

Enthalpy for Pyrolysis for Several Types of Biomass

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This study utilizes a pilot-scale pyrolysis system to determine the enthalpy for pyrolysis for Northern Red Oak (*Quercus rubra*), Western White Pine (*Pinus monticola*), corn stover, and oat hulls. The analytical method uses an energy balance on a pyrolytic reactor. The energy required is measured at a fast pyrolysis reactor temperature near 500 °C using nitrogen as an inert fluidizing agent in a fluidized bed reactor. On a dry basis, the energy necessary to pyrolyze these fuels varies between 0.8 ± 0.2 MJ/kg for oat hulls and 1.6 ± 0.3 MJ/kg for pine.

1. Introduction

The purpose of this study is to quantify the enthalpy for pyrolysis of various types of biomass. With this value known, fast pyrolysis systems can be specifically engineered for particular types of biomass. This is important because it is possible that different types of biomass will have vastly different enthalpies for pyrolysis. Thus, the design of the system may vary with respect to heat transfer issues or sizing of the reactor on the basis of the energy required to carry out the pyrolysis.

Enthalpy for pyrolysis, h_p , is defined as the energy required to raise biomass from room temperature to the reaction temperature and convert the solid biomass into the reaction products of gas, liquids, and char. Restating, it is the total energy consumed by the biomass during pyrolysis, including contributions to both sensible enthalpy and enthalpy of reaction for the pyrolysis of biomass.^{1,2} The sensible enthalpy refers to the energy absorbed by the biomass to raise its temperature only. The enthalpy of reaction is the energy required to drive the pyrolysis reactions. A standard enthalpy approach, at first glance, would seem suitable in quantifying the energy consumed in pyrolysis. This approach requires that the enthalpy of the products and reactants be referenced to a standard temperature. However, the products of pyrolysis are complex in nature with respect to their composition. Also, the sensible enthalpy or specific heat data corresponding to the products and reactants is many times difficult to determine. Often, the enthalpy for pyrolysis is termed in the literature as the heat for pyrolysis. This study chose to employ the former terminology to be consistent with current usage of enthalpy.

A number of previous studies have attempted to measure enthalpy for pyrolysis by a variety of methods. Reed and Gaur² utilized a reducing flame to provide direct heat energy to birch dowels on a 1 to 2 cm scale. They calculated h_p values of 2.9 to 3.5 MJ/kg of biomass. This nonconventional method likely leads to large errors in the enthalpy for pyrolysis calculation. In addition, this process lasted longer than 50 s per sample and more closely resembles slow pyrolysis rather than fast pyrolysis. Pilot plant studies by Morris et al. with spruce and pine have indicated h_p values of 2.5 MJ/kg of oil produced.³ This indirectly suggests that h_p is 1.75 MJ/kg of biomass, neglecting the heat losses of the system and assuming 70% oil conversion. However, the details of this calculation are not given. A hearth furnace under vacuum conditions has also been utilized by Roy and associates⁴ to present significant insight on the energy required to pyrolyze wood chips. At a hearth temperature of 437 °C, the enthalpy for pyrolysis for wood chips with 5.9% moisture is 0.7 MJ/kg.⁴ An uncertainty for the published values is not given, so the accuracy of the results is not known. The enthalpy for pyrolysis is dependent on the reactor temperature due to sensible heat considerations as well as changes in pyrolysis reaction chemistry. This is an important consideration when comparing results from various studies on enthalpy for pyrolysis. The goal of the present investigation is to obtain accurate values of enthalpy for pyrolysis for several kinds of biomass.

2. Apparatus

Many types of reactors have been developed for the fast pyrolysis of biomass, including fluid beds, ablative reactors, circulating fluid beds, entrained flow reactors,

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(2) Reed, T. B.; Gaur, S. The High Heat of Fast Pyrolysis for Large Particles. In *Developments in Thermochemical Biomass Conversion*; Bridgwater, A. V., Boocock, D. G. B., Eds.; Blackie Academic and Professional: New York, 1997; pp 97–103.

