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Citation:

Novel Method for the Determination of Water Content and Higher Heating Value of Pyrolysis Oil

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This research provides a novel approach for the determination of water content and higher heating value of pyrolysis oil. Pyrolysis oil from Napier grass was used in this study. Water content was determined with pH adjustment using a Karl Fischer titration unit. An equation for actual water in the oil was developed and used, and the results were compared with the traditional Karl Fischer method. The oil was found to have between 42 and 64% moisture under the same pyrolysis condition depending on the properties of the Napier grass prior to the pyrolysis. The higher heating value of the pyrolysis oil was determined using an oil-diesel mixture, and 20 to 25 wt% of the oil in the mixture gave optimum and stable results. A new model was developed for evaluation of higher heating value of dry pyrolysis oil. The dry oil has higher heating values in the range between 19 and 26 MJ/kg. The developed protocols and equations may serve as a reliable alternative means for establishing the actual water content and the higher heating value of pyrolysis oil.

INTRODUCTION

Conversion of biomass to pyrolysis oil *via* fast pyrolysis continues to gain more recognition due to environmental consequences and political issues associated with the use of fossil fuel and, more importantly, the fear of energy insecurity in the near future. Pyrolysis oil has potential for various applications, such as combined heat and power and as a source of various chemicals. Currently, its application for electricity generation is still in an infant stage. In the areas of internal combustion engines and aeroderivative turbines, quality issues remain a challenge (Ringer *et al*. 2006). This may be overcome through deoxygenation of most of the chemical species present in the oil. Detailed knowledge about physicochemical and chemical composition of crude pyrolysis oil is crucial, as it can facilitate the design of upgrading processes and provide empirical information to ascertain the degree of deoxygenation. Different analytical techniques have been used for characterization of pyrolysis oil (Venderbosch and Prins 2010; Zheng and Wei 2011; Bridgwater 2012; Imam and Capareda 2012; Jacobson *et al*. 2013; Kanaujia *et al*. 2013; Cheng *et al*. 2014). The preliminary and most important physicochemical properties of pyrolysis oil are water content, higher heating value, and pH. Water content and higher heating value are generally obtained by using a Karl Fisher

titration unit and oxygen bomb calorimeter, respectively, according to various American Society for Testing and Materials (ASTM) and British Standards Institution (BSI) standards (ASTM E203 2001; ASTM D240 2009; BS 2000-12 1993). The Karl Fischer method is an analytical tool for determining the amount of water in samples or products based on the Bunsen reaction between iodine and sulfur dioxide in aqueous or non-aqueous mediums according to Eq. 1 (Aquastar® 2014; Felgner 2014). This reaction is sensitive to pH and may have serious effects on the final result. A pH value between 5 and 8 is said to be the optimum range for accurate water determination. Values outside of this range make the reaction proceed at either a slower or faster rate, resulting in formation of additional water within the system due to side reactions (Aquastar® 2014; Felgner 2014). Consequently, highly acidic or basic samples need to be buffered in order to get reliable results.

$$ROH + SO_2 + R'N \rightarrow [R'NH]SO_3R + H_2O + I_2 + 2R'N \rightarrow 2[R'NH]I + [R'NH]SO_4R \quad (1)$$
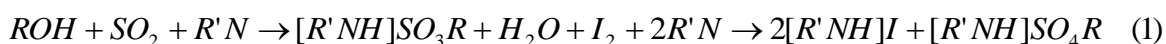
Generally, pyrolysis oil has a pH range between 2 and 3. This raises a serious concern, as water content of the oil cannot be estimated using the Karl Fischer technique under such pH conditions. Water content is a critical factor for estimating a higher heating value (HHV) of the oil. During heating value analysis, the oil is combusted and its water content vaporized by taking away some energy, which must be accounted for in order to estimate the overall energy content of the oil. Determining the water content of pyrolysis oil using the Karl Fischer technique has been mentioned in several previous studies, among which include Uzun *et al.* (2010), Ertas and Alma (2010), and Imam and Capareda (2012). However, detailed information on how it was carried out is not always available. Recently, nuclear magnetic resonance (NMR) spectroscopy has been used to determine the water content of pyrolysis oil. Smets *et al.* (2011) and David *et al.* (2012) used ^{1}H NMR and ^{31}P NMR, respectively, in their studies to determine the water content of pyrolysis oil. However, these methods are only effective for pyrolysis oil with water contents of less than 50 wt%. Samples with higher water contents are underestimated and hence cannot be used for all types of pyrolysis oil. In addition, having an NMR spectrometer in many pyrolysis centers (in the case of decentralized systems where quick checks on the pyrolysis oil may be required) may not be convenient and economically feasible due to time of testing and the high cost of the unit and maintenance requirements. The objective of this study was to develop a step by step method for accurate water content and heating value analysis of pyrolysis oil.

