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# Dyanamic Thermal Analysis of Lignocellulosic Crop Residues

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**Abstract:** Dynamic thermogravimetric analysis (TGA) under nitrogen was used to investigate the thermal decomposition behaviour of three different Canadian crop residues, namely wheat straw (*Triticum aestivum* L.), triticale straw (*Triticosecale*) and flax shive (*Linum usitatissimum*. The effect of milling type, ball mill and cryo-mill and milling time on thermal degradation behaviour of the finely milled biomass particles was investigated. The results showed that for all biomass types subjected to the various milling treatments, weight loss resulting from thermal decomposition occurred between temperatures of 200°C and 800°C. All of the samples showed a mass loss of around 70-75% on reaching 400 °C depending on heating rate, biomass type and milling treatment. Generally, for all heating rates, the degradation of all biomass samples presented a main peak between 340-395 °C and a shoulder between 300-330 °C depending on biomass type and milling treatment. Evaluation of activation energy ($E_a$) values via the Kissenger method offered a fundamental means to describe the thermal decomposition of the crop residues. The activation energy values for the milled wheat straw, triticale straw and flax shives ranged from 179-222.1, 176-227.9 and 194-218.7 kJ $mol^{-1}$, respectively. Determination of activation energy values provides information necessary for understanding the thermal decomposition behaviour of milled wheat straw, triticale straw and flax shives in the context of defining their use as both agro-fillers in thermocomposites and a source material for bioenergy and biochemicals.

**Key words:** Wheat straw · Triticale straw · Flax shives · Thermal decomposition · Milling · Particle size · Kinetic analysis · Kissenger method · Activation energy

## INTRODUCTION

Herbaceous agricultural residues obtained after food crop harvesting is one of the largest sources of annually renewable biomass [1] and herbaceous agricultural residues do not compete directly with food production [2]. Canada has 27 million ha of cropland and produces 75 million metric tons of agricultural crops [3]. Therefore a large amount of agricultural residues are produced every year globally and consequently crop residues can serve as a source material for obtaining bioenergy and developing biobased products [4].

The plastic industry has typically used inorganic fillers such as talc, calcium carbonate, mica and glass or carbon fibers to fill and to modify the performance of thermoplastic materials. The main roles of these inorganic fillers are to provide rigidity and temperature resistance yet these inorganic fillers are costly and abrade processing equipment [5]. Plant biomass flour or fibres [5,6,7] are being increasingly used as organic reinforcing materials (i.e. agro-fillers) in thermoplastic composite materials. Large-scale use of wood flour, loosely defined as wood particles that are small enough to pass through a screen with 850 μm openings, as a filler for thermoplastics has grown from less than 50,000 tonnes in 1995 to nearly 600,000 tonnes in 2002 [8]. Non-wood biomass also has great potential to be utilized as agro-fillers in composite manufacturing. Biomass powder and fibers from non-wood sources such as rice husk, wheat straw, flax, hemp, jute, sisal, pineapple and bagasse have been used to prepare biocomposite materials [5,9]. The primary advantages of using agro-fillers in thermoplastics include low density, low cost, high mechanical properties, nonabrasive nature [5,10] carbon neutrality, biodegradability, availability and renewability [5,11,12].

Although agro-filler represents a good opportunity for effective use of agricultural residues for the production of reinforced polymers, the thermal stability of

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these agro-fillers is an important parameter. Thermoplastics are processed at temperatures close to 200°C [7] and therefore degradation of agro-filler, such as odour development and discoloration, along with a reduction in mechanical properties, due to high temperatures at the time of processing may be detrimental to quality and functionality. Therefore it is essential to investigate the thermal decomposition properties of the agro-fillers.

Thermal decomposition reactions not only play a crucial role in defining biocomposite stability but these reactions are also important during biomass utilization processes, such as gasification, bio-oil (tar) and char formation. [13]. Thermal degradation in the absence of oxygen (i.e. pyrolysis) is considered to be a promising technology that is capable of converting biomass to clean energy and valuable chemicals [4,13,14,15]. The degree of pyrolysis is dependent on many factors, including: composition of biomass, natural resistance of samples, heating rate and temperature [14]. In order to harness pyrolysis as an effective thermoconversion technology, the decomposition behaviours of various crop residues should be studied as this is of importance for obtaining energy (combustible gases) and biochemicals (via condensation of the volatiles released from pyrolysis) from biomass [15]. It is therefore essential to study the fundamentals and mechanisms of biomass pyrolysis [4,15-17].

Thermogravimetric analysis (TGA) can be used to obtain kinetic parameters associated with thermal degradation, which constitutes an important tool in estimating the thermal behavior of biomass under dynamic conditions as this technique provides fundamental knowledge which can be applied to industrial pyrolysis applications [18,19] and defining thermal stability of polymers [7,20]. Kinetic parameters associated with the thermal degradation properties, such as activation energy ($E_a$) pre-exponential factor (A) and reaction order (n) are important factors in defining the thermal decomposition. [7, 21]. Kinetic parameters can be determined experimentally, either isothermally with time variation [21,22], or non-isothermally by varying heating rate [21,23,24]. Some non-isothermal techniques commonly used to determine activation energy include the Kissinger method [23] and the Coats-Redfern method [24].

Thermal degradation characteristics of plant biomass are strongly influenced by chemical composition [6]. The main chemical components of plant biomass are cellulose (30-50%), hemicellulose (15-35%), lignin (10-30%) and the actual values of these components depend on source [4]. Generally, the thermal degradation of biomass involves a number of complex reactions [7]. At heating rates below 100°C/min there are four stages in the thermal decomposition of plant biomass: 1) evaporation of the water present; 2) volatilization of the extractives; 3) decomposition of the hemicelluloses; and 4) subsequent decomposition of cellulose followed by lignin as it is decomposed more slowly within a greater temperature range [7,25].

The thermal degradation behaviour of wheat straw filled recycled thermoplastic composites was investigated by Mengeloglu and Karakus [5]. Also, a few publications have reported on the thermal degradation properties of wheat straw and flax straw and shives [9,22,26-28]. There are no reports, to our knowledge, that investigate the thermal characteristics and kinetic parameters of the triticale straw, an important Canadian crop residue. Kim and Eom [6] used TGA to study the thermal decomposition behaviour of finely milled rice husk (i.e. rice husk flour) in particle size classes ranging from <45μm to between 150-300 μm.

With respect to biomass characterization, it has been reported that the particle size of a sample influences compositional analysis [3,19] as biomass samples with larger particle sizes display higher cellulose, hemicellulose and lignin levels and a lower ash level than the fraction with smaller particle sizes. Bridgeman *et al*. [29] reported that biomass is heterogeneous and difficult to reduce to uniform small particles. Thermogravimetric analysis (TGA) typically uses small sample sizes and use of small amounts of heterogenous samples can lead to large variations, errors and difficulties in data comparison. Thermal degradation properties of reed canary grass and switchgrass were affected by particle size; the temperature at which maximum rate of decomposition occurred was lower for smaller particles [29]. This was attributed to compositional differences as smaller particles contained more inorganic matter and caused a catalytic effect. The work of Bridgeman *et al*. [29] did not strictly examine the effect of particle size on thermal decomposition as the samples were milled with a common milling time and type and particles were separated by sieving according to class size, 90 μm and 90-600μm. The different sized particles possessed different chemical compositions. Nevertheless, particle size, regardless of chemical composition of the particles affects thermal decomposition behaviour via heat and mass transfer effects [30]. Altun *et al*. [31] studied the thermal decomposition of Silopi asphalite, an organic material of petroleum origin that was subjected to different degrees of milling to create different particle sizes.

This work showed that both activation energy and the temperature at which maximum rate of decomposition occurred was higher for smaller particles.

Milling is a particle size reduction process that involves high shear stresses, which generates heat [32]. Ball milling is a commonly used particle size reduction technique [29,33,34] which releases heat [35]. Ball milling has been shown to affect the chemical structure of biomass [34,35]. The work of Schwanniger *et al*. [35] noted that the mechanical treatment of ball milling for time periods of 0 to 60 minutes altered the degree of cellulose crystallinity and polymerization of cellulose in wood samples. In contrast, low temperature milling helps to take the generated heat out of the samples [32,33] and therefore cryo-milled biomass may exhibit different properties compared to ball milled biomass.

In all, effective use of crop residues as either an agro-filler for biocomposites or as a source material for the production of energy and biochemicals requires a fundamental understanding of its thermal degradation properties and reaction kinetics. The objective of this work was to characterize the thermal decomposition process for three Canadian crop residues (wheat straw, triticale straw and flax shive) with thermogravimetric analysis (TGA).Also investigating the effect of milling time and type on the thermal stability and the kinetic parameters of finely ground crop residues for use as an agro-filler in thermoplastic polymer composite with TGA, was another target. Information obtained from this work can be used to evaluate and rationalize the potential for these crop residues as a source of agro-filler, bioenergy and biochemicals.

