevera, T., Rajendran, K., Saradha, S. 2009. Biodiesel production process optimization and characterization to assess the suitability of the product for varied environmental conditions. *Renewable Energy*, 34, 762-765.
- Endalew, A.K., Kiros, Y., Zanzi, R. 2011. Heterogeneous catalysis for biodiesel production from *Jatropha curcas* oil (JCO). *Energy*, 36, 2693-2700.
- Fukuda, H., Kondo, A., Noda, H. 2001. Biodiesel fuel production by transesterification of oils. *Journal of Bioscience and Bioengineering*, 92, 405-416.
- Koizumi, T. 2015. Biofuels and food security. *Renewable and Sustainable Energy Reviews*, 52, 829-841.
- Komers, K., Skopal, F., Stloukal, R., Machek, J. 2002. Kinetics and mechanism of the KOH - catalyzed methanolysis of rapeseed oil for biodiesel production.
- Ma, F., Hanna, M.A. 1999. Biodiesel production: a review. *Bioresource Technology*, 70, 1-15.
- Maçaira, J., Santana, A., Recasens, F., Angeles Larrayoz, M. 2011. Biodiesel production using supercritical methanol/carbon dioxide mixtures in a continuous reactor. *Fuel*, 90, 2280-2288.
- Panwar, N.L., Kaushik, S.C., Kothari, S. 2011. Role of renewable energy sources in environmental protection: A review. *Renewable and Sustainable Energy Reviews*, 15, 1513-1524.
- Picou, L., Boldor, D. 2012. Thermophysical Characterization of the Seeds of Invasive Chinese Tallow Tree: Importance for Biofuel Production. *Environmental Science & Technology*, 46, 11435-11442.
- Quinn, J.C., Davis, R. 2015. The potentials and challenges of algae based biofuels: A review of the techno-economic, life cycle, and resource assessment modeling. *Bioresource Technology*, 184, 444-452.
- Schuchardt, U., Sercheli, R., Vargas, R.M. 1998. Transesterification of vegetable oils: a review. *Journal of the Brazilian Chemical Society*, 9, 199-210.
- Su, Y., Zhang, P., Su, Y. 2015. An overview of biofuels policies and industrialization in the major biofuel producing countries. *Renewable and Sustainable Energy Reviews*, 50, 991-1003.
- Suganya, T., Kasirajan, R., Renganathan, S. 2014. Ultrasound-enhanced rapid in situ transesterification of marine macroalgae *Enteromorpha compressa* for biodiesel production. *Bioresource Technology*, 156, 283-290.
- Terigar, B.G., Balasubramanian, S., Boldor, D. 2010. Effect of Storage Conditions on the Oil Quality of Chinese Tallow Tree Seeds. *Journal of the American Oil Chemists Society*, 87, 573-582.
- Wang, X., Liu, X., Zhao, C., Ding, Y., Xu, P. 2011. Biodiesel production in packed-bed reactors using lipase-nanoparticle biocomposite. *Bioresource Technology*, 102, 6352-6355.
- Wen, D., Jiang, H., Zhang, K. 2009. Supercritical fluids technology for clean biofuel production. *Progress in Natural Science*, 19, 273-284.
- Yan, S., DiMaggio, C., Mohan, S., Kim, M., Salley, S., Ng, K.Y.S. 2010. Advancements in Heterogeneous Catalysis for Biodiesel Synthesis. *Topics in Catalysis*, 53, 721-736.

New Class of Biobased Materials Emerging from Ag-Science Collaboration



Biodegradable polymeric nanoparticles with lignin beads attached to the surface (left) or entrapped (right). The nanoparticles can be customized to deliver molecules, like medications, into targeted cells or tissues. Source: LSU AgCenter.

Tailgating at football games is an important pastime in Louisiana. Barbecues, smokers, and boiling pots are brought to campuses where sausage, gumbo, seafood, and meats are carefully prepared for hungry fans. Can you smell it already? That delicious aroma and taste found in smoked foods is due to science! When the pit master throws hardwood into the smoker, the heat breaks down the lignin in the hardwood plant tissues, creating aromatic smoke that flavors the food.

