

A Simplified Method for the Measurement of Insoluble Solids in Pretreated Biomass Slurries

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Abstract The biochemical conversion of cellulosic biomass to liquid transportation fuels includes the breakdown of biomass into its soluble, fermentable components. Pretreatment, the initial step in the conversion process, results in heterogeneous slurry comprised of both soluble and insoluble biomass components. For the purpose of tracking the progress of the conversion process, it is important to be able to accurately measure the fraction of insoluble biomass solids in the slurry. The current standard method involves separating the solids from the free liquor and then repeatedly washing the solids to remove the soluble fraction, a laborious and tedious process susceptible to operator variations. In this paper, we propose an alternative method for calculating the fraction of insoluble solids which does not require a washing step. The proposed method involves measuring the dry matter content of the whole slurry as well as the dry matter content in the isolated liquor fraction. We compared the two methods using three different pretreated biomass slurry samples and two oven-drying techniques for determining dry matter content, an important measurement for both methods. We also evaluated a large set of fraction insoluble solids data collected from previously analyzed pretreated samples. The proposed new method provided statistically equivalent results to the standard washing method when an infrared balance was used for determining dry matter content in the controlled measurement experiment. Similarly, in the large historical data set, there was no statistical difference shown between the wash and no-wash methods. The new method is offered as an alternative method for determining the fraction of insoluble solids.

Keywords Pretreatment · Fraction insoluble solids · Biomass · Lignocellulosic ethanol · Corn stover

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Introduction

The biochemical conversion of lignocellulosic biomass into liquid fuels and chemicals is a multistep process which presents many technical and economic challenges [1]. One of the most significant challenges is the necessity to break down the biomass into soluble sugars for fermentation in a highly efficient and industrially feasible manner [2]. This is typically done in a two-step process. The first step is a pretreatment process using a catalyst such as ammonia or sulfuric acid, which is meant to hydrolyze and/or solubilize a fraction of the biomass and prepare the biomass for enzymatic hydrolysis. The second step is an enzymatic hydrolysis, which hydrolyzes the cellulose and possibly the residual hemicellulose fraction of the biomass [2, 3]. From a process economic viewpoint, it is generally preferred to carry out these steps at a high total solids concentrations of 10–45% dry matter content (DM), which results in the formation of a heterogeneous slurry with a wide range of insoluble particles in a concentrated sugar liquor [3]. In order to better understand and quantify the efficacy of these conversion processes, it is necessary to measure the fraction of the biomass which has been solubilized and that which remains insoluble. For example, accurate insoluble solid analytical methods for these complex mixtures are essential for calculating conversion yields [4].

The National Renewable Energy Laboratory (NREL) published a Laboratory Analytical Procedure (LAP) in 2005 for evaluating the fraction of insoluble solids for pretreated biomass slurries [5]. This method, referred to as the “standard method” or “washing method” in this paper, involves mixing a known quantity of biomass slurry with excess water and subsequently separating the liquid in order to separate the soluble species from the insoluble solids. By successive separation and water addition steps, the insoluble biomass can be completely separated from the soluble fraction. The fraction of insoluble solids (FIS) can then be determined from the dry mass of biomass present after washing. The washing process is laborious and time intensive, and can vary based on operator technique.

In this paper, we offer an alternative method for measuring FIS that can reduce the analysis time and labor needed to determine the FIS. We propose to calculate the FIS of pretreated biomass slurries through the measurement of the fraction of dry matter in the whole slurry and in the separated liquor fraction. By reducing the number of steps in the process, FIS measurements can be obtained quickly and easily, without the added work of washing the biomass. We present data comparing the two methods for three individual pretreated biomass slurries, which were analyzed with six replicates, and discuss the separate measurements that impact the overall calculations. We also present a comparison of a large number of historical measurements from pretreated samples produced from 2007 to 2009, and show a comparative statistical analysis of this large data set.

The method by which the dry matter content of pretreated materials is determined can impact the final FIS calculations. Pretreated slurries often contain volatile compounds which may be driven off during dry matter determination, changing the percent solids measurement and thus the FIS value [6]. There are two common approaches for determining dry matter content via gravimetric methods using drying ovens [7]. These use either a vacuum oven held at 40 °C or an infrared (IR) drying balance with a temperature set point of 105 °C. The vacuum oven is commonly used when the presence of volatile compounds is suspected; however, their application in the FIS determination process can yield different results based on how the FIS is calculated. In addition to reporting results for FIS, we present data comparing the use of two different drying methods for measuring the total dry matter content of pretreated samples.