## MATERIALS AND METHODS

**Samples:** Triticale straw (*Triticosecale* Wittm. ex A. Camus cv, AC Ultima) samples were provided by Agriculture and Agri-Food Canada, Lethbridge, AB. CPS wheat (*Triticum aestivum* L.), straw was provided by Agriculture and Agri-Food Canada, Saskatoon SK. Flax shives (*Linum usitatissimum* L.; cvs, CDC Bethune) was provided by Biolin Research Inc. Saskatoon, SK.

**Coarse Milling of Samples:** As noted the main steps in wood flour production (and consequently agro-filler production) are size reduction via milling and size classification [8]. Therefore raw samples were milled using a Retsch SM 2000 cutting mill (Retsch GmbH, Haan, Germany) with a 2mm discharge screen. Milled samples were separated using a Retsch AS 200 tap sieve shaker (Retsch GmbH, Haan, Germany) with 20-and 80-mesh sieves shaken for 5 min. The fraction with a particle size range of 180-850μm was used for the experimental work since it has been reported that the particle size of a sample influence compositional analysis [3,29]. Therefore, a common size fraction was used in this work. The sieved samples were kept at-20 °C until analyzed.

**Fine Milling of Samples:** In order to further reduce particle size, coarsely milled samples were either ball-milled at 20 Hz for 0, 10 and 90 minutes using a Retsch Mixer (MM 301) Mill (Retsch GmbH, Haan, Germany) or cryo-milled at 20 Hz for 0, 10 and 90 minutes using a Spex Certiprep 6800 Freezer Mill (Spex SamplePrep, Metuchen, NJ, USA). It should be noted that the particle size of the 0 min time point was the same as the coarsely milled samples (i.e. sample with particle size >180μm and <850μm. Particle size of the fine milled samples was determined using confocal scanning laser microscopy (Leica SP2 AOBS Confocal, Leica Microsystems Inc.) coupled with Imaris 3D/4D real-time interactive data visualization software (Bitplane Scientific Software, South Windsor, CT, USA). The Imaris 3D/4D visualization software determined the sizes of the particles, in terms of diameter, by considering the particles to be spheres. This assumption was valid as the Imaris 3D/4D real-time interactive data visualization software measured the sphercity of the particles. The average sphercity value for all of the particles was 0.803 ± 0.027 which indicated the particles were spherical in nature. Also, using this software the total number of particles was counted and the particles were grouped in ranges according to size. Results were expressed as the number frequency (i.e. the fraction) of particles residing in a certain size classification as affected by crop residue type, milling time and mill type. Notably, the work of Zhu *et al*. [33] investigated how ball milling and cryomilling of poly(ethylene terephthalate) affected particle size distribution, however their work used a laser diffraction particle size analyser to determine the size of the particles. The laser diffraction technique typically determines particle size based on the assumption of sphericity [36] which is in agreement with the method used in this work.

**Chemical Composition Analysis:** Acid insoluble and acid soluble lignin, structural carbohydrates and ash content of the samples were determined according to the NREL procedure for determination of structural carbohydrates and lignin in biomass [37]. The samples were hydrolyzed with a two-step acid hydrolysis procedure. The samples

were subjected to an initial hydrolysis step using 72% $H_2SO_4$ at 30 °C for 1 h, followed by hydrolysis using 4% $H_2SO_4$ at 121 °C for 1 h. Monosaccharides in the hydrolyzate were quantitatively measured with HPLC equipped with a refractive index detector (Agilent 1100, Agilent Technologies Inc., Palo Alto, CA). The HPLC analysis was carried out using a Biorad Aminex HPX-87P column (300×7.8mm, Bio-Rad Laboratories, Hercules, CA) with a Cation H Refill Cartridge guard column (30×4.6mm, Bio-Rad Laboratories, Hercules, CA). The column temperature was 75 °C and the mobile phase was MilliQ water operating at a flow rate of 0.5 mL/min. Acid insoluble lignin was determined gravimetrically as the ash-free acid insoluble residue resulting from the hydrolysis. Acid soluble lignin, the low molecular fraction of lignin present the filtrate, was calculated from the measuring UV absorbance at 320 nm of the liquid phase resulting from the hydrolysis. An absorptivity of 30 $Lg^{-1}cm^{-1}$ was used to convert absorbance readings to mass values [37]. Ash content of the samples was determined as described by [38]. Briefly, the samples were ashed by complete combustion in a muffle furnace (Model F-A1730, Thermolyne Corporation, Dubuque, IA) equipped with a temperature controller (Furnatrol II series 413, Thermolyne Corporation, Dubuque, IA) running a temperature ramp program as follows: 1) ramp from room temperature to 105 °C; 2) hold at 105 °C for 12 min; 3) ramp to 250 °C at 10°C $min^{-1}$; 4) hold at 250 °C for 30 min; 5) ramp to 575 °C at 20°C $min^{-1}$; 6) hold at 575 °C for 180 min; 7) and drop to and hold at 105 °C until removed. The remaining residue in the crucible was taken as the ash content.

It has been reported that water and ethanol extractives present in biomass samples influence compositional analysis [3,39]. Therefore removal of extractives from the biomass was performed as indicated by the NREL procedure [40] for analytical purposes only. As described by Tamaki and Mazza [3], a water extraction was performed for 24 h using a conventional Soxhlet apparatus, which included: extraction tube (85 mL); boiling flask (500 mL); heating mantle (Glas-Col, Terre Haute, IN). After the water extraction was complete, an ethanol extraction was performed for an additional 7 h. The extractive-free biomass was dried in a vacuum oven at 35 °C for 24 h and kept at-20 °C until tested. The extractives obtained via evaporation of the solvent at 40 °C using a rotary evaporator were dried in a vacuum oven at 35 °C for 24 h. The mass of the dried extractives was measured. Research has shown that it is possible to recover wheat straw [5] and flax processing waste (shive) [9] which has no/low economic value for direct use in the production of biocomposites. Thus it should be noted that the material used for this work was subjected to thermal analysis studies in an "as received" state (i.e. crop residues containing extractives).

**Thermogravimetric Analysis:** Thermogravimetric experiments were performed using a thermogravimetric analyzer, (SDT Q600, TA Instruments, New Castle, DE) with high purity nitrogen gas at a flow rate of 100$cm^3$/min as the purge gas to provide an inert environment. The instrument continuously monitored and recorded changes in the mass of the sample as temperature increased. Approximately 10 mg of representative samples were evenly distributed into 90 $\mu$L alumina sample cups (TA Instruments, New Castle, Delaware), loaded onto a balance beam into the furnace and heated from room temperature to 1000°C with heating rates of 10, 20, 50 and 80°C $min^{-1}$. All experiments were performed in triplicate. Thermogravimetric (TG) mass loss curves and differential thermogravimetric (DTG) mass loss rate of change curves were generated and data was analyzed with the TA Universal Analysis program (version 2000, New Castle, DE).

**Reaction Kinetics of Thermal Decomposition:** As noted, the thermal properties of wheat straw, triticale straw and flax shive subjected to different milling treatments was studied by thermogravimetric analysis (TGA). The analysis was performed from 25 to 1000°C, using several heating rates: 10, 20, 50 and 80°C $min^{-1}$. The use of several heating rates was performed in order to evaluate the activation energy of the degradation process of the biomass samples using the method proposed by Kissinger [23]. Kissinger's method derives the activation energy using the peak temperature ($T_p$) [41]. Kissenger's method is based on the fact that the reaction rate, ($d\alpha/dt$), rises to a maximum value with an increase in reaction temperature, which is indicated by a peak in the differential thermogravimetric (DTG) mass loss rate of change curves. Therefore, considering that the reaction rate is dependent on the peak temperature, the peak temperature varies with the heating rate [26,41]. Thus, it is possible to evaluate the activation energy using the following equations [26]:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

Where: $d\alpha/dt$ expresses the conversion rate as a function of time, k is the kinetic rate constant and is a function of temperature $f(\alpha)$ is a function of the reaction mechanism.

$$\alpha = 1 - \frac{m_{(t)} - m_f}{m_0 - m_f} \quad (2)$$

Where: $\alpha$ is the mass fraction reacted at time (t), $m_{(t)}$ is the experimental mass at time (t), $m_f$ is the final mass and $m_0$ is the initial dry mass,

$$k = A\exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

Where: k, the kinetic rate constant, which, according to the Arrhenius equation, is a function of the pre-exponential factor (A), apparent activation energy ($E_a$), absolute temperature (T) in Kelvin and universal gas constant (R= 8.314 J $mol^{-1}$ $K^{-1}$ ).

The temperature-time relation can be computed from the following equation [26]:

$$T = T_0 + \beta t \quad (4)$$

Where: $\beta$ is the constant heating rate (°C $min^{-1}$) and $T_0$ is the initial temperature.