Beyond barbecue, lignin is a low-value byproduct used by industry mostly as a source of biomass for burning. The other two major components of plant tissues, cellulose and hemicellulose, are converted into paper products, sugars, and fuels like ethanol.

However, the lowly lignin is about to get a new use. Researchers are investigating its chemistry in order to create an entirely new class of industrial and biomedical material from this renewable resource. This new class of materials would bring a huge boost to biological industries, as well as generate highly skilled jobs and training for young Louisiana students and researchers.

In the long term, the development of materials with a renewable resource such as lignin can positively impact the environment by gradually moving away from a fossil fuel-based industry to an industry based on green technologies.

The lignin research team – led by Dr. Dorin Boldor, Charles P. Siess Jr. LSU Professor of Engineering in the Department of Biological

and Agricultural Engineering – is a collaboration of researchers from three institutions: LSU, the LSU AgCenter, and the University of Kentucky.

The National Science Foundation (NSF) recently selected the team for a \$4 million Research Infrastructure Improvement Track-2: Focused EPSCoR Collaboration (RII Track-2 FEC) award. These awards focus on “innovative science and engineering pathways to produce new knowledge and novel technologies to solve the challenges of scarcity and variability at the intersection of food, energy, and water systems.”

“We are looking to add value to lignin, an otherwise low-value product, and at the same time, help young researchers pursue research avenues that will place them at the forefront of their field in the biobased economy,” Boldor said.

The team is researching the deconstruction and reconstruction process of lignin at the molecular level so new materials can be created out of its building blocks. The deconstruction process is very challenging because a high level of precision is needed to break down the lignin into the exact size and compounds needed for the rebuilding process, else it would break up into individual atoms.

Once it is deconstructed into lignin monomers, novel chemical processes are used to reconstruct the lignin building blocks into a new class of materials, dubbed “lignin beads.” The researchers are investigating several new medical and industrial applications for these beads.

“The possibilities are vast for these new materials. The impact of this EPSCoR project can be felt in areas ranging from an improved delivery mechanism for bioactive and potential drug compounds through food, development of improved methods for water treatment and purification, and improved separation processes for chemical industries that reduce energy consumption.”

- Dr. Dorin Boldor, LSU AgCenter

One new medical application with enormous potential is a new kind of antimicrobial. Research has shown that some bacterial cell processes are disrupted by specific compounds in lignin beads. The team intends to investigate all of the effects that these beads have on biological cells and tissue. The future holds the possibility of designing an antimicrobial product that targets dangerous bacteria or cancer cells.

Another medical application being researched is the assembly of nanoparticles.

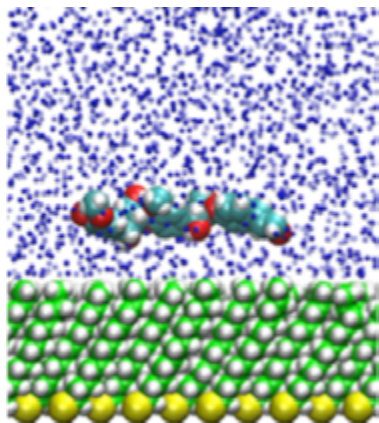


Image from a supercomputer simulation of the molecular behavior changes that occur when a lignin bead (light blue/red) in a solvent solution (dark blue specks) nears a surface (green). Source: LSU AgCenter and Dr. Dorel Moldovan, LSU.

We can make nanoparticles directly out of these structures or attach lignin beads to other nanoparticles,” Boldor said.

Dr. Cristina Sabliov, also with the Department of Biological and Agricultural Engineering, is developing biodegradable polymeric nanoparticles (see front page illustration) that can be customized to hold medication molecules targeted to certain areas of the body. The product is swallowed by the patient and remains intact until it reaches the targeted tissues, like the stomach or intestines, and then the medication is released from the nanoparticle exactly where it is needed.

Still another application is in industrial products, such as thin films and membranes, which are actively being researched for use in water purification and other separation processes. Thin films separate compounds by attracting targeted molecules to the surface and keeping them there until they are ready to be released. Membranes are used to separate chemical or biological compounds by passing them through pores.