Theoretical Background

As mentioned in the introduction, a simple gravimetric analysis of weighing a sample, fully drying the sample, and then re-weighing the sample will give the mass fraction of the total solids, or total dry matter content, including both the insoluble and soluble solid species. A means of differentiating between the insoluble and soluble components is required to determine the fraction of the slurry that is insoluble. By a simple accounting of the different components of the slurry, we have the following relationships (refer to Fig. 1):

$$m_T = m_{is} + m_{ss} + m_w = m_{ts} + m_w = m_{is} + m_l, \quad (1)$$

$$m_{ts} = m_{is} + m_{ss}, \quad (2)$$

$$m_l = m_{ss} + m_w, \quad (3)$$

$$f_{is} \equiv \frac{m_{is}}{m_T}, f_{ss} \equiv \frac{m_{ss}}{m_T}, f_w \equiv \frac{m_w}{m_T}, f_{ts} \equiv \frac{m_{ts}}{m_T}, f_l \equiv \frac{m_l}{m_T}, \quad (4)$$

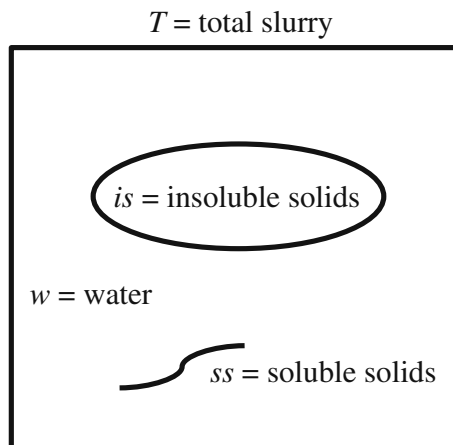
$$x_{is} \equiv \frac{m_{is}}{m_{ts}}, x_{ss} \equiv \frac{m_{ss}}{m_{ts}}, \quad (5)$$

and

$$y_{ss} \equiv \frac{m_{ss}}{m_l}, y_w \equiv \frac{m_w}{m_l}, \quad (6)$$

where m_i is the mass of component i , f_i is the mass fraction of component i as a part of the total slurry, x_i is the mass fraction of solid component i as a part of the total solids, and y_i is the mass fraction of component i as a part of the liquid. The subscripts have the following meanings: T = total slurry, ts = total solids, l = liquid, is = insoluble solids, ss = soluble

Fig. 1 Schematic of components in a biomass slurry



solids, and w = water. These relationships will be useful below as we illustrate the calculations needed for determining the fraction of insoluble solids from experimental data.

Before proceeding further, it is important to note the different mathematical definitions of the terms f_{is} and x_{is} . The term f_{is} is the mass fraction of insoluble solids as a part of the total slurry mass (which includes the water associated with the slurry), where as x_{is} is the mass fraction of insoluble solids as a part of the total solids. In practice, both are commonly referred to as simply the fraction of insoluble solids, leading to potential confusion when reporting quantitative results. In this paper, we will loosely use the term FIS when discussing methods, but we will be clear which term we are using when reporting numerical values. Note also that f_{ts} is referred to as either the fraction of total solids (in the slurry) or as the total dry matter content (DM).

Wash Method

The method outlined in the NREL LAP involves washing the biomass repeatedly with purified water to remove the soluble species [5, 7]. At a conceptual level, the method consists of four experimental steps:

1. Measure f_{ts} of the slurry material by gravimetric analysis (details below).
2. Set aside a slurry sample for washing and measure its mass ($m_{T(uw)}$). The mass of total solids in this sample is $m_{ts(uw)} = f_{ts} m_{T(uw)}$.
3. Wash the sample and concentrate to a reasonable water content (details below). Measure the mass of the washed solids ($m_{T(w)}$).
4. Measure the fraction of total solids in the washed sample ($f_{ts(w)}$) by gravimetric analysis.

