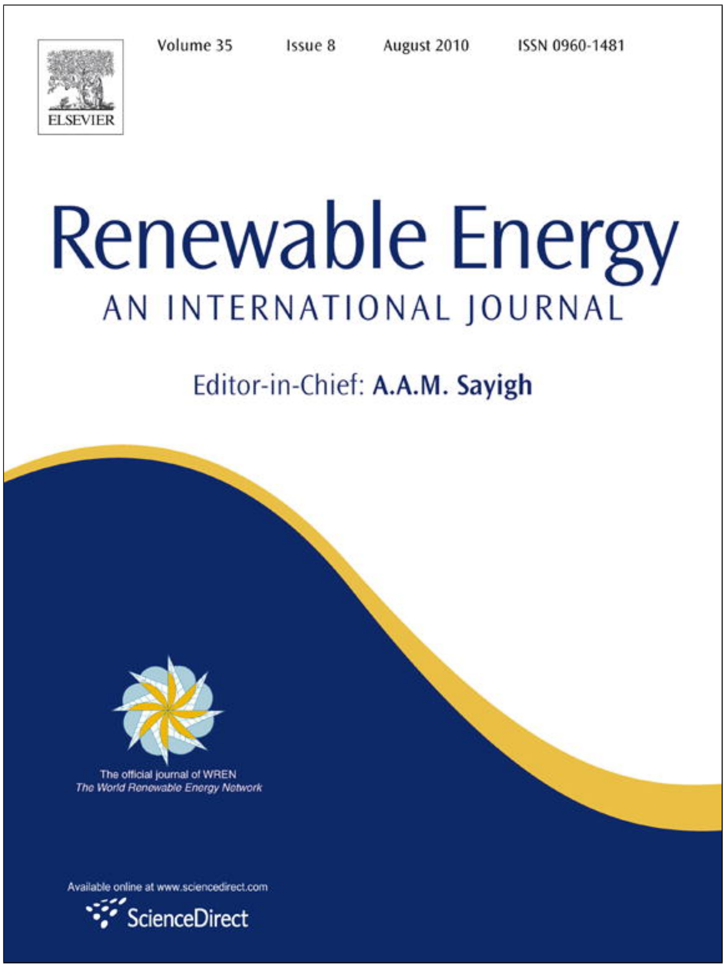
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Characterization of Canadian biomass for alternative renewable biofuel

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ABSTRACT

Biomass represents the renewable energy source and their use reduces the consumption of fossil fuels and limits the emission of CO_2, SO_x, NO_x and heavy metals. They are used in pyrolysis, gasification, combustion and co-combustion. Present study aims to highlight the common biomass available in Canada such as wheat straw, barley straw, flax straw, timothy grass and pinewood. The biomass samples were collected form Saskatoon, Canada and examined for their physical and chemical characteristics using static bomb calorimeter, XRD, TGA, ICP-MS, CHNSO, FT-IR and FT-NIR. The biomass samples were subjected to three-step extraction process, i.e. hexane, alcohol and water extraction separately, after extraction the raffinate biomass was acid hydrolyzed. The acid soluble fractions, which mainly contained degraded sugars, were analysed by HPLC and the lignin content was determined using acid insoluble fraction. The hexane extract (i.e. waxes), alcohol extract and lignin were characterized by FT-IR spectroscopy. Among all the biomass samples pinewood shows lower ash and lignin content, while shows higher calorific value, cellulose and hemicellulose content. The appreciable amount of hexane soluble in pinewood was due to the presence of terpene hydrocarbons. However among the agricultural biomass samples barley straw shows higher ash, wax and lignin content compared to wheat and flax straw. All these properties combined together have shown that pinewood, wheat and flax can act as the potential candidates for bio-energy production.

1. Introduction

Alternative and renewable energy resources have recently become a high priority for many countries and will play a major role in the chemical industry in the near future. These renewable energy resources have become quickly popularized due to their lack of environmental risks and pollution; they are favorable alternatives to fossil fuels and their derivatives. In addition to their sustainable favorability, they are, in general, more evenly distributed over earth's surface than fossil fuels or uranium and may be exploited using less capital-intensive technologies. Hence they increase the scope for diversification and decentralization of energy supplies and the achievement of energy self-sufficiency at a local, regional, and national level [1]. Lignocellulosic biomass represents a renewable and largely untapped source of raw feedstock for conversion into liquid and gas fuels, thermochemical products and other energy-related end products [2].

In all cases, a fundamental characterization of biomass as a feedstock is required for bio-fuel and chemical production, which exhibit very different properties with respect to traditional fossil fuels and their derivatives [3]. In particular, lignin–cellulosic materials are more reactive and have a higher volatility than coals. However, all biomass differs greatly in volatile matter concentration, even the same type of biomass can change in composition based on the climatic conditions and seasonal variation. Furthermore, characterization of biomass is imperative as the chemical composition of biomass affects the conversion processes differently. For example, high nitrogen and ash concentration reduces hydrocarbon yield during thermochemical conversion [2]. Whereas lignin concentration, one of the three basic components of lignocellulosic material does not have a detrimental effect on thermochemical product yield [4]. Biomass feedstock composition determines the theoretical yield from a biochemical conversion, and can thereby have a significant impact on conversion process economics. From this information, the impact of biomass characterization on the expanding biofuel and bioproduct industry can be seen. With knowledge of these complex feedstock compositions and thermal behavior in conversion processes, yield can be predicted, mathematical models can be created to further understand products, economic analysis can be performed, and most importantly, technology can be formed to make biomass conversion more efficient, effective, and better competition for fossil fuel production.

