Review of Biomass Feedstocks and Guidelines of Best Practice

(Full Version)

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1 Executive Summary

This document is the result of the evaluation of biomass feedstocks, from Europe and Latin America, that took place as part of the DIBANET project. That project is co-financed from the 7th Framework Programme for Research and Technological Demonstration of the European Union. (Title: Enhancing international cooperation between the EU and Latin America in the field of biofuels; Grant Agreement No: 227248-2).

The work in Task 2.1 of Work Package 2 (WP2) at DIBANET partners UL, CTC, and UNICAMP involved evaluating, on a number of levels, potential feedstocks for utilisation in the DIBANET acid-hydrolysis process (WP3). In the early stage of the project a wide number of feedstocks were examined and relevant secondary compositional data were sought from the literature. Selected feedstocks were analysed at the laboratories of UL, CTC, and UNICAMP and, from these, a limited number of feedstocks were subjected to more in-depth analysis/evaluation.

Work at UL focused on Miscanthus, cereal straws, and waste papers. The wet-chemical and spectroscopic analysis that was carried out on a wide number of Miscanthus samples have allowed for in-depth understandings to be reached regarding the changes in lignocellulosic composition, and potential biomass/biofuel yields that could be realised over the harvest window. Straws present much less chemical variation but have enough structural carbohydrates to warrant their processing in the DIBANET technology. Waste papers can have amongst the highest total carbohydrate contents of any of the feedstocks studied.

Work at CTC focused on the residues of the sugarcane industry – sugarcane bagasse and sugarcane trash (field residues from harvesting). A large number of samples were collected from a variety of sugar mills and plantations. It has been seen that there can be a significant variation in the composition of different bagasse samples, particularly with regards to the ash content. Sugarcane trash has lower total carbohydrates contents than bagasse but is still a suitable feedstock for DIBANET.

Work at UNICAMP focused on the evaluation of residues from the banana, coffee, and coconut industries. It was found that these also have potential for utilisation in the DIBANET process, however the value of the residues for this end-use is dependent on which part of the plant is utilised. For instance, coffee husks have sufficient structural carbohydrates to allow for decent yields of levulinic acid, formic acid, and furfural in DIBANET, however the leaves of the coffee plant do not. Leaves from the banana plant are also of less value for DIBANET than the other parts of the plant (e.g. stem).

A major output of this Deliverable is the downloadable electronic database that contains all of the WP2 analytical data obtained during the course of the project. It contains analytical data and predicted biorefining yields for a total of 1,281 samples. It can be obtained, free of charge, from the DIBANET website and will be a valuable tool for stakeholders in biorefining projects.

This document presents the data and evaluations that were made regarding biomass feedstocks, and also puts forward “guidelines of best practice” in terms of making the best use of these resources. A shortened version of this document can also be downloaded from the DIBANET website.

2 Introduction

Biomass feedstocks for the production of biofuels and chemicals vary greatly in their chemical compositions. These differences affect the suitability of these feedstocks for conversion and which technologies are most suitable for processing these feedstocks.

The DIBANET project focuses on the conversion of lignocellulosic materials; biomass principally composed of the polymers cellulose, hemicellulose, and lignin. Each of these polymers differs substantially in composition. Cellulose is a homopolysaccharide with its D-anhydro-glucopyranose (a C6 sugar) units linked through β-linked (1→4)-glycosidic bonds. These linkages allow for cellulose molecules to be closely associated through intermolecular and intramolecular hydrogen bonds, hence the recalcitrance of cellulose to hydrolysis (the liberation of the individual sugar units from the polysaccharide).

The term hemicellulose covers a variety of complex carbohydrate polymers that are mostly not extractable in hot water but, unlike cellulose, are extractable in aqueous alkali (1). These constitute the cell-wall polysaccharides of land plants that are not cellulose or pectins (2). Hemicelluloses tend to be branched heteropolysaccharides that are mostly built up of: the pentoses D-xylose and L-arabinose; the hexoses D-glucose, D-mannose, and D-galactose; with smaller amounts of L-rhamnose, in addition to D-glucuronic acid, 4-O-methyl-D-glucuronic acid, and D-galacturonic acid. While the proportions of these substituents vary between hemicellulose and feedstock types, the majority tend to be pentoses (3). Hemicelluloses can also be acetylated.

The major role of lignin in plants is as a supporting agent in cell structure, while it also assists in the resistance of biomass against microbial attack and decay (4). Structurally, lignin can be described as a complex three-dimensional polymer of phenylpropane units. These units are relatives of carbohydrates, coming from the dehydration and cyclisation of sugars. They are mostly either 4-hydroxycinnamyl alcohol (para-coumaryl alcohol, H) or its 3- and/or 3,5-methoxylated derivatives - coniferyl (guaiacyl, G) alcohol, and sinapyl (syringal, S) alcohol, respectively. The phenylpropane units are linked in various ways - directly between the rings, between the propane units, and through ether linkages via the hydroxyl groups (5). Ether linkages between aromatic rings are possible at several positions; thus a three-dimensional structure results (4). These ether linkages are very resistant to cleavage, a factor in explaining the low lignin degradation rates by most biota (3). Lignin is also relatively hydrophobic.

The properties of these three lignocellulosic polymers are clearly very different and, hence, the relative proportions and compositions of these in a given biomass feedstock will be of crucial importance in determining conversion process yields, technical feasibilities, and economics. The composition of the biomass will also influence which conversion mechanism, hydrolysis (e.g. enzymatic hydrolysis, acid hydrolysis) or thermochemical (e.g. pyrolysis, gasification), is most appropriate.

Technologies that process lignocellulose, e.g. DIBANET, have often been termed "biorefineries", a term analogous to oil refineries since, like these, biorefineries can obtain a

variety of end products according to the chemical components of the starting materials and the market demand for end-products.

A major part of Work Package 2 in the DIBANET project involved the evaluation of the potential lignocellulosic feedstocks that exist both in Europe and Latin America. A wide range of feedstocks were considered, as part of a literature review, and those that were considered to have most potential for the economical and sustainable production of the platform-chemicals/biofuels possible from the DIBANET hydrolysis process were selected for analysis and further investigation.

The DIBANET hydrolysis process focuses on the production of platform chemicals from the polysaccharides (cellulose, hemicellulose) of biomass. Levulinic acid (LvA), 4-oxopentanoic acid or γ-ketovaleric acid, is a C5-molecule with both ketone & carboxylic acid functionality which provides interesting synthetic pathways for use as a chemical building block for a wide variety of derivative compounds. It is produced via the controlled degradation of hexoses (C6-sugars) by acid, a process which also produces equivalent molar yields of formic acid as a co-product. Furfural, another valuable platform chemical, is also produced from the degradation of pentoses (C5-sugars).

Carbohydrates that do not ultimately convert to levulinic acid, formic acid, and furfural, or their intermediates (e.g. hydroxymethylfurfural) will instead form humin-type materials. These, along with Klason lignin and acid insoluble ash, are the solid residuals of the DIBANET process. Work Package 4 in the DIBANET project focuses on the thermochemical conversion of these solid residuals.

This diverse array of products from the DIBANET process is feedstock-composition dependent and ultimate determinations of the suitability of a given feedstock cannot be made with confidence without accurate and relevant data regarding biomass composition. There are some existing data in the literature regarding some relevant lignocellulosic feedstocks, however these data are often of insufficient detail to reliably inform such determinations. For example, detergent fibre analytical methods, which can estimate hemicellulose, cellulose, and lignin contents based on the gravimetric measurements of the weights of the ADF, NDF, and ADL fractions of the biomass (6), do not directly measure these polymers or their constituents and so cannot differentiate between the C5 and C6 sugars in hemicellulose.

Hence, there exists a clear need for the analytical work that has taken place as part of the DIBANET project.

3 Biomass Analysis in DIBANET

3.1 Methodologies

The methodology involved in preparing and characterising biomass samples in the DIBANET project was outlined in Deliverable 2.1 of the project ("Participatory Workshop for Biomass Sampling, Analysis"). The standardised analytical procedures, used by DIBANET partners

UL, UNICAMP and CTC in their analysis, can be downloaded from the DIBANET website along with the associated Data Recording Sheets. The steps involved in this analysis are summarised below and in Figure 1 (sample preparation and near infrared (NIR) analysis) and Figure 2 (wet-chemical analysis). These methods are also described in more detail in a recent DIBANET publication (7).

Sample Preparation

1. A representative sample was taken from storage and placed on a tray in preparation for air drying. If it is in a state that allows direct presentation to the analytical cell of the NIR device then it is analysed there without any sample preparation needed. If not, the sample is chopped until it is in a form where it can be presented to the cell (but still be of a heterogeneous particle size).

2. The sample is then left to air dry in the laboratory until the mass loss between 2 consecutive days was less than 0.5%.

3. NIR analysis of this air-dried sample is carried out.

4. Comminution of the biomass, to ensure a more homogeneous particle size distribution, took place. The biomass was processed until all of it was of a particle size less than 850 microns.

5. This ground sample was then analysed in the NIR.

6. The sample was then sieved to provide separate fractions, DS ($180 < x < 850$ microns) and DF (< 180 microns).

7. The DS and DF fractions are stored in air-tight containers for future wet-chemical analysis.

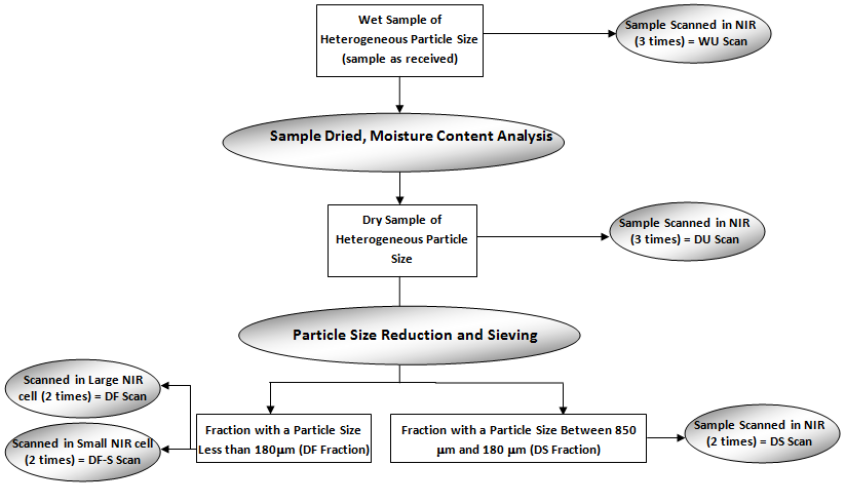

Figure 1: The methodology employed in processing biomass, including the collection of NIR spectra, so that a dry sample of an appropriate particle size can be obtained for subsequent wet chemical analysis.

Wet-Chemical Analysis

1. Sample preparation was targeted to maximise the DS to DF ratio since the DS particle size was considered to be the most appropriate for acid hydrolysis and the accurate determination of polysaccharide sugars contents. Hence, most wet-chemical analysis used the DS fraction of the sample.

2. Ethanol soluble extractives can interfere with the accurate quantification of polysaccharide sugars, Klason lignin, and acid soluble lignin (8). Hence, these were removed using a Dionex Accelerated Solvent Extractor (ASE 200) and quantified (based on the loss in dry matter).

3. The extractives-free material was then hydrolysed using sulphuric acid in a two-stage process (9). This produced a hydrolysate containing the liberated monosaccharides that constituted the structural polysaccharides and the acid soluble lignin. A solid residue, the "acid insoluble residue" (AIR), was also produced.

4. The monosaccharides were quantified using HPAEC-PAD, high performance anion exchange chromatography with pulsed amperometric detection (10). This allowed for the analysis of glucose, xylose, arabinose, galactose, rhamnose, and mannose, with fucose used as an internal standard.

5. Acid soluble lignin (ASL) was quantified using ultraviolet spectroscopy.

6. The AIR fraction was ashed and the ash content subtracted from the AIR content in order to determine the Klason lignin (KL) content.

3.2 DIBANET Analytical Database

A database containing compositional data of samples analysed by DIBANET partners can be downloaded from the DIBANET website at http://www.dibanet.org/chemicaldatabase.php.

It contains the results from the wet-chemical and/or spectroscopic analysis of 1,281 samples. These are presented in a list on the initial page that loads when the database is opened, Figure 3. This list can be filtered according to: the region in which the samples were collected (Latin America or Europe), the sample type (energy crop, agricultural residue, or non-agricultural waste), and certain specific biomass species can also be selected (sugarcane residues, coffee residues, banana residues, coconut residues, and Miscanthus). The list can also be ordered according to the compositional values. Summary statistics (average, maximum, minimum, range, and standard deviation) of the samples in the list are also presented. If a sample is double-clicked an additional page is opened. This presents more detailed compositional data and graphical charts, Figure 4, as well as the NIR-predicted compositional values (if such models exist for that feedstock).

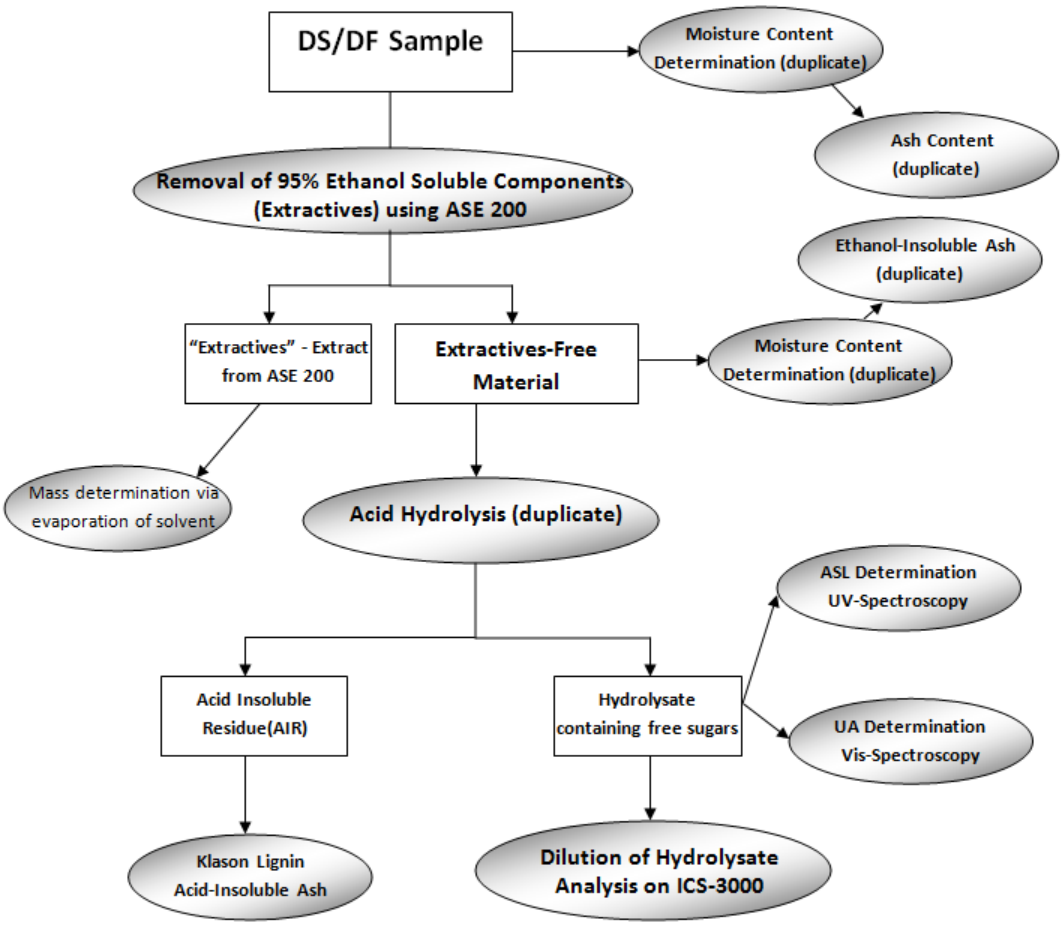

Figure 2: An illustration of the sequential methodology analytical sequence employed for the analysis of structural carbohydrates, lignin, and extractives, in prepared biomass samples.

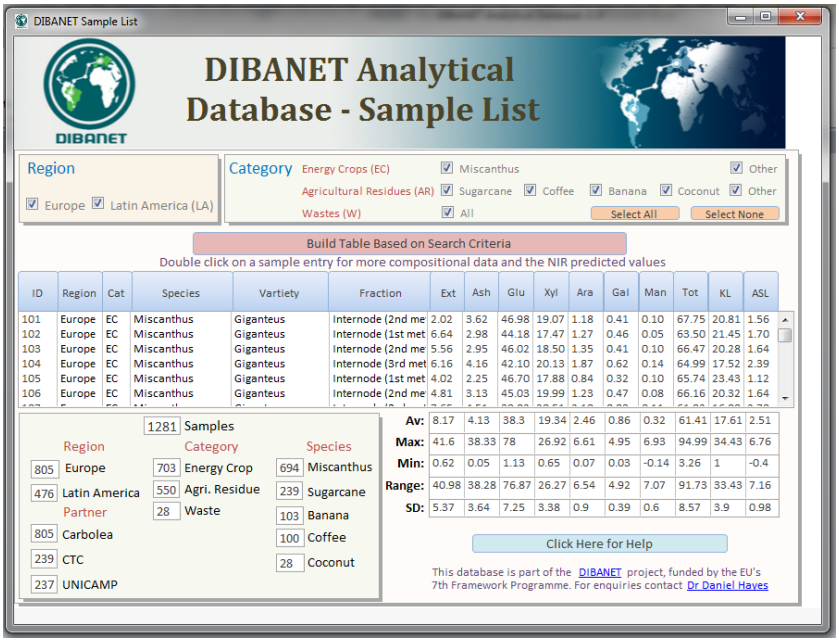

Figure 3: The "Sample List" page of the DIBANET Analytical Database.

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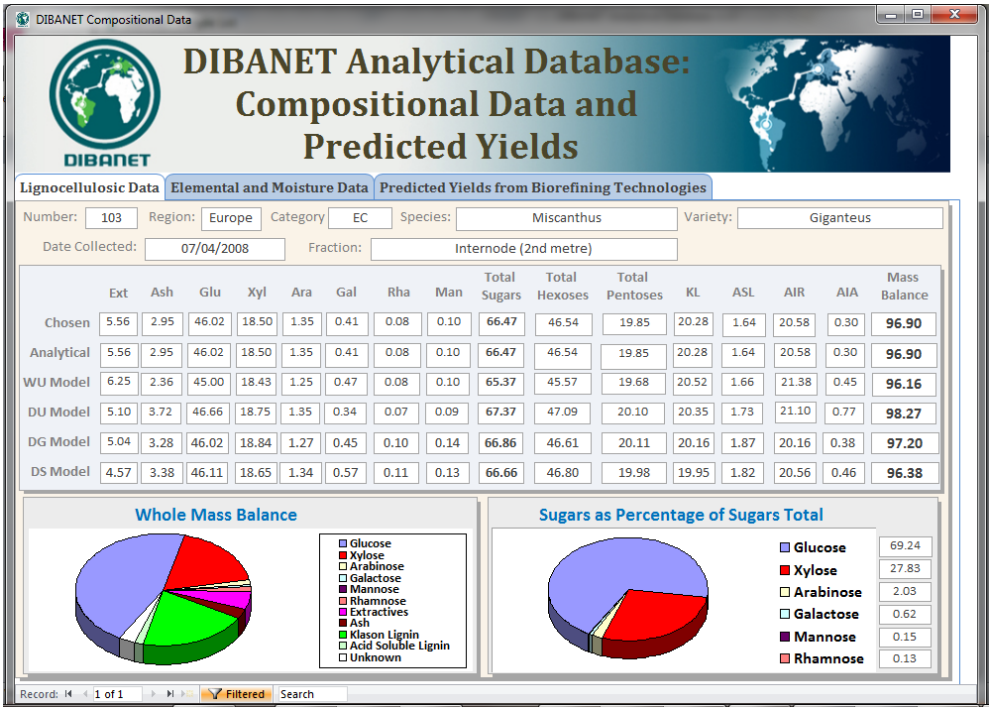


Figure 4: The detailed compositional data page of the DIBANET analytical database.

A tab of this sample detail page, Figure 5, displays the yields of chemicals/biofuels that may be expected if this sample were to be processed in a number of representative biorefining technologies, including the DIBANET acid-hydrolysis process

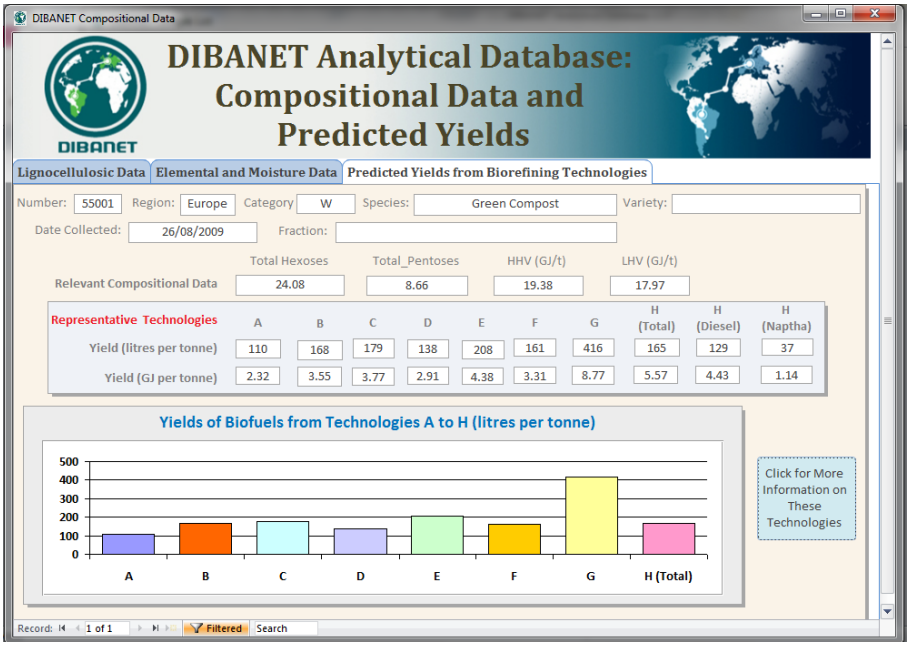


Figure 5: The "Predicted Yields from Biorefining Technologies" subpage of the DIBANET analytical database.

4 European Feedstocks

4.1 Initial Examination of Feedstocks

The evaluation of European feedstocks was carried out by DIBANET partner UL (the University of Limerick, Ireland). A wide range of feedstocks that may have potential for the DIBANET process were identified and some of these were sampled from various locations in Ireland. These feedstocks are listed in Table 1 which also classifies them according to whether they are energy crops (specifically produced for processing in biorefining), agricultural residues, or non-agricultural wastes.

These feedstocks are discussed below and some of the secondary data obtained from the literature are presented in Table 2 and primary data, obtained in the UL laboratories, are presented in Table 3. Note that a limited number of the samples from UL that are discussed in this report have been collected/analysed under other projects.

As discussed in Section 2, data regarding the relative amounts of the individual monosaccharides that constitute the structural polysaccharides are severely lacking in the literature, hence the data are presented simply on a cellulose, hemicellulose, and lignin content basis in Table 2.

Table 1: The potential lignocellulosic feedstocks, identified in Ireland, for utilisation in the DIBANET process. These are classified according to whether they are energy crops, agricultural residues, or non-agricultural wastes.

Energy Crops	Agricultural Residues	Wastes
Miscanthus	Cereal Straws	Municipal solid wastes
Switchgrass	Animal Excreta	Waste Papers
Reed Canary Grass	Spent Mushroom Compost	Garden Wastes/Composts
Short Rotation Coppices (SRC)	Forestry Residues	Sewage Sludge
		Food Waste

Table 2: Secondary data for the cellulose [Cl.], hemicellulose [Hc.], lignin [Lg.], total carbohydrate [Carb.] and ash contents (all in % dry matter), with moisture content (wet basis) [MC], and LHV - lower heating value (MJ/tonne dry feedstock), and HHV - higher heating value (MJ/tonne dry feedstock) for some Irish feedstocks of interest.

Sector	Feedstock	Cl.	Hc.	Lg.	Ash	Carb.	Ref	MC	Ash	LHV_{dry}	HHV_{dry}	Ref
Municipal Solid Waste (MSW)	Office Paper	64.7	13	0.9	11.6	**77.7**	(11)	0	6.7	14061	15375	(12)
	Newspaper	48.3	18.1	22.1	2.0	**66.4**	(11)	0	NA	18389	19720	(13)
	Cardboard	59.7	13.8	14.2		**73.5**	(14)	0	8.4	15661	16900	(15)
	Food Waste	50.8	6.7	9.9		**57.5**	(16)[a]	70	5	12721[b]	14000	(17, 18)
	Leaves and Grass	25.6	14.8	21.6		**40.4**	(16)[c]	60	4	13968 [b]	15000	(17, 19)
	Prunings	35.4	18.4	32.6		**53.8**	(16)	40	3.6	17730 [b]	19000	(17, 20)
	Combined Organic MSW Fraction [d]	45.1	9.2	14.0		**54.3**		65.4	4.7	13419	14657	
Straw	Wheat Straw, Winter and Spring	40	28	17		**68**	(21)	10.3	4.7	17659	18940	(22)
	Oat Straw, Winter and Spring	41	16	11		**68**	(23)	7	7.8	17011	18089	(24)
	Barley Straw, Winter	46	23	15		**69**	(25)	7.3	6.4	16979	18274	(26)
	Rape Straw	45	19	18		**64**	(25)	9	3.8	17532	18637	(26)
Other Agricultural Residues	Poultry Manure	11	16	4		**27**	(27)	30	27.4	12676	13764	(28)
	Poultry Litter[e]	20	20	8		**39.3**		24	21	14171	15317	
	Spent Mushroom Compost	38	19	25	30	**57**	(29)	70.8	30.2	12091[b]	12929	(30)
	Dairy Cattle (lactating) Excreta	25	21	13	9	**46**	(31)					
	Pig Faeces	16.9	20.3	4.9	17.4	**27.2**	(32)					
Forest Residues	Spruce Wood[f]	42.7	25.2	28.2		**67.9**	(33)	51.9	2.1	18246	19533	(34)
	Spruce Needles[g]	28.2	23.3	35.3		**51.5**	(33)		1.5	18686	20120	(35)
	Pine Wood	40.8	25	28.1		**65.8**	(33)		0.1	18873	20217	(36)
	Pine Needles	29.1	22.8	28.4		**51.9**	(33)		1.5	18686	20120	(35)
	Bark[f]	35.9	18.2	35.9		**54.1**	(33)		2.3	18543	19830	(22)
Energy Crops	Miscanthus Leaves	27.3	30.5	23.5		**57.8**	(37)	54.5	0	16387	17600	(38)[j]
	Miscanthus Stems[i]	39.37	26.6	23.64	2.98	**66.0**	(39)	14.2	1.5	18205	19580	(40)
	Miscanthus Winter[j]	34.54	28.16	23.58	1.79	**62.7**		50	0.90	17478	18788	
	Willow Coppice	43.0	21.3	26.6	1.0	**64.3**	(41)	11.4	1.9	18047	19400	(42)
	Reed Canary Grass	45	23	22		**68**	(43)	0	6.4	17900	19144	(44)
	Switchgrass	36.1	24.6	20.6	4.8	**60.7**	(45)	9.8	9	16794	18064	(46)

a = Average of data for two food samples; b = data for the LHV not available, the LHV was calculated according to: LHV = HHV – 1000(0.2205H_2) (47), where H_2 is the % (by dry mass) hydrogen content of the feedstock; c = verge grass data taken; d = fraction taken as being 73.8% food, 16.3% leaves/grass and 9.9% prunings according to (48). e = assumed at 70:30 by mass ratio of poultry manure to wheat straw in litter; f = data for Norway Spruce (Picea abies) used. g = heating value data for pine needles used; h = no heating value data found, data for bamboo leaves used; i = assumed the composition of the spring harvested Miscanthus is equal to the stems; j = a leaf:stem ratio of 29%:71% is used for winter Miscanthus.

Table 3: Primary lignocellulosic, extractives, ash, and elemental data for biomass samples analysed at the University of Limerick. EXTR = 95% ethanol soluble extractives; KL = Klason lignin; ASL = acid soluble lignin; AIR = acid insoluble residue; AIA = acid insoluble ash; ARA = arabinose; GAL = galactose; RHA = rhamnose; GLU = glucose; XYL = xylose; MAN = mannose; TOT = total sugars; C = carbon; H = hydrogen; N = nitrogen; S = sulphur.

Sample	EXTR	Ash	KL	ASL	AIR	AIA	ARA	GAL	RHA	GLU	XYL	MAN	TOT	C	H	N	S
Energy Crops																	
Switchgrass	12.64	11.42	11.45	6.76	13.23	1.77	3.16	2.05	0.45	23.19	9.18	0.71	**38.74**	46.45	6.36	1.15	0.06
Willow Short Rotation Coppice	7.36	1.67	21.84	2.23	21.9	0.05	0.9	1.32	0.49	39.68	12.44	1.91	**56.74**	-	-	-	-
Miscanthus (September)	11.22	3.68	16.8	2.36	18.03	1.22	2.26	0.66	0.16	38.31	18.22	0.12	**59.74**	-	-	-	-
Miscanthus (February)	3.82	2.34	18.14	2.24	19.23	1.08	2.63	0.7	0.17	41.47	22.03	0.21	**67.2**	-	-	-	-
Agricultural Residues																	
Spring Barley Straw	3.73	1.67	19.41	2.27	19.34	0	2.18	0.77	0.15	41.63	23.25	0.41	**68.38**	48.48	6.24	0.56	0.01
Winter Barley Straw	4.64	4.40	18.02	2.18	18.96	0.94	2.56	0.86	0.13	41.65	21.08	0.29	**66.57**	47.51	6.48	0.48	0.05
Spring Oats Straw	3.17	3.93	20.07	2.38	20.67	0.61	2.45	0.95	0.14	42.98	21.47	0.38	**68.37**	48.38	6.36	0.41	0.01
Winter Oats Straw	2.38	4.65	18.22	2.29	19.40	1.18	2.94	1.12	0.17	41.45	21.09	0.31	**67.07**	46.84	6.04	0.40	0.02
Spring Wheat Straw	3.61	4.94	20.56	2.42	22.32	1.76	2.12	0.82	0.14	38.12	21.96	0.45	**63.61**	46.82	6.25	0.77	0.09
Winter Wheat Straw	4.36	3.32	18.77	2.26	20.15	1.39	2.45	0.84	0.16	39.35	23.43	0.45	**66.67**	47.91	6.52	0.39	0.00
Mushroom Compost (Phase 1)	3.16	18.54	23.50	2.76	26.96	3.46	1.93	0.66	0.19	29.14	13.82	0.57	**46.30**	41.08	5.15	2.02	1.77
Mushroom Compost (Phase 2)	2.58	23.44	28.00	0.84	32.25	4.25	1.47	0.62	0.20	21.72	10.30	0.86	**35.17**	40.34	4.99	2.75	2.38
Spent Mushroom Compost	1.82	38.33	32.75	3.19	39.17	6.42	0.75	0.83	0.31	11.06	4.25	0.84	**18.05**	37.87	4.03	1.88	0.74
Pig Excreta	22.11	22.94	15.33	4.77	16.56	1.23	4.15	0.75	0.30	10.20	9.11	0.26	**24.76**	43.43	5.82	3.64	0.59
Dairy Cattle Excreta	11.31	19.56	21.72	3.24	23.32	1.60	2.35	0.83	0.30	22.02	13.50	0.32	**39.31**	43.11	6.10	1.67	0.40
Non-Agricultural Wastes																	
Fresh grass	12.64	11.42	11.45	6.76	13.23	1.77	3.16	2.05	0.45	23.19	9.18	0.71	**38.74**	45.24	6.16	3.52	0.42
Verge grass	3.73	14.52	17.40	-	24.68	7.28	4.00	2.36	0.39	28.86	16.32	0.99	**52.93**	42.19	5.67	1.20	0.05
Green Compost (16 weeks)	2.29	27.55	33.60	2.14	48.55	14.95	0.63	1.48	0.30	18.50	6.03	2.24	**29.18**	43.03	6.08	1.39	0.14
Brown Bin Waste (February)	20.20	23.06	-	-	17.41	-	1.03	1.03	-	20.40	2.74	1.36	**26.56**	-	-	-	-
Brown Bin Waste (May)	7.08	31.78	18.57	-	35.03	16.46	1.45	1.56	0.51	19.79	5.51	1.80	**30.12**	34.76	3.72	2.72	2.48
Waste Wood (Wood-Pallets)	1.44	6.23	28.42	-	29.65	1.22	0.77	1.56	0.17	36.94	6.77	7.87	**53.90**	-	-	-	-
Twigs from a Pyranctha Plant	8.25	3.41	30.58	2.17	30.52	0	2.08	1.83	0.61	24.50	12.26	1.14	**42.42**	-	-	-	-
Leaves of Ivy Plant	14.41	-	20.54	4.58	20.60	0.12	1.48	1.86	1.47	17.76	2.66	1.60	**26.83**	-	-	-	-
Branch of Lawson Cypress Plant	5.25	-	31.69	0.89	31.69	0.03	1.55	4.96	0.28	32.47	6.94	6.46	**52.67**	-	-	-	-
Leaves of Lawson Cypress Plant	23.75	6.69	26.52	2.75	27.07	0.55	3.24	2.43	0.54	12.63	1.34	2.54	**22.73**	-	-	-	-

4.1.1 Energy Crops

4.1.1.1 Miscanthus

Miscanthus is a perennial C_4 rhizomatous grass that has been shown to be highly productive in Europe. Secondary compositional data are presented in Table 2 and secondary data in Table 3. This feedstock is discussed in detail in Section 4.2.

4.1.1.2 Switchgrass

This is a perennial C_4 grass, native to North America, which is established from seeds. It has received much attention in the US as a potential lignocellulosic energy crop (49) due to its low requirements for nutrients and water and its capacity for production on marginal land (50, 51). Its yields are said to be sustainable over reasonably long periods (over 10 years (52)) and, while these yields may in some cases be lower than for Miscanthus, the ability to establish via seeds will result in significantly lower establishment costs (53). There are numerous switchgrass varieties, and these can be classified as belonging either to the lowland or to upland ecotypes. The former tend to be taller and more suited to wet conditions, whilst upland ecotypes are less productive but capable of growth in more arid climates (54). Switchgrass varieties have been shown (55) to vary in their lignocellulosic composition.

Conventional hay harvesting equipment can be used to harvest switchgrass. In contrast to Miscanthus, switchgrass tends to be harvested after senescence to prevent lodging losses (56). A delay in harvest till the spring will, like Miscanthus, result in a decreased moisture content allowing for easier storage and a more suitable feedstock for thermochemical processing. It however is associated with a significant loss in biomass yields (52) although some have found that switchgrass does not shed its leaves over the course of the harvest window to the extent that *Miscanthus x giganteus* does (43). While the crop can be harvested twice a year, a single harvest tends to give higher yields in temperate climates (57), and can be more economic, although this can vary according to the cultivar. It was found that in the upper southeastern region of the USA upland cultivars yielded more biomass in a twice-yearly harvest compared with a one-cut regime (58).

Christian and Riche (43) carried out switchgrass growth trials, in the UK. They found that the average yield was 12 t ha^{-1} y^{-1} (on an oven dry basis) for the four top-yielding varieties (of 8 varieties) in the final year, over six years. Its yields are said to be sustainable over reasonably long periods (approximately 15 years) and, while these yields tend to be lower than Miscanthus, the ability to be established via seeding will result in significantly lower establishment costs (53). However, the productivity of the switchgrass *Shawnee* variety that was sampled by UL researchers from Oak Park in Ireland was very poor. The low yields of the crop are reflected in its analytical data (Table 3); the total sugars and KL contents are very low. In contrast, the ASL, ash, and extractives contents are high. The total mass balance for

this sample was only 81.0%. It is likely that much of the remainder of the mass balance consisted of extractives components not soluble in 95% ethanol.

4.1.1.3 Short Rotation Coppices

These energy crops include the hardwoods willow, poplar, and robina, and have been used extensively in Scandinavia for biomass-fuelled electricity and energy generation (59). Short rotation coppices (SRCs) have relatively high yields, can grow in different climates, and have reasonably low maintenance costs once the crop is established.

SRC plantations are currently established from 20-25 cm long un-rooted stem cuttings that are planted vertically into a seed-bed (60). The average density in Britain is 15,000 cuttings per hectare (61) and the high cost of these cuttings result in significant establishment costs (62). By the end of the first growing season, usually in November, the trees will have reached a height of approximately one to two and a half metres and have up to four stems. These stems are then coppiced at a height of around 5 cm, usually between two weeks after leaf fall and the first bud swells in spring (early March) (63). This technique promotes multiple sprout formation. Little maintenance is required after the second growing season, apart from the monitoring of pathogens. Conventionally, it has been recommended that harvesting should occur in the winter, when the plants are dormant and their leaves have fallen, and be completed by bud swell. Due to the heavy nature of the harvesting machinery, operations are not considered possible when the soil is wet. However, some studies indicate that year-long harvesting is possible, although there are yield losses associated with summer harvesting (64).

The number of years between harvests is defined as the cutting cycle. SRCs generally have cutting cycles of between two and five years (65). There are four important factors to consider when judging the most appropriate cutting cycle.

1. Cost/Revenue Streams: A longer cutting cycle will reduce overall harvesting costs as fewer operations will be required throughout the lifespan of the plantation. However, it would also mean that initial returns from the plantation would occur later.

2. Annual Yield: If maximal biomass production is a target, cutting cycles should be evaluated on what mean annual yields they result in. Armstrong *et al*. (66) found that poplar coppice yield in a four year cycle was 70% greater than for two 2-year cycles. Kopp *et al*. (67) evaluated one, two, and three year cutting cycles and also found that a longer cycle increased annual yields whilst Willebrand *et al*. (68) found that a five-year cycle was the optimum for the Salix *viminalis* variety.

3. Lignocellulosic composition: Szczukowski *et al*. (69) examined chemical variation for six willow-coppice genotypes in relation to cutting frequency (one, two, three years) and found that cellulose content increased with the cutting cycle.

4. Plant/soil stress: Repeated harvesting may result in decreased yields due to increased soil damage and plant stress (70).

Importantly, however, cutting cycles do not have to be fixed, and can be extended for any specific growing season. This may be done if the growth in the planned season of harvest has been poor, or to accommodate the needs of the biorefinery. This adaptability of the harvesting regime (cutting cycle and potential for year-round harvesting) means that SRC may be less susceptible to negative issues regarding predictability of supply than annually harvested crops. There are also a variety of options for the means of harvest and transport of the crop. The harvesters can either cut and chip the SRC in one operation, or harvest the whole stems for later comminution at the biorefinery. Whole stem harvesters are generally less costly and the stems store and air-dry well in the field. Furthermore, chippers at the biorefinery may offer a lower unit cost and a higher chip quality than on-field chippers (71). However, the transport of whole stems may be prohibitively expensive (63). Dry matter losses in storage are minimal for stems but can be significant for chips - if coppice chips of moisture content 50-60% are stored without ventilation or active drying, dry matter losses of up to 3% per month are possible (72).

It is generally considered that coppice plantations can go through seven or eight rotations (i.e. have a lifespan of 21-24 years with a three-year cutting-cycle) before plant vitality falls and yields start to decline (63). It is also the general consensus that the yields will be lower in the first rotation than in subsequent rotations due to the emphasis of root growth in the early years (73). However, there have been significant losses in dry matter associated with pathogenic attack. These have been particularly prominent in the British Isles, while such losses tend to be less significant in Scandinavian regions. Mitchell *et al*. (72) found that, in one crop in England, over 50% of the willow was defoliated (leading to death) due to heavy beetle infestation. Leaf rust is also a problem in the British Isles and the infection also leaves the plants susceptible to secondary infection and attack from other pathogens and pests. The pathogens can also hybridise and form new pathotypes meaning that, while initially appearing resistant, clones may ultimately become susceptible (74). It is considered that the selection of species that are more resistant to attack is a more sustainable and economical approach than the use of chemical agents to protect susceptible varieties. It is also advisable to have a mixture of clones in any plantation, since mono-cultural fields tend to be more susceptible to damage (75).

The data in Table 3 show that the total sugars content of willow coppice is less than that of Miscanthus but still sufficient to warrant the utilisation of this feedstock in the DIBANET process, providing feedstock costs are not excessive. The relative proportions of the different lignocellulosic sugars are also different, with less xylose than Miscanthus but more mannose and galactose.

4.1.1.4 Reed Canary Grass (Phalaris arundinacea)

Reed canary grass (RCG) is a perennial C_3 grass that is: indigenous to northern Europe; adapted to short vegetation periods and low temperatures; can be established by seed; and is safe from overwinter mortalities (57).

It can reach a canopy height of 1.5–3 metres and, like Miscanthus, has a vigorous rhizome system. It has been used as a forage crop, mainly in North America. The crop can be harvested in the late summer or there can be a delayed harvest in the spring. The relatively dry spring crop can be cut with normal hay harvesting equipment.

There has been much research in Scandinavia on the use of RCG for energy and fibre purposes (76-78). The crop is particularly suited for that region due to its toleration of cold climates (77) and its ability to be grown on cut-away peat land.

The estimated lifetime of a plantation is 10 years (79). In trials in Sweden it was found that the highest yields were obtained on humus rich soils and averaged, over 8 harvest years, 9 tonnes of dry matter per hectare when harvested in the autumn, and 7.5 tonnes of dry matter per hectare at the spring harvest (77). An EU study covering several plantations across Europe and fifteen RCG genotypes found that delaying the harvest resulted in yields dropping by between 2% and 37%, depending on the genotype (78). As part of this study, Christian and Riche (43) grew RCG over six years in Rothamstead, England, where it was found that the highest yield was obtained in the second year and that yields decreased as the crop matured further. It was found that there was significant damage to the crop resulting from the larvae of the grass moth, *Opomea*. The stem to leaf proportion (by mass) was on average 75% stem in the spring harvest and 65% stem in autumn.

The data in Table 2 show that RCG has a high total sugars content and so is an attractive feedstock for the DIBANET process. Given that Miscanthus may take several years to attain ceiling yields, RCG may be more attractive as a short to medium-term crop for the farmer who may wish to enter the energy crop sector but is not prepared to risk the significant establishment costs associated with coppices and Miscanthus. In this context, RCG is a suitable energy crop for sites that are available only for short periods such as in an arable rotation. In the longer term, however, the farmer would receive a greater financial return from growing Miscanthus, providing the land is suitable. A biorefinery of a given capacity would also require a lower total area of land to meet its feedstock demand if this land were producing Miscanthus rather than RCG.

4.1.2 Agricultural Residues

4.1.2.1 Straws

Straw is a general term that can cover most solid plant residues from crops. It can include the residues from oilseed rape, rye, barley, wheat, oats, beans, rice, and peas. For example, when wheat or barley is threshed, straw is a by-product that is typically laid back on the field during

the harvest combining process. Some may be collected and used for bedding, feed supplement, or for the production of mushroom compost. However, much is left to rot on the field in order to preserve soil fertility (80, 81).

The yield of straw per unit mass of grain will vary according to the plant type and the local environment. For example, the average yield of wheat straw is 1.3–1.4 kg per kg of grain (82). The chemical compositions of straws will be dependent on the relative proportions of the components of the plant (e.g. leaves, nodes, internodes etc.) and the chemical compositions of these. The harvesting procedure is also important since it determines how well these different components are collected (83).

For straws the amount of residue that needs to be left on the soil to preserve soil fertility and prevent against soil erosion is an important consideration. This is a complex issue and the field residue requirements will vary according to the location and factors such as climate, soil characteristics, tillage type and crop rotations (84). A 2006 white paper by the US Department of agriculture (85) suggested that up to 30% of corn (maize) field residues could be removed from some no-till systems without increased erosion and runoff.

UL researchers have sampled by hand numerous samples of straws comprising several varieties of a number of plant species growing in Ireland. The average compositional values obtained for these different species are presented in Table 3. Section 4.3 discusses in detail the analytical results obtained.

4.1.2.2 Animal Excreta

The composition of animal excreta is a complex issue, being dependant on the class of animal, diet, digestibility of food, bedding, and stage of growth, among other factors. The main animal classes that produce excreta that can be collected for subsequent processing or distribution to biorefineries are cattle, pigs, and poultry. UL researchers have analysed several samples of dairy cattle excreta and pig excreta, some of these results are provided in Table 3. The total sugars content varied between 21% and 46% for the pig excreta and between 33 and 39% for the cattle excreta. Ash and extractives were significant fractions for both excreta types. It was found that hemicellulose (calculated as the total content of non glucan sugars) was the major polysaccharide in the pig excreta (with a content that was up to 89% greater than cellulose) whilst cellulose was the major polysaccharide in dairy slurries. For both excreta types, however, the moisture contents were extremely high (over 90% on a wet basis), indicating that these are unsuitable feedstocks for the energy efficient production of biofuels via thermochemical processes. These moisture contents would also significantly increase the costs involved in transporting these slurries.

Poultry facility waste, which comprises the manure (approx. 70%) and litter base (straw, paper, or wood shavings; approx. 30%), may have more potential (86). It has a much lower moisture content than pig or cattle excreta; between 20 and 50%, depending on husbandry practices (87). Because of this there are existing commercial facilities for the generation of heat and power from this resource. The lignocellulosic analysis of the material, as shown in Table 2, has a higher total carbohydrate content than the other excreta; suggesting that

reasonable yields could be obtained from processing this material in hydrolysis biorefining technologies.

4.1.2.3 Spent Mushroom Compost

Spent mushroom compost (SMC) is the substrate remaining after mushroom production, with approximately 5 kg of SMC produced for each kg of mushrooms (88). In 2001 290 kt (wet basis, or 85 kt on a dry basis) of SMC were produced per annum in the Republic of Ireland (89), with 96% coming from the Border counties (30) (including 70 kt, wet basis, from Co. Monaghan (90)). Importantly, SMC is produced all year round, and hence predictability of supply should be high and seasonality issues avoided. Also, the shift that has been seen over time to larger producers concentrated in a relatively small area is an advantage when organising supply logistics for a biorefinery; transport costs should be relatively low.

