

Pyrolysis of Biomass to Bio-oil in the Classroom: The fabrication and optimization of a miniaturized Biomass Conversion Module

Ms. Amber DeAnn Graviet, Washington State University

Amber Graviet is an undergraduate Chemical Engineering student at Washington State University. with a minor in Mathematics and Chemistry. Over the past year she has been working with Jacqueline Burgher, Dr. Van Wie, and Dr. Golter to create a biomass conversion module for student learning.

Jacqueline K Burgher, Washington State University

Jacqueline Burgher is a graduate student at Washington State University in the Chemical Engineering Department. She received her bachelor's degree from Anderson University, worked in industry, received an MBA from Anderson University and is currently working with Prof. Bernard J. Van Wie on fabricating, optimizing, and implementing a miniaturized gasification system for use in the engineering classroom.

Prof. Bernard J. Van Wie, Washington State University

Prof. Bernard J. Van Wie did his B.S., M.S. and Ph.D., and postdoctoral work at the University of Oklahoma where he also taught as a visiting lecturer. He has been on the Washington State University faculty for 32 years and for the past 18 years has focused on innovative pedagogy research and technical research in biotechnology. His 2007-2008 Fulbright exchange to Nigeria set the stage for him to receive the Marian Smith Award given annually to the most innovative teacher at Washington State University.

Dr. Paul B Golter, Washington State University

Paul B. Golter obtained an MS and PhD Washington State University and made the switch from Instructional Laboratory Supervisor to Post-Doctoral Research Associate on an engineering education project. His research area has been engineering education, specifically around the development and assessment of technologies to bring fluid mechanics and heat transfer laboratory experiences into the classroom.

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Abstract:

This work-in-progress paper focuses on the fabrication and optimization of a miniaturized fast pyrolysis module for hands-on learning of biomass to biofuels conversion in the classroom. Our goals are to help engineering students better understand thermochemical conversion concepts including the specific reactions in pyrolysis, the process of optimizing a system, and the constraints of a system designed for pyrolysis.

The modular design focuses on optimizing the temperature in the reactor by adjusting the energy delivered to the reactor by the resistance wire. In order to achieve pyrolysis temperatures, the length and type of the wire had to be optimized to get the reactor up to temperature. In this study we tested wires of Kanthal 145 alloy and tungsten and varied wire length for optimization. We studied different combinations of these two variables, including varying the wire length from 10 -45 cm with both types of wire. These variables changed the amount of current delivered to the system, which changed the final temperatures with each combination. Understanding the interactions between current delivery and wire type is critical for achieving reactor pyrolysis temperatures.

Temperature plots were analyzed to determine how changing wire type and wire length affect reaction rate and speed at which final temperatures are reached. Qualitative data were also collected to determine how changing the reactor wire length and wire type affected the volume of bio-oil produced. Based on the experimental design, we expected to find an optimal wire length and choose between the better wire type to achieve desired pyrolysis temperature and reaction time so that pyrolysis liquid produced is consistent with literature results where 75% of the biomass weight is converted to pyrolysis liquid with only 12% of the initial biomass weight being converted to water. This design process optimization is expected to lead to a modular system useful in the classroom for communicating reactor design principles and teaching students about optimization of a reactor system with respect to both temperatures achievable and bio-oil yield.

Introduction:

Due to stringent emission requirements the increasing amount of CO_2 emissions and of other greenhouse gases from combustion processes, technologies in renewable energies that decrease these emissions have been streamlined for implementation in industry.¹ Pyrolysis is an effective thermochemical conversion process that helps to cut down emissions while producing a source of useable fuel from renewable resources. In the process of pyrolysis, biomass is heated to 400-600°C in the absence of oxygen, to produce bio-oil.² The products formed in the process are char, oil, tar, water, and fuel gases. It is known that rapid heating yields higher volatile components and temperatures above 600°C will promote gas production.³ Fast pyrolysis, or pyrolysis that occurs in a few minutes, yields a product consisting of a mixture of polar organics (about 75±80 wt%) and water (about 20± 25 wt%) that are created from the thermochemical

break down of hemicellulose, cellulose, lignin and minor amounts of other organics within the biomass.⁴ This study focuses on the bio-oil produced in the reaction. Its composition is complex and depends on the type of biomass being used. Generally the composition of bio-oil for a wood based biomass is 45-50wt% oxygen, up to 10wt% hydroxyacetaldehyde, 5wt% acetic acid, and 3wt% formic acid.²