Biomass is a promising renewable energy. The availability of biomass of the world is 220 billion oven-dry ton (odt) per year or 4500 EJ (10^{18} J) [5]. It is the world's largest and most sustainable energy resource. Increasing the capacity of energy produced from

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biomass one can reduce the fossil fuel consumption. The advantages of this process are to reduce the green house gases in compared to fossil fuels and also solve the difficulties of the dependence of imported fossil fuels for many countries [5]. Biomass refers to plant derived organic matter that is available on a renewable basis. Lignocellulosic biomasses includes agricultural crop waste, forest residues, aquatic plants, energy crops residues etc and are about 50% of the all biomasses. It is mainly consist of cellulose, hemicellulose, and lignin. Cellulose is composed of monomers of glucose, a six sugar linked by β (1–4) glycoside bonds. Hemicellulose is a highly branched carbohydrate and is composed of both hexose and pentose sugar. Lignin is a macromolecular in nature with phenolic character, it is helical and contains ether and carbon–carbon linkages. Lignocellulosic biomass is one of the promising renewable feedstocks for production of biofuels and chemicals due to petroleum oil shortage, fluctuating price of the crude oil and environmental problems. Currently, lignocellulosic biomass resources deserve major interest to produce bio oil, bioethanol, synthesis gas, hydrogen and chemicals. Various roots have been investigated to utilize the waste non-food biomass for fuel. A few studies on biomass conversion processes such as chemical, physical, biological and thermal have been reported [6] and most general outline is presented in Fig. 1.

The use of renewable resources for fuel, such as ethanol derived from lignocellulosic biomass has great potential to replace petroleum fuel. Ethanol is made from the fermentation of sugar viz. glucose which is one of the simplest sugar and can be obtained from the cellulose present in the plant biomass (lignocellulosic biomass). The challenge in using lignocellulosic biomass as an ethanol source is removal of the lignin and hemicellulose from cellulose with rapture of strong cell wall of plant matrix. It is flexible composites of biological polymer such as cellulose, hemicellulose and lignin, which serve to maintain the structural integrity of plant cells [7]. Cell wall polysaccharides can be used as feedstock for biofuel production after being broken down into simple sugar, but this process is strongly inhibited by the presence of lignin, which is a part of a phenolic polymer. Lignin is part of a complex matrix in which cellulose micro fibrils are embedded [8]. The inhibition of saccharification enzyme by lignin may result from the reduced accessibility of cellulose micro fibrils as well as adsorption of hydrolytic enzymes to lignin polymer. Therefore, the characterization of lignocellulosic biomass is important to determine the feasibility of the biofuel production from different feedstocks.

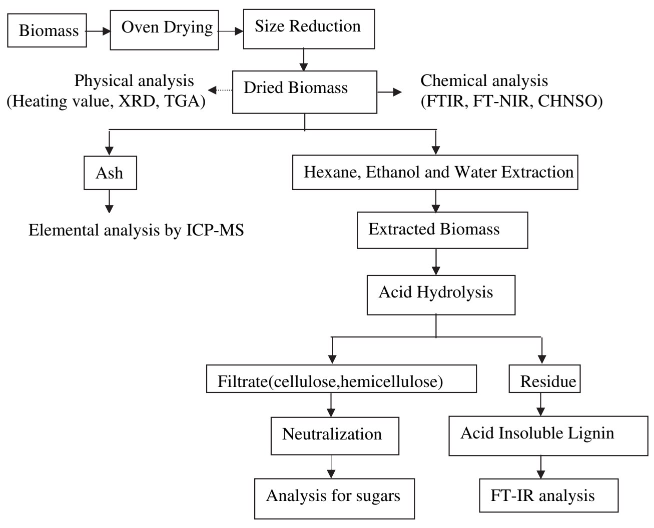

Fig. 1. Schematic diagram of biomass extraction and analysis.

The present study is to select the different origin of biomass such as agriculture residue, wild grass and forest residue which are abundant in Canada and characterize them using thermo-chemical methods. The selected five biomasses such as wheat straw, barley straw, flax straw, timothy grass and pinewood are abundant in Canada. In the prairie provinces of Canada, Saskatchewan produces 7.6 million tonnes of wheat, 4.2 million tonnes of barley and 0.57 million tonnes of flax seed annually based on the average taken over from the production data of the past ten years [9]. Similarly a wild grass variety, i.e. timothy is chosen due to its ability to grow anywhere in Canada. Furthermore there is excess of timothy grass in Canada, which has exported 7000 metric tonnes in 2007. This exceeded more than double, than that (3000 metric tonnes) exported in 2006. In Canada average annual wood cut has been estimated at 167.5 million m^3 creating over 60 million tonnes of residues [5,6]. The annual harvests are taken from approximately 1 million ha, constituting of only about 0.25% of the total forestland in Canada [10].

The basic objective of this study was to select the potential candidates from different Canadian biomass and evaluate the potential of these biomasses as feedstock for the production of biofuel based on their physical and chemical characterization.

2. Materials and methods

The biomass samples were collected from the location of Saskatoon (52.13°N, 106.41°W), Canada. The solvents used in the experiments were reagent grade and distilled in laboratory before use. The extraction and analysis of biomass were carried out using standard NREL methods [11] and repeated the procedure of extraction and analysis three times. The experimental data presented are the average of the three such readings. The overall experimental steps are presented in Fig. 1.

2.1. *Biomass samples*

The biomass such as wheat straw, barley straw, flax straw and timothy grass were harvested during 2008 in Saskatchewan, Canada. The forest residue such as pinewood was collected from local forest of Saskatchewan in 2008 and these biomass samples were stored at room conditions.

Wheat (*Triticum aestivum* L.) plays a major role among the few species widely grown as food sources and likely was central to the beginning of agriculture [12]. Approximately one-sixth of the total arable land in the world is cultivated with wheat. From 1995 onwards wheat production increased at a much higher rate and ultimately increased the biomass production. Canada stands the fourth position in the world in wheat production [13]. Wheat straw is a major agricultural by-product that has been successfully utilized as a raw material in energy sector. Wheat straw could be considered as a natural resource and consists mainly of cellulose, hemicellulose and lignin [14].

Barley is one of the major crops in the world and it is also one of the third major crops in Canada. Barley straw is a significant raw material used in cellulose production as an energy resource and in agriculture as ruminant feed [15]. Like wheat, barley straw is also rich with cellulose, hemicellulose and lignin [16], and found to be the potential candidates for production of bio-fuel.

It is well known that Canada is the largest producer and exporter of flax seed [9]. Flax straw could be considered as a kind of natural resource in renewable energy sector. Several companies utilize flax straw in large scale for production of bio-fuels. It is physically easier to use as a fuel for large commercial users. Flax straw has a per tonne heating value similar to soft coal and cheaper than conventional fuels. There is no report available on chemical composition of flax straw.