EXPERIMENTAL

Materials

Pyrolysis oil was obtained from the pyrolysis of Napier grass in a fixed bed tubular reactor at reaction temperature between 550 and 600 °C, a heating rate of 30 °C/min, and under a nitrogen atmosphere of 30 mL/min. Karl Fischer reagents (CombiSolvent Keto and CombiTitrant 5 Keto) and other reagents used in this experiment were supplied by Merck Millipore Sdn Bhd (Malaysia). Diesel fuel was purchased from a PETRONAS service station in Semenyih, Malaysia. After each production of pyrolysis oil, physicochemical characterizations were carried out within 24 h. The oil was first filtered using PTFE syringe filter with a 0.45 μm pore size and 13

mm diameter. A WalkLAB microcomputer pH meter TI9000 (Trans Instruments, Singapore) was used to determine the pH and Karl Fischer V20 volumetric titrator (Mettler Toledo) for water content according to ASTM E203 (2001). The higher heating value was determined using an oxygen bomb calorimeter (Parr 6100), according to ASTM D240 (2009). Two oil samples were prepared, one as produced (A_{rsmpl}) which serves as the control and the other buffered to pH between 5 and 8 (A_{bfsmpl}). Sodium hydroxide solution (20 to 40 %wt/wt) was used to adjust the pH. At the end of the water analysis, results from the Karl Fischer unit were used in Eq. 4, which was developed from the water balance, as presented below, to determine the overall water content in the oil. Figure 1 shows a schematic diagram of sample preparation for water analysis.
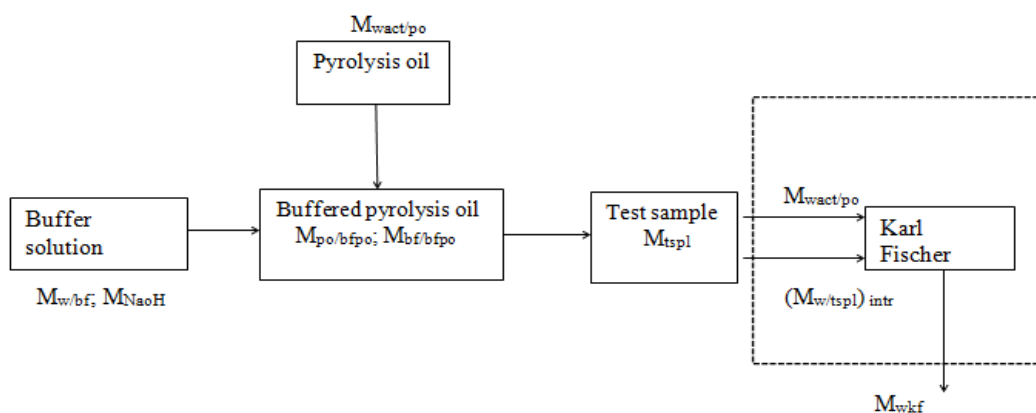

Fig. 1. Schematic diagram for development of water correction model

RESULTS AND DISCUSSION

Water Balance around the System Boundary in Fig. 1

From Fig. 1 and the set of equations below, $M_{w/bf}$ and M_{NaOH} are the mass of the water and that of the sodium hydroxide (NaOH) in the initial buffer solution, respectively. $M_{po/bfpo}$ and $M_{bf/bfpo}$ are the mass of pyrolysis oil buffered and mass of the buffer in the buffered oil. $M_{wac/po}$ is the mass of actual water in the pyrolysis oil, $(M_{w/tspl})_{intr}$ the mass of the water introduced in the test sample, M_{wkf} the mass of the water obtained from the Karl Fischer unit, $M_{po/tspl}$ the mass of the pyrolysis oil in the test sample, $M_{bf/tspl}$ the mass of the buffer in the test sample, $X_{wact/po}$ the percentage of actual water in the pyrolysis oil, x_{wkf} the fraction of water from the Karl Fischer unit, $x_{w/bf}$ the fraction of water in the buffer, and $x_{bf/bfpo}$ the fraction of buffer in the buffered pyrolysis oil.