Since there are negligible soluble solids in the washed solids, i.e. $f_{is(w)} = f_{ts(w)}$, the mass of the insoluble solids in the sample is given by

$$m_{is(uw)} = m_{is(w)} = f_{ts(w)} m_{T(w)}. \quad (7)$$

The mass fraction of the insoluble solids as a part of the total slurry and as a part of the total solids can then be calculated by

$$f_{is} = \frac{m_{is(uw)}}{m_{T(uw)}}, \quad (8)$$

and

$$x_{is} = \frac{m_{is(uw)}}{m_{ts(uw)}} = \frac{f_{is}}{f_{ts}}. \quad (9)$$

Note that the subscript notation (uw) and (w), with the parentheses are included, denotes “unwashed” and “washed”, respectively. The subscript w without parentheses denotes “water”.

No-Wash Method

The proposed method to differentiate between the insoluble and soluble solids requires no washing of the biomass. Conceptually, this method requires just two experimental steps:

1. Measure f_{ts} of the biomass material by gravimetric analysis (details below).
2. Obtain a sample of liquid from the biomass (details below) and measure the mass fraction of (soluble) solids in the liquid (y_{ss}) by gravimetric analysis.

The mass fraction of the insoluble solids as a part of the total slurry and as a part of the total solids can then be calculated by

$$f_{\text{is}} = \frac{f_{\text{ts}} - y_{\text{ss}}}{1 - y_{\text{ss}}}, \quad (10)$$

and

$$x_{\text{is}} = \frac{f_{\text{is}}}{f_{\text{ts}}}. \quad (11)$$

The relationship given by Eq. 10. may not be obvious. It can be derived directly from the relationships given by Eqs. 1–6:

$$\begin{aligned} m_{\text{is}} &= m_{\text{T}} - m_{\text{I}}, \\ f_{\text{is}} &= 1 - \frac{m_{\text{I}}}{m_{\text{T}}} \frac{m_{\text{w}}}{m_{\text{w}}}, \\ f_{\text{is}} &= \frac{y_{\text{w}}}{y_{\text{w}}} - \frac{f_{\text{w}}}{y_{\text{w}}}, \\ f_{\text{is}} &= \frac{(1 - y_{\text{ss}}) - (1 - f_{\text{ts}})}{(1 - y_{\text{ss}})}, \\ f_{\text{is}} &= \frac{f_{\text{ts}} - y_{\text{ss}}}{1 - y_{\text{ss}}}. \end{aligned}$$

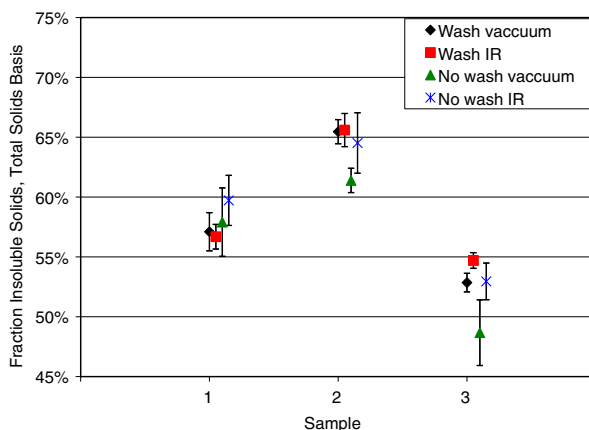
Materials and Methods

Pretreated Materials

Three unique pretreated biomass slurry samples were obtained from three different high solids pretreatment reactors in operation at NREL. Two reactors were of the continuous type, with capacities of 1,000 and 200 kg per day, respectively, and one was a 4 L batch reactor. Pretreated solids were all derived from corn stover feedstocks and dilute acid pretreatment. Pretreatment conditions were in the range of 175–190 °C, 1% (w/w) sulfuric acid concentration in the liquid phase, and residence times between 90 and 300 s. The nominal range of fraction of insoluble solids as a part of the total solids was from 50–65%, and is indicative of high soluble sugar concentrations in pretreated hydrolyzate slurries (Fig. 2). Total dry matter content was in the range of 28–35%, which is consistent with pretreatments considered ‘high solids’ for commercial scale processes. Pretreated slurries were stored in airtight containers at 4 °C before analysis. Table 1 provides compositional data of both the liquid and solid fractions, corresponding to soluble and insoluble solids respectively, for the three pretreated samples used. All three samples have similar solids compositions, while the liquor fractions vary greatly both in sugar concentration and volatile fractions.