(3) Morris, K.; Johnson, W.; Thamburaj, R. Fast Pyrolysis of Biomass for Green Power Generation. 1st World Conference and Exhibition on Biomass for Energy and Industry. Seville, Spain. June 5–9, 2000.

(4) Roy, C.; Lemieux, R.; de Caumia, B.; Blanchette, D. Processing of Woodchips in a Semicontinuous Multiple-Hearth Vacuum-Pyrolysis Reactor. In *Pyrolysis Oils from Biomass: Producing, Analyzing and Upgrading*; Soltes, E. J., Milne, T.A., Eds.; American Chemical Society: Washington, DC, 1988.

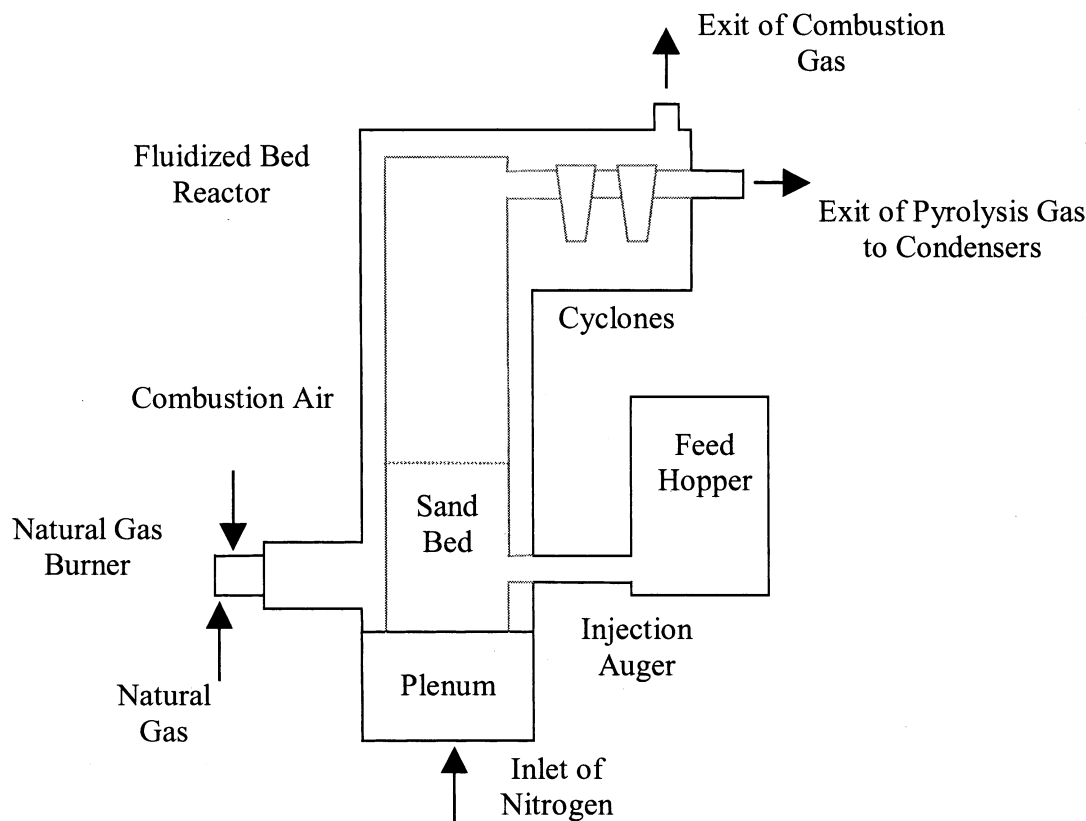


Figure 1. Pyrolysis reactor system.

and rotating cone reactors.⁵ Among the most commonly employed are fluidized beds, which are used in the present study because of their favorable heat transfer and mass transfer characteristics.⁶

