THERMO-CHEMICAL BIOMASS CONVERSION BY PISTON COMPRESSION OF SURROUNDING GAS

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Introduction

Thermo-chemical biomass conversion by pyrolysis to bio-oil, biochar, and non-condensable gases is a part of an attractive path to an alternative energy source because of the upgrade in heating value and density. ¹ This is a short note intended to highlight the prospects of the use of a piston to compress a gas that surrounds biomass in a cylinder so that the biomass may be heated for thermo-chemical conversion to bio-oil, biochar, and non-condensable gases. An example calculation is presented where argon and small amounts of biomass (110 ppm) are injected into a high compression engine turning at low speed (15 rpm). This strategy is found to have bio-products, energy recovery, and power requirements that are similar to those reported in the literature for fluidized-bed fast pyrolysis reactors.

The typical 4-stroke cycle is: intake, compression, power, and exhaust; this is replaced with: intake, compression, expansion, and exhaust. The intake stroke draws in a two-phase mixture of compression gas and pulverized biomass. The compression stroke heats the compression gas nearly adiabatically by PdV work and transfers energy to the pulverized biomass by combined natural/forced convection and radiation. The expansion stroke rapidly decreases the temperature and pressure of the bio-products and compression gas. The exhaust stroke forces the bio-products and compression gas from the cylinder. During the rapid cooling of the pyrolysis vapors during the expansion stroke bio-oil could condense in the cylinder. This could be addressed by having the exhaust valve situated so that the piston could "shovel" liquid products from the cylinder during the exhaust stroke. The heat released by condensation of the pyrolysis vapor is not included in the following calculations.

Energy Balance - Reactor Temperature Estimation

In this section, we formulate equations to predict the temperature of the compression gas and the biomass in the reactor. The compression gas is the gas that is injected into the cylinder along with the biomass. Consider a closed control volume around the compression gas that is uniform and excludes the biomass. The change in internal energy of the compression gas (U_g) is $\Delta U_g = Q_g - W_g$. Here, Q_g is the heat transfer into the compression gas from the surroundings, and W_g is energy transfer from the compression gas to the surroundings. Note that $\Delta U_g = c_{vg}n_g\Delta T_g$, where T_g is the temperature of the compression gas, c_{vg} is the molar specific heat at constant volume of the compression gas, and n_g is the number of moles of the compression gas. The pressure work on the compression gas volume (V_g) is $W_g = PdV_g$; so, the time-rate form of the energy balance is

$$c_{vg}n_g\frac{dT_g}{dt} = \dot{Q}_g - P\frac{dV_g}{dt}.$$
(1)

Inspection of Eq. 1 implies that the time-rate of change of temperature is increased by the volume decrease and decreased by heat transfer to the surroundings. The compression is isentropic if $\dot{Q}_g = 0$.

The heat transfer of the compression gas to the surroundings is

 $\dot{Q}_g = \dot{Q}_{wg} + \dot{Q}_{bg}$, where \dot{Q}_{wg} is the heat transfer from the walls to the compression gas and \dot{Q}_{bg} is the heat transfer from the biomass to the compression gas. Radiation and combined natural/forced convection are included in both terms. The walls are assumed to have the properties of steel² and the biomass is assumed to have the thermo-physical properties of cornstover.³

The biomass is assumed to be a collection of independent spheres that act as a lumped mass; so, the temperature change is predicted as

$$m_b c_b \frac{dI_b}{dt} = -\dot{Q}_{bg} + \dot{Q}_{bwr} + \dot{Q}_{\Delta h_p},\tag{2}$$

where \dot{Q}_{bwr} is the heat transfer from the biomass to the walls by radiation and $\dot{Q}_{\Delta h_p}$ is the rate of energy loss due to pyrolysis. The mass and specific heat of the biomass (m_b and c_b) are assumed to be constant through the themro-chemical conversion process; however, individual fractions of m_b are permitted to evolve as computed by the Diebold⁴ mechanism. The heat of pyrolysis reaction is taken to be $\Delta h_p = 538 \text{ kJ/kg.}^5$ The mass-loss-rate due to pyrolysis (\dot{m}_p) is taken to be rate at which the Diebold⁴ model predicts the virgin and active cellulose decompose; so, $\dot{Q}_{\Delta h_p} = \Delta h_p \dot{m}_p$. This is a crude treatment which should be revisited.

