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EFFECTS ON BOILER EFFICIENCY STANDARDS OF PULVERIZING COAL

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ABSTRACT

This paper examines the effects of particle size on the calorific value of hydrocarbons, shedding light on the thermodynamics of pulverizing coal in a commercial power plant. Both laboratory testing results and energy balances around an actual pulverizer are presented.

Although tacitly known to any power plant engineer, efficient combustion may be seen in two parts: preparation of the material's surface/mass ratio, and then its combustion with the proper air/fuel mix and associated mechanics. This work attempts to put a thermodynamic face on the first part. A theory is presented which demonstrates that a hydrocarbon's surface/mass ratio affects its potential to release its full chemical energy. This theory has been generally supported in this work by laboratory testing of pure substances; however this testing was not conclusive and should be repeated. If an optimum surface/mass is not achieved, unburned combustibles will result - and this regardless of subsequent air/fuel mixtures and/or burner sophistications. This work is suggests that an optimum surface/mass ratio exists for each hydrocarbon substance (and coal Rank); however, once this optimum has been reached, a higher surface/mass provides no further benefit.

Since surface tension describes a material's free energy, an aspect of surface tension, termed hydrogen bonding free energy, was shown to relate to the Δcalorific value penalty associated with non-optimum surface/mass ratio. A correlation was developed relating surface/mass ratio to observed an Δcalorific value penalty and hydrogen bonding free energy. This correlation's form may be applied to coal if supported with additional research.

The impetus for this work was the ASME Performance Test Code 4's allowance of pulverizer shaft power to influence boiler efficiency's "credit" term, thus affecting efficiency. It was demonstrated that surface/mass affects calorific value and thus efficiency. However, there is no observable difference between grinding a hydrocarbon to a given surface/mass ratio, versus manufactured spheres.

Although laboratory preparation of coal samples should emulate pulverizer action, this work suggests that a renewed and careful review of laboratory procedures is required. Recommendations are provided for critique and debate.

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NOMENCLATURE

A_M = As-Fired surface area/mass ratio, cm^2/gm
A_0 = Surface area/mass ratio associated with complete availability of chemical energy, cm^2/gm
CV = Calorific Value
D_{Mj} = Mean particle size for case j
ΔE = Observed difference in CV, ΔkJ/kg (ΔBtu/lbm)
= $CV(A_0) - CV(A_M)$
G = Gibbs free specific energy
H = Total specific energy
k = Boltzmann's constant
K = Equilibrium constant for chemical reaction
m_{AF} = As-Fired fuel flow, lbm/hr
NG^P = Non-Free specific energy, pulverizer output
P = Pressure
P_{SHAFT} = Brake shaft pulverizer power, Btu/hr
R = Gas constant
s = Specific entropy
T = Temperature
U = Internal energy
γ^T = Total surface tension, Newton/meter
γ^H = Hydrogen bonding free energy, Newton/meter
Γ_M = Transfer constant, $gram(m/J)^2$

INTRODUCTION, PULVERIZERS AND CALORIMETRICS

This section discusses the development of theoretical fundamentals used to understand why any combustible fuel's surface/mass ratio may influence how efficiently it burns. This section is followed by presentation of experimental evidence. Both sensitivity studies and monitoring of a commercial coal pulverizer were also completed which support the conclusions.

The process of mixing a sample of coal with the notion of testing divisions of the sample for calorific value as a function of particle size - and expecting absolute uniformity of the samples - was not considered a profitable path. Coal's mineral matter (metal oxides and rocks) will grind differentially and will intrinsically bias results. A new approach employed plastics, formed into spheres of unusually tight tolerances. These included: Acrylic (PMMA), Acetate, PVC and Teflon (PTFE). The materials tested ranged from 12.7 mm diameter spheres, to samples ground to between 1.190 and 0.595 mm mean diameters (i.e., 16 to 30 mesh). Typically three to six sizes (plus the ground) were employed for each plastic. This testing led to several surprising conclusions regarding the role that surface/mass ratio plays, and offers suggestions for future development of coal pulverizer fineness criteria.

Testing spheres of pure chemicals demonstrated that the act of burning material with progressively higher surface/mass ratios (smaller particles), explains an expected full release of chemical energy (complete combustion under ideal conditions). However, this work also suggests that fineness has a definable limit; there is no difference between an infinitely small particle versus this limiting value. For all materials, this work demonstrated that any possible changes in internal energy (i.e., grinding samples) did not affect calorific value, only surface/mass ratio. For brittle materials such as Acrylic and coal, other than affecting surface/mass, and thus surface energy, grinding has no other energetic effects once temperature equilibrium was achieved.

In addition to laboratory testing, a detailed energy balance was conducted on a pulverizer using operational data obtained from the 610 MWe Boardman Coal Plant. It was demonstrated that the contribution of pulverizer shaft power to system energy balances, if any, was well within the limit of error and could not be determined solely from an As-Tested heat balance. This highlights the importance of the laboratory studies conducted in determining the effects of grinding. Boardman test results tend to support our laboratory findings, that allowing pulverizer shaft power to influence boiler efficiency is not correct. Pulverizer action affects the surface/mass ratio of brittle materials, its shaft power affects house electrical loads.

One objective of this work was to address the requirement of ASME's Performance Test Code 4 (2008) to include pulverizer shaft power as a "credit" in its determination of boiler efficiency; from its page 94:

> "§5-15.5, QrBX Auxiliary Equipment Power Credits, Btu/hr [P_{SHAFT}]. Typical auxiliary equipment includes pulverizers, gas recirculating fans, hot primary air fans, and boiler circulating pumps. ... ."

The other side of the understanding the grinding of coal lies with specifying how the material is prepared for calorific testing. Discussions with several laboratories specify that calorimetric samples are prepared as follows, as employed when multiple samples are being analyzed:

> For production runs, samples are ground or crushed such that 95% of the material passes a 60 Mesh (0.25 mm), mixing the coarse with fines (ASTM D2013 specifies 100% pass); then calorific testing the mix per D5865.

It is postulated that such practices may allow bias to the measured calorific value at two levels: 1) given there may be harsh sensitivity to calorific value (CV) versus the material's mean surface/mass ratio; and/or 2) coarse particles may well bias CV in a strongly non-linear manner. This paper attempts to at least "box" these questions. Bear in mind that a power engineer's common experience when testing coal-fired systems, results in an essentially random pattern (say within ±1%) of measured CVs when acquiring samples over as little as 30 minutes from the same stream. We are now suggesting it may be that such variations are due to laboratory techniques as much as coal's vagaries.

The efficiency of a steam generator is dependent on the thermodynamic balancing of product and reactant streams: ideal combustion products less losses found in the exiting streams; reactants consisting of the fuel stream's full potential of chemical energy, the As-Fired, and combustion air and miscellaneous input streams. In all methods of determining boiler efficiency, it is tacitly assumed that the described As-Fired fuel is available to deliver its full chemical energy. For purposes of this work, we wish to suggest metrics descriptive of this full chemical energy (i.e., a pulverizer's output); and whether a pulverizers' shaft power can directly affect fuel's internal energy.

Although the authors believe that pulverizing coal is emulated in the laboratory when preparing a sample for calorimetric testing (Lang, 2009), and this work suggests confirmation of this belief, we also recognize definitive proof awaits. We suggest continued research and testing.

