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Model of Fast Pyrolysis of a Small Volume-Fraction of Biomass Within a Gas of Transient Temperature and Pressure

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A simple model and results for the decomposition of pulverized cellulosic biomass within a non-oxidizing gas of transient temperature and pressure is presented. This model is used to predict the performance of a novel thermo-chemical biomass conversion scheme termed the reciprocating biomass conversion reactor (RBCR). Calculations indicate that complete thermo-chemical conversion can be completed within the compression and expansion strokes of a repurposed 4-stroke motor. Approximately 70% (by weight) of the bio-products are in the form of bio-oil. The performance of the RBCR is predicted to be favorable when compared to the state of the art, which is considered to be the fluidizied bed reactor (FBR). The biomass feedrate is increased by ≈ 100%, and the energy required for conversion to bio-oil is reduced by ≈ 50%.

I. Introduction

The power required for straight and level flight of an aircraft is approximately[1] a function of the aircraft weight to the power 3/2. This well understood effect of aircraft weight on aircraft performance implies that the simplest route to implementation of alternative energy carrier and conversion systems requires similar power-to-weight ratios to those currently available. The power-to-weight ratio requirement and the maturity of the jet engine are arguments for the development and use of "drop-in" aviation fuel derived from biomass. Aviation bio-fuel can be produced by converting biomass to bio-oil via fast pyrolysis, and subsequent upgrading to aviation fuel.[2–10]

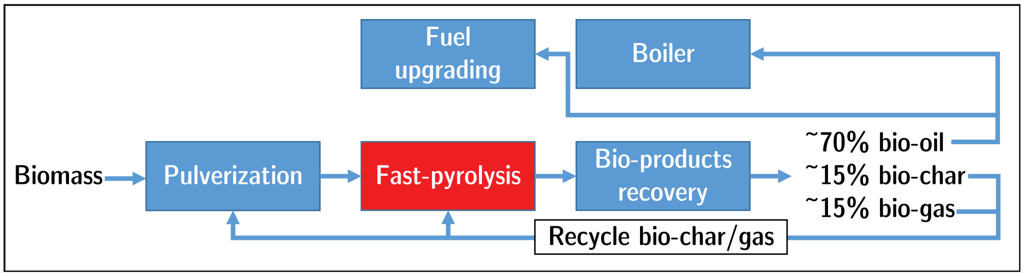

Figure 1. Flow chart for thermo-chemical conversion of biomass by fast pyrolysis. Biomass is pulverized, pyrolyzed, and the bio-oil is recovered for use in a boiler (directly for heat or electricity), or upgraded for use as bio-diesel or aviation fuel.[11] The bio-char and bio-gas can be recycled for use as an energy source for the required energy for pulverization and fast-pyrolysis. The approximate fractions of bio-products are taken from the literature.[12] The contribution of this paper is to predict the performance of a novel means to thermo-chemically convert biomass by fast pyrolysis.

Fast pyrolysis is a process where biomass is decomposed in an environment without an oxidizing agent at temperatures of approximately 500°C for short times (Fig. 1). Thermo-chemical biomass conversion by fast pyrolysis to bio-oil, bio-char, and bio-gas is a part of an attractive path to an alternative energy source because of the upgrade in heating value and density[13] so that it may be easily transported as part of a

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new distribution network.[11,14] Effective methods of biomass conversion to bio-oil are of interest because bio-oil represents a deployable energy carrier with favorable source characteristics (e.g., in-situ production and carbon-neutral).[15–20] Biomass is pulverized, pyrolyzed, and the bio-products are recovered (Fig. 1). Bio-oil can be used directly in boilers (i.e., for heating or electricity), or upgraded for use as a fuel.[11]

There are a number of reactor types for fast pyrolysis: entrained flow reactor, wire mesh reactor, vacuum furnace reactor, vortex reactor, rotating reactor, microwave reactor, fluidized-bed reactor, and the circulating fluidized-bed reactor.[12,21–30] Some of these reactors are complicated and require a large external energy source for operation.