$$M_{wact/po} + (M_{w/tspl})_{intr} = M_{wkf}$$

(2)

$$M_{wact/po} = M_{wkf} - (M_{w/tspl})_{intr}$$

$$X_{wact/po} = \left[\frac{M_{wact/po}}{M_{po/tspl}}\right] \times 100$$

(3)

Substitute Eq. 2 in 3 to obtain the following:

$$X_{wact/po} = \left[\frac{M_{wkf} - (M_{w/tspl})_{\text{int}r}}{M_{po/tspl}} \right] \times 100$$

$$= \left[\frac{x_{wkf} \times M_{tspl} - (x_{w/bf} \times M_{bf/tspl})}{M_{po/tspl}} \right] \times 100$$

$$X_{wact/po} = \left[\frac{x_{wkf} \times M_{tspl} - (x_{w/bf} \times M_{bf/tspl})}{(1 - x_{bf/bfpo}) \times M_{tspl}} \right] \times 100$$

$$= \left[\frac{x_{wkf} \times M_{tspl} - (x_{w/bf} \times x_{bf/bfpo} \times M_{tspl})}{(1 - x_{bf/bfpo}) \times M_{tspl}} \right] \times 100$$

$$= \left[\frac{\left[x_{wkf} - (x_{w/bf} \times x_{bf/bfpo}) \right] \times M_{tspl}}{(1 - x_{bf/bfpo}) \times M_{tspl}} \right] \times 100$$

$$= \left[\frac{x_{wkf} - x_{w/bf} \times (x_{bf/bfpo})}{(1 - x_{bf/bfpo})} \right] \times 100 \tag{4}$$

Experimental values of water content in the pyrolysis oil for both buffered and raw sample are shown in Fig. 2. The result revealed that Karl Fischer titration system underestimates the amount of water present in the pyrolysis oil for the unbuffered samples. For example, a sample with pH value of 2.83 had water content of 32.22 wt%, while the corresponding sample buffered to pH of 5.25 gave 63.91 wt% water content. This trend of increasing water content in the buffered samples was observed in this study. In addition, the time to reach the end point was faster with the buffered samples and consumes less regents compared to the unbuffered samples. Pyrolysis oil pH adjustment can therefore be seen as a major requirement toward the determination of its actual water content. This requires careful attention since accurate determination of higher heating value of the pyrolysis oil is dependent on how well the water content is quantified.

Pyrolysis oil is usually combined with other materials such as cotton, alcohol (methanol, ethanol), and diesel to determine its higher heating value in an oxygen bomb calorimeter due to the level of moisture that is associated with it. Initial tests of pyrolysis oil mixed with methanol following ASTM D240 (2009) did not give consistent results under similar conditions due to rapid changes in the sample weight during the preparation stage and bomb assembly. This is attributed to the low molecular weight and high vapor pressure of methanol. Similar behavior was also observed when cotton was used. The change in weight was not rapid compared to that of the methanol. Another trial of pyrolysis oil with diesel fuel was conducted, and the results seemed better than that of the methanol and cotton. An optimum higher heating value of pure diesel fuel was then

determined by varying the sample mass as shown in Table 1. Diesel with a mass of around 0.520 g gave a higher heating value of 42.0958 MJ/kg, which is comparable to the literature value (GREET 2010; Engineering Tool Box 2014b) and was used in the subsequent analysis. Different proportions of pyrolysis oil were mixed with this mass of diesel to find an optimum ratio. From the heating value analysis (Table 2), pyrolysis oil between 20 and 25% of the total mixture gave the same range of heating values. This range can therefore be regarded as optimum for pyrolysis oil-diesel mixtures for heating value analysis using a bomb calorimeter.
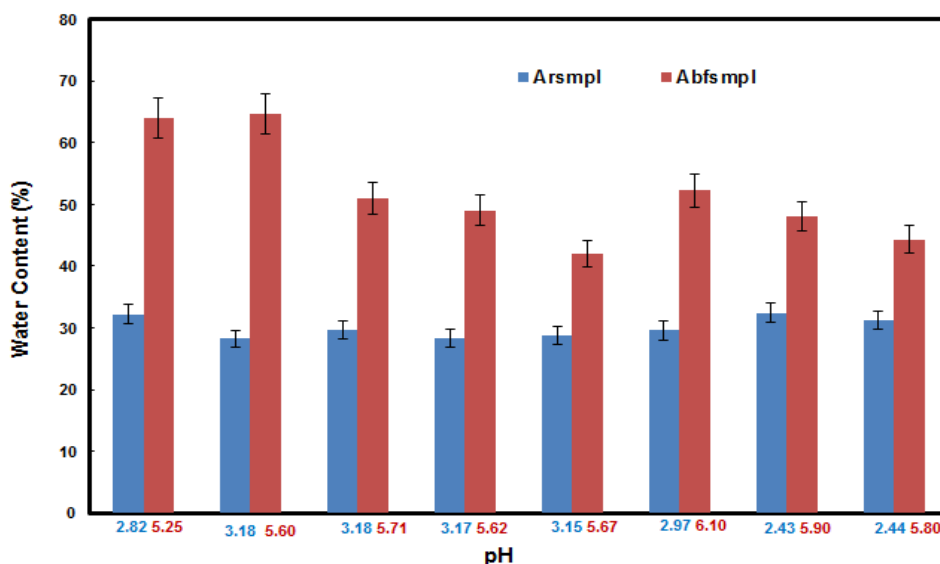
Fig. 2. Water content of pyrolysis oil from Karl Fischer titration. Arsmpl, raw pyrolysis oil sample as produced; Abfsmpl, buffered pyrolysis oil sample. Data reported as average ± standard deviation.