As shown in Figure 1, the main components of the reactor system include a fluidized bed, a natural gas burner, a plenum, a feed hopper, and two cyclones in series. The main reactor is a fluidized bed of sand in which nitrogen enters through the plenum at the base of the unit. The average particle diameter of the sand is 730 μm , using a standard sieve analysis. The sand originates from near Eau Claire, Wisconsin (Red Flint Sand and Gravel), and is approximately 95% silica, 2% iron oxide, 0.9% aluminum oxide, with the balance being trace amounts of other oxides. The diameter of the reactor is 16.2 cm and stands 1 m in height with a sand depth of 32 cm. The natural gas burner is rated at 44 kW and is directly plumbed to natural gas lines and compressed combustion air. The hot gases from the combustion burner flow through the annulus around the fluidized bed, providing heat to the reactor system. The plenum, located at the base of the reactor, is the inlet for the inert nitrogen, which is the fluidizing gas for the sand bed. A feed hopper is also connected to the reactor via a dual auger system. The first auger (not shown) meters the biomass from the feed hopper into an injection auger which then supplies the reactor with biomass. Another feature of the reactor system is a set of cyclones in series contained in a hot gas-heating jacket which is an extension of the annulus around the

bed. The nitrogen and pyrolysis gases exit the freeboard and enter these cyclones. The exit of the cyclones is considered the exit of the reactor system.

The unit is fitted with various thermocouples and pressure taps to monitor operating conditions. In addition, a variable-frequency drive controls the feed rate of the biomass, and a mass flow controller monitors the nitrogen flow. The natural gas flow and the airflow to the burner are regulated, and pressure drops across the corresponding incorporated orifice plates are recorded. A data acquisition system monitors and records all system components.

3. Energy Balance on the Pyrolysis Reactor

The energy flows for the pyrolytic reactor are illustrated in Figure 2. There are two primary heat flows as well as three flows of enthalpy. The first inflow, represented by $H_{N_2, \text{in}}$, is the enthalpy introduced to the reactor from the nitrogen flowing into the system. The second inflow of energy, Q_{in} , is associated with the heat transfer into the system that results from the combustion of natural gas in the burner. Included in the energy outflows is the enthalpy, $H_{N_2, \text{out}}$, associated with the exiting nitrogen. In addition, a heat loss, Q_{Loss} , also is considered in the analysis. Last, the enthalpy flow, H_p , is consumed by the biomass in the pyrolysis process. The resulting energy balance, eq 1, is used to describe the system.

$$H_p = Q_{\text{in}} + H_{N_2, \text{in}} - H_{N_2, \text{out}} - Q_{\text{Loss}} \quad (1)$$

During each pyrolysis test, the system was brought to steady state with respect to the bed temperature. All

(5) Bridgwater, A. V.; Peacocke, G. V. C. Fast Pyrolysis Processes for Biomass. *Renewable Sustainable Energy Rev.* **2000**, *4*, 1–73.

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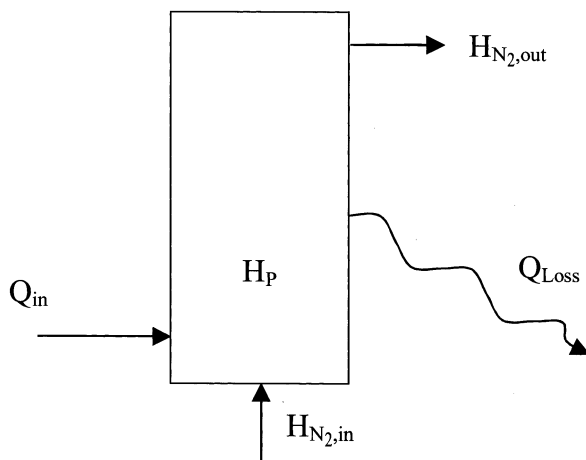


Figure 2. Energy flows.

parameters remained constant at their initial values except for the mass flow rate of the biomass which was adjusted until a constant bed temperature near 500 °C was achieved in approximately 30 min. From this point, the biomass rate remains steady and pertinent data of the system was analyzed to evaluate the heat flows given in eq 1.