Mushroom compost is a mixture of 60-70% straw, 28-34% poultry litter, and 2-4.5% gypsum (91). It is made in a series of stages, termed phases. In the first phase the components (e.g. straw, litter, gypsum) are mixed and then placed in long windrows for a period of up to 2 weeks with the resulting product being termed Phase I compost. The second phase takes up to 18 days and takes place indoors in plastic tunnels that allow for the environment to be controlled so that any unwanted organisms or diseases in the compost can be controlled. Once the compost is of a quality suitable for mushroom production the compost is mixed with "spawn", a monoculture of mushroom mycelium on grain (92). This compost is termed Phase II. Phase III involves the spawning and growth of the mycelium and takes place under controlled conditions. It is considered complete when the mycelia have fully colonised the compost.

Mushroom producers either receive Phase II or Phase III composts. Once the compost is fully colonised mushroom production involves placing a casing layer of peat on top of the compost. This layer promotes the formation of promordia; mushroom pins. Approximately three weeks after this point the first crop (first flush) of mushrooms can be harvested. The compost can then be rewet allowing for the harvesting of subsequent flushes at approximately 7 day intervals. Typically, in Ireland, up to three flushes are harvested from each compost shipment. The remaining material is known as SMC and can sometimes be sterilised ("cooked out") by heating for 12 hours at 70^{o}C.

There are serious issues concerning the disposal of SMC. The compost is considered an unwanted waste by most producers, and dumping is very apparent in some counties - bags of SMC can be found lying at the side of the road or dumped in quarries in Tyrone, Armagh and Monaghan (30). SMC can be disposed by a contractor at a charge of approximately €10 per tonne; a study found that 72% of all SMC in Ireland is applied to land (93). There are problems associated with this use, however. A survey (94) in Co. Monaghan reported significant deterioration of the four main cross border rivers in the area. It was also found that the amount of phosphorus being generated by local agriculture was well in excess of the County's nutrient capacity.

The overall composition of SMC will vary according to the time of year, the amount of peat casing put on by the grower, the compost manufacturers, and the amount of water added to

the mushroom by the grower. The chemical composition of the ultimate spent material will be significantly different from the composite of the materials that make up the mushroom compost and casing layer, however, due to the effects of the composting process and mushroom growth.

The average moisture content of SMC has been measured as 65%, and the volatiles and ash contents, on a dry basis, as 61% and 39%, respectively (93). There has been some research on the use of Irish SMC for energy generation (30). The high moisture content, however, indicates that combustion of this feedstock would not be an effective utilisation of the material – the HHV of SMC is around 12.2 MJ/kg on a dry basis, but moisture content results in the effective heating value being around 2.4 MJ/kg (91).

While there are several sources detailing the moisture content and calorific value of SMC, there are less data on carbohydrate and polysaccharide contents (29, 95, 96). Jordan *et al*. (92) carried out an examination of the composition of SMC in Ireland in order to determine its suitability as a fertiliser. The mean values for a number of samples are presented in Table 2. It was considered by UL researchers that if the cellulose and hemicellulose contents presented in Table 2 were reflective of the real polysaccharide composition of SMC then this represents an attractive feedstock for biorefining given that it would be approximately 57% carbohydrate and potentially provided to the biorefinery for a gate fee.

To investigate further, UL researchers have collected a number of samples of spent mushroom compost (from different mushroom supplier and representing different numbers of mushroom harvests (flushes)) and analysed these. Some samples of mushroom compost, at various stages in the production cycle, were also collected and analysed. Some of the results obtained are presented in Table 3. It can be seen that there is a significant drop in total carbohydrate content from Phase I to Phase II compost. All of the major constituent sugars experience a drop over this period. Regarding the SMC, Table 3 shows that the total sugars content falls significantly further, down to 18.1%.

Table 3 also shows that, while the sugars content of SMC is less than that of the mushroom compost, the KL content is greater. An increased KL content may suggest an improved heating value and hence potential for utilisation in thermochemical biorefining schemes; however in this case the ash content also increases. Even without considering the technological problems that high ash content feedstocks bring to thermochemical processes, the situation regarding dealing with the post-treatment waste (approximately 1 tonne of ash for every 3 dry tonnes of sample) would be a great concern. The high moisture contents of this feedstock (over 65%) would, in any case, preclude SMC from being a practical, in energy terms, feedstock for thermochemical processing.

These data therefore suggest that SMC is not an attractive feedstock for hydrolysis or thermochemical biorefining technologies. This is in great contrast to what the literature review of the secondary data suggested. However, these secondary data were flawed in that they only used gravimetric methods for determining the polysaccharides contents and these can often be misrepresentative, particularly with feedstocks that might contain high contents of proteins and sugar degradation products.

4.1.2.4 Forestry Residues

Wood with a smaller diameter than 70 mm (branches and the tops of trees) is generally not harvested in roundwood operations. Depending on the age of the tree, the species, the tree-density, and the wood/foliage mix (97), the amount of forest residues can vary from 50 to 100 tonnes per hectare on an oven dry basis (98). In Ireland, spruce is the most abundant species and it produces approximately twice the amount of forest residues compared to pine and birch due to its long crown (99). It has been estimated that, with Sitka spruce (*Picea sitchensis*) harvested down to a diameter of 70 mm, forest residues (including needles) after clearfelling constitute about 30% of total above ground biomass (97). However, not all soils will be suitable for residue extraction (100), and the residue harvesters used will not be capable of collecting all the biomass available (47). The utilisation of forestry residues will require the development of the appropriate infrastructure (both in terms of harvesting machinery and in integrating residue collection into current forestry practices) but this has already been done extensively in countries such as Finland (99).

Table 2 contains secondary compositional data for the wood and needles from Norway spruce and pine. It can be seen that the woods have higher total carbohydrate contents than the needles, although there are likely to be sufficient lignocellulosic sugars in these needles to allow for their processing in hydrolysis technologies such as DIBANET.

The residues from the sawmill industry are other potential feedstocks. In 2006 approximately 2.176×10^6 m^3 of timber was used in Irish sawmills (101). This is said to have resulted in the production of 1.079×10^6 m^3 of sawmill residues. These residues can be classified as bark, woodchips, or sawdust and these have current uses in panelboard mills and for the generation of process heat/power. However, it has been estimated that the remaining quantities of residues could still be a significant resource for biorefining (86). The compositions of the woodchips and sawdust should be similar to the woody materials listed in Table 2. That table also presents compositional data for Norway spruce bark which, despite having a lower carbohydrate content than spruce wood, is still suitable for the DIBANET process. This bark also has a relatively high lignin content and a relatively low ash content, suggesting that the acid hydrolysis residues that would be obtained from the DIBANET process should have a good higher heating value and so be attractive for thermochemical processing (e.g. gasification).

4.1.3 Non-Agricultural Wastes

It has been estimated that, in 2005, a total of 3,050,052 tonnes (wet basis) of municipal solid waste (MSW) were generated in Ireland (102). Approximately 72% of this was biodegradable, Figure 6 categorises this biodegradable municipal waste (BMW) and revises the figures to dry tonnes according to the moisture contents provided by (103). BMW is composed of wood, various papers and cardboards, organics, and textiles. Some of these components of BMW are discussed below.

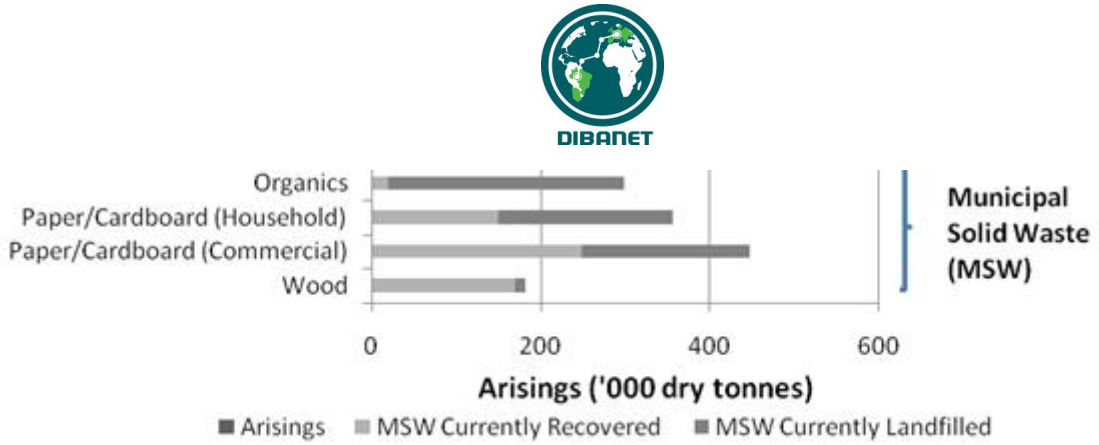


Figure 6: The arisings, in 2005, of lignocellusic municipal wastes in Ireland.

Waste Paper/Cardboard: An earlier paper by a UL researcher assumed that 50% of all the paper/cardboard from the commercial sector is chemically and energetically equivalent to office paper, 40% is equivalent to cardboard and 10% to newspaper with the proportions shared equally between these three for the household sector. The secondary data obtained for these three categories (Table 2) show that these have very attractive total carbohydrate contents, suggesting that these could be suitable feedstocks for processing in hydrolysis biorefining technologies such as DIBANET. Paper and cardboard samples are discussed in further detail, along with the primary analytical data that were obtained for these in the UL laboratories, in Section 4.4.

Wood: Waste wood can come from the construction and demolition industry as well as other sectors. The lignocellulosic data presented for spruce and pine woods in Table 2 suggests that these may also be attractive feedstocks for biorefining via the DIBANET process. Table 3 presents primary compositional data for a sample of waste wood collected from a waste-processing facility. This resource primarily consisted of discarded wood-pallets. It has a lesser total sugars content than the wood feedstocks in Table 2 but this content is still considered to be sufficient for the feedstock to be used in the DIBANET process.

Textiles: Textiles can be produced from petroleum, animal wools, or from plants such as cotton and flax. However, no reliable data on the proportions of plants to the total mix were found, hence this resource is not accounted for in this study.

Organic Waste: This fraction can be considered to be the remaining BMW that is not paper, wood, or textiles. It is primarily composed of food waste and waste plant materials (either grasses/leaves or prunings). Table 2 presents some secondary data that were obtained for the lignocellulosic compositions of these materials and Table 3 presents some primary data obtained in the Carbolea laboratories. "Brown Bin Waste" is the term given for the material collected in organic-waste household bins in Dublin. Table 3 presents analytical data for two brown-bin samples, one collected in February and the other in May. It was noted that the sample collected in February had more food waste and less garden waste than the sample collected in May. However, for both samples the total sugars contents is low and can be considered insufficient to warrant processing in technologies such as DIBANET.

The other non-agricultural wastes in Table 3 represent green (garden) wastes. It can be seen that the foliage (e.g. fresh grass, leaves) have significantly less total sugars contents that the more woody material (branches, twigs). It is considered that such foliage is also unsuitable for processing in DIBANET. A sample of green waste after 16 weeks of composting was also

collected (the "Green Compost" sample in Table 3). This sample also has a low total sugars content and a high ash content and also can be considered unsuitable for the DIBANET process.

Hence, it is clear that unsorted green waste contains insufficient lignocellulosic sugars to warrant processing in DIBANET. However certain fractions of green waste (i.e. the woody material) can be suitable.

4.1.4 Conclusions

A summary of the literature review and wet-chemical analysis of a wide range of biomass feedstocks in Ireland is provided below, along with guidelines of best practice (highlighted in green).

Need for Analytical Data

- The yields that may be obtained from processing feedstocks in the DIBANET process will be highly dependent on the relative amounts of the different lignocellulosic sugars in the structural polysaccharides.
- The amount of solid residues produced from the DIBANET process, i.e. the feedstock for subsequent thermochemical processing (gasification), will be dependent on the polysaccharide, lignin, and ash contents.
- Much of the compositional data in the literature is not specific enough to accurately inform estimates of the potential yields that might result from processing feedstocks in the DIBANET process.
- Hence, primary analysis of a number of feedstocks by DIBANET partners was necessary.
- DIBANET partner UL undertook an investigation of a range of Irish lignocellulosic feedstocks. These included energy crops, agricultural residues, and wastes.

Energy Crops

- Miscanthus is a highly productive crop that has a significant amount of structural carbohydrates, it is most suitable for the DIBANET process.

- Reed canary grass and willow coppices also have attractive lignocellulosic compositions.

- Switchgrass also has a good lignocellulosic composition, providing it is productive. However, experimental plots of switchgrass in Ireland have experienced poor yields.

- If the land is productive and available for a significant period of time (10+ years), the production of Miscanthus, rather than coppices or reed canary grass, should be favoured.

- If the land is only to be used for energy crop production in the short term then reed canary grass is preferable to Miscanthus due to its significantly lower establishment costs.

- The longer cutting cycle of coppices, and the potential for year-round harvesting, are attractive properties and may help to minimise supply cycle constraints associated with the provision of energy crops to biorefineries.

- However, the biomass/yield losses associated with pathogenic attack on coppices in parts of Europe can be significant and need to be seriously addressed/considered by farmers.

Agricultural Residues

- Straw is a significant resource that has a lignocellulosic composition suitable for the DIBANET process.

- In order to preserve soil fertility, not all of the straw can be removed from the land. How much straw needs to be left will be dependent on local factors including climate, soil characteristics, tillage type, and crop rotations.

- Pig and cattle excreta have insufficient levels of structural carbohydrates to warrant their processing in the DIBANET process. Alternative end-uses for these resources need to be sought.

- Furthermore, their high moisture contents will make transportation difficult/expensive and will prohibit their utilisation in thermochemical biorefineries.

- Poultry litter, however, does appear to be a suitable feedstock for the DIBANET process given that it has greater structural carbohydrate contents.

- This feedstock also has a significantly higher dry matter content than the other animal wastes and so logistical problems regarding transportation are likely to be less.

- The secondary data for spent mushroom compost suggested that it had a structural carbohydrate content that was sufficient to warrant the utilisation of the feedstock in the DIBANET process.

- However, the primary data obtained at UL show much lower carbohydrate contents.

- Spent mushroom compost is not suitable for the production of biofuels via thermochemical or hydrolysis technologies. Alternative end-uses for this resource need to be sought.

- Forestry residues (wood and leaves) are suitable for utilisation in the DIBANET process but this will require a significant investment in the infrastructure required for their collection and transport.

- Sawmill residues are also of value for biorefining but there are other current end-uses for these resources.

Non-Agricultural Wastes

- Municipal wastes are predominately composed of waste papers, food waste, garden waste, and waste woods.
.
- Waste food does not contain sufficient lignocellulosic sugars to warrant its utilisation in the DIBANET process.

- Garden/green waste contains various types of materials such as grasses, leaves, twigs, and branches.

- Only the more woody materials have lignocellulosic compositions suitable for the DIBANET process.

- Garden/green waste taken as a composite (i.e. a sample from a compost pile) does not have a favourable proportion of wood to foliage. Hence, the sourcing of green waste for biorefineries needs to be specifically tailored to high-carbohydrate materials. This may necessitate for separate collection schemes or for processes to sorting the woody material from the total green-waste resource.

- Waste paper and cardboard materials can have total carbohydrate contents in excess of any other feedstock discussed in this report. They are extremely attractive feedstocks for the DIBANET process providing they can be sourced at reasonable prices.

At an early DIBANET meeting it was decided that only a limited number of feedstocks would be selected for processing in the DIBANET conversion technologies (principally the acid hydrolysis process developed in Work Package 3). The early evaluations that took place in Work Package 2 helped to inform the choice as to which feedstocks would be selected. It was decided that Miscanthus would be the main feedstock from Europe and that sugarcane bagasse and sugarcane trash would be the main feedstocks from Latin America.

Miscanthus was selected because of its high productivity and relatively low maintenance costs and attractive environmental profile. The analysis and observations regarding this feedstock are discussed in detail in Section 4.2.

As part of DIBANET Work Package 2 near infrared spectroscopy (NIRS) quantitative calibration models for the important mass constituents were also developed for Miscanthus. It was also decided that NIRS models would be developed for straws and paper wastes since these were found to have attractive total sugars contents and represented a significant waste resource that could sustain a number of commercial-scale biorefineries. Some of the analytical results obtained from straws are discussed in Section 4.3 and some of the results from papers in Section 4.4.

4.2 Miscanthus

4.2.1 Background

4.2.1.1 Grass Components

Miscanthus is a perennial C_4 rhizome grass that originated from Asia but was introduced to Europe in the 1930s. At that time its main use was as an ornamental grass. However, the development of Miscanthus *x giganteus*, a sterile hybrid of the M. *sinensis* and M. *sacchariflorus* varieties, led to increased interest in utilizing this variety as an energy crop due to its high yields. The crop is also attractive because it has minimal requirements for fertilizer and pesticides. Miscanthus is closely related to sugar cane, and the two often hybridise in the wild (104).

Miscanthus is classified as a grass. Figure 7 provides an illustration of the major anatomical components of most grasses. The below ground component of plants is usually termed the root and is of little relevance for most biomass schemes. The above ground "shoot" component consists of a stem and leaves. The stem can bear one, two or more cotyledons, depending on the plant (monocotyledons and dicotyledons). All grasses are monocotyledons.

Graminaceae is the term given for the grasses. It chiefly covers herbaceous plants, but also some more woody species such as cereals, bamboo, and reeds. The mainly-holocellulose components of biomass (e.g. cereal straw and sugar cane bagasse) tend to have less established markets than the more valuable components of cereals and sugar canes (e.g. barley/wheat and sucrose) whose high prices preclude their use in lignocellulosic fractionating technologies.

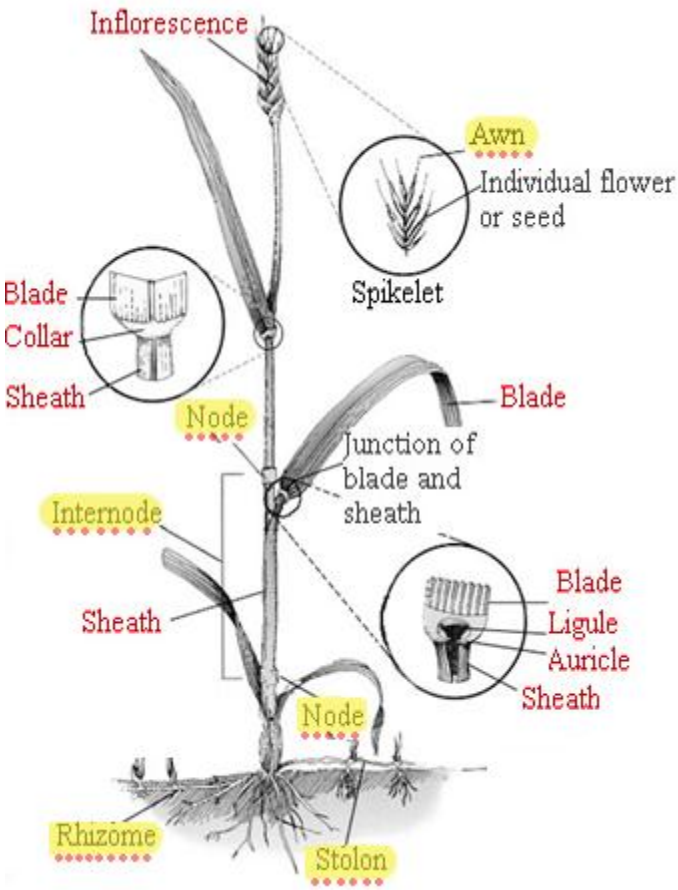


Figure 7: An illustration of the main fractions of most grasses. Taken from (105).

The stems are mostly hollow, cylindrical and interrupted at intervals by swollen joints or nodes from which the leaves originate. The parts of the stem between the nodes are termed the internodes. At the tip of a growing shoot sits the terminal bud of the shoot that is surrounded by the leaf (or flower) primordias.

The lower portion of the leaf forms a sheath, which encloses and protects the young shoots. The second half of the leaf then opens out into the leaf blade. The midrib is the major vein structure of the leaf. Although it has only a small proportion of the cross sectional area (e.g. 6-13% in grasses), it can comprise 18-28% of the leaf weight and contain 14-24% of the lignified tissues in the leaf (106).

4.2.1.2 Establishment and Development Cycle of Miscanthus

There are numerous varieties of Miscanthus that have been grown experimentally (107) but fewer varieties tend to be grown commercially. In Ireland Miscanthus *x giganteus* is the only commercial crop that has been established so far, although there have been experimental plots

of other varieties, principally M. x *sinensis*. Elsewhere in Europe, particularly in the regions that experience colder winters, M. x *sinensis* has been grown commercially

Establishment

M. *x giganteus* is sterile, and so must be propagated vegetatively. This can either involve the planting of rhizome cuttings or plantlets (significantly more expensive). The plantlets are much more susceptible to frost-mortality and so tend to be planted later (April to May) than rhizomes (March to April). Rhizomes can be collected from nursery fields where Miscanthus has already been established – these are broken up, collected and planted using existing agricultural equipment such as potato harvesters and planters.

Miscanthus can grow on a wide variety of soils (e.g. sandy soils as well as high organic matter content soils) and, while the ideal pH range should be between 6.6 and 7.5, it can tolerate more acidic/alkaline conditions (104). The main problems associated with the establishment of Miscanthus crops are those relating to over-wintering. Miscanthus plantations in the northern regions of Europe *(*M. *x giganteus* varieties in particular) have suffered from poor survival over the winter in the first year after planting (108). Trials at a site in Cashel, Co. Tipperary, showed that micro-propagated plants are much more susceptible for winter mortality than rhizome propagated plants – there was a 95% survival rate for the rhizomes but the survival rate for the micro-propagated plants was only 17% (108). The level of winter-failure was attributed to killing by late spring frosts of the first shoots produced. If this happens, the plants will not re-sprout. The failure of the micro-propagated plants to develop a sufficient rhizome system to retain enough reserves for early shoot growth may be the reason for their high mortality. Overwintering is only a problem in the establishment year of the plantation, after that period the rhizomes are developed enough to escape frost mortality.

Other Miscanthus genotypes, such as M. *x sinensis*, are more resistant to cold winters due to their higher frost resistance. However, in periods where winter rhizome destruction is not a problem, M. *x giganteus* yields tend to be higher than those of *sinensis*. The reasonably mild winters experienced in Ireland, particularly the west coast, may reduce the risk of overwintering for rhizome-propagated plants. However, the establishment costs for Miscanthus are currently significant, between €1,060 and €2,555 per hectare in Ireland (109).

Growth

Spring growth will start once daytime temperatures exceed 10^{o}C. In May, June, and July, growth is very rapid and results in cane-like stems that may reach a height of 3 m or more. Once the canopy closes, the lower layers of leaves begin to senesce. Shoot growth continues through August and September with full senescence occurring following the first frosts of the autumn. During the end of the growing season, nutrients are translocated from the stems and leaves to the rhizomes for storage and utilisation the following season. The efficient use of nutrients by Miscanthus varieties means that fertilisation levels need not be high. The low fertiliser and pesticide requirements of Miscanthus mean it is a relatively environmentally friendly crop - Spink & Britt (110) identified Miscanthus as being one of the most environmentally benign alternatives to permanent set-aside land.

Fertilisation should be carried out after the harvest but before shoots grow sufficiently high that they become damaged by the equipment. While the plots at Cashel are still productive in their later years, ten years after planting potassium deficiency became relevant and tenth year yields from unfertilised plots were significantly lower than for fertilised plots (111).

If Miscanthus is harvested in the autumn, extra leaf mass is taken from the field (112). This means that less will decay on the ground and, hence, less nutrients will be transferred to the soil. More (perhaps up to 100%) fertilisation will therefore be required (113).

Harvesting Window

Harvesting of Miscanthus is carried out annually and can take place using conventional harvesting equipment. It can occur after crop senescence until just before re-growth in the following spring. It is important that the crop has senesced so that translocation of assimilates to the rhizomes has occurred. Irish growth will cease at the first frosts of autumn or winter. After this period crop senescence accelerates, nutrients are sequestered to the rhizomes, and moisture falls. Harvesting is necessary before spring growth to avoid sprout damage. Current practices involving Miscanthus seem to be geared towards harvesting the biomass in the spring before the start of the growing season (114). The reasoning behind this is that the later that the harvest can be carried out, the lower will be both the moisture content and the inorganic mineral content; these are important qualities in biomass combustion.

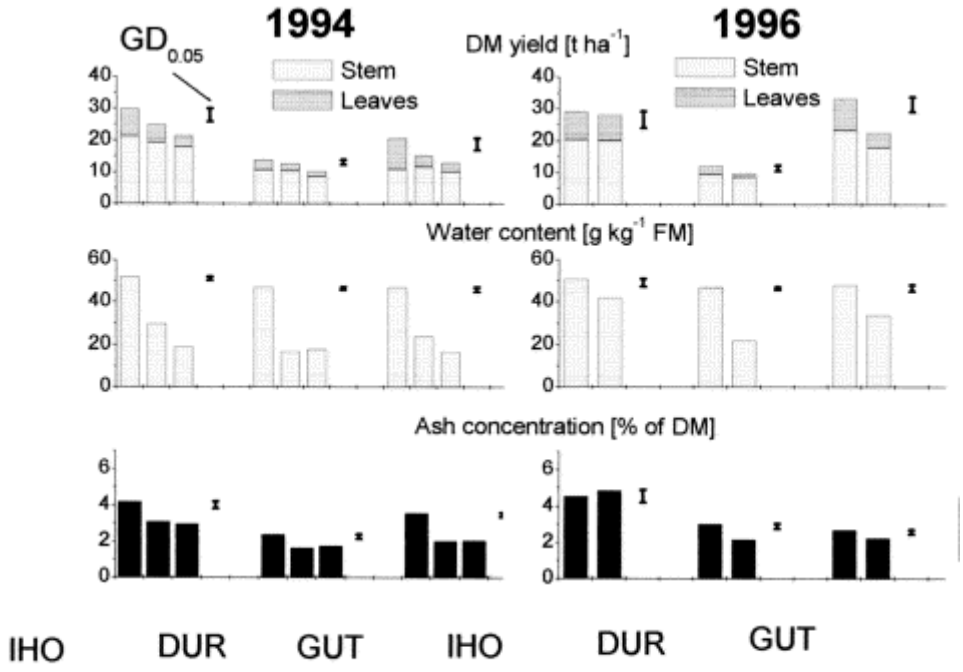


Figure 8: Miscanthus dry matter yield, moisture content, and ash concentration at three sites for harvests at December and February (for the crop grown in 1994 and 1996) and at March (for the 1994 crop). These dates are plotted from left to right for each site. The three different locations in Southern Germany are Inger Hof (Iho), Durmersheim (Dur) and Gutenzell (Gut) - Taken from Lewandowski and Heinz (115).

The research of Lewandowski and Heinz (115) illustrates well the dynamics involved over the harvest window. Figure 8 shows the effects, at three locations, of delaying the harvest. *Miscanthus* that was grown in 1994 was harvested in December, February, and March. *Miscanthus* that was grown in 1996 was harvested in December and February. It can be seen that, except for one site in 1996, delaying harvest to February always resulted in a loss of yield, while the moisture content also fell dramatically. On average, dry matter yields were reduced by 18% between December and February and by an additional 16% in 1995 between February and March. Figure 8 shows that the principal reason for this reduction in dry matter was due to the loss of leaves; the stem component does not decrease to a great degree in most cases. The concentrations of carbohydrates and lignin per tonne of harvested biomass are likely to change significantly given the proportional increase in the stem component that is associated with a late harvest. With regards to the ash content, a harvest delay from December to February reduced this significantly but a delay from February to March did not.

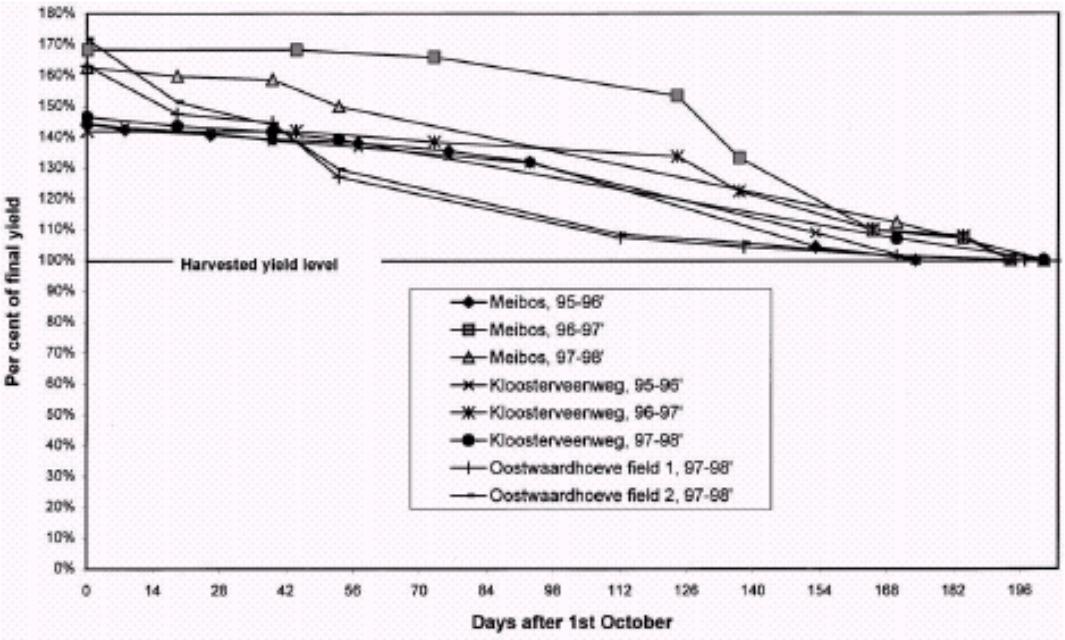


Figure 9: Decrease in the harvestable amount of Miscanthus over the course of six months after the 1st of October, expressed in terms of the final yield harvested in April, for various years and locations in The Netherlands. Taken from (116)

Experiments at the Cashel site also back-up these data – the ceiling figures of between 14 and 16 t dry matter ha^{-1} y^{-1} that were attained after the first four years of growth, were figures for the March harvest. They found that there were dry matter losses of almost 40% which occurred between the first air frost in autumn and final harvest in March (111). Figure 9 shows, for several years and stands in The Netherlands, that the standing harvestable-biomass after senescence can be as much as 70% higher than that available in the spring (116).

4.2.1.3 Yields

Research throughout Europe has found that the yields associated with different Miscanthus varieties can vary dramatically, e.g. between 2 and 44 tonnes of dry matter (DM) per hectare (57). Highest yields tend to occur in warmer, sunnier, southern European climates although, in such locations, water availability becomes a limiting factor. In more northern areas, where global radiation and average temperatures are lower, and hence become the limiting factors, yields without irrigation are more typically 8-25 t DM ha^{-1} (57).

It generally takes several years for annual productivity to reach ceiling yields, representative of the time required for full establishment of the Miscanthus stand. For example, it was found in that, in southern Germany, autumn yields of Miscanthus *x giganteus* increased from about 2-3 t DM ha^{-1} in the first year after planting to 22-30 t DM ha^{-1} in the third year (111). It has also been reported that the period required to obtain ceiling yields is longer in temperate climates (up to 6 years) than in warmer climates (within 2 years). For example, a site at Trinity College Dublin took 5 years to reach its ceiling yield of 14 t DM ha^{-1} (Clifton-Brown, personal communication 2003).

4.2.1.4 Costs Involved in Miscanthus Production

There have been extensive studies on the costs and profitabilities of various Miscanthus scenarios (43, 62, 114, 117, 118). Bullard and Nixon (114) estimated the cost for Miscanthus plantations in the UK. They assumed a ceiling yield of 18 oven dry tonnes (odt) per ha that was reached after 3 years. Bullard and Nixon (114) assumed a unit price for rhizomes of 7.5 cents, resulting in total rhizome costs per hectare (with a plantation density of 20 000) of €1,500. Given land preparation and planting operations, the total establishment costs were estimated at approximately €2,000/ha. Annual husbandry costs (fertiliser, herbicides) were low at approximately €100/ha. They found that the cost of harvesting one hectare of Miscanthus using a baling system and subsequently storing for 6 months was €305/ha. The associated cost for chopping the Miscanthus with a forage harvester was €316/ha. It was assumed that 20% of the stand biomass was lost through storage and harvesting losses. The result of their studies was that the break-even cost for the production of baled Miscanthus, with no subsidies, was €69/odt. This fell to €33/odt when set-aside support was included.

The assumption of a yield of 18 odt $^{-1}$ ha^{-1} in that study was somewhat optimistic. A subsequent paper by Bullard (117) considered Irish conditions, among those of other countries, and varying yields. Break-even costs, under no subsidy, ranged from €72.9 for 12 odt/ha to €37.96 for 24 odt/ha. Venturi *et al*. (62) found that the break even cost, excluding land costs, was €40 per tonne for baled Miscanthus and €28 per tonne for chopped Miscanthus. They found that the corresponding costs for chipped and whole stem willow were €50 and €35, respectively.

4.2.1.5 Lignocellulosic Analysis of Miscanthus in the Literature

Most analysis on Miscanthus has focussed on its moisture content, energy value, and ash composition – all important qualities for combustion (119). Less data exist for the lignocellulosic components of the feedstock. The general characteristics of grasses should apply in that there should be a large concentration of cellulose and hemicellulose with the hemicellulosic fraction being closely related to xylans, with a low concentration of glucomannans present.

Kaack *et al*. (120) examined various properties of M. x *giganteus* stems, selected at 5 different points in the harvest window (between mid-November and mid-March) at a stand in Denmark. These properties included the stem length, internode length, and the number of internodes per stem. It was found that the average stem length increased from 197 cm at the first harvest to 206 cm at the second harvest, but then decreased linearly over time to 169-170 by the last two harvests. Furthermore, the maximum number of internodes (12) was found in the second harvest period, but this value fell to 9 by the last harvest. These reductions were attributed to lodging occurring because of abscission of internodes during the period from December to March.

One of the most extensive characterisations of Miscanthus was carried out by Visser and Pignatelli (39). The results of their analyses are provided in Table 4. The samples used were composed of a 52% basal section, 33% centre section and 15% top of the stem of a second-year crop of Miscanthus *x giganteus*. They also found a degree of polymerisation of approximately 1,300 for cellulose. Table 4 also provides data from other sources, including those obtained by Papatheofanous *et al*. (121) for M. x. *sinensis* (using detergent analysis methods).

Table 4: Lignocellulosic contents of Miscanthus, taken from several sources.

Source	**% Dry Matter**				
	(122)	**(39)**	**(123)**	**(121)**	**(124)**
Variety	Giganteus	Giganteus	Giganteus	Sinensis	Sinensis
Section	Stems	Stems	Spring harvest	Spring harvesy	Stems
Cellulose	38.2			43.1	
Hemicellulose	24.3			26.7	
Glucan	39.5	38.8	45.6		48.3
Xylan	19.0	24.3	22.5		19.0
Arabinan	1.8	2.3	2.3		1.4
Galactan	0.4	0.6	0.4		0.5
Mannan			0.2		
Uronic acids	1.8	-			
Total Lignin	25.0	25.2	26.5	22.1	23.5
Klason Lignin	24.1	23.6	26.0		
ASL	0.9	1.6	0.5		1.6
Solvent Extract.	4.2*a	2.2*b	1*c		
Water Extract.	1.4				
Ash	2.0	3.0	2.8	3.9	5.7

**a = ethanol:toluene (2:1); *b = ethanol; *c = dichloromethane*

A paper by Le Ngoc Huyen *et al*. (125) is especially relevant. It discusses the sampling at two points in the harvest window of a two year stand of *M. x giganteus*, an early harvest (November) and a late harvest (February the next year). These dates corresponded to a dry matter yield of 21 t DM ha^{-1} in the early harvest and 15 t DM ha^{-1} in the later harvest. These samples were then either analysed whole or separated into the following fractions which were then analysed separately: leaves, sheaths, lower internode section, upper internode section. These internode sections were selected by numbering each internode from the base of the stem and selecting the basal section (number 2, represented by IN2 in Table 5) and the apical regions (number 11, represented by IN11 in Table 5). All other internodes and all nodes were discarded and not analysed. The analytical protocol involved obtaining the neutral detergent fibre (NDF) fraction which was then hydrolysed using the conventional two-stage acid hydrolysis procedure and the liberated sugars quantified by high-performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD). The analyses of acetyl content and numerous lignin components were also carried out. The values for sugars, acetyl, lignin etc. in the paper are presented on a % NDF basis; however, Table 5 has corrected these for the NDF content of the sample so that they are on a whole mass basis. Interesting points to take from Table 5 are that the ratio of xylose to arabinose is approximately three times higher in the internodes than it is in the leaves and sheaths, it was suggested that this indicates a higher proportion of primary cell walls in the leaves/sheaths. Lignin was also highest in the lower internode section, as would be expected. Galactose is higher in the leaves and sheaths than in the nodes and the values for the acetyl content seem quite high for all fractions, particularly when compared to other lignocellulosic feedstocks, e.g. 1.7% in wheat straw (126). Interestingly Le Ngoc Huyen *et al*. (125) found barely any uronic acids in their analysis (0.01% of dry matter NDF).

Table 5: The relative amounts (% dry matter) of lignocellulosic constituents in the various anatomical fractions of Miscanthus x giganteus harvested in November and February. S/G = syringyl/guaiacyl lignin ratio. Data adapted from (125)

Constituent	**Amount (% dry matter) For Corresponding Fraction**								
	Early Harvest (November)					**Late Harvest (February)**			
	Whole	IN 2	IN11	Green Leaves	Green Sheath	Whole	IN 2	IN11	Sheath
NDF	76.37	89.16	91.05	76.86	78.27	86.75	91.19	91.13	83.98
Arabinose	2.49	1.19	1.35	3.50	3.38	2.41	1.40	1.65	3.27
Galactose	0.47	0.28	0.24	1.03	0.89	0.30	0.30	0.28	0.94
Glucose	37.82	46.74	46.00	30.07	35.30	43.78	46.04	45.23	36.66
Xylose	16.90	15.85	18.10	15.59	16.15	18.81	16.53	17.62	16.54
Xyl/Ara Ratio	6.78	13.37	13.73	4.44	4.78	7.81	11.90	10.73	5.07
Total Sugars	57.68	64.05	65.65	50.20	55.71	65.31	64.27	64.78	57.41
Acetyl	3.22	3.04	3.06	2.54	2.89	2.98	3.16	2.99	2.94
KL	14.40	19.87	15.67	13.41	12.78	16.68	17.36	17.35	15.25
S/G Ratio	0.56	0.64	0.64	0.43	0.34	7.81	0.83	0.83	0.48

Table 5 shows that there is a clear increase in the NDF content of the whole plant associated with the later harvest as opposed to the early harvest. That would be attributable to the loss in

leaves that occurs over this period. However, regarding the composition of the NDF fraction itself, the authors concluded that the major influence due to harvesting date was on the cell wall phenolic fraction of the whole biomass (lignin composition, phenolic acids) whereas no significant differences were found for the glucan or total lignin content. The authors also undertook experiments involving the enzymatic saccharification of these samples and found that the lower internode sections were the most recalcitrant, whereas the leaves and sheaths displayed similar susceptibilities to the enzymatic conversion of cellulose and arbinoxylans (being 2.5 to 3 times greater than for the internodes). It was theorised that the lignins in the leaves/sheaths were less recalcitrant than those in the internodes.

Hodgson *et al*. (127), as part of the European Miscanthus Improvement project that included the growth of 15 Miscanthus genotypes at a plot in Rothamsted Research in the UK, analysed five of these genotypes for their acid detergent lignin (ADL), cellulose (acid detergent fibre (ADF) – ADL), hemicellulose (NDF-ADF) and ash contents and compared these properties between November (early) and February (delayed) harvests. The results are provided in Table 6. It can be seen that there are clear differences in compositions between the genotypes; for example, M. *x giganteus* and *sacchariflorus* were generally higher in lignin and cellulose and lower in hemicellulose than the M. x *sinensis* genotypes. There were less significant differences between the harvest dates, although the ash contents did fall.

Table 6: Cell wall composition of Miscanthus species and genotypes in November and February harvests. Ho:Lg = Holocellulose content divided by lignin content. Lig = lignin, Cell = cellulose, Hc = hemicellulose. Taken from (127).

Variety (M. x)	**Genotype**	**Amount of Contituent (% DM) According to Each Harvest Date**									
		November Harvest					**February Harvest**				
		Lig.	**Cell.**	**Hc.**	**Ho:Lg**	**Ash**	**Lig.**	**Cell.**	**Hc.**	**Ho:Lg**	**Ash**
Giganteus	EMI01	12.0	50.3	24.8	6.3	2.7	12.6	52.1	25.8	6.2	2.7
Sacchariflorus	EMI05	12.1	49.1	27.4	6.3	2.3	12.1	50.1	28.1	6.5	2.2
Sinensis (hybrid)	EMI08	9.3	43.1	33.1	8.2	3.5	9.7	45.3	33.0	8.1	2.7
Sinensis	EMI11	9.7	47.6	34.0	8.0	3.2	10.3	45.5	30.6	7.7	3.0
Sinensis	EMI15	9.2	46.7	33.0	8.8	2.4	9.3	52.2	30.3	8.9	2.2

4.2.1.6 Miscanthus in Ireland

All commercial Miscanthus plantations in Ireland are of the M. x *giganteus* variety. There have been a number of other varieties grown at the Oak Park Teagasc experimental site in Carlow, where Miscanthus has been in production for over 15 years. Miscanthus has also been grown in Cashel, Co. Tipperary, since 1997. The primary use for commercially-grown Miscanthus is as a fuel, supplied as co-feed with peat in the Bord na Móna power station in Edenderry, Co. Offaly. Up to 30% biomass as a co-feed is mandated for 2015 and the power plant operator expects that Miscanthus will contribute 10% to the total fuel mix. As a result of this end use for the crop it is typically harvested in the Spring (March/April) so that the ash, moisture contents, and leaf:stem ratios are at a minimum. There are currently no uses for early harvest, i.e. wet, Miscanthus in Ireland.

The total area of land under Miscanthus cultivation in Ireland has expanded in recent years, primarily as a result of the introduction of the "Bioenergy Grant Scheme for Willow and Miscanthus" which provides establishment grants, up to €1 300 per hectare, to cover 50% of the costs. According to the official statistics for applications made to this scheme 599 hectares were planted in 2007, 752 in 2008, 704 in 2009 and 182 hectares in 2010, totalling 2,238 hectares over this period. In comparison, funding was sought for establishment grants for a total of 577 hectares of willow short rotation coppice plantations over this same period. Data are available on a per-county basis and these are provided (for the combined 2007-2010 period) in Table 7. It can be seen that the counties of Cork, Kilkenny, Limerick, Tipperary, and Wexford contribute 65% of the total Miscanthus area. This is in contrast to the coppice plantations where these counties only contribute 18.1% towards the total (with no hectares planted in Limerick and Kilkenny) with Meath (24.5%), Cavan (17.1%), and Monaghan (12.4%) contributing the majority of the plantations. In 2011 the Sustainable Energy Authority of Ireland (SEAI) launched the "Bioenergy Mapping Scheme" website. This can be accessed at http://maps.seai.ie/bioenergy/ (last accessed by the Author on 16/4/11) and allows the known locations of numerous crops to be plotted on a map of Ireland. Figure 10 shows this map when all known Miscanthus plots were selected.

Table 7: The total hectares (ha) applied for Miscanthus establishment grants, by county, in Ireland over the period 2007-2010

County	Total ha	% of Total
Carlow	39.4	1.76
Cavan	15.4	0.69
Clare	11.3	0.51
Cork	327.6	14.64
Donegal	6.9	0.31
Dublin	0.0	0.00
Galway	99.8	4.46
Kerry	109.5	4.89
Kildare	37.4	1.67
Kilkenny	233.6	10.44
Laois	49.8	2.22
Limerick	365.4	16.33
Longford	17.9	0.80
Louth	10.6	0.47
Mayo	37.3	1.67
Meath	31.7	1.42
Monaghan	16.4	0.73
Offaly	32.6	1.46
Roscommon	25.7	1.15
Sligo	6.9	0.31
Tipperary	351.7	15.72
Waterford	97.6	4.36
Westmeath	62.4	2.79
Wexford	203.3	9.09
Wicklow	47.5	2.12%

Styles *et al*. (109) undertook, for Irish conditions, a life-cycle-assessment for a 16 year (14 harvests) Miscanthus plantation. This involved taking, from the literature, the costs associated with each activity in the life cycle and inflating these to 2006 prices. The paper considered the

use of the feedstock for electricity/heat production and assumed payment prices for Miscanthus at 70, 100 and 130 € t^{-1} DM for mid, low, and high estimates. It was found that annualised production costs for Miscanthus ranged from €430 to €559 ha^{-1}, equivalent to between €37 and €48 t^{-1} DM. Under the mid-costs and mid-price scenario the annual gross margins for Miscanthus production were €326-383 ha^{-1} with these margins rising to up to €586 ha^{-1} when using the low cost estimates. It was found that most of the Miscanthus scenarios were highly competitive with all other agricultural land uses with the exception of dairy.

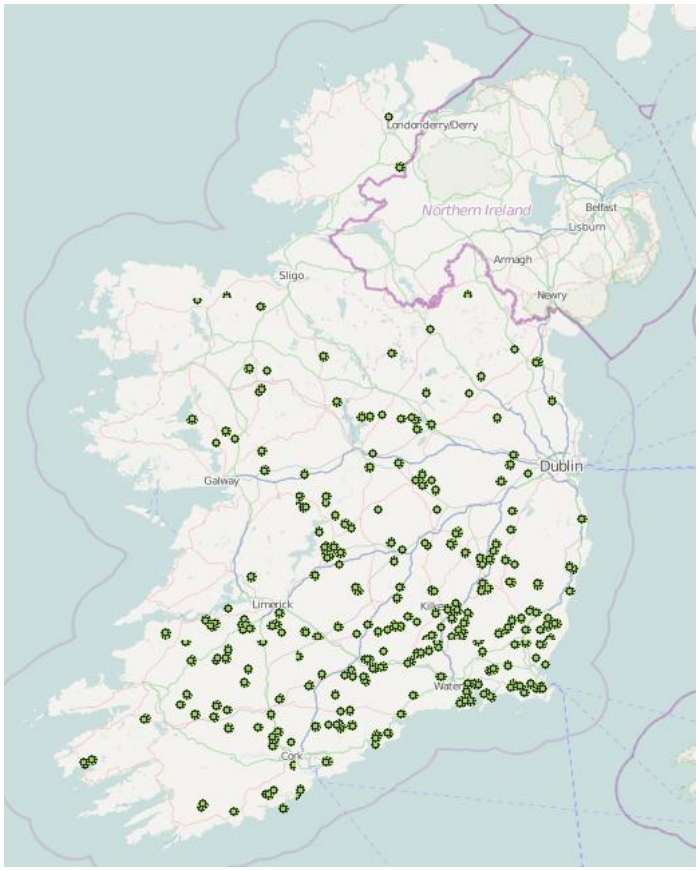


Figure 10: A map showing the Miscanthus plantations across Ireland. Taken from http://maps.seai.ie/bioenergy/ on 16/4/11

Walsh (128) carried out a reasonably simplistic evaluation in the Irish context. She assumed a productivity of 15 dry tonnes per hectare and found that annual costs were €803/ha (including a €480 land rental), equating to a cost of €53.53 per tonne with no subsidy or €25.80 with set-aside payments.