INTRODUCTION, FREE ENERGY

Although the amount of academic literature on micro-combustion is vast, reaching back to the 1900s, it has fallen off precipitously over the past 20 years. The authors believe that there are but few viable works which relate combustion theory to either coal fineness associated with industrial pulverizers, or in critiquing laboratory procedures against theory. This said, we choose to separate the mechanics of mixing coal particles with combustion air (i.e., combustion mechanics), from a more fundamental understanding of why we grind coal. Although this work has experimental flaws, and these are discussed, it attempts to bridge thermodynamics to pulverizer performance.

Consider the most fundamental of thermodynamic principles, the description of free energy as given by:

$$G = H - Ts \qquad (1)$$

$$= U + Pv - Ts \qquad (2)$$

First, note that Eq.(2) is routinely differentiated holding pressure constant, then holding temperature constant. It can be easily demonstrated that $(\partial \Delta G / \partial T)_P = -\Delta s$, given that use of the internal energy term (U) is taken in the broadest sense of: chemical, surface, deformation, etc. This expression leads to one of the most important relationships in thermodynamics, that free energy of any reaction is related to thermo-chemical properties; i.e., $\Delta G^0 = -RT\,ln K$, where K is the reaction's equilibrium constant.

The action of a pulverizer is one of grinding combustible material; i.e., increasing its surface/mass ratio. In describing this process, consider that we are not concerned with changes in standard states (ΔG^0) of products less reactants, but rather in the consequences of not of grinding well. The goal here is to relate thermo-chemical properties to a pulverizer's ability to deliver all available chemical energy. Thus consider use of Eq.(2) as only applied to the product stream from a pulverizer, relative to ideal conditions, considered to be some finite surface/mass ratio (an optimum fineness). This difference can be thought of as a "non-free" energy of the product stream, a penalty; we chose the symbol ΔNG^P:

$$\Delta NG^P = (U + Pv - Ts)_{IDEAL} - (U + Pv - Ts)_{ACTUAL} \qquad (3)$$

where the "ideal" represents full release; in the differential:

$$dNG^P = dU + d(Pv) - d(Ts) \qquad (4)$$

In Eq.(4), it becomes obvious that as the full chemical potential is realized, dNG^P approaches zero (there is no non-free energy). However, if grinding a solid hydrocarbon insufficiently we must expect, upon burning, to produce less than the ideal products of CO_2, H_2O and SO_2. Tars, CO, unburned material, etc. will result, and the right-hand side of Eq.(4) must reflect that: $\int dNG^P > 0.0$.

If we consider that the right-hand side of Eq.(4) relates to insufficient grinding, then the larger the particle will yield a higher Δenergy penalty. We chose to define this penalty as ΔE; that is a calorific effect which is observable in the laboratory using a constant volume (V), constant temperature (T), bomb calorimeter. Thus the Pdv and sdT terms of Eq.(4) are zero. For completeness, changes in ΔE reflect a single reacting material (N=1); summarized as $\partial(\Delta E)_{T,V,N}$.

$$\partial(\Delta E)_{T,V,N} = (\partial U)_{T,V,N} + v(\partial P)_{T,V,N} - T(\partial s)_{T,V,N} \qquad (5)$$

In Eq.(5), $T(\partial s)_{T,V,N}$ is the irreversible loss which describes inefficient grinding, and where the $v(\partial P)_{T,V,N}$ term will have small numerical impact when conducted in a modern bomb calorimeter using high O_2 over-pressure.

To resolve the left side of Eq.(4), it was hoped that an index could be developed which encompassed all hydrocarbons, plastics to coal - a modeling nexus. Various thermo-chemical and mechanical properties were considered. An initial effort to describe dNG^P focused on the mechanical property of the Hardgrove Grindability Index, or HGI (ASTM D409). If this could be established for plastics, results might then be compared to coal which is routinely tested for this Index. However, testing plastics, given their malleable nature, resulted in melting the material when submitted to harsh grinding. Numerous other properties where investigated. We then turned to the use of surface tension. Note that the classic definition of total surface tension (γ^T), as a form of free energy, is defined by $(\partial \Delta G / \partial A_M)_{P,T,N}$; that is the relationship between free energy and surface/mass ratio.

However, two important variances to the classical use of surface tension must be considered. First, it is postulated that non-free energy is inversely related to surface tension. Second, recall that although surface tension may relate to a variety of systems (solid-liquid, vapor-solid, etc.), of interest here is the surface energy of a decomposing solid hydrocarbon (it is being burnt). Current teaching considers three components comprising total surface tension of a solid: free energy associated with dispersive forces, dipolar-dipolar interactions, and the free energy of hydrogen bonding (γ^H).

Attractive forces between molecules, in the classical sense, and, for our work, as found between branches of the same molecule per coal's interfacial layering (and as one would expect in any complex molecular structure such as DNA), may be defined as an approximate function of separation distances. For a wetted coal at the molecular level these may be viewed broadly as three types: dispersive forces having no impact on combustion; dipole-dipole interactions of non-water components (e.g., hydroxyl to matrix terminations); and hydrogen free bonding associated with water, for coal as a R-H...B type interaction (Birdi, 2009). We believe the latter effect can be related to coal's decomposition. For coal we see complexity between both hydrogen and the hydroxyl group to the coal's matrix, favoring the poorer Ranks but given their higher water & ash contents, adding considerable complexity. It is postulated that, as the consumption of outer hydrogen atoms implies combustion, overcoming the free energy of hydrogen bonding - or an equivalent effect - must therefore be inversely proportional to changes in NG^P with respect to surface/mass. This leads to Eq.(6). In this equation we have dropped the partial restraints anticipating that upon integration effects will cancel.

$$\partial NG^P/\partial A_M = \partial(\Delta E)/\partial A_M \propto 1.0 / (\gamma^H A_M) \tag{6}$$

Values for γ^H for polymers were obtained from Owens & Wendt (1969). A general study of γ^H values for coals was suggested by Tampy, *et al.* (1988). However, specific study of γ^H for unique coal types, such as anthracite and Powder River Basin (PRB) coals, appears wanting. This is understandable given the presence of coal's water and its high total surface tension; of course total drying will drive off volatiles, thus affecting CVs.

Note that whether a classically wetted solid, or a thin vapor film in contact with a combusting sphere, the physical property of surface tension as a free (potential) energy must hold. When applied to a solid hydrocarbon, it is assumed that the free energy of inter-molecular hydrogen forces - however normalized - offers a modeling nexus for all combustibles, plastic balls to coal. When integrating elements of Eq.(6), regarding the product stream, Eq.(7) is developed. As a definite integral, Eq.(7) suggests that a definable surface/mass ratio, A_0, yields a total release of chemical energy driving ΔE to zero.

$$\int_{A_M}^{A_0} \partial A_M/(\Gamma_M \gamma^H A_M) = \int_{\Delta E(A_M)}^{\Delta E_0} \partial \Delta E(A_M) \tag{7}$$

Integration limits are from an observed surface/mass (A_M) associated with a measured calorific value, to a surface/mass (A_0) associated with complete availability of chemical energy. The constant Γ_M was introduced into Eq.(7) as a transfer constant, converting the potential energy associated with hydrogen bonding to chemical release. If Eq.(7) is viable, Γ_M should be found constant for all hydrocarbons provided that the population of outer-layer hydrogen atoms allows for a measurable γ^H (or may otherwise be defined as discussed below). As a function of temperature it is anticipated that: $\gamma^H = f(\mathrm{kT})$. Γ_M has the reciprocal units of specific energy times energy flux, or (kg/kJ)/(J/m^2).