The energy flows associated with the nitrogen were calculated on the basis of an average specific heat value⁹ associated with the temperature of the nitrogen and the reference temperature. The flow rate of nitrogen is precisely known from the mass flow controller monitoring the nitrogen flow. The inlet and exit temperatures of the nitrogen were monitored with thermocouples. The nitrogen heat flows were then calculated with the following equations in which T_{ref} is defined as 25 °C.

$$H_{N_2,in} = \dot{m}_{N_2} C_{p,in} (T_{in} - T_{ref}) \quad (2)$$

$$H_{N_2,out} = \dot{m}_{N_2} C_{p,out} (T_{out} - T_{ref}) \quad (3)$$

The following equation represents the method used to calculate Q_{in} :

$$Q_{in} = H_{RP} + \sum_R \Delta H_i - \sum_P \Delta H_i \quad (4)$$

The term, H_{RP} , represents the enthalpy of combustion of the natural gas. The second term refers to the sensible enthalpy of the entering reactants. In this study, this reactant enthalpy is considered to be equal to zero since the reactants enter at essentially the reference temperature of 25 °C. The third term symbolizes the sensible enthalpy of the exiting producer gas from the combustion process at the exit of the heat jacket. The enthalpy of combustion was calculated from specific knowledge of the gas and airflow rates at steady state. The molar analysis of the natural gas was provided on a daily basis from the local supplier.⁷ Typically, the natural gas was greater than 95% methane in composition on a molar basis. With this knowledge, the heat of combustion of the gas was calculated assuming complete consumption

of the fuel and standard methods were used for this analysis which can be found in most engineering thermodynamic textbooks.⁸ The energy flow corresponding to the exiting hot gas from the burner is calculated by an average specific heat method similar to that of the nitrogen heat flows. The flow rate of the products of combustion is known since the rates of natural gas and air into the burner are established. Therefore, from a chemical balance, the amounts of carbon dioxide, nitrogen, oxygen, and water vapor are known. The corresponding average specific heat⁹ can be calculated for each gas constituent since the temperature of the hot gas was monitored. Thus, the enthalpy associated with the exiting hot gas is defined as follows with the reference temperature equal to 25 °C.

$$\sum_P \Delta H_i = \sum_i (\dot{m}_i C_{p,i} (T_{Hotgas} - T_{ref})) \quad (5)$$

The last unknown for defining the enthalpy for pyrolysis is the heat loss, Q_{Loss} , associated with the overall system. This value is extremely difficult to accurately calculate using theoretical methods due to the nature of the system's complex geometry, gas flows, and surface temperature gradients. An alternative method was developed in which water was injected into the system as a liquid at 25 °C and raised to the bed temperature. The resulting nitrogen/water vapor mixture exits the system similar to the product flow from biomass pyrolysis. For water, eq 1 is solved for the heat loss term and rewritten as follows:

$$Q_{Loss,W} = Q_{in} + H_{N_2,in} - H_{N_2,out} - H_W \quad (6)$$

Note that the enthalpy associated with water, H_W , is similar in nature to that of the enthalpy for pyrolysis of a biomass, H_P , and accordingly replaces this term. They are similar in the respect that both enthalpies are endothermic. In this test, the enthalpy for water, H_W , is the amount of energy required to take liquid water at room temperature and raise it to steam at the reactor temperature. The properties of water are well-known, and this energy requirement can be calculated from most thermodynamic sources. The enthalpy change associated with steam at 500 °C is 3.38 MJ/kg with a reference temperature of 25 °C.⁸ For a specific mass flow of water into the reactor system, the energy associated with converting liquid water to the resulting steam is quantified. As a result, $Q_{Loss,W}$ can be calculated for the processing of water in the reactor.