A very useful yield prediction model was designed using measurements from a four year old field trial of M. x *giganteus* in Cashel (111). It assumed that rainfall was not limiting and that

fertiliser application was adequate; hence growth was dependent on air temperature and solar radiation. By linking empirical growth and climate parameters (129), with data from meteorological stations in Ireland, a geographic map was produced to indicate the potential primary production of above-ground dry matter, as shown in Figure 11. The yields predicted by the model were the standing biomass yield in early autumn when the first frost occurred. The predictions for the trial site over two years were 17.3 and 18.4 t ha^{-1}, 27% and 31% higher than the December-harvested dry matter yields of 13.6 and 14.0 t ha^{-1}. While the overestimation may be partly due to the relative simplicity of the model, the dry matter loss experienced between senescence and harvesting could also be responsible.

The model predicted substantial interannual variation in yields, mainly as a consequence of the changes in the length of the frost free period. Nixon and Bullard (130) developed a similar model for the United Kingdom. This model also incorporated soil series data for England and Wales to allow the user to also calculate potential yields where water availability may be a limiting factor.

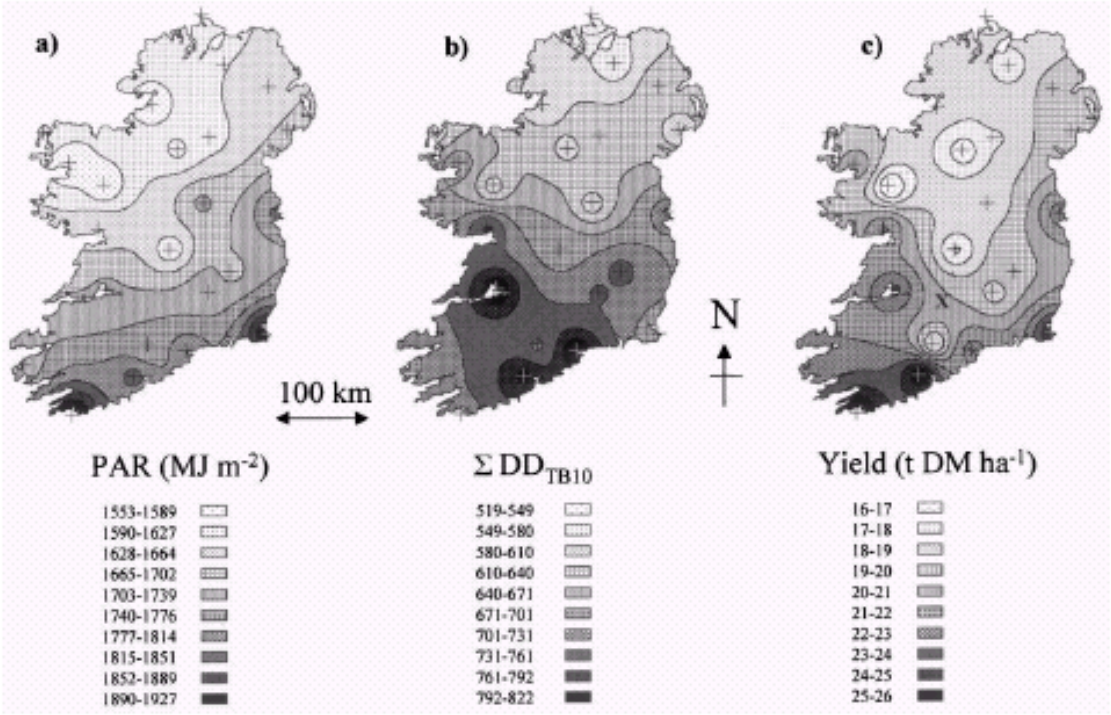


Figure 11: Miscanthus modelled productivity maps for Ireland. (a) Total annual mean radiation (MJ/m^2); (b) degree days above 10^oC; (c) mean simulated yield at the end of the growing-season for M. x giganteus. Taken from (111).

The MiscanMod model (131) that was subsequently developed by Clifton-Brown has allowed predictions of the production potential throughout Europe for M. *x giganteus*, based on local climatic conditions (temperature, radiation, rainfall and soil water holding capacity).

4.2.2 Miscanthus Sampling Strategy

The sampling of many Miscanthus samples took place prior to DIBANET in a research project at Carbolea funded by the Irish Department of Agriculture. In this project plants were sampled from stands for each month during the period of October 2007 to April 2008 (or until the stand had been harvested). Seven different stands were used. These were chosen to reflect variations in stand age and the success in plant establishment. These sites are listed below:

- Adare-H: A plantation that was in its third year at a farm of Joe Hogan in Adare, Co. Limerick.
- Adare-C: A plantation in its second year at a farm of Joe Hogan in Adare, Co. Limerick.
- Shannagolden: A plantation in its second year at a farm in Shanagolden, Co. Limerick.
- Langton: A first-year crop at a farm of Paul Langton in Co. Kilkenny.
- Clonmel: A first-year crop at a farm of Ann Kehoe in Co. Tipperary.
- Carlow-F: A crop that was in its thirteenth year at the Teagasc Oak Park Research Centre in Carlow, Co. Carlow.
- Carlow-G: A crop that was in its thirteenth year (different site) at the Teagasc Oak Park Research Centre in Carlow, Co. Carlow.

The dates at which samples were collected from each site are presented in Figure 12. If more than one plant was sampled then this is represented by stacked points on the chart.

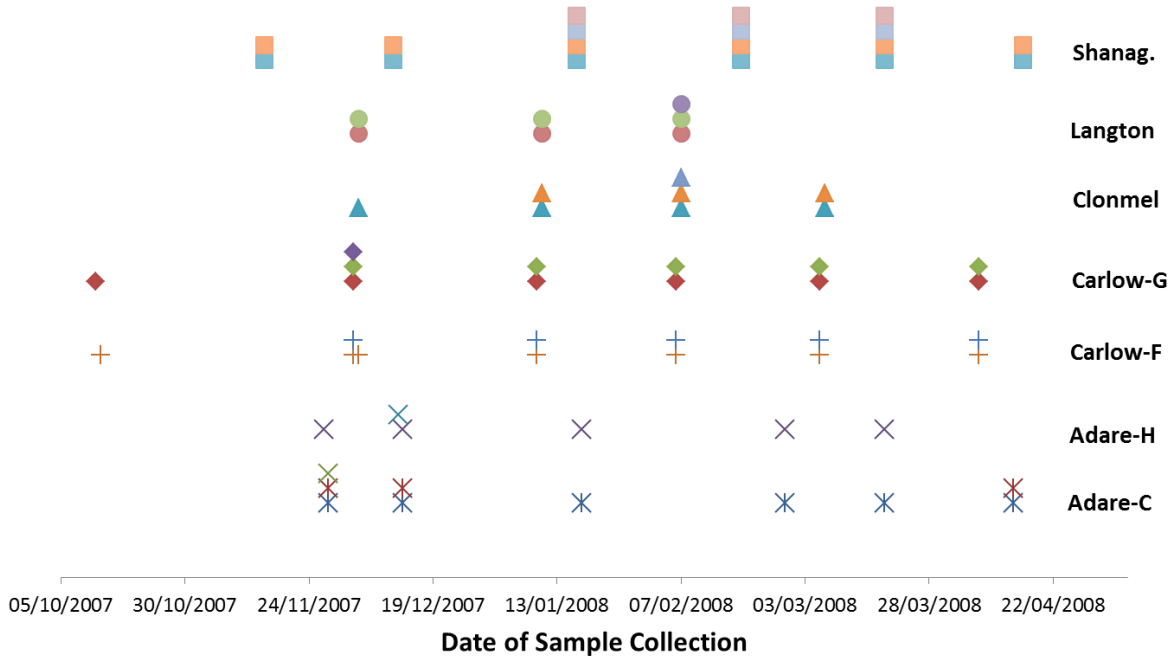


Figure 12: Chart representing the number of Miscanthus plants collected, according to date and site location, during the period October 2007 to April 2008.

The plant sampling methodology involved the random selection, at a location within the field, of a whole plant. All of the plantations listed above featured the Miscanthus x *giganteus* variety and a plantation density of 1 plant per metre squared. It was easy to determine, according to the distribution of the stems, the boundaries of each plant. Separate fractions of the plant were collected. The general methodology involved is outlined below:

1. The "live" leaf blades ("K" fraction) were considered to be those blades that were more than 60% green (determined upon visual inspection). These were separated from the sheath at the ligule and placed in airtight plastic bags.

2. The "live" leaf sheaths ("M" fraction) were the sheaths attached to the live leaf blades and they were removed from the plant and collected in separate bags.

3. The "dead" leaf blades ("F" fraction) were those that were judged, upon visual inspection, to be less than 60% green. These were removed and collected separately.

4. The "dead" leaf sheaths ("H" fraction) were then also collected.

5. In some instances there were inflorescences at the top of the plant. These "flowers" (the "FL" fraction) were collected separately.

6. At this stage the remainder of the plant that had not been sampled consisted of the stems. These were cut at a height of 5 cm above the ground. Then each stem was cut at distances of 1 metre. The first 1 metre section was labelled X1, the second X2, etc. In order to fit the stem sections into the airtight bags it was necessary to cut them into billets of approximately 15 cm in length. Care was taken so that the stems were only cut at internode, rather than node, sections.

7. The samples were then brought to the Carbolea laboratories and stored in a freezer.

8. At a later point the stem sections were removed from the freezer and allowed to equilibrate to room temperature (the bags were still sealed to prevent moisture loss). The node sections were then cut from these stems resulting in the formation of two separate samples for each stem section. For example, the X1 fraction would provide an X1N sample corresponding to the nodes collected from that sample and an X1T sample corresponding to the internodes sections collected from that sample.

A total of 77 Miscanthus *x giganteus* plants were collected from these seven sites between October 2007 and April 2008. The separation of these plants into the anatomical fractions described above resulted in the production of 479 samples.

As part of the DIBANET project more samples of Miscanthus were collected in order to improve the near infrared spectroscopy models that are key parts of the project. On 9/2/10 a total of 8 WP (whole plant) samples were collected from the Adare-H site and 8 WP samples from the Adare-C site. These samples involved either the collection of a set of whole biomass

stems (including the leaf blades, leaf sheaths and flowers) or the collection of a certain metre fraction of these plants (WP1 = first metre, WP2 = second metre etc.). A further 13 WP samples were collected from the Carlow-G site on 17/2/10; three of these WP samples were from a stand of the Miscanthus x *sinensis* variety. On 29/9/10 a further 8 WP samples were collected from the Adare-H site and 7 WP samples from the Adare-C site. The Adare-C site was returned to on 27/10/10 for the collection of a further 4 WP samples and the Adare-H site was returned to on 10/11/10 for the collection of a further 9 WP samples. On 6/10/10 seven WP samples were collected from the Shanagolden site with three more WP samples collected from this site on 27/10/10.

On 15/10/09 samples of several Miscanthus varieties other than *giganteus* were collected from an experimental plot in the Teagasc Oak Park Research Facility. These samples comprised two *sinensis* plants and 7 other varieties. The F, H, K, and M fractions of these plants were collected separately, as described above. However, the stem sections were not cut to separate the internode and node sections – instead the X1, X2 etc. stem sections were retained for analysis. On 9/2/10 a further 13 stem sections, this time of the Miscanthus *x giganteus* variety, were collected from the Adare-H (7 samples) and the Adare-C (6 samples) sites.

In November 2010, it was decided that more leaf samples were needed so a total of 8 F samples, 6 H samples, and 12 K samples were collected from the Adare-H and Adare-C sites.

In addition to the samples that were collected by the Author, 16 samples of harvested Miscanthus cultivars other than M. x *giganteus* were sent to the Carbolea laboratories from Dr. Eppel-Hotz in Germany. Since these were received dry, no wet NIR analysis was possible for these samples. These samples were labelled "HP" to differentiate them from the other plant fractions that were collected.

Table 8 provides a summary of the total number of samples collected/received.

The DIBANET project involved the analysis of a large number of the samples that were collected. This analysis was either by wet-chemical means or using the near infrared spectra of the samples to predict their lignocellulosic composition as described in a recent publication (7).

Table 8: Summary of the different plant sections collected, according to Miscanthus variety. F = "dead" leaf blades, H = "dead" leaf sheaths, K = "live" leaf blades, M = "live" leaf sheaths, FL = flowers, X1-4 = stem section from the first-fourth metre section of the plant, X1T-X4T = internode section from the first-fourth metre section of the plant, X1N-X4N = node section from the first-fourth metre section of the plant, WP = whole plant sample, WP1-WP3 = whole plant sample from the first-third metre section of the plant, HP = harvested plant (supplied from Germany).

Variety	Leaf Sections				Whole Stem Sections				Internode Sections					Node Sections				Whole Plant Sections				HP	TOTAL
	F	H	K	M	FL	X1	X2	X3	X4	X1T	X2T	X3T	X4T	X1N	X2N	X3N	X4N	WP	WP1	WP2	WP3		
Giganteus	72	84	30	7	3	6	5	2	0	77	61	38	2	73	65	39	2	27	15	15	7	0	630
Sinensis	2	2	2	2	2	2	2	0	0	0	0	0	0	0	0	0	0	1	1	1	0	0	17
Other	6	6	5	5	4	7	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	16	53
TOTAL	80	92	37	14	9	15	11	2	0	77	61	38	2	73	65	39	2	28	16	16	7	16	700

4.2.3 Variations in Lignocellulosic Composition Within a Plant

Table 9 presents compositional data for the various anatomical fractions of a plant that was sampled on October 12th 2007 from a 13-year old Miscanthus x *giganteus* stand in Oak Park, Carlow. The stem of the plant was close to 3 m in height meaning that there were three stem sections corresponding to each metre (0-1 m, 1-2 m, 2m +). At a later point these stem sections were separated into the internode and node samples. Each plant fraction was weighed while wet and its moisture content determined, allowing the relative proportion of stem/leaf fractions to be determined. According to total dry matter, 66.2% of the plant was stem sections (nodes or internodes) and 33.8% was leaf sections. These leaf sections were either: dead leaf blades ("F"), dead leaf sheaths ("H"), live leaf blades ("K"), or live leaf sheaths ("M"). There were no flowers on this plant. The only location in which flowering *giganteus* plants were observed was Shanagolden, a stand where Miscanthus was in its second year of production. The compositional data of flowers sampled from a plant at this location are also provided in Table 9.

Data in Table 9 labelled with an asterisk have been predicted using near infrared spectroscopy models developed on the spectra of wet samples. All other data have been determined with reference analytical (wet-chemical) methods. Table 9 also provides data for the whole plant ("WP"); this has been determined as the weighted average of the data of all the fractions of the plant. The data for the whole stem ("X"), and each metre of the stem (nodes and internodes combined, e.g. X1) have also been calculated as the weighted average of the relevant stem sections.

For all of the plants sampled, the internode sections contributed the majority of the dry matter to the total stem weight. For example, the first metre internode section (X1T) of the 2+ m plant described in Table 9 contributed 91.2% to the total mass balance for the first metre section of the stem, with the remainder coming from the nodes. The X1T section also contributed 34.6% to the total dry matter of the plant, with 22.4% coming from X2T section and only 3.6% from the X3T section. Regarding the leaves, the K fraction contributed 15.1% of the total dry mass, the F fraction 11.3%, the M fraction 3.5% and the H fraction 3.9%. Note that these mass data are not provided in Table 9, instead that Table provides the concentrations of various constituents by plant fraction.

There are several important observations regarding the 3-stem-sections plant in Table 9:

- Glucose is the largest constituent in all plant sections, this carbohydrate is clearly representative of the cellulose, which is the major polysaccharide in Miscanthus.
- Xylose is the second most abundant carbohydrate in the samples, 18.9% of the total mass balance of the whole plant (WP), followed by arabinose with 2.06%. The concentration of galactose is approximately 3 times less, in the whole plant, than that of arabinose, whilst mannose and rhamnose are minor constituents. This suggests that, as outlined in the literature (125), the hemicellulose in Miscanthus is principally an arabinoxylan with approximately one arabinose residue in the polysaccharide for every 10 xylose residues.

Table 9: Compositional data for a Miscanthus x giganteus plant that was over 2 m in height and a plant of the same variety that was less than 1 m tall.

Plant Fraction	Extr. (%)	Ash (%)	Ara. (%)	Gal. (%)	Rha. (%)	Glu. (%)	Xyl. (%)	Man. (%)	Total Sugars	AIR (%)	KL (%)	ASL (%)	AIA (%)	TOTAL (%)	Ara :Xyl	Hc :Cel	Nitr. (%)
A plant Over 2 m High (3 Stem Sections - X1, X2, X3)																	
Live leaf blades, K	12.19	4.60	3.40	1.07	0.27	30.15	17.55	0.16	52.60	14.59	13.83	4.93	0.76	88.15	0.19	0.74	1.87
Live leaf sheaths, M	8.40	2.58*	2.88	0.86	0.11	41.30	20.70	0.21	66.06	17.64	16.66	2.17	0.98	95.86	0.14	0.60	0.43
Dead leaf blades, F	4.56	5.07	3.74	1.09	0.30	37.15	20.50	0.29	63.07	19.52	17.87	3.13	1.65	93.70	0.18	0.70	0.45
Dead leaf sheaths, H	3.93	3.00	3.03*	0.79*	0.20*	40.51*	20.59*	0.18*	66.03*	20.19	18.81	1.81	1.38	92.85	0.15	0.61	0.23
Stem, Internode 1m, X1T	6.27	2.06*	1.13	0.54	0.08	46.49	17.74	0.05	66.04	21.32	21.00	1.31	0.32	96.69	0.06	0.42	0.22*
Stem, Node 1m, X1N	6.73	1.79	1.70	0.65	0.09	41.54	19.07	0.14	63.19	22.25	22.08	1.66	0.17	95.46	0.09	0.52	0.28*
Whole Stem, 1m, X1	6.31	2.04*	1.18	0.55	0.08	46.06	17.86	0.06	65.79	21.41	21.10	1.34	0.31	96.58	0.07	0.43	0.22*
Stem, Internode 2m, X2T	7.19	3.15*	1.33	0.38	0.08	46.07	19.42	0.04	67.33	18.05	17.67	1.66	0.38	96.99	0.07	0.46	0.15
Stem, Node 2m, X2N	6.79*	2.67*	2.28*	0.91*	0.05*	39.59*	20.46*	0.27*	64.55*	18.80*	19.01*	2.23*	0.00*	94.28	0.11	0.61	0.47*
Whole Stem, 2m, X2	7.15*	3.11*	1.41*	0.43*	0.08*	45.51*	19.51*	0.06*	67.09*	18.11*	17.79*	1.71*	0.34*	96.76	0.07	0.47	0.18*
Stem, Internode 3m, X3T	6.61	7.02	2.77	0.84	0.16	38.26	21.15	0.17	63.37	14.10	13.59	4.13	0.51	94.72	0.13	0.66	1.01*
Stem, Node 3m, X3N	11.66*	10.03*	3.34*	1.30*	0.14*	34.12*	20.71*	0.38*	62.20*	16.01*	14.87*	3.44*	2.70*	99.99	0.16	0.76	0.85*
Whole Stem, 3m, X3	6.94*	7.21*	2.81*	0.87*	0.16*	37.99*	21.12*	0.19*	63.29*	14.23*	13.68*	4.09*	0.66*	95.06	0.13	0.66	1.00*
All Stem, X	6.66*	2.73*	1.36*	0.53*	0.08*	45.39*	18.66*	0.07*	66.13*	19.77*	19.45*	1.64*	0.34*	96.56	0.07	0.46	0.25*
Whole Plant, WP	7.21*	3.28*	2.06*	0.69*	0.14*	41.82*	18.85*	0.12*	63.73*	18.90*	18.30*	2.33*	0.61*	94.79	0.11	0.52	0.52*
Flower (another plant)	4.33	4.08	5.61	1.45	0.18	29.69	26.92	0.30	64.15	20.24	19.94	3.57	0.30	96.07	0.21	1.16	0.98
A plant Less Than 1 m High (1 Stem Section - X1)																	
Live leaf blades, K	12.23*	5.68*	3.57*	1.18*	0.24*	29.47*	18.12*	0.21*	51.13*	15.95*	13.39*	4.89*	2.17*	88.97*	0.13	0.61	1.69*
Dead leaf blades, F	7.06*	8.37*	3.75*	1.16*	0.47*	30.65*	18.51*	0.34*	54.07*	19.39*	16.15*	4.04*	3.96*	90.50*	0.08	0.53	0.74*
Dead leaf sheaths, H	4.90*	3.10*	2.96*	0.71*	0.05*	42.80*	22.37*	0.10*	68.52*	18.50*	17.94*	2.27*	1.66*	97.21*	0.13	0.69	0.33*
Stem, Internode 1m, X1T	5.02*	3.25*	1.62*	0.60*	0.13*	42.70*	20.11*	0.07*	65.86*	18.25*	17.36*	2.41*	0.58*	93.28*	0.09	0.55	0.24*
Stem, Node 1m, X1N	4.88*	3.72*	2.87*	1.03*	0.06*	37.24*	21.28*	0.28*	64.51*	19.70*	19.10*	2.67*	1.10*	93.14*	0.14	0.64	0.53*
Whole Stem, 1m, X1	5.00*	3.32*	1.81*	0.67*	0.12*	41.88*	20.28*	0.10*	65.66*	18.47*	17.62*	2.45*	0.66*	93.26*	0.13	0.61	0.29*
Whole Plant, WP	6.98*	4.75*	2.71*	0.88*	0.20*	37.16*	19.75*	0.17*	60.66*	18.08*	16.45*	3.27*	1.74*	92.32*	0.08	0.53	0.69*

* = Data supplied by NIRS calibration; Extr. = extractives; Ara. = arabinose; Gal. = galactose; Rha. = rhamnose; Glu. = glucose; Xyl. = xylose; Man. = mannose; AIR = acid insoluble residue; KL = Klason lignin; ASL = acid insoluble lignin; AIA = Acid insoluble ash; Hc:Cel = Hemicellulose to cellulose ratio; Nitr = nitrogen.

- This arabinose to xylose ratio (Ara:Xyl in Table 9) varies according to the plant fraction. Arabinose is proportionately greatest in Miscanthus flowers and is also present in higher concentrations in the leaf blades compared with the stems, as noted in the literature (125). Arabinose is also present in higher concentrations in the nodes than in the corresponding internode section and the concentrations in both nodes and internodes increase with height up the stem.

- The xylose concentration also increases with stem height, however, meaning that the Ara:Xyl ratio value is constant between the first and second metre stem sections; however, it almost doubles for the third metre section.

- The galactose concentration also increases with stem height and is consistently higher in the nodes than in the internodes.

- After cellulose and hemicellulose, lignin is the most abundant polymer in these plant fractions. It is present in low concentrations in the live leaf blades and upper sections of the plant and in greatest concentrations in the lower stem sections. This is logical given that more structural support is required in these lower sections whereas the leaves and upper parts of the plant are more focussed towards photosynthesis. These results are consistent with those in the literature.

- Lignin is consistently at higher concentrations in the nodes than it is in the corresponding internode sections (with the difference being between 1 and 2%). This is also logical given the previously mentioned concept of structural support.

- Acid soluble lignin (ASL) follows an inverse relationship with Klason lignin (KL); it is present in greater quantities in the leaves and upper sections of the plant than it is in the lower stem sections.

- The glucose content follows similar trends to the KL content. It is lowest in the live leaf blades and lower in the upper stem sections than it is in the lower stem sections. However, in contrast to KL, its content is consistently greater in the internode section than it is in the corresponding node section.

- Table 9 also provides data for the hemicellulose to cellulose ratio (Hc:Cel). It is assumed that all of the glucose present came from cellulose and that hemicellulose is the sum of all other sugars. This ratio ranges from 0.42 for the X1T section to 0.74 for the K section and 0.76 for the X3N section. The ratio is 1.16 for the flowers sample showing that cellulose is not the major polysaccharide in this fraction.

- Ash content is higher in the leaf blades and upper stem sections and lowest in the lower parts of the stem. There is also consistently more ash in the nodes compared with the corresponding internode section. Ash and acid insoluble ash (AIA) contents are higher in the dead leaf fractions compared with the corresponding live leaf fractions, and the AIA also contributes a greater proportion of the total ash in these dead sections. The AIA:Ash ratio is also greater in the sheaths than the leaf blades for

both the dead and live leaves with the ratios for these sheaths being greater than for any other fraction.

- The extractives content is greatest in the live leaf blades as would be expected given that the leaves' primary role is for photosynthesis and the assimilation of primary metabolites (132). The live leaf sheaths also have large extractives contents. With the exception of sample X3N, the extractives content does not change greatly with stem height.

- The nitrogen content is greatest in the live leaf blades; expected as nitrogen is an important part of the photosynthetic pathway of C_4 plants (132). The nitrogen contents of the stem sections generally increase with plant height. Nitrogen is also present at higher than average concentrations in the flowers.

Table 9 also includes analytical data for the anatomical fractions of a much smaller plant. This plant was the same age as the taller plant and sampled, from the same stand, on December 4th 2007. The leaf fractions were 144.4% of the dry mass of the stem sections with most of the leaves being dead. Some important differences between this and the taller plant are listed below:

- Higher ash content in all sections.

- Lower stem lignin content than the X1 fraction of the 2+ m plant. The KL content is instead more similar to that of the X2 section of the taller plant. This is logical given that the stems of the smaller plant were much thinner and were required to give less structural support than the lower stem sections of taller plants.

- Glucose content in the stem is also lower.

- Xylose and ASL contents of the X1 sections that are greater than those for the X1 sections of the taller plant and more similar to the upper sections of that plant.

Table 9 provides a column for the total mass balance for the samples ("TOTAL"). This is the sum of the following contents: Extractives, ash, total sugars, KL, and ASL. AIA and AIR are not included because these are represented in the ash and KL concentrations. The nitrogen content is not included because it is possible that some of the nitrogen would end up in the KL. It can be seen the total mass closure for all samples is less than 100% and is significantly lower for the live leaf blade samples (where it is less than 90%) than it is for the other plant fractions. The remainder of the mass balance could come from uronic acids (which range between 1.01 and 1.96% of total mass for the 31 samples that were analysed), acetyl groups liberated from the acid hydrolysis of hemicellulose, and extractives components that are not soluble in 95% ethanol but will be present in the hydrolysate.

A hot water extraction step may be employed instead of or as a precursor to ethanol extraction. Given the amount of laboratory work involved in the extraction of samples this was not considered to be practical for all samples. However, towards the end of the research a

solvent controller was purchased for the automated extraction system in the Carbolea laboratory. This allowed for experiments to be made comparing ethanol extraction vs. water extraction vs. a sequential water then ethanol extraction for selected samples. Samples covering a variety of ethanol-soluble extractives contents were selected for this analysis and the results are provided in Table 10. A column shows the difference between the 95% ethanol soluble extractives and the total amount of ethanol extractives removed in the sequential extraction, and the final column in the Table expresses the extractives removed by ethanol extraction as a percentage of the total amount of extractives removed in the sequential extraction.

Table 10 shows that the extractives removed by ethanol extraction, for the samples analysed, accounted for between 46 and 77% of the extractives removed in the sequential extraction of the sample. This proportion tends to be higher for the lower stem section samples than for the upper stem section and leaf samples. Importantly, for the live leaf samples the difference between the extractives removed in ethanol extraction versus those removed in the sequential extraction is large (close to 10% for some samples). This difference will bring the total mass balances for these samples much closer to 100%.

Table 10: Amounts (% DM) of 95% ethanol-soluble extractives, hot-water-soluble extractives, and the extractives removed after first employing a water extraction and then an ethanol extraction. Values are % of the dry mass of the sample and the numbers in the brackets represent the standard deviation of duplicates (SDD). Diff = (water + ethanol extraction) – (ethanol extraction) and % ethanol is the percentages of water + ethanol extractives represented by the ethanol extraction.

Sample	Month	Variety	# Stem Sections	95% Ethanol Extractives (%)	Water Extractives (%)	Water + Ethanol Extr. (%)	Diff (%)	% Ethanol
Live Leaf Blade	Dec	Giganteus	2	9.64 (0.09)	14.98 (0.05)	18.83 (0.19)	9.19	51.19
Live Leaf Blade	Nov	Giganteus	3	9.24 (0.22)	12.14 (0.07)	16.54 (0.01)	7.3	55.86
Live Leaf Blade	Oct	Sinensis	2	9.49 (0.02)	13.37 (0.16)	17.43 (0.14)	7.94	54.45
Live Leaf Blade	Oct	Sinensis	2	11.42 (0.20)	15.89 (0.03)	20.77 (0.34)	9.35	54.98
Live Leaf Sheath	Oct	Sinensis	2	7.46 (0.37)	9.96 (0.18)	11.56 (0.16)	4.1	64.53
Dead Leaf Blade	Jan	Giganteus	2	5.10 (0.05)	7.02 (0.09)	10.20 (0.16)	5.1	50.00
Dead Leaf Blade	Nov	Giganteus	3	9.45 (0.24)	13.14 (0.55)	17.13 (0.28)	7.68	55.17
Dead leaf sheaths	Nov	Giganteus	3	6.12 (0.24)	7.76 (0.11)	12.01 (0.09)	5.89	50.96
Dead Leaf Sheath	Jan	Giganteus	3	2.21 (0.14)	2.47 (0.18)	4.80 (0.01)	2.59	46.04
X1 Node	Nov	Giganteus	3	6.38 (0.04)	8.49 (0.19)	10.56 (0.09)	4.18	60.42
X1 Node	Feb	Giganteus	3	8.31 (0.16)	11.95 (0.26)	14.47 (0.32)	6.16	57.43
X1 Internode	Jan	Giganteus	3	12.60 (0.39)	14.33 (0.01)	16.27 (0.07)	3.67	77.44
X3 Internode	April	Giganteus	3	4.64 (0.11)	7.98 (0.07)	9.61 (0.02)	4.97	48.28
WP (All Plant)	Oct	Giganteus	2	12.68 (0.16)	15.14 (0.12)	17.53 (0.12)	4.85	72.33
WP (1st metre)	Feb	Giganteus	3	4.14 (0.21)	4.10 (0.10)	6.34 (0.11)	2.2	65.30

4.2.4 Variations in Lignocellulosic Composition Between Varieties

In addition to plants of the Miscanthus *x giganteus* variety some plants of the Miscanthus *x sinensis* variety were also collected and analysed as were 6 plants of different experimental varieties that were growing in a plot at the Teagasc Oak Park Research Centre in Carlow. These plants were much shorter than Miscanthus *x giganteus*. This is normal, in regions where Miscanthus *x giganteus* grows well and Miscanthus *x sinensis* is less productive (133). *Sinensis* plants can have an advantage over *giganteus* plants in cold climates, however, as this variety is more cold resistant, particularly in the establishment phase. It was found that sinensis, and the other varieties that were analysed, tended to have higher xylose and arabinose contents than the Miscanthus *x giganteus* plants sampled but lower glucan contents. Hence, the hemicellulose to cellulose ratio tended to be higher in these samples.

A total of 16 samples of non-giganteus varieties that were harvested in the month of March (i.e. mostly composed of stem material) were also supplied to the Carbolea laboratories from a plant breeding station in Germany. The analytical data obtained for these samples were compared with the average whole-plant composition of 4 Miscanthus x *giganteus* plants of three-stem-sections that were sampled by in Ireland in March (2 from Shanagolden site and 2 from the Carlow site). It was found that the xylose contents of the German samples were greater than for the *giganteus* plants. Indeed, the minimum xylose-content German sample had a xylose content that was greater than the maximum xylose content *giganteus* sample. The same is true for the arabinose content of the samples whilst the opposite is the case for the Klason lignin content (it is higher in the *giganteus* samples). Also, on average, the glucose contents of the German samples are lower than that of the *giganteus* samples. The net effect is that the hemicellulose to cellulose ratio increases from an average of 49% for the *giganteus* samples to an average of 59% for the German samples (ranging from 55 to 61%). This is a 20.4% increase in relative terms. The average total sugars content of these German samples is 1.84% greater than the average content for the *giganteus* samples. The effects that these changes in the relative proportions of carbohydrates would have on the yields in biorefining technologies would depend on the relative efficiencies of those processes (see Section 4.2.7). For example, Technology E can achieve similar yields of ethanol from pentose and hexose sugars whilst technology C yields substantially less ethanol per tonne of pentose sugars than it does per tonne of hexose sugars. Using the average data for the German and *giganteus* samples, the German samples would yield an extra 10 litres of ethanol per dry tonne of Feedstock using technology E, but only an extra 3 litres per tonne using Technology C.

4.2.5 Variations in Harvestable Biomass over the Harvest Window

Section 4.2.2 detailed the sampling protocol that took place, between the months of October 2007 and April 2008 over 7 Miscanthus stands. Section 4.2.2 also provides details for these sites and Figure 12 shows when each plant was sampled from each location. The plants were collected for two reasons:

1. To examine how the relative mass proportions of the leaves and stems changes over the harvest window; and

2. To provide samples of varying physiochemical compositions in order to expand the concentration ranges and spectral variation of samples for NIRS calibrations.

In order to satisfy the second requirement, some plants that were different from the majority of the plants in the stand were selected. This selection was primarily based on plant height. Using the example of the Shanagolden site, the majority of the plants were over 2 m in height meaning that they had three stem sections (X1, X2, X3); however, in order to increase spectral variability some smaller plants (e.g. those with only one or two internode sections) were sampled from the field. These smaller plants typically were on the boundaries of the plantation and appeared similar to the typical plants seen in the first-year plantations (Langton and Clonmel).

As described in Section 4.2.2, all the standing biomass of one plant was always sampled. The small plants had a much lower total stem mass than the taller plants that were selected from the same site. It is known that the proportion of leaves will fall over time after senescence; hence observing differences between plants of differing total stem mass can only occur in a relatively short window where the effects of leaf loss over time do not become dominant.

Figure 13 plots the total leaves weight, expressed as a percentage of the total stem weight, for all plants collected from stands in the month of January 2008. Total dry leaf mass is defined as the sum of the dry weights of dead leaf blades, dead leaf sheaths, live leaf blades, and live leaf sheaths, whilst total dry stem mass is defined as the sum of the dry weights of all the internode and node sections for that plant. Figure 13 shows that the percent leaves is related to the total stem weight of the plant. A 3rd order polynomial regression curve is fitted to the datapoints, providing an R^2 of 0.936. Hence, a more productive plant will grow taller and the relative mass proportion of leaves will fall as the stems increase in diameter and lignify.

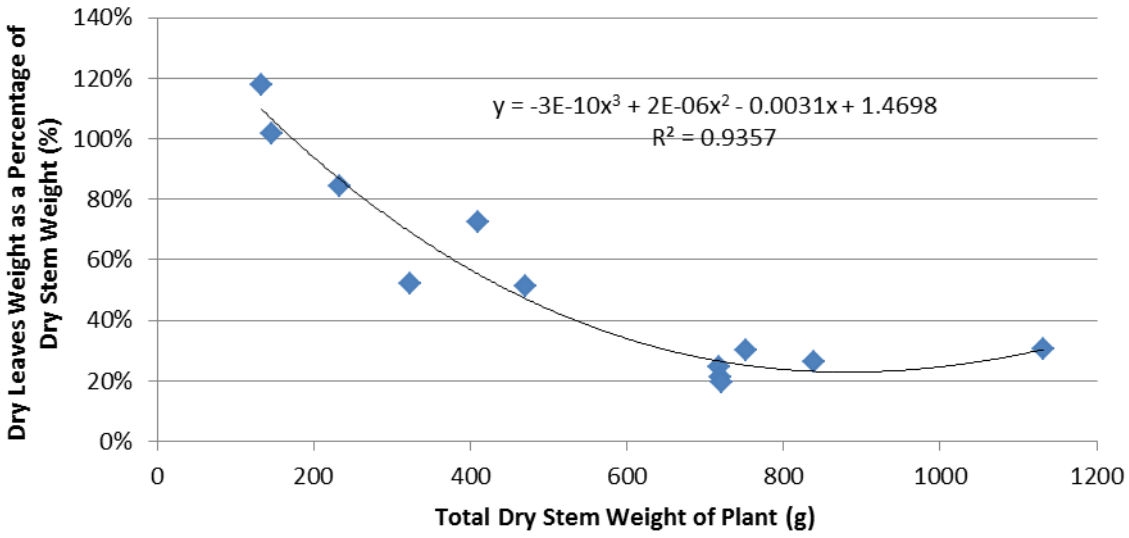


Figure 13: The amount of total leaves (leaf blades plus leaf sheaths), expressed as a percentage of total dry stem weight, for plants of varying total dry stem weights.

Figure 13 shows that an experiment cannot examine the effects of harvest time on the stem/leaves proportions if the heights/weights of the plants are also a varying factor. Therefore, for this examination only plants that had the same number of stem sections were compared over the harvest window. Four sites will be examined below:

Shanagolden Site

This stand was in its second year of production and the majority of the plants sampled had three stem sections. Figure 14 plots the variation in the percent leaves over time for such plants. The first two plants were sampled on November 15th 2007. There was a significant amount of leaves on both these plants, with an average of 17% of the total dry mass of both plants being either live leaf blades or live leaf sheaths, and a further 17% of the total dry mass being either dead leaf blades or dead leaf sheaths. When the stand was visited one month later the proportion of live leaves had fallen substantially to an average of 3.3% of the total dry mass of the plant. Over this month the leaves had lost their colour, becoming "dead" according to the classification outlined in Section 4.2.2. However, it was noticed that leaf fall was not substantial at this point and most of the leaves were still present on the plant (the amount of dead leaf fractions, expressed as a percentage of total plant mass, on both plants rose to an average of 28%, from 17% the previous month).

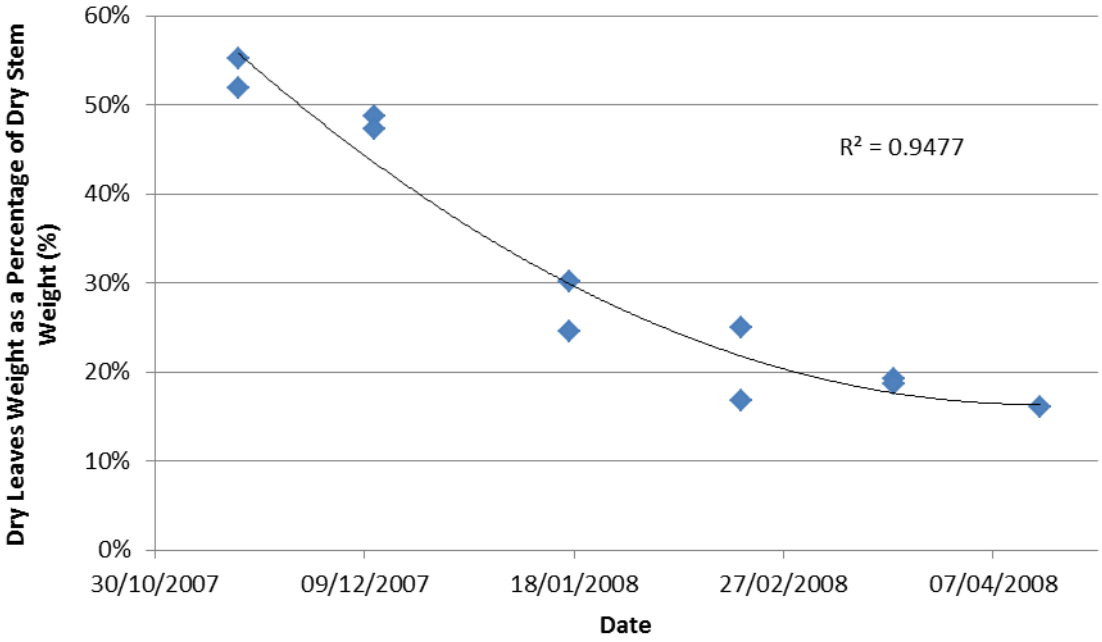


Figure 14: The amount of total leaves (leaf blades plus leaf sheaths), expressed as a percentage of total dry stem weight, for plants with at least three stem sections that were sampled from the Shanagolden site.

When the stand was again visited in January 2008 it was readily apparent that many of the leaves had fallen from the plant. Two plants (of three stem sections) were sampled at this time and these had no live leaves/sheaths present and the contribution that dead leaf fractions made

to the total mass balance of the plants fell to an average of 21%. Furthermore, the majority of the dead leaf mass was provided by the sheaths rather than the leaf blades. These sheaths are encased around the stem and less prone to breakage/displacement from the stem than the leaf blades.

Over the subsequent months the relative proportion of total dead leaves continued to fall but at a substantially lower rate. The principal reason for the continued reduction was the continued fall over time of the leaf blades that still remained on the plant. The last plant from this stand was sampled on April 16th 2008. The amount of dead leaf blades that were still present on the plant at this point only contributed 0.84% of the total dry mass of the plant. In contrast, the proportion of total plant mass provided by the dead sheaths remained relatively constant over time. This is illustrated in Figure 15; the values are lower at the first sample date since fewer sheaths could be characterised as "dead" at this time.

Typically in Ireland Miscanthus stands are harvested in March or April. If the plant sampled on April 16th 2008 is used to represent the stand at harvest then it can be assumed that the leaf fractions of the crop comprise 13.8% of the total mass balance, i.e. their mass is 16% of the total stem mass. The average percent leaves of the two plants collected in November 2007 was 53.0% of stem mass or 34.7% of total plant mass. If it is assumed that the dry stem mass is constant over the harvest window, then the extra leaf material present in the early harvest represent a potential extra 31.9% in total dry matter yield. With an assumed April yield of 12 dry tonnes per hectare, this would translate to a November yield of 15.8 dry tonnes per hectare.

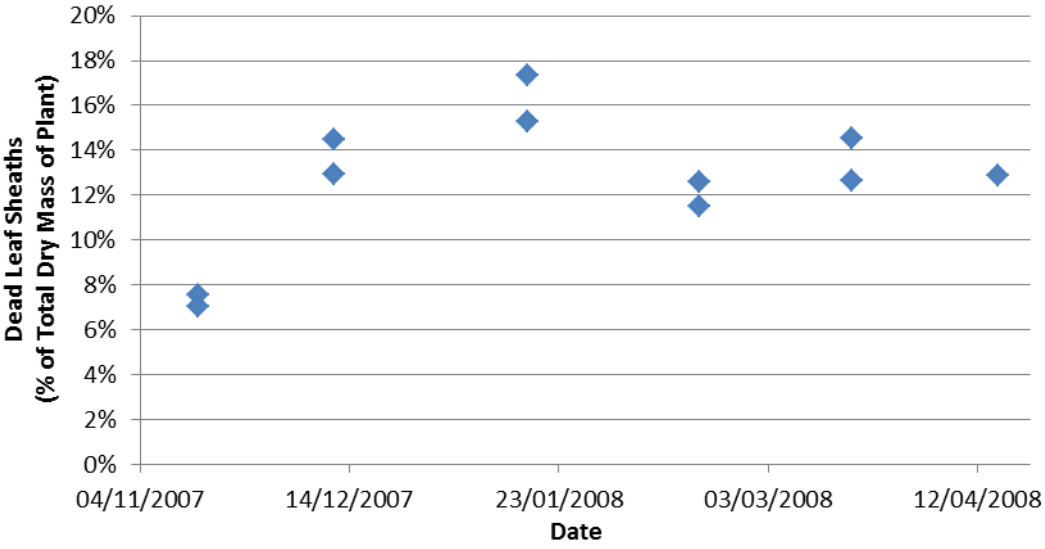


Figure 15: The amount of dead leaf sheaths, expressed as a percentage of the total dry weight of the plant, for plants with at least three stem sections that were sampled from the Shanagolden site.

Adare-H Site

This stand was in its third year of production. All of the plants sampled from this location had three stem sections. Figure 16 plots the variation in the percent leaves over time. The plot is similar to that seen for the 3-stem-section plants at Shanagolden, Figure 14. A third order polynomial regression line is fitted to the datapoints, the R^2 value here is 0.9698. The last samples were collected on April 13th 2008, and the leaf fractions were on average 13.0% of the total stem mass, compared with the leaves being 56.4% of total stem mass for the first sample (collected on November 27th 2007). The relative advantage of an early harvest in this instance is an increase in total dry matter yield of 38.4%. Therefore, if the late harvest provides a yield of 12 tonnes per hectare the early harvest would provide a yield of 16.6 dry tonnes per hectare.

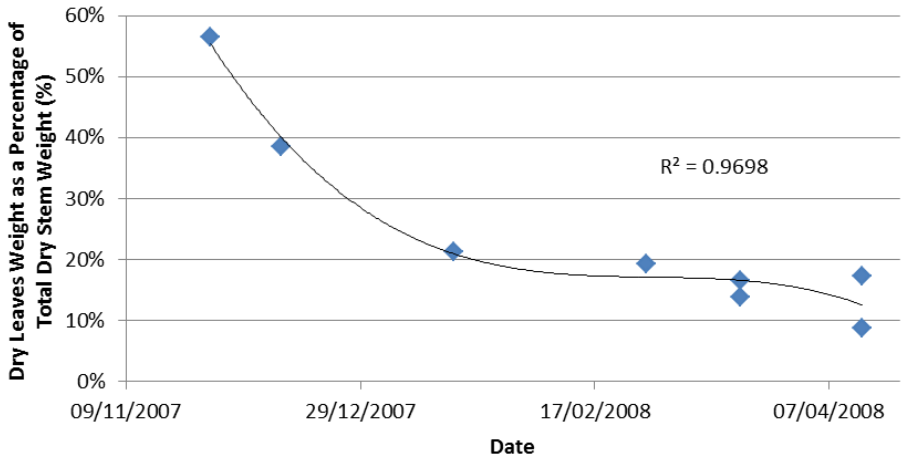


Figure 16: The amount of total leaves (leaf blades plus leaf sheaths), expressed as a percentage of total dry stem weight, for plants with at least three stem sections that were sampled from the Adare-H site.

