Biomass Compositional Analysis Tools and Techniques: A Review

Pragya Yadav[1*] & A K Sarma[2]
[1]SSS National Institute of Bioenergy, Kapurthala Punjab & IKGPTU, Kapurthala Punjab (Corresponding Author)
[2]SSS National Institute of Bioenergy, Kapurthala, Punjab
[1]pragyayadav21@gmail.com, [2]draksarma@gmail.com

Abstract:

Biomass is soft, heterogeneous organic material comprising of carbohydrates, fats and proteins. The relative abundance of the constituent polymers depends up on the source of biomass. In biomass of plant origin (most widely used), the major components are carbohydrates (cellulose & hemicelluloses) and lignin commonly referred as ligno-cellulosic biomass. It is postulated that conversion of lignocellulosic biomass to biofuels is a challenging task owing to the composition variation coupled with resistance to modification. In order to address these issues, various characterization tools and techniques have been developed over the last century. In this article, an overview of the biomass composition analysis techniques that have co-evolved with interest in biofuels and bioenergy is presented. The article envisages the developments in the lingo-cellulosic biomass characterization starting from Weende Method (1859, initially developed for the estimation and analysis of crude fibre in food) to Klason Lignin Method (1923, for quantification of lignin) to USDA Forest Products Laboratory Method (1920-40). Later in 1944, Saeman et al optimized the chromatographic techniques that had been adopted as TAPPI standard for pentosan determination. These methods are currently used in biorefinery for quantitative determination of carbohydrate and lignin in wheat and corn stover. Another significant contribution is the Dietary Fibre Method (1953) of Hipsley thereafter the term "dietary fibre" was used to describe plant cell wall material composed of cellulose, hemicelluloses and lignin. Nelson and Leming proposed the Monoethanolamine method for gravimetric estimation of cellulose after removal of lignin. In 1963, Van Soest proposed the Detergent Fibre method for fractionation and compositional analysis of lignocelluloses. AOAC has recognized Prosky Dietary Fibre method (1984) and Uppsala Method (1985) as official methods. Acetyl Bromide method (1997) is considered a consistent method for determining the digestibility of lignin and overcomes some of the issues associated with the previous methods yet is limited by xylan degradation. The latest development includes the NREL Methods (2000) where comprehensive laboratory analytical procedures (LAP) have been developed for the determination of structural carbohydrate and lignin in biomass. However, NREL methods are known to underestimate the cellulose content due to sulphonation of cellulose at high sulphuric acid concentration. Amongst the spectroscopic techniques NIR, MIR and Raman Scattering spectroscopy is pioneer in the field as they are inexpensive, expedient and provide broad spectrum of compositional data of macromolecules.

Keywords

Biomass characterization; compositional analysis; lignocelluloses; spectroscopy; bioenergy; biorefinery

Introduction

Lignocellulose is the plant biomass widely used for biofuel production. Typically, lignocelluloses is made up of cellulose (40–60%), hemicellulose (20–40%), and lignin (10–24%)[1]. Cellulose is the most abundant biopolymer on earth, composed of β-D-glucopyranose moieties linked via β-(1, 4) glycosidic bonds[2,3] . Hemicellulose is branched heteropolysaccharide composed of small subunits of pentose sugars (xylose and arabinose) and hexose sugars (galactose, glucose, and mannose)[4]. One of the major challenges in the sustainable development of the biofuel industry is the cost effective degradation of various components of the ligocelluloses [3]. Accurate biomass compositional analysis helps in estimation of conversion yields and process economics for biofuel production [2]. This review aims to study the chronological development of biomass compositional tools and techniques and identify the merits and demerits of the same. The above information will be used to lay a research direction for upcoming researchers.

Material & Methods

The authors completely relied on scientific databases such as Science Direct, Web of Science, Scopus and Google Scholar for the literature search. We searched using keywords and also researched related secondary references and suggestions made by the search engines. Based on this search, tools and techniques of biomass characterization will be the primary focus of this review. This paper will review the major developments in the biomass characterization methods and thereafter a comparison of existing lab methods is conducted to see the current day procedures adopted worldwide.