Assuming that the heat loss associated with the processing of water is similar to that of any biomass analyzed at comparable reactor conditions, then all of the parameters on the right side of eq 1 are known. The heat flow Q_P of the particular biomass being tested can then be calculated. Continuing a step further, the enthalpy for pyrolysis on a mass basis can be calculated as shown by eq 7 for any biomass.

$$h_p = \frac{H_P}{\dot{m}} \quad (7)$$

To validate this method, the enthalpy change of a well-known high-temperature process was evaluated in the pyrolysis reactor and compared to a calculated value

(7) Northern Natural Gas. http://www.nng.enron.com/dob/etfr_chromatograph.html.

(8) Moran, M. J.; Shapiro, H. N. *Fundamentals of Engineering Thermodynamics*, 2nd ed.; John Wiley & Sons: New York, 1992.

(9) NIST Chemistry Webbook. NIST Standard Reference Database, 69, 2001. <http://webbook.nist.gov/chemistry>.

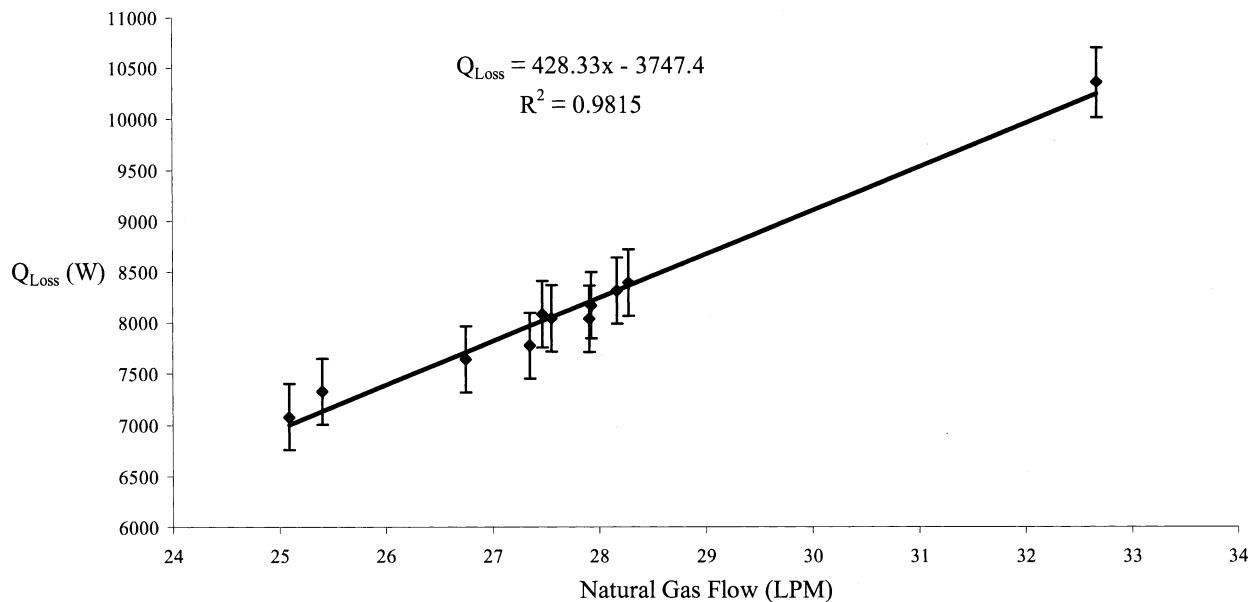


Figure 3. Heat loss without injection of biomass.

from published data. The energy associated with the conversion of liquid methanol (99.9% pure) to methanol vapor can be readily calculated from tabulated data of the specific heats and latent heats of evaporation for methanol. The outcome of this validation test is presented in the next section along with the results for several biomass fuels.