Table 1. Mass of Diesel Sample and Corresponding Higher Heating Value Determined using Oxygen Bomb Calorimeter

S/No	Mass of diesel (g)	Higher heating value (MJ/kg)
1	1.8809	15.7740
2	1.8972	15.8024
3	1.8886	15.7812
4	1.0112	26.3450
5	1.1143	26.9872
6	1.0243	26.4534
7	0.8011	39.1913
8	0.8112	39.2312
9	0.8094	39.2067
10	0.5200	42.0958
11	0.5210	42.0976
12	0.5200	42.0958

Each value is an average of three replicates; the standard deviations are within 3%

Table 2. Proportion of Pyrolysis Oil in the Mixture and Higher Heating Values

S/No	MD (g)	MPO (g)	M_{mix} (g)	%PO	HHV$_{mix}$ (MJ/kg)
1	0.5086	0.5183	1.0269	50.4723	23.4914
2	0.5022	0.3140	0.8162	38.4710	28.3958
3	0.5031	0.3176	0.8207	38.6987	28.5504
4	0.5254	0.1509	0.6763	22.3126	**34.9818**
5	0.5201	0.1522	0.6723	22.6387	**34.4399**
6	0.5071	0.1560	0.6631	23.5259	**34.7009**
7	0.5057	0.1600	0.6657	24.0349	**34.4296**
8	0.5057	0.1281	0.6338	20.2114	**34.7687**

MD, mass of diesel; MPO, mass of pyrolysis oil; M_{mix}, mass of mixture of diesel and pyrolysis oil; HHV$_{mix}$, higher heating value of the mixture. Each value is an average of three replicates; the standard deviations are within 3%.

Estimation of Actual Higher Heating Value of Dry Pyrolysis Oil

Estimation of the actual higher heating value of dry pyrolysis oil was carried out using Eq. (6), which was developed through the total energy balance shown below.

$$M_D \times HHV_D + M_{po} \times \left(HHV_{po} \right)_{wet} = M_{mix} \times HHV_{mix}$$

$$\left(HHV_{po} \right)_{wet} = \frac{M_{mix} \times HHV_{mix} - M_D \times HHV_D}{M_{po}} \tag{5}$$

But $M_{po} \times \left(HHV_{po} \right)_{wet} = M_{dry} \times \left(HHV_{po} \right)_{dry} - M_w \times LH_w$

$$\left(HHV_{po} \right)_{dry} = \frac{M_{po} \times \left(HHV_{po} \right)_{wet} + M_w \times LH_w}{M_{drypo}}$$

$$= \frac{M_{po} \times \left(HHV_{po} \right)_{wet} + x_{wac/po} \times M_{po} \times LH_w}{M_{drypo}}$$

$$\left(HHV_{po}\right)_{dry} = \frac{M_{po} \times \left(HHV_{po}\right)_{wet} + x_{wac/po} \times M_{po} \times LH_w}{(1 - x_{wac/po}) \times M_{po}}$$

$$= \left[\frac{\left(HHV_{po}\right)_{wet} + x_{wac/po} \times LH_w}{(1 - x_{wac/po})}\right]\frac{M_{po}}{M_{po}}$$