Timothy grass is commonly grown for cattle feed and, in particular, as hay for horses. It grows to about 3 ft in height and resembles cereal wheat both in leaf and placement of seed head on top of the stalk. It is relatively high in fibre, especially when cut late. It makes a very high energy feed, so that it is preferred for work horses [17]. So this biomass can be utilised for bio-fuel production.

Pinewood biomass is generated in the process of making of small pieces, which is a source of waste biomass [18]. An example of this is the 65 MW of plant in Williams Lake that uses about 600,000 tonnes of saw mill residue per year and numerous smaller power plants throughout Canada.

2.2. Physical properties of biomasses

The dried biomass samples were pulverized and ground in a Wiley Mill (0.5 mm) prior to analysis. The physical characteristics of biomass samples such as proximate analysis by ASTM methods [19-21] and calorific value, XRD and TG analysis were obtained by using NREL methods [11].

2.2.1. Proximate analysis

The moisture content of the biomass was determined using the procedure given in ASTM 3173-87 [19]. The ash content was determined in laboratory muffle furnace (Holpack, USA) as per ASTM 3174-04 [20]. For the ash content, 1.0 g of biomass sample was taken in crucible and placed in muffle furnace maintained at 575 ± 10 °C for 4 h. Then the crucible was removed from the furnace and placed in the desiccator. The above process of heating and cooling was repeated until constant weight was obtained. This process allows removal of the volatiles and unburnt carbon.

The volatile matter in the biomass was determined by the procedure given in ASTM D 3175-07 [21]. The biomass sample (1.0 g) was taken and placed in muffle furnace maintained at 950 ± 10 °C for 7 min. Then the crucible was removed from the furnace and placed in the desiccator. The loss of weight was given the volatile matter in the biomass.

2.2.2. Calorific value

The calorific values were determined in a static bomb calorimeter; a sealed Parr 1108, using NREL method [11] and detail procedure described by Hubbard et al. [22] Sample pellets of 1.0 g was used for each analysis. A cotton thread was attached to the platinum ignition wire and placed in contact with the pellet. The bomb was filled with oxygen at 25 °C with 1.0 cm^3 of water added to the bomb. The calorimeter was placed in an isothermal jacket with an air gap separation of 10 mm between all surfaces. The electrical energy for ignition was determined from the change of potential across a 1256 or 2900 µF capacitor when discharged from about 40 V through a platinum wire. The bomb calorimeter was submerged in a calorimeter cane filled with distilled water. The calorimeter jacket was maintained at constant temperature by circulating water at 25 °C.

2.2.3. XRD analysis

The XRD analysis was performed using Rigaku diffractometer (Rigaku, Tokyo, Japan) using Cu Kα radiation at 40 kV and 130 mA in the scanning angle of 5–50° at a scanning speed of 0.5° min^{-1}.

2.2.4. TGA

TG analysis of the biomass samples were performed using PerkinElmer instrument, Pyris Diamond TG/DTA. The purpose of TGA is to understand the devolatilization characteristics of the biomass samples with temperature. Therefore, 0.5 mg of sample was taken and studied the devolatilization characteristics from 20 to 650 °C at the rate of 10 °C/min. The rate of purge gas (Nitrogen) flow was 60 mL/min.

2.3. Chemical analysis of biomasses

The chemical analysis of biomass samples were performed using CHNSO, ICP-MS, FT-IR and FT-NIR test methods.

2.3.1. CHNSO

The common organic elements such as C, H, N, S and O were analyzed in PerkinElmer Elementar CHNSO analyzer. The sample (1.0 mg) was used in a tin boat assortment for percentage composition of C, H, N and S analysis and the percentage O was determined by means of difference.

2.3.2. ICP-MS

The analysis of some common elements present in the ash was determined by ICP-MS. A standard sample contained metals viz. Mg, Al, Ca, P, Mn, Fe, Cu, Zn and Sr were used for the calibration (signal intensity vs. mass to charge ratio) of ICP-MS. A full scan m/z 40–250 was carried out for quantification study.

2.3.3. FT-IR

The FT-IR spectra of biomass samples were obtained by using PerkinElmer, FT-IR spectrum GX. The biomass (10 mg) was well mixed with 200 mg of KBr and the mixture was compressed for preparation of pellets. Each spectrum was the average of 64, co-addition of scans with a total scan time15 s in the IR range of 600–4000 cm^{-1} at 2 cm^{-1}.

2.3.4. FT-NIR

Each sample (10 mg) was put in a non-NIR absorbing glass vial (PIKE technologies, Madison, WI) of an FT-NIR spectrometer (Excalibur 3100, Varian Inc., Palo Alto CM) equipped with an NIR integrating sphere (Integrat IR™, PIKE technologies, Madison, WI). A constant weight was applied on the sample to ensure uniform compactness and kept the sample sealed from ambient air. The spectra cover a range of 4000–10,000 cm^{-1} with a spectral resolution at 8 cm^{-1}. Each spectrum shown in Fig. 6 was the average of 64; co-addition of scans with a total scan time15 s in the NIR range of 4000–10,000 cm^{-1}.

Table 1
Proximate, ultimate and calorific value of biomass.

Biomass	Proximate analysis (wt%)				Ultimate analysis (wt%)					Calorific value (MJ/kg)
	Moisture	Ash	Volatile matter	Fixed carbon[a]	C	H	N	S	O[b]	
Wheat straw	6.0 ± 0.2	1.3 ± 0.1	78.3 ± 0.2	14.4 ± 0.2	41.6 ± 0.2	6.1 ± 0.2	0.14 ± 0.02	0.06 ± 0.01	52.1 ± 0.3	20.3 ± 0.2
Barley straw	6.9 ± 0.3	9.8 ± 0.1	78.5 ± 0.1	4.8 ± 0.2	41.4 ± 0.1	6.2 ± 0.1	0.63 ± 0.02	0.01	51.7 ± 0.2	15.7 ± 0.3
Flax straw	7.9 ± 0.3	3.0 ± 0.2	80.3 ± 0.2	8.8 ± 0.3	43.1 ± 0.2	6.2 ± 0.2	0.68 ± 0.03	0.09 ± 0.01	49.9 ± 0.3	17.0 ± 0.2
Timothy grass	5.0 ± 0.2	1.1 ± 0.1	77.9 ± 0.2	16.0 ± 0.3	42.4 ± 0.2	6.0 ± 0.2	1.03 ± 0.02	0.15 ± 0.02	50.4 ± 0.2	16.7 ± 0.3
Pinewood	5.8 ± 0.4	1.5 ± 0.2	82.4 ± 0.1	10.3 ± 0.2	49.0 ± 0.2	6.4 ± 0.1	0.14 ± 0.01	0.01	44.4 ± 0.4	19.6 ± 0.2

[a] % Of fixed carbon calculated from difference of moisture, ash and volatile matter content.