4. Results

This study evaluated enthalpy for pyrolysis for two types of wood: oak (*Quercus rubra*), a hardwood, and pine (*Pinus monticola*), a softwood. In addition, two herbaceous materials were analyzed: corn stover and oat hulls. It is important to note that all testing was performed utilizing a pilot scale reactor that operates at slightly positive pressures (~4 kPa). To promote fast pyrolysis, a small biomass particle size was utilized in

this study and therefore, all biomass has a critical dimension of 1 mm or smaller. A reactor temperature of approximately 500 °C is used because oil yield is optimized for many types of biomass near this temperature.

The heat loss, Q_{Loss} , of the system was calculated when there was no injection of biomass or other material into the reactor except for the inert fluidizing gas nitrogen. As a result, eq 1 could then be simplified by noting that the enthalpy for pyrolysis, H_p , is zero. Since the remaining heat flows could be calculated readily, values for the heat loss could directly be found. Figure 3 shows the relationship between the heat loss and the flow rate of the burner for the prescribed conditions. The data illustrates a strong linear correlation of the heat loss with respect to the natural gas flowing to the burner. The procedure was repeated for the situation

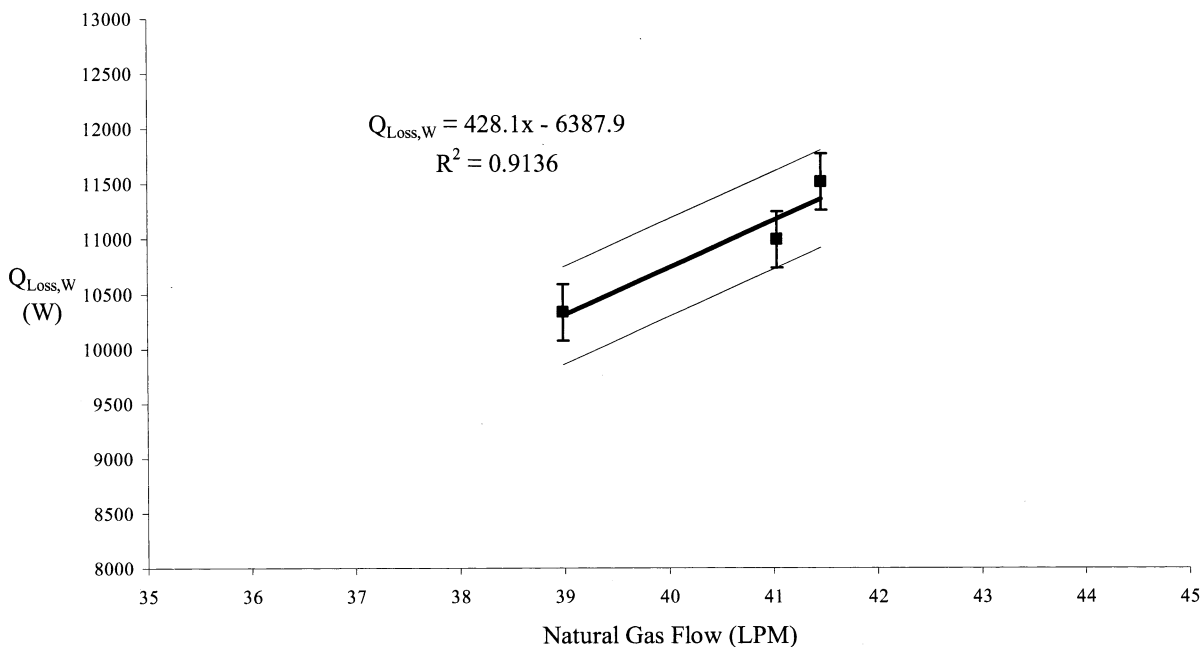


Figure 4. Heat loss with water injected.