$$ln\ (A_M/A_0) = -\Gamma_M \gamma^H \Delta E(A_M) \tag{8A}$$

$$A_M = A_0\ exp\ (-\Gamma_M \gamma^H \Delta E) \tag{8B}$$

Eq.(8B) has similitude with the Arrhenius relationship (1889) for chemical reactions, teaching that reaction rates are proportional to *exp*(-ΔEnergy/RT). Note that what is claimed by Eq.(8A) is that the effects of not pulverizing properly (producing large coal particles and $\Delta E > 0.0$) is not a direct function of the coals' chemical energy (calorific value), nor its base chemistry (other that being a hydrocarbon, and given $\gamma^H > 0.0$); but is only a function of particle size! Eq.(8) suggests that the only influence on efficient grinding is the free energy associated with hydrogen bonding γ^H. By examining the slopes of a semi-log plot of Figure 3, Γ_M was determined by best fit to be 13.0, given γ^H has units of Newton/meter, and ΔE in kJ/kg; recall that 1.0 Newton/meter = 1.0 Joule/meter^2; thus:

$$A_M = A_0\ exp\ (-13.0\ \gamma^H \Delta E) \tag{9}$$

EXPERIMENTAL EVIDENCE

A spherical shape optimizes surface/mass ratio. For the same mass, multiple spheres versus a few will increase surface/mass as the square of the ratio of diameters. The grinding of coal produces, in the mean, spherical shapes. Although this work is concerned about the grinding of coal, given its heterogeneous nature and combined with any mineral matter, grinding to various sizes for direct testing of Eq.(9) was initially questioned. It was believed the presence of mineral matter alone would guarantee differential grinding effects. It is interesting that in the literature one can find numerous academics forming tar balls, hair balls, etc. used for study. Indeed, the authors first turned to making sucrose spheres, then obtained pure hydrocarbon crystals from helpful colleagues at a national laboratory. For various reasons, none of these initial efforts were successful. We then turned to precision plastic spheres used to confirm theoretical understanding. Although the plastic sphere work should be repeated, current results suggest that controlled coal experimentation with commercial pulverizers, or their laboratory equivalent, might prove beneficial.

The plastic spheres are tightly manufactured, having typical diameter and spherical tolerances < ±0.025 mm. Through selection, a whole number of spheres could be made to match approximately the largest sphere's mass; thus developing a constant mass per test sample for each material; see Figure 1 and Table A1. Note that to minimize errors associated with the modern calorimeter, a highly sensitive instrument, the mass of all samples should remain ≈constant. Table 1 lists the materials tested with their associated base data (columns 2, 3 & 6).

A test procedure is outlined in Appendix A. This has been improved from its original intent, and now forms recommendations for an improved testing protocol with the hope this work might be repeated with enhanced accuracy. Although performing Hardgrove Grindability testing was not successful, grinding to a 16x30 Mesh was achieved; this afforded a mean particle diameter of 0.595 mm (0.023 inch). Attempts to grind to smaller sizes were not successful as all the plastics used were too malleable; we encourage further efforts, possibly considering a crushing mechanism. For each material and each size, five calorimetrics were performed; excluding Acetate, a total of 85 tests were run on four plastics and 17 sizes. Of the 17 sizes tested, 3 sizes produced outlying data; of these all but one was explained by aged material whose manufacturing date was at least 5 years older than the next oldest. Bear in mind that polymer manufacturing (for PVC and Teflon) cannot guarantee that same number of monomers will results from lot to lot. Such manufacturing issues in combination with the fact that plastics chemically degrade, suggests that future testing use material from the same lot and of recent manufacture.

Of the remaining tests, a reduction in the standard deviation by one-half was typically achieved by rejecting no more than two in any given five runs for Acrylic and PVC. Although this would appear to be a high rejection, actual standard deviations (computed by Excel based on measured CVs) were reduced as follows: for Acrylic from ±4.83 to ±1.27 ΔBtu/lbm; and for PVC from ±9.66 to ±3.07 ΔBtu/lbm. Typical results are indicated in Fig. 2, note that the outlying data for this material (PVC) was manufactured 8 years before the next oldest. Teflon results scattered wildly as the sample size increased; the presented data represents a few consistent points aligning with general trends. Standard deviations for Teflon's CV were reduced from ±5.68 to ±1.21 ΔBtu/lbm. However this was achieved by rejecting 26 samples out of 51 Teflon tested; although of these, 21 of the rejected were associated with the largest sizes (7/32, 1/4 and 5/16 inch).

Testing Acetate was not successful, yielding an unacceptable data scatter. Note that the first of the listed values encompass all CVs tested (several sizes were repeated). Note also that there appeared no correlation between standard deviations and the material's base CV.

Because of these testing difficulties, the authors strongly encourage repeating this work using only Acrylic and anthracite; preparation and testing techniques are provided in Appendix A.

Figure 3 presents results associated with Acrylic, PVC and Teflon. Although for Acrylic, conditions approaching zero ΔE are not well defined, the broad results support Eq.(7)'s assumption of a finite integral; that an assumed infinitely large surface/mass is not required (vs. a finite A_0).

The "theory" as presented by dashed lines in Figure 3, employed the best fix value for A_0 and γ^H, used to confirm Eq.(9). **We find remarkable agreement between the results seen in Figure 3 and published γ^H values; see Table 1 (columns 4 vs. 5).** For example, the literature value of Acrylic's γ^H is 4.3, while the as-tested, based on Eq.(9), was 4.27 milli-Newton/m. In summary, these results allow the determination of ΔE as a function of an unique particle size (Mesh size). For example, this has been computed in Table 2 for a 30 Mesh criteria, and that Mesh which yields zero ΔE. From a computed ΔE we can then determine the relative change in boiler efficiency versus a full release of CV.

The technique developed by this work is also remarkable as holding witness to the strange behavior of Teflon, see Figure 3. We observe that although Teflon's CV is low, its γ^H is akin to Acrylic, but yet it produces ΔE penalties which lie between Acrylic and PVC. However, Teflon's A_0 is extreme at 115,264 cm^2/gm; this, versus 83.073 and 985.645 cm^2/gm for Acrylic and PVC respectively. And yet, with such apparent inconsistencies, the data of Fig. 3 remains consistent, noting that the first Teflon point is the 16x30 Mesh grind, the others being spheres. The answer may be that in describing Teflon, Eq.(9) is describing a highly malleable material, that A_M/A_0 approaches unity for such materials.

Figure 1: Typical As-Tested Configurations (using constant mass, variable surface area)

Table 1: Properties and γ^H Results of Materials Tested

Material	Calorific Value (Btu/lbm)	Density (gram/cm^3)	Listed Hyd. Bonding Free Energy, γ^H (10^{-3} Newton/m)	As-Tested (Best Fit) Hydrogen Bonding Free Energy, γ^H (10^{-3} Newton/m)	Comments
Acrylic (PMMA)	11535	1.1835	**4.3**	**4.27**	Tested 6 sizes: 1/2 to 1/16 inch, and 16x30 Mesh.
Acetate w/Diethyl Phthalate	8713	1.2800	**(n/a)**	**---**	Tested 7 sizes; CVs varied wildy, no viable results.
Polyvinyl Chloride (PVC)	8900	1.3050	**0.0 to 1.1**	**0.87**	Tested 4 sizes: 1/2 to 3/16 inch and 16x30 Mesh.
Teflon (PTFE)	2250	2.1750	**3.5 to 4.1**	**4.03**	Tested 7 sizes: 5/16 to 1/32 inch and 16x30 Mesh.