Result & Discussion

The authors found that Krasznai et. al [5] have made a detailed study on 'Compositional analysis of lignocellulosic biomass: conventional methodologies and future outlook' and the same has been summarised in the table [1]

highlighting the major developments in lignocellulosic biomass characterization methods. Table 2 sums up the widely used wet lab practices adopted worldwide for the compositional studies of lingo-cellulosic biomass [5-18].

Table1: Major developments in lignocellulosic biomass characterization

Method	Contributor	Significance
Weende	Hennerberg and Stohmann (1859)	• for estimation and analysis of crude fiber in food • still routinely used in agriculture
Klason lignin	Klason (1923)	• for the quantification of lignin in biomass • accepted as a TAPPI standard • still in use
USDA FPL	USDA Forest Products Laboratory (FPL, 1920-40)	• applied the Klason lignin methods to wood • later adopted the methods of Saeman et al. for the saccharification of wood and cellulose.
Saeman pentosan	Saeman et al.(1944)	• Saeman et al. optimized the chromatograph techniques that had been adopted as a TAPPI standard for pentosan determination • these methods have recently been applied in biorefinery for the quantitative determination of carbohydrate and lignin in wheat and corn stover
Dietary fiber	Hipsley (1953)	• Hipsley coined the term “dietary fiber” in 1953 to describe plant cell wall materials composed of cellulose, hemicellulose, and lignin that are indigestible by the human digestive tract. This term became a basis for future work in the agricultural and food sciences.
Monoethanolamine	Nelson and Leming(1957)	• For gravimetric quantification of cellulose after the removal of lignin and other carbohydrates; they determined the optimal conditions for this process, and its usefulness with application to three types of agricultural residues
Permanganate method	Tasman and Berzins (1957)	• developed a permanganate method for lignin to measure the Kappa number of wood in the pulp and paper industry . • its limitations have resulted in minimal use.
Detergent fiber methods	Van Soest (1963)	• used for the fractionation and compositional analysis of plant-based materials, including lignocellulose; these included neutral and acid detergent fiber analyses (NDF and ADF, respectively).
Moore and Johnson Method (modified USDA FPL)	Moore and Johnson (1967)	• for the analysis of pulp and wood sugars at the USDA FPL • method was found to underestimate pentose content.
Trifluoroacetic acid	Fengel and Wegner (1979)	• for the determination of cellulose and hemicellulose by proxy of their hydrosylate sugars; • two methods were described for materials with high and low lignin content
Grohmann	Grohmann et al. (1984)	• method involved the modification of the Moore and Johnson methods for the use of a milder acid hydrolysis technique.

		• rarely been used in recent years
Prosky dietary fiber	Prosky et al.(1984)	• an enzymatic and chemical dietary fiber method that allowed retention of the cell wall, • allowing for the quantification of cell wall components; the technique has been designated as an AOAC official method
Uppsala method	Theander (1985-86)	• to estimate the composition of cell wall components using a chemical approach and a variety of techniques. • It was adopted as an AOAC method, following inter-laboratory studies by Milne et al. and Theander et al., for the quantification of soluble and insoluble polysaccharides. • susceptible to contamination and overestimated Klason lignin values
Acetyl bromide	Lu and Ralph(1997)	• consistent method for determining the digestibility of lignin, and • overcomes some of the issues associated with some of the previous methods • limited by xylan degradation
Nrel methods (laboratory analytical procedures)	National Renewable Energy Laboratory (NREL, 2000);	• laboratory analytical procedures (LAPs) have been developed for the determination of structural carbohydrates and lignin in biomass in recent years

Table 2: A summary of Lab methods for compositional analysis of lingo-cellulosic biomass