Table 1. Flow Rates and Temperatures of Reactor System with Uncertainty

	natural gas flow SLPM	burner air flow SLPM	enthalpy of combustion J/L	nitrogen flow SLPM	biomass rate kg/h	inlet nitrogen temperature °C	outlet nitrogen temperature °C	burner gas exit temperature °C	bed tempera- ture °C
methanol	41.7 ± 0.20	583.8 ± 18.4	32558.7 ± 2.9	260.0 ± 5.0	5.19 ± 0.10	25 ± 5	461.6 ± 2.0	464.4 ± 2.0	496.2 ± 2.0
oak	40.7 ± 0.21	581.3 ± 18.5	32553.8 ± 3.2	260.0 ± 5.0	7.13 ± 0.10	25 ± 5	422.4 ± 2.0	451.5 ± 2.0	500.0 ± 2.0
oat hulls	40.4 ± 0.21	581.5 ± 18.5	32573.1 ± 3.0	260.0 ± 5.0	10.22 ± 0.10	25 ± 5	444.7 ± 2.0	458.0 ± 2.0	495.7 ± 2.0
pine	41.5 ± 0.20	580.7 ± 18.5	32626.0 ± 2.9	260.0 ± 5.0	6.05 ± 0.10	25 ± 5	446.9 ± 2.0	467.1 ± 2.0	503.5 ± 2.0
corn stover	39.4 ± 0.21	578.4 ± 18.6	32593.5 ± 2.9	260.0 ± 5.0	7.13 ± 0.10	25 ± 5	435.7 ± 2.0	435.3 ± 2.0	512.8 ± 2.0

Table 2. Energy Flows of Reactor System with Uncertainty

	$H_{N_2,in}$ kW	Q_{in} kW	$H_{N_2,out}$ kW	Q_{Loss} kW	H_p kW
methanol	0.00 ± 0.026	16.69 ± 0.247	2.32 ± 0.046	11.47 ± 0.443	2.89 ± 0.510 ^a
oak	0.00 ± 0.026	16.32 ± 0.244	2.11 ± 0.042	11.02 ± 0.443	3.20 ± 0.508
oat hulls	0.00 ± 0.026	16.10 ± 0.245	2.23 ± 0.044	10.91 ± 0.443	2.97 ± 0.509
pine	0.00 ± 0.026	16.58 ± 0.248	2.24 ± 0.045	11.37 ± 0.443	2.97 ± 0.510
corn stover	0.00 ± 0.026	15.96 ± 0.240	2.43 ± 0.044	10.50 ± 0.443	3.03 ± 0.507

^a Enthalpy change due to vaporization for methanol.

in which water was injected into the reactor. The heat loss when water is injected into the system mimics the conditions present during the pyrolysis of biomass. Figure 4 illustrates the results of the water tests in which the heat loss data is fitted to a linear relation. Applying the individual uncertainty of each data point, the largest absolute uncertainty of the fitted linear equation can be established. The absolute largest error (443 W) for the fitted line is shown in Figure 4 as the surrounding lighter lines. With the bed temperature near 500 °C, the heat loss at steady state can be closely calculated for the pyrolysis of biomass by applying the gas flow rate to the fitted curve.

To verify the method presented, a substance with a known enthalpy at the exit temperature, methanol (99.9% pure), was tested in the reactor. To begin, the reactor was brought to steady state at around 500 °C. Once at steady state, the natural gas was adjusted to a higher setting in the range of Figure 4. This adjustment to the higher setting is needed to provide the additional energy required used by the reactants once they are injected. Immediately, methanol was injected using a peristaltic pump at a controlled rate. The rate of injection was adjusted until the system came to steady state at near 500 °C. The flow rate was then measured and recorded. Using the governing equations described, the corresponding energy flows for the system could be calculated as detailed previously. The heat loss, Q_{Loss} , was calculated by inserting the natural gas flow in the linear relationship established in Figure 4. By determining the mass flow rate at steady state, the energy required to process the methanol on a mass basis could be calculated directly. The theoretical energy required for raising methanol from a liquid state at 25 °C to a vapor at 496 °C is based on the following information. The energy to vaporize methanol at 64.6 °C is 35 210 J/mol.¹⁰ The constant specific heat of the liquid methanol is 83.3 J/mol-K.¹¹ The constant specific heat of the vapor is calculated from a linear fit of data presented

(10) Majer, V.; Svoboda, V. *Enthalpies of Vaporization of Organic Compounds: A Critical Review and Data Compilation*; Blackwell Scientific Publications: Oxford, 1985; p 300.