Table 2 is also interesting when comparing Acrylic and PVC that the ΔE penalty appears to have no functionality with E_0. The ΔE penalty at 30 Mesh for Acrylic is almost half that for PVC, but PVC has the lower CV. Further Acrylic requires only a 50 Mesh, versus PVC at 300, to achieve zero ΔE. Note that errors made with E_0 will not affect the slope seen in Figure 3.

Table 2: Sensitivity to a 30 Mesh

Material	Calorific Value, E_0 (kJ/kg)	ΔE Penalty at 30 Mesh (kJ/kg)	Mesh Size for $\Delta E = 0.0$
Acrylic	26830	136.66	50
PVC	20701	220.76	300
Teflon	5234	9.788	[very high]

Figure 4 presents Eq.(9) when considering only its exponential portion; i.e., plotted as the ratio A_M/A_0. Fig. 4 is presented only to suggest that such a plot developed for various coal Ranks would be illuminating for guiding grinding/crushing specifications for individual coal Ranks. Note that Figure 4 accents inconsistencies associated with the test data; it emphasizes both the promise and the need for repeat testing using improved techniques and materials. The great difference observed regarding PVC is caused by its low γ^H value versus those for Acrylic and Teflon.

The most serious result associated with this work lies with the fact that depending on how samples are prepared, measured CVs could well vary outside the repeatability error associated with the modern bomb calorimeter (typically with standard deviations < 0.10%). It could be that sample preparation could well contribute to the traditional variability found in coal-fired sampling.

PULVERIZER SENSITIVITIES

The energy flows in and out of an operating pulverizer were examined to determine the sensitivity of the heat balance to the pulverizer shaft power. Operational data (presented in Appendix B) was obtained from a Foster Wheeler pulverizer at the Boardman 610 MWe unit, burning PRB coal. The objective of this study was to understand the measurement accuracy required to determine if pulverizer shaft power could influence classical energy balances; i.e., the internal energy of the dry coal stream, aside from Primary Air heating.

To balance the energy around the pulverizer four input/output streams were considered: dry coal, water in the fuel, dry air, and moisture in the air. Upon mixing with hot Primary Air, a portion of fuel water evaporates, increasing the moisture in the exiting "dirty air" stream up towards the point of saturation. Temperatures of the inlet streams were measured and held constant. Outlet streams were assumed at equilibrium. Sensitivity studies assumed the boundary temperatures were constant given that the measured air temperatures were considered highly reliable (571.6 ^{o}F and 133.3^{o}F). Inlet and outlet enthalpies were then determined such that evaporation of fuel water could be computed. For these computations it was assumed that: seal air was small and could be ignored; radiation losses were constant; and pyrite losses were small and were ignored. The question then was to gage the effect of adding shaft power to the energy streams, and thus determining its possible impact on exiting fuel moisture and exiting air humidity.

Pulverizer testing was conducted twice given the first test results indicated the exit air stream was not saturated. The second test results confirmed a non-saturated state (results of the first test are reported here). The coal moisture at the pulverizer inlet was sampled at 30.55% moisture. Coal moisture at the exit was computed at 20.41% assuming no shaft power contribution. The computed exiting air relative humidity was computed at 74.27%. Taking the air to saturation would drive the coal's moisture to 15%.

When applying the As-Tested 0.317 MWe brake shaft power to the energy balance - again, assuming a constant boundary temperatures - resulted in altering exit fuel moisture from 20.41% to 19.58% by weight. The capacitances of the system will, of course, favor the air streams. When lowering the fuel moisture by 1.0% weight, from 30.55%, assuming no shaft power contribution, the exit fuel moisture was altered from 20.41% to 19.58%. Grab sample testing indicated that exit fuel moisture, for the As-Tested conditions was approximately 21% with an uncertainty of ±1%. Testing practices would suggest that looking for a ±1% change is a marginal exercise. Also, consider that the pulverizer tested rotated at 32 rpm, which is hardly sufficient to add measurable frictional dissipation via mechanical work to the air stream.

Test results confirm that the energy balance around the pulverizer may be only marginally sensitive to shaft power. If assuming shaft power is consumed in altering the fuel's surface/mass ratio, decreasing the ΔE term - and does nothing to alter the coal stream's internal energy - then the energy balance performed appears to produce nominal expectations. Again, such surface/mass effects should be emulated when testing coal for calorific value following established laboratory practices.

AN ALTERNATIVE APPROACH

An approach is offered which employs Eq.(9) using a commercial pulverizer; i.e., emulating a "laboratory instrument". If we assume A_0 of Eq.(9) is constant for a given hydrocarbon, we can then equate two conditions:

1) where no grinding occurs, a $\Delta E(A_{M1})$ found at the pulverizer inlet (Hammer Mill outlet); and
2) where optimum grinding occurs found at the pulverizer outlet, thus $\Delta E(A_{M2}) = 0.0$:

$$A_{M1}/A_{M2} = \mathit{exp}\,[-13.0\,\gamma^{H}\,\Delta E(A_{M1})\,] \qquad (10)$$

Eq.(10) leads directly to an energy flow balance with measure shaft power (P_{SHAFT}), by multiplying ΔE by the pulverizer's fuel flow; note the negative sign remembering ΔE is a penalty, and the units conversion:

$$\begin{aligned} P_{SHAFT} &= -\,m_{AF}\,\Delta E(A_{M1}) \\ &= [m_{AF}/(13.0\,\gamma^{H}\,2.326)]\,\mathit{ln}\,(D_{M1}/D_{M2})^2 \qquad (11) \end{aligned}$$

Eq.(11) allows the back-calculation of an <u>effective</u> γ^H for the wet, As-Fired coal based on measured coal flow, shaft power and assumed input/output particle sizes:

$$\gamma^{H} = [0.066142\,m_{AF}/P_{SHAFT}]\,\mathit{ln}\,(D_{M1}/D_{M2}) \qquad (12)$$

For Boardman's As-Tested conditions the mean particle size from its Hammer Mills was taken as $D_{M1} = 8.0$ mm (5/16 inch). Boardman's pulverizer output was taken at an assumed optimum of a mean 200 Mesh ($D_{M2} = 0.074$ mm). With these assumptions, an effective γ^H value was typically computed at 30 milli-N/m. Given the complexity of water's presence ... its effects on coal's micro-pores, the interrelationship between pure water's free energy versus the dry coal's free energy at the molecular level ... the range of effective γ^H must lie between pure water and the available laboratory evidence for low-water coal. For high Rank coals this value was estimated from the literature at 10 milli-N/m (Birdi, 2009). Pure water's value is 51.0 milli-N/m for combined dipolar and hydrogen bonding; this, from a total surface tension of 72.8 milli-N/m (note that dispersive forces have no effect on combustion).

To test Eq.(12), four years of operational data was obtained for the Boardman pulverizers. Through use of a selection criteria, only high-load data was analyzed (the criteria included: > 595 MWe; uncorrected pulverizer current x voltage > 225 kW; and indicated fuel flow > 117.5 k-lbm/hr). Remarkably different effects were observed, indicating that for a degraded pulverizer (or correctly stated, for a pulverizer which was "out-of-normal") the computed effective γ^H was demonstrated as quite sensitive. Figure 5 indicates a well behaved Pulverizer Mill E indicating an essentially constant effective γ^H; and this given use of different PRB coals and variable air flows, fuel moistures and PA temperatures. The plot for Pulverizer Mill E was found similar as seen for 4 other Mills, all well-behaved. However, Figures 6 & 7 presents Pulverizer Mills A & B whose mean output coal particle size must be degraded (assuming the Hammer Mill output was constant). Pulverizer Mill B's effective γ^H was found the most inconsistent among the seven Mills studied; both Mills A & B were judged to be in need of servicing.