The function (Eq. 5) is deduced via Eqs. (1-4) as follows [26]:

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E_a}{RT_p} + \ln\left(\frac{AR}{E_a}\right) \quad (5)$$

Where: $T_p$ is the peak temperature in degrees of Kelvin obtained from the DTG curve.

It should be noted that equation 5 is valid for first order reactions (i.e. n=1). The activation energy is calculated from the slope of the straight line from equation 5 while the pre-exponential factor (A) is calculated from the y-intercept of the straight line generated from equation 5 [26].

**Statistical Analysis:** Statistical analysis was conducted using SAS Institute Inc. Software, version 9.1 (SAS Institute, 2001). Data were subjected to analysis of variance (ANOVA) with replication using the SAS PROC GLM procedure with biomass, mill type, milling time and heating rate as fixed effects. Least square (LS) means and Least Significant Difference (LSD) at 5 % significance level were generated using the SAS PROC GLM procedure.

## RESULTS AND DISCUSSION

**Chemical Composition:** Table 1 presents the acid insoluble lignin (AIL), acid soluble lignin (ASL), total lignin (TL) (sum of AIL and ASL), total sugars and ash content of the CPS wheat straw (WSC); flax shives from cv. CDC Bethune (FSB); and triticale straw from cv, AC Ultima (TSU). All results are expressed on a dry basis. It can be seen that the wheat straw exhibited AIL, ASL and TL contents, ~ 19, 1.2 and 20%, respectively. The triticale straw sample displayed lower ASL and TL content, ~17 and 18%, respectively. The total sugars content of wheat and triticale straw samples were comparable, ~ 67 and 68%, respectively. These results agree with the work of Tamaki and Mazza [3]. With respect to extractives wheat and triticale contained comparable amounts of total extractives, ~ 13 and 15%, respectively. The ethanol soluble extractives were present in lower quantities in both wheat and triticale straws, ~ 3.4 and 1.6 %, respectively. The water soluble extractives were present in higher amounts of ~9 and 13%, respectively. The flax shives had the highest AIL content ~27% which is in agreement with values reported in the literature [3,42,43]. The total sugars content for flax shives analyzed was ~56 %, which is slightly higher than the values presented by Tamaki and Mazza [3]. Compared to the wheat and triticale straw the flax shives contained lower amounts of both ethanol and water extractives, ~ 1.3 and 5 %, respectively. Table 1 shows that the wheat straw demonstrated the lowest ash content, 1.36 % followed by the flax shives and triticale straw, which presented values of 2.08 and 2.36%, respectively.

Table 1: Chemical Composition of Wheat Straw, Triticale Straw and Flax Shives

| Sample | Moisture Content (%) | Ash(%) | Extractives(%) | Acid Insoluble Lignin(%) | Acid Soluble Lignin(%) | Total Lignin(%) | Glucans(%) | Xylans(%) | Galactans(%) | Arabans(%) | Mannans(%) | Total Sugars(%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| WSC | 3.60±0.11 | 1.36±0.12 | 9.12±1.36 (WS)<br>3.43±0.18 (ES)<br>12.55±1.51 (T) | 19.52±0.18 | 1.17±0.01 | 20.69±0.18 | 42.14±0.25 | 21.36±0.27 | 0.86±0.14 | 1.69±0.14 | 0.92±0.03 | 66.97±0.58 |
| FSB | 5.40±0.11 | 2.08±0.06 | 4.79±0.46 (WS)<br>1.34±0.03 (ES)<br>6.14±0.43 (T) | 26.70±0.03 | 0.82±0.01 | 27.52±0.02 | 33.41±0.30 | 18.58±0.13 | 1.33±0.05 | 0.44±0.05 | 2.12±0.12 | 55.89±0.59 |
| TSU | 6.16±0.07 | 2.36±0.18 | 13.15±0.35 (WS)<br>1.55±0.06 (ES)<br>14.69±0.29 (T) | 17.40±0.03 | 1.25±0.01 | 18.65±0.04 | 41.14±0.15 | 23.73±0.17 | 1.02±0.02 | 2.09±0.02 | 0.19±0.02 | 68.16±0.30 |

The sample types are coded as follows: CPS wheat straw (WSC); triticale straw, cv. AC Ultima (TSU); and flax shives, cv. CDC Bethune (FSB)
Total sugars content (%) is the sum of glucans, xylans, galactans, arabans and mannans present in the biomass samples
Water soluble extractives (WS); ethanol soluble extractives (ES); and total extractives (T)

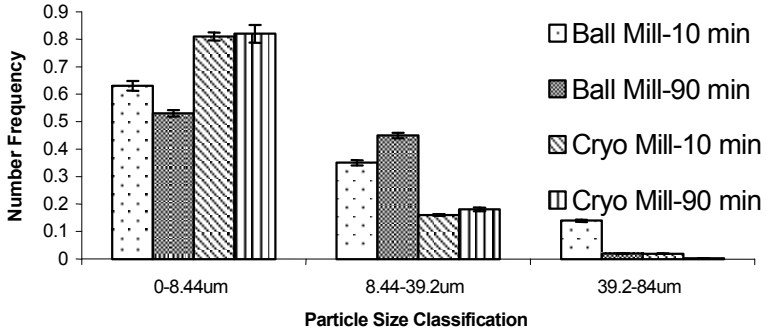


Fig. 1: Effect of milling time and type on particle size: Wheat straw

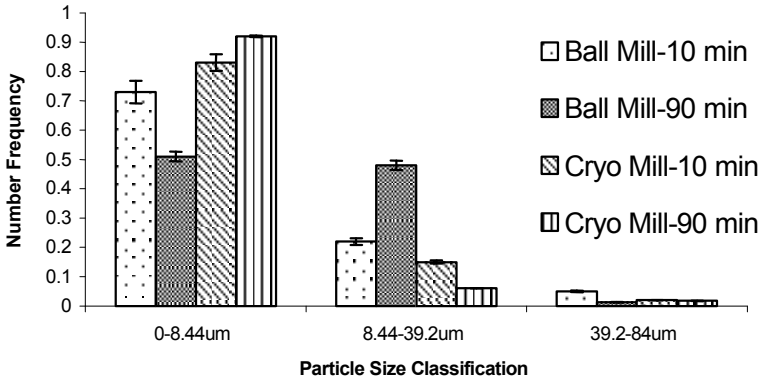


Fig. 2: Effect of milling time and type on particle size: Triticale straw

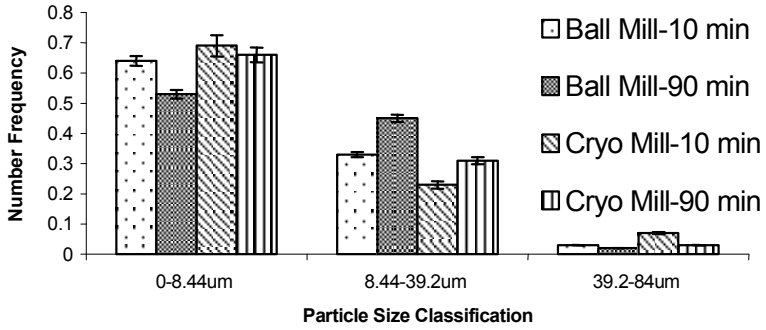


Fig. 3: Effect of milling time and type on particle size: Flax shive

**The Effect of Milling Type and Time on Particle Size:** Figures 1-3 show the number frequency (i.e. the fraction) of the particles residing in a certain size classification as affected by crop residue type, milling time and mill type. All of the ball-milled and cyro-milled samples, regardless of biomass type, exhibited particles sizes less than 85µm which is in agreement for the particle sizes for ball milled wood reported by Schwanniger *et al*. [35]. Statistical analysis indicated that all of the number frequency values demonstrated coefficients of variation values of ≤5%. The wheat straw samples ball milled for 10 minutes (BM-10) had a number frequency of 0.63 for particles belonging in the 0-8.44 µm particle size class and a number frequency of 0.35 for particles belonging in the 8.44-39.2 µm particle size class, wheat straw samples ball milled for 90 minutes (BM-90) had a number frequency of 0.53 for particles belonging in the 0-8.44 µm particle size class and a number frequency of 0.45 for particles belonging in the 8.44-39.2 µm particle size class, wheat straw samples cryo-milled for 10 minutes (CM-10) had a number frequency of 0.81 for particles belonging in the 0-8.44 µm particle size class and a number frequency of 0.16 for particles belonging in the 8.44-39.2 µm particle size class, wheat straw samples cryo-milled for 90 minutes (CM-90) had a number frequency of 0.82 for particles belonging in the 0-8.44 µm particle size class and a number frequency of 0.18 for particles belonging in the 8.44-39.2 µm particle size class. The triticale straw samples ball milled for 10 minutes (BM-10)

had a number frequency of 0.73 for particles belonging in the 0-8.44 μm particle size class and a number frequency of 0.22 for particles belonging in the 8.44-39.2 μm particle size class, triticale straw samples ball milled for 90 minutes (BM-90) had a number frequency of 0.51 for particles belonging in the 0-8.44 μm particle size class and a number frequency of 0.48 for particles belonging in the 8.44-39.2 μm particle size class, triticale straw samples cryo-milled for 10 minutes (CM-10) had a number frequency of 0.83 for particles belonging in the 0-8.44 μm particle size class and a number frequency of 0.15 for particles belonging in the 8.44-39.2 μm particle size class, triticale straw samples cryo-milled for 90 minutes (CM-90) had a number frequency of 0.92 for particles belonging in the 0-8.44μm particle size class and a number frequency of 0.06 for particles belonging in the 8.44-39.2 μm particle size class.