The fluidized-bed reactor (FBR) is representative of the current state of the art; the FBR requires a condenser to cool the bio-products to quench the secondary pyrolysis reactions;[26] the condenser is an active cooling component that leads to heat loss and system inefficiency. The primary pyrolysis reactions create the pyrolysis vapor which condenses to bio-oil; the secondary pyrolysis reactions adversely affect the bio-oil quality and should be avoided.[12,13,22,26,31]

II. Reciprocating Biomass Conversion Reactor (RBCR) Cycle

A cycle has been proposed[32,33] utilizing rapid heating/conversion and cooling of a small volume-fraction of pulverized biomass suspended in a gas within a cylinder; the scheme is called the reciprocating biomass conversion reactor (RBCR). The process flowchart is presented as Fig. 2. In a typical Diesel engine, the 4-stroke cycle is: intake, compression, power, and exhaust; in the proposed conversion scheme, this is replaced with: intake, compression/heating, expansion, and exhaust. The idealized cycle for the proposed biomass conversion scheme proceeds as follows:

1. *Intake:* A two-phase mixture of an inert fluidizing gas (Ar, N2, or a CO/CO2 mixture) and a small volume-fraction of pulverized biomass are input into the cylinder of a high compression-ratio engine.
2. *Compression/heating:* An external power source (e.g., an electric-motor) turns the crankshaft driving the piston to compress and heat the biomass/fluidizing-gas mixture within the cylinder. Process heat is transferred from the fluidizing gas to the biomass; this process heat is sufficient to thermo-chemically convert the biomass to bio-products by fast pyrolysis.
3. *Expansion/cooling:* The expansion stroke rapidly decreases the temperature and pressure of the fluidizing-gas/bio-products mixture within the cylinder, quenching the undesirable secondary pyrolysis reactions. A significant fraction of the energy required to compress the system is recovered as the pressure is reduced through expansion.
4. *Exhaust:* The exhaust stroke forces the fluidizing-gas/bio-products mixture from the cylinder.

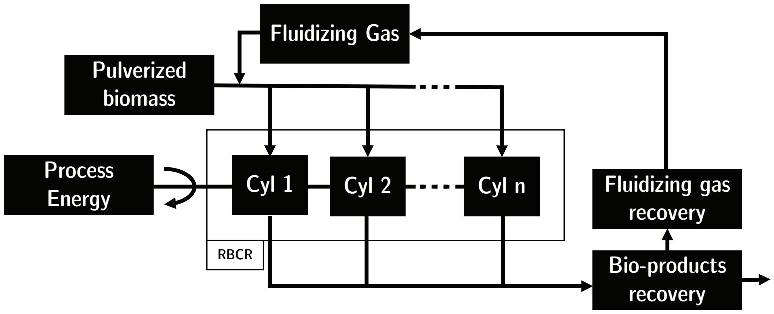

Figure 2. Reciprocating biomass conversion reactor (RBCR) process flowchart.

This cycle has the potential to reduce operating costs of thermo-chemical conversion by reducing the required input energy to the system and improving the quality of the bio-products by quenching undesirable secondary pyrolysis reactions. The instant following desired biomass conversion, the bio-products and fluidizing gas reside within the cylinder at an elevated temperature and pressure. This is surplus process heat, and in contrast to the state of the art, the surplus process heat is transferred and reused mechanically through the crankshaft to another piston/cylinder during the expansion stroke. In this paper, a model is formulated and used to predict the useful biomass conversion parameter space of the RBCR.