And finally, Eq.(11) is interesting in that it implies the lower the γ^H value implies that an increased shaft power is required to grind per unit mass of fuel. This would be anticipated for the harder and drier, higher Rank coals. An increasing presence of fuel hydrogen and fuel water at the molecular level - considering their undoubted complexity in forming an <u>effective</u> γ^H - may well benefit the pulverization process, reducing ΔE and shaft power for the same surface/mass. Of course this statement does not apply to coal's surface moisture.

CONCLUSIONS AND SUGGESTIONS

- Testing spheres made of pure chemicals demonstrated that burning hydrocarbons with progressively higher surface/mass ratios reduces unburned material and trends towards realizing full chemical potential.

- There is no observable difference in predictable characteristics between grinding a hydrocarbon (to <16 Mesh), versus manufactured spheres.

- This work demonstrated that changes in measured calorific value of pure substances is due entirely to surface/mass ratio and the material's free energy associated with inter-molecular hydrogen bonding.

- This work suggests that grinding solid hydrocarbons affects surface/mass ratio which impacts measured calorific value; and, through this, boiler efficiency. Low surface/mass materials result in degraded calorific value, resulting in unburned hydrocarbons, the creation of tars, CO, etc. Such effects are quite apart from poor combustion mechanics which will also degrade efficiency. This suggests that burner design must strive for a mean particle size $\leq A_0$.

- It is recommended that laboratory testing continue using Acrylic and anthracite, following the testing procedures outlined in Appendix A; this testing should confirm Eq.(9). Appendix A addresses the faults found with this work (i.e., use of non-uniform material, sample preparation, etc.).

- It is recommended that testing continue by verifying Eq.(12), and thus eliminating the delicate ΔE determinations. Eq.(12) employs measurements which can be made repeatedly through on-line monitoring. If developed for various Ranks, we can then turn to Eq.(9) to develop fineness criteria. Consideration should be given to changing a hammer mill's output then testing for a constant γ^H.

- This work has demonstrated that surface/mass ratio and free energy associated with hydrogen bonding are the only metrics required to describe insufficient grinding. Although judgement suggests that the present criteria of 95% of material passing a 60 Mesh, mixing coarse with fines, may not be sufficient, we also recognize that laboratory grinding such that 100% passes a 120 Mesh, may drive off water and volatiles thus affecting a laboratory tested CV to a greater extent than surface/mass. Testing programs involving crushing, versus grinding, should be critiqued.

- This work suggests, based on thermodynamics, that fuel water (or any chemical which increases an effective γ^H) may play an important role in pulverization; that higher effective wetted surfaces (at the molecular level) reduces shaft power, and would tend to reduce ΔE. This statement does not apply to affects caused by surface moisture and its obvious effects on CV.

- This work suggests a separation of the effects of a pulverizer's output, versus the mechanics of combustion *per se*. If a pulverizer associated with a new Steam Generator did not deliver intended fineness, Eq.(9) could provide a tool to correct guarantees of boiler efficiency by back-computing a ΔE penalty applied to the design calorific value.

- In general, results of this work suggest viewing coal calorific values with a jaundiced eye. Traditional data scatter observed with grab sampling, may be as much a function of laboratory equipment and testing techniques - haphazard preparation resulting in variable surface/mass ratios - as to fuel's intrinsics.

These conclusions and suggestions have been presented in the belief that both changes and further research are required to better understand coal. The authors encourage any responsible research organization concerned with the power industry to take up our work, apply critical review, and proceed with continued development.

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NOTES and ERRATA

Since ASME publication, the principal author has collected many comments and clarifications concerning points on physical chemistry, pulverizer function and applications. They have been incorporated here by revision. He is especially grateful to Bill Smith, President, Exothermic Engineering, LLC, Liberty, Missouri for his critique.

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APPENDIX A:

The following procedure is recommended for material preparation and calorific testing of Acrylic and anthracite.

1) Two materials will be tested, Acrylic and anthracite, according to the following:
   a) Acrylic spheres, $C_5H_8O_2$, Polymethyl-Methacrylate (PMMA), CAS 9011-14-7, shall be tested as specified by Table A1. Listed sample weights consider both sphere size and typical calorimetric limits imposed on lab equipment. It is suggested that Acrylic spheres should be prepared by Engineering Laboratories, Oakland, NJ (**www.PlasticBalls.com**). The manufacturer shall provide assurance that the same lot of raw material is used to produce all sizes, and that all spheres are produced within the same six month period; this will necessitate a special order.
   b) Anthracite ground material shall be tested as specified by Table A2. The material should be acquired from the Coal and Organic Petrology Laboratories, The Pennsylvania State University, University Park, PA (**n8h@psu.edu**). When ordering, emphasizes must be placed on obtaining uniform material; i.e., special order as appropriate.

2) It is important that the material not be handled with exposed skin for fear of surface contamination.

3) The same calorimetric equipment shall be used for all tests involving the same material (i.e., charging machine, bomb, water jacket, vessel, etc.); it shall be identified by manufacturer, model and serial numbers. It is strongly recommended that if a production calorimeter is used, that the LECO Model AC600 isoperibol calorimeter be used.

4) A portion of the Acrylic spheres shall be ground (or crushed) following the sieve sizes specified in Table A1. Sifting used to prepare test samples shall be conducted such that less than <1.0% of the material does not pass the coarse criteria, and >99% of the material is captured by the finer. Material lying outside this criteria shall be discarded. It is recognized this criteria may be difficult to achieve given Acrylic; new lab techniques may be required such that the material is not melted, possibly involving a more isothermal process of crushing, versus traditional grinding. Material shall be obtained from all Acrylic sphere sizes.

5) At least 60 grams of delivered anthracite shall be ground to between 6 and 7 Mesh, followed by at least 48 hours of continual mixing; from this lot, additional samples shall follow. Grinding and mixing shall be conducted in a nitrogen environment to minimize oxidation. After mixing, a portion of the anthracite shall then be ground following the sieve sizes specified in Table A2, again in a nitrogen environment. Sifting used to prepare test samples shall be conducted such that less than <1.0% of the material does not pass the coarse criteria, and >99% of the material is captured by the finer; discard material lying outside this criteria.

6) It is important that the indicated sample weights (see Tables) be conserved within ±0.0005 gram for Acrylic, and within ±0.005 gram for all ground samples. Acrylic weights have been computed to the whole sphere using the best available density; if the prepared lot of Acrylic varies, then the weight of a single Acrylic 1/2 inch sphere shall be used to set the remaining weights.

7) After weighting, all samples shall be placed in a desiccator for at least 48 hours until tested; this includes both delivered spheres and the ground material. In summary, prepare all samples, grind as specified, and then desiccate all samples.

8) Prepared samples shall be tested for calorific value following ASTM standard D5865-10a; see Tables for the number of tests per size.

9) Calibration of the calorimeter shall be completed using 10 benzoic acid tests at 25 ^{o}C calorimetric temperature, using routine procedures. Calibrations shall be conducted before each material tested. Calibration shall be completed once, at the start of a given material testing; its resultant Calibration Factor shall not be altered.

10) All calorimetric testing shall be conducted using a ΔT Mode; automatic determination of equilibrium is allowed with manual confirmation. All testings and calibrations, shall be completed within 2 days.