This experimental design is based on other research investigating different pedagogical approaches that have been implemented in STEM courses. At Washington State University the use of hands-on learning modules are being used to enhance student learning and to promote critical thinking, with outcomes showing gains in conceptual understanding that are not seen with traditional lecture-based classes.⁵ The pedagogy used in the study at Washington State University implemented miniaturized fluid mechanic modules to complete experiments reflective of concepts traditionally communicated via lecture. Ahmadu Bello University in Zaria, Nigeria also ran a study on how Desktop Modular Learning (DML) affected student learning for heat transfer concepts. It was concluded using a flashlight survey that the Desktop Modular Learning/Hands-on Learning (DML/HAL) learning helped to promote students' teamwork skills, grasping of important facts, persistence of concepts, as well as visualization of ideas, peer interaction, and curiosity. A survey consisting of 25 questions that focused on the Seven Principles of Good Undergraduate Education and placed them in a five-point Likert scale reflected the students' experiences in the classroom. The study noted, "An overwhelming 96% [of students] were of the opinion that they are better able to remember important facts, while 88% agree they have a more thorough understanding of ideas and concepts, and 94% said they are better able to visualize ideas" when using the DML/HAL system in the classroom.⁶ It has also been shown that research based lectures have made more of an impact than traditional lecture to improve students' conceptual understanding, engagement, and retention in physics based programs.⁷

Based on what is known about active learning, discovering where a pyrolysis unit could fit into existing curriculum to communicate heat transfer would be an appropriate area to investigate. By building a module of pyrolysis, students will have the opportunity to do hands-on experiments that focus on concepts taught within thermodynamics, biological processing, and transport phenomena/heat transfer. Certain parameters on the module can be manipulated, which allow students to optimize the amount of bio-oil produced by changing either the wire length or voltage. This will allow the class to include both hands-on learning as well as traditional lecture, and should help to eliminate social exclusion, improve the quality of learning, and create an environment of equal opportunity for different type of learners within the classroom.⁸.

This work in progress paper focuses on the optimization of a pyrolysis module to be implemented within the classroom. To create the module, we divided the optimization into two experiments with each experiment focusing on different concepts to communicate to students biomass conversion. The first experiment involves selecting a wire that can reach a temperature range of 200 °C – 400°C without breaking or oxidizing. We tested various wire lengths and voltages with two wires, tungsten and Kanthal 145 alloy consisting of 0-0.08% C, 0-.7% Si, 20.5-23.5% Cr, 5.3% Al, and 69.02-73.2% Fe .⁹ Kanthal 145 alloy is a material that is used as a

heating element within small appliances, such as toasters, and in industrial furnaces, while Tungsten is commonly used within light bulbs. The second experiment involved tests to optimize the wire length and to reach the highest maximum pyrolysis temperature between the range of 200-800 °C, the low and medium temperature range of pyrolysis.

Experiment One:

Methods:

The first part of the modular design focuses on determining the type of resistance wire that should be used as a heating element in the system to achieve desired pyrolysis temperatures. To keep the module simple and straightforward for student use, computer paper was used as the biomass. This choice was made because paper is a ubiquitous biomass source and because the majority of students know paper is made of trees. Prior to the biomass being placed into the reactor, the biomass was mashed with DI water to create a paste and then dried for 24 hours at 120°F to remove moisture. The biomass was then inserted into a 10-cm length 3-mm outer diameter, 1-mm inner diameter quartz reaction tube. A type K probe thermocouple was attached to the outside of the reactor to collect the temperatures at 1-second intervals during each trial of the experiments. Figures 1 and 2 show the experimental setup both in the hood and as a diagram for the pyrolysis module that can be replicated as a hands-on activity.



Figure 1: The physical experimental setup within the lab



Figure 2: A pictorial diagram outlining the experimental setup.