The flax shive samples ball milled for 10 minutes (BM-10) had a number frequency of 0.64 for particles belonging in the 0-8.44 μm particle size class and a number frequency of 0.33 for particles belonging in the 8.44-39.2 μm particle size class, flax shive samples ball milled for 90 minutes (BM-90) had a number frequency of 0.53 for particles belonging in the 0-8.44 μm particle size class and a number frequency of 0.45 for particles belonging in the 8.44-39.2 μm particle size class, flax shive samples cryo-milled for 10 minutes (CM-10) had a number frequency of 0.69 for particles belonging in the 0-8.44 μm particle size class and a number frequency of 0.23 for particles belonging in the 8.44-39.2 μm particle size class, flax shive samples cryo-milled for 90 minutes (CM-90) had a number frequency of 0.66 for particles belonging in the 0-8.44 μm particle size class and a number frequency of 0.31 for particles belonging in the 8.44-39.2 μm particle size class.

For the wheat and triticale straw biomass types regardless of milling time, the cryo-milled samples contained a larger proportion of particles in the 0-8.44 μm particle size class, 0.81-0.92, compared to the ball-milled samples, 0.53-0.73. Also for both the wheat straw and triticale straw samples, prolonged ball-milling time increased the proportion of particles with a larger particle size while prolonged cyro-milling time did not affect particle size distribution. Comparable results were obtained by Zhu *et al*. [33] as it was reported that poly(ethylene terephthalate) ball milled at ambient temperatures showed an initial increase in particle size upon increased milling time followed by a decrease at very long milling times (10 h) after which a stationary value was attained. Notably, these long milling times were not investigated in the present work. Alternatively, in cyromilling, the particle size decreased with milling time, until the particle refinement reached a stationary value at 10 h of milling.

Particle size distribution results for the flax shive samples indicated that flax shives were relatively insensitive to both prolonged ball and cryo-milling times. The flax shive samples that were cryomilled showed a slightly higher proportion of particles in the smallest (0-8.44 um) particle class size compared to the ball milled samples yet the effect of milling time on particle size distribution was not as pronounced for the flax shive as wheat and triticale straw. The reason for this result may be explained in terms of structure and chemical composition. Flax shive is core flax fiber, which, comes from the inside of the flax stem after primary flax fibres are removed via a retting process which removes cellulosic fibres [9]. Thus, flax shive contains less cellulose and more lignin than wheat and triticale straw. It has been reported that plant material with higher lignin content appears to be more difficult to mill [29], which may explain the observed insensitivity of the flax shive samples to increased milling times.

**Thermal Decomposition Behavior:** The thermal degradation of the three types of biomass, wheat straw, triticale straw and flax shives, as affected by milling (time and type) was determined by thermogravimetry. Representative mass loss/thermogravimetric (TG) curves at each heating rate for the coarse milled wheat straw, triticale straw and flax shives are shown in Figure 4a, 5a and 6a, respectively. For all samples, the mass loss increased with temperature. Also, the curves for all samples start at ~150 °C, as data analysis was performed after water present in the sample had evaporated. Table 2 provides a summary of the degree of thermal decomposition of the crop residues at various temperatures. The mass loss for all samples up to approximately 200 °C was minimal as there were no observed differences between of mass loss among samples as affected by biomass type and milling treatment as the amount of mass remaining was ~ 99% for all samples. This indicates that all samples tested were thermally stable at 200 °C indicating suitability for use in composites processing [7,12]. The majority of mass loss occurred between 200 and 400 °C. All of the samples showed a mass loss of around 70-75% upon reaching 400 °C depending on heating rate, biomass type and milling treatment. There were significant differences ($p \leq 0.05$) with respect to mass loss between the crop residue types subjected to common milling treatment and heating rate.

Table 2: Degree of Thermal Decomposition of Wheat Straw, Triticale Straw and Flax Shives, as Affected by Temperature, Milling Treatment, and Heating Rate