11) Records for each run shall include:
a) start and end temperatures of the jacket and bucket/bomb assembly shall be accurately recorded for each test, record temperatures to at least four significant digits (e.g., 25.01 ^{o}C);
b) ignition start and end times;
c) combustion vessel's start and end pressures, if possible (or the charging pressure);
d) weights of the samples to ±0.0002 gram;
e) calorific values at constant volume;
f) the lab's ambient psychrometrics; and
g) any other relevant data and/or observations.

Table A1: Testing Acrylic Spheres

No. of Tests	Diameter or Mesh Size	No. of Spheres per Sample	Sample Mass (gram)
10	1/2 inch	1	1.2693
10	1/4 inch	8	1.2693
10	3/16 inch	19	1.2718
10	1/8 inch	64	1.2693
10	1/16 inch	512	1.2693
10	14 to 16 Mesh	---	1.2693
10	50 to 60 Mesh	---	1.2693
10	170 to 200 Mesh	---	1.2693

Table A2: Testing Anthracite

No. of Tests	Encompassing U.S. Mesh Sizes	U.S. Mesh Opening (mm)	Sample Mass (gram)
10	6 to 7 Mesh	2.6050	1.0000
10	14 to 16 Mesh	1.3000	1.0000
10	50 to 60 Mesh	0.2735	1.0000
10	120 to 140 Mesh	0.1150	1.0000
10	170 to 200 Mesh	0.0810	1.0000

APPENDIX B:

The following tables describe basic operating conditions, input and output data employed for pulverizer sensitivity studies. The authors encourage its use for further benchmark and standards research.

Table B1: Pulverizer Operating Conditions

Pulverizer Input Streams	Flow (klb/hr)	Press. (psiA)	Temp. (deg F)
Coal	114.70	14.55	39.18
Primary Air	192.7	16.5	571.6
Fuel-Air Mixture	307.5	15.7	133.3

Table B2: Pulverizer Energy Balance Inlet Conditions

Pulverizer Input Streams	Flow (klb/hr)	Enthalpy (Btu/lbm)	Energy (kBtu/hr)
Dry Coal	79.662	1.951	155.43
Moisture in Coal	35.039	7.239	253.63
Moisture in Air	0.8864	1321.38	1171.31
Dry Air	191.86	131.34	25199.74

Table B3: Pulverizer Energy Balance Outlet Conditions

Pulverizer Power & Outlet Streams	Flow (klb/hr)	Enthalpy (Btu/lbm)	Energy (kBtu/hr)
Brake Shaft Power	---	---	1082.584
Dry Coal *	79.662	27.692	2205.99
Moisture in Coal	20.427	101.318	2069.66
Moisture in Coal (with shaft power)	19.397	101.318	1965.24
Moisture in Air	15.498	1151.74	17849.96
Moisture in Air (with shaft power)	16.529	1151.74	19036.95
Dry Air *	191.86	24.260	4654.505

* Pulverizer air stream was not affected by shaft power.

Figure 2: PVC Sphere Results (manufacturing dates shown)