III. Closed Control-Volume Energy Balance

Here, we analyze a closed, transient control volume, presented as Fig. 3, which surrounds one cylinder of the RBCR shown in Fig. 2. There is a well-mixed and evenly distributed fluidizing gas and biomass/bio-products mixture in this control volume; the fluidizing gas and biomass are separated in Fig. 3 only to clearly show the direction of energy flow. In Fig. 3, Q is the energy that is transferred into a control volume by heat transfer, W is is the energy that is transferred out of a control volume by work, and ΔH_P is the change in enthalpy required to pyrolyze the biomass. The subscripts b, g, and w represent the biomass, fluidizing gas, and wall, respectively. Two subscripts in succession indicate "from a to b," e.g., Q_{gb} is the energy transferred from the fluidizing gas to the biomass by heat transfer. Additionally, we assume that the pressure of the fluidizing gas and biomass are equal, $P_g = P_b = P$.

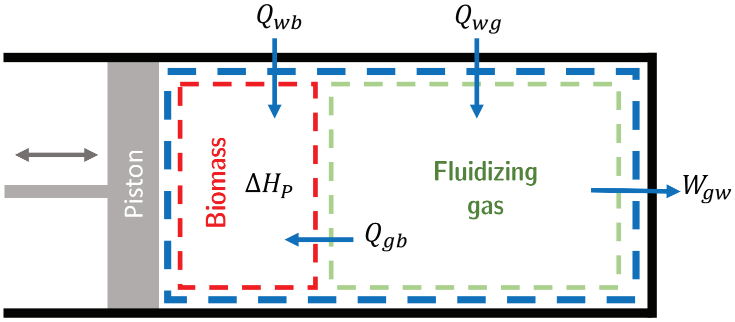

Figure 3. Transient closed control volume for analysis of the compression and expansion strokes of the RBCR. The red marks the closed control volume for the biomass, the green marks the closed control volume for the fluidizing gas, and the blue marks the control volume enclosing the cylinder for one cycle. We assume a well-mixed and evenly distributed fluidizing gas and biomass/bio-products mixture in this control volume; they are separated only to clearly show the direction of energy flow.

The change in internal energy for the fluidizing gas is $\Delta U_g = c_{vg} n_g \Delta T_g$ and the work term is $W_{gw} = P\Delta V_g$. Here, c_{vg}, n_g, ΔT_g, and V_g are the constant-volume molar specific heat, number of moles, change in temperature, and volume of the fluidizing gas, respectively. The first law for the control volume of the fluidzing-gas is written as

$$\begin{aligned} \Delta U_g &= Q_g - W_g = -Q_{gb} + Q_{wg} - W_{gw} \\ \Delta U_g &= c_{vg} n_g \Delta T_g = -Q_{gb} + Q_{wg} - P\Delta V_g. \end{aligned} \tag{1}$$

The change in enthalpy of the biomass, ΔH_b, includes the change in sensible enthalpy, ΔH_S, and enthalpy of pyrolysis reactions, ΔH_P, as $\Delta H_b = \Delta H_S + \Delta H_P = \Delta U_b + \Delta(PV_b)$. We assume that there is no volumetric change of the biomass. The change in enthalpy due to pyrolysis is $\Delta H_P = m_P \Delta h_P$, and the change in sensible enthalpy is $\Delta H_S = m_b c_b \Delta T_b$. Here m_p, Δh_P, m_b, c_b, and ΔT_b are the pyrolyzed mass, mass-specific enthalpy of pyrolysis, biomass mass, biomass specific heat, and change in biomass temperature, respectively. The first law for the control volume for the biomass is written as

$$\begin{aligned} \Delta U_b &= Q_b - W_b = Q_{gb} + Q_{wb} - W_b \\ \Delta U_b &= m_b c_b \Delta T_b + m_P \Delta h_P - V_b \Delta P = Q_{gb} + Q_{wb} \end{aligned} \tag{2}$$