A much larger set of historical pretreated slurry samples with a much larger range of insoluble solids content were used to further compare the two FIS measurement methods. These samples came from the three pretreatment reactors described above. They were generated over the period of 3 years (2007–2009) for a variety of experiments and represent a wide range of pretreatment conditions. All samples were dilute sulfuric acid pretreated samples. Both wash and no-wash method FIS data were gathered as part of standard sample analysis.

Fig. 2 Fraction insoluble solids as a part of the total solids (x_{is}) determined using four different measurement methods



Wash Method

The biomass samples were washed according to the method outlined in the NREL LAP for FIS determination [5]. Biomass was washed by the centrifugation method described in the LAP, using a Sorvall (Evolution RC) centrifuge. Approximately 75 g of biomass slurry was weighed into 250-ml centrifuge bottles. Samples were then spun at 12,000 rpm (24,000 rcf) for 10 min and the supernatant was decanted with minimal insoluble solids loss. Approximately 200 ml of DI water was then added to each centrifuge bottle, the biomass was re-suspended by hand mixing, and then spun again in the centrifuge. The process was repeated until the glucose levels measured in the supernatant were below 0.02 g/L as

Table 1 Pretreated sample composition by insoluble solids fraction and liquor content fraction.

Pretreated sample number	1	2	3
Solids composition (% DM)			
Ash	4.3	3.4	3.7
Protein	0.0	2.6	1.9
Lignin	25.0	25.9	25.3
Glucan	59.6	60.9	59.1
Xylan	7.7	6.8	5.1
Minor Sugars	1.5	2.0	1.3
Acetate	1.4	1.2	0.1
Liquor composition (g/L)			
Glucose	19.78	11.99	35.53
Xylose	82.15	59.23	100.17
Minor sugars	24.14	9.65	19.78
Acetic acid	4.60	9.72	16.27
HMF	1.22	0.65	3.93
Furfural	0.87	3.69	2.55

Note the difference in the concentration of volatile components (acetic acid, HMF, furfural) for the three samples

measured using a glucose analyzer (Yellow Springs Instruments Inc. model no. 2700 Select). Samples were then weighed, and their dry matter content was determined by one of the two drying techniques described below. To reach glucose levels below the desired concentration, the centrifugation process was repeated five to six times.

No-Wash Method

For the no-wash (direct) method, a solid–liquid separation was performed to obtain a liquor sample for dry matter content determination. This was carried out by centrifuging 75 g of the whole slurry samples for 10 min at 12,000 rpm (24,000 rcf) in a floor-standing centrifuge (Sorvall Evolution RC). The liquor was then decanted and filtered through a Glass Fiber filter using a vacuum filtration system. The liquor fraction was then analyzed for dry matter content. Although 75 g of sample was used to obtain liquor in this study, it is possible to obtain enough liquor for this analysis from less than 10 g of sample, depending on the liquid content of the sample.

Drying Ovens

Two types of drying oven were used to determine the impact of drying technique on the dry matter measurements necessary for the calculations. The same drying methods were used to measure the dry matter content of the whole slurry (f_{is}), of the washed slurry ($f_{is(w)}$), and of the separated liquor (y_{ss}). A vacuum oven (VWR model 1430) pulling a vacuum of 431 mmHg and set to 40 °C was used as a low temperature drying method. The low-temperature oven was used to minimize volatile loss during drying. Samples of 0.5 to 2.5 g were dried for 48 h or until there was no significant change in mass noted between 4-h periods. The second drying oven was a semi-automated IR balance (Mettler Toledo, model HR83 Halogen), designed specifically for measuring the dry matter content of wet samples. The oven had a maximum temperature of 105 °C and dried the biomass until less than 0.01% change in dry matter content was detected over a 1 min timeframe. Sample size ranged from 0.5 to 2.5 g, and the samples were evenly distributed on the sample pan. For liquid samples, or slurry samples with high liquid content, disposable quartz pads were used to enable more even and rapid drying.