Adare-C Site

This stand was in its second year of production and the majority of the plants growing in this plantation were over 2 m in height. Figure 17 presents the variation in the percent leaves over time for plants of three stems sections. The percent leaves for two plants that only had two stem sections, collected on November 28th 2007, are also plotted. The second order polynomial regression line is only fitted to the three-stem-section plants datapoints. This stand was harvested earlier than the Adare-H and Shanagolden stands meaning that the last samples were collected on February 28th 2008. This is the probable reason why the percent leaves for the latest datapoint (17.0%) is greater than the percent leaves for the last datapoints for three-stem-section plants from other sites.

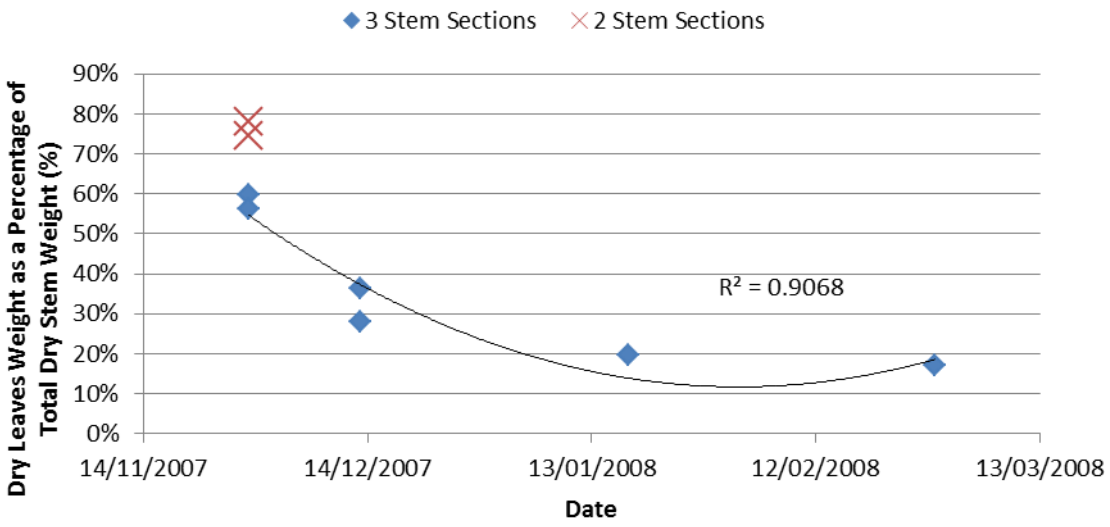


Figure 17: The amount of total leaves (leaf blades plus leaf sheaths), expressed as a percentage of total dry stem weight, for plants with three stem sections (diamond) and two stem sections (crosses), that were sampled from the Adare-C site.

Carlow-F and Carlow-G Sites

These sites had Miscanthus plants in their 13th year of growth. The sites had been established and maintained in the same way but were separated by a field of another crop. The results for both sites have been combined and are presented, for plants with three stem sections, in Figure 18. Plants were sampled from these sites on the 12th and 13th of October 2007, an earlier sampling date than for the other locations. The datapoints from the two plants that were sampled on these dates provide extra interesting information about the dynamics seen in leaf:stem proportions in Miscanthus stands following senescence. There are only minor differences seen in the percent leaves between 13/10/07 and 3/12/07. That indicates, as also suggested by the data for the plants collected from the Shanagolden site over the first two dates, that leaves are not lost to a significant degree over this period. As with the Shanagolden site, however, the leaves did change in colour over this period meaning that the dead leaf blades were more abundant than the live leaf blades in the December samples. A 5th order polynomial regression line fits the datapoints reasonably well and provides an $R^2$of 0.9825.

The last samples were collected on April 7th 2008 and the leaf fractions were on average 15.0% of the total stem mass for these samples, compared with the leaves being an average of 53.4% of total stem mass for the first two samples. The relative advantage of an early harvest in this instance is an increase in total dry matter yield of 33.4%. Hence, if the late harvest provides a yield of 12 tonnes per hectare the early harvest would provide a yield of 16.0 tonnes per hectare.

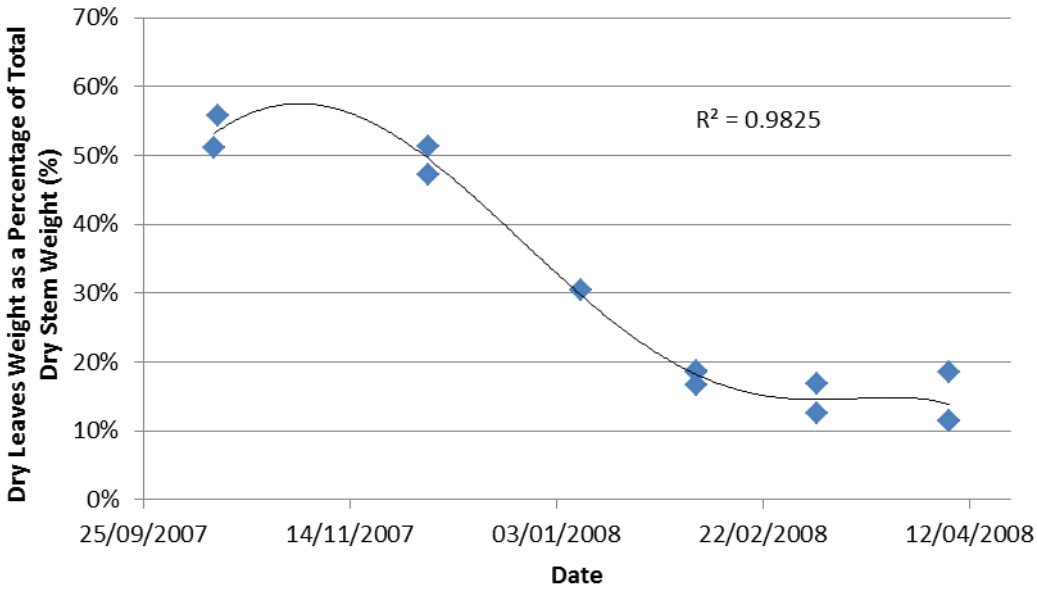


Figure 18: The amount of total leaves (leaf blades plus leaf sheaths), expressed as a percentage of total dry stem weight for plants with three stem sections that were sampled from the Carlow-F and Carlow-G sites.

Combination of Data Across All Sites

Figure 19 combines all of the leaf data of the three-stem sections plants for the 4 sites. A polynomial regression curve is fitted to this plot and, while the R^2 value is less than for the individual sites, it is reasonable considering that Figure 19 covers stands of differing ages.

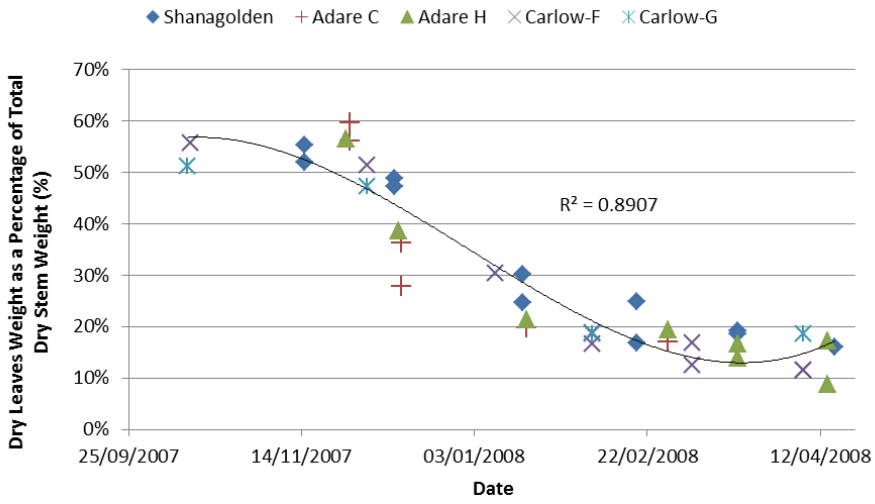


Figure 19: The amount of total leaves (leaf blades plus leaf sheaths), expressed as a percentage of total dry stem weight for plants with three stem sections for the Shanagolden, Adare-C, Adare-H, Carlow-F, and Carlow-G sites.

4.2.6 Variations in Lignocellulosic Composition over the Harvest Window

Examinations were conducted to see if there were changes in the chemical composition of the samples over the harvest window. These tests were done on certain plant fractions and on the plant as a whole (which involved the weighted average of the compositions of each fraction). Where wet-chemical data were available these were used, but in their absence wet NIRS models (7) were used to predict the composition of each sample. Table 11 presents the R^2 and Pearson correlation coefficient (r) values indicating the relationship (or absence of a relationship) between composition and date for whole plant samples at the Carlow, Adare-H, Adare-C and Shanagolden sites. Since the plants at the Adare-C and Shanagolden site were of the same stand age their data are also combined in Table 11. For each of these sites only the plants of over 2m height (i.e. 3 stem sections) were used for comparison. Table 11 also presents correlation coefficient values for the samples grouped according to their number of stem sections. The groups for 2 and one stem section plants include samples from the Langton and Carlow sites as well as samples from Carlow, Adare, and Shanagolden. The value for r was tested to see if it was significant at p = 0.05, using the t-test value for correlation and determining from this the p value using the 2-tailed t-distribution with (n-2) degrees of freedom. If this value was less than 0.05 then the correlation can be considered to be statistically significant at the 95% confidence interval. Such statistically significant correlations are highlighted in bold in Table 11.

Some of the important observations regarding these data are discussed below:

- For most groups there is a statistically significant (α = 0.05) negative correlation between extractives content and later dates for sample collection. This can be explained by the decrease in the relative proportion of leaves, a fraction that had higher extractives content than the stems.

- There are also statistically significant negative correlations for ash, arabinose, galactose, rhamnose, ASL, AIA, and nitrogen. These can also be explained by the higher concentrations of these constituents in the leaves, particularly the live leaf blades.

- In contrast, there are statistically significant positive correlations between constituent value and harvest date for KL (Figure 20 for the Carlow sites), AIR, and total sugars. This is also rational given that the concentrations of these constituents is greater in the stems whose contribution to total mass balance increase over time.

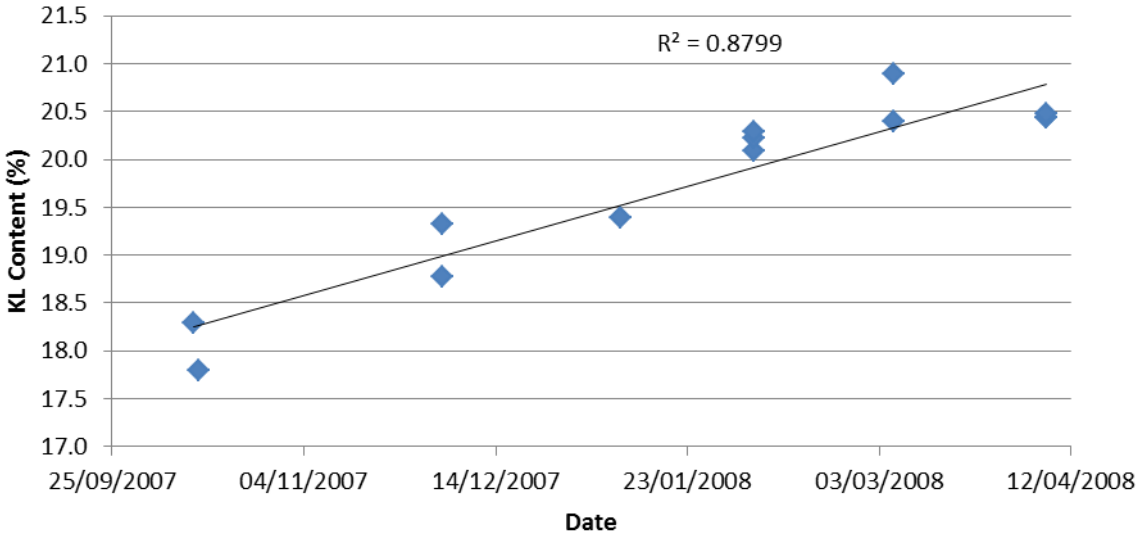


Figure 20: Relationship between Klason lignin (KL) content of whole-plant samples and sample collection date for the samples of 3-stem-section plants collected from the Carlow sites.

Table 11: R^2 and Pearson correlation coefficients for the relationship between constituent concentration and date of sample collection for Miscanthus whole-plants according to either plant location or whether the plants were less than 1 m high (one stem section), between 1 and 2 m high (2-stem section), or over 2 m high (3 stem-section).

	Carlow		**Shanagolden**		**Adare-H**		**Adare-C**		**Adare-C and Shanagolden**		**All 3-Stem Section Plants**		**All 2-Stem Section Plants**		**All 1-Stem Section Plants**	
No. of Samples	13		11		5		6		17		35		22		9	
Constituent	R^2	r	R^2	r	R^2	r	R^2	R	R^2	R	R^2	r	R^2	r	R^2	r
Extractives	0.475	-0.689	0.504	-0.710	0.348	-0.590	0.001	-0.028	0.290	-0.538	0.238	-0.488	0.517	-0.719	0.323	-0.569
Ash	0.382	-0.618	0.555	-0.745	0.575	-0.758	0.322	-0.567	0.543	-0.737	0.417	-0.645	0.554	-0.745	0.318	-0.564
Arabinose	0.750	-0.866	0.670	-0.818	0.340	-0.583	0.185	-0.430	0.606	-0.779	0.623	-0.789	0.451	-0.672	0.206	-0.454
Galactose	0.640	-0.800	0.677	-0.823	0.975	-0.988	0.221	0.470	0.423	-0.651	0.397	-0.630	0.447	-0.668	0.312	-0.558
Rhamnose	0.660	-0.813	0.227	-0.477	0.825	-0.908	0.451	-0.671	0.202	-0.449	0.326	-0.571	0.465	-0.682	0.247	-0.497
Glucose	0.603	0.776	0.757	0.870	0.733	0.856	0.335	0.579	0.701	0.837	0.542	0.737	0.650	0.806	0.490	0.700
Xylose	0.004	0.067	0.153	0.391	0.719	0.848	0.067	-0.258	0.155	0.394	0.065	0.255	0.270	0.519	0.292	0.540
Mannose	0.004	-0.059	0.196	-0.443	0.734	-0.857	0.015	0.122	0.164	-0.405	0.084	-0.290	0.066	-0.258	0.002	-0.044
Total Sugars	0.262	0.512	0.471	0.686	0.902	0.950	0.063	0.250	0.436	0.660	0.314	0.560	0.678	0.823	0.642	0.801
AIR	0.641	0.801	0.770	0.878	0.908	0.953	0.563	0.750	0.660	0.813	0.574	0.757	0.467	0.683	0.335	0.579
Klason Lignin	0.880	0.938	0.793	0.891	0.839	0.916	0.156	0.395	0.665	0.815	0.645	0.803	0.522	0.722	0.501	0.708
ASL	0.675	-0.821	0.771	-0.878	0.856	-0.925	0.769	-0.877	0.770	-0.877	0.626	-0.791	0.587	-0.766	0.711	-0.843
AIA	0.158	-0.397	0.474	-0.688	0.536	-0.732	0.016	-0.127	0.396	-0.630	0.271	-0.521	0.451	-0.671	0.062	-0.249
Nitrogen	0.138	-0.371	0.501	-0.708	0.662	-0.814	0.025	-0.159	0.456	-0.675	0.226	-0.476	0.336	-0.579	0.697	-0.835

Statistical Tests

Table 12: Results from ANOVA tests to determine if there is a significant difference in the constituent value means of the "Early" and "Late" WP samples.

Constituent	Test	Degrees of Freedom	F Value	Significance of Difference
Extractives	ANOVA	21	11.259	P < 0.01
Ash	ANOVA	21	17.258	P < 0.01
Arabinose	ANOVA	21	62.728	P < 0.01
Galactose	Welch	9.650	26.936	P <0.01
Rhamnose	ANOVA	21	18.924	P < 0.01
Glucose	Welch	9.948	29.221	P <0.01
Xylose	ANOVA	21	3.403	
Mannose	ANOVA	21	4.838	P < 0.05
Klason Lignin	ANOVA	21	33.518	P < 0.01
Acid Soluble Lignin	ANOVA	21	37.231	P < 0.01
Nitrogen	ANOVA	21	6.355	P < 0.05
Hemicellulose to cellulose ratio	ANOVA	21	26.835	P < 0.01
Leaves content (as %age of dry stem weight)	Welch	16.261	82.399	P <0.01

Using SPSS Version 18, One Way ANOVA was used to test for significant differences in the means of various constituents between whole plants sampled in the "Early" harvest window (October, November, December) and whole plants selected in the "Late" harvest window (March, April). In all cases the means were compared for the samples of Miscanthus *x giganteus* plants with three stem sections and the whole plant composition was determined as the weighted average of the compositions of the different fractions (leaves, nodes, internodes etc.). Table 12 summarises the results of these tests. It shows whether an ANOVA test or a Welch F test was used (the former being used under conditions where the variances of the groups were the same) and provides the F value and degrees of freedom for each of these tests. It also specifies the significance level of the difference with either P < 0.01, P < 0.05, or no value (indicating that the difference between the means was not significant). Figure 21 plots the means, of the Early and Late groups, for the glucose, xylose, Klason lignin, leaves to stems percentages, and hemicellulose to cellulose percentages whilst Figure 22 has the corresponding plots for the extractives, ash, arabinose, galactose, rhamnose, mannose, ASL, and nitrogen contents.

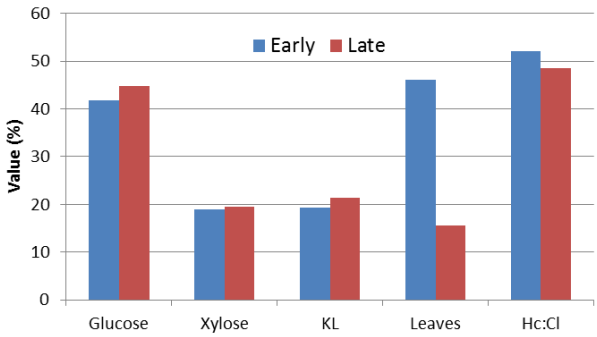


Figure 21: Comparison of the means for "Early" and "Late" harvest WP samples. KL = Klason lignin; Leaves = leaves weight (as a percentage of stem weight); Hc:Cl = Hemicellulose content as a percentage of cellulose content.

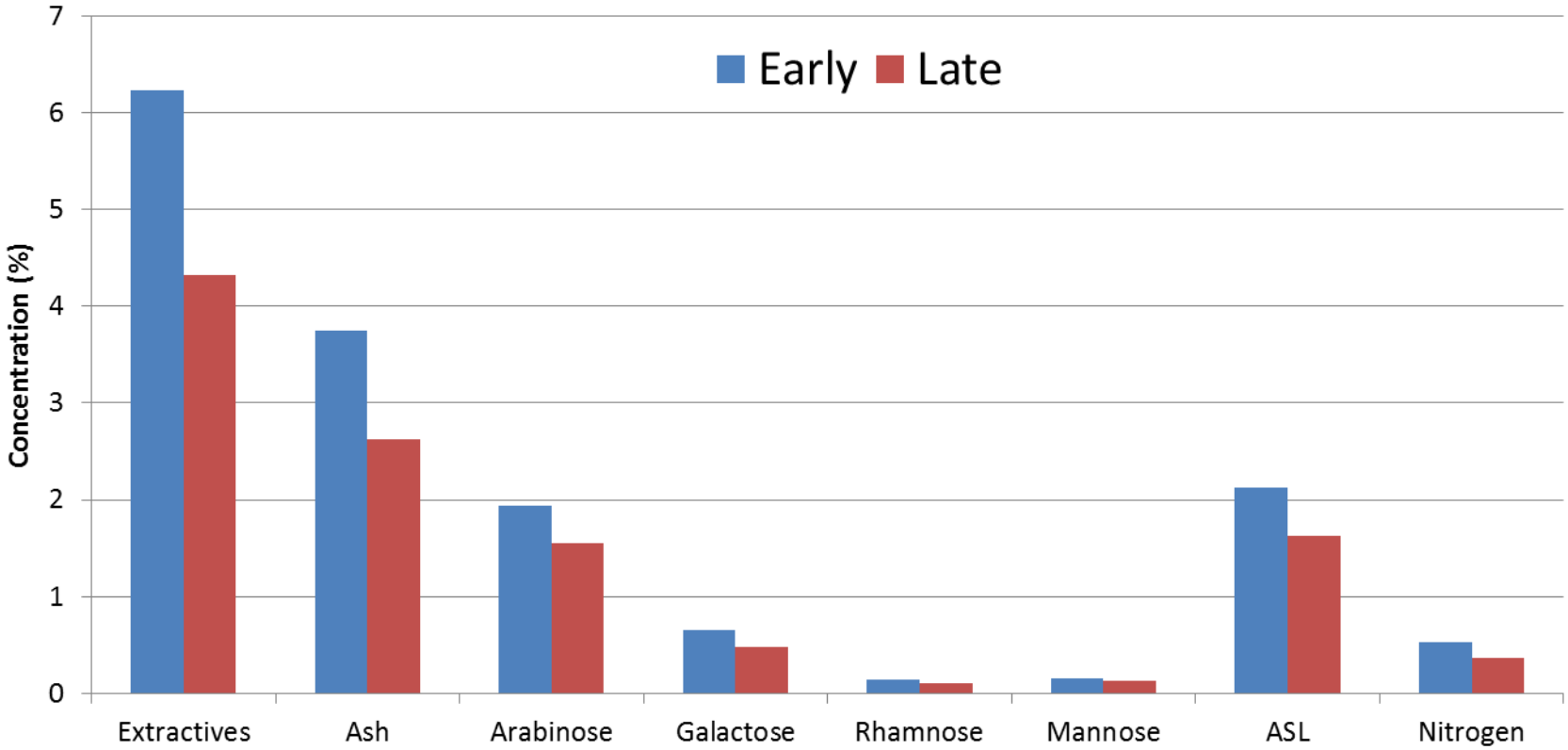


Figure 22: Comparison of the means for "Early" and "Late" harvest WP samples. All samples were of Miscanthus x giganteus samples of a height greater than 2m. ASL = acid soluble lignin.

Changes within Individual Plant Fractions

Many of the trends seen in Table 11 and Table 12 can be explained by the changes in the relative proportions of stems and leaves over time. Whether or not the compositions of separate plant fractions change over time was also examined. The correlation statistics, using the same plants and groupings as in Table 11, are presented for the dead leaf blades in Table 13, for the dead leaf sheaths in Table 14, and for the whole-stems (the weighted average of all internode and node sections of the plant) in Table 15. Some observations about these data are summarised below:

- For all groups there is a statistically significant positive correlation between sample collection date and the galactose content of the dead leaf blades. This was confirmed in an ANOVA that compared the galactose contents for the dead leaf blades between samples collected in an "Early" harvest and those in a "Late" harvest. Levene's test resulted in the rejection of the null hypothesis that the variances of the groups are the same so the Welch F value was used. It was found that there was a significant effect of harvest period $F(1,17.529) = 74.088$, $P < 0.01$.

- For all groups, except Adare-H, there is a statistically significant positive correlation between sample collection date and the mannose content of the dead leaf blades. This was also confirmed in an Early/Late harvest AVOVA; $F(1,40) = 71.320$, $P < 0.01$.

- These trends may not necessarily be related to chemical changes in these leaf blades over time, but may instead be related to the types of leaves that stay on the plant for longer periods and those that fall earlier.

- Most of the other relationships seen for the dead leaf blades are inconsistent between locations and groups.

- There are no consistent strong correlations between harvest date and constituent concentration for the dead leaf sheath samples.

- There are statistically significant positive correlations between harvest date and KL and AIR concentrations for the whole-stems of 3-stem-section and 2-stem-section plants. The Pearson correlation coefficient values for the one-stem-section plants are similar but not statistically significant (at $\alpha = 0.05$) due to the limited number of samples of these plants. These observations were explored with ANOVA tests comparing Early/Late harvests and are summarised in Table 16 which shows that there are significant differences ($P < 0.05$) for the 2-stem section and 3-stem section plants. This relationship could exist because KL is required for structural support and stems with lower contents are likely to be more prone to lodging (only the standing stems were sampled).

Table 13: R^2 and pearson correlation coefficients for the relationship between constituent concentration and date of sample collection for Miscanthus dead leaf blades according to either plant location or whether the plants were less than 1 m high (one stem section), between 1 and 2 m high (2-stem section), or over 2 m high (3 stem-section). All of the plants used to calculate these values for the Carlow, Shanadolden and Adare sites had three stem sections.

	Carlow		**Shanagolden**		**Adare-H**		**Adare-C**		**Adare-C and Shanagolden**		**All 3-Stem Section Plants**		**All 2-Stem Section Plants**		**All 1-Stem Section Plants**	
No. of Samples	13		11		5		6		17		35		22		9	
Constituent	R^2	r	R^2	r	R^2	r	R^2	r	R^2	r	R^2	r	R^2	r	R^2	r
Extractives	0.349	0.591	0.294	-0.542	0.457	-0.676	0.516	-0.719	0.364	-0.603	0.001	-0.035	0.089	-0.298	0.143	-0.378
Ash	0.321	-0.566	0.165	-0.406	0.640	0.800	0.070	-0.265	0.041	-0.202	0.055	-0.235	0.171	-0.414	0.097	0.311
Arabinose	0.468	0.684	0.108	0.329	0.323	0.568	0.330	0.575	0.117	0.342	0.229	0.479	0.084	0.289	0.089	0.298
Galactose	0.923	0.961	0.790	0.889	0.885	0.941	0.840	0.916	0.747	0.864	0.799	0.894	0.673	0.821	0.719	0.848
Rhamnose	0.571	-0.756	0.368	-0.606	0.756	0.870	0.369	-0.608	0.146	-0.382	0.118	-0.344	0.254	-0.504	0.576	0.759
Glucose	0.563	-0.750	0.002	0.049	0.037	-0.192	0.060	-0.245	0.002	0.047	0.198	-0.445	0.087	0.295	0.143	-0.379
Xylose	0.052	-0.228	0.000	0.018	0.161	-0.402	0.182	-0.426	0.002	-0.041	0.050	-0.225	0.170	0.412	0.537	-0.733
Mannose	0.701	0.837	0.511	0.715	0.699	0.836	0.804	0.897	0.510	0.714	0.440	0.664	0.323	0.568	0.803	0.896
Total Sugars	0.208	-0.456	0.107	0.326	0.001	0.034	0.007	0.081	0.087	0.295	0.029	-0.172	0.217	0.466	0.121	-0.348
AIR	0.261	-0.511	0.238	0.488	0.346	0.588	0.214	0.463	0.156	0.395	0.003	-0.058	0.022	-0.148	0.307	0.554
Klason Lignin	0.308	-0.555	0.104	0.322	0.272	0.522	0.122	0.350	0.054	0.231	0.027	-0.163	0.001	0.025	0.006	0.077
ASL	0.709	0.842	0.431	-0.656	0.674	-0.821	0.044	0.210	0.239	-0.489	0.002	-0.045	0.087	-0.294	0.010	-0.098
AIA	0.111	-0.333	0.305	0.552	0.607	0.779	0.124	0.353	0.207	0.455	0.012	0.110	0.063	-0.251	0.130	0.360
N	0.906	0.952	0.209	0.457	0.692	-0.832	0.446	0.668	0.043	0.206	0.219	0.468	0.011	-0.103	0.078	0.279

Table 14: R^2 and Pearson correlation coefficients for the relationship between constituent concentration and date of sample collection for Miscanthus dead leaf sheaths according to either plant location or whether the plants were less than 1m high (one stem section), between 1 and 2 m high (2-stem section), or over 2m high (3 stem-section). All of the plants used to calculate these values for the Carlow, Shanadolden and Adare sites had three stem sections.

	Carlow		**Shanagolden**		**Adare-H**		**Adare-C**		**Adare-C and Shanagolden**		**All 3-Stem Section Plants**		**All 2-Stem Section Plants**		**All 1-Stem Section Plants**	
No. of Samples	13		11		5		6		17		35		22		9	
Constituent	R^2	r	R^2	r	R^2	r	R^2	r	R^2	r	R^2	r	R^2	r	R^2	r
Extractives	0.385	-0.620	0.766	-0.875	0.006	0.080	0.038	0.196	0.074	-0.271	0.130	-0.360	0.028	-0.168	0.110	-0.331
Ash	0.213	-0.461	0.420	-0.648	0.660	-0.813	0.079	0.281	0.293	-0.541	0.286	-0.535	0.168	-0.410	0.020	0.141
Arabinose	0.466	-0.682	0.105	-0.324	0.600	0.775	0.046	0.214	0.056	-0.238	0.027	-0.164	0.047	-0.217	0.020	0.142
Galactose	0.143	-0.378	0.382	-0.618	0.256	0.506	0.261	0.511	0.088	-0.297	0.022	-0.147	0.024	0.155	0.614	0.783
Rhamnose	0.031	-0.177	0.000	-0.005	0.909	0.953	0.051	-0.225	0.022	0.148	0.013	0.114	0.041	0.203	0.104	-0.323
Glucose	0.053	0.230	0.467	0.683	0.287	-0.535	0.725	-0.851	0.040	0.201	0.004	0.064	0.017	-0.130	0.014	0.119
Xylose	0.216	0.464	0.207	0.455	0.065	-0.254	0.000	-0.019	0.131	0.362	0.124	0.352	0.004	-0.067	0.007	-0.086
Mannose	0.289	0.538	0.132	-0.363	0.000	0.005	0.398	0.631	0.041	-0.202	0.006	0.079	0.127	0.356	0.270	0.520
Total Sugars	0.079	0.282	0.411	0.641	0.001	-0.029	0.337	-0.580	0.025	0.157	0.040	0.201	0.004	-0.064	0.091	0.301
AIR	0.118	0.343	0.045	0.211	0.069	-0.262	0.232	0.482	0.019	-0.136	0.006	0.075	0.044	0.209	0.003	0.059
Klason Lignin	0.146	0.382	0.367	0.606	0.007	-0.084	0.023	0.151	0.002	0.039	0.051	0.226	0.042	0.205	0.034	-0.185
ASL	0.071	0.266	0.276	-0.525	0.276	0.525	0.922	0.960	0.008	0.088	0.033	0.182	0.002	0.044	0.009	0.093
AIA	0.027	-0.164	0.343	-0.586	0.635	-0.797	0.002	0.048	0.289	-0.538	0.154	-0.392	0.126	-0.355	0.041	0.202
N	0.008	0.087	0.000	0.021	0.081	0.284	0.863	0.929	0.034	0.184	0.025	0.159	0.215	0.464	0.022	0.148

Table 15: R^2 and Pearson correlation coefficients for the relationship between constituent concentration and date of sample collection for Miscanthus stems according to either plant location or whether the plants were less than 1m high (one stem section), between 1 and 2 m high (2-stem section), or over 2m high (3 stem-section). All of the plants used to calculate these values for the Carlow, Shanadolden and Adare sites had three stem sections.

	Carlow		**Shanagolden**		**Adare-H**		**Adare-C**		**Adare-C and Shanagolden**		**All 3-Stem Section Plants**		**All 2-Stem Section Plants**		**All 1-Stem Section Plants**	
No. of Samples	13		11		5		6		17		35		22		9	
Constituent	R^2	r	R^2	r	R^2	r	R^2	r	R^2	r	R^2	r	R^2	r	R^2	r
Extractives	0.167	-0.409	0.273	-0.522	0.160	-0.400	0.004	-0.063	0.167	-0.409	0.109	-0.330	0.321	-0.567	0.072	-0.268
Ash	0.172	-0.414	0.098	-0.313	0.398	-0.631	0.025	0.158	0.053	-0.229	0.080	-0.282	0.384	-0.620	0.059	-0.243
Arabinose	0.081	0.285	0.040	-0.200	0.673	0.820	0.815	0.903	0.005	0.067	0.044	0.211	0.071	-0.267	0.001	0.027
Galactose	0.010	-0.102	0.311	-0.558	0.614	-0.783	0.661	0.813	0.087	-0.295	0.031	-0.175	0.257	-0.507	0.154	-0.392
Rhamnose	0.095	-0.309	0.090	0.300	0.880	-0.938	0.168	0.410	0.098	0.313	0.000	-0.020	0.108	-0.328	0.072	-0.268
Glucose	0.133	-0.365	0.218	0.467	0.157	0.396	0.122	-0.349	0.177	0.421	0.003	0.055	0.297	0.545	0.079	0.281
Xylose	0.000	-0.014	0.081	0.285	0.778	0.882	0.000	0.017	0.124	0.352	0.047	0.217	0.055	0.235	0.224	0.474
Mannose	0.106	0.326	0.021	-0.146	0.452	-0.672	0.128	0.357	0.006	-0.079	0.003	0.051	0.045	-0.211	0.004	0.061
Total Sugars	0.026	-0.160	0.079	0.281	0.549	0.741	0.013	-0.116	0.111	0.333	0.009	0.095	0.352	0.594	0.167	0.409
AIR	0.560	0.748	0.673	0.821	0.477	0.691	0.389	0.624	0.603	0.776	0.436	0.660	0.376	0.614	0.389	0.623
Klason Lignin	0.769	0.877	0.604	0.777	0.426	0.653	0.001	-0.023	0.435	0.659	0.359	0.599	0.357	0.598	0.391	0.625
ASL	0.114	0.337	0.185	-0.431	0.099	-0.315	0.073	0.270	0.144	-0.379	0.003	-0.052	0.172	-0.414	0.363	-0.602
AIA	0.059	-0.243	0.196	-0.443	0.318	-0.564	0.342	0.585	0.054	-0.233	0.064	-0.253	0.529	-0.728	0.040	0.201
N	0.004	0.062	0.074	-0.271	0.394	-0.628	0.113	0.336	0.075	-0.275	0.005	-0.068	0.070	-0.265	0.005	-0.073

Table 16: ANOVA tests to determine if there is a significant difference in the Klason lignin and acid insoluble residue (AIR) means of "Early" and "Late" whole stem samples for giganteus plants of differing heights. Note there was only one sample in the "Early" category for 1 m height plants.

Constituent	Plant Height	Mean for "Early"	Mean for "Late"	Test	Degrees of freedom	F Value	Significance of Difference
Klason Lignin	>2 m	20.25	21.72	Welch	11.916	15.885	P < 0.01
AIR	> 2 m	20.90	22.41	ANOVA	21	16.405	P < 0.01
KL	1-2 m	18.45	21.16	Welch	5.878	11.885	P < 0.05
AIR	1-2 m	19.34	21.83	Welch	6.215	13.225	P < 0.05
KL	< 1 m	17.62	20.21	ANOVA	4	6.949	
AIR	< 1 m	18.47	21.42	ANOVA	4	6.061	

4.2.7 Projected Biorefining Yields According to Time of Harvest

This section links the trends seen in total dry matter yield and the chemical composition of the crop available for harvest (at the time of sample collection) to potential yields from processing the harvested Miscanthus in several biorefining technologies. Six different hydrolysis technologies are examined; these are discussed in detail in an earlier paper (86), and will be summarised here:

(A) – Dilute acid hydrolysis of biomass in two plug-flow reactors (134). This can be considered to representative of a near-commercial dilute-acid hydrolysis facility.

(B) – Dilute acid hydrolysis of cellulose in a counter-current reactor with an uncatalysed steam hydrolysis pre-treatment (135, 136). This more efficient process (for cellulose hydrolysis) may be commercially viable in the future.

(C) – Concentrated acid hydrolysis of biomass (137). This technology, and the predicted yield, is similar to that employed by BlueFire Ethanol (138) which is planning to construct a commercial-scale biorefinery to produce ethanol from lignocellulosic wastes.

(D) – Enzymatic hydrolysis of biomass. Involves a dilute acid pre-treatment and separate fermentation of the monosaccharides from cellulose and hemicellulose (sequential hydrolysis and fermentation – SHF) (139). Cellulase enzymes are produced in a separate reactor to that for hydrolysis. This is the likely setup of the first commercial enzymatic hydrolysis facilities planned by companies such as Iogen.

(E) – Enzymatic hydrolysis and fermentation of biomass via consolidated bioprocessing (CBP) (136) with a liquid hot water pre-treatment step (140). Here hydrolysis of cellulose, fermentation of the sugars and production of cellulases all take place in one reactor and involve a single micro-organism. This process can be considered to potentially be the most efficient and economical enzymatic hydrolysis technology (141); however, it is currently not

sufficiently developed for commercialisation. There is substantial ongoing research, however, (142-144) and it is expected that such a process could be viable before 2020.

(F) – The DIBANET process which involves the dilute acid hydrolysis of lignocellulosic polysaccharides and subsequent dehydration of the products to levulinic acid and co-products (145, 146). Polysaccharide-derived hexoses yield levulinic acid (LA) and formic acid (FA) (50% LA and 20% FA by mass hexoses are assumed (146)). Hemicellulose-derived pentoses yield furfural (50% by mass (146)), which can be converted to LA (93% conversion by mass (147)). Here it is assumed that all furfural is converted to LA and that ethyl levulinate (EL) is then produced via esterifying LA with fuel-grade ethanol (with a yield of EL that is 95% of the theoretical maximum). EL can be used in regular diesel engines up to 20% (146). According to their molar masses, approximately 400 kg of ethanol is required per tonne of LA.

Technologies A to E produce ethanol, the following formulae are used to calculate the yield of ethanol according to the hexose and pentose contents of the feedstock and the efficiencies of the technology (86):

$$E_{cl} = \frac{1110^{a} \cdot 0.5111^{b}}{(0.789)^{c}} \frac{100 - Cl_{con}}{100} \frac{H_{cl}}{100} \frac{F_{gl}}{100}$$

$$E_{hc} = \frac{1136^{d} \cdot 0.5111^{b}}{(0.789)^{c}} \frac{H_{hc}}{100} \frac{F_{hc}}{100}$$

Where:

E_{cl} – litres ethanol per tonne of cellulose, dm^3/t;

E_{hc} – litres ethanol per tonne of hemicellulose, dm^3/t;

Cl_{con} – cellulose consumed by cellulases, %;

H_{cl} – hydrolysis efficiency for cellulose to glucose, %;

H_{hc} – Hydrolysis efficiency for hemicellulose to sugars, %;

F_{gl} – the fermentation efficiency of glucose;

F_{hc} – the fermentation efficiency of hemicellulosic sugars.

a – the mass yield of glucose per tonne of cellulose with 100% conversion efficiency is 1,110 kg due to the conversion from the polymeric to the monomeric form;

b – the theoretical maximum mass yield of ethanol via conventional fermentation (100% efficiency) is 51.11%;

c – the density of ethanol is 0.789 kg/ dm^3;

d – the mass yield of pentoses per tonne of pentose-sugars with 100% conversion efficiency is 1,136 kg due to the conversion from the polymeric to the monomeric form;

The data for the Shanagolden site was used to examine the variations in potential ethanol/levulinic acid yields over the harvest window. As described in Section 4.2.4, the average percent weight leaves (calculated in terms of the total stem mass) at the last date for sample collection is used as a baseline for an expected yield of 12 dry tonnes per hectare, and any changes in this percentage are used to change the expected total yield at that point in the harvest window (Figure 23). It is assumed that stem dry mass is constant over the window. These yields are then linked to the whole plant compositions determined from either wet chemical or NIR-predicted data (these are represented by the total hexose and pentose curves in Figure 23), in order to calculate the expected biorefinery yields per hectare, Figure 24. Only the data for 3-stem section plants (the modal class) are used.

Table 17 shows that Technology E has the highest yields of ethanol from both the pentose and hexose sugars. Correspondingly, this technology achieves the highest yields at any given point in the harvest window. These yields are greatest in the "Early" harvest scenario. Figure 23 shows that the pentose content is stable over the course of the harvest window while the glucose content rises. This represents an increase in the cellulose content of the standing stock of biomass over the harvest window. Figure 25 shows how these changes in the composition of the feedstock influence the yields of end-products per tonne of feedstock according to technologies A to F. So that technologies A to E can be compared with the DIBANET process (F) the end products are quantified in energy terms (GJ/tonne feedstock). For DIBANET, the mass proportion that LA contributes to EL is used to ascertain the energy value contribution provided by the LA produced from the biomass. Figure 25 shows an increase in yields per tonne for each technology over time. The net effect of this dynamic is that the slopes of the curves representing decreased ethanol/levulinic acid yields per hectare with a delayed harvest, Figure 24, are less than that of the curve for total biomass yield, Figure 23.

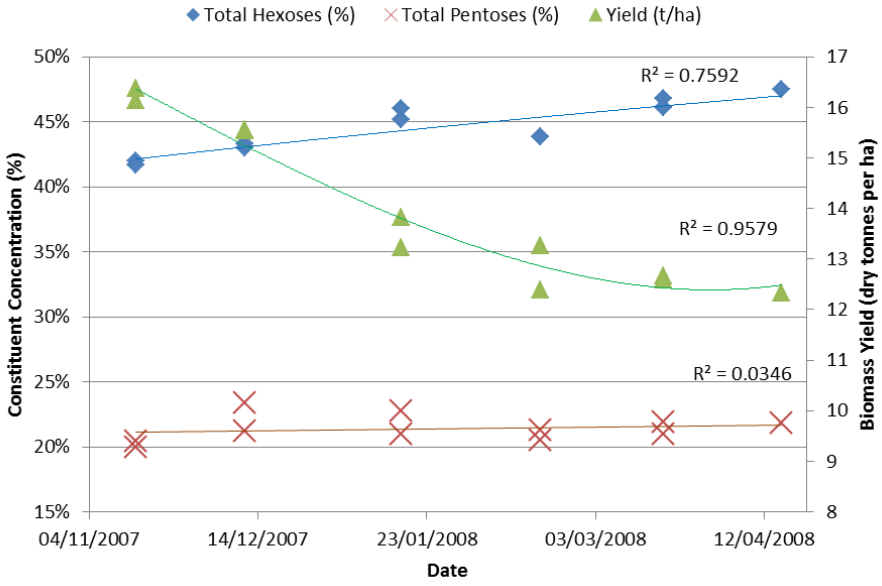


Figure 23: Miscanthus yield (dry tonnes per hectare), and the total hexose and pentose contents of the feedstock, at various points in the harvest window on the Shanagolden site.

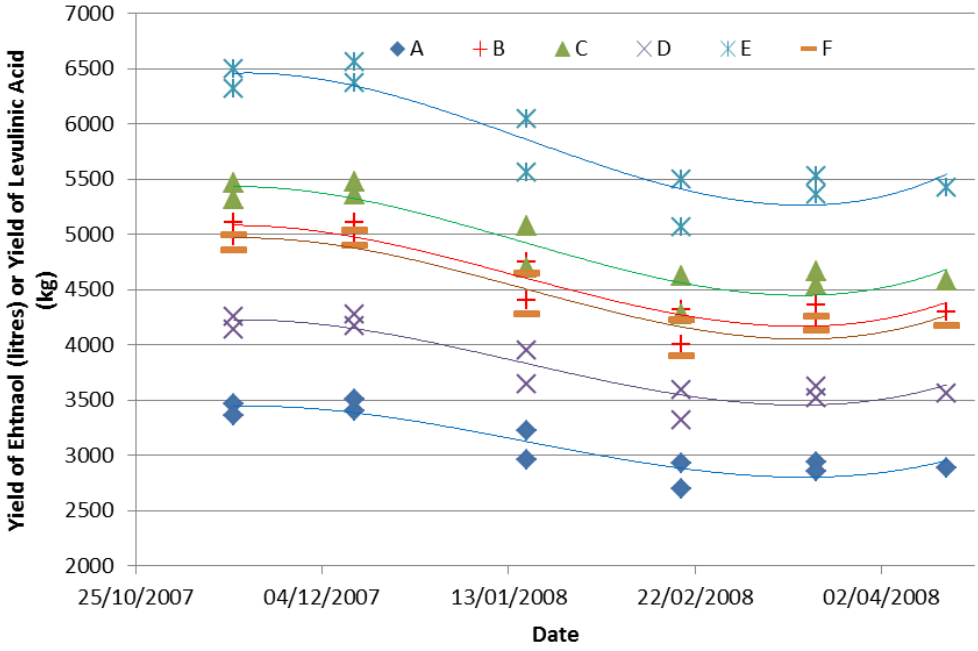


Figure 24: Yield of ethanol (litres per hectare) and levulinic acid (kg per hectare) from processing, using technologies A to F, the projected standing stock of biomass on the Shanagolden site at various points in the harvest window. A = near-term dilute acid hydrolysis process; B =advanced dilute acid hydrolysis process; C = near-term concentrated acid hydrolysis process; D = near-term enzymatic hydrolysis process; E = advanced enzymatic hydrolysis process; F = DIBANET process projections.

Figure 26 illustrates this point by using the example of the yields of LA from the DIBANET process. These are expressed in terms of a percentage increase in LA yield per hectare associated with earlier harvests, compared to that which would be experienced from harvesting the biomass at the latest point in the harvest window. It can be seen that a maximum improved yield of up to approximately 20% can be achieved with an early harvest. This is lower than the 31.9% increase in dry matter yield discussed in Section 4.2.4. Furthermore, there is a significantly lower change in the expected yield in the months of October and November and March and April than for the interim period. These two periods fit the concept of the "Early" and "Late" harvest categories, Section 4.2.6, reasonably well. Considering the "Early" window, the harvest of biomass could be taken towards the latter part of this period, perhaps at a point where more of the nitrogen has translocated to the rhizomes, with little negative effect on biomass yield. Yield considerations become important moving beyond the "Early" period until the "Late" period is reached whereupon yields and compositions will be stable for several months. Hence, the exact date of harvesting samples in the "Late" window could be flexible according to other considerations (e.g. consistency of supply rates of feedstock to the biorefinery, weather conditions etc.).

Table 17: Conversion factors and yields for the ethanol-producing hydrolysis technologies A-E. A = near-term dilute acid hydrolysis process; B = advanced dilute acid hydrolysis process; C = near-term concentrated acid hydrolysis process; D = near-term enzymatic hydrolysis process; E = advanced enzymatic hydrolysis process.