[b] % Of O calculated from the difference of C, H, N and S.

Table 2
ICP-MS analysis of some common elements present in ash (ppm).

Element	Wheat straw	Barley straw	Timothy grass	Flax straw	Pinewood
Mg	22,534	16,490	20,479	64,006	34,297
Al	11,613	2583	585	637	4961
Ca	–	–	–	47,385	150,621
P	14,381	17,768	22,796	21,780	27,244
Mn	383	288	684	1139	1247
Fe	5820	2690	1041	1904	52365
Cu	163	134	147	229	3879
Zn	123	95	203	448	3222
Sr	231	229	153	497	558

The data presented is the average of three analysis.

2.4. Determination of extractives in biomass

The biomass samples (100 g) were extracted with n-hexane, ethanol and distilled water respectively by Soxhlet extraction apparatus and each solvent extraction were carried out for 6 h. In first step the extraction of n-hexane soluble compounds was carried out to separate the class of compounds such as non-polar lipids, hydrocarbon compounds and terpenoids, etc. The hexane raffinated biomass was extracted with alcohol to separate polar compounds such as chlorophyll, polar waxes, sterol and other minor constituents. The final raffinate biomass was extracted with water to separate inorganic materials and non-structural sugars, etc. The solvent in each extract was removed in rotary evaporator under reduced pressure (Figs. 7–9).

The final raffinate biomass (after Soxhlet extractions) was acid hydrolyzed using H_2SO_4 for conversion of hemicellulose and cellulose to sugars by NREL method [11]. The acidic sugar solution was neutralized by calcium carbonate. Then the sugars were analysed by Hewlett-Packard HPLC equipped with an RI detector. The analysis was performed by an Aminex HPX 87P column (Bioad, Hercules, CA) equipped with a deashing guard cartridge (BioRad). Degassed HPLC grade water was used as the mobile phase at the rate of 0.6 mL/min with an ambient column temperature (35 °C) and the injection volume was 20 µl with a run time of 20 min. The mixed sugar standards viz. cellulobiose, glucose, xylose, galactose, arabinose and mannose were used for quantification. The weight percentage of these compounds in the sample was determined by comparing with respective standards.

The FT-IR analysis of hexane extract (wax), ethanol and lignin were carried out using the similar method as discussed above. For comparison, only the spectra of barley straw, flax straw and pinewood are presented.

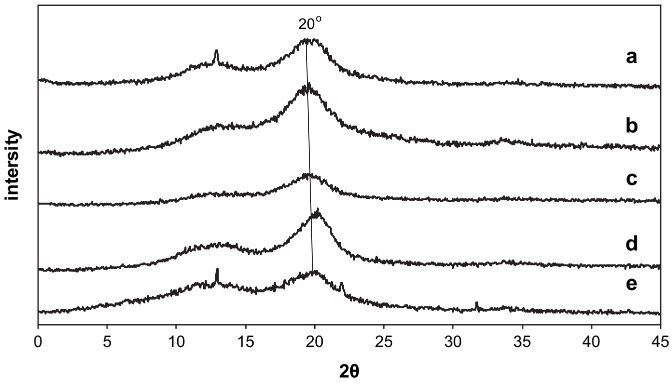

Fig. 2. XRD analysis of biomass samples: a-timothy grass, b-flax straw, c-barley straw, d-pinewood, e-wheat straw.

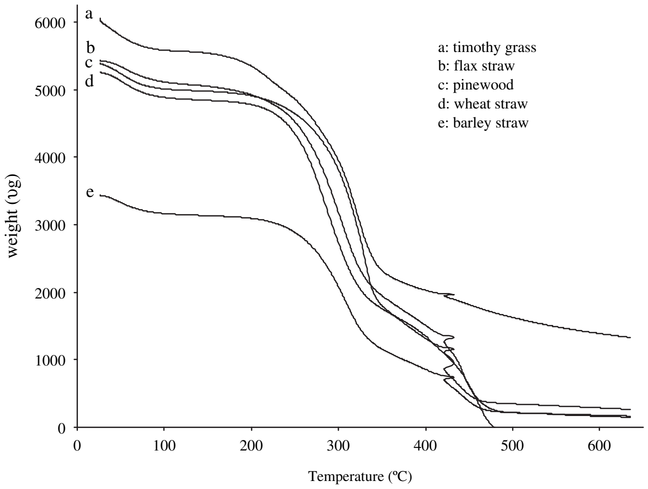

Fig. 3. TG analysis of biomass samples.

3. Results and discussion

3.1. Characteristics of biomasses

The proximate composition, ultimate composition and calorific values of wheat straw, barley straw, flax straw, timothy grass and pinewood are shown in Table 1. The calorific value of the biomass samples was determined using the method described above. During this it was observed that wheat straw, pinewood shows high calorific value compared to barley straw and timothy grass. Moreover the calorific value of pinewood in present study, i.e. 19.6 ± 0.2 MJ/Kg closely resembles the value (20 MJ/Kg) reported by Demirbas [23]. This high calorific value of wheat straw and pinewood shows that these are comparatively the potential biomass for the production of bio-energy.