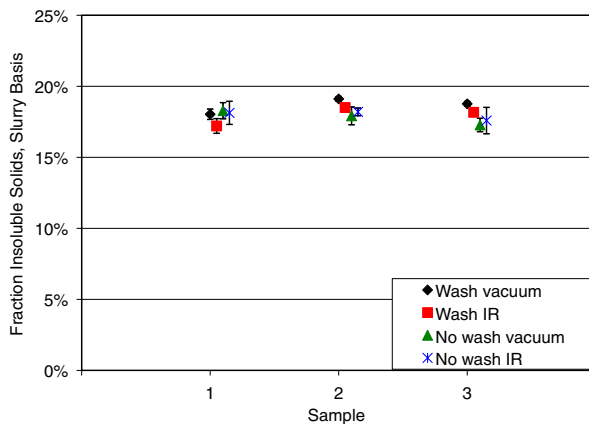
For each of the three pretreated biomass samples analyzed specifically for this study, measurements were repeated a total of six times for each FIS determination method to achieve an acceptable level of certainty in the analysis. The values reported from the historical data set are averages from two to three measurements for each sample.

Results and Discussion

Comparison of the Methods Using Three Specific Samples

Figure 2 shows the measured values for FIS as a fraction of the total solids (x_{is}) calculated in four different ways for the three pretreated hydrolyzate slurry samples: wash method using a vacuum oven for gravimetric analysis, wash method using an IR drying balance for gravimetric analysis, no-wash method using the vacuum oven, and no-wash method using the IR balance. Figure 3 shows the same data, but with the FIS represented as a fraction of the total slurry (f_{is}). The error bars represent the experimental uncertainty for a 95% confidence interval for the average values of the six sample replicates. In general, the

Fig. 3 Fraction insoluble solids as a part of the whole slurry (f_{is}) determined using four different methods of measurement



uncertainties are greater for the values of x_{is} (Fig. 2) than for the values of f_{is} (Fig. 3), due to the propagation of error through the extra calculation needed to determine x_{is} .

Sample 1 shows good agreement among all four methods for the measurement of FIS (Fig. 2), as all of the values are within each other's region of uncertainty. For samples 2 and 3, there are statistically significant differences shown between measurement methods when measuring x_{is} . However, the observed differences for these samples are not consistent with either the oven type used or the FIS measurement method. To compare the differences in FIS determination methods further, the differences between the values for each method from the sample mean (averaged over all methods) were calculated and then averaged over the three pretreated samples analyzed (Figs. 4 and 5). Uncertainty values in the data measurements were propagated through this calculation. The no-wash vacuum method gave results for x_{is} that were on average 2% lower than the other three methods, as is seen in Fig. 4. Figure 5 shows that the f_{is} value determined from the wash vacuum method is higher than the values obtained by the other methods; however, this difference is less than 1%, which is much less than the needed accuracy for yield calculations. Especially when compared to the scatter in the historical data (Fig. 8), this difference is indeed small. All the FIS methods can therefore be said to be similar to the standard method in all cases except when measuring x_{is} with the no-wash method and using the vacuum oven.

Fig. 4 Average difference in x_{is} from the sample mean for all three pretreated samples

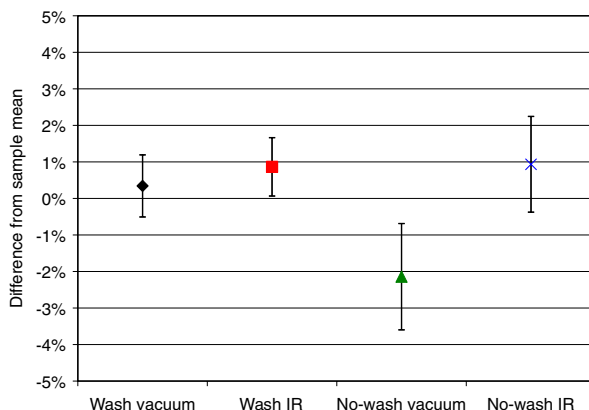
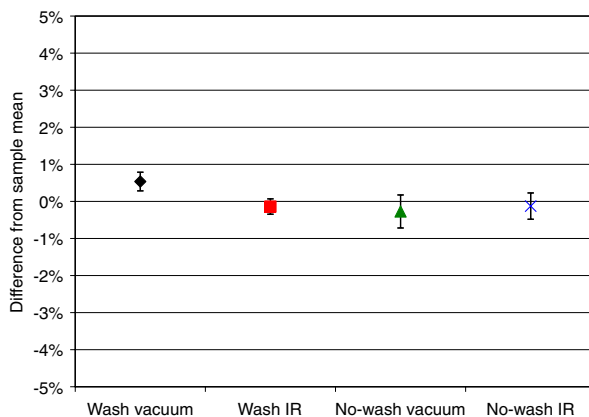


