**Miniature Biomass Conversion Unit, Conceptual Idea No. 2: Mass Transport and Thermochemical Reactions**

Learning objectives – At the end of this project, students will be able to:

* *Describe the key differences between pyrolysis, gasification, and combustion.*
* *Determine how to configure the miniature tubular biomass conversion reactor to run experiments on pyrolysis, gasification and combustion.*
* *Describe key products of pyrolysis and methods to identify them.*
* *Write the overall reactions for combustion and gasification.*
* *Qualitatively perform a pyrolysis reaction and look for key metrics.*
* *Predict gasification and combustion product compositions based on reactant composition.*
* *Perform combustion experiments and determine rates of reaction.*
* *Calculate the Damköhler number and infer rate limiting phenomena (between kinetics and mass transfer) for the tubular biomass conversion reactor.*
* *Perform an energy balance on reacted gas as it passes forward toward the thermocouple to model the spike in thermocouple temperatures.*

Each team will receive the following materials:

* One 18-V variable power supply (Shared)
* One LCD screen temperature reader that connects to type-K thermocouples (Shared)
* One fan (Shared)
* 2 ring stands (Shared)
* 2.5 feet of 22-gauge Kanthal® alloy wire
* 2 sets of stainless steel adaptors for tube ends
* Two male type-K thermocouple connectors
* Two female type-K thermocouple connectors
* 2.5 feet of thermocouple wire
* 3 type-K butt-welded thermocouples (you can find the junction by carefully running your hand over the wire and feeling for the bump)
* Two 3 mm OD, 2 mm ID quartz tubes, 8 cm long
* Two 12 mm OD, 10 mm ID quartz tubes, 8 cm long
	+ Slotted ~2 mm on each end for wire – need to cut with wafer saw using a diamond blade
* Silver tape
* 60 mL Syringe
* Teflon® Tubing
* One syringe pump
* 6.5 mm toothpicks shaved to ~1 mm diameter, then trimmed to 6 mm
* Biochar (optional)

Toothpick and biochar compositions are important for the exercises and are listed in Table 1 as determined using a CHN analysis instrument. The biochar may be made in a spoon reactor, whereby the toothpick is put in an inert environment, e.g., N2, for 60 minutes at 700°C.

Table 1: Typical elemental analysis of the reactants for pyrolysis, combustion, and gasification, based on data reported of Gartner et al. [1].

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Sample Type | O(mass %) | C(mass %) | H(mass %) | N(mass %) |
| Generic Toothpick | 48.2 | 45.5 | 6.25 | 0.04 |
| Biochar | 0.22 | 98.4 | 1.24 | 0.14 |

**Variable List and Values for Calculations**

$A\_{s}=$ *area of reaction surface including front facing cross section of the biochar and cylindrical biochar surface over which the flame front overlaps, [cm2]*

$C\_{O\_{2}}^{o}$*= O2 concentration of feed gas for the experiment, [mol/cm3]*

$C\_{O\_{2}}^{s}$*= O2 concentration in equilibrium with surface, [mol/cm3]*

$C\_{P\_{product gas}}=$ *heat capacity of product gas, [J/g/K]*

$D\_{biochar}= $*diameter of biochar, [cm]*

$D\_{eq}= $*equivalent diameter for annulus, [cm]*

$Da=$ *Damköhler number, dimensionless*

$Gz=$ *Gratz number, dimensionless*

$k\_{c}$*= mass transfer coefficient, [cm/s]*

$k\_{r}=$ *reaction rate constant, [1/s]*

*kproduct gas= thermal conductivity of product gas [J/s/cm/K]*

$ρ\_{product gas}=$*density of product gas, [g/cm3]*

$Pr=$ *Prandtl number, dimensionless*

$Re=$ *Reynolds number, dimensionless*

$\left(-r\_{O\_{2}}\right)\_{Actual}=$ *actual rate of O2 consumption, [mol/cm3/s]*

$Sc=$ *Schmidt number, dimensionless*

$\overbar{u}=$ *average velocity of incoming gas stream [cm/s]*

$\dot{v}=$ *volumetric flowrate [cm3/s]*

$μ\_{product gas}=$ *viscosity of product gas, [g/cm/s]*

**Exercises**

1. Compare and contrast pyrolysis, gasification, and combustion. How are they the same? How are they different?
2. You were given both a toothpick and biochar as possible reactants. For each of the following choose which reactant you will use and justify why you propose to use it:
	1. Pyrolysis
	2. Gasification
	3. Combustion
3. Just as important as the carbon input to a reaction is the composition of gas that you add to the reaction. Each of these reactions uses either or both N2 and O2 as the incoming fluid reactant. Answer the following questions below:
	1. Pyrolysis: Describe the typically abundant products in a pyrolysis reaction. Tell what the composition of an incoming gas stream should be and why .
	2. Gasification: Tell what gasifying agents (gases) may be used to perform gasification and which is most practical for use in the classroom. Write the overall reactions for gasification when using an O2 gasifying stream referring to literature for mechanisms to support the stoichiometric equations you provide. Describe how one might run a gasification process after inserting the biomass. Tell what mole fraction ranges one might use for the incoming reactant gas and tell why you would select these ranges.
	3. Combustion: Write the overall reaction for combustion and describe ranges for the incoming mole fractions of O2 and N2.