The percentage of ash in wheat straw, barley straw, flax straw, timothy grass and pinewood were found to be 1.3 ± 0.1, 9.8 ± 0.1, 3.0 ± 0.2, 1.1 ± 0.1 and 1.5 ± 0.2% respectively. According to this study it was observed that, barley shows high percentage of ash compared to the other biomass under study. The common elemental composition of ash is presented in Table 2. The elements such as Ca, P, Mn, Fe, Cu, Zn, Sr were detected in high amount in

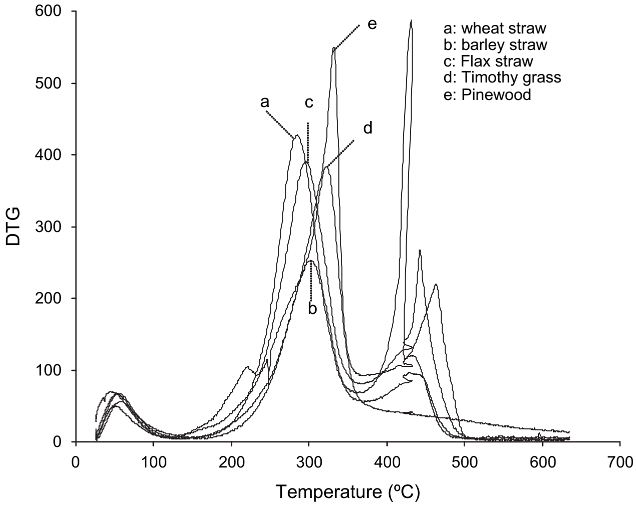

Fig. 4. DTG analysis of biomass samples.

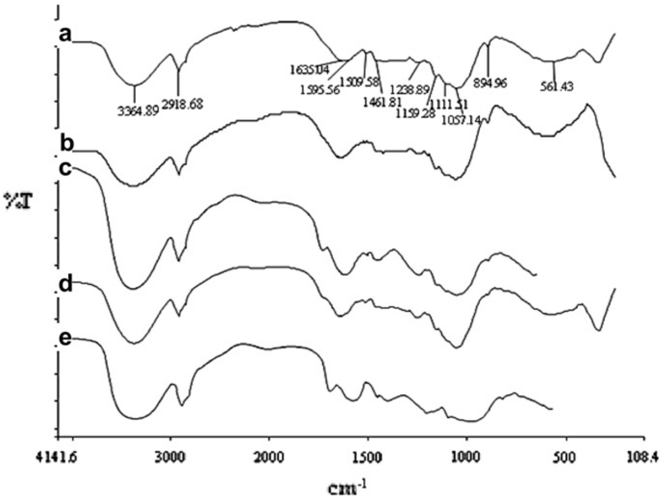

Fig. 5. FT-IR spectra of biomass samples: a-wheat straw, b-barley straw, c-flax straw, d-timothy grass, e-pinewood.

pinewood as compared to the other biomass samples, similarly Ca was detected in very high amount (i.e. 150,621 ppm) in pinewood and it was completely absent in wheat straw, barley straw and timothy grass.

The XRD analysis of various biomass samples are presented in Fig. 2. The intense X-ray diffraction peak was detected at 25°. The calculated areas of wheat straw: 325,881, barley straw: 541,938 flax straw: 525,051, timothy grass: 775,801 and pinewood: 581,217 in comparative square units. Among all these biomass samples the maximum crystallinity was obtained for timothy grass and minimum in case of wheat straw. The crystallinity of the surface is mainly related to the wax content (high molecular mass hydrocarbons and fatty components) in the biomass [14]. However, the overall crystallinity of biomass depends on wax, cellulose content and also depends on the complex nature of bonding [24] between cellulose, hemicellulose and lignin. Therefore, further study on nature of bonding between major chemical classes in the biomass is necessary to justify the XRD observation. During the hexane extraction, it was observed that, pinewood extract contained appreciable amount of hexane soluble materials because the pinewood contained high amount of terpeneoids, which are soluble in non-polar solvent (i.e. hexane). Therefore the pinewood hexane extract recovered terpenoids along with small fractions of waxy materials. As pinewood and flax straw shows less amount of waxy materials along with significant crystallinity, this accounted them suitable biomass for bio-fuel production.

The behavior of biomass materials during devolatilization was related to the presence of chemical constituents such as cellulose, hemicellulose and lignin [25]. The devolatilization behaviors of different lignocellulosic biomass were quite different (Fig. 3). The onset temperature of devolatilization was in the range of 200–250 °C, which corresponds to 5% weight loss with respect to the final weight loss. The main weight loss ends at 310–350 °C for all biomass and then followed by a slow and continuous weight loss. The former step was due to the primary devolatilization, where as the later was attributed to the degradation of heavier chemical structures in the solid matrix [26]. Quantitatively, the volatile matter released in the primary devolatilization was more important than in the secondary devolatilization, accounting for more than 50% of the final volatile matter released at 500 °C. Important observation was marked by Biagini et al. [3] regarding the devolatilization of hemicellulose, cellulose and lignin. For hemicellulose, they used xylan as a standard molecule in their study. The onset temperature was 253 °C and maximum weight loss was at 299 °C. The volatile matter released after primary devolatization was 76.3 wt%. Similarly in cellulose the onset temperature was 319 °C and maximum devolatization occurred at 354 °C. The volatiles released after the primary step of devolatization was 79.6 wt%. Whereas, in case of lignin it is decomposed in a wider range of temperature compared to hemicellulose and cellulose. The onset temperature was comparable to xylan. However, the primary devolatilization could be completed at 482 °C. The maximum weight loss was occurred at 361 °C. The *final weight loss* in case of lignin (60.2 wt%) was lowest in compared to hemicellulose and cellulose.

The weight loss as shown in Fig 3 can be explained as follows: the weight loss at temperature less than 100 °C was for loss of easily volatiles, 100–130 °C for loss of water, 130–250 °C for volatile compounds, 250–350 °C for hemicellulose, 350–500 °C for cellulose, lignin and >500 °C for lignin. A long tail of devolatilization was observed in timothy grass, which may be due to high percentage of mannose or lignin content, whereas pinewood completely devolatilised at ~500 °C. The devolatilization characteristics of wheat and flax straw were very close and comparable to pinewood as shown in Fig. 3. The primary devolatilization of pinewood and the secondary devolatilization of wheat straw were found to be highest as shown in Fig. 4. However the rate of loss of volatiles for barley straw was much slower as compared to the other biomass and that is due to its high lignin and wax contents.