Fig. 5 Average difference in f_{is} from the sample mean for all three pretreated samples



There are other statistical analyses that could be performed to further probe the contributions of the measurement methods (wash vs. no wash) and the drying techniques. A detailed analysis of variance was performed, and it was found that both the measurement method and drying technique do separately and in combination cause statistically significant differences in the measured values. However, since the overall differences are small, we do not report such a detailed analysis here and instead present the effects of the measurement method and drying technique in combination. Uncertainty values and p values for the differences between the methods are given in Table 2, which support the qualitative observations that were made from Figs. 4 and 5. Although the differences between the methods are small, it is useful to discuss possible explanations for the differences observed.

Table 2 Statistical analysis of the differences between the FIS measurement methods.

Methods compared	Difference (%)	Uncertainty (95%)	p value
FIS, total solids basis (x_{is})			
Wash vac–wash IR	−0.52	1.16%	0.37
Wash vac–direct vac	2.48	1.69%	0.005
Wash vac–direct IR	−0.59	1.56%	0.45
Wash IR–direct vac	3.01	1.66%	0.001
Wash IR–direct IR	−0.07	1.53%	0.93
Direct vac–direct IR	−3.08	1.96%	0.003
FIS, total slurry basis (f_{is})			
Wash vac–wash IR	0.67	0.33%	0.0002
Wash vac–direct vac	0.81	0.51%	0.003
Wash vac–direct IR	0.66	0.43%	0.004
Wash IR–direct vac	0.13	0.49%	0.59
Wash IR–direct IR	−0.01	0.41%	0.95
Direct vac–direct IR	−0.14	0.57%	0.61

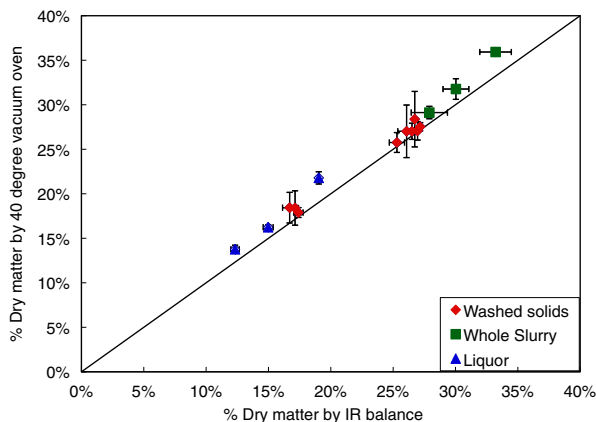
A p value less than 0.05 indicates that the difference is significant within a two-sided 95% confidence interval

Comparison of the Drying Methods

Besides the presence of the washing step in the standard method, the difference in the two ovens used for dry matter determination affect the two calculations differently, and therefore must be examined for possible impacts to the values. Figure 6 compares dry matter measurement methods for each of the data points in the study. The vacuum oven method gives slightly higher % dry matter values than the IR balance, as can be seen from deviation from the line showing perfect agreement. This is consistent with the hypothesis that the biomass retains more of the volatile compounds during drying in the vacuum oven than in the IR balance, which operates at a higher temperature and therefore may drive off more volatiles. However, if the volatile fraction remained in both the whole slurry and liquor fractions during dry matter determination, as is the case when using the vacuum oven, then the values for x_{is} calculated via the direct method would be lower when compared to results using the IR oven. This is due to the calculation itself, which, when both the whole slurry and liquor DM content increase, the calculated x_{is} values decrease. This is consistent with the data in Fig. 2 showing higher x_{is} values for the IR oven samples than the vacuum oven samples for the direct calculation method. For the washing method, a decrease in dry matter content due to volatile evaporation would correspond to lower f_{is} values and higher x_{is} values. This trend in the washing methods is not reflected in Figs. 2 and 3, suggesting other causes for their variation. In only one of the samples was the difference in FIS values significantly different for the two drying methods. This is likely due to the volatile species being removed by the washing procedure since they are part of the soluble fraction.