| Sample | Milling Treatment | Heating Rate (°C min$^{-1}$) | Mass Remaining (%) at Various Temperatures | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | 200°C | 300°C | 400°C | 500°C | 600°C | 800°C |
| WSC | Coarse | 10 | 99.6±0.06$^{a1}$ | 85.7±6.09$^{a1}$ | 29.4±0.80$^{a1}$ | 24.1±0.69$^{a1}$ | 22.1±0.69$^{a1}$ | 20.4 ± 0.71$^{a1}$ |
| | BM-10 | 10 | 99.5±0.02$^{a1}$ | 80.4±0.18$^{b1}$ | 26.9±1.04$^{b1}$ | 21.8±0.95$^{b1}$ | 19.8±0.91$^{b1}$ | 18.1 ± 0.9$^{b1}$ |
| | BM-90 | 10 | 99.4±0.01$^{a1}$ | 75.4±0.10$^{c1}$ | 26.8±0.39$^{bc1}$ | 23.5±0.32$^{a12}$ | 21.4±0.28$^{ab12}$ | 19.8 ± 0.26$^{a1}$ |
| | CM-10 | 10 | 99.6±0.03$^{a1}$ | 81.9±0.22$^{b1}$ | 28.8±0.30$^{ac1}$ | 23.5±0.40$^{ac1}$ | 21.5±0.43$^{ac1}$ | 19.8 ± 0.44$^{a1}$ |
| | CM-90 | 10 | 99.5±0.04$^{a1}$ | 81.3±0.20$^{b1}$ | 27.6±0.95$^{bc1}$ | 22.4± 0.97$^{bc1}$ | 20.5±0.99$^{bc1}$ | 18.8 ± 1.01$^{a1}$ |
| TSU | Coarse | 10 | 97.7±3.05$^{a2}$ | 80.9±2.99$^{a2}$ | 32.7±1.26$^{a2}$ | 27.4±1.02$^{a2}$ | 25.3±0.91$^{a2}$ | 23.61 ± 0.83$^{a2}$ |
| | BM-10 | 10 | 99.9±0.01$^{a2}$ | 81.3±0.03$^{a1}$ | 22.6±0.22$^{b2}$ | 18.0±0.25$^{b2}$ | 16.1±0.31$^{b2}$ | 14.54 ± 0.30$^{b2}$ |
| | BM-90 | 10 | 99.8±0.01$^{a1}$ | 78.3±0.07$^{b2}$ | 25.1±0.24$^{b1}$ | 20.2±0.24$^{c2}$ | 18.2±0.25$^{c2}$ | 16.51 ± 0.26$^{b2}$ |
| | CM-10 | 10 | 99.4±0.005$^{a1}$ | 81.9±0.23$^{a1}$ | 30.9±1.17$^{c2}$ | 25.7±1.23$^{d2}$ | 23.7±1.26$^{ad2}$ | 22.17 ± 1.29$^{a2}$ |
| | CM-90 | 10 | 99.4±0.006$^{a1}$ | 81.8±0.31$^{a1}$ | 30.4±1.30$^{c1}$ | 25.3±1.39$^{d1}$ | 23.3±1.41$^{d1}$ | 21.73 ± 1.42$^{a2}$ |
| FSB | Coarse | 10 | 99.6±0.09$^{a1}$ | 83.7±0.30$^{a1}$ | 30.2±1.24$^{a1}$ | 23.9±1.05$^{a1}$ | 21.6±1.04$^{a1}$ | 19.7 ± 1.08$^{a1}$ |
| | BM-10 | 10 | 99.6±0.01$^{a12}$ | 82.3±0.11$^{a1}$ | 29.5±0.58$^{ab3}$ | 23.6±0.62$^{ab3}$ | 21.4±0.66$^{ab3}$ | 19.5 ± 0.67$^{a1}$ |
| | BM-90 | 10 | 99.6±0.01$^{a1}$ | 77.9±0.28$^{b2}$ | 30.0±0.93$^{a2}$ | 24.1±0.9$^{a1}$ | 21.8±0.89$^{a1}$ | 19.9 ± 0.87 $^{a1}$ |
| | CM-10 | 10 | 99.6±0.02$^{a1}$ | 83.7±0.25$^{a1}$ | 28.8±0.87$^{ac1}$ | 22.9±0.85$^{ac1}$ | 20.8±0.84$^{ac1}$ | 18.9 ± 0.84$^{a1}$ |
| | CM-90 | 10 | 99.6±0.02$^{a1}$ | 82.1±0.07$^{a1}$ | 28.04±0.26$^{bc1}$ | 22.2±0.26$^{bc1}$ | 20.1±0.23$^{bc1}$ | 18.2 ± 0.21$^{a1}$ |
| WSC | Coarse | 50 | 99.7±0.04$^{a1}$ | 90.74±0.27$^{a1}$ | 31.5±1.49$^{ab1}$ | 23.9±1.38$^{ab1}$ | 21.6±1.34$^{a1}$ | 19.8 ± 1.32$^{a1}$ |
| | BM-10 | 50 | 99.6±0.005$^{a1}$ | 90.8±0.14$^{a12}$ | 31.2±0.44$^{a1}$ | 23.3±0.42$^{a1}$ | 20.9±0.44$^{a1}$ | 19.1 ± 0.46$^{a1}$ |
| | BM-90 | 50 | 99.6±0.01$^{a1}$ | 88.6±0.08$^{b1}$ | 31.5±0.76$^{ab1}$ | 24.82±0.89$^{bc1}$ | 22.38±0.92$^{a1}$ | 20.5 ± 0.94$^{a1}$ |
| | CM-10 | 50 | 99.7±0.01$^{a1}$ | 91.6±0.12$^{a1}$ | 32.8±0.58$^{bc1}$ | 24.5±0.58$^{ac1}$ | 22.2±0.57$^{a1}$ | 20.3 ± 0.58$^{a1}$ |
| | CM-90 | 50 | 99.7±0.02$^{a1}$ | 91.0±0.04$^{a1}$ | 31.7±0.70$^{ac1}$ | 23.3±0.72$^{a1}$ | 20.9±0.74$^{a1}$ | 19.1 ± 0.75$^{a1}$ |
| TSU | Coarse | 50 | 99.6±0.006$^{a1}$ | 91.1±0.44$^{a1}$ | 34.8±2.49$^{a2}$ | 27.9±2.45$^{a2}$ | 25.5±2.49$^{a2}$ | 23.8 ± 2.47$^{a2}$ |
| | BM-10 | 50 | 99.9±0.04$^{a1}$ | 93.1±0.16$^{a2}$ | 25.6±0.59$^{b2}$ | 18.6±0.87$^{b2}$ | 16.6±0.89$^{b2}$ | 14.9 ± 0.91$^{b2}$ |
| | BM-90 | 50 | 99.9±0.02$^{a1}$ | 91.6±0.10$^{a2}$ | 25.9±0.61$^{b2}$ | 19.9±0.61$^{b2}$ | 17.7±0.58$^{b2}$ | 15.7 ± 0.65$^{b2}$ |
| | CM-10 | 50 | 99.6±0.31$^{a1}$ | 91.5±0.34$^{a1}$ | 34.8±0.42$^{a2}$ | 27.9±0.24$^{a2}$ | 25.5±0.24$^{a2}$ | 23.8 ± 0.24$^{a2}$ |
| | CM-90 | 50 | 99.6±0.006$^{a1}$ | 91.3±0.04$^{a1}$ | 33.7±0.15$^{a2}$ | 26.9±0.13$^{a2}$ | 24.5±0.12$^{a2}$ | 22.8 ± 0.11$^{a2}$ |
| FSB | Coarse | 50 | 99.7±0.01$^{a1}$ | 90.9±0.12$^{ab1}$ | 36.2±0.89$^{a2}$ | 25.3±1.12$^{a1}$ | 22.6±1.14$^{a1}$ | 20.5 ± 1.14$^{a1}$ |
| | BM-10 | 50 | 99.8±0.01$^{a1}$ | 90.6±0.15$^{ab1}$ | 34.7±0.64$^{b3}$ | 24.2±0.64$^{ab1}$ | 21.7±0.61$^{a1}$ | 19.6 ± 0.60$^{a1}$ |
| | BM-90 | 50 | 99.7±0.02$^{a1}$ | 88.9±0.16$^{a1}$ | 33.7±0.59$^{bc3}$ | 25.7±0.56$^{a1}$ | 22.9±0.55$^{a1}$ | 20.8 ± 0.52$^{a3}$ |
| | CM-10 | 50 | 99.7±0.01$^{a1}$ | 91.4±0.20$^{b1}$ | 35.9±0.86$^{a2}$ | 24.1±0.78$^{a1}$ | 21.5±0.80$^{ac1}$ | 19.4 ± 0.81$^{a1}$ |
| | CM-90 | 50 | 99.7±0.02$^{a1}$ | 90.7±0.24$^{ab1}$ | 34.7±1.12$^{ac2}$ | 23.5±1.11$^{b1}$ | 21.1±1.09$^{bc1}$ | 19.1 ± 1.09$^{a1}$ |

The sample types are coded as follows: CPS wheat straw (WSC); triticale straw, cv. AC Ultima (TSU); and flax shives, cv. CDC Bethune (FSB)

Coarse is coarse milled samples, BM-10 is samples ball milled for 10 minutes, BM-90 is samples ball milled for 90 minutes, CM-10 is samples cryomilled for 10 minutes and CM-90 is samples cryomilled for 90 minutes.

Within common biomass type and common heating rate values followed by different letters within columns are significantly different ($p \leq 0.05$)

Within common milling time, milling type and heating rate values followed by different numbers within columns are significantly different ($p \leq 0.05$)

For the coarse milled samples with particle sizes between 180-850µm (i.e. samples not subjected to ball or cryo milling) heated at a rate of 10 °C min$^{-1}$ more mass remained in the triticale straw samples (32.7%) followed by the flax straw samples (30.2%) and the wheat straw samples (29.4%), implying that the triticale straw and flax shives are more thermally stable in this temperature region compared to wheat straw. This may be due to a combined effect of the lower ash content and low lignin content exhibited by the wheat straw compared to the triticale straw and flax shive samples (Table 1). Plant materials with high lignin content have been shown to exhibit increased thermal stability [7,12] and plant materials with high ash content have been shown to exhibit decreased thermal decomposition [6]. Interestingly, when the same samples were heated at a rate of 50°C min$^{-1}$ more mass remained in the flax shive samples (36.2%) and the triticale straw samples (34.8%) followed by the wheat straw samples (31.5%).

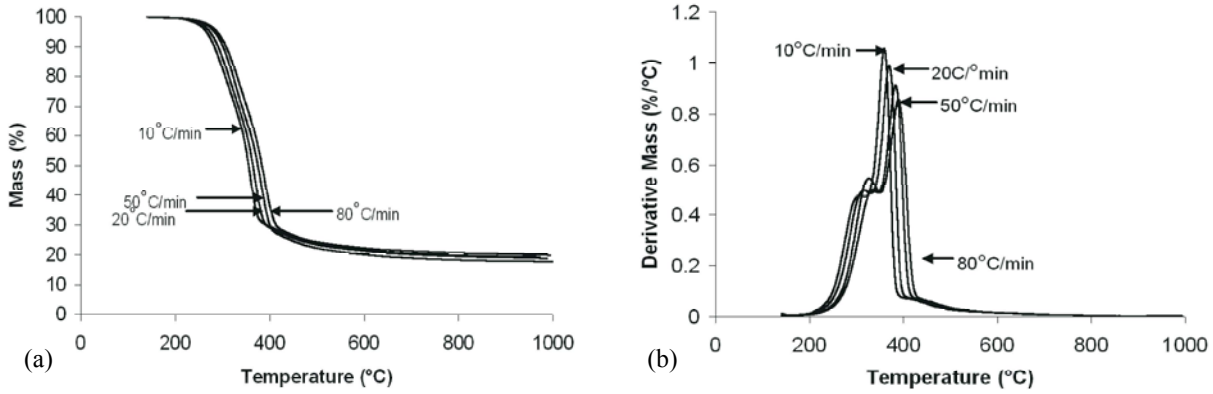


Fig. 4a: Representative TGA thermogram of biomass sample: Wheat straw-coarse milled sample at various heating rates

Fig. 4b: Representative DTG thermogram of biomass sample: Wheat straw-coarse milled sample at various heating rates

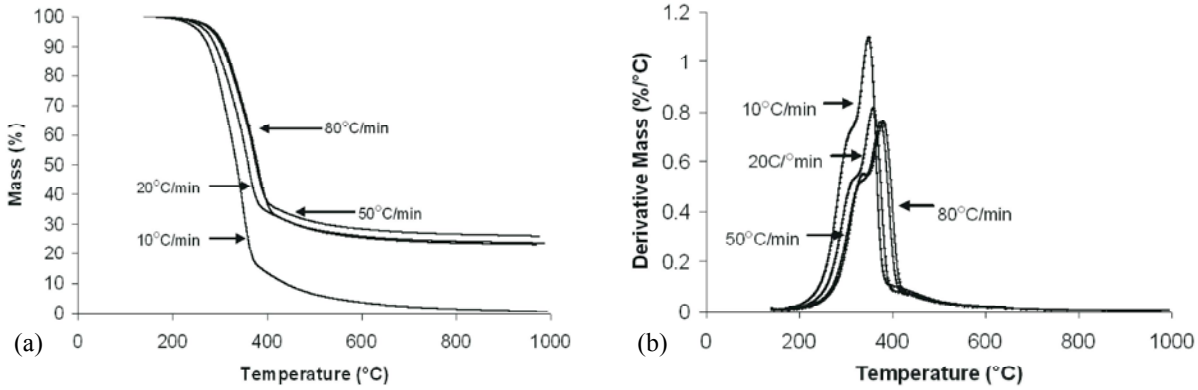


Fig. 5a: Representative TGA thermogram of biomass sample: Triticale straw-coarse milled sample at different various heating rates