To determine which wire to use in Experiment 2, we performed a series of qualitative experiments comparing the Kanthal 145 alloy and Tungsten wires by observing the durability and oxidation of the wire under different voltages and wire lengths. These experiments occurred in air and were not placed in a vacuum environment, which led Tungsten to shorten its lifetime as a heating element. A wire in this experiment was classified as durable when it did not show signs of oxidation or did not break. The wire was considered oxidized if discoloration occurred during the trial. Different experiments were conducted with both types of wire, which included varying the wire length from 10-45 cm and changing the initial voltage at the start of the experiment with 10 V and increasing by an increment of about 1.3 V with each additional experiment up to 18.5V. The wires were treated differently as noted in table 2 and 3 because Tungsten has a larger voltage drop, meaning that the input voltage into the system was not the same as the output. This required the Tungsten wire to undergo more trials to help understand the range of the voltage drop and how it affected the temperature achieved using the given wire. Both the input voltage and the wire length changed the amount of current delivered to the system which in turn affected the final temperature in the reactor. The relationship between wire length, voltage, resistance and are shown in Equations 1 and 2^{10}

$$V = IR \tag{1}$$

where: V = voltage;

$$I = current;$$

and R = resistance.

$$R = \frac{\rho L}{A} \tag{2}$$

where: ρ = resistivity;

L = length of wire;

and A = area.

The resistivity for Tungsten and the Kanthal 145 alloy wire is a measured value that quantifies the amount that a material resists the flow of electric current. Table 1 lists the resistivity for Tungsten and Kanthal 145 alloy at room temperature (ρ_0).

Table 1: The Resistivity of Tungsten and Kanthal 145 alloy at 20°C.

Resistivity for Tungsten and Kanthal at 20°C (n Ω m)		
Tungsten	50	
Kanthal	145	

Table 2 and 3 shows the experimental design for testing the two types of wire and the conditions including wire length and voltage for these runs.

Tungsten			
Wire Length (m)	Initial Voltage (V)	Output Voltage (V)	
0.305	4.7	4.7	
0.305	4.7	4.1	
0.305	9.3	4.1	
0.305	9.3	4.5	
0.305	14	4.1	
0.305	14	3.6	
0.305	18.6	3.5	
0.305	18.6	3.9	
0.25	18.6	2.2	
0.25	16.1	2.1	
0.25	15.4	2	
0.25	13.2	2	
0.25	12.1	2	
0.25	10.8	1.8	
0.25	9.5	1.9	
0.25	8.1	2	
0.25	6.5	1.9	
0.25	4.5	2.1	
0.25	2.5	2	
0.1	18.6	1.2	
0.1	16.1	1.2	
0.1	15.4	1.2	
0.1	13.2	1.4	
0.1	12.1	1.5	
0.1	10.8	1.5	
0.1	9.5	1.6	
0.1	8.1	1.5	
0.1	6.5	1.5	
0.1	4.5	1.6	
0.1	2.5	1.8	
0.05	18.6	1.1	
0.05	16.1	1.2	
0.05	15.4	0.7	
0.05	13.2	0.9	
0.05	12.1	0.8	
0.05	10.8	0.7	
0.05	9.5	1.1	
0.05	8.1	1.2	
0.05	6.5	1.4	
0.05	4.5	1.8	
0.05	2.5	13	

Table 2: Tungsten Testing Parameters for Experiment 1

	Kanthal				
Wire Length (m)	Initial Voltage (V)	Output Voltage (V)			
0.095	14	14			
0.2	18.5	18.5			
0.2	14	14			
0.25	14	14			
0.35	18.5	18.5			
0.45	18.4	18.4			
0.3	18.5	18.5			
0.4	18.5	18.5			
0.4	14	14			

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Results:

After completing the comparative tests between the Kanthal 145 alloy wire and Tungsten wire, results indicate the Kanthal 145 alloy had a higher durability, with no oxidation or breaking. Comparatively, during the testing the Tungsten wire would oxidize and ultimately result in breakage during trials. Figure 3 represents an image of an oxidized Tungsten wire.



Figure 3: Tungsten after 30 minutes of use at an average temperature of 450 °C.

Figure 4 shows the relationship between input voltage and output temperature in both the Tungsten and Kanthal 145 alloy. There were four different lengths of wire for each wire type tested, and Figure 4 shows how different wire lengths yielded different overall temperatures. The trend observed with the Tungsten wire length showed the shorter the wire, the faster oxidation occurred and the more likely it was for the wire to break. The Kanthal 145 alloy did not show any signs of breaking or oxidizing in the first experiment using different wire lengths and voltages. As the wire length increased, it the temperature of the wire also increased.

The decision about which wire to continue with in Experiment 2 was influenced by both the temperatures the wires could reach as well as the wire's resistance to oxidation and breakage. The Kanthal 145 alloy reached a high temperature of 800°C with the 35-cm wire, and the 30-cm wire reached a temperature of 500°C. The Tungsten wire reached a high temperature of 346°C with the 30.5-cm wire and an input voltage of 6V. Because of these results, the Kanthal 145 alloy was chosen for the second experiment because it did not oxidize or break during any of the trials and reached a higher maximum temperature compared to Tungsten as seen in Figure 5.