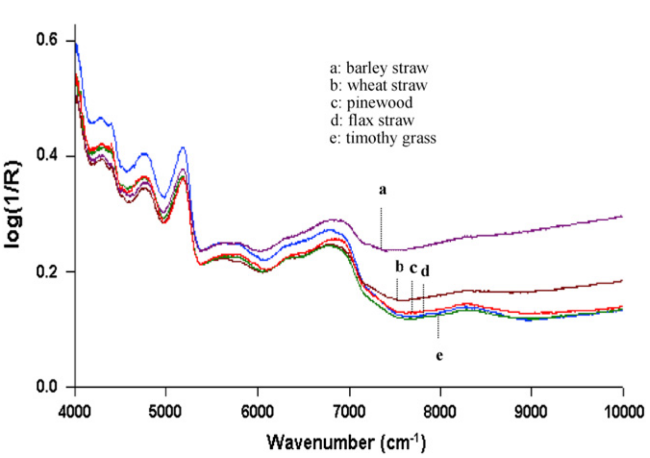

Fig. 6. FT-NIR spectra of biomass samples.

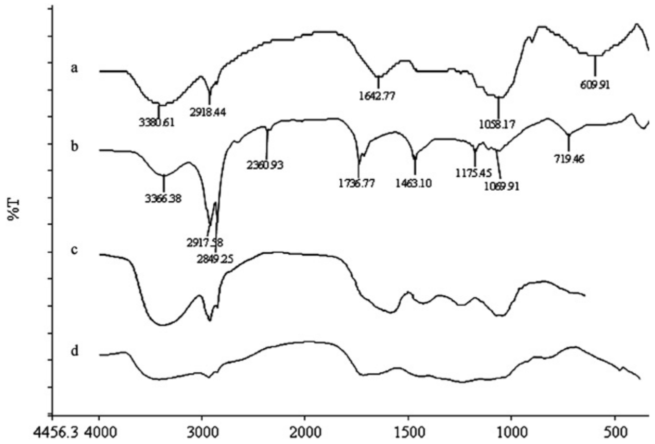

Fig. 7. FT-IR spectra of barley straw and its extractives: a-biomass, b-wax, c-ethanol extract, d-lignin.

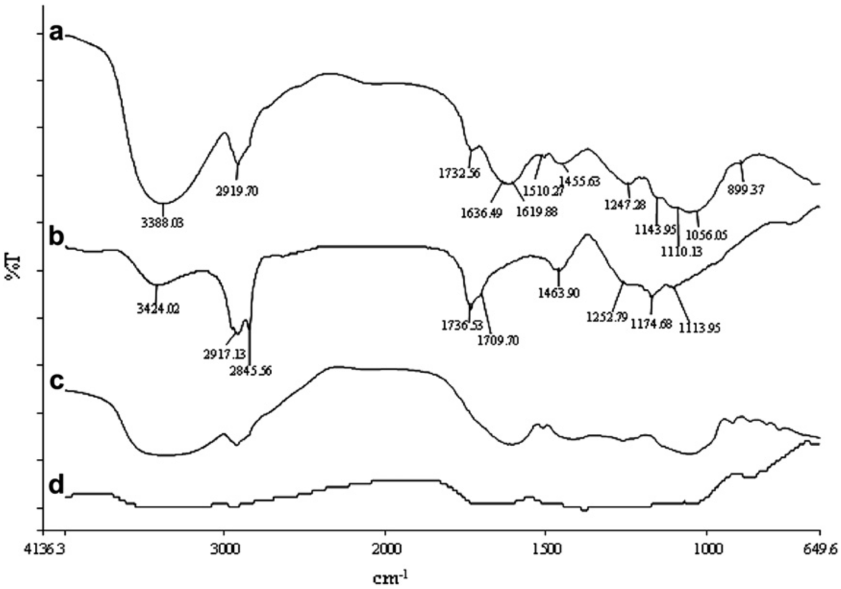

Fig. 8. FT-IR spectra of flax straw and its extractives: a-biomass, b-wax, c-ethanol extract, d-lignin.

CHNSO analysis of biomass samples showed no marked difference as presented in Table 1. The pinewood contained high percentage of C (49.0%), H (6.4%) and low percentage of N (0.14%) and S (0.01%). Canadian encyclopedia reported that the hydrogen content of pinewood is 5.98% [10] and Nunez-Regueira et al. [27] reported that the pinewood of Spain origin contained C: 48.3–55.4%, H: 5.2–7.7%, N: 0.16–1.6% and S: 0.14–0.45% which agrees well with this study. The organic element composition of wheat, barley and flax straw was found to be almost similar, whereas timothy grass contained slightly high percentage of N and S. For example, high nitrogen and ash concentrations reduce hydrocarbon yields during thermochemical conversion [2]. A significant fraction of herbaceous biomass consists of inorganic constituents, commonly referred to ash, which cannot be converted into energy. The inorganic material commonly associated with oxygen, sulphur and nitrogen containing functional groups. These organic functional groups can provide suitable sites for inorganic species to be associated chemically in the forms of cations or chelates [28].

The FT-IR studies (Fig. 5) revealed that the most prominent peaks in the spectrum originate from –OH stretching vibration (3370–3420 cm^{-1}) and CH_2 and CH_3 asymmetric and symmetric stretching vibrations (2935–2915 cm^{-1}). These vibrations are expected from hemicellulose, cellulose and lignin. Very intense peaks in the region 1742–1620 cm^{-1} originate from the stretching mode of carbonyls mainly ketones and esters [29]. Mainly these bands are expected from waxes such as fatty acids, fatty esters, high molecular mass aldehydes/ketones.

In FT-NIR spectroscopy (Fig. 6), chemical species absorb throughout the spectrum region (4000–10,000 cm^{-1}). The most informative range of NIR spectra was 5500–9000 cm^{-1}. The comparative NIR analysis of each biomass is presented in Fig. 6. The spectral range from 8700 to 8000 cm^{-1} contained absorption bands corresponding to the second overtone of C–H stretching vibrations, where as the first overtone C–H stretching bands appeared in 5988–5813 cm^{-1}. The peak at 6990 cm^{-1} is due to first overtone of O–H (stretching) [30,31]. So the functional group identified by FT-IR was confirmed by FT-NIR spectra. However, a NIR spectrum is