	(Biorefining Technology) (Reference)				
	(A)	**(B)**	**(C)**	**(D) (139)**	**(E) (139)**
Cellulose consumed by cellulases (%)	0	0	0	6	4
Hydrolysis of cellulose to glucose (%)	50 (134)	84 (135)	87 (137)	75	98
Hydrolysis of hemicellulose to sugars (%)	85 (136)	55 (136)	95 (137)	82.5	93
Kg hexoses per tonne cellulose [a]	555	932	966	783	1044
Kg sugars per tonne hemicellulose [b]	966	625	1079	937.2	1056
Ethanol from glucose (% of theoretical) [c]	90 (134)	95 (135)	95 (135)	87.5	93.5
Ethanol from hemicellulose sugars (% of theoretical) [c, d]	59 (148)	86 (139)	59 (148)	59	93.5
Litres Ethanol per tonne cellulose	324	574	594	444	633
Litres Ethanol per tonne hemicellulose	369	348	412	358	640

a = the mass yield of glucose per tonne of cellulose with 100% conversion efficiency is 1110kg; b = the mass yield of pentoses per tonne of pentose-sugars with 100% conversion efficiency is 1136kg; c = the theoretical maximum mass yield of ethanol is 51.11%; d = for the near-term commercial technologies (A, C, D) a lower efficiency is used since high yields have not yet been demonstrated at commercially-viable production rates.

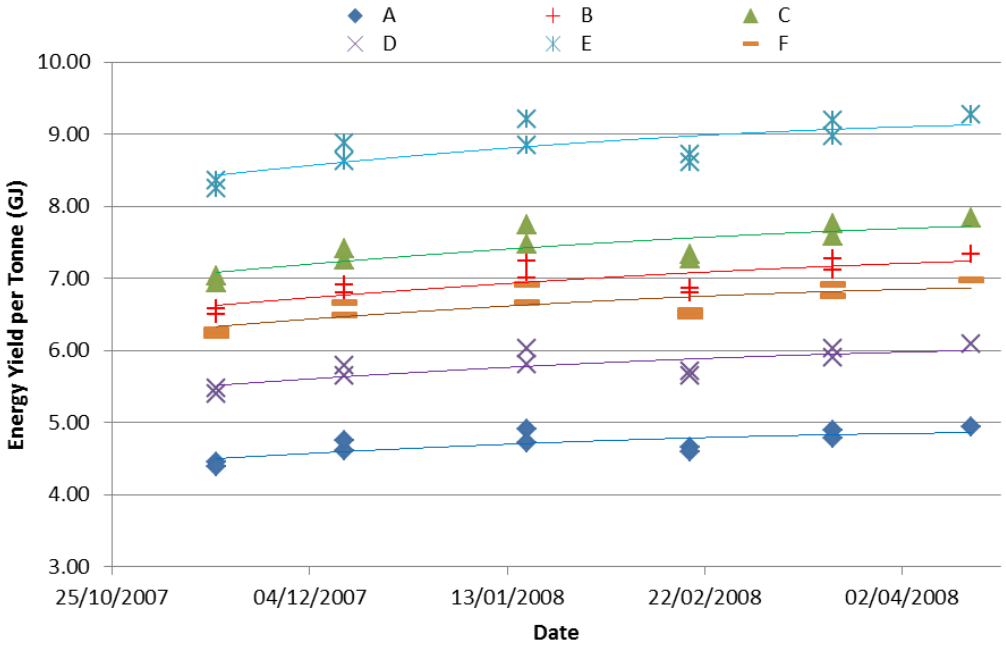


Figure 25: Energy yield (GJ) per tonnes of processing Miscanthus collected at various points in the harvest window through technologies A to F. A = near-term dlute acid hydriolysis process; B =advanced dilute acid hydrolysis process; C = near-term concentrated acid hydrolysis process; D = near-term enzymatic hydrolysis process; E = advanced enzymatic hydrolysis process; F = DIBANET process projections.

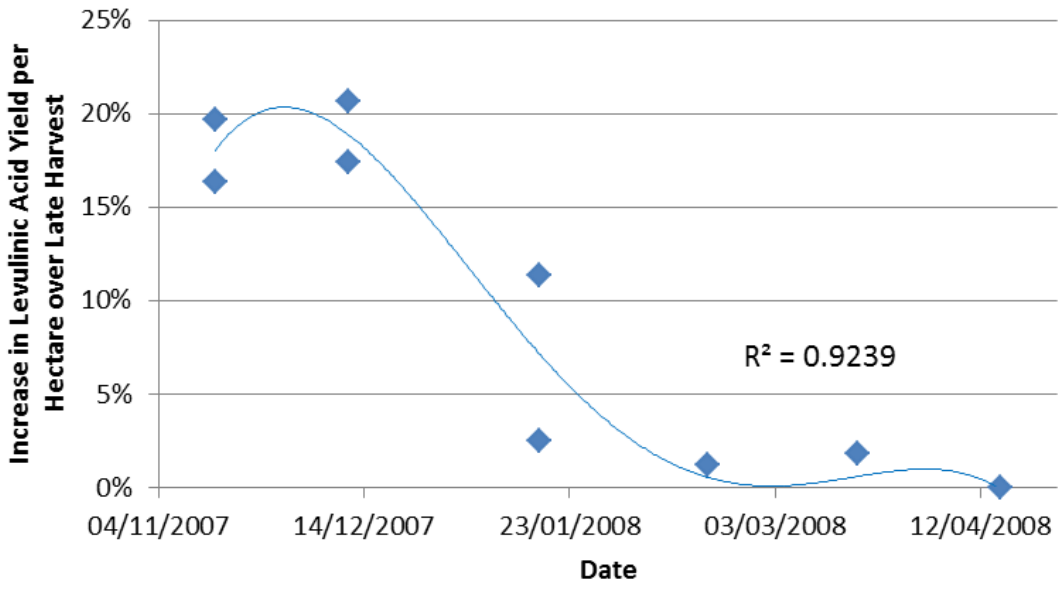


Figure 26: The increased yield per hectare of levulinic acid, over that experienced from the latest point in the harvest window (the datapoint from April), associated with earlier harvests.

Technologies A, C, and D are considered to be the near term options for commercial facilities and, of these, C provides by far the greatest yields. However, this process requires that the moisture content of the material is not significantly greater than 10%. The high moisture contents (over 50%) seen for Early harvest samples may therefore prohibit processing these in C. The ethanol yields from a Late harvest of process C are greater than the Early harvest yields of technologies A and D, therefore the relative advantage of an Early harvest may only be relevant for biorefining once more modern technologies (B, E, F) are commercially viable. When such a point is reached, the maximum potential ethanol yield, of approximately 6,250 litres per hectare per year associated with processing an Early harvest through technology E, is significantly greater than the expected ethanol yields from current first-generation biofuel crops such as wheat (3142 l/ha), barley (2065 l/ha), and sugar beet (4685 l/ha) in Ireland (149). Indeed, the "Late" harvest ethanol yields from technology E would also be greater than all these first-generation alternatives.

4.2.8 Summary and Guidelines of Best Practice

Guidelines of best practice are highlighted in green.

Miscanthus as an Energy Crop for Biorefining

- Miscanthus is a productive energy crop that does not require significant time or expense for maintenance after plantation. It can be productive for up to 20 years without the need for replantation.

- The lignocellulosic composition of the crop once at full production is highly attractive for use in biorefining technologies.

- The stem fractions of the plant, when processed in biorefining technologies, will provide higher chemical/biofuel yields than the leaf fractions. This is due to their higher total sugars contents and increased heating values. The lower acid soluble lignin, protein, and extractives contents in the stem sections are also likely to present fewer complications in many conversion processes (e.g. acid and enzymatic hydrolysis).

- The total sugars content of the crop in its first year of production is significantly less than in subsequent years. The total biomass yield of the crop is also less in this first year.

- Given this situation, **the commercial harvest of the first year growth of Miscanthus** and the subsequent transport of this crop to the biorefinery is not economical and **is not advised**.

- Instead, the crop should be cropped after the first year of growth with the biomass either left on the land for soil conditioning or used for other local uses.

Miscanthus Varieties

- Miscanthus x giganteus is the only Miscanthus variety in commercial production in Ireland. Other crops, e.g. sinensis, are grown experimentally but their yields in experimental plots have tended to be significantly lower than that of Miscanthus x giganteus.

- Hence, if climatic conditions are suitable for the growth of Miscanthus x giganteus (i.e. the winters are relatively mild) then this variety should be favoured in order to attain maximal yields.

- The non-giganteus varieties that have been analysed in this projected tended to have higher hemicellulose contents than giganteus but lower cellulose contents. Hence, more sugars may be liberated in pretreatment processes (e.g. dilute acid hydrolysis) with these varieties.

- The development of Miscanthus varieties has traditionally been focused on improving the resistance of the crop to cold winters or on maximising biomass yields.

- More recently research/breeding activities have considered improving the biorefining characteristics of the crop (e.g. polysaccharide contents, recalcitrance of the lignocellulosic matrix). Hence, future varieties may offer significant advantages over Miscanthus x giganteus for biorefining.

Harvest Window for Miscanthus x giganteus

- The harvest window for Miscanthus is between October and April.

- Between October and early December a relatively small amount of standing biomass is lost as leaf fall. This period is termed the "Early Harvest" in this report.

- Between mid-December and the end of February there is a rapid loss of leaves from the plant.

- By March the only remaining leaf materials tend to be the sheaths. These are lost from the plant at a much slower rate than the leaf blades. Hence, the loss of standing biomass is much less after March. This period is termed the "Late Harvest" in this report.

- The best time for harvesting Miscanthus will be dependent on how the crop will be processed.

- The dry biomass yield associated with an Early Harvest can be approximately 30% more than that associated with a Late Harvest.

- If the maximal biomass yield is the primary desire the crop should be harvested in the ``Early´´ period. The crop will have a significant amount of moisture (approximately 50% on a wet basis) at this time.

- An Early harvest will not provide a feedstock suitable for most thermochemical biorefining technologies (e.g. pyrolysis, gasification) since these will require lower moisture contents.

- An Early harvest is feasible for most hydrolysis biorefining technologies providing they do not use pretreatment method that require dry feedstock (e.g. ionic liquids).

- An early harvest will remove leaves that would, in a Late harvest, fall to the field. The amount of carbon and nitrogen provided to the soil would therefore be reduced.

- The removal of leaf material from the land can be addressed with increased fertiliser input.

- The amount of extra fertilisation required could be minimised by harvesting the crop towards the later period of the Early Harvest Window. This delay will allow for more of the nutrients present in the plant to translocate from the leaves to the rhizomes where they will be stored for utilisation in the subsequent year of plant growth. From the start to the end of this Early window the plant will change colour (leaves will be classified as "dead" rather than "live") but relatively little leaf material will be lost from the plant.

- There are significant changes in lignocellulosic composition of the standing plant over the harvest window. The most important of these are an increase in the glucan and Klason lignin content.

- On a dry mass per-tonne basis the biomass collected during the Late harvest period is of more value for biorefining processes (hydrolysis and thermochemical) than the biomass collected in the ``Early´´ harvested period.

- If a feedstock payment scheme at a biorefinery, using the hydrolysis platform, is based on total sugars content then the Late harvest crop would be worth approximately 10% more per tonne than the Early harvest crop.

- This dynamic means that the advantage of an Early harvest (as opposed to a Late harvest) is less in biofuel terms (approximately 20%) than in biomass terms (approximately 30%).

- Farmers should consider their own local practices to determine whether the potential extra 20% in revenue per hectare associated with an Early harvest is sufficient to cover the extra costs associated with the harvest and transport of a wet crop and with the need to increase fertilisation levels.

- Considering the needs of the biorefinery, it is not practical or economical to receive all of the feedstock in a relatively short window since this will necessitate for larger storage facilities or for a need to utilise multiple biomass feedstocks over the course of a year.

- Hydrolysis biorefineries could receive Miscanthus for seven months of the year (from the start of the Early window to the end of the Late window).

- If Miscanthus is to be received at biorefineries over the whole course of the harvest window it may be necessary for the facility to pay variable prices for the crop over this period. For example, such a scheme could compensate farmers that harvest late in the window since they would otherwise receive less revenue per hectare under a flat-rate payment scheme.

- Alternatively the biorefinery could enter onto contracts with each feedstock supplier so that Miscanthus is supplied in a staggered manner using different months for harvest in different years. In this way, the total revenue over the lifespan of a plantation would be consistent between suppliers.

- Due to their requirements for low moisture-content feedstocks, the effective harvest window for Miscanthus is much lower for many thermochemical biorefineries. It is unlikely/unpractical for a thermochemical facility to operate throughout the year using Miscanthus as a sole feedstock. Hence, thermochemical biorefineries processing Miscanthus will also require the supply of other feedstocks in periods outside of the reduced harvest window.

4.3 Straws

Summary statistics for the samples analysed are presented, according to species type, in Table 18. These results show that, as with the Miscanthus samples, the principal constituent of the straws is glucose. This is a sugar that will primarily be present in the polysaccharide cellulose. Xylose is the second most abundant constituent, closely followed by Klason lignin. Arabinose is the next most abundant sugar but is present in concentrations approximately 10 times less than that of xylose. Galactose is present in concentrations that are typically around three times less than arabinose, whilst rhamnose and mannose are minor components, although mannose is present in slightly higher concentrations than it is in many of the Miscanthus samples. Among all the samples, the arabinose to xylose ratio ranged from 0.09 to 0.14 and the galactose to xylose ratio from 0.03 to 0.05. In both cases the lowest ratios were for the winter barley group and the highest ratios for the winter oats group. The inverses of these arabinose to xylose ratios (i.e. xylose to arabinose ratios) are between 7.1 and 11.2; these values are below the ratio of 13 determined in the research of Sun *et al*. (150), however that paper involved the analysis of Chinese straws.

Table 18 shows that, generally, there is a low variation between different varieties of a certain species. For example, the range in glucose content for of all winter wheat samples analysed was only 0.82%. However, there is a greater variation in lignocellulosic components between different species (as can be seen for in the quantiles plots of the glucose, xylose, and arabinose contents in Figure 27). For example, the average glucose content of spring-oat-straw is approximately 5% higher than that of spring-wheat straw.

While the variation between all samples is greater than the variation within species groups, it is still quite low. For example, the standard deviation is less than 2% and the range less than 10% for all constituents. This limited variability should be attractive in the sense that it improves the confidence that can be associated with any predictions of potential biofuel yields. This is perhaps even true for unknown varieties of the straw types listed above since no single sample of a given variety type has been observed, in these data, to deviate greatly from the properties of the other samples of that type. This limited variation would, however, make the job of developing precise NIRS calibrations much harder since it would mean that the model would require lower standard errors of prediction in order to achieve the same r-squared value as for a dataset where the compositional values were more varied. It is very uncommon for NIR model standard errors to be less than the errors associated with the wet-chemical analysis methods employed, hence accurate and precise NIRS models for straw compositional statistics are likely to require extremely accurate reference methods.

Estimates have been made by UL researchers regarding the arisings of cereal straws in Ireland. Specific data for straw production in Ireland are lacking, hence these are estimated based on data for the harvested area and yields (151) and on the straw/grain ratios for each feedstock (152, 153). A total figure of 0.96×10^6 tonnes (on a dry basis) is calculated for the maximum harvestable straw available. The mushroom industry requires one tonne of straw per 2.5-3 tonnes of compost (80), meaning that a production of 290 kt of compost (89) will require about 90 kt of (predominately wheat (152)) straw, hence this figure is taken from the predicted total yield of wheat straws. Other current uses for straws are for animal feed and bedding or as a soil amendment (81).

Another study estimated that between 80 kt and 325 kt of the total straw resource could be available for energy purposes (152). These figures are distributed proportionately between the various available straw types according to cereal production figures (151), with the total straw arisings under three scenarios presented in Table 19. These scenarios are (i) all straw produced potentially available for biorefining; (ii) 319 kt of total straw potentially available (equivalent to 325 kt minus the estimated production of rapeseed straw) ; (iii) 78 kt of total straw potentially available (80 kt minus the estimated production of rapeseed straw).

Table 18: Summary statistics for the average, standard deviation, maximum, minimum, and range of the compositional values of the different straw species, and of all straw samples.

Straw Type	Extr.	Ash	KL	ASL	AIR	AIA	ARA	GAL	RHA	GLU	XYL	MAN	TOT
Average Values													
Spring Barley	3.73	1.67	19.41	2.27	19.34	-0.02	2.18	0.77	0.15	41.63	23.25	0.41	68.38
Winter Barley	4.64	4.94	18.02	2.18	18.96	0.94	2.56	0.86	0.13	41.65	21.08	0.29	66.57
Spring Oats	3.17	3.93	20.07	2.38	20.67	0.61	2.45	0.95	0.14	42.98	21.47	0.38	68.37
Winter Oats	2.38	4.65	18.22	2.29	19.40	1.18	2.94	1.12	0.17	41.45	21.09	0.31	67.07
Spring Wheat	3.61	4.94	20.56	2.42	22.32	1.76	2.12	0.82	0.14	38.12	21.96	0.45	63.61
Winter Wheat	4.36	3.32	18.77	2.26	20.15	1.39	2.45	0.84	0.16	39.35	23.43	0.45	66.67
All	3.80	4.04	18.95	2.27	19.89	0.94	2.48	0.89	0.15	41.08	21.91	0.36	66.86
Standard Deviation													
Spring Barley	2.14	0.28	0.35	0.11	0.38	0.26	0.06	0.04	0.01	1.36	0.21	0.04	1.67
Winter Barley	1.48	1.11	1.15	0.11	0.99	0.48	0.14	0.10	0.01	0.97	0.76	0.09	1.32
Spring Oats	1.01	1.62	0.34	0.21	0.65	0.31	0.04	0.06	0.02	1.23	0.69	0.11	0.90
Winter Oats	1.00	0.20	0.29	0.04	0.52	0.27	0.04	0.02	0.01	0.82	0.08	0.03	0.83
Spring Wheat	1.40	0.66	1.07	0.42	1.09	0.13	0.19	0.04	0.02	1.48	0.50	0.13	2.16
Winter Wheat	0.67	0.46	0.11	0.08	0.44	0.35	0.09	0.02	0.01	0.34	0.58	0.06	0.39
All	1.48	1.48	1.16	0.18	1.27	0.62	0.27	0.12	0.02	1.76	1.12	0.10	1.82
Maximum Values													
Spring Barley	6.41	1.91	19.86	2.38	19.71	0.36	2.23	0.82	0.15	42.80	23.41	0.46	69.82
Winter Barley	6.59	6.25	19.53	2.36	20.21	1.56	2.72	1.02	0.15	43.18	21.99	0.46	68.23
Spring Oats	4.29	6.12	20.54	2.62	21.56	1.02	2.49	1.00	0.16	44.20	22.15	0.52	69.42
Winter Oats	3.43	4.84	18.50	2.32	19.99	1.49	2.98	1.14	0.17	42.59	21.16	0.36	68.25
Spring Wheat	4.77	5.40	21.59	2.73	23.44	1.85	2.31	0.85	0.16	39.56	22.53	0.55	65.94
Winter Wheat	4.80	3.64	18.88	2.31	20.72	1.89	2.58	0.86	0.16	39.73	24.29	0.54	67.21
All	6.59	6.25	21.59	2.73	23.44	1.89	2.98	1.14	0.17	44.20	24.29	0.55	69.82
Minimum Values													
Spring Barley	1.53	1.29	19.01	2.11	18.84	-0.17	2.09	0.73	0.14	39.69	22.94	0.36	65.97
Winter Barley	2.23	3.36	16.42	2.04	17.16	0.38	2.41	0.73	0.12	40.42	20.02	0.18	64.11
Spring Oats	1.87	2.70	19.72	2.13	19.98	0.27	2.41	0.90	0.12	41.73	20.52	0.27	67.50
Winter Oats	1.24	4.42	17.83	2.25	18.85	0.91	2.90	1.09	0.16	40.71	20.97	0.28	66.34
Spring Wheat	2.06	4.47	19.45	1.94	21.27	1.61	1.93	0.78	0.13	36.61	21.62	0.30	61.67
Winter Wheat	3.39	2.99	18.67	2.14	19.81	1.14	2.38	0.82	0.15	38.91	23.04	0.42	66.39
All	1.24	1.29	16.42	1.94	17.16	-0.17	1.93	0.73	0.12	36.61	20.02	0.18	61.67
Range in Values													
Spring Barley	4.88	0.62	0.85	0.27	0.87	0.53	0.14	0.09	0.01	3.11	0.47	0.10	3.85
Winter Barley	4.36	2.89	3.11	0.32	3.05	1.18	0.31	0.29	0.03	2.76	1.97	0.28	4.12
Spring Oats	2.42	3.42	0.82	0.49	1.58	0.75	0.08	0.10	0.04	2.47	1.63	0.25	1.92
Winter Oats	2.19	0.42	0.67	0.07	1.14	0.58	0.08	0.05	0.01	1.88	0.19	0.08	1.91
Spring Wheat	2.71	0.93	2.14	0.79	2.17	0.24	0.38	0.07	0.03	2.95	0.91	0.25	4.27
Winter Wheat	1.41	0.65	0.21	0.17	0.91	0.75	0.20	0.04	0.01	0.82	1.25	0.12	0.82
All	5.35	4.96	5.17	0.79	6.28	2.06	1.05	0.41	0.05	7.59	4.27	0.37	8.15

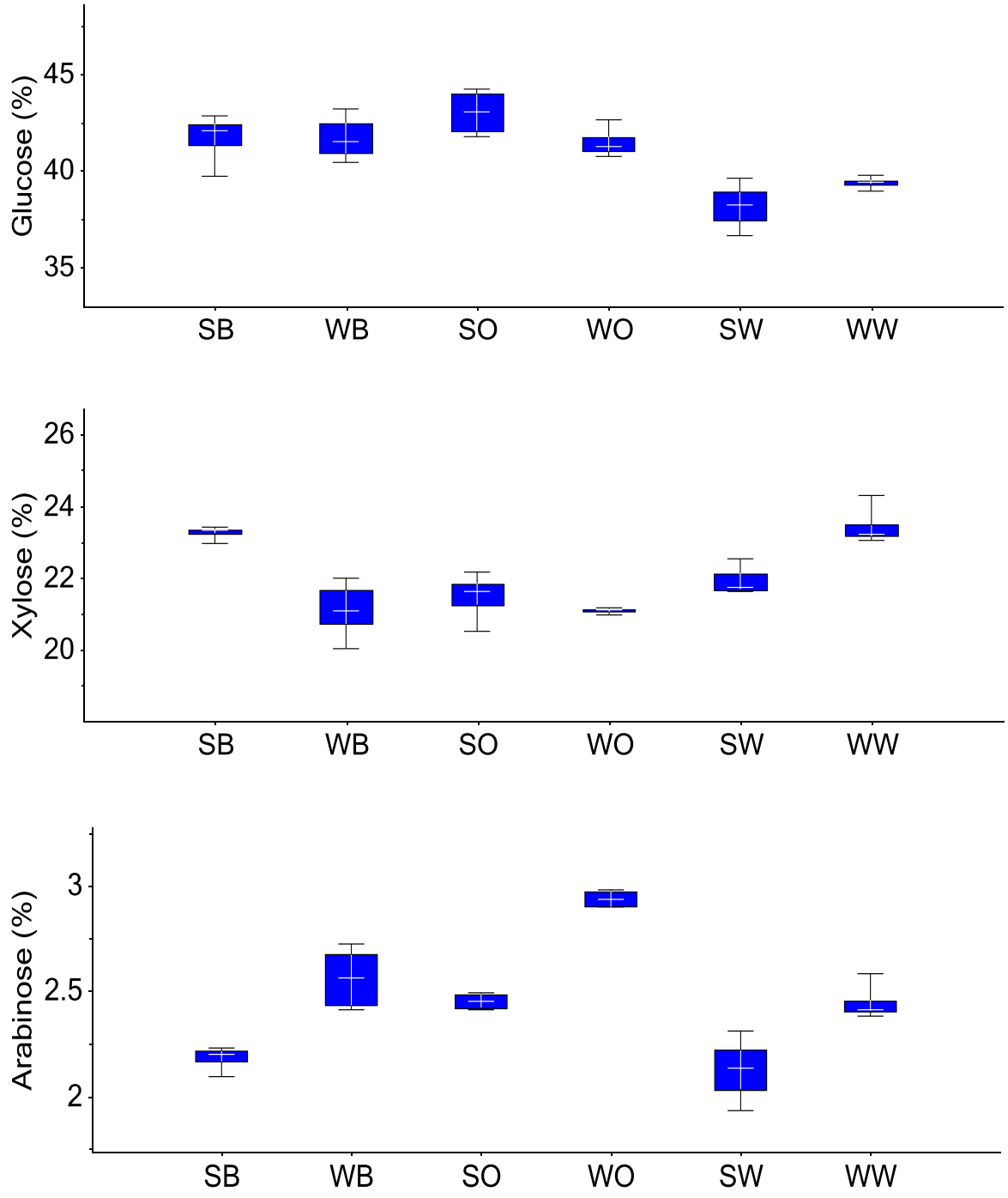


Figure 27: Quantile plots involving spring barley (SB), winter barely (WB), spring oats (SO), winter oats (WO), spring wheat (SW), and winter wheat (WW) for: (a) glucose; (b) xylose; and (c) arabinose.

Table 19: Estimates of the quantities of straw produced in three scenarios. (i) Total amounts of straw produced; (ii) upper estimate of practical resource available for end-use; (iii) lower estimate of practical resource available for end-use. Straw ratio = straw yield as a proportion of total grain yield. Straw – SMC takes away the wheat straw quantities that are estimated to be used by the mushroom compost industry (89).

Species	Area in June 2006 ('000 ha) (151)	Yield (t/ha) (151)	Straw ratio	Straw yield (odt/ha)	Total Resource ('000 odt)	Straw – SMC ('000 odt)	% (total)	Upper Quantity Scenario ('000 odt)	Lower Quantity Scenario ('000 odt)
Wheat									
Winter	59.2	9.8	0.55	4.6	271	208	21.8%	71	17
Spring	28.3	7.8	0.62[a]	4.1	116	89	9.3%	30	7
Oats									
Winter	9.3	8.0	0.86	5.8	54	54	5.7%	19	5
Spring	11.1	6.4	0.86 [b]	4.7	52	52	5.4%	18	4
Barley									
Winter	15.1	7.9	0.56	3.8	57	57	5.9%	19	5
Spring	151.9	6.7	0.55	3.1	476	476	49.8%	162	40
TOTAL					1,045	955		319	78

a = the spring wheat straw/grain ratios were not investigated in (152); the percentage difference seen (from a German study (153)) in the straw/grain ratio compared with the winter variety is used to approximate the Irish spring variety ratio from that of the winter variety; b = winter oats straw/grain ratio is used.

Summary

- Straws have suitable carbohydrate contents for utilisation in the DIBANET process.
- The variation in composition between different varieties within a species is relatively low.
- The range in composition is greater between species but still less than seen in other feedstocks, e.g. Miscanthus.
- This lower range will allow for increased confidence in the values for the expected yields from biorefining, since these will be based on the expected composition.

4.4 Waste Papers

Table 20 presents the extractives, ash, and lignocellulosic data for the DS fractions of a number of paper and cardboard samples that have been analysed in the UL laboratories. It can be seen that many of these samples have high total sugars contents, with values ranging from 65.3% (for the fast food wrapping) to 94.54% (for the Tetrapak cartons). This suggests that these samples could be excellent feedstocks for hydrolysis biorefining technologies, such as DIBANET, although the $CaCO_3$ filler in office paper may affect acid-catalysed hydrolysis. Amongst the sugars, glucose is by far the most abundant, usually followed by xylose. Mannose is a much more important sugar, in proportional mass terms, in these samples than it is in many other samples (e.g. sugarcane bagasse, sugarcane trash, Miscanthus, straws). Indeed, it is the second most abundant sugar in the newspaper and white-bag samples. This is a reflection of the paper coming from woody materials, rather than herbaceous feedstocks, a fact that is also responsible for the arabinose and xylose contents being lower than seen for Miscanthus and bagasse samples.

In softwoods galactoglucomannan is the principal hemicellulose component and constitutes around 20% of the dry weight (154). The glucose to mannose ratio is about 1:3, whereas the ratio of galactose to glucose can vary from 1:1 to 1:10 (47). Arabinoxylans are also present in softwoods but at lower quantities (2). In hardwoods, the xylans are the principal hemicellulose, but the type of xylan found is typically a glucuronoxylan rather than an arabinoxylan. The concentration of this xylan in hardwoods varies between 15 and 30% by weight (155). In a few species, for example in some birches, the xylan content can reach as high as 35% (47).

Paper made from hardwoods tends to be smoother than paper from softwoods but softwood paper also tends to be weaker. The fibres from hardwoods and softwoods can be blended into a single paper type, with the proportional quantities varying according to preferences for strength, whiteness, roughness etc.

The type and severity of pulping used will determine the amount of lignin that is retained in the final paper. Table 20 shows that the KL content of the paper/cardboard samples varies greatly (from 1% for printouts to 26.4% for newspapers). Given that the ASL and extractives contents of the samples are relatively small, the only other major contributor to the total mass balance, apart from the sugars and KL, is the ash content. This also varies substantially, from 1.3% for the Tetrapak sample to 34.9% for the glossy paper sample. Under a situation where the ash content is constant, for a given particle size fraction, between two samples and increase in the KL content will usually be accompanied by a decrease in the total sugars content. This would mean that the relative advantage provided by hydrolysis or thermochemical biorefining processes would shift since the KL has proportionately higher carbon, and proportionately lower oxygen, contents than the polysaccharides. However, even in instances where the KL content is increased, some of these paper/cardboard samples are not ideal feedstocks for thermochemical processing due to their high ash contents and since the paper additives may cause problems in some gasification schemes.

Waste Paper Arisings in Ireland

Approximately 67% of the recovered biodegradable municipal waste (BMW) in 2005 was paper and cardboard, however only 2.6% of this was recycled in Ireland, a drop from 31% in 2004 due to the closure of a paper mill (102). Ireland exported 387 kt (on an oven dry basis) of collected paper/cardboard, with 39.3% sent to the UK and 27.1% sent to Asia (102). The specific make-up of this paper/cardboard stream is not known, however it can be calculated from the data that 62.4% of it came from the commercial sector, with 37.6% coming from households.

A paper by a UL researcher (86), using secondary chemical data, assumed that 50% of all the paper/cardboard from the commercial sector was chemically and energetically equivalent to office paper, that 40% was equivalent to cardboard and 10% to newspaper. The proportions were shared equally between these three for the household sector.

In this report these proportions are maintained and it is assumed that the composition of office is equal to that of printer paper (Table 20) and that the composition of cardboard is equal to that of the food cardboard packaging sample (Table 20). Under these assumptions, the weighted averages of the compositional values for these samples provided the data for the "Household", "Commercial" and "Export" (62.4% commercial and 37.6% household) categories in Table 20.

Summary

- There is a large range in the total sugars contents of the paper and cardboard samples analysed in the UL laboratories, however even the sample that has the lowest total carbohydrate content had a sufficient sugar content to warrant its processing in DIBANET.

- The lignocellulosic composition of these wastes is significantly different from that of herbaceous feedstocks (e.g. Miscanthus, straws, sugarcane residues). For example, the mannose content is higher and the xylose content lower.

- Klason lignin also varies substantially between samples (1-26%), this will greatly influence the amount of solid residues that may be expected after the DIBANET hydrolysis process.

4.5 Projected Biorefining Yields from Waste Feedstocks

Section 4.1.4 concluded that the main waste feedstocks in Ireland that were suitable for utilisation in the DIBANET process (and other biorefining technologies) were straws and waste papers.

Sections 4.3 and 4.4 present estimates for the quantities of these wastes that might be practical for biorefining. From these it is possible to estimate the biofuel/chemical yields that may be possible from processing these resources.

A scenario is presented whereby all of the paper that is exported from Ireland, whose composition is estimated in Table 20, is instead biorefined, with the resource estimates provided by the EPA (102) used (Section 4.4). In addition, the upper estimates for the practical and sustainable quantities of barley, wheat, and oat straws that can be used, see Table 19, are also biorefined.

The calculated total biofuel yields, in million litres (million kg for process F) and terajoules (TJ), from processing these feedstocks in Technologies A to H (with technology F being the DIBANET process) are presented in Table 21. For each process the yields are summed across all feedstocks to provide a total biofuel energy yield which is then expressed as a percentage of the total energy demand, estimated for the year 2010 (156), for petrol and diesel transport fuels in the Irish Republic.

Table 21 shows that exported paper/cardboard contributes the greatest quantity of biomass (54.9% of the total), followed by spring barley straw (22.9%), whilst the other feedstocks contribute much less to the total biomass resource. These total quantities of biomass allow for between 1.76% and 3.34% of the estimated current demand for petrol and diesel transport fuels in Ireland to be met. This is a significant amount and is possible from using sustainable quantities of residues and wastes.

The removal of straws from the field, rather than letting them contribute to the soil organic matter, can be a contentious issue, however the scenario put forward still allows for the retention of a portion of these straws on the land (152). The alternative is that only the waste paper/cardboard resource is biorefined. This scenario results in between 1.03% and 1.97% of the estimated 2010 demand for petrol and diesel transport fuels in Ireland to be met. Taking the yield from technology E as an example, this level of biofuel supply is 58.5% of the level of biofuel supply in the straw and paper scenario. Therefore, the drop in output is less than the loss in total biomass. This is a result of the exported paper resource offering superior yields per tonne to the straws in the hydrolysis biorefining technologies. However, if instead technology G was used to process these national resources of biomass then the biofuel yield in an exported-paper only scenario would be 51.4% of the biofuel yield in a straw and exported paper scenario. This is because paper provides lower yields per tonne, compared with straws, in this process.

Table 20: Primary lignocellulosic, extractives, ash, and elemental data for paper and cardboard wastes analysed at the University of Limerick. EXTR = 95% ethanol soluble extractives; KL = Klason lignin; ASL = acid soluble lignin; AIR = acid insoluble residue; AIA = acid insoluble ash; ARA = arabinose; GAL = galactose; RHA = rhamnose; GLU = glucose; XYL = xylose; MAN = mannose; TOT = total sugars; C = carbon; H = hydrogen; N = nitrogen; S = sulphur.

Sample	EXTR	Ash	KL	ASL	AIR	AIA	ARA	GAL	RHA	GLU	XYL	MAN	TOT	C	H	N	S
Food Wrapping Paper	2.34	17.21	14.79	0.61	19.87	5.08	0.49	0.77	0.09	49.96	7.73	6.35	65.39	-	-	-	-
Brown Paper Bags	2.08	4.64	7.85	0.86	9.47	1.62	0.59	0.54	0.06	70.32	9.35	5.09	85.95	44.59	6.45	0.12	0.02
White Paper Bags	0.80		25.65	0.56	26.18	0.53	0.60	0.41	0.07	57.24	6.27	6.97	71.56	-	-	-	-
Envelopes	2.65	8.93	2.00	0.74	2.44	0.44	0.22	0.17	0.05	67.06	13.74	2.30	83.54	41.48	6.20	0.07	0.02
Glossy Paper (Advertisements)	0.98	19.57	6.29	0.61	10.21	3.93	0.28	0.33	0.06	58.76	8.37	3.87	71.67	38.67	5.48	0.04	0.01
Food Packaging (Cardboard)	1.40	8.87	10.97	0.67	13.25	2.28	0.63	0.68	0.06	63.36	9.84	5.60	80.16	43.21	6.29	0.04	0.03
Cereal Boxes	1.08	10.01	12.90	0.64	14.85	1.95	0.68	0.97	0.09	56.88	9.17	5.81	73.61	43.92	6.14	0.08	0.01
Birthday Cards	1.12	13.41	5.87	1.16	7.12	1.25	0.22	0.28	0.09	64.53	15.35	2.02	82.51	42.81	5.26	0.29	0.10
Till Receipts	2.62	10.60	4.69	0.54	5.43	0.74	0.15	0.10	0.04	68.36	11.98	1.25	81.88	42.07	6.00	0.08	0.00
Printer Paper	0.62	11.43	1.00	0.72	1.00	0.00	0.07	0.13	0.04	70.64	13.27	0.98	85.14	39.76	5.80	0.03	0.01
Newspapers	2.63		26.44	0.53	26.49	-0.03	1.14	2.05	0.16	46.41	6.29	11.86	67.91	-	-	-	-
Tetrapak	2.03	1.17	1.65	0.64	1.65	0.00	0.42	0.18	0.04	77.64	11.70	4.56	94.54	56.78	8.70	0.01	0.00
Household	1.13	9.26	7.53	0.68	8.45	0.91	0.40	0.54	0.06	65.31	11.20	3.92	81.43	-	-	-	-
Commercial	1.55	6.77	12.80	0.64	13.58	0.75	0.61	0.95	0.09	60.14	9.80	6.15	77.74	-	-	-	-
Export	1.29	8.32	9.51	0.67	10.38	0.85	0.48	0.70	0.07	63.36	10.67	4.75	80.04	-	-	-	-

Table 21: Expected total biofuel yields from processing the estimated national resources of straws and paper considered available for biorefining technologies. The yields are in million litres of ethanol for processes A, B, C, D, E, G, million kg of levulinic acid for process F, million litres of diesel from H (D, million litres of naptha from H (N) and million litres of diesel and naptha for process H. The yields are also expressed in energy terms (TJ). These total energy outputs from each technology are expressed as a percentage of total estimated petrol and diesel demand in Ireland in 2010. H (D) = FT-diesel; H (N) = FT-naptha.

Feedstock	**Dry Tonnes per Year**	**Million Litres of Product (million kg for Process F)**										**TJ**									
		A	**B**	**C**	**D**	**E**	**F (kg)**	**G**	**H**	**H (D)**	**H (N)**	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**H (D)**	**H (N)**
Spring Barley	161,863	37.59	54.02	58.04	45.44	70.11	53.71	68.42	27.17	21.15	6.02	792	1,138	1,223	957	1,477	1,105	1,441	916	729	187
Winter Barley	19,317	4.35	6.32	6.78	5.29	8.14	6.24	8.03	3.19	2.48	0.71	92	133	143	112	171	128	169	108	86	22
Spring Oats	17,667	4.09	5.96	6.38	4.98	7.65	5.87	7.45	2.96	2.30	0.65	86	126	134	105	161	121	157	100	79	20
Winter Oats	18,502	4.21	6.10	6.54	5.11	7.86	6.03	7.51	2.98	2.32	0.66	89	128	138	108	166	124	158	101	80	21
Spring Wheat	30,318	6.55	9.38	10.09	7.91	12.22	9.35	12.36	4.91	3.82	1.09	138	198	213	167	257	192	260	165	132	34
Winter Wheat	70,830	16.06	22.86	24.60	19.31	29.90	22.87	29.74	11.81	9.19	2.62	338	482	518	407	630	471	627	398	317	81
Exported Paper	387,000	102.20	167.85	175.94	133.67	196.17	153.20	142.54	56.59	44.06	12.54	2,153	3,536	3,706	2,816	4,133	3,153	3,003	1,908	1,519	390
TOTAL	705,496	175	272	288	222	332	257	276	110	85	24	3,688	5,740	6,075	4,671	6,995	5,295	5,815	3,696	2,941	755
% of 2010 Demand												1.76%	2.74%	2.90%	2.23%	3.34%	2.53%	2.78%	1.76%		
% of 2010 Demand (Only Exported Paper is Biorefined)												1.03%	1.69%	1.77%	1.34%	1.97%	1.51%	1.43%	0.91%		

5 Latin American Feedstocks

5.1 Initial Examination of Feedstocks

According to the responsibilities outlined in the DIBANET Description of Work, two feedstocks (sugarcane bagasse and sugarcane trash) were to be studied and characterised by DIBANET partner CTC (see Section 5.2) whilst other Latin American feedstocks were to be studied by UNICAMP. The section presents the initial evaluations made, in 2010, by UNICAMP regarding the suitability of a number of feedstocks for the DIBANET process. This evaluation would lead to the selection of a subset of three feedstocks for more detailed analysis and the development of near infrared spectroscopy (NIRS) models. References in this section are made to secondary and primary analytical results.

5.1.1 Residues from the Coffee Industry

In the crop year 2011/2012 the world coffee production was 7.8 Tg, with Brazil being the largest producer with 2.6 Tg (157). The production of coffee results in a high volume of residues. At different stages, from harvesting to the processing and consumption, several residue types (leaves, spent-ground, pulp and husks) are produced, with the husks being the major residues; for every 1 kg of coffee beans produced, approximately 1 kg of husks are generated (158). Concerns about the deleterious effects associated with the handling of these wastes has led to an increasing interest in utilizing them in alternative processes (e.g. biorefining).

In Brazil, the most common way of preparing coffee occurs by dry methods. In these the coffee bean dries under the sun, or in pre dryers and artificial dryers, resulting in residues that approximate around 50% of the picked weight. These residues can be used as organic compost for producers on the same plantations or on other plantations, but the majority is rejected.

It appears (Table 22) that, based on their total sugars content of 63.0%, coffee husks may represent an attractive feedstocks for the DIBANET process. This total sugars content was the second highest amongst the 10 different Latin American feedstocks analyzed at UNICAMP (Table 22).

5.1.2 Soy Peel

Soy is a major global crop with 92.2 million hectares under cultivation, resulting in a worldwide production of 216 million tonnes of beans. The greatest producers of soy are the USA (32%), followed by Brazil (28%), Argentina (21%), China (7%) and India (4%). In

Brazil 23.2 million hectares of land under soy cultivation produce 65 million tons of bean. Soy peel represents a major residue from the processing of soy and composes around 8% of the entire bean. Some, but not all, of the peel produced is used in animal feed and there is a desire to seek alternative end uses for this residue. On the basis of its total sugars content (Table 22) soya peel appears to be a suitable feedstock for the DIBANET process.

5.1.3 Bamboo

Bamboo is a tropical plant that is located in many southern Asian countries (e.g. China, India, Thailand and Vietnam) as well as a number of Latin American countries, especially Brazil. Brazil has the most varieties of bamboo in Latin America; according to a report of the United Nations from March 2005 the country has more than 200 species of bamboo. However, the full potential of these Brazilian bamboos for utilization as energy crops are not utilized, in contrast to the situation in other countries such as China and India. Furthermore, in Asia bamboo can be harvested in 5 years, whilst in Brazil there are places where, because of the favorable climate and soil, it can be harvested in only 3 years, with greater yields than in the Asian harvests. Also beneficial is the fact that the plant is highly resistant to stress and can survive in unfavorable seasons and arid climates. According to Table 22 bamboo presents a good amount of total sugars (about 62.00%), and hence represents another viable feedstock for the DIBANET process.

5.1.4 Banana Residues

Banana is the most consumed tropical fruit in the world. Brazil is the country that has the biggest consumption per person, around 29.8 kg/habitant,year, while the consumption in the world is of 9.0 kg/habitant,year. Annually about 95.6 Tg of bananas are produced, with a total production of 7.2 Tg in Brazil, the world's fifth largest producer (FAO, 2011). The production and marketing conditions of banana result in large quantities of residues. About 30-40% of the fruits are discarded, and for each 1 Mg of harvested banana, approximately 4 Mg of lignocellulosic residues (3 Mg of stem, 160 kg of stalk, 480 kg of leaf and 440 kg of husks) are generated.

The industries that use the mature banana as raw material in their processes face some problems due to the residues generated. These residues can cause environmental contamination due to incorrect disposal and decomposition, leading to the production of harmful and odorous leachates and gases (159). According to the analytical work conducted during DIBANET banana residues can contain between 40-46% of total sugars. This is less than other feedstocks but may still be considered sufficient to warrant utilizing this material in biorefining processes, particularly if it can be obtained at low/no/negative costs. Given that there are numerous types of banana residues with different compositions, this feedstock warrants further investigation.

5.1.5 Rice Husks

Rice is considered the most important sustenance plantation in many developing countries, especially in Asia and Oceania. It is a staple diet for about 2.4 billion people, and according to estimates there will be a demand to serve double this population by 2050. In terms of total production, rice is the third most important bean in the world, behind wheat and corn/maize. The worldwide yearly production of rice in 2007 was about 650 million tons. Latin America occupies the second place in production and the third in consumption, and Brazil is the ninth greatest country in terms of rice production, with around 13.36 million tonnes produced. Each kilogram of picked bean is accompanied by the production of 1-1.5 kg of chaff. It is estimated that around 650-975 million tons of rice chaff is produced per year globally. A great part of this quantity is used for cattle feed but large volumes are also disposed as waste.

The options for disposal of the rice chaff are limited by the low density of the soil and the slow degradation when it is in the soil. Nowadays, field-burn is a fundamental practice to remove the rice chaff, but this results in air pollution that can be detrimental to public health. Rice husks have several characteristics that suggest they can be suitable raw materials for biorefining. For instance, they have high contents of cellulose and hemicelluloses (see Table 22).

5.1.6 Eucalyptus Sawdust

Another potential biorefinery feedstock is eucalyptus sawdust. It is produced in large quantities by sawmills and the disposal of these residues can also be an environmental concern. Brazil has a highly developed forest plantation state, dominated by eucalyptus species with an estimated planted area of more than 3 million hectares. Brazil is the largest producer of eucalyptus in the world, resulting in the production of 30 million tons per year of wood residuals. From this quantity of residuals, 0.62 million tons correspond to sawdust (waste). It is urgent to find solutions to the fate of 0.62 million tons of sawdust stored in open, cause pollution in areas that could be harnessed for agriculture or other economic activity.

5.1.7 Acai Seed

Açaí (*Euterpe oleracea*) is a tropical palm tree that occurs naturally in the Amazon region. Brazil is the largest world producer of açai with 112,676 tons/year of the fruit. Its spherical grape-sized fruits are green when young and ripen usually to a dark purple (Strudwick & Sobel, 1988). An important reloading point for açaí is the city of Belém in Pará State, Brazil, where fruits can be collected throughout the year. However, a major harvesting period exists during the ‘‘dry-months’’ from August to December. Usually, the fruits are used to prepare a liquid with creamy texture by macerating the pericarp and mixing it with different amounts of water, yielding commercially available açaí pulp (Lichtenthäler et al.,2005). In the producing region, açaí is integrated in the daily dietary habits of the native people and is normally used in main meals for lunch or dinner. In modern Brazilian society, it has gained interest as a

nutritionally valuable wellness product (Strudwick & Sobel,1988). Meanwhile, açaí is favoured as an ingredient in fruit beverages beyond the Brazilian borders and is exported mainly to the USA or to Europe (Sabbe, Verbeke, Deliza, Matta, & Van Damme, 2009).