IV. Ideal Model as Explanation of Cycle

We can create a simple model of biomass decomposition in an RBCR to illustrate its utility and working principles. Heat transfer to the RBCR walls is not considered, $Q_{wb} = Q_{wg} = 0$, and all the biomass is pyrolyzed: $m_P = m_b$. Additionally, the change in pressure term is considered to be small for the biomass solid, $V_b \Delta P \ll m_b c_b \Delta T_b$, and $V_b \Delta P \ll m_P \Delta h_P$. Eqs. 1 and 2 are rewritten as

$$\Delta T_g = -\frac{Q_{gb} + P\Delta V_g}{c_{vg} n_g}, \tag{3}$$

and,

$$Q_{gb} = m_b c_b \Delta T_b + m_b \Delta h_P. \tag{4}$$

The fluidizing gas of an RBCR is presented in pressure-volume and temperature-state space in Fig. 4. In that figure, the states 1-4 are label and undergo:

1. **1-2** Isentropic compression of the fluidizing gas, requiring W_{in}. The compression is fast relative to any possible heat transfer process, so $Q_{gb} = \Delta T_b = 0$.
2. **2-3** Isobaric heat transfer from the fluidizing gas to the biomass for conversion, Q_{gb}. The biomass undergoes "complete" conversion at a specified temperature typical of fast pyrolysis.
3. **3-4** Isentropic expansion of the fluidizing gas, extracting, W_{out}. The expansion is fast relative to any possible heat transfer process, so $Q_{gb} = \Delta T_b = 0$.
4. **4-1** Isochoric heat transfer from the biomass to the fluidizing gas, Q_{gb}. This quenches the undesirable secondary pyrolysis reactions.

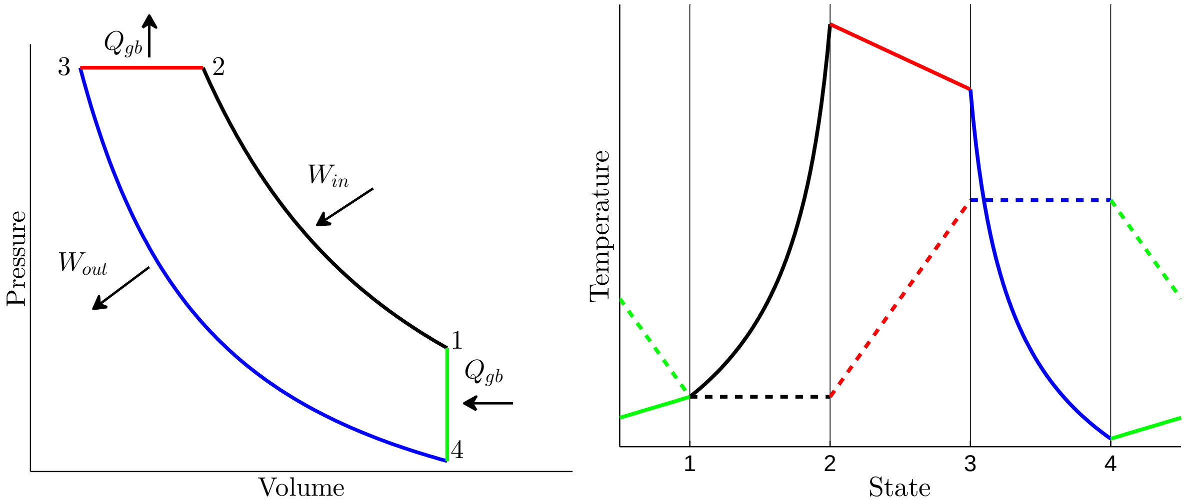

Figure 4. ***Left:*** **RBCR cycle of fluidizing gas in pressure-volume space. Cycle proceeds counter clockwise. 1-2: W_{in} work required for isentropic compression of the fluidizing gas. 2-3: Q_{gb} is the isobaric heat transfer from the fluidizing gas to the biomass. 3-4: W_{out} is the work extracted by isentropic expansion of the fluidizing gas. 4-1: Q_{gb} is isochoric heat transfer from the biomass to the fluidizing gas.** ***Right:*** **RBCR cycle in temperature-state space. Solid lines represent the fluidizing-gas temperature. Dashed lines represent the biomass temperature.**