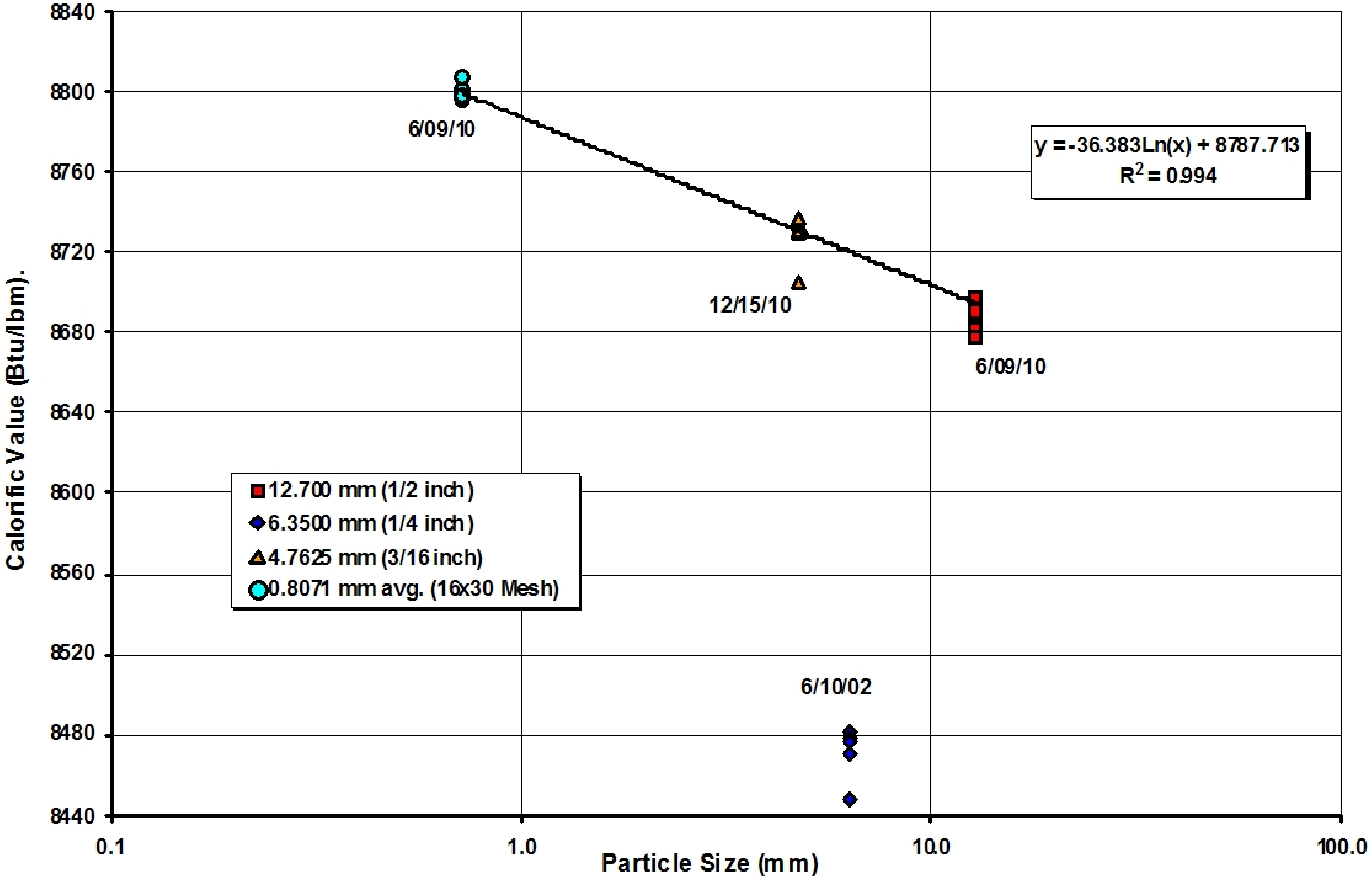


Figure 3: Surface/Mass vs. Energy Difference, As-Tested and Theory

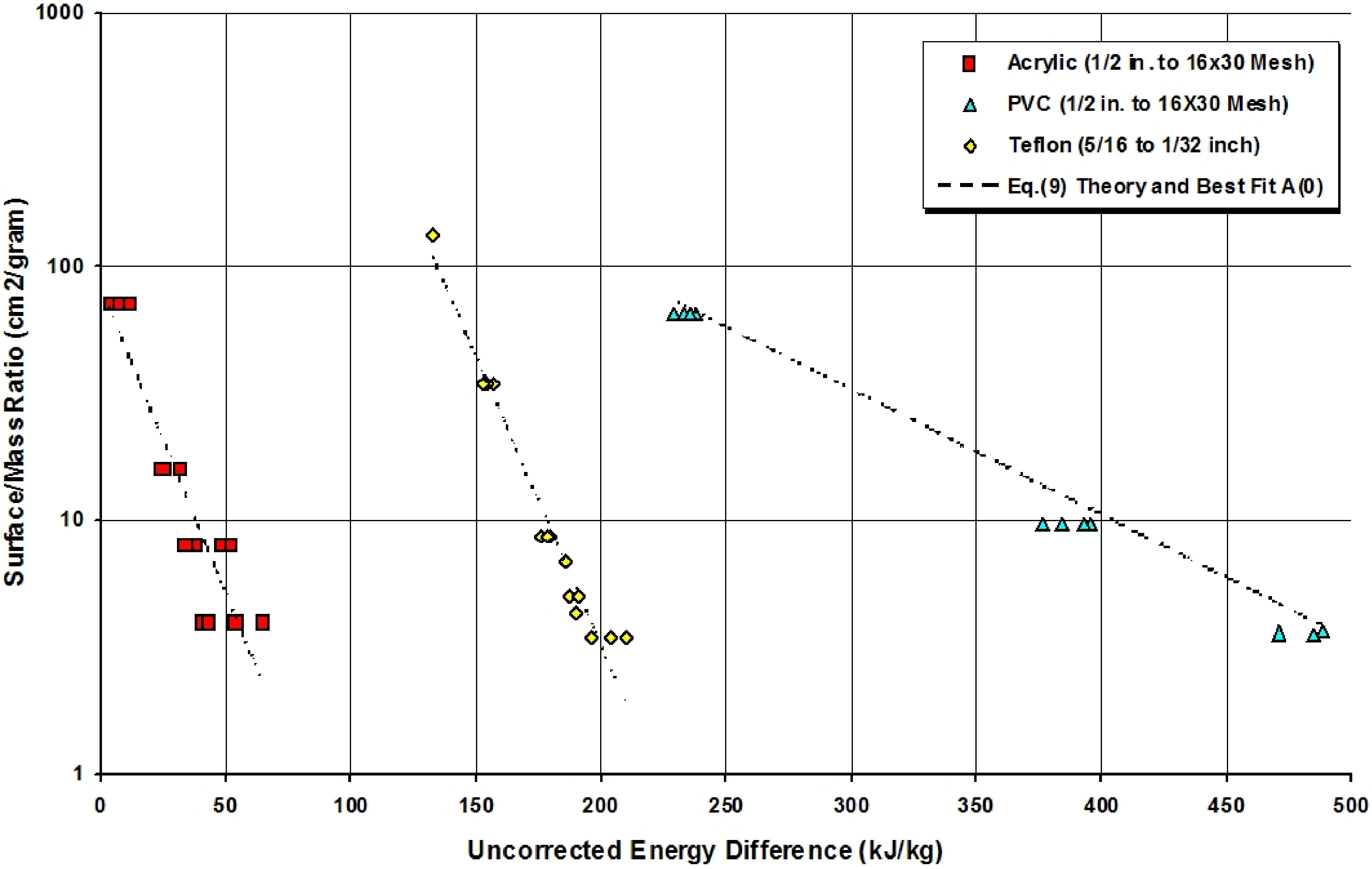


Figure 4: Ratios of Surface/Mass vs. Energy Diff., As-Tested and Theory

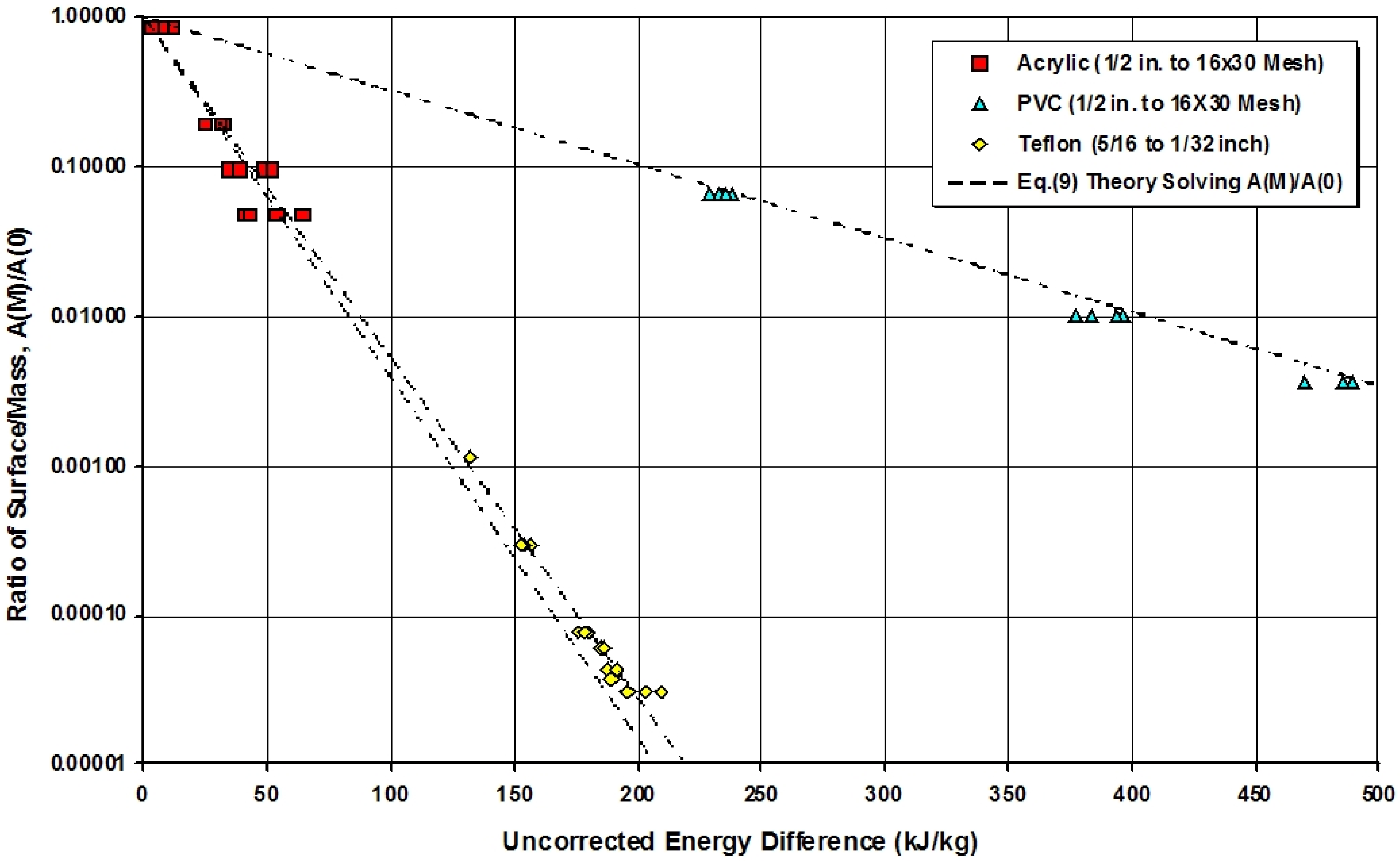
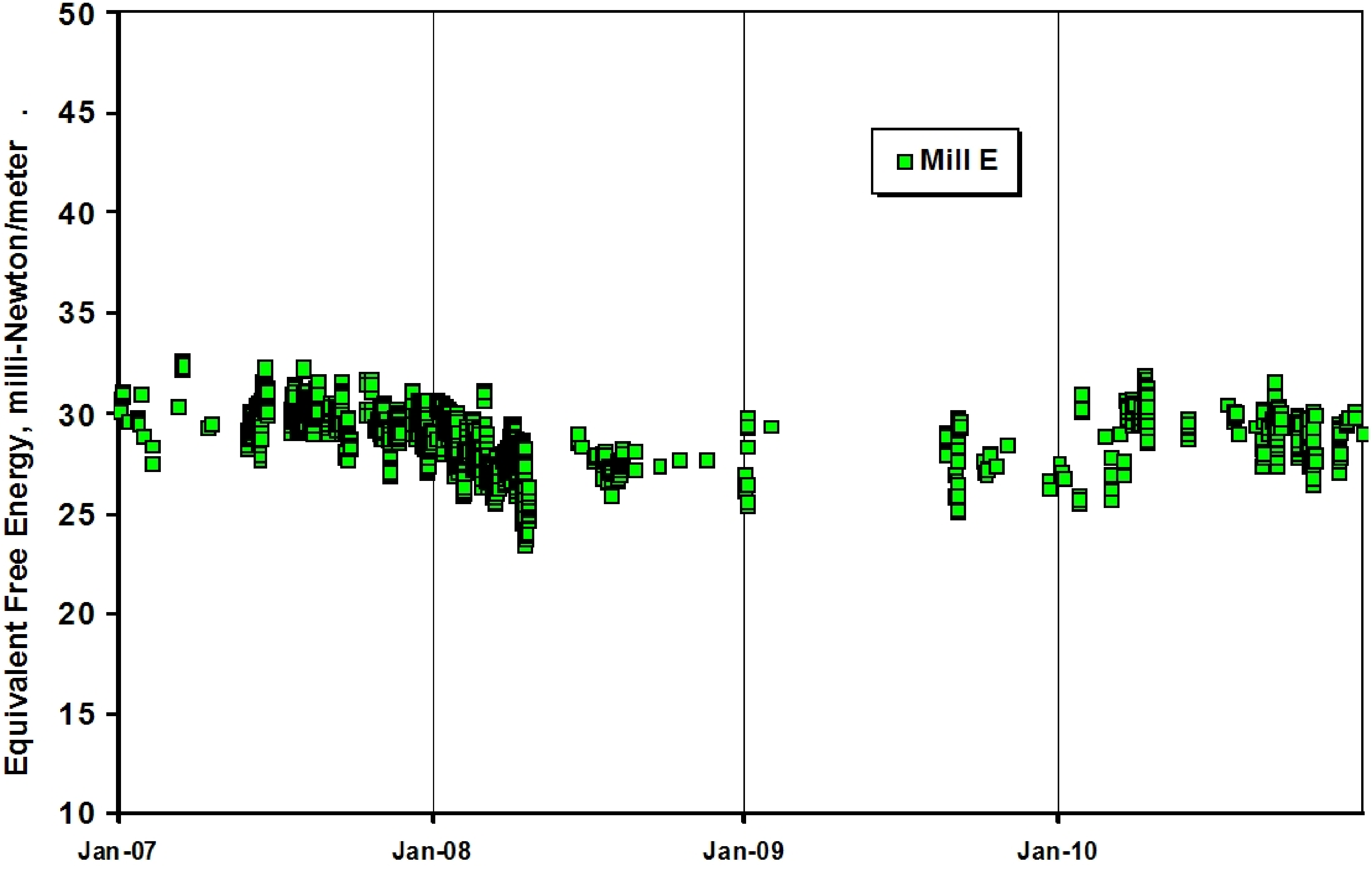