Figure 4: A side-by-side comparison of Tungsten to Kanthal 145 alloy wire under different output voltages. The graphs show that as the wire length increases in both the Tungsten and Kanthal 145 alloy the temperature will increase.

Discussion:

Experiment 1:

The results in Experiment 1 narrowed the choice of resistance wire used within the module to the Kanthal 145 alloy. This was chosen because of the higher temperatures it can achieve when paired with the system and because of its durability in terms of preventing oxidation. Results corroborated that the Kanthal 145 alloy is a superior choice over the tungsten wire because of its capacity to transport current to reach desired temperatures and because it does not break with oxidation.

Experiment 2:

Methods:

After completing Experiment 1 on the two types of wire, the Kanthal 145 alloy wire was selected and then quantitatively tested to find the wire length that reaches the pyrolysis temperature range and produced the maximum amount of bio-oil. Temperature profiles of the experiments were graphed and analyzed to help select the wire length that reached the desired temperature range of pyrolysis. The voltage of the tests was between 18.3-18.5 V and the wire was varied from 5-cm to 45-cm. During the experiment qualitative data was collected on the amount of bio-oil produced within the reactor.

Results:

Figure 5 shows the temperature profiles from the reactor using different lengths of the Kanthal 145 alloy wire tested at 18.5 V. The results show that 35-cm resulted in the highest temperature reaching a value of 800°C. Further experiments were completed to investigate how the voltage affects the wire breakage. As more experiments were performed, it became evident that an optimum range existed for the wire length. Longer wires of 45-cm and shorter wires of 5-cm both broke during trials, indicating a range of 9.5-35-cm is optimum in this system.



Figure 5: Temperature of the reactor compared to the varying the wire length of Kanthal 145 alloy.

Testing was also done on Kanthal 145 alloy comparing wire lengths of 20, 30, and 40-cm at the maximum voltage on the power supply, 18.3-18.5V. The voltage was held constant in the experiments for all lengths of the Kanthal 145 alloy. It was used to complete the quantitative experiment on the three different wire lengths. The results of the observational experiment

showed that the 30-cm wire length resulted in the highest maximum temperature for the system and produced the most bio-oil.

Discussion:

The results in Experiment 2 showed that a wire between 30-35-cm delivers current to the reactor to achieve the highest maximum temperature of 800°C for a fast pyrolysis reaction. The results also indicated that the distance between coils around the reactor may have been a contributing factor to the temperature reached within the reactor. This is corroborated by both experimental observations and consideration of transport phenomena. First, during the second part of Experiment 2, the biomass had to be covered by the wire to fully heat the particles and achieve pyrolysis temperatures. If the coils did not encompass the biomass, bio-oil would not be produced within the quartz reactor. The wire needed to cover the whole biomass length in the reactor; when the wire was shorter than the biomass length, the distance between coils increased, leading to inconsistencies of heating between trials. Coils with a shorter distance between each rotation concentrate thermal energy and allow improved heating of the biomass to conversion temperatures. After noticing this effect, the coil distance between each rotation was kept consistent.

Results also indicate a wire shorter than 30-cm dramatically increases the time to heat the entire biomass, taking 5-10 minutes, which indicates a shorter wire yields both less bio-oil and a slower heating rate. A slower heating rate will yield less volatiles and allows for secondary reactions between char and volatiles.³ A high maximum oil yield can be produced by using fast pyrolysis and by fast uniform heating of the biomass particles.¹¹ This effect is also not optimal for this system because implementing it in a classroom should be done within a short amount of time, and taking 5-10 minutes for one experiment is too long.

From this investigation, a template for a hands-on implementation on heat transfer effects on pyrolysis reactions has been developed and optimized for use with the Kanthal 145 alloy. The Appendix includes a full description of how to implement the pyrolysis module into the chemical engineering classroom, focusing on the effects of heat transfer from coil distance. This module can be implemented in a transport phenomenon or thermochemical conversion course, illustrating the notable difference in pyrolysis products between each respective pyrolysis reaction.