Interest of the potential of the açaí (Euterpeoleracea, Mart) for biorefining was evaluated using the seed residue. This has a high content of total sugars, about 70.00%, with a notable predominance of mannose (Table 22).

5.1.8 Elephant Grass

Elephant grass is a lignocellulosic material that has attracted interest as a potential energy source (e.g. through combustion) due to its high calorific value, its abundance, its cheap production costs, and its rapid growth (Gómez et al, 2012). Table 22 shows that its total sugars content, approximately 50%, is also attractive for the DIBANET process.

5.1.9 Coconut

Brazil produces about 1.5 billion coconuts annually. Fibers are obtained from the mesocarp of the coconut fruit, which constitutes about 25% (160). Coconut husks are hard lignocellulosic agro-wastes that represent 15–20% of the coconut composition. The coconut shell and fibers can be easily used for biorefining concept due to the attractive levels of carbohydrate components (hemicelluloses and cellulose), and such an end use will solve the environmental problems that may result from the inadequate disposal of these wastes in nature (Mantia et al,2005).

5.1.10 Conclusions

UNICAMP analysed a set of feedstocks from Latin America (10 different biomasses) for the DIBANET project. These were: açai seed, coconut husks and fibers, eucalyptus sawdust, rice husks, soy peel, coffee husks, elephant grass, banana residues and bamboo (Figure 28). Chemical and physical properties, costs for transportation these residues, total production of biomasses and their residues as evaluated by national and international agencies (such as EMBRAPA, ICO, IAC), carbohydrate content and energy balance were analysed for the feedstocks selection. Table 22 shows the compositional data obtained from the analyses of these 10 different feedstocks. Once these criteria were evaluated, 3 biomasses were chosen by UNICAMP according to the suggestion of Chilean partner, Fundacion Chile, in the sustainability context: banana residues (stem and stalk), coffee husks and coconut residues (husks and fibers). These biomasses were chosen based on: the total sugars content, the total production in Brazil of these residues, and on the viability for collection and transportation of these samples.

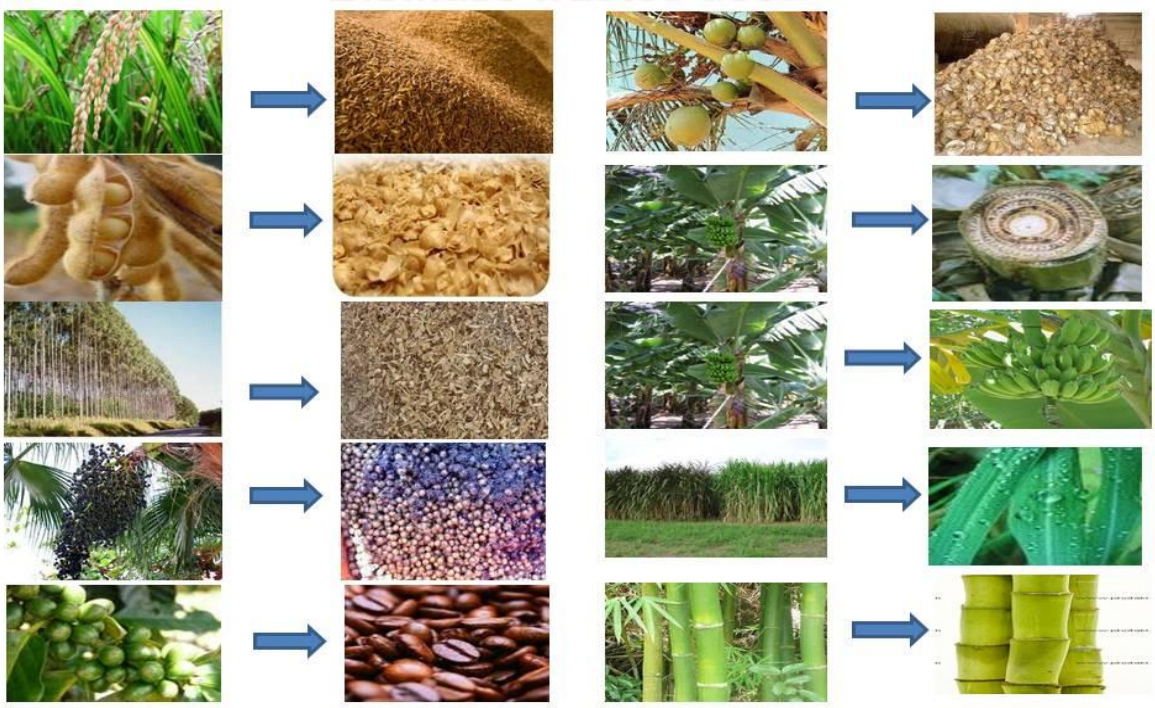


Figure 28: Illustrations of some of the feedstocks analysed at UNICAMP: Rice husks, soy peel, eucalyptus sawdust, açai seed, coffee husks, coconut shell, banana stem, banana stalk, grass and bamboo.

Table 22: Compositional data obtained at UNICAMP for 10 Latin American biomass feedstocks. All values in % of dry matter.

Feedstock	Ara	Gal	Rha	Glu	Xyl	Man	Total Sugars	Total Lignin	Extractives	Ash	Mass Balance
SOY BEAN	4,64	3,13	0,92	35,05	9,85	4,31	57,90	7,58	6,81	4,14	77,00
RICE HUSKS	1,70	0,83	0,13	36,17	16,65	0,49	55,98	23,90	2,32	12,5	95
SADWUST	0,26	1,23	0,25	38,79	9,72	0,35	50,60	32,87	8,12	0,63	92
BAMBOO	0,81	0,32	0,06	44,65	14,78	0,07	61,57	17,64	12,62	2,81	95
GRASS	3,56	1,22	0,10	27,52	16,12	0,24	48,84	15,61	11,54	12,66	89
COCONUT	1,79	0,71	0,30	32,41	14,37	0,35	49,94	35,87	1,41	2,63	90
AÇAÍ SEED	0,69	1,43	0,17	8,66	3,18	53,59	67,71	17,26	9,5	0,46	95
BANANA Stalk	2,89	1,18	0,27	26,83	6,94	1,46	39,56	10,68	22,85	10,33	84
BANANA Stem	2,37	0,72	0,16	36,32	5,36	0,61	45,53	8,38	25,15	10,30	90
COFFEE	1,62	1,54	0,51	35,33	21,89	1,68	62,55	24,46	4,21	4,00	95

5.2 Sugarcane Residues

5.2.1 Background

5.2.1.1 Sugarcane Production

Sugarcane is classified under the Poaceae (grasses) family and is a close relative of Miscanthus. An extremely large number of sugarcane varieties have been developed in order to improve yields, sugar contents, pest resistance, and to optimise the crop towards the region in which it is grown.

Sugarcane is a semi-perennial C_4 plant with the plantation cycle depending on the environmental properties of the region of production. For example, in Brazil the cycle usually lasts six years enabling five cuts to be taken (161). The crop is grown for the production of sugar, which can be extracted from the plant and refined for sale on the open market or used for the production of bioethanol. Around 20 million hectares of sugarcane were planted and 1.3 billion wet tonnes of cane produced in the 2006/2007 season with Brazil being the greatest contributing country with plantations covering 7 million hectares (161). According to a report by Centro de Tecnologia Canavieira (CTC), in Brazil the average productivity of the plant is 70 wet tonnes per hectare per annum (162).

Sugarcane ideally requires two different growing seasons in order to attain maximal yields and high sugar production. A warm and wet season allows the growth of the crop and then a cooler and drier season will enable the maturation of the plant and the accumulation of sucrose in the stems (161). The first cut of the crop typically occurs a year or more after planting. Following cutting the stems will grow back and are harvested each year, although yields tend to decline with the stage of the cycle.

There are a variety of important compositional characteristics of sugarcane. The Pol (short for polarisation) value is the apparent sucrose content, typically expressed as a percentage of the total dry mass of the cane. In varieties of sugarcane grown for sugar production the pol content of the sugarcane juice varies from 8 to 15% (163). Fibre is the term given to the sugarcane bagasse which is considered to be the total of the insoluble solids derived from cane after the milling stage. CTC (162) reported a 14.2% pol content and a 12.7% fibre content for sugarcane produced in a plantation in Sao Paulo state, which achieved a yield of 87.1 wet tonnes of cane per hectare.

Only the stem of the crop contains sufficient sucrose to warrant its processing in sugar mills. The other parts of the crop, principally the leaves and tops, are often referred to as the “trash” of the plant. It has been estimated that for each tonne of harvested cane 140 kg of trash will exist (161). Traditionally, manual harvesting practices of sugarcane have been carried out, and these still take place in developing countries, although they are being gradually phased out in favour of mechanical harvesting techniques (for example, the Brazilian government has targeted 2020 as a date when all harvesting will be mechanical). Manual harvesting practices require the crop to be burnt prior to the chopping of the stems by workers. This will burn the leaves of the crop but not damage the stems and roots. Mechanical harvesting usually involves

a combine harvester which cuts the crop at the base of the stalk, strips off the leaves, and chops the cane into reasonably consistent lengths which are then blown into a transporter traveling alongside. The “trash” is blown back onto the field.

5.2.1.2 Sugarcane Bagasse

Following harvesting the cane is transported to a sugar mill where it needs to be processed quickly in order to avoid the loss of sugar. This means that sugar mills only operate during the harvesting season, between April and December in the Brazilian state of Sao Paulo, and between June and December in Australia.

Figure 29 shows a simplified representation of a sugar mill (164). The process firstly involves washing the cane to remove excess soil and impurities and it is then crushed/shredded/chopped before proceeding to a series of mills that contain three to five rollers. Hot water, or a combination of hot water and impure sugarcane juice, are sprayed onto the crushed cane after it leaves each mill. This is done in order to extract the juice from the cane. Lime is then added to the juice and it proceeds to a clarifier where soluble and insoluble impurities coagulate and settle at the bottom of the tank. This residue is filtered to produce a filter cake that can be used as an animal feed supplement and a fertiliser. Subsequent stages involve the clarified juice being evaporated to produce a syrup that is about 65% solids and 35% water (165). This syrup is then clarified and the sugar starts to crystallise in vacuum pans. The mixture of syrup and crystals is known as massecuite and these are separated in a centrifuge device. The liquor component here is referred to as molasses and it returns to a vacuum pan for the production of more crystals which form part of a second masscuite which is again put through a centrifuge. A third crystal production cycle can then occur but the molasses that follow from this are of low sugar content and cannot be processed further. This type of molasses is known as blackstrap molasses (165) and has use as an animal feed and as a feedstock for ethanol production.

All of the above stages are not necessary in sugar mills that produce bioethanol from the feedstock. The process involves the fermentation of the sugarcane juice, or of a mixture of the juice and molasses. Typically the juice is clarified and partially evaporated in order to increase the sugar concentration prior to fermentation and it is at this stage when molasses can be added. Yeasts are used for the fermentation and the resulting product is a “wine” with an ethanol concentration of between 7 and 10% (161). After recovery, via centrifugation, of the yeasts, ethanol is produced via the distillation of the “wine” and the subsequent dehydration of the hydrated bioethanol.

According to data, provided by CTC, and which represent the average figures for nearly 60 mills in the Brazilian state of Sao Paulo, one tonne of sugarcane will produce 86 litres of hydrated bioethanol in a bioethanol-only scheme or 100 kg of sugar and 23 litres of hydrated bioethanol that comes from the fermentation of the molasses (162).

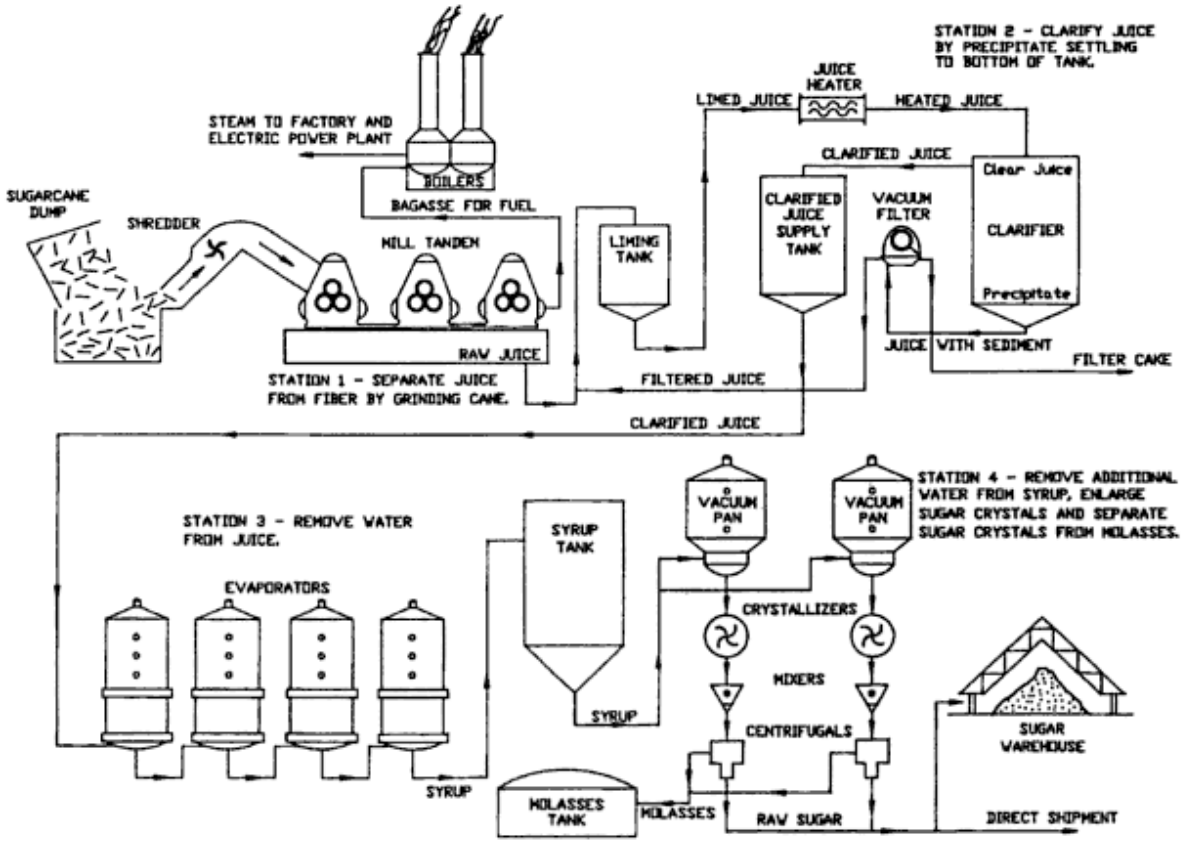


Figure 29: A simplified flow-diagram representation of a sugar mill. Taken from (164)

As can be seen in Figure 29 sugarcane bagasse (SB) is the term given to the residual solid material that is left after the milling of the cane. Ideally the maximum amount of pol (sucrose) would be extracted during the milling process with little left in the SB. Any extraction inefficiencies will be to the detriment of the profitability of the sugar mill. The following formula has been defined to determine the pol extraction efficiency of the milling process (166):

$$Pol_{Extraction} = 100 * \left(1 - \frac{Pol_b * Fibre_c}{Fibre_b * Pol_c}\right)$$

Where c = sugarcane, and b = bagasse.

Hence, if sucrose is efficiently removed the bagasse will represent a predominately lignocellulosic feedstock. Taking the example of Brazilian sugar cane, one wet tonne of sugarcane that is processed at the mill will yield approximately 280 kg (wet) of SB (167). Typically SB has a moisture content of between 45 and 55% on a wet basis (165). It can be seen therefore that SB is an extremely significant output of the sugar mill. Taking again the

example of Brazil, it was estimated that 160 million wet tonnes of SB were produced in 2008 (168).

The primary use for this resource is as a heat and steam provider to satisfy the energy needs of the sugar production or fermentation processes. It has been estimated that a minimum of 50% of the bagasse is required for this (169). In many cases the surplus bagasse represents a problematic waste that could lead to safety issues (e.g. spontaneous combustion) if stored for a long period of time. For that reason some mills deliberately burn the SB at a low efficiency in order that more of it will be consumed for energy production (170). It has been estimated that the use of SB in boilers could be reduced by up to 36% if more efficient combustion schemes are employed (170).

There has been a significant amount of research into the utilisation of SB in biorefining technologies that may produce saleable chemicals from the polysaccharides (167, 170-172) or bio-oils via the pyrolysis of this residue (168, 173).

Table 23 summarises the compositional values of SB found in a literature review as part of the DIBANET project. These samples cover several countries. There are significant differences between these samples. For example ,the range in glucan/cellulose content is 11.5%, with the most concentrated sample having a cellulose content that is 33.8% greater (in relative terms) than the least concentrated sample. Hence, there are likely to be significant differences in the yields of conversion products (e.g. ethanol, levulinic acid) when processing different bagasse samples in biorefining technologies.

Table 23: Secondary compositional data (% of dry matter) for sugarcane bagasse samples obtained from various locations.

Reference	Source	Cl.	Hc.	Glu.	Xyl.	Ara.	Gal.	Man.	Extr.	KL	ASL	Ash
(174)	Hawaii	42.9			25.2	1.4				19.0	6.6	4.9
(170)	Australia									22.3		
(171)	Brazil	45.5	27.0						4.3*b	21.1*a		2.2
(175)	Reunion	45	26							20		2.1
(176)	Brazil	34.1	29.6							19.4*a		7.9
(177)	Mexico			38.9	20.6	5.6				23.9		
(178)	Hawaii			44	26	2				23		
(179)	Thailand			40.2	22.5	2.0	1.4	0.5		25.2		
(180)	Brazil			41.3	21.8	1.8	0.5	0.3		20.5	2.9	4.1
(181)	Argentina *c			43.1	25.0	1.5	0.4	0.3		23.2*a		2.5
(182)	China	43.6	33.5							18.1*a		2.3
(183)	India		27	34					17			4

*Cl. = cellulose; Hc. = hemicellulose; Glu. = glucan; Xyl. = xylan; Ara. = arabinan; Gal. = galactan; Man. = mannan; Extr. = extractives; KL = Klason lignin; ASL = acid soluble lignin; *a – total lignin; *b – 95% ethanol-soluble extractives; *c – the data for this sample are presented on an (ethanol-toluene) extractives-free basis (this sample also had 1.2% uronic acids, and a 3% acetyl content).*

Other authors have noted that there can be a wide variation in the ratio of arabinose to xylose (0.019 to 0.247) and xylose to glucuronic acid (7.4-100) (170, 184-186). The cellulose in SB has also been isolated and characterised. A study by Sun *et al*. (182) involved testing three different isolation techniques (which focus on the removal of all other structural components leaving the cellulose as a solid residue) on extractives-free samples of Chinese SB. It was

found that the degree of polymerisation of the "cellulose" fraction varied between 1,185 and 1,406, according to the method of isolation. Sindhu *et al*. (183) determined a degree of crystalinity of 63.6% for Indian SB cellulose.

5.2.1.3 Sugarcane in Brazil

Figure 30: Sugarcane production in Brazil

The sugarcane industry, Figure 30, is of a significant importance to the Brazilian economy. It has been estimated that the sugarcane sector in the 2009/2010 season contributed US$32 billion to the economy, equivalent to 2% of GDP. A total of 580 million tonnes of sugarcane were processed, resulting in the production of 33 million tonnes of sugar, 29 billion litres of ethanol, 165 million tonnes of bagasse, and 128 million tonnes of straw. There are currently close to 400 sugar mills and 72,000 sugarcane farms in the country. Sao Paulo is the state with the most amount of land under sugarcane cultivation and approximately 200 mills although there are significant levels of production in the states of Parana and Minas Gerais. The total area of land producing sugarcane, and the total production of sugar and ethanol, has increased significantly since the launch of the PROALCOOL program in 1971, Figure 31, with land use typically shifting from livestock to cane production.

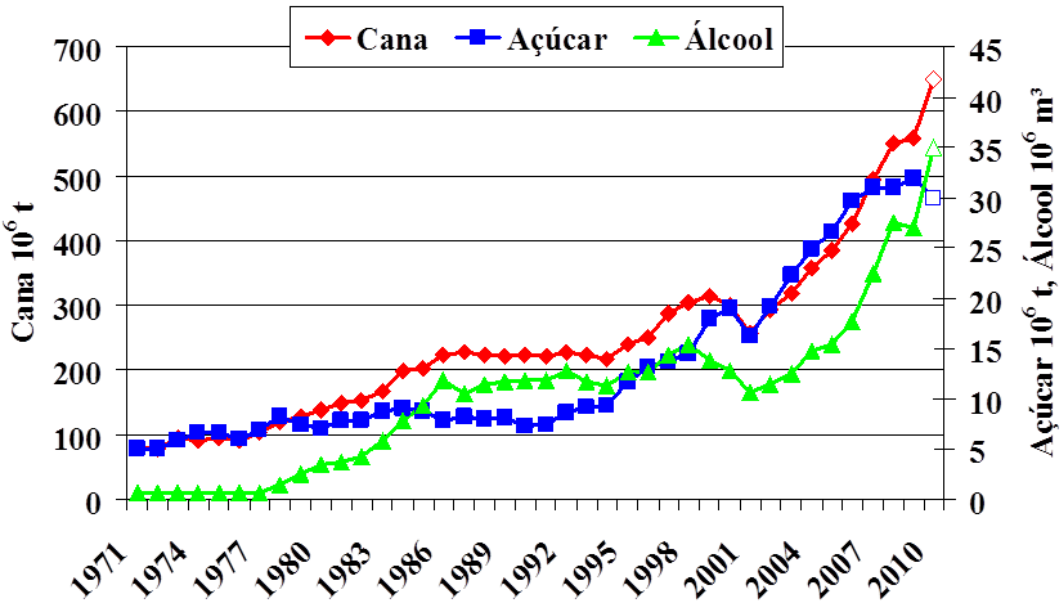


Figure 31: Expansion of the production levels of sugarcane (cana), sugar (acucar), and alcohol (alcool).

The ethanol that is produced in sugar mills can either be sold as a fuel, mixed with petroleum, or sold for other end uses. The Brazilian Ministry of Agriculture, Livestock and Supply estimated that the ethanol production in the 2008/2009 season amounted to 27.3 billion litres with 13.3 billion litres being sold as hydrated ethanol for use in flex-fuel vehicles and 6.3 billion litres being mixed with gasoline (with a gasoline to ethanol proportion of 75:25).

Numerous varieties of sugarcane are grown commercially in Brazil. The types of varieties and the proportions that these contribute to total sugarcane production have changed over time as new varieties have been developed and older varieties become susceptible to diseases and pathogens. Organisations, such as CTC, are responsible for the development of new sugarcane varieties with the aim of improving the yield of biomass and sucrose and the resistance to pathogenic-attack. These varieties are designed and tested for their productivity in different soil, climatic, and cropping climates. Table 24 summarises the main sugarcane varieties that are currently grown on commercial scales in Brazil. These are classified according to the most appropriate copping or soil conditions for the crop.

Table 24: List of the major sugarcane varieties currently grown in Brazil. Classified according to the harvest period or soil fertility.

Early Harvest	Mid Harvest	Late Harvest	For Less Fertile Soils
SP80-3250	SP79-1011	SP79-1011	SP79-2313
SP80-1842	SP80-1816	SP79-2313	RB72-454
RB76-5418	RB85-5113	SP79-6192	RB78-5148
RB83-5486	RB85-5536	RB72-454	RB80-6043
RB85-5453		RB78-5148	RB83-5486
RB83-5054		RB80-6043	
		RB84-5257	

Table 25 shows information for the relative distribution between the top 20 sugarcane varieties in 2009. These varieties constitute 84.6% of the total sugarcane area under cultivation. Figure 33 presents pie charts summarising the distributions, within states, of the major different varieties. These compositions of these varieties have been determined but only for parameters relevant to sugar production, there has been no detailed study regarding the variations in lignocellulosic composition between the bagasses obtained, Figure 32, from these varieties. Table 26 does, however, present some relevant data pertaining to the yield of sugarcane, sugarcane trash (dry basis), and the trash/stalk mass ratio for three different sugarcane varieties that were sampled in the Piracicaba and Ribeirao Preto regions of Sao Paulo. Data are given for the first harvest (after 18 months) and for the harvest in the second and fourth year of production. It can be seen from Table 26 that these trash to stalk ratio can vary significantly between varieties, with the minimum being 11% (variety SP80-1842 in the first/fourth harvest) and the maximum being 17% (variety RB72454 in the fourth harvest), a relative difference of 54.5%.

Table 25: The proportions that the top 20 sugarcane cultivars contributed to the total sugarcane area under cultivation in Brazil in 2009.

Variety	% of Total Sugarcane Area Under Cultivation
RB867515	20.1
SP81-3250	12.1
RB72454	7.5
RB855453	6.7
SP83-2847	5.0
RB835486	4.4
RB855536	4.3
RB855156	3.2
SP79-1011	2.8
RB835054	2.5
SP80-1842	2.4
SP80-1816	2.3
SP80-3280	2.2
SP91-1049	1.6
DIVERSAS	1.6
RB92579	1.6
SP89-1115	1.2
RB845210	1.2
PO88-62	1.1
RB855113	0.8

Table 26: The sugarcane and trash yield and the trash to stalk mass ratio for three sugarcane varieties harvested in two regions in Sao Paulo over three harvests.

Variety	Stage of Cut	Sugarcane Yield (tonnes/ha)	Trash Yield (dry tonnes/ha)	Trash/Stalk Ratio
SP79-1011	1st harvest	120	17.8	15%
	2nd harvest	92	15.0	16%
	4th harvest	84	13.7	16%
SP80-1842	1st harvest	136	14.6	11%
	2nd harvest	101	12.6	13%
	4th harvest	92	10.5	11%
RB72454	1st harvest	134	17.2	13%
	2nd harvest	100	14.9	15%
	4th harvest	78	13.6	17%
Average		**104**	**14.4**	**14%**

Figure 32: Pictures of sugarcane bagasse, the harvest of sugarcane, and the retention of sugarcane trash on the field.

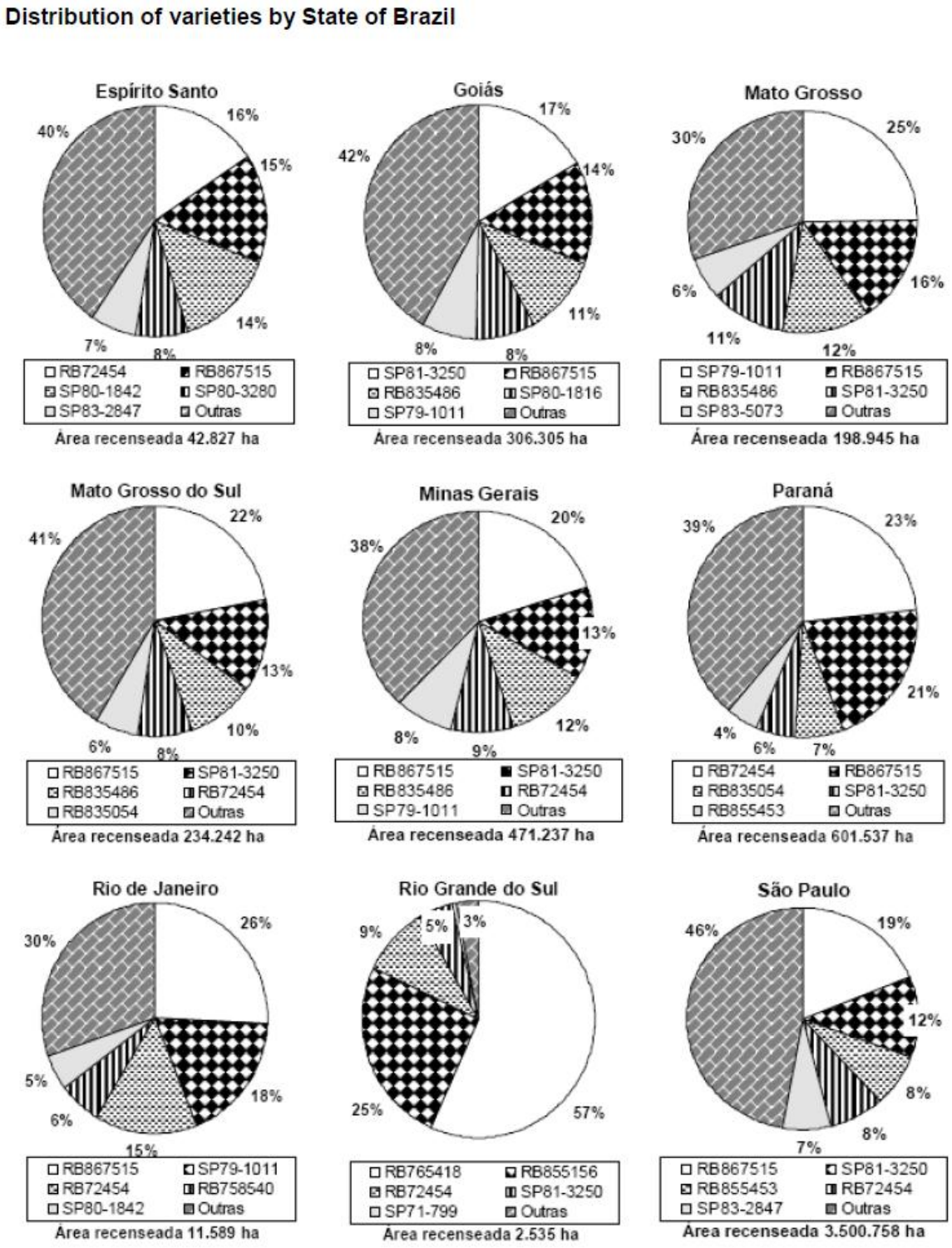


Figure 33: Distribution of sugarcane varieties according to state (2008/2009 season).

5.2.2 Sampling Strategy for Bagasse and Trash

Between July 2010 and November 2010 a total of 202 samples of sugarcane bagasse were collected from 16 different mills in Sao Paulo state, Figure 34. The bagasse was sampled directly from the process flow coming out from the final mill in the facility, Figure 35. In most cases it was not possible to identify the sugarcane variety that was being processed in the mill at the time of sample collection; however 9 different varieties were identified over the whole sample collection period. The samples were stored in airtight plastic bags that were kept in freezers at CTC for preservation. At a later point these samples were defrosted, the NIR spectra of the wet form of the samples was collected and the samples were then air dried, ground, and sieved, with several additional NIR spectra collected at different points in this sample preparation protocol. A subset of these prepared samples were then analysed via wet chemical techniques.

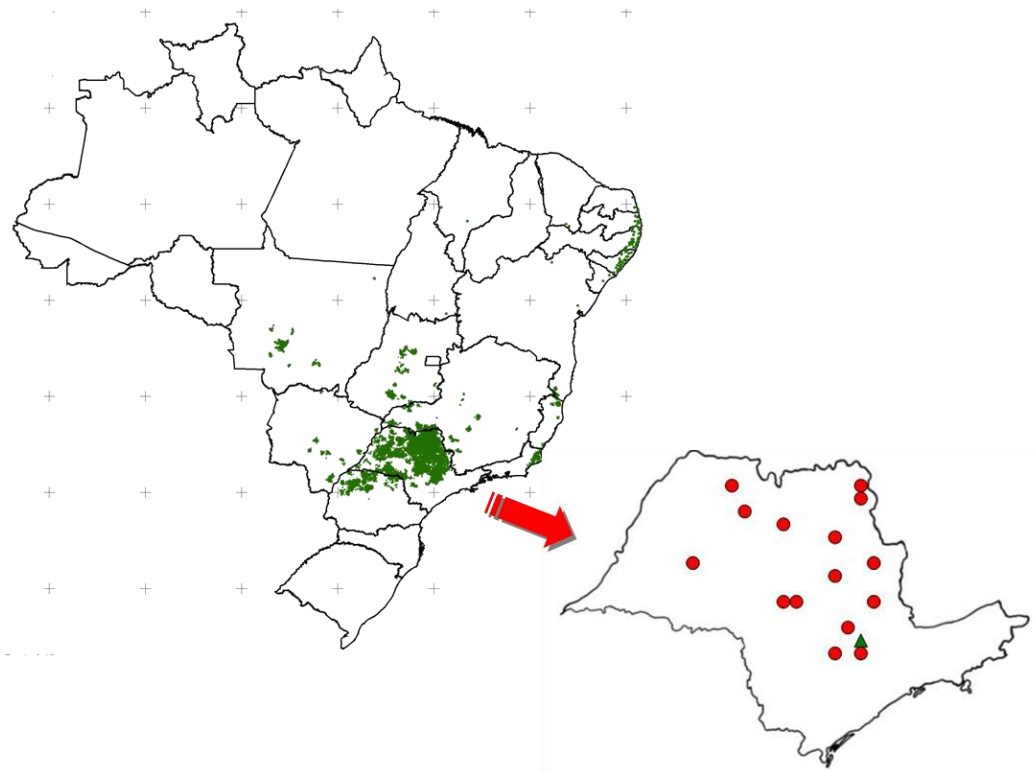


Figure 34: Map of sugarcane producing regions (green) in Brazil, top left, and of the sugar mills in Sao Paulo state (red circles) from which bagasse was sampled in the DIBANET project, bottom right. The location of DIBANET partner CTC is highlighted with a green triangle in the bottom right figure.

In the same period a total of 37 samples of sugarcane trash were also sampled. These were collected from experimental sugarcane plots at CTC as well as from commercial plantations after the mechanical harvest of the cane, Figure 35. It was not possible to identify the sugarcane variety for every sample that was collected, however at least 8 different varieties were identified when sampling sugarcane trash. These trash samples were stored, processed, and analysed in the same manner as the bagasse samples.

Figure 35: Sampling of sugarcane trash in the field (left), the point at which sugarcane bagasse was sampled at the sugar mill (right).

5.2.3 Analytical Results

5.2.3.1 Bagasse

Table 28 and Table 29 present some summary statistics and histograms for compositional parameters of bagasse. The histograms represent the distribution of component values, on a whole mass basis, across this data set. A model normal distribution is included, for comparison, as a red curve on these histograms. For all components the distribution statistics are provided in whole mass (WM) basis, and for relevant components these are presented on an ash free (AF) basis.

As expected, the major components of the bagasse samples analysed are glucose, xylose and Klason lignin. The concentrations of these components, provided in Table 28 and Table 29 are comparable to those in Table 23. The glucose sugars liberated in the hydrolysis step would primarily have come from cellulose whereas xylose would have come from hemicellulosic polysaccharides (xylans). The other hemicellulosic sugars that were analysed for in this experiment were arabinose, which had an average value of 2.17% on a whole dry mass basis, and galactose, which had an average value of 0.56% on a whole dry mass basis. The ratio of arabinose to xylose contents ranged from 0.07 to 0.12, within the ranges discussed in Section 5.2.1.2. The ratio of galactose to xylose contents ranged from 0.019 to 0.036. The other hemicellulosic carbohydrates analysed for, mannose and rhamnose, are only present in minor

quantities, as expected. Hence, the main hemicellulose in sugarcane bagasse appears to be arabinoxylan, as described in the literature.

Table 27 provides the correlations between many of the chemical components (the WM data were used in all instances), absolute *r* values greater than 0.5 are highlighted in bold. Some of the correlations are to be expected; for example the positive correlations between many of the ash components (e.g. acid insoluble ash and total ash), and the positive correlation between glucan and total sugars contents. There is a significant negative correlation (r = -0.724) between the ash and glucose content. As a reflection of this there are also negative relationships between glucose and: AIR (r =-0.658) and AIA (r =-0.688). Table 29 shows that the ranges in glucose and total sugars contents are significantly less when expressed on an ash-free basis compared with on a whole mass basis. Table 28 shows that that the histogram for ash content is highly skewed, with the majority of samples having ash contents less than 5% and a smaller number of samples having significantly higher ash contents. High ash contents in bagasse may be the result of the collection of significant amounts of soil material, in addition to sugarcane, due to poor harvesting practices.

The variations in sugars contents will result in significantly different yields if these samples were to be processed in biorefining technologies. For example, under the assumed yields of the DIBANET process (see Section 4.2.7), the yield would range from a minimum of 271 litres to a maximum of 333 litres per tonne of feedstock (a relative difference of 23%).

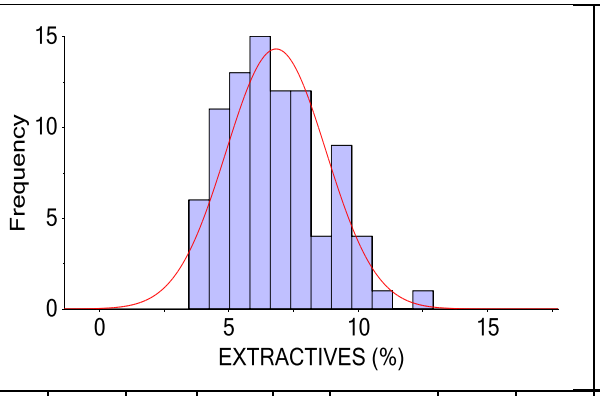
Given the operational frameworks of the sugar mills that the bagasse samples were collected from it was not possible to ascertain the variety of sugarcane that was being sampled nor whether it had been manually or mechanically harvested. Hence, it was not possible to determine compositional variations that may exist according to variety or harvesting practice. No statistically significant correlations were found between compositional parameters and date of sample collection.

For most constituents there was not a significant difference in the average compositions between different mills, however there were interesting variations in the average ash content between mills as illustrated in the quantiles plot in Figure 36.

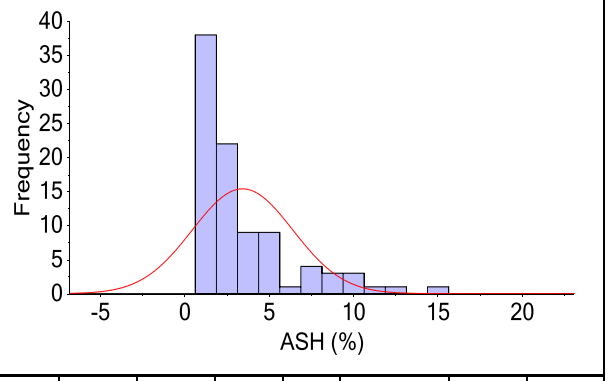
Table 27: Correlation coefficients between the various constituents for the sugarcane bagasse samples analysed. Absolute values greater than 0.5 are highlighted in bold.

	ASH	**KL**	**ASL**	**AIR**	**AIA**	**ARA**	**GAL**	**RHA**	**GLU**	**XYL**	**MAN**	**TOT**
EXTR	0.005	-0.387	-0.426	-0.204	0.092	-0.110	0.110	-0.002	-0.423	**-0.511**	0.120	**-0.509**
ASH		-0.409	-0.463	**0.770**	**0.844**	0.136	0.302	-0.008	**-0.724**	-0.458	0.215	**-0.693**
KL			0.174	-0.009	-0.447	-0.264	-0.372	-0.384	0.304	0.488	-0.092	0.388
ASL				-0.297	-0.416	0.308	0.058	0.286	0.424	**0.503**	0.012	0.523
AIR					**0.875**	-0.021	0.255	-0.200	**-0.658**	-0.473	0.421	**-0.646**
AIA						0.105	0.382	-0.063	**-0.688**	**-0.626**	0.414	**-0.713**
ARA							**0.628**	0.478	-0.149	0.213	0.173	0.063
GAL								0.359	-0.311	-0.316	0.405	-0.281
RHA									-0.051	0.028	0.315	0.022
GLU										**0.641**	-0.486	**0.937**
XYL											-0.332	**0.861**
MAN												-0.438

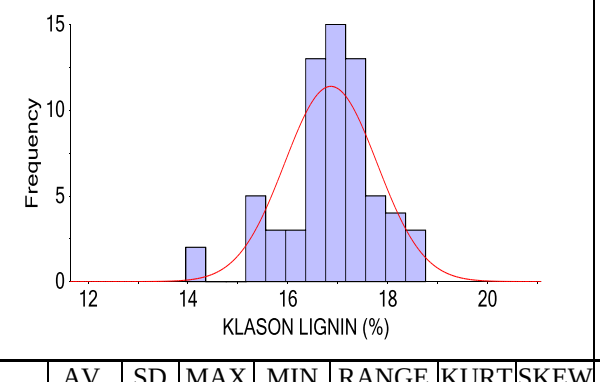
Table 28: Histograms and associated statistics for extractives, ash, Klason lignin, acid soluble lignin, acid insoluble residue, and acid insoluble ash for the bagasse samples analysed via wet-chemical means. WM = mass basis, AF = ash-free basis.



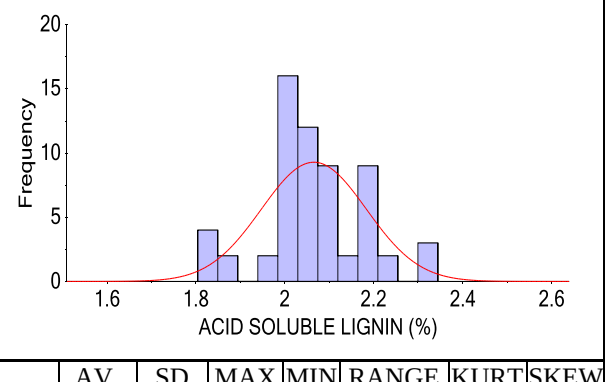
	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	6.83	1.93	12.90	3.46	9.44	0.02	0.49
AF	7.13	1.79	11.67	3.64	8.02	-0.39	0.23



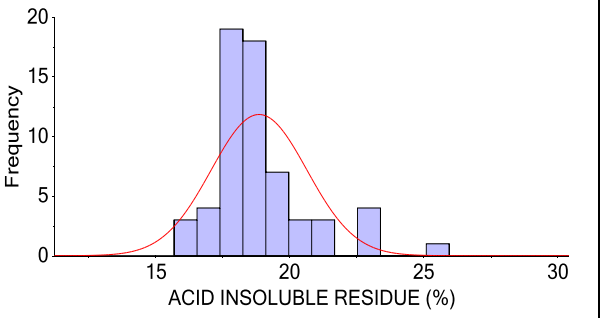
	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	3.43	2.99	15.66	0.63	15.03	3.32	1.85



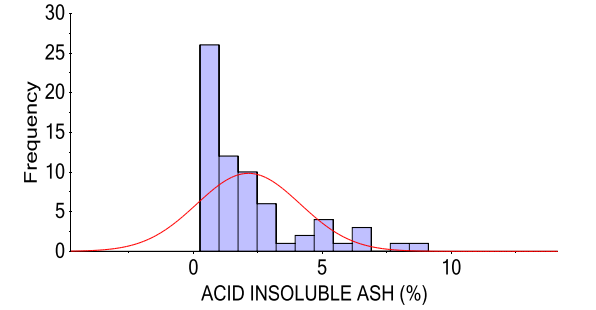
	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	16.87	0.92	18.76	13.96	4.80	1.28	-0.71
AF	17.59	0.95	19.95	14.64	5.31	2.13	-0.68



	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	2.07	0.12	2.35	1.80	0.54	0.38	0.05
AF	2.15	0.11	2.38	1.90	0.48	-0.24	0.05

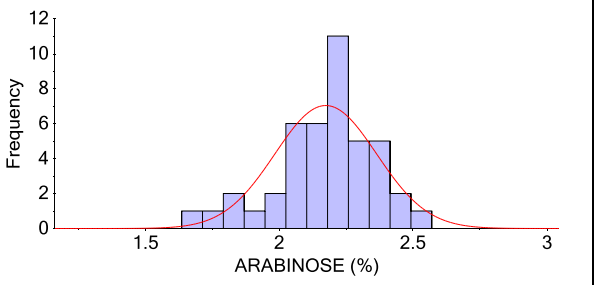


	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	18.86	1.79	25.96	15.70	10.26	4.01	1.73

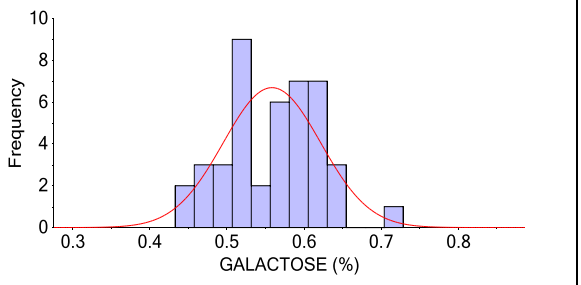


	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	2.15	2.01	9.13	0.27	8.85	2.05	1.61

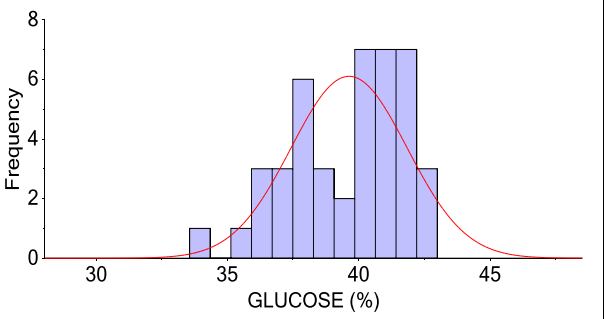
Table 29: Histograms and associated statistics for the structural sugars contents of the bagasse samples analysed via wet-chemical means. WM = whole mass basis, AF = ash-free basis.