Fig. 5b: Representative DTG thermogram of biomass sample: Triticale straw-coarse milled sample at various heating rates

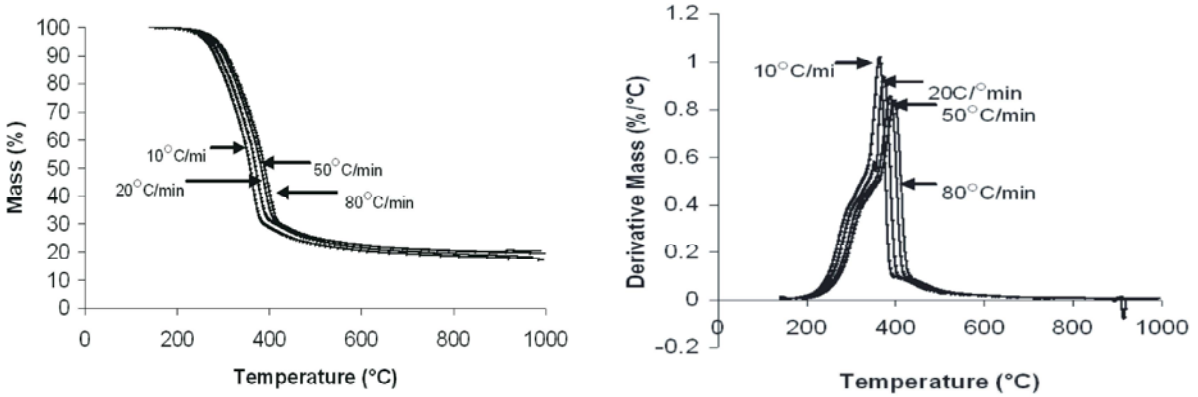


Fig. 6a: Representative TGA thermogram of biomass sample: Flax shive-coarse milled sample at different various heating rates

Fig. 6b: Representative DTG thermogram of biomass sample: Flax shive-coarse milled sample at various heating rates

With respect to thermal decomposition within biomass type as affected by milling treatment, there were observed differences. For both wheat and triticale straw types, samples that were ball milled showed significantly ($p \leq 0.05$) less mass remaining at 400 °C than the coarse milled and cryo-milled samples. There was no noticeable

effect of milling treatment on the degree of thermal decomposition at 400 °C for the flax shive samples. A possible explanation is that prolonged ball milling may decrease the degree of crystallinity of the cellulose present in the wheat and triticale samples. Schwanniger *et al*. [35] has reported that ball milling decreases the degree of crystallinity of the cellulose which has also been shown to reduce thermal stability [44]. Interestingly, Zhu *et al*. [33] reported that both ball milling at ambient temperatures and cryomilling decreased the crystallinity of poly(ethylene terephthalate), however it was indicated that amorphization mechanisms are different as ball milling created oriented amorphous particles while cryomilling created general/non-oriented amporhous particles, which may affect thermal stability. Ball milling did not affect the flax shive samples in the same manner as the wheat and triticale samples as these samples had already undergone the degradative retting process that removes cellulosic fibres [9].

Data for all of the samples indicted that at temperatures over 500 °C a slow mass loss occurred up to the final temperature (800 °C) where the mass loss curves became relatively flat. Regarding the mass remaining for the coarse milled samples with particle sizes between 180-850µm (i.e. samples not subjected to ball or cryo milling) heated at a rate of 10 °C $min^{-1}$, more mass remained in the triticale straw samples (23.6%) followed by the flax shive samples (19.7%) and wheat straw samples (20.4%), implying that the triticale straw was more thermally stable in this temperature region (800 °C) compared to flax shive and wheat straw. The same trend was observed for samples heated at 50 °C $min^{-1}$. This result may again be explained by compositional differences. The combined effect of the higher ash content [6] and lower lignin content [7,12] exhibited by the wheat straw compared to the triticale straw may have reduced its thermal stability. Although the flax shives possessed higher lignin content and lower extractives content which has been reported to increase thermal stability [7,12,44], it possessed a lower cellulose content which too has been shown to enhance thermal stability [7,12,44]. This result seems to indicate that high cellulose content affects thermal stability more than high lignin content in this temperature range.

With respect to thermal decomposition within biomass type as affected by milling treatment, there were only observed differences for the triticale straw type, samples that were ball milled showed significantly less mass remaining at 800 °C than the coarse milled and cryo-milled samples. This result is difficult to rationalize, however, the enhanced effect of balling milling on decreasing the thermal stability of triticale straw may be due to the fact that the triticale samples possessed less lignin than the wheat straw and flax shive samples. d'Almeida *et al*. [12] indicated that biomass samples with higher lignin contents show less degree of degradation compared to biomass samples with lower lignin content. Also, extractives have been implicated in affected the degree of decomposition [7,44]. Shebani *et al*. [44] noted that the removal of extractives from wood improved its thermal stability. It was also noted that removal of hot water extractives, in comparison to ethanol soluble extractives, caused more improvement in the thermal stability of wood. Tritcale straw contained the highest level of extractives and the ratio of water soluble extractives to ethanol soluble extractives was the highest at ~9:1 (Table 1). This may have caused the ball milled triticale straw to be less stable and exhibit enhanced decomposition.

It can also be seen from Table 2 that for all of the samples it was observed that at a given temperature, when a slower heating rate (10°C $min^{-1}$) was used, the samples exhibited a the higher the degree of degradation compared to data from the higher heating rate (50°C $min^{-1}$) which has significant at $p \leq 0.05$. This may be due to the fact that the response time for the sample to attain the necessary temperature for thermal decomposition (i.e. pyrolysis) increased at lower heating rates, which was in favour of thermal degradation [7,26]. The differential thermogravimetric (DTG) curves (first derivative of TGA mass loss versus temperature thermograms) of the three crop residues, wheat straw, triticale straw and flax shives, as affected by milling (time and type) were obtained. Representative DTG curves at each heating rate for the coarse milled wheat straw, triticale straw and flax shives are shown in Figure 4b, 5b and 6b, respectively. In the DTG curves for all samples, weight loss resulting from thermal decomposition occurred between temperatures of 200°C and 800°C. Thermal decomposition rate increased over the 200-400 C, also with increased heating rate the DTG curves being shifted towards a higher temperature zone and the peak temperature ($T_p$) corresponding to the maximum loss of mass shifted to higher temperature values which was significant at $p \leq 0.05$.

Generally, for all heating rates, the degradation of all biomass samples presented a main peak between 340-395 °C and a shoulder between 300-330 °C depending on biomass type and milling treatment. The first event (shoulder) can be associated with the decomposition of hemicellulose and the slow degradation of lignin [7]. The second event (main peak) at approximately 340-395 °C can be attributed to the degradation of cellulose.

Table 3: Thermal Parameters Obtained from Differential Thermogravimetric (DTG) Curves for Wheat Straw, Triticale Straw and Flax Shives