Several industry partners are already on board, including the Louisiana Forestry Association, the Louisiana Chemical Manufacturing Initiative, and the Kentucky Association of Manufacturers.

Due to the complexity and molecular scale of these tiny building blocks, the team assembled for this research is quite interdisciplinary, including scientists in computer science, chemistry, biology, and five engineering thrusts – agricultural, chemical, industrial, mechanical, and biological.

The team is composed of Boldor (principal investigator), Dr. Dorel Moldovan (co-PI, LSU College of Engineering), Sabliov (co-PI, LSU AgCenter), Dr. Sue Nokes (Lead co-PI, University of Kentucky), and Dr. Bert Lynn (co-PI, University of Kentucky). Senior collaborators include Dr. Carlos Astete and Dr. Pranjali Muley (LSU AgCenter); Dr. Lavrent Khachatryan, Dr. Elizabeth Martin, and Dr. Jangwook Jung (LSU); and Dr. Jian Shi, Dr. Stephen Rankin, and Dr. Barbara Knutson (University of Kentucky).



Dr. Dorin Boldor, LSU AgCenter

Alumni Spotlight - Tyler Ortego



Tyler Ortego is a coastal engineer and avid entrepreneur with a passion for commercializing promising technologies in the public sector. He uses his prior experience as a water resources engineering consultant to identify opportunities, navigate red tape, and get proprietary products specified into public sector contracts.

He is a graduate of LSU Engineering, holding both a BS ('04) and MS ('06) in biological engineering, and his academic training focused on biological processes, wetland science, and coastal engineering. His research focused on oyster growth and mechanical properties of biologically enhanced concrete for use in shoreline protection structures.

Ortego started his career at a consulting firm in Baton Rouge, Louisiana, supporting subdivisions and commercial development. He then moved to Houma, Louisiana, where he worked on several large wetland restoration, flood protection, and related mitigation projects.

He is one of the inventors of the OysterBreak and OysterKrete technologies and the founder and supervising professional of ORA Estuaries. He has experience in all stages of implementing large-scale, high-profile coastal protection and restoration projects. Key projects at ORA Estuaries include large-scale oyster sampling, living shorelines design, and assessment of ecosystem functions of natural reefs. Ortego is also certified as an oyster biologist with the Louisiana Oyster Lease Damage Evaluation Board.

Electromagnetic Heating for Lignocellulosic Biomass Conversion to Liquid Fuels

Dideolu J. Daniel* and Dorin Boldor^

^corresponding author – Dorin Boldor, Charles P. Siess Professor of Engineering, LSU Department of Biological and Agricultural Engineering

*Dideolu J. Daniel, graduate student, Department of Biological and Agricultural Engineering

INTRODUCTION

The need for liquid fuels produced at a sustainable rate not only requires that we harness cheap and quality starting biomaterials, it also calls for conversion methods which will require minimum energy input and guarantee a high return on limited resources. Pyrolysis, a thermochemical conversion technique, involves the heating of biomass at temperatures ranging from 300 to 7000C within a residence time of less than two seconds at atmospheric pressure. Bio-oils obtained via this method are coke neutral, have low sulfur and nitrogen content, and are readily converted to liq-

uid fuels without incurring the capital of a high-pressure system.¹ In addition to the liquid biofuel fraction, a solid biochar and gasses are also obtained, which can be used for various industrial, processing, and agricultural applications.

In several investigative studies, researchers in BAE designed a novel electromagnetic heating mechanism for running pyrolysis experiments using several biomasses, including lignocellulosic biomass energy cane (*Saccharium complex*) bagasse, invasive Chinese tallow trees (*Triadica sebifera* L.), pine sawdust, lignin, and cellulose.

The pyrolysis system used consisted of a low-frequency induction heater that heated a stainless steel tube which held the biomass. The biomass was compactly packed within the tube, and an auger was sometimes used to mix the reactor. Nitrogen gas was used both to purge the oxygen from the system prior to pyrolysis and as a carrier gas to move the pyrolysis vapors out of the reactor into the collection system to be condensed and collected. The condensate was collected into the collection flask placed in an ice bath (Figure 1).