**Experiments**

For assembly refer to Figure 1. You must first wire the thermocouple to the male and female connectors. *Be gentle* as these wear and can break. You only get the number you are issued. Thread the thermocouple wire through the center of the smaller diameter quartz reactor tube until the butt-weld is at the center of the reactor. Then insert either the toothpick or biochar into the quartz reactor. Ensure this reactant is in the center and the butt-weld remains at the center of the toothpick or biochar. Route the ends of the thermocouple wire through each of the stainless steel tee fittings through silicone gaskets to ensure electrical isolation. Around the quartz tube, wrap 20 cm of Kanthal®-A1 alloy wire 12 times with ~1 mm between each coil. Then, if you are doing a combustion or gasification experiment, you will need a partially silvered quartz glass tubing convection and radiation shield notched on each end so the resistance wire can enter and exit. Slip the shield around the quartz reactor with the wire exiting on either end. For the pyrolysis experiment you need not provide the shield as the resistance wire can heat the contents to pyrolysis temperatures without shielding. The wire ends will connect to the alligator clips joined to wires routed to the DC voltage source. It is critical that one ensures every piece is electrically isolated. This includes the resistance wire and the thermocouple. The stainless steel will accept electrons and this will disrupt the voltage delivery or the thermocouple reader.

Instructors: To make the mixtures for the gasification experiment you need specific amounts of both N2 and O2. Air is not acceptable as a source as the higher O2 levels will lead to combustion over gasification. TA’s will need to fill syringes beforehand or if in the lab students can access the gases, *but only after a proper gas cylinder and regulator safety orientation*.



**Figure 1: a) left hand side of assembled reactor; b) diagram of right hand side of reactor system; c) complete setup of the system where the shield fits over the recessed portion of the nuts connected to tee fittings. Resistance wire exits through notches at the two opposite ends of the shield. Thermocouple wires exit by grooves in the shield fit onto tee edges.**

Reminder – Configure the system for each reaction:

1. Pyrolysis: No outer shield
2. Gasification & Combustion: Outer shield with 70% shielding. The outer shield fits nicely onto the smaller diameter recessed portion of the nuts that screw onto the tee fittings. Resistance wires pass through notched openings on the two opposite ends of the shield and are connected to the power supply with alligator clips.

**Pyrolysis**: This experiment is qualitative only. Configure the system with a toothpick and N2 in the syringe. Start by flushing the system with N2. Then, with a consistent flowrate of 7-10 mL/min turn on the power source and syringe pump at the same time. Observe the reaction that occurs.

1. Write down observations for the pyrolysis reaction.
2. Take apart the system. There will be a sticky oil coming out of the reactor. It has a distinct smell. Write down observations based on the smell and viscosity of the oil.

**Gasification:** Assemble the system with ~4 mg of biochar (that has been weighed and recorded) in the center and provide a borosilicate shield masked on the inside with aluminum foil tape to provide 70% coverage with the remaining 30% uncovered space to serve as a viewing window. The thermocouple should be positioned at the biochar center. Attach the syringe pump to the incoming tube and flush with N2. For the experiment, have a syringe of N2and one with a mixture of O2 (10-15%) and N2 (85-90%).

Once flushed, immediately replace the N2 syringe with one containing a mixture of O2 and N2 and start the syringe pump (7-10 mL/min) while initiating the DC power source. Observe what happens during the reaction.

1. Why is the reactor flushed with N2 before beginning the gasification experiment?
2. What are the products produced in the reactor during gasification?
3. Using the data from table 1, what is the molar ratio of carbon to hydrogen in the biochar?

**Combustion:** Configure the system with an 6 cm toothpick shaved to an approximate 1 mm diameter, i.e., ~30 mg, and have syringes filled with 100%, 75% and 50% O2 and the balance N2. Alternatively, configure the system with biochar in the reactor running 6 total experiments at voltages of 12 V and 18 V and entrance gas streams of 100%, 75%, and 50% O2. Record each experiment by video to track the flame front as it proceeds down the length of the biomass.