The combined natural/forced heat transfer coefficients are found from correlations.² The natural convection to the walls⁶ and to the biomass⁷ are assumed to be steady by non-dimensional analysis. Thermo-physical properties for the compression gas are calculated using Cantera⁸ with appropriate thermodynamic data.⁹

Example Calculation of Conditions

The proposed arrangement is to use a cylinder from a high compression ratio ($\approx 20:1$) reciprocating engine at low-speed ($\approx 15-60$ rpm) driven by an external energy source. Eqs. 1 and 2 are integrated in time through the compression/expansion strokes of one cycle for one cylinder of a 7.3 L International Harvester Diesel Engine turning at 15 rpm. The compression gas is argon; the biomass is comprised of spherical particles 190 µm in diameter with thermo-physical properties of corn stover.³ A time-history of reactor pressure *P*, compression gas temperature T_g , and biomass temperature T_b for the reactor is presented as Fig. 1. The maximum temperature of the biomass is over 500 °C at a pressure of over 60 bar. The heating rate exceeds 600 °C/s during the compression stroke and then is rapidly cooled at over -500 °C/s during the expansion stroke. The temperature of the compression-gas/biomass-products is calculated to be below ≈ 0 °C at the end of the expansion stroke; no phase changes are included in this calculation.



Figure 1. Calculation of reactor pressure *P* (dashed), compression gas temperature T_g in (dashed-dot), and biomass temperature T_b (solid) for a reciprocating engine used for thermo-chemical biomass conversion.

For this calculation, 143 mg of corn stover that pyrolyzes as cellulose is assumed to have been injected as a "dusty gas" (as defined by Marble¹⁰) into 1 cylinder of the reactor; for the 8-cylinder/4-stroke process, this results in a 0.6 kg/hr processing rate of biomass. By volume, the concentration of the ground stover is calculated to be 112 ppm. The requirement for compression-gas feed is 200 mg/s/cylinder. For the 8-cylinder/4-stroke process this requires 5.4 kg/hr of argon.



Figure 2. Pressure-Volume diagram for reciprocating engine for thermochemical biomass conversion.

The compression/expansion strokes are presented in pressurevolume space in Fig. 2 with arrows indicating the cycle direction. This pressure-volume diagram presents an advantage of the reciprocating reactor by illustrating the potential to do *PdV* work during the expansion stroke that can be extracted from each cycle to be used in another cylinder of the reactor on the same crankshaft (noting that compression occurs every 90° per crankshaft revolution in an 8-cylinder engine). Assuming 80% mechanical efficiency and including the energy required to comminute the biomass, \approx 750 W are required to run the apparatus at 15 rpm.



Figure 3. Weight fractions vs. time for the proposed thermo-chemical conversion cycle computed from Diebold's mechanism. VC: Virgin Cellulose, CW: Char and H₂O, AC: Active Cellulose, PV: Pyrolysis Vapor, SG: Secondary Gas, ST: Secondary Tar.

In Fig. 3, the evolution of the biomass weight fraction is presented per the mechanism of Diebold. At the end of an expansion stroke, very little secondary gas is produced, and over 70% of the biomass is in the form of pyrolysis vapor. The virgin and active cellulose is degraded primarily between 1.5-2.0 s. This phenomena manifests itself in the calculated biomass temperature (Fig. 1) 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.

Discussion

In Boateng et al.¹¹ and Mullen et al.¹², the researchers report a figure of merit termed "energy recovery;" this is the estimated ratio of the heat of combustion of the bio-products to that of the feedstock and required input heat. In Boateng et al.¹¹, the researchers report a balance of input biomass to bio-products of 60.7% bio-oil, 12.9% bio-char, and 11.3% non-condensable gas; this infers a mass-loss of 15.2%, which is attributed to bio-products being trapped in the lines and the reactor. They report an energy recovery of 50-55% based on bio-oil as a product. In this report, we use the mass balance and the heating values reported in that work for the energy recovery estimate for the proposed method of thermo-chemical conversion; the result is an energy required to comminute the corn stover, ³ the energy recovery is 59%.

The feed-rates computed here are comparable to those found in the literature for bench-scale fluidized-bed fast pyrolysis. For example, Boateng et al.¹¹ report feed-rates of 2.5 kg/hr of switch grass with 4.8 kg/hr of N₂ as a fluidizing gas. Mullen et al.¹² report 1.0-1.6 kg/hr of corn cobs or corn stover with the same apparatus. With the proposed cycle, it is calculated that 0.6 kg/hr of corn stover could be processed with 5.4 kg/hr of Ar required as a compression gas.

Conclusion

In this work, we assess the feasibility of using piston compression for biomass conversion. The biomass is injected as a "dusty gas" into the cylinders of a reciprocating engine along with a compression gas for thermo-chemical conversion. Much of the energy required to compress the gas by PdV work can be recaptured for use in another cycle of piston compression on a shared camshaft, yielding an efficient apparatus. The bio-products and compression gas can be routed through a cyclonic separator, as in other fast pyrolysis methods.¹³ For the proposed cycle, per the mechanism of Diebold, very little secondary gas is produced, and over 70% of the biomass is in the form of pyrolysis vapor. Engine speed can be tuned to a desired time-temperature history to alter the fractions of the bio products. Additionally, it is not clear that the Diebold⁴ mechanism is appropriate for the calculated reactor pressures of over 60 bar; Mok and Antal¹⁴ and others have found a significant effect of pressure on the heat of pyrolysis and the rate at which bio-products are formed.

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