Method	**Fraction measured**	**Limitations**
Proximate, Weende, or Crude fiber	Portion of plant cell wall, complete cellulose recovery	Most non-cellulosic polysaccharides and lignin removed May underestimate fiber content by more than 50%
Neutral detergent fiber (NDF)	Incompletely digestible feed fraction, almost complete recovery of grass cell walls	Pectin almost completely removed protein and starch removal can be problematic
Acid detergent fiber (ADF)	Portion of plant cell wall, complete cellulose recovery	A major portion of lignin is solubilized
ADF minus ADL	Cellulose	Same as ADF and ADL
NDF minus ADF	Hemicellulose	Same as NDF and ADF
Acid Detergent Lignin(ADL)	Lignin	Lignin solubilization
Dietary fibres	Complete recovery of cell wall polymers	Protein and starch removal
Uppsala dietary fibres	Total cell wall recovery and composition	Complex and tedious
Crampton & Mnayard	Cellulose	Xylan contamination and cellulose degradation
Klason Lignin	Lignin	Under/over -estimate lignin content
Monoethanolamine (MEA)	Cellulose after lignin and carbohydrates rermoved	Time consuming & hemicellulose content may be not be fully removed

USDA FPL	Reducing sugars and lignin in woody samples	Limitations of reducing sugar assay
Trifuoroacetic Acid	Cellulose and hemicellulose	Incomplete hydrolysis may occur
UK	Plant Cell wall non –starch polysccharides	Lignin not quantified
DFRC	Lignin	Xylan degaradation
NREL LAP TP-510-42618	Structural carbohydrates and lignin	Underestimated cellulose content due to sulphonation of cellulose at high sulphuric acid conc.

The study shows that NREL LAP methods are very useful for compositional analysis of woody and herbaceous biomass. The scope for better analytical methods comes from three major limitations of current methods:

1. New or improved methods should focus on better characterization of existing components or for detection of novel components . For example, a method to specifically quantify lignin is much needed over the current gravimetric method, which is prone to interferences [6]. In another case, novel methods are needed for measurement of Uronic acid present as sugar conjugates after analytical hydrolysis such as 4-O-methylglucuronoxylose. Although, HPLC seems promising for the uronic acid analysis yet the lack of commercial standards makes quantification difficult [7]. Thus, improved methods for measurement of the sugars degraded during hydrolysis could significantly improve the carbohydrate analysis.
2. Improvements in the throughput and efficiency of present analytical methods are needed so as to make the characterization techniques more cost-effective and faster. One of the research groups [7] has suggested the automation of the two-stage hydrolysis (the core of the carbohydrate and lignin measurement procedure) so as to improve the efficiency of the procedure.
3. There is a need to validate the performance of the above methods on a broader spectrum of biomass substrates. As per the requirements, we can alter these methods or develop new methods to ensure more and more biomass types can be used for bio-energy production. For example, industrial residues (e.g., corn fiber and municipal solid waste) and other emerging biofuel feedstocks.

   Besides, routine lab methods spectroscopic techniques such as near-infrared (NIR) spectroscopy coupled with multivariate calibration method is also widely used in biomass characterization [19, 20]. In fact, spectroscopic techniques are faster and technically easier to generate compositional analysis results. However, the production of good quality data sets using NIR model depends on results from wet chemical analysis. The higher variability of the underlying analysis method is prone to show errors during NIR analysis. Hence, the relevance of wet chemical analysis cannot be undermined.

Conclusion

The authors conclude that due to concerted efforts of the researchers worldwide the present set of tools and techniques for biomass characterization has emerged. The growth and expansion bio-energy industry is significantly impacted by it. Hence, to ensure better faster and more accurate biomass compositional analysis of lignocellulosic biomass the authors have critically reviewed the existing methods and also recommended the way forward.