V. Transient RBCR Control Volume

The model presented in Sec. IV is illustrative, so it may introduce the idea of the RBCR cycle; however, this analysis is not detailed enough for comparisons to other thermo-chemical conversion schemes. A more detailed treatment will be presented in this section to predict the transient response of the RBCR. Differential equations are formulated from the application of the first law to the fluidizing gas and the biomass/bio-products in the reactor (Eqs. 1 and 2).[32, 33] The time-rate form of Eq. 1 is

$$\frac{dT_g}{dt} = \left(-\dot{Q}_{gb} + \dot{Q}_{wg} - P\frac{dV_g}{dt} \right) / (c_{vg} n_g). \tag{5}$$

Inspection of Eq. 5 implies that the time-rate of change of temperature is increased by cylinder volume decrease and decreased by heat transfer to the surroundings. Additionally, the dV_g/dt term is prescribed by considering the kinematic motion[34] of the piston.

The biomass is assumed to be a collection of independent spheres that act as a lumped mass, m_b, with a constant volume and specific heat c_b. However, individual fractions of m_b are permitted to evolve as computed by the first-order kinetics mechanism in Diebold[35] (Fig. 5). Additionally, the rate of energy loss due to pyrolysis, $\Delta\dot{H}_P = \dot{m}_P \Delta h_P$ is included in the calculations. So, Eq. 2 can be rewritten to predict the biomass temperature (T_b) change as

$$\frac{dT_b}{dt} = \left(\dot{Q}_{gb} + \dot{Q}_{wb} - \Delta\dot{H}_P + V_b \frac{dP}{dt} \right) / (m_b c_b). \tag{6}$$

The dP/dt term can be related to the time rate of change of the fluidizing-gas temperature and volume change through the differentiation of the logarithm of the ideal gas law as

$$\frac{dP}{dt} = P \left(\frac{1}{T_g}\frac{dT_g}{dt} - \frac{1}{V_g}\frac{dV_g}{dt} \right). \tag{7}$$

The rate of heat loss from the pyrolysis reactions requires the calculation of the rate at which the biomass is decomposed. This is modeled with a kinetics mechanism found in the literature. The emerging nature of the biomass pyrolysis modeling field[28, 36–52] presents a number of options to model the production rates of bio-products. Our choice of mechanism is based on the favorable comparison of experimental data[53, 54] of cellulose pyrolysis kinetics at high heating rates to the results predicted from the Diebold[35] model. The first-order kinetic rates of Arrhenius form, $k_i = A_i \exp(E_i/(R_u T_b))$, are tabulated for each component in Diebold.[35] Inspecting Fig. 5, the rate of mass production of each component can be written as

$$\dot{m}_{VC} = -k_{CA} m_{VC} - k_{CC} m_{VC}, \tag{8a}$$
$$\dot{m}_{CW} = k_{CC} m_{VC} + k_{AC} m_{AC}, \tag{8b}$$
$$\dot{m}_{AC} = k_{CA} m_{VC} - k_{AC} m_{AC} - k_{AG} m_{AC} - k_{AV} m_{AC}, \tag{8c}$$
$$\dot{m}_{PV} = k_{AV} m_{AC} - k_{VG} m_{PV} - k_{VT} m_{PV}, \tag{8d}$$
$$\dot{m}_{SG} = k_{AG} m_{AC} + k_{VG} m_{PV}, \tag{8e}$$
$$\dot{m}_{ST} = k_{VT} m_{PV}. \tag{8f}$$

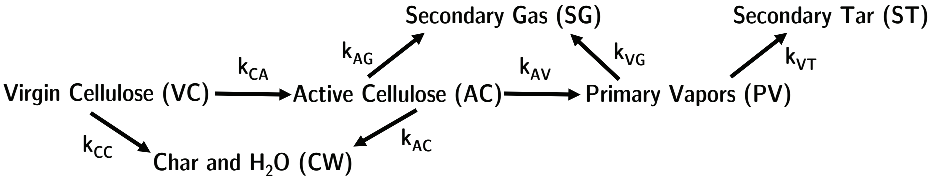

Figure 5. Mechanism for cellulose pyrolysis adapted from Diebold.[35]