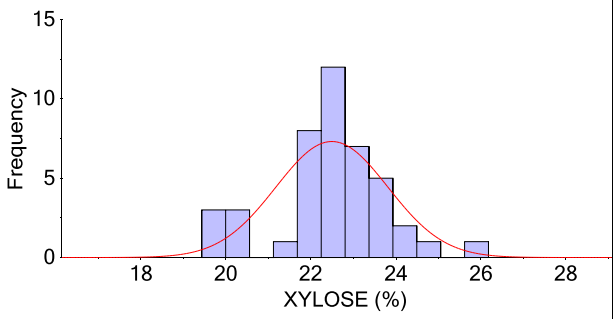
	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	2.17	0.19	2.57	1.64	0.93	0.76	-0.70
AF	2.27	0.22	2.83	1.65	1.17	1.41	-0.61



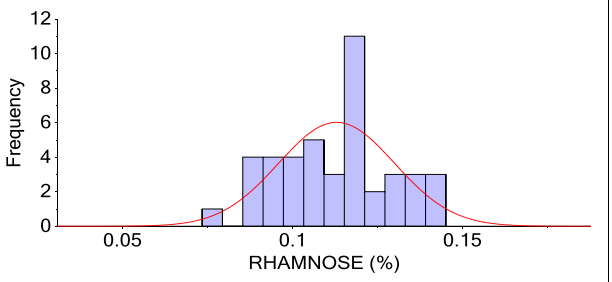
	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	0.56	0.06	0.73	0.43	0.30	0.02	0.10
AF	0.59	0.08	0.78	0.44	0.35	0.25	0.06



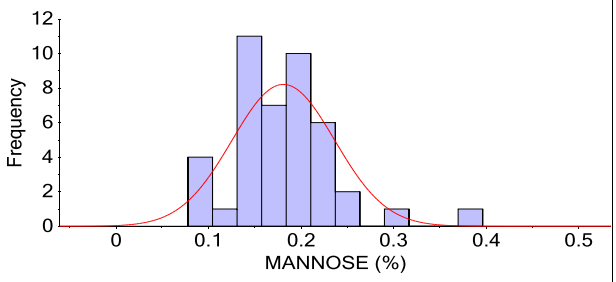
	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	39.65	2.21	43.01	33.57	9.44	-0.12	-0.64
AF	41.41	1.52	44.00	38.39	5.61	-0.81	-0.27



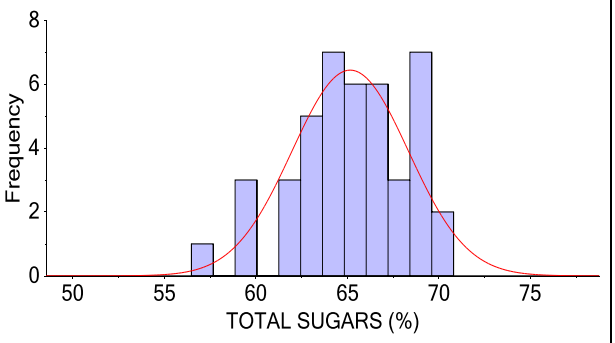
	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	22.50	1.32	26.19	19.44	6.75	1.20	-0.20
AF	23.53	1.22	26.55	20.21	6.35	1.22	0.15



	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	0.11	0.02	0.15	0.07	0.07	-0.47	-0.04
AF	0.12	0.02	0.16	0.07	0.09	0.14	-0.04



	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	0.18	0.06	0.40	0.08	0.32	4.46	1.32
AF	0.19	0.06	0.41	0.08	0.33	3.32	1.30



	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	65.17	3.18	70.82	56.50	14.33	0.14	-0.56
AF	68.10	2.24	72.76	63.86	8.90	-0.70	0.22

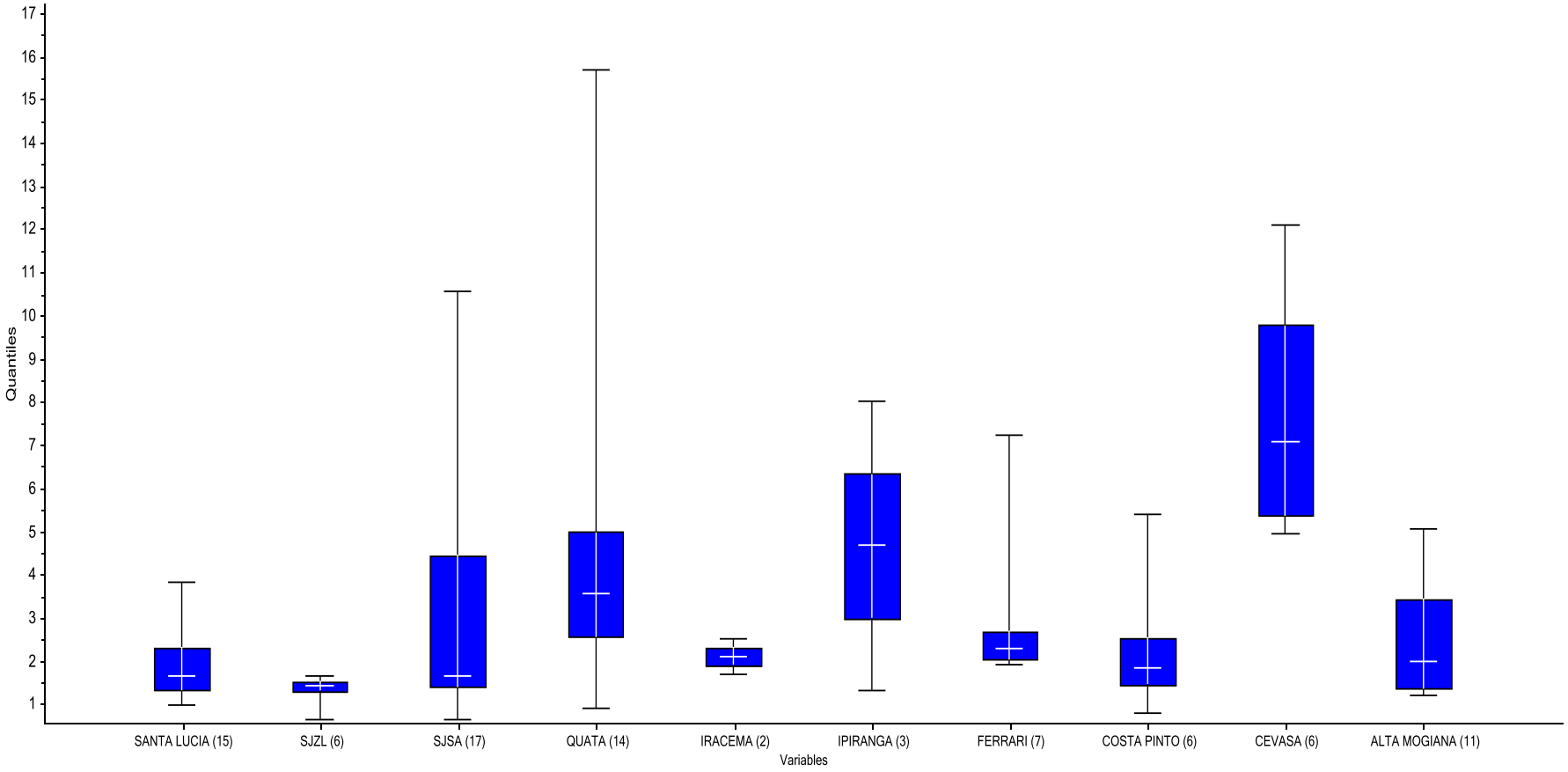


Figure 36: Quantiles plot for the ash contents obtained for bagasse samples collected from a number of mills (number of samples in brackets).

5.2.3.2 Trash

Table 31 and Table 32 present summary statistic and histograms for the sugarcane trash samples that were analysed. Some of these statistics are also presented, along with those for sugarcane bagasse, in Table 30.

Table 30: Summary statistics for the sugarcane bagasse and trash samples analysed. AVG = average, SD = standard deviation, KL = Klason lignin, ASL = acid soluble lignin, ARA = arabinose, GAL = galactose, RHA = rhamnose, GLU = glucose, XYL = xylose, MAN = mannose, TOT = total sugars. For each sample category and constituent the highest value is highlighted ion bold (except for the "MIN" category where the lowest value is highlighted in bold).

	EXTR	**ASH**	**KL**	**ASL**	**ARA**	**GAL**	**RHA**	**GLU**	**XYL**	**MAN**	**TOT**
AVG Trash	9.00	5.62	15.89	2.92	3.11	0.84	0.11	34.63	21.09	0.34	60.11
AVG Bagasse	6.83	3.43	16.87	2.07	2.17	0.56	0.11	39.65	22.50	0.18	65.17
MAX Trash	12.34	8.97	17.83	3.42	3.59	0.99	0.15	37.64	22.97	0.50	64.57
MAX Bagasse	12.90	15.66	18.76	2.35	2.57	0.73	0.15	43.01	26.19	0.40	70.82
MIN Trash	4.95	3.78	13.85	2.41	2.83	0.65	0.09	30.69	19.21	0.20	54.23
MIN Bagasse	3.46	0.63	13.96	1.80	1.64	0.43	0.07	33.57	19.44	0.08	56.50
Range Trash	7.38	5.20	3.97	1.01	0.76	0.33	0.07	6.95	3.76	0.30	10.35
Range Bagasse	9.44	15.03	4.80	0.54	0.93	0.30	0.07	9.44	6.75	0.32	14.33
SD Trash	1.84	1.34	0.92	0.24	0.20	0.08	0.01	1.53	1.06	0.07	2.37
SD Bagasse	1.93	2.99	0.92	0.12	0.19	0.06	0.02	2.21	1.32	0.06	3.18

Important observations about these trash samples are noted below:

- Lower values, compared to bagasse, for the average, maximum, minimum and ranges of the major sugars glucose and xylose. This results in the total sugars content also being lower.

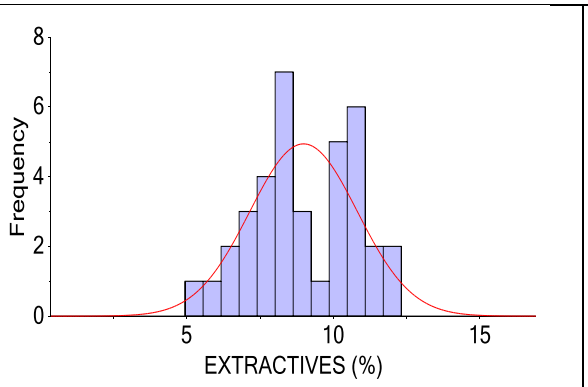
- Higher values for the minor polysaccharide sugars arabinose, galactose, and mannose.

- The net effect of these differences in sugar contents would result in the predicted yield of levulinic acid in the DIBANET process being 292 litres per dry tonne for an average trash sample compared with 317 litres per dry tonne for an average bagasse sample, a relative difference of 8.6%.

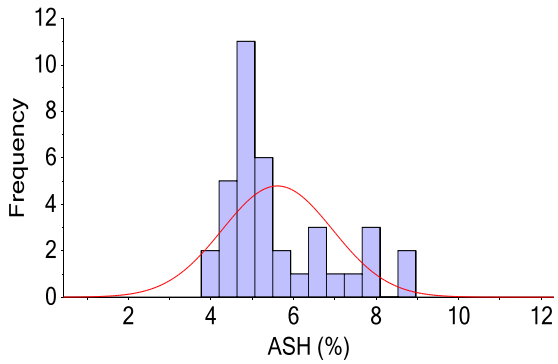
- Klason lignin contents tend to be lower in trash samples, compared with bagasse samples, however acid soluble lignin contents are higher.

- Ash and extractives contents that are, on average, higher than those of sugarcane bagasse but less varied.

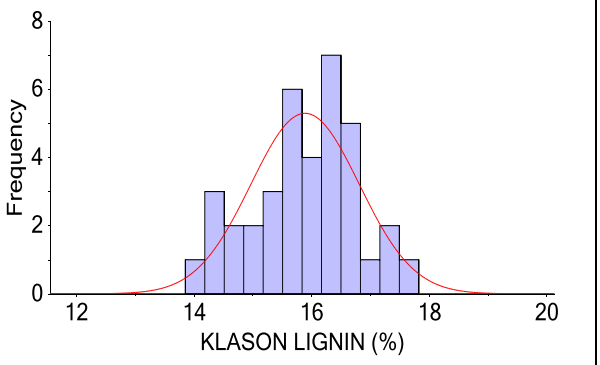
Table 31: Histograms and associated statistics for extractives, ash, Klason lignin, acid soluble lignin, acid insoluble residue, and acid insoluble ash for the trash samples analysed via wet-chemical means. WM = mass basis, AF = ash-free basis.



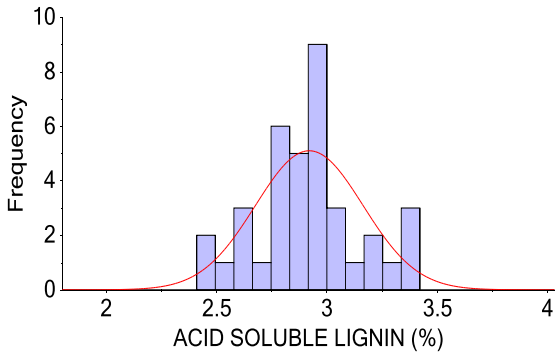
	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	9.00	1.84	12.34	4.95	7.38	-0.74	-0.18
AF	9.53	1.91	13.08	5.21	7.87	-0.62	-0.17



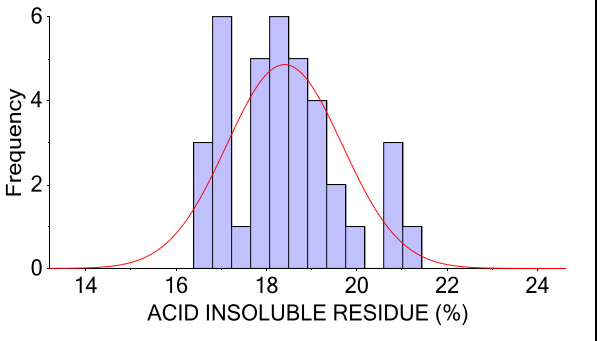
	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	5.62	1.34	8.97	3.78	5.20	0.28	1.14



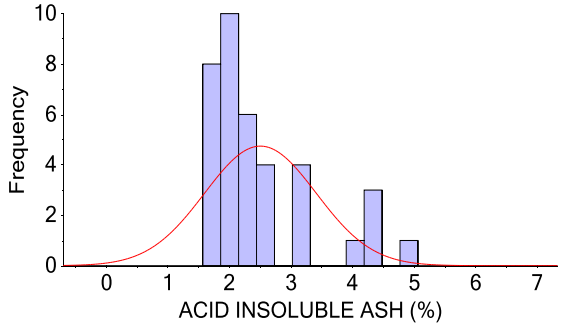
	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	15.89	0.92	17.83	13.85	3.97	-0.26	-0.26
AF	16.84	1.00	18.68	14.85	3.83	-0.78	-0.31



	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	2.92	0.24	3.42	2.41	1.01	-0.03	0.14
AF	3.09	0.26	3.63	2.54	1.09	-0.15	0.07

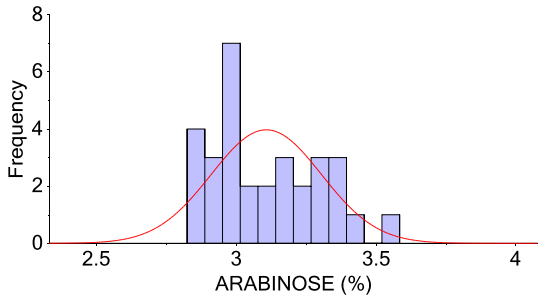


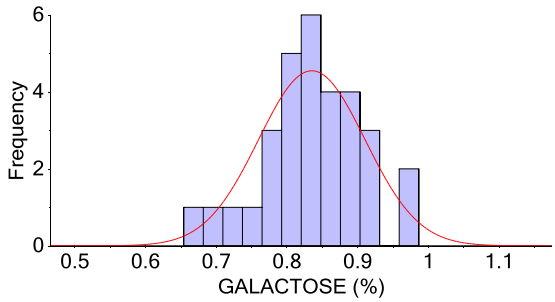
	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	18.41	1.28	21.45	16.40	5.05	-0.01	0.57



	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	2.51	0.91	5.07	1.57	3.50	1.07	1.39

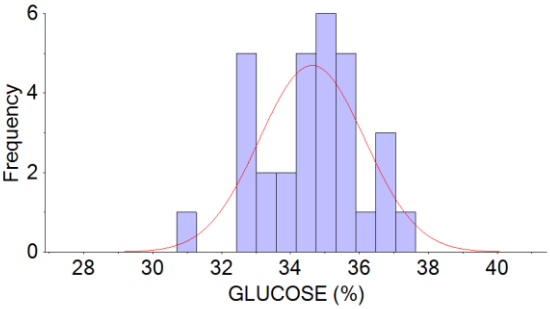
Table 32: Histograms and associated statistics for the structural sugars contents of the bagasse samples analysed via wet-chemical means. WM = whole mass basis, AF = ash-free basis.

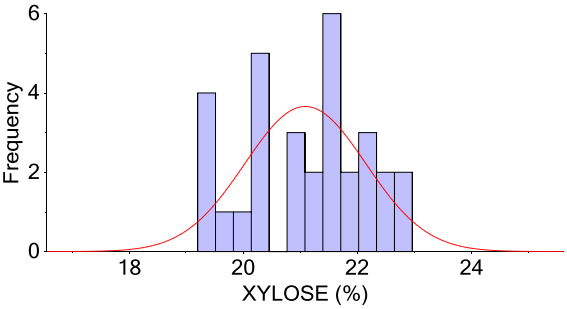




	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	3.11	0.20	3.59	2.83	0.76	-0.62	0.53
AF	3.29	0.20	3.74	2.98	0.76	-0.42	0.67

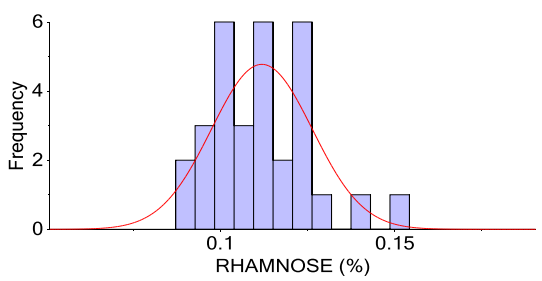
	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	0.84	0.08	0.99	0.65	0.33	0.27	-0.31
AF	0.88	0.08	1.07	0.70	0.37	0.83	-0.07

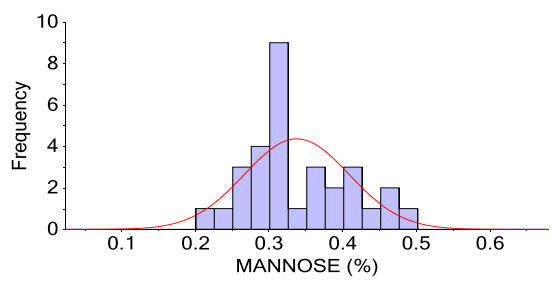




	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	34.63	1.53	37.64	30.69	6.95	0.25	-0.26
AF	36.62	1.50	39.28	32.28	7.00	1.31	-0.70

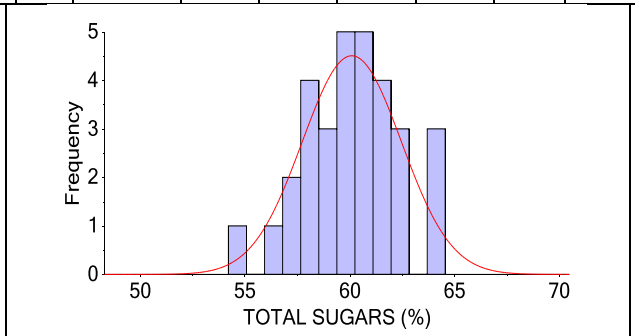
	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	21.09	1.06	22.97	19.21	3.76	-0.78	-0.18
AF	22.31	1.07	24.15	20.30	3.85	-0.75	-0.19





	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	0.11	0.01	0.15	0.09	0.07	1.26	0.74
AF	0.12	0.02	0.16	0.09	0.07	0.81	0.62

	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	0.34	0.07	0.50	0.20	0.30	-0.27	0.45
AF	0.36	0.08	0.55	0.21	0.33	-0.06	0.50



	AV.	SD	MAX	MIN	RANGE	KURT	SKEW
WM	60.11	2.37	64.57	54.23	10.35	0.13	-0.20
AF	63.58	2.30	67.64	57.04	10.60	0.89	-0.57

5.2.4 Discussion, Guidelines of Best Practice

Summary notes and guidelines (highlighted in green) are provided below:

- Both sugarcane bagasse and sugarcane trash have sufficient amounts of lignocellulosic sugars to justify their processing in hydrolysis biorefining technologies.

- The compositions of the bagasse samples that were analysed tended to be more varied than those of the trash samples analysed.

- Ash, in particular, can vary significantly in bagasse samples. There also seems to be a tendency for the ash contents of bagasse to be higher in some mills.

- The ash content can be particularly important for thermochemical biorefining technologies and also can affect the amount of acid required in acid-hydrolysis processes.

- Hence, it is recommended that careful determinations and observations, over a period of time, of the ash contents, associated with the harvesting/milling process of any mill that is being considered for a biorefining scheme, be carried out.

- Operational practices of sugar mills in Brazil do not allow the sampler to trace the bagasse sample being collected to a particular location, sugarcane variety, or harvesting practice. Hence, the effects of variations in these on lignocellulosic compositions, and the suitability of a sample for biorefining, cannot yet be ascertained.

- However, all commercial sugarcane variety development to date has focussed on traditional quality parameters related to sugar production (e.g. sucrose content). The increasing interest in the use of sugarcane residues for biorefining may allow for targeted improvements to be made in the relevant physicochemical characteristics in the future (e.g. increased cellulose content and reduced Klason lignin content for feedstocks intended for enzymatic hydrolysis).

- No significant relationship between harvest date and the lignocellulosic composition of the bagasse was found.

- All of the sugarcane trash should not be collected from the field since this will lead to deterioration in soil fertility. The amount of material that should be left in the field will depend on local characteristics and fertilisation practices (for example, if sugarcane vinasse is applied to the land then it may be acceptable to remove a larger amount of trash for biorefining).

- Using the average lignocellulosic compositions of sugarcane bagasse and sugarcane trash determined in DIBANET analyses along with the estimated arisings presented in Section 5.2.1.3 (165m dry tonnes of bagasse and 128m dry tonnes of straw), the total potential yields possible from processing these feedstocks in representative

technologies A-F are presented in Table 33. These potential levels of ethanol production are far in excess of the current ethanol output from sugarcane sucrose in Brazil (29 billion litres). However, using all of the bagasse and trash resources is neither practical nor environmentally acceptable. As discussed in Section 5.2.1.2 approximately half of the bagasse produced in a sugar mill will be required to supply process heat and steam for the production of sucrose and first-generation ethanol. Furthermore, all of the sugarcane trash should not be removed from the land or soil quality will deteriorate. However, even if the figures in Table 33 are halved, the potential production levels of ethanol/levulinic-acid from practicable resources of sugarcane residues are still large and will significantly increase (more than double) the ethanol output from sugarcane in Brazil.

Table 33: Potential ethanol and levulinic acid yields (in billion litres and petajoules (PJ) from processing all of the estimated sugarcane bagasse and sugarcane trash arisings in biorefining technologies A-F.

	Billion Litres of Ethanol					**Billion Litres Levulinic Acid**
	Tech. A	**Tech. B**	**Tech. C**	**Tech. D**	**Tech. E**	**Tech. F (DIBANET)**
Bagasse	36.6	52.4	56.4	44.2	68.2	52.2
Trash	26.3	37.1	40.0	31.4	48.8	37.3
TOTAL	62.9	89.5	96.3	75.6	117.1	89.6
	Total Energy Yield (PJ)					
Bagasse	771	1104	1187	930	1437	1075
Trash	554	781	842	662	1029	768
TOTAL	1325	1886	2030	1593	2466	1843

- The manual harvesting of sugarcane is being phased out in Brazil and other countries in favour of mechanical harvesting. This will mean that the crop will no longer be burnt prior to harvest meaning that the total quantities of trash resources available nationally will increase over time.

5.3 Banana Residues

5.3.1 Background

5.3.1.1 Components, Production, and Utilisation

Banana plantations are native in Southeast Asia regions and cultivated throughout the tropics. Bananas are the main fruit in international trade and the most popular one in the world, with an annual production of about 100 Mt. In terms of volume they are the first exported fruit, while they rank second after citrus fruit in terms of value. Banana plantations have been developed in approximately 115 countries, and are found in abundance in tropical and subtropical areas. The main exporters are located in South East Asia and South America (Table 34), with India leading the production. Brazil is in fifth position.

Table 34: World production of bananas.

Country	Area Harvested (ha)	Production (tonnes)	Yield (t/ha)
India	844,000	31.897.900	37.79
China	413,853	9.848.895	23.80
Philippines	449,610	9.101.340	20.24
Ecuador	215,647	7.931.060	36.78
Brazil	486,991	6.978.310	14.33
Others	2,361,843	36.357.314	15.39
World	4,771,944	102.114.819	21.40

Banana is the common name for the herbaceous plants of the genus Musa and is cultivated mainly for its fruit (159). Figure 37 provides an illustration of the main components of banana. It is a large herb, with a succulent, very juicy stem which is a cylinder of leaf-petiole sheaths composed of long fibres and strongly overlaps called pseudostems. Each pseudostem bears fruit only once before dying and being replaced by another pseudostem. The perennial portion of the plant which generates the new pseudostem is the rhizome. The pseudostem consists of concentric layers of leaf sheath and crown of large leaves which are amongst the largest of all plants. Each pseudostem can produce a bunch of bananas. The bunch are sustained by the stalk, also known as the peduncule.

Banana biomass residues comprise three main items which are the stalks, the peels and the pseudostems. About 30-40% of the fruits are discarded, and for each 1 Mg of harvested banana, approximately 4 Mg of lignocellulosic residues (3 Mg of stem, 160 kg of stalk, 480 kg of leaf and 440 kg of husks) are generated. Presently, this large amount of residues represents an important source of environmental contamination caused by the incorrect disposal and decomposition, producing harmful and odorous leaching, and gases (159). The

development of new applications for these agricultural residues could be an interesting income for banana producers and for a regional economy.

After harvesting, the pseudostem is traditionally wasted for which it is normally left in the soil plantation as organic fertilizer or mixed with the rejected fruits to make animal feed. Banana leaves are widely used as plates and for lining cooking pits and for wrapping food for cooking or storage. However, this will eventually turn into waste after it has served its purpose. Improved processes have made it possible to utilize banana fibre for many purposes such as paper, rope, table mats and handbags.

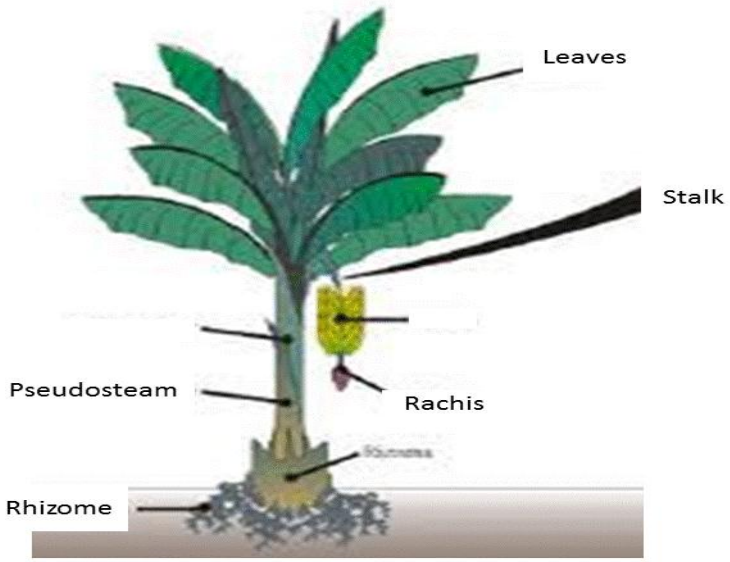


Figure 37: The main components of banana (Castro et al., 2008).

5.3.1.2 Bananas in Brazil

In Brazil, bananas are cultivated in all Brazilian states, from the coastal strip to the high lands of the interior, which leaves Brazil in fifth place in terms of world production. Most of the production comes from the Northeast, which produces 38% of the national total, followed by the Southeast (32%), North (11.7%), South (15%) and Midwest (4%) (Figure 38). Banana differs from other species of fruiting plants, it presents a continuous flow of production from the first year of cultivation, attracting producers who obtain a return on invested capital quickly.

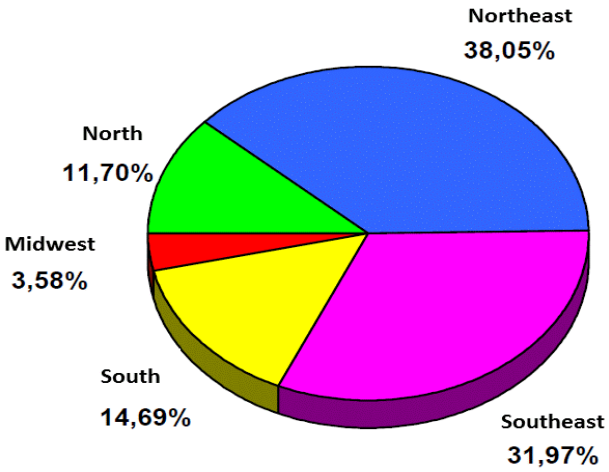


Figure 38: Brazilian production of banana by region (www.sidra.ibge.gov.br/bda/pesquisa).

Over the past thirty years, the banana production nearly doubled, from 277k ha in the harvest of 1978 to 486k ha in the harvest of 2010. In this year, the national harvest of banana represented a quantity of 6.98 Mt and an average yield of 14.4 tons per hectare, resulting in an increase of 2.9% and 2.8%, respectively, compared with data from the previous harvest (Figure 39).

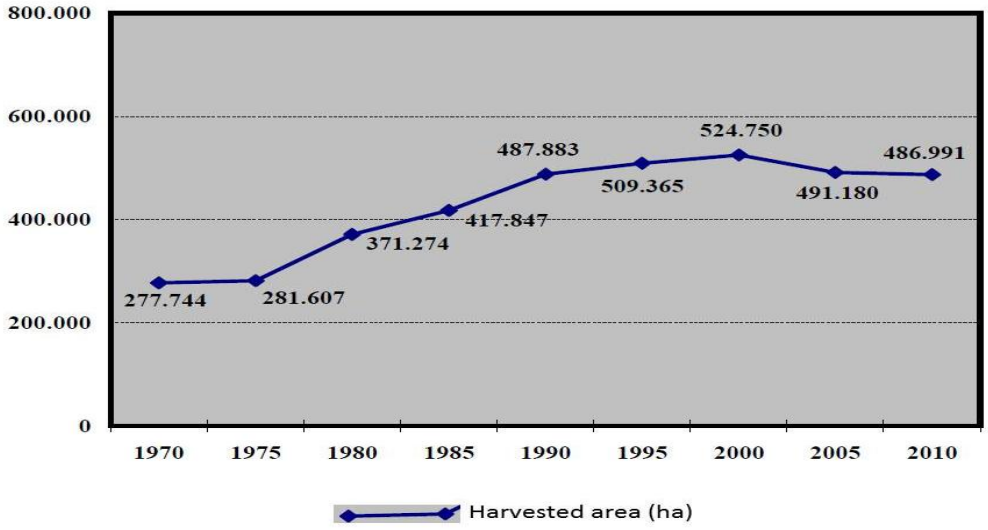


Figure 39: Banana production in Brazil (IBGE, 2011).

There are approximately 180 varieties of banana trees, and 35 of these occur in Brazil. The banana cultivars most widespread in Brazil are: Prata, Pacovan, Prata Anã, Maça, Mysore, Terra e D‟Angola, which are used solely for the domestic market; and Nanica, Nanicão and Grande Naine, used solely for exportation. On a smaller scale, are planted “Ouro‟ (AA), ”Figo Cinza‟ and “Figo Vermelho‟ (ABB), “Caru Verde‟ and “Caru Roxa‟ (AAA). The

Prata, Anã and Pacovan varieties are responsible for approximately 60% of the area cultivated with banana in Brazil. In Table 35 are shown the characteristics of the main varieties of banana in Brazil.

Table 35: Characteristics of the main varieties of banana in Brazil.(Cruz das Almas, 2004).

Characteristics	**Varieties**									
	Prata	Pacov.	Prata Anã	Maçã	Ouro	Nani.	Nanicã	Grande Neine	Terra	D'Angola
Postage	High	High	Med	Med-High	Med-High	Low	Med-Low	Med-Low	High	Med
Density (plants/ha)	1.11	1.11	1.66	1.66	1.66	2.50	1.60	2.00	1.11	1.66
Bunchweight (Kg)	14	16	14	15	8	25	30	30	25	12
Number of fruits/bunch	82	85	100	86	100	200	220	200	160	40
Number of bunches/bunch	7.5	7.5	7.6	6.5	9	10	11	10	10	7
Yield without irrigation(t/ha)	13	15	15	10	10	25	25	25	20	12
Yield with irrigation (t/ha)	25	40	35	na	Na	na	75	45	na	na

5.3.1.3 Lignocellulosic Analysis of Banana Residues in the Literature

Oliveira *et al*. (187) examined the chemical composition and structure of components from different morphological parts of 'Dwarf Cavendish' banana plant (petioles/midrib, leaf blades, floral stalk, leaf sheaths and rachis) to evaluate their potential as eventual raw materials for chemical processing. All fractions were characterised on carbohydrates, lignin, extractives, proteins and ash content. The results on general chemical composition of different morphological parts of banana are presented in Table 36.

The results of analyses showed a remarkable variability in structure and the amounts of the main macromolecular constituents. The pseudo-stem (leaf sheaths and floral stalk) presented a low content (about 13%) and particular structure of lignin. The leaf sheaths of the banana plant presented relatively high cellulose content (>37%). On the other hand, floral stalk, the other counterpart of pseudo-stem, differs significantly from leaf sheaths with a low proportion of cellulose. Therefore, the leaf blades contain, according to recently published results, unusually high amounts of lipophilic extractives, namely steryl glycosides that are valuable additives in functional food products. Most of the banana plant fractions contained also remarkable amounts (up to about 22%) of structural hemicelluloses (probably xylan and xyloglucan).

Bilba et al. (188) 2007 evaluated the composition of banana fibres (Table 37). Two parts of a banana-tree were studied, leaves (BL) and the pseudo-stem core (BC). Their results showed that BL samples contained less cellulose than BC, with the amount of hemicelluloses comparable for the samples. Lignin, extractives and moisture content were the highest for BL samples.

Table 36: Chemical composition of different morphological regions (%, dry weight).

Components	Petioles/midrib	Leaf blades	Floral stalk	Leaf sheaths	Rachis
Ash	11.6	19.4	26.1	19.0	26.8
Extractives[a]	5.9	16.1	17.6	12.6	17.6
Dichloromethane	1.2	5.8	1.4	1.4	1.5
Ethanol/toluene	0.9	2.6	1.1	2.1	1.4
Water[b]	3.8	7.7	15.1	9.1	14.7
Lignin	18.0	24.3	10.7	13.3	10.5
Insoluble[a]	16.8	22.0	9.8	12.6	9.6
Soluble	1.2	2.3	0.9	0.7	0.9
Holocellulose[a]	62.7	32.1	20.3	49.7	37.9
Hemicellulose A[a]	14.8	6.7	2.8	7.2	3.9
Hemicellulose B[a]	6.7	1.9	2.7	4.2	3.6
α -Cellulose[a]	39.5	20.7	14.4	37.1	28.4
Cellulose[a]	31.0	20.4	15.7	37.3	31.0
Pentosanes[a]	16.2	12.1	8.0	12.4	8.3
Starch	0.4	1.1	26.3	8.4	1.4
Proteins	1.6	8.3	3.2	1.9	2.0

[a] Corrected for ashes content; [b]Corrected for starch content.

Table 37: Botanical composition of studied fibers (wt%).

Sample	Leaves (BL)	Pseudo-Stem Core (BC)
Cellulose	25.75±1.42	31.27±3.61
Hemicellulose	17.08±1.11	14.98±2.03
Lignin	24.84±1.32	15.07±0.66
Partial Amount, PA	67.67±3.85	61.32±6.30
Extractives	9.84±0.11	4.46±0.11
Moisture	11.69±0.03	9.74±1.42
Ashes	7.02±0.79	8.65±0.10
Sum[a]	96.22±4.78	84.77±7.93

Between brackets, 95% probability confidence intervals assuming a normal distribution. [a] Cumulative standard deviation (SD).

Cordeiro et al., (189) studies the potentialities of banana pseudo-stems growing in Madeira Island (Portugal). First, the raw material was both studied as a whole (type I) and as the outer bark part (type II), which is richer in cellulose fibres. The main components of the two types of material were quantified, and showed that the polysaccharide content was high enough (about 60–70%), and that the lignin content was very low (approximately 12%). The only discouraging finding was the relative high amounts of ashes and extractives, 14.1% and 8.1%, for the whole material (type I) and outer bark material (type II), respectively, corresponding mainly to polar extractives (95–96% of the total extractives) (see Table 38). These values are relatively high when compared with other feedstocks. Nevertheless, in some cases the amount of extractive components can be very high as for example for C. cardunculus L., 15–18% (190), or Arundodonax, 14–23% (191).

The results of the monosaccharides composition analysis from pseudo-stem shows that glucose is the predominant monomer in this raw material with 74%, followed by xylose (13.1%), arabinose (9.1%), galactose (2.5%) and mannose (1.3%).

Table 38: Chemical composition of banana crops (% w/w).

	Ashes	**Extractives**			**Lignin**	**Holocellulose[a]**	**Cellulose[a]**
		Diethyl ether	Ethanol/toluene	Water			
Type I	13.9	0.6	4.6	8.9	12.0	60.1	34.5
Type II	14.6	0.4	2.3	5.4	12.7	65.2	40.2

[a]Corrected taking account residual lignin. The relative errors of these data are in the range of ± 2-3%. Type I: the whole material. Type II: the outer bark material, which seemed to be richer in fibres.

Guimarães et al. (192) studied fibres from Brazil, the results available are show in Table 39.

Table 39: Chemical composition of banana fibres.

Component (%)	**Banana**
Moisture	8.57±0.19
Ash	4.14±0.92
Holocellulose	50.92±0.34
Cellulose	50.15±1.09
Hemicelluloses	0.77±0.58
Klason lignin	17.44±0.19
Crystallinity (%)	39

Arredondo *et al*. (193) evaluated the ethanol production from banana fruit and its lignocellulosic residues. The results obtained in the energy evaluation show a positive energy balance for the four production routes evaluated; therefore, they can be considered renewable energy sources. The banana fruit and its organic residues are feedstocks that can be used to produce ethanol through hydrolysis, fermentation and distillation.

5.3.1.4 Environmental Considerations

Bananas residues give the advantage of producing a renewable feedstock for biofuels/bioproducts, so reducing the environmental issues that the world is now currently dealing with, such as global warming and air pollution. Bananas residues consist of the by-products resulting from harvesting and processing as well as the fruit itself (when discarded due to imperfections which make them unsuitable for sale). A portion of the waste is intended for animal feed, but significant amounts normally are dumped in landfills, river, oceans and unregulated dumping grounds forming huge masses of putrefying wastes that attract rodents, insects, scavengers, spread diseases, contaminate water sources and generate fouls odours.

This environmental impact can be reduced greatly by converting these residues and waste into chemicals.

The feedstock can be beneficial to many tropical developing countries not only in Brazil, but other countries like India, Indonesia and Malaysia where bananas are abundant. With the increasing fuel price and depleting fossil fuels, biorefining offers an option for waste management that yields green energy that can contribute to the growth of a country's economy and also a boost to supporting industries such as fertilizer and food production. The banana hydrolysate produced can be used for levulinic acid production, diesel miscible biofuels, bioethanol and other important chemicals. Analyzing the environmental considerations, Brazil has the potential to convert banana residues to energy as the process requires simple infrastructure, the feedstock is easy to be handled and has a high content of carbohydrates.

5.3.2 Sampling Strategy for Banana Residues

One hundred and three samples of banana residues have been collected. The banana residues were from different botanical fractions (stem, stalk, leaf, rhizome, husks and rachis) collected during the period March 2010 to March 2012 in Brazil. Fifty three of the samples originated from the North and Northeast regions, while 50 came from the South and Southeast. The sample set included distinct cultivars, such as: Prata, Pacovam, Prata Anã, Maça, D"Angola, Nanica, Terra, Grande Neine, Ouro, Preciosa, Calipso, Maravilhaand Caturra (see Table 40).

Table 40: Summary of the total number of samples collected/received.

Variety	Stem	Stalk	Leaves	Rhizome	Rachis	Husks	Total
Maça	6	14	2	5		1	
Nanica	2	4					
Ouro	2	3				1	
Prata	2	4					
Caturra	1	2	2		1		
Bucaneiro	1	1					
Calipso	1	1					
Prataanã	1	1					
Grande Neine	1	1					
Terra	2	1	2				
Pacovam	1	1					
Preciosa	1	1					
Maravilha	1	1					
-*	17	13			2		
Total	39	48	6	5	3	2	**103**

**unidentified*

5.3.3 Analytical Results

Table 41 and Figure 40 present, respectively, the compositional data for the various anatomical fractions of banana and histograms for compositional parameters of bananas, determined via reference analytical (wet-chemical) methods as part of the DIBANET project.

There are several important observations regarding the information in Table 41 and Figure 40:

- Glucose is the largest constituent in all plant fractions; this carbohydrate is clearly representative of cellulose, which is the major polysaccharide in Banana residue.

- Xylose is the second most abundant carbohydrate in the samples, 12-18% of the total mass balance of the whole plant (WP), followed by arabinose with 3-11%. The concentration of galactose is approximately 2 or 3 times less, in the whole plant, than that of arabinose, whilst mannose and rhamnose are minor constituents. This suggests that, as outlined in the literature, the hemicellulose in banana is probably xylan and xyloglucan (187).

- The arabinose concentration varies according to the plant fraction. Arabinose is proportionately greatest in Banana leaves and rhizome compared with the stems and stalk. The same occurs for galactose, with high concentration in the leaves and rhizome fractions.

- The xylose concentration is the same for leaves and rhizome, however, in smaller concentrations than that of the other botanical fractions.

- After cellulose and hemicellulose, lignin is the most abundant polymer in these plant fractions. The values for the lignin content found in banana plant, 9–23%, are those typically reported for a large variety of gramineaceous species and very similar to the values found in other annual plants (9–26%) or in non-wood fibres (12–24%) (190, 191). Interestingly, the lignin content varies significantly in different fractions of the banana plant (Table 41).

- Again, leaves and rhizomes present the same and the highest content of lignin, compared against other fractions. This is expected given that more structural support is required in these fractions, especially for the rhizome.

- The leaves of the plant are more focussed towards photosynthesis, with highest extractives content. These results are consistent with those found in the literature (187, 188).

- The lowest lignin content was determined in the stem and stalk fractions.

- Acid soluble lignin (ASL) follows an inverse relationship with Klason lignin (KL) for the rhizome fraction.

- The total sugars content follows different trends to the KL content. It is lowest in the stem and stalk fractions. However, in contrast to KL, its content is consistently greater in the stalk and stem.

- All morphologic parts of banana plant contained considerable amounts of ashes (3-10%). The high ash content in stem and rachis is, probably, due to their important function in nutrient transport.

- The extractives content is greatest in the stem and leaf as would be expected given that the leaves' primary role is for photosynthesis and the assimilation of primary metabolites (132).

- The total mass balance for the samples ("TOTAL") represents the sum of the following contents: Extractives, ash, total sugars, KL, and ASL. AIA and AIR are not included because these are represented in the ash and KL concentrations. It can be seen the total mass closure for all samples is less than 100% and is significantly lower for the leaf and stalk samples (where it is less than 80%) than it is for the other plant fractions. The remainder of the mass balance could come from uronic acids and acetyl groups liberated from the acid hydrolysis of hemicellulose, and extractives components that are not soluble in 95% ethanol but will be present in the hydrolysate.

- A hot water extraction step may be employed instead of, or as a precursor to, ethanol extraction. Given the amount of laboratory work involved in the extraction of samples this was not considered to be practical for all samples.

- The total sugar results presented for the DIBANET project by UNICAMP are similar to those reported in the literature (187, 192). In some cases even higher, with carbohydrates content greater than 45% of the total composition.

5.3.4 Summary and Guidelines of Best Practice

- The banana fruit and its organic residues are feedstocks that can be used for biorefining technologies. Through these processes, agricultural waste can be used to produce ethanol and reduce environmental concerns. The stem, rachis and stalk fractions of the plant, when processed in biorefinery technologies, will provide higher chemical/biofuel yields. This is due to their higher total sugars contents and increased heating values.

- However, the leaves are not such a good resource due to the lowest sugars content (only 37%). The rhizome also cannot be used for biorefining processes because is not a residue, rather it is a part of the banana plant used for planting.

Table 41: Compositional data for banana fractions, whole biomass%.