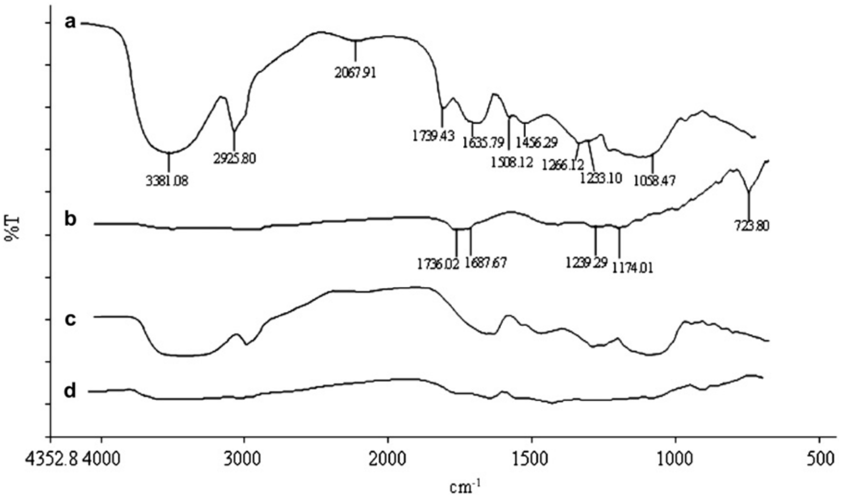

Fig. 9. FT-IR spectra of pinewood and its extractives: a-biomass, b-wax, c-ethanol extract, d-lignin.

Table 3
Extractives in g from 100 g of biomass.

Biomass	Hexane extract	EtOH extract	Water extract	Cellulose	Hemicellulose	Lignin
Wheat straw	1.7 ± 0.1	2.1 ± 0.2	10.3 ± 0.3	34.6 ± 0.2	29.3 ± 0.3	21.3 ± 0.3
Barley straw	5.3 ± 0.1	4.6 ± 0.2	8.5 ± 0.2	32.5 ± 0.4	25.7 ± 0.2	23.0 ± 0.5
Flax straw	1.5 ± 0.2	8.0 ± 0.3	10.0 ± 0.2	28.7 ± 0.2	26.8 ± 0.2	22.5 ± 0.4
Timothy grass	3.1 ± 0.3	5.4 ± 0.2	8.0 ± 0.4	31.5 ± 0.2	27.5 ± 0.3	24.0 ± 0.6
Pinewood	3.6 ± 0.2	6.8 ± 0.3	4.5 ± 0.2	39.0 ± 0.3	34.0 ± 0.3	12.0 ± 0.5

a unique representation of a substance or a mixture. Signals from bands such as C–O, C=O, O–H and O–CH_3 as well as first and second overtones were included within this region.

3.2. Biomass extractives

The yield of hexane, alcohol and water extracts for different biomass samples are presented in Table 3. In terms of total extract, the flax straw has maximum (19.5 wt%) and wheat straw has minimum (14.1 wt%), whereas both flax and wheat straw shows least amount of waxy materials. Similarly pinewood contained low percentage of water soluble extracts (4.5 wt%). To determine the total sugar content in the raffinate biomass, it was treated with dilute H_2SO_4 and in the process of acid hydrolysis the oligomers brake down into monomers. The conversion is required because the HPLC only detects the sugars in its monomeric forms. The detailed chemical composition of sugars is shown in Table 4. During this study it was observed that, all the extracts shows no significant difference in the percentage of glucose, where as large deviation in the percentage of cellulobiose, xylose, galactose, arabinose and mannose was observed. The composition of sugars in wheat straw, flax straw and pinewood are comparable but barley straw contained high percentage of galactose, whereas timothy grass contained high percentage of mannose. Small fractions of sugar are also expected in the water extract of the biomass samples, for which the analysis is not done.

In the FT-IR study of extractives (Figs. 7–9), the prominent peaks were at 1056, 1248, 1265, 1506 and 1603 cm^{-1} represented C–H and O–H bending frequencies which were indicators of lignin [7,29]. According to Moore and Owen [32], the most characteristics bands of lignin were at 870, 1263, 1506 and 1601 cm^{-1}. In our analysis, the wax contains less intense –OH peak (2956–2850 cm^{-1}), which indicates that wax is partially free from –OH group but long chain fatty acids are not completely separated. The peak at 800 and 1463 cm^{-1} was due to the C–H and CH_3 asymmetric scissoring deformations. A very unique set of absorption peaks originating from β-diketones was observed in the spectrum: keto tautomer displayed a doublet at ~1730 cm^{-1}. Other apparent peaks are assigned to stretching vibrations in the esteric type of compounds; =O–C–O–C at 1250–1270 cm^{-1} and O=C–O–C at 1090–1045 cm^{-1}. So the IR spectrum of pinewood hexane extracts show that the absence of peak –OH band (2956–2850 cm^{-1}). Though the total hexane extract was appreciable in pinewood due to the presence of terpenoids. The less intense lignin spectrum in IR of pine-wood reflects its low lignin percentage and similarly explained the lignin intense spectrum in case of timothy grass and barley straw.

Table 4
Percentage composition of sugars in biomass.

Name of sugar	Wheat straw	Barley straw	Flax straw	Timothy grass	Pinewood
Cellulobiose	–	–	1.0 ± 0.1	1.3 ± 0.2	2.2 ± 0.4
Glucose	53.6 ± 0.2	55.7 ± 0.5	52.6 ± 0.6	52.0 ± 1.1	51.8 ± 1.5
Xylose	16.0 ± 0.5	15.2 ± 0.7	11.2 ± 0.5	17.1 ± 0.4	7.2 ± 0.5
Galactose	1.0 ± 0.1	15.6 ± 0.6	3.4 ± 0.3	2.9 ± 0.3	5.9 ± 0.3
Arabinose	18.6 ± 0.7	13.1 ± 0.5	28.5 ± 0.5	3.9 ± 0.3	28.6 ± 0.4
Mannose	9.8 ± 0.6	0.3 ± 0.1	3.3 ± 0.4	22.7 ± 1.0	4.2 ± 0.2

4. Conclusion

Greater utilization of natural, renewable resources is vital for an economically viable and environmentally sound society. The biomass samples selected for this study such as wheat straw, barley straw, flax straw, timothy grass and pinewood are abundant in Canada. The physico-chemical characterization of all these samples showed that, the pinewood is the potential candidate for the bioenergy production due to high calorific value, devolatilization, cellulose and hemicellulose content, besides low ash and lignin content. The physico-chemical properties of agricultural residue such as wheat and flax straw followed closely with pinewood. It is also evident from the above discussion that timothy grass and barley straw are not suitable feedstock for bioenergy production due to high temperature with long time for devolatilization, high lignin content and low calorific value. The study of all these biomass samples in the light of bio-fuel production ensures that these biomasses can be utilized for gasification, bio-oil and bio-alcohol production and may meet the demand of the second generation biofuel. This is the first systematic report on chemical characterization of Canadian biomass. However, the conversion of these solid biomass samples to liquid fuel (bio-oil and bio-ethanol) and estimation of the fuel properties is on progress.