| Sample | Milling Treatment | Heating Rate (°C min$^{-1}$) | $T_p$(°C) | $M_p$(%) |
|---|---|---|---|---|
| WSC | Coarse | 10 | 358.2 ± 0.58$^{a1}$ | 53.7 ± 0.41$^{a1}$ |
| | BM-10 | 10 | 357.2 ± 0.35$^{a1}$ | 57.2 ± 0.87$^{b1}$ |
| | BM-90 | 10 | 345.9 ± 0.31$^{b1}$ | 55.2 ± 0.46$^{b12}$ |
| | CM-10 | 10 | 358.3 ± 0.06$^{a1}$ | 54.6 ± 0.43$^{b1}$ |
| | CM-90 | 10 | 359.1 ± 0.13$^{a1}$ | 56.4 ± 0.83$^{b1}$ |
| TSU | Coarse | 10 | 349.5 ± 0.47$^{a2}$ | 50.27 ±2.45$^{a2}$ |
| | BM-10 | 10 | 351.6 ± 0.07$^{b2}$ | 58.1 ± 0.16$^{b1}$ |
| | BM-90 | 10 | 342.5 ± 0.13$^{c2}$ | 55.5 ± 0.26$^{c1}$ |
| | CM-10 | 10 | 348.6 ± 0.36$^{a2}$ | 50.8 ± 0.64$^{a2}$ |
| | CM-90 | 10 | 348.1 ± 0.13$^{a2}$ | 51.1 ± 1.02$^{a2}$ |
| FSB | Coarse | 10 | 363.3 ± 0.58$^{a3}$ | 53.9 ± 1.15$^{a1}$ |
| | BM-10 | 10 | 361.3 ± 0.93$^{b3}$ | 55.0 ± 0.70$^{a2}$ |
| | BM-90 | 10 | 349.4 ± 0.83$^{c3}$ | 53.5 ± 0.78$^{a2}$ |
| | CM-10 | 10 | 363.8 ± 2.65$^{a3}$ | 55.2 ± 3.25$^{a3}$ |
| | CM-90 | 10 | 363.7 ± 0.47$^{a3}$ | 57.9 ± 0.29$^{b1}$ |
| WSC | Coarse | 50 | 382.3 ± 1.51$^{a1}$ | 55.5 ± 1.18$^{a1}$ |
| | BM-10 | 50 | 384.8 ± 0.42$^{b1}$ | 58.2 ± 0.29$^{b12}$ |
| | BM-90 | 50 | 374.2 ± 1.83$^{c1}$ | 56.2 ± 1.31$^{a1}$ |
| | CM-10 | 50 | 384.4 ± 0.41$^{b1}$ | 55.1 ± 0.70$^{a12}$ |
| | CM-90 | 50 | 385.6 ± 0.15$^{b1}$ | 56.9 ± 0.44$^{a1}$ |
| TSU | Coarse | 50 | 372.1 ± 1.44$^{a2}$ | 49.1 ± 1.25$^{a2}$ |
| | BM-10 | 50 | 378.9 ± 0.93$^{b2}$ | 58.8 ± 0.85$^{b1}$ |
| | BM-90 | 50 | 368.5 ± 0.21$^{c2}$ | 56.3 ± 0.41$^{c1}$ |
| | CM-10 | 50 | 374.3 ± 1.25$^{d2}$ | 49.8 ± 0.30$^{a1}$ |
| | CM-90 | 50 | 373.9 ± 0.09$^{d2}$ | 50.6 ± 0.08$^{a2}$ |
| FSB | Coarse | 50 | 388.0 ± 0.98$^{a3}$ | 54.4 ± 1.56$^{a1}$ |
| | BM-10 | 50 | 388.2 ± 0.50$^{a3}$ | 56.6 ± 0.27$^{b2}$ |
| | BM-90 | 50 | 376.3 ± 0.91$^{b3}$ | 54.4 ± 1.05$^{a2}$ |
| | CM-10 | 50 | 391.5 ± 2.99$^{c3}$ | 57.0 ± 1.79$^{b2}$ |
| | CM-90 | 50 | 388.0 ± 1.25$^{a3}$ | 55.9 ± 1.98$^{b1}$ |

The sample types are coded as follows: CPS wheat straw (WSC); triticale straw, cv. AC Ultima (TSU); and flax shives, cv. CDC Bethune (FSB)

Coarse is coarse milled samples, BM-10 is samples ball milled for 10 minutes, BM-90 is samples ball milled for 90 minutes, CM-10 is samples cryomilled for 10 minutes and CM-90 is samples cryomilled for 90 minutes.

Tp is temperature at peak on DTG curve; Mp is % mass loss at peak temperature

Within common biomass type and common heating rate values followed by different letters within columns are significantly different ($p \leq 0.05$)

Within common milling time, milling type and heating rate values followed by different numbers within columns are significantly different ($p \leq 0.05$)

Depolymerization of hemicellulose has been noted to occur around 150-350 °C, random cleavage of the glycosidic linkage of cellulose has been noted to occur around 275-350 °C and the degradation of lignin has been noted to occur between 250-500 °C [7,16]. Decomposition due to reactions such as dehydration, decarboxylation and decarbonlyation, which result in the production of volatile compounds, char and ash, all occur at this temperature range [16,22].

To further investigate the thermal decomposition behavior of crop residue samples as affected by milling treatment, the temperature at which the fasted rate of mass loss occurred ($T_p$) as well as the corresponding mass losses at peak temperature ($M_p$) were obtained from the TG and DTG curves. Both values ($M_p$ and $T_p$) are presented in Table 3 for all samples subjected to the 10 and 50 °C min$^{-1}$ heating rates. There were significant differences with respect to $T_p$ and $M_p$ values between the crop residue types subjected to different milling times and types. For the coarse milled samples with particle sizes between 180-850µm (i.e. samples not subjected to ball or cryo milling) higher $T_p$ values were seen in the flax shives, followed by the wheat straw and then the triticale straw. While for the $M_p$ values less mass was lost from the triticale straw samples at $T_p$ compared to the wheat straw and flax shive samples. This implies that while the rate of triticale straw decomposition is more rapid at lower temperature than wheat straw and flax shives the degree of its decomposition is less. This result is possibly due to its higher extractives content and lower lignin content (Table 1) which decreases thermal stability [7,12,44] yet the higher ash content associated with triticale straw may has hindered degree of degradation as high ash content has been noted to negatively affect thermal decomposition [6].

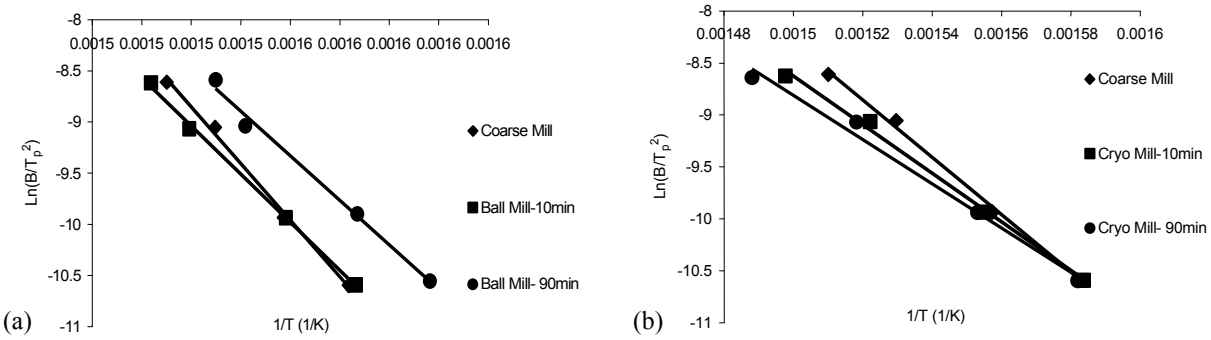


Fig. 7a: Kissenger method plot of $\ln(\beta/T_p^2)$ against 1/T for ball-milled wheat straw samples. The line represents the linear regression of the points.

Fig. 7b: Kissenger method plot of $\ln(\beta/T_p^2)$ against 1/T for cryo-milled wheat straw samples. The line represents the linear regression of the points.

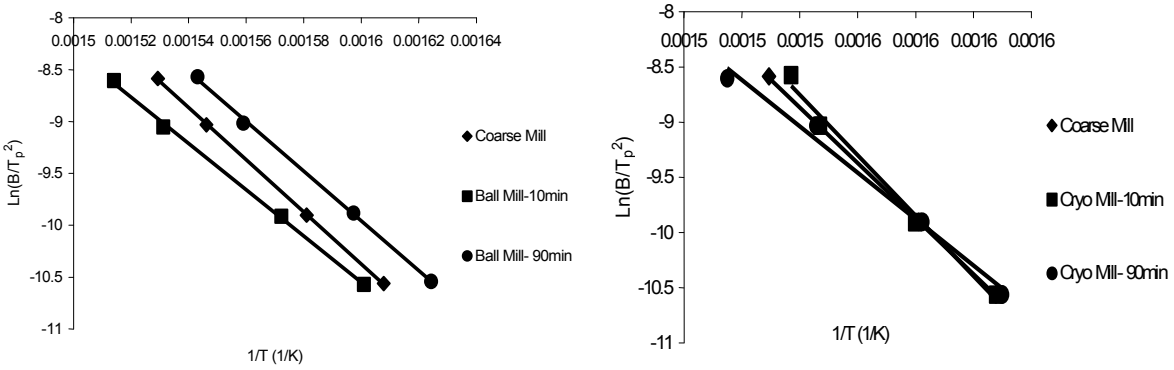


Fig. 8a: Kissenger method plot of $\ln(\beta/T_p^2)$ against 1/T for ball-milled triticale straw samples. The line represents the linear regression of the points.

Fig. 8b: Kissenger method plot of $\ln(\beta/T_p^2)$ against 1/T for cryo-milled triticale straw samples. The line represents the linear regression of the points.