$$= \left[\frac{\left(HHV_{po}\right)_{wet} + x_{wac/po} \times LH_w}{(1 - x_{wac/po})}\right] \tag{6}$$

where M_D, M_{po}, and M_{mix} are the mass of diesel, pyrolysis oil, and mixture of pyrolysis oil and diesel, respectively, HHV_D, $(HHV_{po})_{wet}$, $(HHV_{po})_{dry}$, and HHV_{mix} are higher heating value of diesel, wet and dry pyrolysis oil, and mixture of pyrolysis oil and diesel, respectively, LH_w is the latent heat of water of evaporation (2.2 MJ/kg) (Engineering Tool Box, 2014a), and $X_{wac/po}$ is the actual fraction of water in the pyrolysis oil from Eq. 4.

A summary of higher heating values of dry pyrolysis oil obtained from following the above protocols and Eqs. 4 and 6 is presented in Table 3. These higher heating values are comparable to the literature value of between 16 and 21 MJ/kg (Mortensen *et al*. 2011; Imam and Capareda 2012; Bridgwater 2012). However, some values in the table are higher than this range due to treatment applied to the source biomass material prior to the pyrolysis.

Table 3. Summary of Higher Heating Value Analysis of the Pyrolysis Oil

S/No	M_D	M_{po}	M_{mix}	%PO	HHV$_{mix}$	(HHVpo)$_{wet}$	HHV$_D$	LH$_w$	x$_{wact}$	(HHVpo)$_{dry}$
	(g)				(MJ/kg)					(MJ/kg)
1	0.5217	0.1428	0.6645	21.4898	34.2765	5.7098	42.0958	2.2600	0.6391	19.8230
2	0.5225	0.1430	0.6655	21.4876	34.3151	5.8856	42.0958	2.2600	0.6455	20.7178
3	0.5230	0.1400	0.6630	21.1161	35.0543	8.7493	42.0958	2.2600	0.5200	20.6760
4	0.5254	0.1509	0.6763	22.3126	34.9818	10.2124	42.0958	2.2600	0.5100	23.1940
5	0.5071	0.1560	0.6631	23.5259	34.7009	10.6627	42.0958	2.2600	0.4900	23.0787
6	0.5205	0.1496	0.6701	22.3250	34.9980	11.3415	42.0958	2.2600	0.4800	23.8968
7	0.5227	0.1464	0.6691	21.8801	35.2345	12.6626	42.0958	2.2600	0.4400	24.3875
8	0.5057	0.1600	0.6657	24.0349	35.3920	14.2038	42.0958	2.2600	0.4200	26.1259

M_D, mass of diesel; M_{PO}, mass of pyrolysis oil; M_{mix}, mass of mixture of diesel and pyrolysis oil; HHV$_{mix}$, higher heating value of the mixture; HHV$_{po}$, higher heating value of wet pyrolysis oil; (HHV$_D$, higher heating value of diesel, (LH$_w$, latent heat of evaporation of water, (x_{wact}, fraction of actual water in the pyrolysis oil. Each value is an average of three replicates; the standard deviations are within 3%.

CONCLUSIONS

1. Water content and higher heating value analysis of pyrolysis oil produced from Napier grass in a fixed bed tubular reactor was conducted. Water content determination of the pyrolysis oil using Karl Fischer titration is dependent on the pH value of the oil. A pH value between 5 and 8 has been found to give better and accurate water content quantification using Karl Fischer titration. Typical pyrolysis oil is in the pH range of 2 to 3; therefore, the pH value of the oil needs to be adjusted before Karl Fischer titration in order to obtain an accurate pH determination.

2. Sodium hydroxide was used to buffer the oil sample to pH between 5.25 and 6.10 and compared to an un-buffered oil sample. An equation for actual water content in the pyrolysis oil after the pH adjustment was developed and used and the results were compared with the traditional method. The pyrolysis oil was found to have a water content between 42 and 64%, depending on the initial properties of the Napier grass biomass used prior to the pyrolysis.

3. A higher heating value of the pyrolysis oil was determined using an oil-diesel mixture; 20 to 25 wt% of the oil in the mixture gave similar results for several trials. Also, a model for calculating the higher heating value of dry pyrolysis oil was developed and applied. Dry oil has a higher heating value between 19 and 26 MJ/kg. Finally, the developed protocols and models can be used to establish the actual water content and the higher heating value of any type of pyrolysis oil.

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