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References

[1] Jones MR. Biomass for energy. In: Kitani O, Hall CW, editors. Biomass handbook. New York: Gordon Breach Science Publ.; 1989 [section 1.2.2].

[2] Sanderson MA, Agblevor F, Collins M, Johnson DK. Compositional analysis of biomass feed stocks by near infrared reflectance spectroscopy. Biomass Bioeng 1996;11:365–70.

[3] Biagini E, Barontini F, Togonotti L. Devolatilization of biomass fuels and biomass components studied by TG/FTIR technique. Ind Eng Chem Res 2006;45:4486–93.

[4] Lynd LR, Cushman JH, Nichols RJ, Wyman CE. Fuel ethanol from cellulosic biomass. Science 1991;251:1318–23.

[5] Anon. Survey of energy resources, World energy council. 20th ed. Oxford: Elsevier Ltd; 2004. p. 267.

[6] Mohan D, Pittman CU, Steele PH. Pyrolysis of wood/biomass for bio-oil: a critical review. Energy Fuels 2006;20:848–89.

[7] Xiao B, Sun XF, Sun RC. Chemical, structural and thermal characterization of alkali soluble lignins, hemicelluloses and cellulose from maize stems, rye straw and rice straw. Polym Degrad Stab 2001;74:307–19.

[8] Chundawat SPS, Venkatesh B, Dale BE. Effect of particle size based separation of milled corn stover on AFEX pretreatment and enzymatic digestibility. Biotechnol Bioeng 2007;96:219–31.

[9] Agricultural statistics. Information of Government of Saskatchewan website.

[10] Anon, The Canadian encyclopedia, historical foundation of Canada. In: Forestry (accessed 2008).

[11] Anon. Biomass feedstock composition and property database. U.S.A: National Renewable Energy Laboratory; 2005.

[12] Harlan JR. The early history on wheat. In: Evans LT, Peacock WJ, editors. Wheat science today and tomorrow. Cambridge, UK: Cambridge University Press; 1981. p. 1–19.
[13] Slafer GA, Satorre EH. Wheat: ecology and physiology of yield determination. Binghamton, New York: Food Products Press, Howarth Press Inc; 2000. pp. 1–12.
[14] Zhang L-H, Dong L, Wang L-J, Wang T-P, Zhang L, Chen XD, et al. Effect of steam-explosion on biodegradation of lignin in wheat straw. Bioresour Technol 2008;99:8512–5.
[15] Wisniewska SK, Nalaskowski J, Witka-Jezewska E, Hupka J, Miller JD. Surface properties of barley straw. Coll Surface B: Biointerfaces 2003;29:131–42.
[16] Strehler A, Stutzle W. Biomass residues. In: Hall DO, Overend RP, editors. Great Britain: John Wiley and Sons; 1987. p. 86–88.
[17] Logsdon G. All fresh is grass. U.S.A: Ohio University Press; 2004. p.174–188.
[18] Kumar A, Sokhasanj S, Flynn PC. British Columbia's beetle infected pine: biomass feedstock for producing power. BIOCAP Canada Foundation; 2005.
[19] ASTM D 3173-87. Standard method for determination of moisture content in biomass. Philadelphia, PA: Am. Society for Testing Materials, International; 2003.
[20] ASTM D 3174-04. Standard method for ash in the analysis sample of coal and coke. Philadelphia, PA: Am. Society for Testing Materials, International; 2004.
[21] ASTM D 3175-07. Standard method for volatile matter in the analysis sample of coal and coke. Philadelphia, PA: Am. Society for Testing Materials, International; 2007.
[22] Hubbard W, Scott D, Waddington G. In: Rossini F, editor. Experimental thermochemistry. Interscience Publ; 1956 [Chapter 5].
[23] Demirbas A. Calculation of higher values of biomass fuels. Fuel 1997;76:431–4.
[24] Meshitsuka G, Isogai A. Chemical structures of cellulose, hemicellulose and lignin. In: Hon DN, editor. Chemical modification of lignocellulosic materials. New York: Marcel Dekker Inc.; 1996. p. 11–34.
[25] Raveendran K, Ganesh A, Khilar KC. Pyrolysis characteristics of biomass and biomass components. Fuel 1996;75:987–98.
[26] Fisher T, Hajaligol M, Waymack B, Kellogg D. Pyrolysis behaviour and kinetics of biomass derived materials. J Anal Appl Pyrol 2002;62:331–49.
[27] Nunez-Regueira L, Rodriguez-Anon J, Proupin J, Romero-Garcia A. Energy evaluation of forest residues originated from pine in Galicia. Bioresour Technol 2003;88:121–30.
[28] Livingston WR. Biomass ash characteristics and behaviour in combustion, gasification and pyrolysis systems. Doosan Babcock Energy Ltd; 2007.
[29] Himmelsbach DS, Khalili S, Akin DE. The use of FT-IR microspectroscopic mapping to study the effects of enzymatic retting of flax (*Linum usitatissimum* L.) stems. J Sci Food Agric 2002;82:685–96.
[30] Gonzalez-Saiz JM, Esteban-Diez I, Sanchez-Gallardo C, Pizarro C. Monitoring of substrate and product concentrations in acetic fermentation process for onion vinegar production by NIR spectroscopy: value addition to worthless onions. Anal Bioanal Chem 2008;391:2937–47.
[31] Ye XP, Liu L, Hayes D, Womac A, Hong K, Sokhansanj S. First classification and compositional analysis of corn stover fractions using fourier transform near-infrared techniques. Bioresour Technol 2008;99:7323–32.
[32] Moore AK, Owen NL. Infrared spectroscopic studies of solid wood. Appl Spectros Rev 2002;36:65–86.