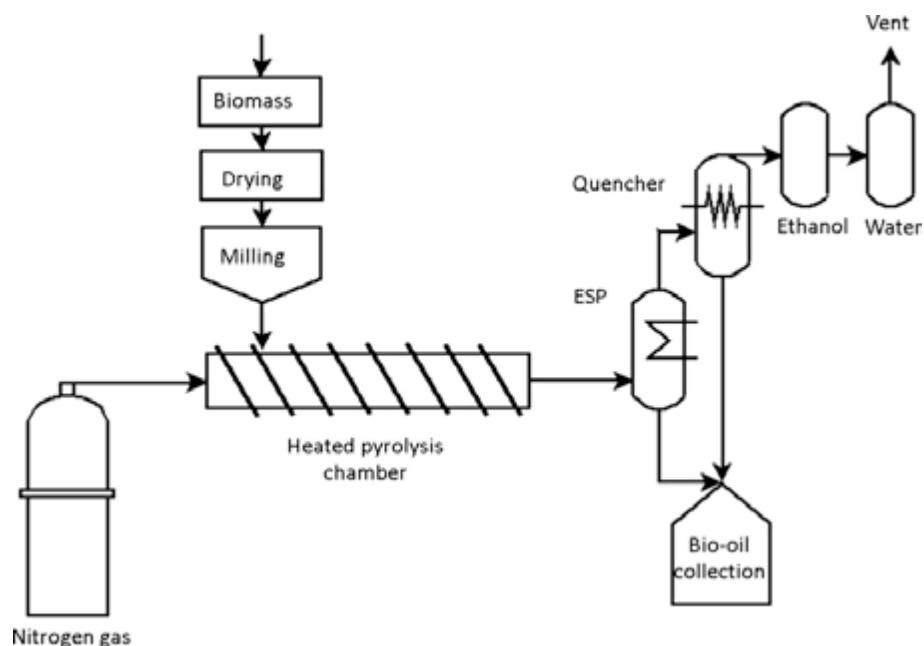


Figure 1. Flowchart for pyrolysis upgrading in an induction heater (from Henkel et al., 2016, permission from publisher requested).

The induction heating mechanism ensured rapid heating rates with the ability to maintain uniform temperatures during experimental runs. The researchers recorded the highest biofuel yield at 500°C for both biomasses and noted that at higher temperatures the higher decomposition rate of the biomass resulted in the reduction in more gases and char yields. Taking this a step further, the investigators hypothesized that the type and particle size ranges might play a key role in the quality of bio-oil obtained after pyrolysis, particularly for energy cane bagasse (*Saccharum complex*) and Chinese tallow tree (*Triadica sebifera* L.) biomass.² Pulp, paper, and forest companies in the United States use more than 36% of the total annual timber harvest as source for raw materials and in the process, generate large amounts of lignin as byproducts.³ Companies using wood pulp from trees and processes that generate cellulosic bioethanol (including sugar mills) produce large quantities of lignin. Thus, lignin is a readily available feedstock that can be used for biofuel production.

When biomass material undergoes pyrolysis, the resulting biofuel is comprised of a mixture of complex organic molecules, such as phenols and furans, due to the breaking down of cellulose, hemicellulose, and lignin during pyrolysis. Under fast pyrolysis conditions, the resulting bio-oil is high in oxygen content. The high oxygen content makes the oil less energy-dense and more prone to degradation reactions, thus making it uncompetitive with hydrocarbons derived from conventional petroleum.

To reduce the oxygen content of bio-oils, various catalysts were used to enhance pyrolysis vapors (prior to being condensed into the liquid) via an upgrading process. The challenge with performing in situ catalysis is that for maximum oil yields, pyrolysis starts to be more efficient at temperatures more than 500°C, at which a catalytic process loses significant amount of liquid due to cracking and decomposition into non-condensable gases. On the other hand, contraire to in situ catalytic upgrading, ex situ catalytic upgrading of biomass has been

proven to increase the yield and rate of deoxygenation at lower temperatures (below 400°C) that prevent liquid losses to cracking and other decomposition reactions. In this research, an ex situ microwave-assisted catalytic upgrading process was developed to improve the biofuel quality and increase the catalyst longevity. Investigations into the fundamental catalytic requirements for deoxygenation of pyrolysis vapors and the role of microwaves in catalyst activity and heating efficiency were undertaken.