The mass-specific heat of pyrolysis reaction is taken to be $\Delta h_P = 538$ kJ/kg.[53] The mass-conversion-rate due to pyrolysis, $\dot{m}_P$, is assumed to be the rate at which virgin and active cellulose is decomposed; so, the rate of change in enthalpy due to the pyrolysis reactions is

$$\Delta\dot{H}_P = \dot{m}_P \Delta h_P = \left(k_{CC} m_{VC} + k_{AC} m_{AC} + k_{AG} m_{AC} + k_{AV} m_{AC} \right) \Delta h_P \tag{9}$$

Radiation and combined natural/forced convection are included in the heat-transfer terms in Eqs. 5 and 6; the heat-transfer coefficients are modified to account for transpiration effects, where appropriate.[55] The walls are assumed to have the properties of steel[56] and the biomass is assumed to have the thermo-physical properties of cornstover.[57] The convection to the walls[58] and to the biomass[59] is assumed to be steady by non-dimensional analysis. Thermo-physical properties for the fluidizing gas are calculated using Cantera[60] with the appropriate thermodynamic data[61] fitted to polynomials of temperature.

The system of Eqs. 5, 6, and 8 are integrated in time to calculate the evolution of pressure, biomass temperature, fluidizing-gas temperature, and conversion fractions for the compression and expansion strokes of the RBCR. The initial conditions are:

1. The biomass begins as virgin cellulose (VC) (Fig. 5).
2. The initial biomass and fluidizing-gas temperatures are $T_b = T_g = 22$°C.
3. The mass of the biomass m_b, and the biomass radius r_b are specified for one cycle.

MATLAB[62] is used to perform the integration for a prescribed cycle period which is determined by the engine speed; the results for the integrations presented herein are not sensitive to the ODE solver tolerance or algorithm, bringing confidence in the calculation result.

VI. Example Calculation

In this section, results are presented that describe the reactor performance per the formulation presented in the previous section. The core of the reactor is a 7.3 L 8-Cylinder 4-Stroke Diesel Engine. Intended for use in trucks, the engine has a bore of 106 mm and a stroke of 104 mm, and is cycled at 100 rpm. The volumetric compression ratio is 22.4, and we assume that the dynamic compression ratio is 75% of this value.

A mixture of argon and spherical biomass particles 50 μm in diameter with thermo-physical properties of corn stover is injected into the intake of the engine (properties from Mani et al.[57]).

A time-history of reactor pressure P, fluidizing-gas temperature T_g, and biomass temperature T_b is presented as Fig. 6 (left). The maximum temperature of the biomass is over 500°C and the heating rate exceeds 5000°C/s during the compression stroke; these temperatures and heating rates are consistent with those found in the literature for fast pyrolysis.[26] The bio-products are rapidly cooled at over -5000°C/s during the expansion stroke; the rapid bio-product cooling rates will quench the undesirable secondary pyrolysis reactions. For context, -60°C/s cooling in a bench-scale fluidized bed reactor has been reported in the literature.[31] Furthermore, those researchers investigated the temporal effect on fractional condensation and found that the water and acid content of the bio-products increased with increasing time after volatiles formation, affirming the idea that "[t]he [secondary pyrolysis] reactions should be stopped quickly after volatile evolution in order to maximize bio-oil yield."[31]