Sulfuric acid was applied to all of the materials as a catalyst to increase hemicellulose hydrolysis during pretreatment. Sulfuric acid was applied between 1–4% w/w dry biomass, and was effectively less than 1% w/w liquid fraction in the pretreated slurry for which FIS is measured. This is due to significant dilution by steam injection during the pretreatment process. Sulfuric acid is a non-volatile substance and should therefore be considered when measuring the dry matter content of pretreated biomass. Since it is a non-volatile, soluble component, it will effectively add to the mass fraction of the “soluble solids”. During the wash method for determining FIS, the sulfuric acid is washed out as part of the washing process, and therefore does not affect the final f_{is} measurement. For the no-wash method, the soluble solids content is directly accounted for in the calculation of f_{is} (Eq. 10), and hence the presence of sulfuric acid will not affect values of f_{is} . In both methods the presence

Fig. 6 Comparison of dry matter content measurements by use of a vacuum oven and an IR balance



of sulfuric acid may influence the measurement of x_{is} , but its contribution can be accounted for, if desired, by the amount of its addition.

Considering the data presented and the impact of the dry matter determination method on the final FIS calculation, the determination of FIS by the standard washing method is equivalent, within experimental uncertainty, to the proposed direct, no-wash method when DM is measured using an IR balance. However, the data suggest that FIS determination is somewhat method dependent, and varied by as much as 5% for the samples analyzed for this study (Fig. 2). It is thus important to better understand experimental uncertainties that may affect the final calculation to minimize these variations. Surprisingly, the data do not show a lower uncertainty for the IR balance DM method when compared to the vacuum oven method, nor for the direct method for measuring the FIS when compared to the washing method. In the authors' experience, the handling of the material during washing steps and during the vacuum oven drying can introduce a lot of variability to the data, especially when different scientists perform the procedures. This is not observed in this study, most likely because a single, highly experienced scientist performed all the experiments. A round-robin type analytical study of these methods may show more variation in the washing and vacuum oven drying methods.

Comparison of the Methods Using a Historical Data Set

To further understand how the two measurement methods compare in the course of standard laboratory analysis, we compiled a population of pretreated samples with FIS data from the past 3 years at the National Renewable Energy Laboratory. These samples were analyzed over the course of normal research and represent a wide variety of pretreated materials. Several analysts evaluated these samples, and the vacuum oven was used for the majority of the solids determinations. In total, 87 samples with the necessary data were identified.

Figures 7 and 8 show the data correlation between the wash and no-wash methods for the dataset for both the x_{is} and the f_{is} calculations, respectively. In order to assess whether the wash and no-wash FIS methods give equivalent results using this data set, a linear fit

Fig. 7 Comparison of x_{is} data from the wash and no-wash methods for a large sample set collected over a 3-year period

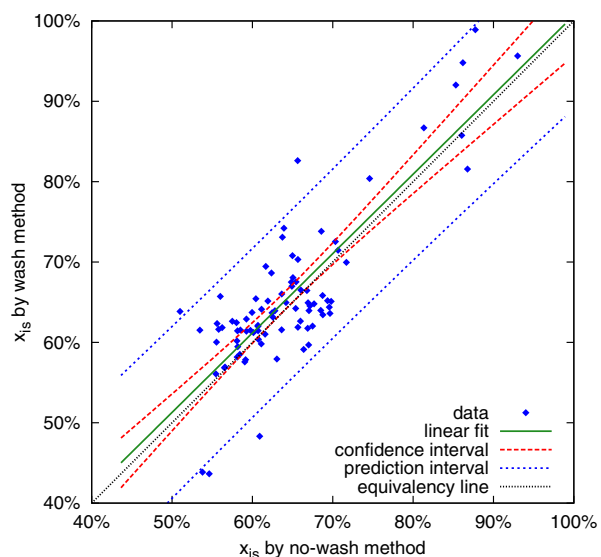
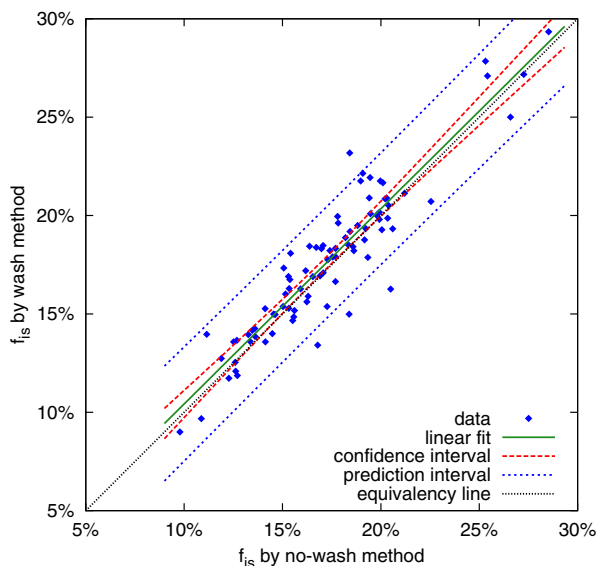