References

1. Sharma, H.K., Xu, C. & Qin, W. Review of physicochemical properties and analytical characterization of lignocellulosic biomass. Waste Biomass Valor (2017). https://doi.org/10.1007/s12649-017-0059-y
2. Sluiter, A., Sluiter, J., & Wolfrum, E. (2013). Methods for biomass compositional analysis. *Catalysis for the Conversion of Biomass and Its Derivatives*. Retrieved from http://www.edition-open-access.de/proceedings/2/9
3. https://www.nature.com/articles/srep40262
4. Safari, F., Tavasoli, A., & Ataei, A. (2016). Gasification of Iranian walnut shell as a bio-renewable resource for hydrogen-rich gas production using supercritical water technology. *International Journal of Industrial Chemistry*. https://doi.org/10.1007/s40090-016-0093-9
5. Krasznai, D. J., Champagne Hartley, R., Roy, H. M., Champagne, P., & Cunningham, M. F. (2018). Compositional analysis of lignocellulosic biomass: conventional methodologies and future outlook. *Critical Reviews in Biotechnology*, *38*(2), 199–217. https://doi.org/10.1080/07388551.2017.1331336
6. Foyle T, Jennings L, Mulcahy P. Compositional analysis of lignocellulosic materials: evaluation of methods used for sugar analysis of waste paper and straw. Bioresour Technol. 2007;98:3026–3036.
7. Sluiter, J. B., Ruiz, R. O., Scarlata, C. J., Sluiter, A. D., & Templeton, D. W. (2010). Compositional analysis of lignocellulosic feedstocks. 1. Review and description of methods. *Journal of Agricultural and Food Chemistry*, *58*(16), 9043–9053. https://doi.org/10.1021/jf1008023
8. Ralph J. Lignin structure: recent developments. Proceedings of the 6th Brazilian Symposium Chemistry of Lignins and Other Wood Components. Guaratingueta, Brazil, 1999, 97–112.
9. TAPPI. TAPPI Test Method T222 om-02. Acid-insoluble lignin in wood and pulp. Atlanta, GA:

Technical Association of the Pulp and Paper Industry Press; 1988.
10. K€urschner K, Hoffer A. A new quantitative cellulose determination. Chem Zeit. 1931;55:161–181.
11. Cunningham RL, Carr ME. Pretreatments of wheat straw for separation into major components. Biotech Bioeng Symp. 1984;14:96–103.
12. Van Soest PJ. Use of detergents in the analysis of fibrous feeds. I. Preparation of fiber residues of low nitrogen content. J Assoc Off Anal Chem. 1963;46: 825–829.
13. Van Soest PJ. Use of detergents in the analysis of fibrous feeds. II. A rapid method for the determin- ation of fiber and lignin. J Assoc Off Anal Chem. 1963;46:829–835.
14. Van Soest PJ, Wine RH. Use of detergents in the analysis of fibrous feeds. IV. Determination of plant cell-wall constituents. J Assoc Off Anal Chem. 1967;50:50–55.
15. Goering HK, Van Soest PJ. Forage fiber analyses (apparatus, reagents, procedures, and some applications). Agric Handb. 1970;379:1–20.
16. Van Soest PJ. Nonnutritive residues: a system of analysis for the replacement of crude fiber. J Assoc Off Agric Chem. 1966;49:546–551.
17. Milne TA, Chum HL, Agblevor F, et al. Standardized analytical methods. Biomass Bioenergy. 1992;2: 341–366.
18. ASTM. Standard test method for determination of carbohydrates in biomass by high performance liquid chromatography. West Conshohocken, PA: ASTM; 2001.
19. Wolfrum, E. J.; Sluiter, A. D. Improved multivariate calibration models for corn stover feedstock and dilute-acid pretreated corn stover. Cellulose 2009, 16 (4), 567–576.
20. Hames, B. R.; Thomas, S. R.; Sluiter, A. D.; Roth, C. J.; Templeton, D. W. Rapid biomass analysis - new tools for compositional analysis of corn stover feedstocks and process intermediates from ethanol production. Appl. Biochem. Biotechnol. 2003, 105, 5–16