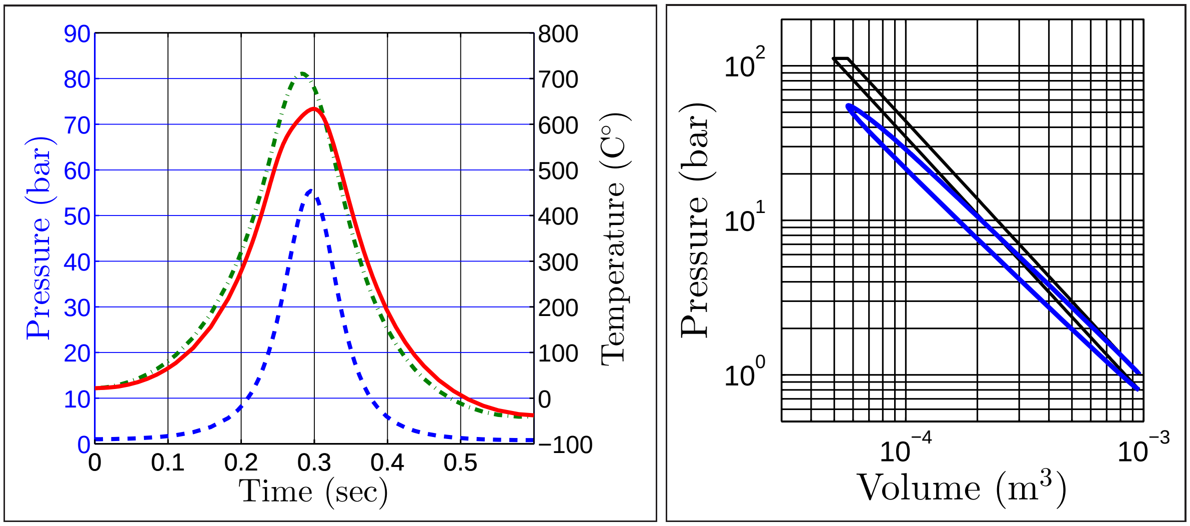

Figure 6. Compression (0-0.3 s) and expansion (0.3-0.6 s) strokes for the pilot-scale experiment. *Left:* Calculation of reactor pressure P (blue, dashed), fluidizing-gas temperature T_g (green, dashed-dot), and biomass temperature T_b (red, solid) for a reciprocating engine used for thermo-chemical biomass conversion. *Right:* Calculated pressure-volume diagram for reciprocating engine for thermo-chemical biomass conversion. The solid blue line is the RBCR cycle predicted by the differential equations described in Sec. V, and the solid black curve is the ideal RBCR cycle described in Sec. IV.

The compression and expansion strokes are shown as Fig. 6 (right) in pressure-volume space (the cycle proceeds counter clockwise). The compression requires input energy, but a significant fraction of this energy can be extracted during the expansion stroke to compress the gas within another cylinder on the same crankshaft. The energy required for one cycle is the area between the curves in Fig. 6 (right). The solid blue curve in Fig. 6 (right) is the RBCR cycle predicted by the differential equations described in Sec. V, and the solid black curve is the ideal RBCR cycle described in Sec. IV. The solid black curve marking the ideal RBCR cycle reaches a higher pressure because we neglected heat transfer to the biomass and the wall during the compression stroke.

In Fig. 7, the biomass weight fraction evolution is presented per the Diebold[35] mechanism. The virgin and

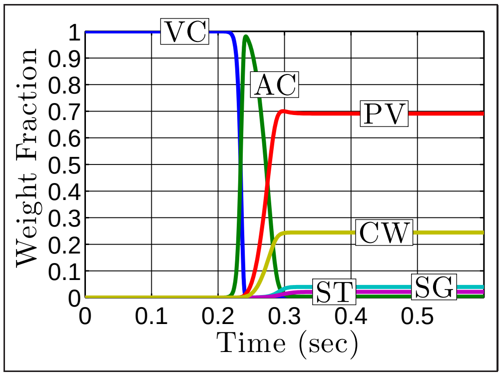

Figure 7. Compression (0-0.3 s) and expansion (0.3-0.6 s) strokes for the pilot-scale scale experiment. Calculated weight fractions vs. time for the proposed thermo-chemical conversion cycle computed from Diebold[35] mechanism. VC: Virgin Cellulose, CW: Char and H_2O, AC: Active Cellulose, PV: Pyrolysis Vapor, SG: Secondary Gas, ST: Secondary Tar.

active cellulose is degraded primarily between 0.2-0.3 s. This phenomena manifests itself in the calculated biomass temperature (Fig. 6 (left)) as a slight change in heating rate; this is because appreciable amounts of energy are being utilized for the heat of pyrolysis during that time ($\Delta \dot{H}_P$ in Eq. 6). At the end of an expansion stroke, 70% (by weight) of the biomass is converted to pyrolysis vapor. Little undesirable secondary gas and tar are produced because the rapid expansion quenches all reactions within cylinder.