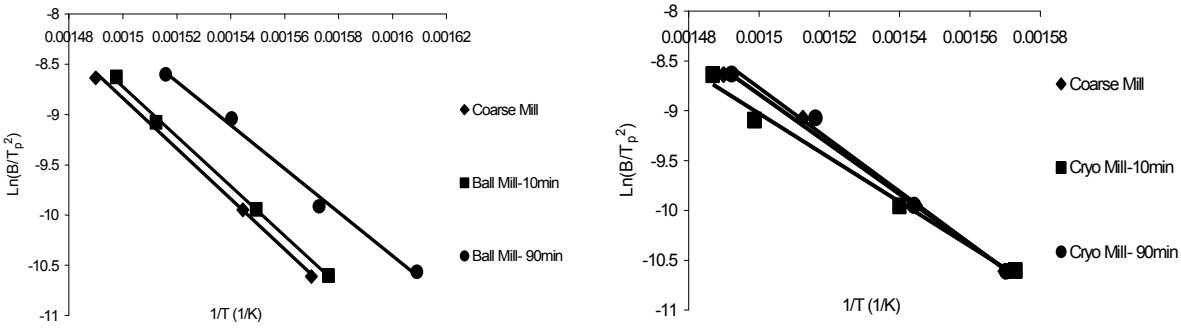


Fig. 9a: Kissenger method plot of $\ln(\beta/T_p^2)$ against 1/T for ball-milled flax shive samples. The line represents the linear regression of the points.

Fig. 9b: Kissenger method plot of $\ln(\beta/T_p^2)$ against 1/T for cryo-milled flax shive samples. The line represents the linear regression of the points.

**Apparent Activation Energy of Thermal Decomposition:** Use of a different biomass types as reinforcing fillers in polymers composite necessitates quantification of the kinetic parameters associated with the thermal decomposition process of the different biomass types [20]. The Kissenger method, outlined in Yang *et al*. [26], was used to determine two important kinetic parameters: apparent activation energy ($E_a$) and pre-exponential factor

(A). The apparent activation energy represents the amount of energy required for the thermal degradation to occur and the pre-exponential factor is a constant used in the Arrhenius equation to calculate the reaction rate coefficient [16,26]. Figures 7-9 represent the Kissenger method plots of $\ln(\beta/T_p^2)$ against 1/T used to obtain the apparent activation energy and pre-exponential factor (A) of the main decomposition process (i.e. related to the main peak on the DTG curve) for the triticale straw, wheat straw and flax shive samples subjected to different milling conditions. Results for the kinetic parameters along with the correlation coefficient ($R^2$) are reported in Table 4. The correlation coefficients were between 0.991-0.999 and consequently the first order reaction equation used represented the data reasonably well [45]. Thus, these results validated the use of a first order equation to describe the reaction kinetics of the thermal decomposition of wheat straw, triticale straw and flax shives. The $E_a$ values for the wheat straw, triticale straw and flax shives ranged from 179-222, 176-227 and 194-218 kJ $mol^{-1}$, respectively. These $E_a$ values presented in Table 4 correlates very well with reported data for flax, 187 kJ $mol^{-1}$ [12], wheat, oat, barley and Ethiopian mustard, 167-228 kJ $mol^{-1}$ [19] and pure cellulose, 203 kJ $mol^{-1}$ [12]. In general there were no significant differences in $E_a$ values between biomass types at common milling times and milling types indicating comparable energy requirements for thermal decomposition. Also, there were no significant differences in the pre-exponential factor (A) between biomass types at common milling times and milling types indicating comparable energy requirements for thermal decomposition. With respect to thermal decomposition within biomass type as affected by milling treatment, there were differences. In most cases the coarse milled wheat straw and triticale straw samples possessed higher $E_a$ and pre-exponential factor values compared to the wheat and tritcale straw samples subjected to ball milling and cryo-milling for various times. These results are in agreement with a study examining the influence of particle size on the thermal decomposition of $CaCO_3$ (inorganic material) which showed that the activation energy of the thermal decomposition of $CaCO_3$ decreased as particle size decreased. This result was attributed to a greater the fraction of "CaCO, molecules" located on the surface of smaller particles with regards to the bulk mass. Therefore, the activation energy decreased because of the "extra" energy stored on the surface of the smaller particles [30]. The $E_a$ values obtained for the coarse milled flax shive samples and cryo-milled were not significantly different even though particle sizes were very different between these milling conditions However, the ball milled flax shive samples possessed $E_a$ values that were significantly lower. Milling treatment did not affect the pre-exponential factors determined for the flax shive samples. This work shows that for all biomass types coarse milled samples show potential for application as an agro-filler in composite

Table 4: Kinetic Parameters of Wheat Straw, Triticale Straw and Flax Shives

| Sample | Milling Treatment | $E_a$ (kJ $mol^{-1}$) | Ln(A) ($min^{-1}$) | $R^2$ |
|---|---|---|---|---|
| WSC | Coarse | $222.1 \pm 10.33^{a1}$ | $41.9 \pm 1.97^{a1}$ | 0.998 |
| | BM-10 | $201.5 \pm 5.79^{ab1}$ | $37.9 \pm 1.13^{a1}$ | 0.998 |
| | BM-90 | $187.9 \pm 6.16^{bc1}$ | $35.9 \pm 1.21^{a1}$ | 0.991 |
| | CM-10 | $190.9 \pm 11.17^{bc1}$ | $35.8 \pm 2.16^{a1}$ | 0.996 |
| | CM-90 | $179.4 \pm 2.34^{c1}$ | $33.6 \pm 0.46^{b1}$ | 0.990 |
| TSU | Coarse | $227.96 \pm 24.45^{a1}$ | $43.7 \pm 4.79^{a1}$ | 0.999 |
| | BM-10 | $187.9 \pm 24.5^{b1}$ | $35.6 \pm 1.28^{b1}$ | 0.999 |
| | BM-90 | $186.0 \pm 6.5^{b1}$ | $35.8 \pm 2.66^{b1}$ | 0.999 |
| | CM-10 | $203.7 \pm 18.7^{b1}$ | $38.9 \pm 3.58^{ab1}$ | 0.991 |
| | CM-90 | $176.5 \pm 4.67^{b1}$ | $33.6 \pm 0.92^{b1}$ | 0.991 |
| FSB | Coarse | $218.7 \pm 12.72^{a1}$ | $40.9 \pm 2.44^{a1}$ | 0.999 |
| | BM-10 | $198.9 \pm 6.09^{b1}$ | $37.2 \pm 1.18^{a1}$ | 0.998 |
| | BM-90 | $194.7 \pm 13.2^{b1}$ | $37.1 \pm 2.58^{a1}$ | 0.993 |
| | CM-10 | $200.4 \pm 28.02^{a1}$ | $37.3 \pm 5.3^{a1}$ | 0.991 |
| | CM-90 | $207.5 \pm 9.32^{a2}$ | $38.7 \pm 1.78^{a1}$ | 0.992 |

The sample types are coded as follows: CPS wheat straw (WSC); triticale straw, cv. AC Ultima (TSU); and flax shives, cv. CDC Bethune (FSB)

Coarse is coarse milled samples, BM-10 is samples ball milled for 10 minutes, BM-90 is samples ball milled for 90 minutes, CM-10 is samples cryomilled for 10 minutes and CM-90 is sampled cryomilled for 90 minutes.

$E_a$ is apparent activation energy; and LnA is the natural logarithm of pre-exponential factor (A).

Within common biomass type, values followed by different letters within columns are significantly different ($p \leq 0.05$)

Within common milling time and milling type, values followed by different numbers within columns are significantly different ($p \leq 0.05$)

polymers as a less energy intensive milling treatment can be performed that yields particles which show good thermal stability. However, if the application is for generating bioenergy (gas, bio-oil, char) and biochemicals then possible ball milling could be employed as this treatment creates biomass particles that exhibit degradation behaviour that is more energetically favourable.

## CONCLUSIONS

Thermogravimetric analysis carried out under a nitrogen environment was used to determine the thermal decomposition behaviour and kinetic paratmeters of three types of Canadian crop residues, wheat straw, triticle straw and flax shives in order to provide data to help promote their use as agro-fillers in thermocomposites and as a source material for bioenergy and biochemicals. The results of this study show that for all samples, mass loss resulting from thermal decomposition occurred between temperatures of 200°C and 800°C. Thermal decomposition rate increased over the 200-400 C and the majority of mass loss occurred between 200 and 400 °C. All of the samples showed a mass loss of ~ 70-75% on reaching 400 °C depending on heating rate, biomass type and milling treatment. Generally, for all heating rates, the degradation of all biomass samples presented a main peak between 340-395 °C and a shoulder between 300-330 °C depending on biomass type and milling treatment. The activation energy ($E_a$) values for the coarse milled wheat straw, triticale straw and flax shives were, 222.1, 227.9 and 218.7, kJ $mol^{-1}$, respectively. The $E_a$ values for the ball milled and cryo milled wheat straw, triticale straw and flax shives ranged from 176 to 207 kJ $mol^{-1}$, respectively. In most cases the ball milled samples possessed lower Ea values. These results provide important information required to better understand the degradation mechanisms of different types of crop residues and supplies information which can be used to determine optimized polymer processing conditions and further develop industrial applications and processes.

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