Figure 5: Boardman's Mill E



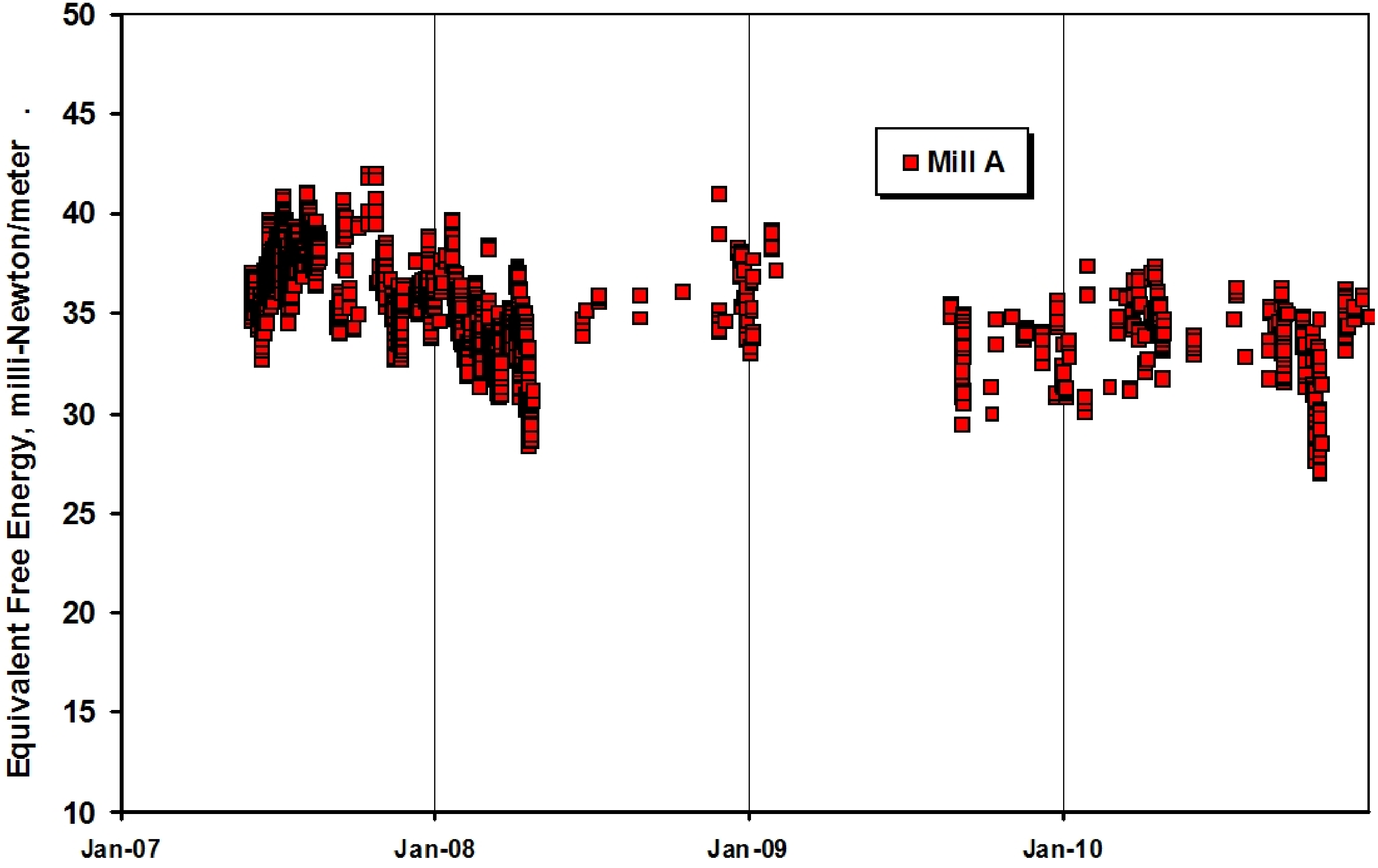


Figure 6: Boardman's Mill A

Figure 7: Boardman's Mill B