PROCEDURES AND RESULTS

The type of feedstock fed into the biomass system needs to be prepared in suitable ration in order to guarantee a high level of output. Other factors which affect the rate of pyrolysis are the pyrolysis temperature, efficiency of the reactor, chemical makeup of the biomass, starting moisture content, and the particle size of the biomass. While most of these have been extensively investigated by researchers with a view to produce efficient biofuels, little attention has

been paid to the particle size ranges of the biomass. To address these oversights, BAE researchers have arrived at an optimum particle size range that not only produces low-water biofuels but also improves the efficiency of its production. By varying the particle size during pyrolysis, the resulting biomasses were low in water content with optimum results being obtained at a particle size range of 0.5 to 1.4 mm.

To study the effects of temperature on product yields and quality for lignin and cellulose components during pyrolysis, researchers have attempted to quantify the contribution of each component on the yield and bio-oil composition. In comparison research led by Dr. Pranjali Muley – in conjunction with Dorin Boldor, Charles P. Siess Jr. Professor of Engineering at LSU – pinewood sawdust was heated to high temperatures ranging from 500 to 7000C using a lab-scale induction heating reactor.⁴ Using this approach, they could examine the water content, chemical composition, and energy content of products obtained at the temperatures using an induction heating reactor. Further, they investigated the catalytic upgrading and pyrolysis of pinewood sawdust using an induction heating reactor and a microwave reactor at temperatures of 290, 330, and 370°C.

In a summary of procedures, pyrolysis of biomass was carried out in an induction heater, and the exiting bio-oil vapors were upgraded by passing them through a catalyst bed heated using either a microwave reactor or a second induction heater. Traditional- and induction-heated catalyst bed processes were compared with various performance indices of the microwave process in terms of yield, catalyst efficiency, and quality of produced bio-oil.

PYROLYSIS RESULTS

By calculating the product yield, we discovered that within the energy cane biomass, the oil yield slightly increased, with particle size ranging from less than 0.5 mm to 0.5 – 1.4 mm, while gas and char yields decreased. Furthermore, an increase in particle size did not produce a corresponding change in the bio-yield. In fact, the highest yield recorded was 48% for particle size range less than 1.4 mm. For the Chinese tallow tree biomass, yield of bio-oil at the smallest particle size was just 25%, as compared to a 44% for energy cane.

Compared with traditionally heated catalyst bed reactors, higher-quality bio-oil was obtained with the induction heating reactor, producing an increased yield of aromatic hydrocarbons and reduced oxygen content. Coke deposition was also reduced for the induction heating reactor, with high-energy efficiency reaching 85%. As temperatures increased from 5000C to 7000C, the char yield for each biomass decreased. However, the temperature change caused only a minor decrease in cellulose char yields compared to the other two biomasses.

A suitable explanation for this is that cellulose is more thoroughly broken down at lower reaction temperatures than lignin and sawdust. The high char yield recorded was due to the superior thermal stability provided by the complex molecular structure of lignin and its higher fixed carbon content. On the other hand, cellulose has a simpler molecular structure, thus making it easier to be broken down during pyrolysis at lower temperatures.

As for the liquid yield, it decreases with temperature increase, with a higher minimum for cellulose than for lignin at 7000C. The highest liquid yield of 55.28% was obtained from pine sawdust at 6000C. A large part of the cellulose is derived from

cellulose, since the maximum liquid yield for cellulose and lignin was 44.68% and 22%, respectively.

Analysis of the gas fractions indicated that gas yield increases with temperature increases and when taken alongside the declining biochar masses, correlated to an increase in biomass breakdown at higher temperatures. The higher heating value (HHV) of the liquid fraction from pine sawdust was the highest at 5500C. The bio-oil obtained from pine sawdust has much higher carbon content and thus, a higher heating value. Gas chromatography-mass spectrometry (GC-MS) showed that most of the liquid consisted of phenolic and oxygenated hydrocarbons. Thus, pine sawdust, lignin, energy cane, and other types of biomass proved useful as a biofuel feedstock in terms of product quality.