VII. Comparison to the State of the Art

The input energy per unit mass of biomass required to thermo-chemically convert biomass to bio-products is a figure of merit to be used to compare the proposed conversion scheme to the state of the art. An estimate of the energy (1 MJ/kg) required to comminute (pulverize) the biomass to 50 microns in diameter is included.[57] The ratio of power available from bio-oil production to the power consumed by the thermo-chemical conversion process, η, is also a figure of interest.

In Table 1, we compare an RBCR constructed from a 7.3 L diesel engine and a small fluidized bed reactor (FBR) found in the literature in Boateng et al.[31] They will be compared because they have nearly the same size/footprint, and thus, by crude assumption, similar capital costs. For the fluidized-bed reactor, the input energy per unit mass of biomass (e_{in}) includes the energy from the heaters (Table 9 in Boateng et al.[31]). Calculations predict that there is significantly less energy required to operate the RBCR per unit mass of biomass, and the biomass feedrate is significantly increased. Additionally, calculations indicate that the RBCR concept is scalable because of the favorable volume/surface-area ratio. This assertion is based on calculations of the RBCR at smaller and larger scales than those provided here (these are omitted for brevity).

Table 1. Comparison of reciprocating biomass conversion reactor (RBCR) with the small-scale fluidized-bed reactor found in Boateng et al.[31] Tabulated are: number of cylinders, bore, stroke, engine speed, mass flow of fluidizing gas $\dot{m}_{FG}$, input energy per unit mass of biomass required to thermo-chemically convert the biomass e_{in}, the feedrate of biomass $\dot{m}_b$, and ratio of power available from bio-oil out to the power required to operate the reator, η.

Make/Model	Disp.	Cyl.	Bore mm	Stroke mm	RPM	$\dot{m}_{FG}$ kg/hr	e_{in} MJ/kg	$\dot{m}_b$ kg/hr	η (-)
Ford/Powerstroke (RBCR)	7300 cc	8	104	106	100	38 (Ar)	1.8	4.3	7.6
Small Fluidized Bed	-	-	-	-	-	4.8 (N_2)	3.5	2.2	3.5

VIII. Conclusion

A simple model and results for the decomposition of pulverized cellulosic biomass within a gas of transient temperature and pressure has been presented. Preliminary results indicate that complete thermo-chemical conversion can be completed within the compression and expansion strokes of a repurposed 4-stroke motor; this warrants further study on the topic.

Relative to the state of the art (which we consider to be the fluidized bed reactor), calculations predict that, for a comparable footprint, the proposed reciprocating biomass conversion reactor (RBCR) will increase the biomass throughput by ≈100% and decrease the mass-specific energy requirement by ≈50% to thermochemically convert biomass to bio-oil, bio-char, and bio-gas by fast-pyrolysis.

The transformative increase in efficiency relative to the state of the art is derived from the expansion stroke. The instant following desired biomass conversion, the bio-products and fluidizing gas reside within the cylinder at an elevated temperature and pressure. This is surplus process heat, and in contrast to the state of the art, the surplus process heat is transferred and reused mechanically through the crankshaft to another piston/cylinder during the expansion stroke. The expansion stroke rapidly quenches the undesirable secondary pyrolysis reactions an order of magnitude more quickly than the state of the art. This should improve the bio-oil quality because the residence time within the reactor can be more accurately controlled.

Acknowledgments

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