Fig. 8 Comparison of f_{is} data from the wash and no-wash methods for a large sample set collected over a 3-year period



and 95% confidence interval for the fit were determined for both the f_{is} and x_{is} data. Since the equivalency ($x = y$) line falls within the confidence interval of the linear fit, it can be concluded that the methods are equivalent within statistical uncertainty. Prediction intervals are also plotted in Figs. 7 and 8. The linear regression line of the data is shifted slightly towards the wash method, indicating that the wash method results in slightly higher f_{is} and x_{is} values. This is consistent with the method comparison data generated specifically for this study (Figs. 4 and 5). The data exhibit a high degree of scatter within the sample set, as evidenced by the large prediction intervals. The average width of the prediction intervals for f_{is} and x_{is} are 5.8% and 22%, respectively, much larger than the error bars shown for the methods in Figs. 4 and 5. These larger prediction intervals are partly, but not completely, due to the fewer number of measurements used to obtain the reported values (2–3 vs. 6). Again, the x_{is} measurement has a wider prediction interval due to propagation of error from the total solids measurement. These prediction intervals are more indicative of what uncertainties can be expected when making these measurements on a day-to-day basis. It is not clear from these data which method is more prone to error. The high degree of variability may be due to sampling and DM measurement errors, which can vary depending on free liquid content of a given sample. A detailed study of these potential sources of error would be of value in future work.

It must be noted again that this work was limited to material from dilute sulfuric acid pretreatment processes, and therefore must be carefully considered before being directly applied to alternatively pretreated materials or other slurry systems. Other pretreatment systems such as ammonia fiber expansion and steam explosion yield slurries with very low levels of solubilized solids. Theoretically, the calculation used in the direct method should be accurate as long as all dry matter measurements are made correctly; however, the authors have not verified this. It has been observed by the authors that the wash method is not suitable for measuring the FIS of materials that have been lightly pretreated and have little or no solubilized solids. This was primarily due to difficulty in dewatering the material through centrifugation for accurate dry matter measurements of the solid fraction, as well as poor measurement of solids concentrations below 3% using the standard oven methods

(data not shown). The direct calculation method may show an improvement in accuracy over the washing method. This would be best verified by doing an additional comparison study on a large sample set that included a variety of differently pretreated materials.

Conclusions

In the study, it was found that there were small differences in the measured FIS based on the method of measurement, be it from a direct calculation or from a quantitative washing. However, when using a direct calculation and DM values obtained from an IR balance, we obtained the same FIS values, within experimental uncertainty, as compared to the current NREL standard method. When compared within a large data set of samples spanning a period of 3 years, the two methods of measuring FIS were also found to be statistically similar. Both methods exhibited a wide degree of variability in the historical data set, most likely due to sampling and DM determination errors. This ability to calculate FIS without having to wash the slurry sample, a time consuming and labor intensive step, will allow for much faster and more efficient FIS determinations. Both the direct calculation method and the standard washing method are sensitive to the method of measuring dry matter content, due to the presence of volatiles in many pretreated hydrolyzate slurries. This study was based on dilute acid pretreated hydrolyzate slurries, and therefore the simplified method should be verified before use with biomass slurries generated under different pretreatment chemistries.

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