UPGRADING RESULTS

Microwave heating produced bio-oil with higher aromatic compounds and deposition of lower coke, an improvement over bio-oils prepared with non-upgraded methods. At the higher temperature of 3700C, we obtained deoxygenated aromatic hydrocarbons up to a 65% yield. The HHV of the bio-oil obtained from the catalytic-upgrading of the pyrolysis vapors increased with the catalyst temperature (HHV means a higher energy content per unit volume).

Heat loss resulting from heat transfer between carrier and catalyst was also reduced with the microwave heating mechanism. The amount of power input needed for catalyst bed heating was lower compared to that for the conventional and induction heating processes, which improved the process efficiency. Already, microwave processes have been scaled up in the food processing industry, and with the discovery stemming from this research, such designs can be adapted to

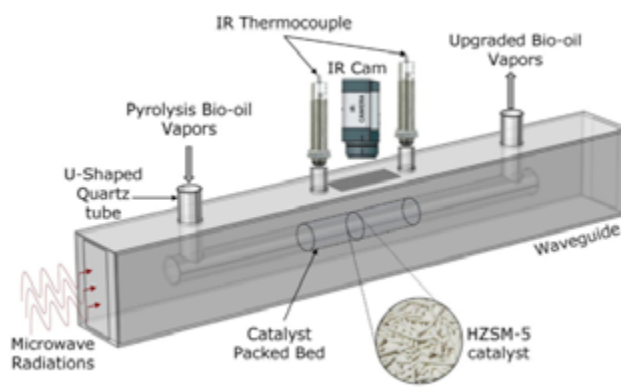


Figure 2. A travelling wave microreactor used for the thermocatalytic upgrading of biomass pyrolysis vapors (from Muley et al., 2016).

produce biofuel from renewable sources in alternative energy plants where biofuel upgrading is important.

Further works on justifying how initial moisture content and final bio-oil water content intermix could help in adapting the pyrolysis process to industrial-scale biofuel applications are underway as researchers manipulate temperature changes and different biomass materials pivotal to the success of sustainable, strong, and nimble production of renewable energy from plants.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the following LSU students, staff, and personnel that contributed to these research efforts over the last few years: Dr. Pranjali Muley, Charles Henkel, Dr. Beatrice Terigar, Akanksha Kanitkar, Nicholas Gerbo, Dr. Sundar Balasubramanian, Laura Picou Fennel, Brianna Bourgeois, Shreya Purohit, Gustavo Aguilar, Mohammad Barekati-Gourdazi, Mohamad Abu-Laban, Dr. Divine Bup Nde, Dr. Carlos Astete, Dr. Cong Chen, Dr. Deepti Salvi, James Allen, Niyaz Methrath-Liyakathali, Casey McMann, Dr. Cristina Sabliov, Jeffrey Ortego, James Palmer, Chris Arauz, Angela Singleton, Donna Elisar, Danielle Bayham.

The research summarized in this article was funded by USDA NIFA via the Hatch Program (project # LAB 94146), USDA NIFA (award# 2011-38821-30873), NSF CBET (award #1437810 and #1258821), NSF EP-SCoR (award #OIA-1632854), Louisiana Board of Regents (ITRS Program, Award No. LEQSP (2007-10)-RD-B-01), Louisiana Board of Regents Enhancement Program, the U.S. Department of Transportation (SunGrant Initiative, Award No. AB-5-61770.LSU1), and the Louisiana Soybean and Grain Research and Promotion Board. Published with the approval of the director of the Louisiana Agricultural Experiment Station as manuscript #2017-xxx-xxxx.

REFERENCES

1. McKendry P. (2002) Energy production from biomass (part 2): conversion technologies. *Bioresource Technol* 83: 47–54.
2. Urbatsch L. (2000) Chinese tallow tree (*Triadica sebifera* (L.) small plant guide. Natural Resources Conservation Service (NRCS).
3. U.S. Department of Energy (2016). 2016 Billion-Ton Report: Advancing domestic resources for a thriving bio economy, Volume 1: Economic Availability of Feedstocks (No. M.H. Langholtz, B.J. Stokes, and L. M. Eaton (Leads), ORNL/TM-2016/160). Oak Ridge National Laboratory, Oak Ridge, TN.
4. Mulley PD, Henkel C, Abdollahi KA, et al. (2016) A critical comparison of pyrolysis of

cellulose, lignin, and pine sawdust using an induction heating reactor. *Energy Conservation and Management* 117: 273-280.