1. Write the overall stoichiometrically balanced combustion reaction.
2. Using the data from Table 1, calculate the gas composition of the exit streams for when you begin with an 6 cm long wooden toothpick shaved to ~ 1 mm diameter, i.e., ~30 mg, and provide 60 mL of entrant gas consisting of 50% O2 if the balance is N2. Assume all of the O2 entering the system is available for combustion provided there is sufficient biomass for reaction.
	1. Determine the relative molar amounts of C, H and O available in the toothpick.
	2. Determine the exit gas composition.
	3. Determine remaining biomass if any.
	4. If a GC or an Orsat analysis system is available confirm the composition of exiting combustion gas.
3. Take out your cell phone to record the reaction; you should see a visible reaction front that looks like a large spark moving along the length of the reactor.
4. Calculate the Reynolds number for gas phase O2 were it to remain unreacted as it passes beyond the leading edge of the toothpick biomass through the annular space surrounding a 1 mm toothpick within a 2 mm diameter quartz micro-reactor in a combustion experiment receiving 60 mL of reactant gas consisting of pure O2 initially at 25 $℃$ where the entire gas content is pushed through the reactor at a rate of 5.1 mL/min but rises to and burns at 600 $℃$ as it reaches the biomass.
5. Align the timing of the data from the thermocouple with the data from the video.
	1. Assuming the reactor is 8 cm long, determine the length of the toothpick from the video.
	2. Determine the maximum temperature in each reaction from the temperature data and determine the time it took for the reaction front to reach the maximum temperature. Record the total time for each reaction.
	3. Using the length calculated from the toothpick in question (5a), record the total time in the video for the reaction front moving down the length of the toothpick. Using these two values, determine the average velocity (reaction speed) for each experiment.
6. The Damköhler number can be expressed as follows for this experiment:

$$Da^{†}=\frac{reaction rate}{convective mass transport rate}=\frac{k\_{r}C\_{O\_{2}}^{°}A\_{s}}{\overbar{u}A\_{x}C\_{O\_{2}}^{°}}= \frac{1}{(1-\frac{\dot{v}}{A\_{s}k\_{c}})}$$

Note the simplified form to the far right is derived in the Appendix of the work by Gartner et al. (*Miniature Biomass Conversion unit for Learning the Fundamental of Heterogeneous Reactions Through the Analysis of Heat Transfer and Thermochemical* Conversion, Gartner et al., ASABE, In Press, 2020) and is necessary because the intrinsic kinetic rate constant, *kr*, is not known, nor is the surface concentration of O2. However, because all the O2 is consumed the actual surface reaction rate can be measured and equated to the rate of transport of O2. It is then a simple matter to solve for the surface concentration of O2 and the reaction rate constant. Simple substitution results in the right hand side above. Rework the solution as follows in your own step-by-step process to make sure you understand it.

1. This analysis is entirely experimental, and we do not have a value for the reaction rate constant, *kr*. To reach a solution, derive the right hand side version of the Damköhler number using a measured reaction rate and estimate of O2 concentration at the surface from a transport model.
2. Calculate the Damköhler number for each experiment for several assumptions about the percent of the flame front actually engulfs the end of the biochar. (hint: This affects the *As* value used in the calculation. )

$A\_{s}= \frac{πD\_{biochar}^{2}}{4}+\frac{πD\_{biochar}×\% flame overlapping biochar}{100}$

1. Given your results from (3), is the combustion process reaction or convective mass transfer controlled in this system? Justify your answer.
2. Make a professional looking graph with O2 convective transport rate, CO2·$\dot{v}$, on the abscissa, and dL/dt, representing the rate at which the combustion reaction proceeds, on the ordinate with a point for each experiment conducted at the different O2 concentrations. Add trend lines for the 12 V and 18 V experiments, for which average temperatures are *850 °C* and *672 °C*.
	1. Please explain from a reaction rate vs. mass transfer rate point of view why the trends appear to be linear. Also, consider which of the two voltages has a steeper slope? Why might this be the case? (Again, think about reaction kinetics and mass transfer).
	2. Using the overall reaction stoichiometry for combustion as shown below, determine the flowrate, average velocity, Reynolds number, and the appropriate tube side heat transfer correlation based on the Reynolds number and Graetz number, at a distance L of 1 cm downstream of the reaction front, for combustion product gases once they are formed at the flame front and as they pass through the annular space surrounding a 1 mm toothpick held within a 2 mm quartz reactor. Assume a total of 60 mL of 100% O2 at a temperature of 25$℃$ flows initially at 5.1 mL/min from a feed syringe and as the O2 enters the reactor it quickly rises to 800$℃$, combusts as it reaches the leading edge of the toothpick, and product gases proceed at an average temperature of 800$℃$ down the annular space.

**References**

[1] J. Gartner, M. Garcia-Perez, D. Thiessen, B. Van Wie, Miniature biomass conversion unit for learning the fundamentals of heterogeneous reactions through the analysis of heat transfer and thermochemical conversion, Transactions of the American Society of Agricultural and Biological Engineers (In Press 2020).