(11) von Reis, M.A. Die spezifische Wärme flüssiger organischer Verbindungen und ihre Beziehung zu deren Molekulargewicht. *Ann. Phys.* [3], **1881**, 13, 447–464.

Table 3. Enthalpy for Pyrolysis, Corrected Theoretically to Dry Basis

	h_p MJ/kg	moisture % (dry basis)	$h_{p,dry}$ MJ/kg
methanol	2.00 ± 0.36 ^a	0.0	2.00 ± 0.36 ^a
oak	1.61 ± 0.26	8.0	1.46 ± 0.28
oat hulls	1.04 ± 0.18	10.2	0.78 ± 0.20
pine	1.77 ± 0.31	7.5	1.64 ± 0.33
corn stover	1.53 ± 0.26	8.8	1.35 ± 0.28

^a Enthalpy change due to vaporization for methanol.

by Stromsoe and results in a value of 62.94 J/mol-K.¹² Thus, the calculated value of the change in enthalpy of methanol is 2.05 MJ/kg for the prescribed conditions. The experimentally measured value of the enthalpy change for methanol was 2.00 ± 0.36 MJ/kg in this study. The two values are in excellent agreement. With this verification of the method, strong confidence in the results for h_p was gained.

This same process was repeated for oak, corn stover, oat hulls, and pine. The pertinent flow rates and temperatures for each test case are shown with their respective uncertainty in Table 1. The values listed represent an average of roughly 10 min of collected steady-state data sampled every 10 s. In addition, Table 2 quantifies the corresponding energy flows for each different reactant. Table 3 summarizes the results of these tests. All biomass had acceptable and typical moisture content between 8.0% and 10.2% water on a dry basis.

Table 3 contains a correction of the enthalpy for pyrolysis to a dry biomass basis. These values were calculated assuming that the unbound water is removed with energy equivalent to 3.38 kJ/kg of water in the reactor. However, if a biomass with higher moisture content is used, the energy required will increase correspondingly.

Furthermore, Table 3 includes an uncertainty for each enthalpy for pyrolysis value. This uncertainty is largely dependent on the heat loss calculation for each substance. In this study, the resulting uncertainty ranged between 16.1% and 17.5%.

(12) Stromsoe, E. Heat capacity of alcohol vapors at atmospheric pressure. *J. Chem. Eng. Data* **1970**, 15, 286–290.

5. Conclusions

This study provides a method for measuring enthalpies for pyrolysis, which is not readily available in the existing literature. The average value of the enthalpy for pyrolysis of the biomass tested is approximately 1.5 MJ/kg when the biomass has typical moisture content of 8% to 10%. The values for the woody biomass are higher than those of the herbaceous materials. A potential difference in the heat for pyrolysis values could be attributed to the lignocellulosic composition differences. Further work could be performed in which specific compositions of cellulose, hemi-cellulose, and lignin are studied in comparison to the required heat for pyrolysis for each type of biomass. If the biomass is exceptionally dry, the average value theoretically drops

to a corrected value of 1.3 MJ/kg. Although endothermic, this value is quite small and may be considered thermo neutral, depending on the design parameters of the system. The obvious way to improve the accuracy of this method is to reduce heat loss from the external burner and the pyrolysis reactor. A significant decrease in the heat loss will likely lower the uncertainty of the enthalpy for pyrolysis measurement. However, uncertainties in the range of 16–18% are probably satisfactory for the design of many fast pyrolysis reactors.

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