5. Muley, P.D. Henkel, C.E., Aguilar, G., Klason, K.T., and D. Boldor, 2016. Ex situ thermo-catalytic upgrading of biomass pyrolysis vapors using a travelling wave microwave reactor. *Applied Energy*. 183:995-1004. Doi:10.1016/j.apenergy.2016.09.047.

6. Henkel, C., Muley, P.D., Abdollahi, K.K., Marculescu, C., and D. Boldor. 2016. Pyrolysis of Energy Cane Bagasse and Invasive Chinese tallow tree (*Triadica sebifera* L.) Biomass in an Inductively Heated Reactor. *Energy Conversion and Management*. 109:175-183. Doi: 10.1016/j.enconman.2015.12.013.

7. Aguilar, G., Muley, P.D. and D. Boldor. 2015. Effect of Biomass Particle Size on Yield and Composition of Pyrolysis Bio-Oil Derived from Chinese Tallow Tree (*Triadica sebifera* L.) and Energy Cane (*Saccharum complex*) in an Inductively Heated Reactor. *AIMS Energy*, 2015, 3(4): 838-850. doi: 10.3934/energy.2015.4.838.

8. Muley, P.D., C.E. Henkel, K.K. Abdollahi, and D. Boldor, 2015. Pyrolysis and Catalytic Upgrading of Pinewood Sawdust Using an Induction Heating Reactor. *Energy & Fuels*. 29:7375-7385. doi: 10.1021/acs.energyfuels.5b01878.

9. Fennell, L.P. and D. Boldor. 2014. Dielectric and thermal properties of sweet sorghum biomass. *Journal of Microwave Power and Electromagnetic Energy*. 48 (4), 1-11.



Biological Engineering Welcomes New Faculty

Dr. Yongchan Kwon received his PhD from the Department of Fine Chemical Engineering and Applied Chemistry at Chungnam National University in South Korea under the supervision of Professor Dong-Myung Kim. He was a postdoctoral research fellow in the Department of Chemical and Biological Engineering at Northwestern University under the direction of Professor Michael C. Jewett, and his doctoral work focused on the cell-free protein synthesis system as an alternative platform for protein production and synthetic biology applications. Dr. Kwon is interested in achieving not only high levels of enzyme production and functionality, but also establishing high-throughput screening methods. He also focused on cell-free metabolic pathway engineering for the biosynthesis of functional biomolecules, such as the heme prosthetic group. As an assistant professor, he is currently working on cell-free synthetic biology applications encompassing expanding the chemistry of life, advancing genome engineering, and standardizing cell-free systems for contributing to the synthetic biology community and production of natural products using novel cell-free systems. Dr. Kwon joined the BAE faculty in August 2017.

Dr. Jangwook “Philip” Jung received a BS in Chemical and Biological Engineering from Inha University in South Korea, an MS in Chemical Engineering from the University of Cincinnati and a PhD in Biomedical Engineering from the University of Chicago and the University of Cincinnati. Since 2010, he has served as a postdoctoral fellow at the University of Wisconsin-Madison, designing composite hydrogels for stem cell differentiation by mimicking the microenvironments of the developing hearts. Since 2013, he has worked as an AHA postdoctoral fellow and Research Associate at the University of Minnesota-Twin Cities in the areas of 3D biomaterial composites for engineering

extracellular microenvironments to direct cell behaviors. One of his main projects is to differentiate pluripotent stem cells into functional cardiomyocytes with engineered biomaterials and to identify novel mechanisms of signaling with systems biology approaches. Dr. Jung joined the BAE faculty in August 2016.