Applications in the Classroom:

This paper is a work in progress that focuses on the development of a pyrolysis module that can be used in the classroom to promote hands-on learning. The module can potentially be used to exemplify specific theories within Chemical Engineering courses. Transport phenomena and Bioprocessing Engineering are courses that would benefit the most from the module, due to the energy transport effects that can be observed between the wire and quartz tubing wall as well as allowing students to observe the changes in amount of bio-oil produced. A transport experiment utilizing this module can be viewed in Appendix 1. Future implementation will take place in the coming school year of 2015/2016. The module will be split into two different experiments that will be applied within an introductory engineering course and within higher division courses within Chemical Engineering. Our group will be focusing on motivational factors with psychometrically validated surveys.

Conclusion:

This study focused on optimizing the wire type and length for a pyrolysis module formulated for hands-on learning. The results of the experiments show that a wire with a high resistivity and high resistance to oxidation should be used as the module's heating element. The optimization indicated a Kanthal 145 alloy wire with 35 centimeters in length gave a maximum temperature of 800°C, achieving pyrolysis temperature over a 3 minute time span.

The development of the module focuses on optimizations that students can re-create to learn about pyrolysis or can be manipulated to focus on specific concepts within Chemical Engineering like transport phenomena. Implementations in the classroom can include an experimental design whereby students alter the coil distance to investigate the changing heat transfer effects.

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References:

1. Poskrobko, S., & Krol, D. (2012). Biofuels: Part II. Thermogravimetric research of dry decomposition. *Journal of Thermal Analysis and Calorimetry*, 109(2), 629-638.

2. Bahng, M., Mukarakate, C., Robichaud, D., & Nimlos, M. (2009). Current technologies for analysis of biomass thermochemical processing: A review. *Analytica Chimica Acta*, 651(2), 117-138.

3. Rezaiyan, J., & Cheremisinoff, N. (2005). *Gasification technologies: A primer for engineers and scientists*. Boca Raton: Taylor & Francis.

4. Bridgwater, A., Meier, D., & Radlein, D. (1999). An overview of fast pyrolysis of biomass. *Organic Geochemistry*, *30*(12), 1479–1493-1479–1493.

5. Van Wie, B., Thiessen, D., Golter, P., & Brown, G. (2012). Adoption of a Non-Lecture Pedagogy in Chemical Engineering: Insights Gained from Observing an Adopter. Journal of STEM Education, 13(5), 52-61.

6.Abdul, B., Van Wie, B., Babauta, J., Golter, P., Brown, G., Bako, R., Olaofe, O. (2011). Addressing Student Learning Barriers in Developing Nations with a Novel Hands-on Active Pedagogy and Miniaturized Industrial Process Equipment: The Case of Nigeria. International Journal of Engineering Education, 27(2).

7. Frazer, J., Timan, A., Miller, K., Dowd, J., Tucker, L., & Mazur, E. (2014). Teaching and physics education research: Bridging the gap. Reports on Progress in Physics, 77, 1-17.

8. Niemi, H. (2002). Active learning—a cultural change needed in teacher education and schools. Teaching and Teacher Education, 18(7), 763–780.

9. Kanthal. (n.d.). Kanthal A (Ribbon (flat wire)). Retrieved March 14, 2015, from http://kanthal.com/en/products/material-datasheets/ribbon-flat-wire/kanthal-a/

10. Kasap, S. (2006). Principles of electronic materials and devices (3rd ed.). Boston: McGraw-Hill.

11. Van de Velden, M., Baeyens, J., Bremsc, A., Janssens, B., & Dewil, R. (2010). Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction. Renewable Energy, 35(1), 232–242.

Appendix 1:

Activity Worksheet: Heat transfer in Pyrolysis

A: Experimental Procedure

- 1. Weigh .05 g of biomass and insert into the reactor
- Wrap 25 cm Kanthal wire around reactor

 note number of coils and distance between coils
- 3. Connect Reactor to Thermocouple
- 4. Attach wire to power supply
- 5. Turn on power supply and set to 18.5 V
 - a. Record data and place into table
- 6. Repeat with different coil distances/number of coils

Dimension and constants: Reactor length=10cm Wire length and gauge= 25cm and 28 Wall thickness of reactor= 2mm Inner diameter of reactor= 1mm

Experimental Data

Output Voltage (V)	Number of coils	Distance between coils (mm)	Maximum Temperature reached (°C)

Questions:

- 1. Explain fundamentally what occurred as you changed the distance between the coils?
- 2. What occurs when there is a decrease in the number of coils on the reactor?
- 3. How does the wall thickness of the reactor effect the maximum temperature of the biomass?