Dr. Elizabeth Martin earned her PhD in biomedical sciences from Tulane in 2013 and has a BS from LSU in 2005. Since 2013, she has worked in two postdoctoral positions at the Tulane School of Medicine – most recently in cancer research – and is continuing that work at LSU. Prior to arriving here, Dr. Martin’s work included evaluation of decellularized breast cancer extracellular matrix in the induction of tumor metastatic recurrence, determining effects of the extracellular matrix on the biologic properties of cancer cells, and evaluation of decellularized tumors as mechanisms for novel breast cancer 3D culture and use in cancer biomaterials. Her earlier work included proteomic analysis of patient serum for potential prognostic markers of heterotopic ossification, evaluation of signaling pathways involved in the formation of ectopic bone following injury in high-impact blast injuries in military personnel, and additional studies that include the evaluation of alterations in the miRNA biogenesis pathway during stem cell differentiation, with a focus on the Argonaute proteins. Dr. Martin joined the BAE faculty in August 2016.

CURRENT OFFICERS:

President

Aaron Hargrove, senior, biological engineering & mathematics secondary major

Vice President

Grace Bingham, senior, biological engineering major & biology minor

Treasurer

Emily Patterson, junior, biological engineering major & robotics engineering minor

Secretary

Calvin Rome, senior, biological engineering major

Fundraiser Chair

Mitchell St. Pierre, senior, biological engineering major & robotics engineering minor

Fundraiser Co-Chairs

Darshil Patel, junior, biological engineering pre-med
Maryn Cavalier, junior, biological engineering pre-med
Ryan Agsunod, sophomore, biological engineering pre-med

BIOLOGICAL ENGINEERING STUDENT ORGANIZATION (BESO)

Before the 2017–2018 academic year began, the Biological Engineering Student Organization's executive team spoke to incoming freshmen at the college's Encounter Engineering (E2) summer camp to promote BESO and the Department of Biological and Agricultural Engineering. Through this event, students were introduced to some of the upperclassmen in biological engineering and the unique intradepartmental dynamic between students and their peers, as well as with the faculty. Team members highlighted the closeness of the department, the academic accomplishments of students and faculty alike, as well as the opportunities that stem from the department's environment. Additionally, BESO kicked off the year with an Icebreaker Beach Party to welcome freshmen to the department and reunite with friends after the summer vacation.

BESO aims to broaden its members' knowledge of the different professional paths they may take. This semester, the group was honored to receive a presentation from Dr. Jorge Isaza from the Surgical Specialty Center in Baton Rouge about the applications of biomedical engineering in the medical field and his personal

experiences applying to and attending medical school. Much of his work involves collaboration with biological engineers in order to study the biomechanics of the vertebral column and improve upon prosthetic devices.

For students interested in attending graduate school, BESO held a video conference with Kameron Kilchrist, fifth-year PhD student, and Camryn Johnson, fourth-year PhD student, who are currently attending Vanderbilt University. As LSU BAE alumni, they were able to provide a unique perspective and advice on relevant courses, research, and internship programs to aid students applying to graduate school. Kilchrist met with students for lunch to discuss his research on investigating the mechanism of cellular uptake, intracellular trafficking, and Vanderbilt's graduate program.

Additionally, Sarah Davis and Dr. Jeffrey Gimble joined BESO to speak on their experiences in industry. Both Davis (BAE alumna), biomedical engineering consultant at DaviSolve Consulting, LLC, and Dr. Gimble, Chief Scientific Officer of LaCell, LLC, discussed job prospects in the biomedical field and provided guidance on joining the workforce.

Prior to the Thanksgiving holiday, BESO held the 36th Annual Sweet Potato & Popcorn Rice Sale. The event was organized by the group's officers and made possible by the volunteer work of both BESO officers and members. Sweet potatoes and popcorn rice were purchased from Garber Farms and sold on the corner of Highland Road and South Stadium Drive per tradition.

Next semester, BESO plans to continue inviting outstanding speakers to expand its members' understanding of the possibilities they have by obtaining a BE degree. The organization is also excited to implement a workshop that will help students with their applications for internships, graduate school, and medical school.

**Department of Biological &
Agricultural Engineering**

149 E. B. Doran Building
Baton Rouge, LA 70803

Telephone: (225) 578-3153
Fax: (225) 578-3492