Plant Fraction	Extr.	Ash	Mois.	Ara.	Gal.	Rha.	Glu.	Xyl.	Man.	Total Sugars	AIR	KL	ASL	AIA	TOTAL	Calor. Value
Average																
Stem	15.12	10.00	8.11	3.23	1.23	0.19	48.24	6.76	1.30	61.00	7.84	7.21	1.70	9.00	87.00	16.13
Stalk	12.53	9.70	9.39	3.34	1.70	0.32	34.62	8.73	3.74	52.40	9.90	8.90	2.80	0.8	79.00	15.53
Leaves	14.89	3.95	5.84	5.8	1.76	0.60	22.24	6.30	0.93	32.12	22.49	18.91	4.05	4.04	75.00	-
Rhizome	5.18	5.43	6.95	5.71	2.35	0.29	33.10	6.31	1.38	47.00	22.18	20.47	2.14	0.58	82.00	-
Rachis	10.69	9.96	9.81	3.88	1.46	0.32	33.80	9.46	1.59	45.11	11.19	10.27	2.67	0.99	81.00	-
Max																
Stem	27.96	6.67	12.09	3.31	1.49	0.22	48.52	7.16	1.79	61.06	20.06	10.87	2.22	2.00	-	-
Stalk	26.42	6.76	20.76	3.74	1.94	0.36	36.27	10.23	6.13	55.31	11.89	11.42	3.51	3.66	-	-
Leaves	18.54	3.67	6.54	5.94	1.77	0.63	22.55	6.51	0.96	38.37	27.06	22.23	6.05	7.62	-	-
Rhizome	8.93	3.74	9.30	5.83	2.42	0.29	33.53	6.42	1.53	49.73	19.11	18.93	2.29	0.92	-	-
Rachis	10.96	4.96	12.23	3.95	1.46	0.29	34.14	9.31	1.48	50.63	19.40	13.41	3.02	5.99	-	-
Min																
Stem	4.1	1.19	4.06	3.16	0.96	0.16	47.95	6.35	0.81	60.83	8.31	8.94	1.76	0.63	-	-
Stalk	2.74	3.88	4.38	2.93	1.53	0.29	23.27	6.05	1.89	41.05	10.20	9.32	2.76	0.98	-	-
Leaves	12.06	2.53	4.42	5.71	1.72	0.55	21.80	6.11	0.89	36.02	26.43	20.04	4.72	4.20	-	--
Rhizome	3.05	2.38	4.12	5.59	2.29	0.28	32.67	6.20	1.24	48.57	17.80	16.89	1.61	0.18	-	-
Rachis	10.42	4.08	7.39	3.77	1.42	0.28	33.37	8.98	1.47	49.31	12.54	11.51	3.01	1.03	--	-
Range																
Stem	23.86	5.48	8.03	0.15	0.53	0.06	0.57	0.81	0.98	0.23	11.75	2.53	0.46	1.37	-	-
Stalk	23.68	2.88	16.38	0.81	0.41	0.07	13.00	4.18	4.24	14.26	1.80	2.00	0.80	2.68	--	-
Leaves	6.48	1.14	2.12	0.23	0.05	0.08	0.75	0.40	0.10	2.30	0.53	1.20	1.30	3.20	-	-
Rhizome	5.88	1.36	5.17	0.24	0.13	0.01	0.96	0.20	0.30	1.20	1.35	2.00	0.58	0.74	-	-
Rachis	0.54	0.88	4.84	0.18	0.04	0.01	0.85	0.33	0.20	1.30	6.97	2.00	0.01	5.00	-	-
Standard Deviation																
Stem	0.28	0.07	0.12	0.05	0.01	0.03	0.23	0.10	0.08	0.45	0.10	0.10	0.00	0.20	-	-
Stalk	0.36	0.15	0.11	0.04	0.03	0.01	0.47	0.12	0.24	0.64	0.43	0.45	0.10	0.02	-	-
Leaves	0.24	0.03	0.06	0.11	0.05	0.01	0.20	0.11	0.02	0.50	0.21	0.20	0.11	0.01	-	-
rhizome	0.18	0.20	0.09	0.17	0.09	0.01	0.61	0.16	0.20	0.81	0.44	0.46	0.05	0.03	-	-
Rachis	0.50	0.32	0.09	0.13	0.03	0.00	0.55	0.25	0.01	0.94	0.53	0.40	0.02	0.13	-	-

Extr. = 95% ethanol-soluble extractives; Ara. = arabinose; Gal.= galactose; Rha. = rhamnose; Glu. = glucose; Xyl. = xylose; Man. = mannose; AIR = acid insoluble residue; KL = Klason lignin; ASL = acid insoluble lignin; AIA = Acid insoluble ash; Nitr = nitrogen; Total = mass balance.

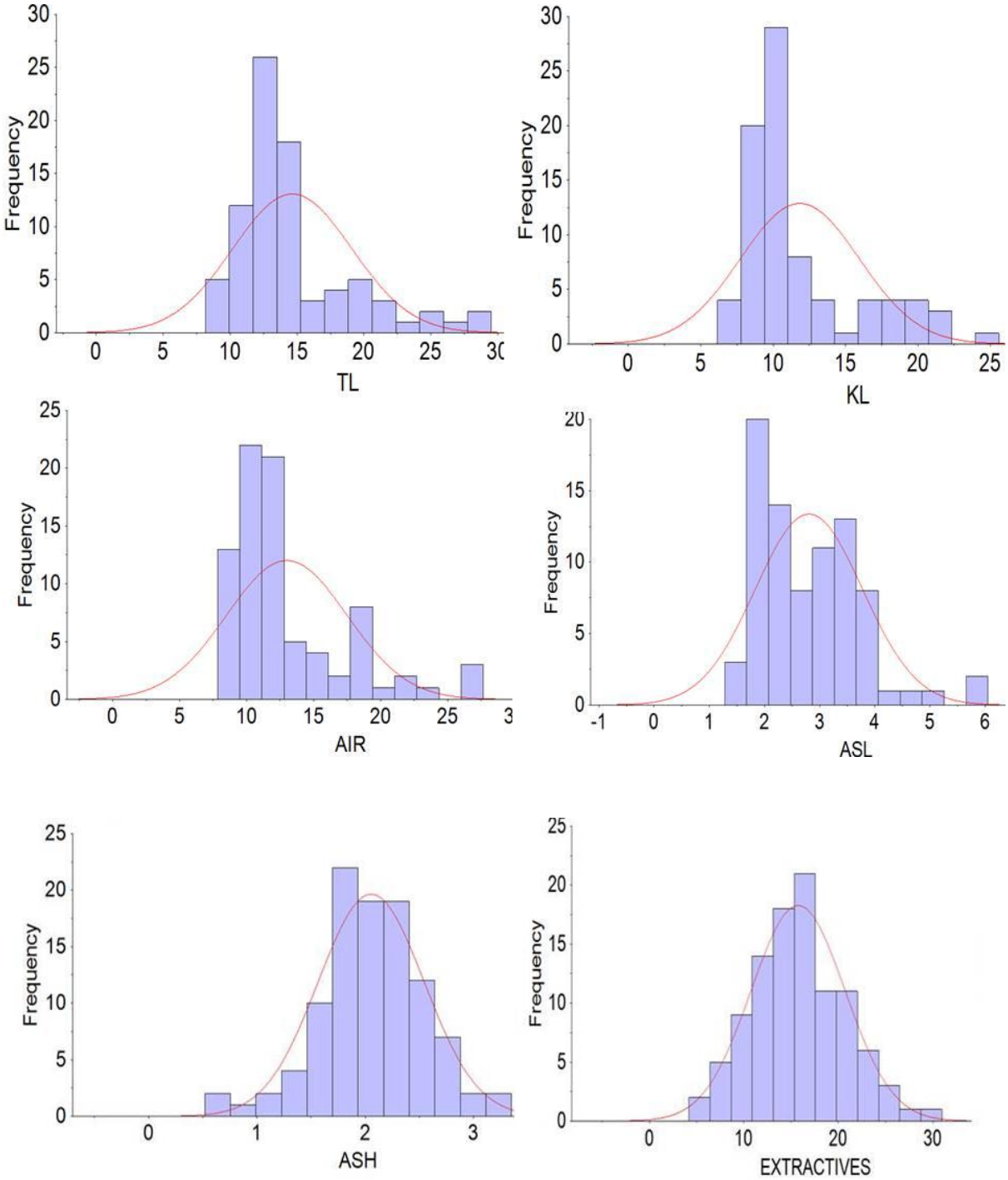


Figure 40: Histograms for extractives, lignin total (TL), Klason lignin (KL), acid soluble lignin (ASL), acid insoluble residue (AIR) , and ash for the banana samples analysed via wet-chemical means.

5.4 Coconut Residues

5.4.1 Background

5.4.1.1 Components, Production, and Utilisation

Coconut (*Cocosnucifera*) is a member of the palm family. It is grown in about 93 countries over an area of 11.8 million hectares (194). In the last decade, coconut increased without substantial alterations in planting areas. According to FAO (2011), in 1998, the world production was approximately 49 Mt, over a harvested area of 11.2 million hectares, whilst in 2010 the production was approximately 60.7 million tonnes, harvested in the same area; representing an increase of overall productivity.

About 80% of the harvested area with coconut is found in Asia (India, Philippines, Indonesia, Sri Lanka, and Thailand) and the remainder distributed among Africa, Latin America, Oceania and the Caribbean. Indonesia is the largest producer of coconut, followed by the Philippines and India. However, in area harvested, the Philippines stands out with greater acreage (Table 42).

Table 42: World production of cocounts, and total area harvested.

Country	Area Harv (ha)	Production (1.000 t)
Indonesia	2,950,000	19,500,000
Philippines	3,379,740	15,319,500
India	1,940,000	10,894,000
Brazil	287,016	2,759,044
Sri Lanka	394,840	2,210,800
Thailand	245,725	1,483,927
Mexico	178,500	1,246,400
Vietnam	138,300	1,086,000
Papua New Guinea	203,000	677,000
Malaysia	174,000	455,408
Others	1,339,505	5,081,057
World	**11,230,626**	**60,713,136**

When using irrigated production systems and appropriate pest management and plant nutrition, coconut production starts from the third year, reaching an average production of 200 fruits/tree,year from the seventh year, when production stabilises.

Coconut residues like husks are attractive due to their high proportions of well-defined polymeric structures of cellulose, hemicellulose and lignin with 28, 38 and 32.8%, respectively. Coconut-derived cellulose has been considered as one of the renewable sources for the production of environmental friendly bioethanol.

The coconut palm is used for decoration as well as for its many culinary and non-culinary uses; virtually every part of the coconut palm has some human use. Coconut shell is the non-food part of coconut, which is hard lignocellulosic agro-waste. Coconut shell is 15–20% of coconut. The coconut husk, or mesocarp, is composed of fibers called coir. The coir can be extracted from either mature or immature fruits, which constitutes about 25% of the nuts (usually 1.1 million tonnes of coconut husk are produced annually in the world). The inner stone, or endocarp, is the hardest part of the nut called shell. Adhering to the inside wall of the endocarp is the testa, with a thick albuminous endosperm, the white and fleshy edible part of the seed. Figure 41 shows the coconut composition.

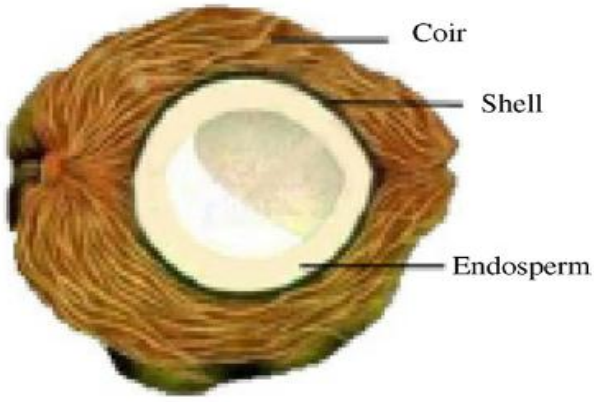


Figure 41: Illustration of the components of a coconut (195).

Brazil has a high potential for the production of coconut, producing annually about 1.5 billion coconuts (FAO, 2012), mainly in the northeast region, in a cultivated area of 273,810 ha. The annual yield of coconut per tree in Brazil is about 140 coconuts compared to 120 coconuts in several countries from Asia and Africa.

Coconut fibre is one of the least expensive among various natural fibers available in the world. It is not brittle like glass fibers, is amenable to chemical modification, and is non-toxic. But the waste from its disposal causes environmental problems, because the biomass in the form of coconut husks is often wasted, due to the lack of market development efforts. This is being looked into by many producing countries. The immature coir fiber is extracted and sold to industries or the husks are used in handcrafts. In Brazil, coir fibers are also substituting for fern trees (Samambaia tree, which is in danger of extinction) in being used for the production of pots for keeping young plants. The coir fibre and pith have been used for traditional fibre applications in woven carpets, ropes, brushes, and matting. Novel markets for the resistant coir fibre have been developed for erosion control mats and horticultural products.

In addition to financing and investment, implementation of residue utilisation technology requires the organization of the husk collection locally and marketing of the end-product. In many tropical countries coconut husks are abundantly available but not used economically. In other countries, like India and Sri Lanka, the coir industry is well established and provides labour and income in rural communities. In the Philippines, the concept of a fully integrated

coconut biorefinery plant has been worked out, combining the processing and marketing of food and non-food coconut products at local centralized conversion plants.

5.4.1.2 Coconut in Brazil

Coconut production has advanced on Brazil in recent years. In 1990 the country ranked 10th in the world ranking, with a production of around 477,000 tonnes of coconut. Currently the country is the fourth largest producer in the world with a production of about 2.8 million tonnes, harvested in an area of 287,000 ha of coconut trees. Brazilian production is responsible for more than 80% of total South American coconut production. This leadership position is given to the country by the increase in technological issues such as fertilization, intensive farming systems, improved varieties, which led to increased productivity and, especially, to the advancement of the agricultural frontier with coconut cultivation.

From Bahia, coconut production spread across the northeast coast, where favorable conditions for cultivation were found, and later ended up adapting in other regions of the country. In 1990 the coconut cultivation was restricted to North and Northeast regions. Nowadays, the cultivation of coconut trees is seen in almost all states of the Brazilian federation (Figure 42).

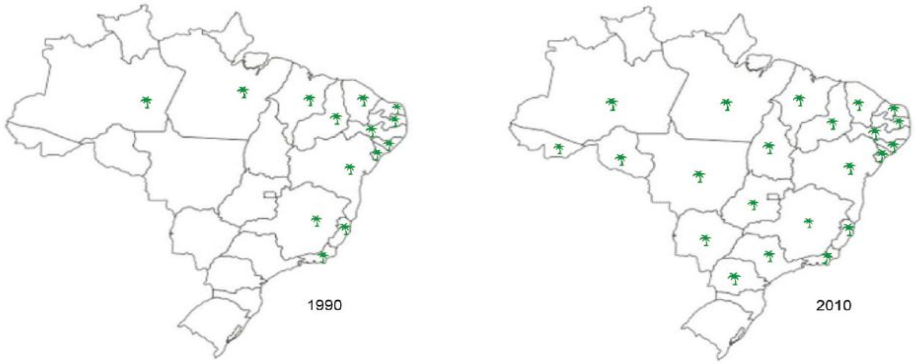


Figure 42: Advancement of coconut cultivation in the Brazilian states between 1990 and 2010.

Brazil has about 280,000 hectares under coconut production, distributed practically in almost all the national territory with production equivalent to two billion fruits (FAO, 2011). Even considering the increase in harvested area since 1990, the levels of production have increased significantly from the end of 1990 (Figure 43).

The productivity of coconut cultivation in Brazil has doubled from 1990 to 2009, from 3,400 fruits/ha to about 7,000 fruits/ha.

Coconut production in Brazil is growing rapidly, based on two different segments: the production of coconut for consumption of dried coconut and coconut production for fresh

coconut water. The planted area in the country is distributed among three coconut varieties: Gigante, Anão and the hybrid (the result of the intersection with Gigante and Anão), Figure 44.

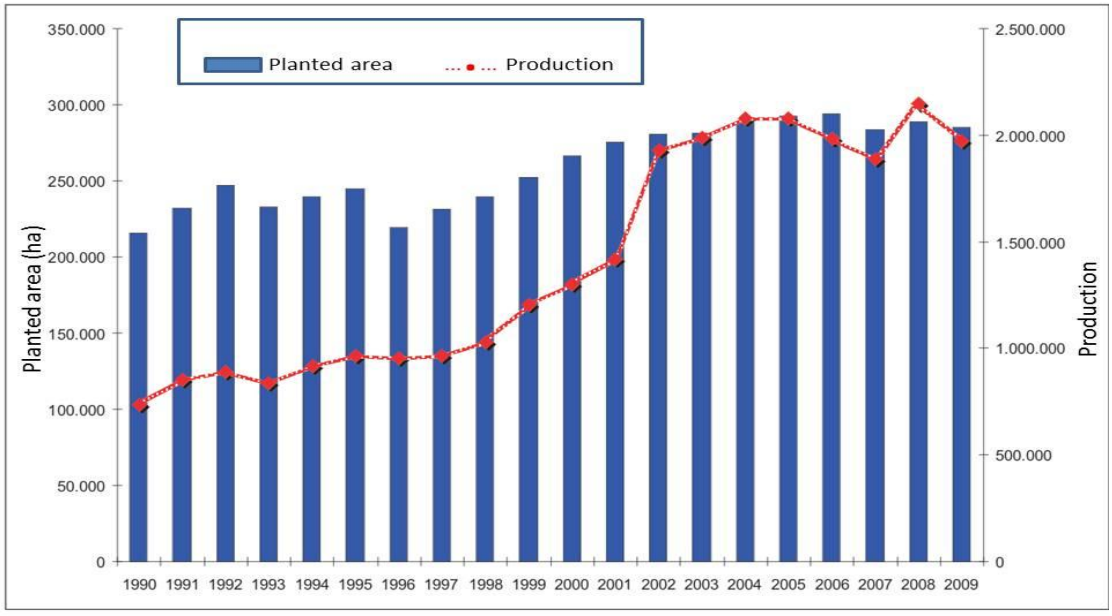


Figure 43: Planted area and production of coconut in Brazil from 1990 to 2009 (IBGE – Produção Agrícola Municipal, 2009).

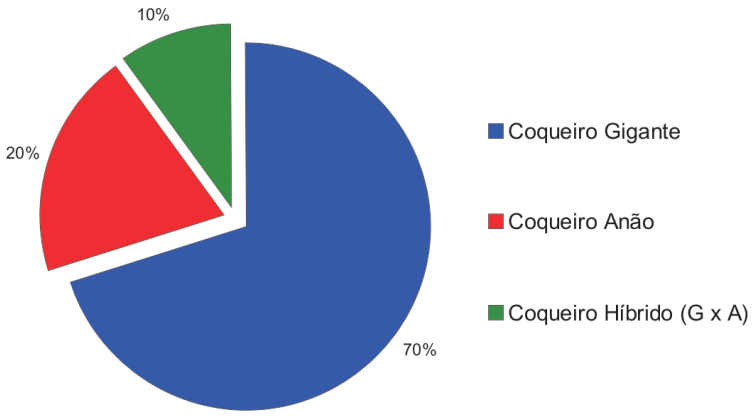


Figure 44: Distribution of varietal groups exploited commercially in Brazil (WANDERLEY e LOPES, 2010).

Figure 45 shows the different varieties of coconut. Figure 45 (A) represents the group of coconut variety "Gigante", also known as mestizo and/or common. Palm trees of this variety may reach 35m in height at maturity. They start to produce within 5 to 7 years of life and may

reach up to 70 years. The collection of this type of coconut occurs 11 to 12 months after flowering (196). Figure 45 (B) shows the Anão variety which presents a higher productivity than the Gigante group. According to Aragon *et al.* (196), these plants, starting production on average 2 to 3 years after planting, with an average yield of 150 to 200 fruits/tree,year and a lifetime of 30 to 40 years. Hybrids, the result from crossing varieties of Anão and Gigante, (Figure 45 (C)) have been successful. These hybrids have a number of advantages over the Gigante and Anão varieties Table 43).

Figure 45: Varieties of coconut (A) Gigante, (B) Anão, (C) Hybrids.

Table 43: Major agronomic characteristics of coconut varietal groups.

Characteristics	Varieties		
	Anão	**Hybrids**	**Gigante**
Start of flowering (years)	2-3	3-4	5-7
Life cycle	30-40	50-60	60-80
Fruit Size	Small	Intermediate	Big
Growing	Slow	Intermediate	Fast
Fruit production (fruits/tree,year)	150-200	130-150	60-80
Productivity of fruits (fruits/ha)	30,000-40,000	20,000-24,000	8,000-12,000

5.4.1.3 Lignocellulosic Analysis of Coconut Residues in the Literature

Vaithanomsat *et al.* (197) evaluated the potential of coconut husks for bioethanol production. The results showed that the coconut husk contained 39.31% alphacellulose, 16.15% hemicellulose, 29.79% lignin and 28.48% extractives. High lignin and extractive contents in the coconut husk indicated the need for pretreatment of this raw material prior to ethanol fermentation. Overall, the results showed that ethanol production from agricultural residues such as coconut husk was promising.

Van Dam *et al.* (198) analysed the constituents of fibre and pith fractions of coconut husk for polysaccharide (cellulose, pectin, and hemicellulose) and lignin contents (Table 44 and Table 45). Detailed carbohydrate analysis of the fibre indicated a glucose (cellulose) content of approximately 33% in the cell wall, together with 12% xylose as the major component of the hemicellulose fraction. Coir pith only contains 16% glucose. The effects of maturing on the chemical composition of the husk was analysed and a significant increase in glucose (cellulose) was observed, while for other sugars no dramatic change in relative amounts could be measured.

Table 44: Chemical composition of different coconut varieties and different fractions.

Variety	Hot water extractive (%)	Alpha cellulose (%)	Hemi-cellulose	Uronic acid (%)	Acid insoluble lignin (%)	Acid soluble lignin (%)	Total lignin (%)	Ash(%)
CATD Fibre	2.3 (0.1)	35.1 (0.3)	16.8 (0.3)	4.6 (1)	32.7(1.1)	1.0 (0.3)	33.6 (0.9)	2.6 (0.4)
CATD Pith	9.8	20.8	15.7	6.6	42.4	1.0	43.5	6.1
AGAT Fibre	2.9 (0.0)	35.1 (0.8)	17.4 (0.1)	3.8(1)	34.6 (0.1)	1.4 (0.1)	36.0 (0.1)	3.0 (0.3)
AGAT Pith	15.0	21.1	13.4	5.5	44.6	1.5	46.1	7.9
TGAT Fibre	2.0 (0.1)	34.9 (0.5)	17.6 (0.8)	4.9 (0)	34.5 (0.2)	1.3 (0.1)	35.8 (0.1)	1.6 (0.2)
TGAT Pith	11.9	22.7	16.6	5.7	43.7	1.3	44.9	3.5
LAGT Fibre	2.1 (0.2)	35.2 (0.3)	17.6 (0.5)	4.7 (2)	34.6 (0.5)	1.3 (0.1)	35.7 (0.8)	2.7 (0.2)
LAGT Pith	12.6	20.0	15.5	5.5	45.7	1.2	46.9	7.2
RIT Fibre	2.0 (0.4)	33.3 (0.2)	18.0(0.3)	4.8 (2)	35.4 (0.3)	1.3 0.1)	36.6 (0.1)	2.3 (0)
RIT Pith	12.6	20.5	15.00	5.3	45.9	1.4	47.3	5.5

Table 45: Sugar composition of coconut.

Fraction (wt. %)	Fibre	Pith
Arabinose	0.8	3.1
Xylose	12.6	3.7
Mannose	0.1	0.4
Galactose	0.3	1.8
Glucose	32.8	16.0
Rhamnose	0.1	0.2
Uronic Acid	4.2	7.1
Total	**46.7**	**25.2**

Two parts of a coconut-tree were also studied by Bilba *et al.* (188): the husks of the fruit shell (CH) and the "fabric" located at the bottom of the leaves (CF), coming from the young leaves' sheaths. For coconut, although partial amounts were equal, contribution repartition of cellulose, hemicellulose and lignin was not the same in husk and fabric fibres. Lignin content was higher in CH fibres while the relative amounts of cellulose and lignin were similar in CF fibres, showing that the CH fibres should be more rigid than CF fibres (Figure 46).

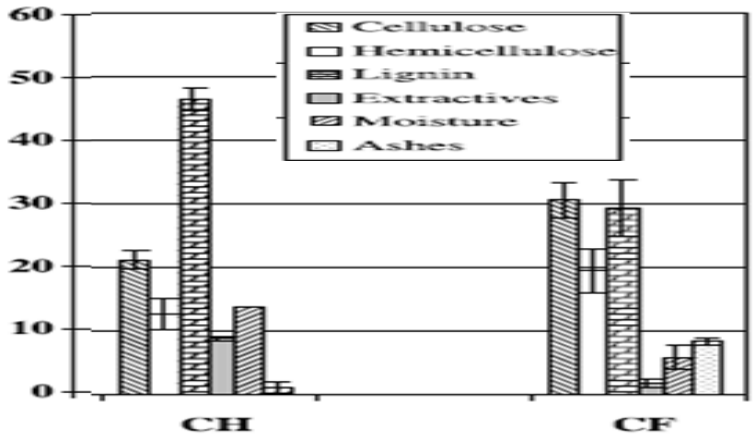


Figure 46: Bar diagrams of botanical components of coconut.

5.4.2 Sampling Strategy for Coconut Residues

Thirty samples of coconut residues have been collected. The coconut residues were from different botanical fractions (15 husks and 15 coir) collected during the period of March 2010 and August 2012 in Brazil. All of them originated from the North and Northeast regions. In most cases it was not possible to identify the coconut variety. The samples were stored in airtight plastic bags that were kept in freezers for preservation. At a later point these samples were defrosted, the NIR spectra of the wet form of the samples was collected and the samples were then air dried, ground, and sieved, with several additional NIR spectra collected at different points in this sample preparation protocol. A subset of these prepared samples were then analysed by wet-chemical techniques.

5.4.3 Analytical Results

Table 46 presents the compositional data, obtained in analysis by UNICAMP, for the various anatomical fractions of coconut. Figure 47 and Figure 48 present selected histograms of these data.

There are several important observations regarding Table 46:

- As expected, the major components of the coconut samples analysed are glucose and Klason lignin.

- The hemicellulosic sugars that were analysed in this experiment were xylose which had an average value of 13 and 16% on a whole dry mass basis for coconut coir and coconut husks, respectively; arabinose, with approximately 3.00% for both; and galactose, which had an average value of 1.6 and 1.0% on a whole dry mass basis, for coir and husks, respectively.

- The other hemicellulosic carbohydrates analysed for, mannose and rhamnose, are only present in minor quantities, as expected.

- High contents of ethanol extractives were determined (12-28%). The literature provides values for the content of hot-water extractives in fibres of 2-3% (198).

- Low amounts of ash content were found.

- Husks presented a higher content of total sugars and lignin than the fibres.

- The coconut husks have higher lignin contents than other biomasses, e.g. banana residues; therefore these will bear higher calorific values. The calorific value is higher in lignin and extractives since these contain less oxygen than the polysaccharides present in the holocellulose (cellulose and hemicellulose).

- Acid soluble lignin (ASL) follows a direct relationship with Klason lignin (KL) for the two fractions.

- The total sugars content follows a direct relationship with Klason lignin (KL) for the two fractions.

- The total sugars presented for the DIBANET project by UNICAMP show similar results to those reported in the literature (197, 198), with values greater than 37% of the total composition.

5.4.4 Summary and Guidelines of Best Practice

• Both coconut husks and coirs have sufficient amounts of lignocellulosic sugars to justify their processing in hydrolysis biorefining technologies.

• The compositions of the coir samples that were analysed tended to show more variation than those of the husks samples analysed.

• The low ash content in coconut samples, is a good parameter, since the high ash content affects the acid hydrolysis increasing the acid consumption and causes problems with corrosion during incineration if a high content of alkali metals are present. Ash also retards the enzymatic hydrolysis, since the ash cations would transfer into the solution and affect the cellulase activity.

• Overall, the results showed that the production of ethanol, levulinic acid, and other bioproducts from agricultural residues such as coconut husk and fibers is promising.

Table 46: Composition (% of dry matter) of different coconut fractions.

Plant Fraction	Extr. (%)	Ash (%)	Mois. (%)	Ara. (%)	Gal. (%)	Rha. (%)	Glu. (%)	Xyl. (%)	Man. (%)	Total Sugars	AIR (%)	KL (%)	ASL (%)	AIA (%)	Calor. Value
Average															
Coir	28.19	2.08	10.16	2.99	1.57	0.40	32.35	13.11	0.79	36.78	30.55	21.66	1.09	0.45	17.45
Husks	12.51	0.75	9.65	3.17	0.99	0.38	31.73	16.21	0.78	46.60	30.26	25.98	2.00	0.40	18.37
Max															
Coir	41.60	3.24	15.37	3.54	1.97	0.44	34.72	14.71	1.27	53.84	35.45	35.08	2.38	3.46	-
Husks	21.44	2.65	14.50	4.00	1.37	0.55	33.96	18.89	2.16	56.50	33.37	33.19	2.08	2.89	-
Min															
Coir	1.41	0.61	6.39	1.85	0.72	0.30	29.10	11.69	0.35	47.90	28.21	27.81	1.30	0.16	-
Husks	7.69	0.29	7.54	2.03	0.65	0.32	28.05	13.52	0.36	49.63	28.01	27.44	1.21	0.20	-
Range															
Coir	40.19	2.36	8.98	1.69	1.25	0.14	5.62	3.02	0.92	5.94	7.24	7.19	1.08	3.3	-
Husks	13.75	2.3	6.96	2.00	0.72	0.54	5.91	5.37	1.80	6.87	5.37	5.75	0.87	2.69	-
Standard Deviation															
Coir	0.55	0.20	0.12	0.22	0.12	0.02	0.42	0.27	0.09	0.35	0.27	0.31	0.08	0.20	-
Husks	0.62	0.07	0.12	0.23	0.08	0.03	0.71	0.27	0.10	0.83	0.21	0.73	0.07	0.05	-

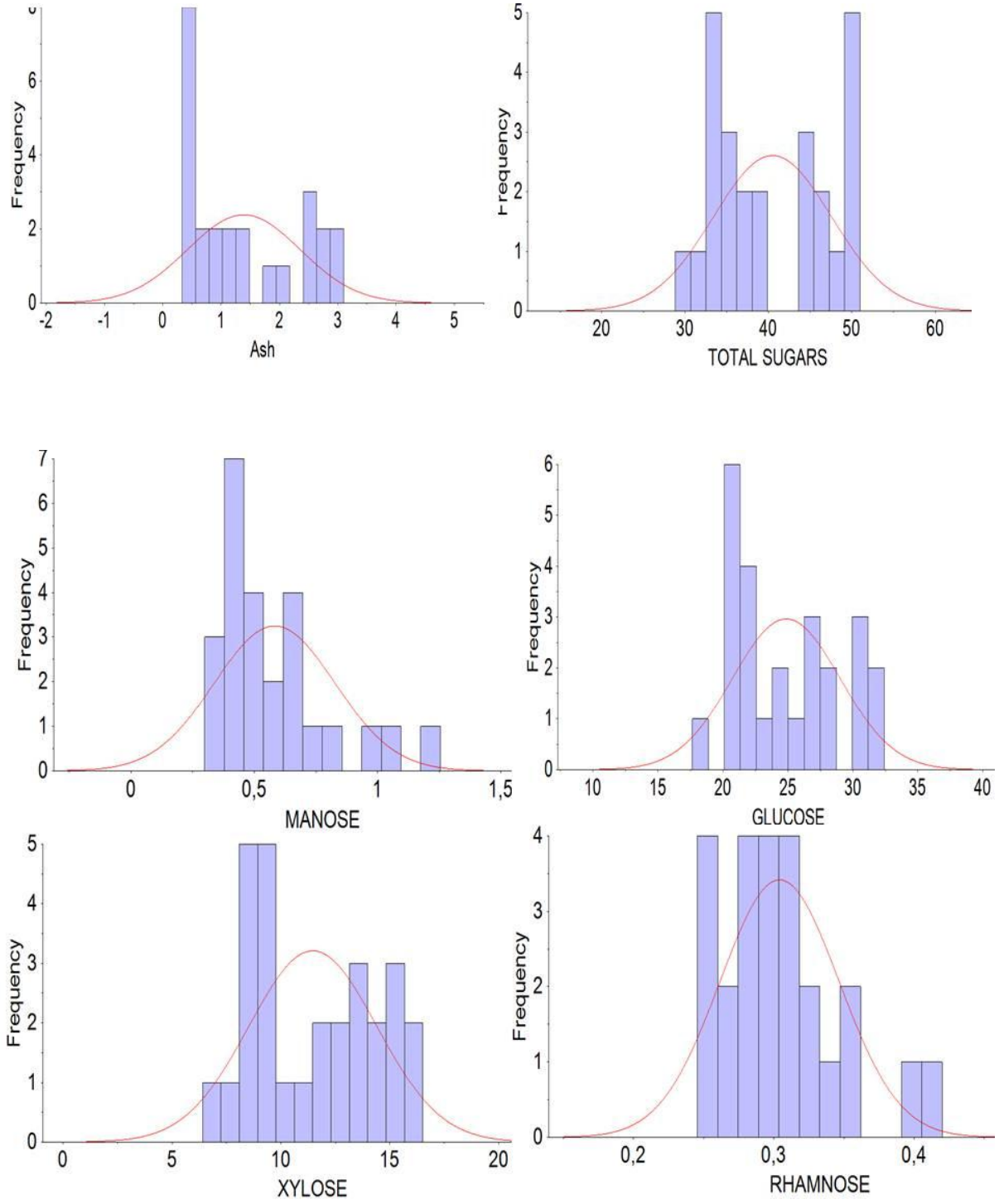


Figure 47: Histograms for the coconut samples analysed via wet-chemical means.

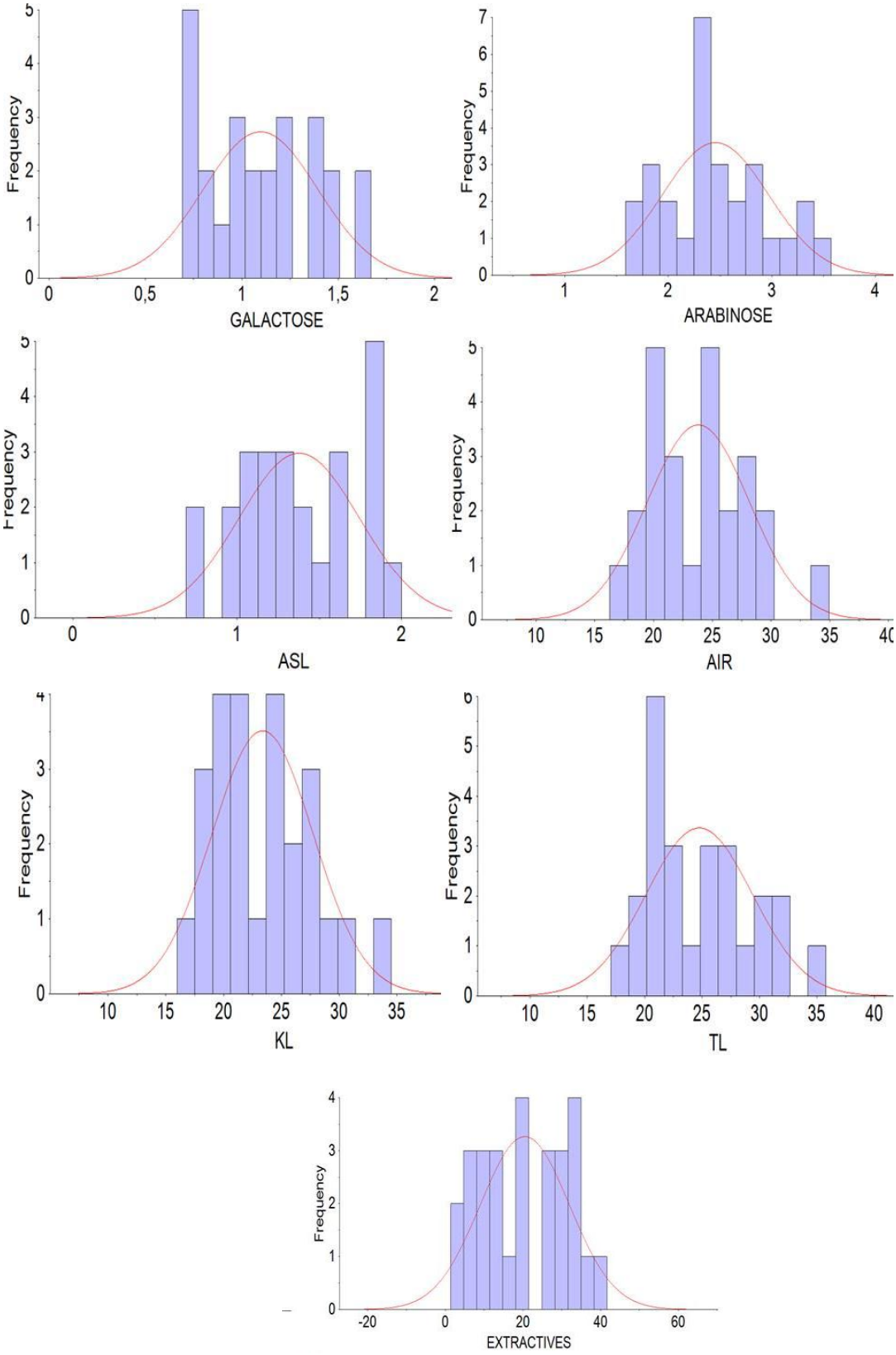


Figure 48: Histograms for the coconut samples analysed via wet-chemical means (ASL:acid soluble lignin, AIR: acid insoluble residue, KL: Klason Lignin and TL: total lignin.

5.5 Coffee Residues

5.5.1 Background

5.5.1.1 Components, Production, and Utilisation

Coffee is one of the world's most popular beverages and important commodities. It has grown steadily in commercial importance over the last 150 years. The province of Kaffa in Ethiopia is considered to be the original habitat of Arabica coffee and Central Africa is reckoned to be the native of robusta coffee.

Globally, 25 million small producers rely on coffee for their living. Brazil, Vietnam and Colombia account for more than half of the world's production. The global coffee production per year on average accounts to approximately 7 million metric tons. According to the International Coffee Organization (ICO), output of coffee brew in the 2011-12 season is estimated at 130 million bags. Over 2.25 billion cups of coffee are being consumed all over the world every day. Over 90% of coffee production takes place in developing countries, while consumption is mainly in the industrialized economies.

With extensive and wide spread cultivation of coffee across the globe, at present Brazil is the largest producer and exporter of coffee in the world and the second largest consumer. The production of coffee in Brazil in the last 5 years ranged from 2.0 to 2.7 million tons. Thus, this commodity is quite relevant to the country's economy.

Coffee is an important plantation crop belonging to the family Rubiaceae, subfamily Cinchonoideae and tribe Coffeae. The Rubiaceae members are largely tropical or subtropical comprising nearly 400 genera and 4,800-5,000 species. The sub-genus Coffeae is reported to comprise over 80 species, which are prevalent in Africa and Madagascar. Coffee is a perennial plant and evergreen in nature. It has a prominent vertical stem with shallow root system, the feeder roots of arabica coffee penetrate relatively deeper into the soil whereas robusta has feeder roots concentrated very close to the soil surface.

Processing is a major activity in the coffee industry and converts raw coffee fruit into liquid coffee. The two basic methods of coffee processing, which differ in complexity and the quality of the resultant raw coffee and the liquor, are the wet and dry methods.

Coffee grounds are highly pollutant due to the presence of organic material that demands a great quantity of oxygen in order to degrade. Simply piled up they can ferment and lead to spontaneous combustion, as has occurred in some storage sites. They can thus not be thrown away untreated.

With such a polluting industrial residue being produced in great quantity, the identification of more rational uses has become necessary. To study the feasibility of these uses it is necessary to know the composition of the coffee residues.

Coffee generates large amount of coffee by-products/residues during processing. Depending upon the method of coffee cherries processing, i.e. wet or dry process, different residues are

obtained. Coffee husks are the major solid residues from the handling and processing of coffee, since for every 2kg of coffee beans produced, approximately 1 kg of husks are generated. The coffee husks represent 12% dry-weight of the whole berry, composed essentially by carbohydrates, proteins and minerals (especially potassium) and it also contains appreciable amounts of tannins, polyphenols and caffeine.

Proposed alternative uses for coffee husks include employing this solid residue as a supplement for animal feed, direct use as fuel, fermentation for the production of a diversity of products (enzymes, citric acid and flavoring substances), use as a substrate for growth of mushrooms and use as adsorbents. However, considering the high amounts generated, there is still a need to find other alternative uses for this solid residue. Given that such residue consists mainly of the pulp and hull of the coffee fruit, it presents a high concentration of carbohydrates and thus can be viewed as a potential raw material for biofuel production.

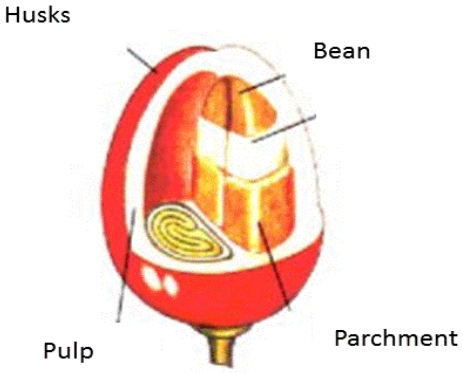


Figure 49: Structure of the coffee plant.

5.5.1.2 Coffee in Brazil

Coffee production in Brazil is responsible for about a third of all coffee, making Brazil by far the world's largest producer, a position the country has held for the last 150 years. In 2007, 2,249,010 metric tonnes were produced, with 80% of coming from Arabica coffee. In the 2012-2013 season Brazil will produce around 50.4 million bags (each bag 60 Kg) of coffee, according to the Ministry of Agriculture. The output of the country will include 38.1 million bags of arabica and 12.3 million bags of robusta coffees. Presently, according to reports, 25% of the robusta production has been completed so far and around 15% of it is not presently available in the market as the drying and peeling processes are not yet completed. Brazil is the largest producer of arabica coffee and second largest in robusta (Figure 50).

Although Brazil is the world's largest coffee producer, Brazilian firms do not dominate the international coffee industry. Coffee plantations cover about 27,000 km^2 (10,000 sq mi) of the country; of the approximately six billion trees, 74% are arabica and 26% robusta. The states São Paulo, Minas Gerais and Paraná are the largest producers (Figure 51) due to suitable landscapes, climate, and rich soil. Most plantations are harvested in the dry seasons of June through September.

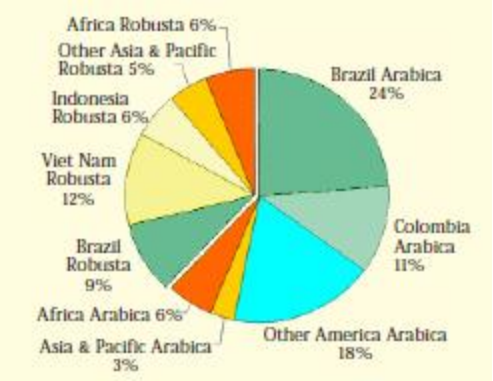


Figure 50: Coffee production.

Figure 51: Map of coffee production zones in Brazil, shown in orange.

Like in other coffee-producing countries, Brazil has a large workforce associated with the crop. Some 3.5 million people are involved in the industry, mostly in rural areas, which generates seven million indirect and direct jobs.

5.5.1.3 Lignocellulosic Analysis of Coffee Residues in the Literature

Pandey *et al.* (199) evaluated the potential opportunities for economic utilization of agro-industrial residues, such as coffee pulp and coffee husk, through biotechnological means. Table 47 shows the composition of coffee pulp and coffee husk as reported by some authors. The composition of coffee pulp differs from that of coffee husk, although the nature of the compounds in both of them are rather similar. There may be difference in percent composition

of the constituents, depending upon the processing mode and efficiency, crop variety, cultivation conditions such as soil type, etc.

Table 47: Composition of coffee pulp and husks.

Components	1 [a,d]	2 [b,d]	3 [c,e]
Carbohydrates	50	44	57.8
Proteins	10	12	9.2
Fibres	18	21	-
Fat	2.5	-	2
Caffeine	1.3	1.25	1.3
Tannins	1.8-8.56	-	4.5
Polyphenols	-	1	-
Pectins	-	-	12.4

D: coffee pulp and E: coffee husks.

Urbaneja *et al.* (1996) used diluted sulphuric acid for hydrolyzing the coffee pulp. The authors obtained xylose, arabinose, fructose, glucose, sucrose, and maltose. Arabinose was the largest constituent followed by glucose. The overall efficiency of the hydrolysis was 64 and 67% for total and reducing sugars, respectively.

Gouvea *et al.* (158) evaluated the feasibility of ethanol production by fermentation of coffee husks by *Saccharomyces cerevisiae*. The results indicated that coffee husks present excellent potential for residue-based ethanol production. The high contents of carbohydrates are expected, indicating that this solid residue seems quite promising for ethanol production, given the high percentage of sugars that are readily available for fermentation (Table 48).

Silva *et al.* (200) evaluated the use of coffee grounds in the Brazilian soluble coffee industry. This residue is used as a fuel in the boilers of the same industry; data about their utilization are presented and analysed, discussing the actual technology and the advantages of improving the drying of the biomass with the exhaust combustion gases. After that, an experimental study was reported on the characteristics of this material, which are important for the combustion process, including the transport, storage and drying, the mean diameter of the particles, talus angle, apparent and real density, sphericity, surface area, terminal velocity, spontaneous ignition temperature and heat of combustion. Compared to other biomasses, coffee grounds can be considered as an excellent fuel, because they show a higher heat of combustion compared to others usually used, such as sugarcane bagasse and rice husks, among others. With some technological effort to improve the conditions of utilization of this fuel in the boilers, the soluble coffee industry could become self-sufficient in thermal energy.

Shenoy *et al.* (201) studied the bioethanol production from coffee pulp waste. Theoretical ethanol yield of dried coffee and wet coffee was found to be 9.35 and 40%, respectively. They concluded that dry and wet coffee pulps were potential source of ethanol production that had been unexploited to date.

Table 48: Chemical composition of coffee husks (% dry basis).

	Coffee husks	Sticky coffee husks
Protein	8-11	9-10
Lipids	0.5-3	0.7-1.2
Minerals	3-7	5-6
Total carbohydrates	58-85	83-85
Cellulose	43	16-25
Hemicellulose	7	9-11
Lignin	9	6-10
Caffeine	~1	0.6
Tannins	~5	0.8-1.2

5.5.2 Sampling Strategy for Coffee Residues

One hundred and two samples of coffee residues have been collected by UNICAMP for the DIBANET project. The coffee residues were from different botanical fractions (husks, leaf, and lesser quantities of bean and toasted coffee). These were collected during the period of June 2011 to September 2011 in Brazil. All samples originated from the Southeast and South. The sample set included distinct cultivars, such as Etiopia, Robusta, Arabica, among others not identified.

The DIBANET project involved the analysis of a large number of the samples from Latin America that were collected. This analysis was either by wet-chemical means or using the near infrared spectra of the samples to predict their lignocellulosic composition.

5.5.3 Analytical Results

Table 49 shows the compositional data for the various anatomical fractions of coffee and Figure 52 presents histograms for selected constituents.

There are several important observations regarding Table 49:

- Glucose is the largest constituent in all plant fractions, except for the coffee bean, where mannose is the main sugar and for toasted coffee, where galactose is the main carbohydrate.

- Important are the low extractives and ash contents on the husks. These are better than the results reported in the literature (202).

- The total mass balance for husks is close to 100%, the remaining 8% probably comes from hot-water extractives.

- The leaves composition is very far from the total composition. Other solvents should be tested and the fraction analysed again.

- Lower values, compared to other biomasses, for the average, maximum, minimum and ranges of the major sugars glucose and xylose were found for leaves, bean and toasted coffee. This results in the total sugars content also being lower.

- Klason lignin contents tend to be lower in bean samples, compared to husks samples, however acid soluble lignin contents are higher.

- The different fractions of coffee presented a wide range of chemical compositions; high total sugars contents were found for the husks and beans whilst, for the leaves and toasted coffee, very low total sugars contents were measured.

- The total sugars contents presented for the DIBANET project by UNICAMP show similar results to those reported in the literature (197, 198).

5.5.4 Summary and Guidelines of Best Practice

- Coffee production requires an elevated degree of processing know-how and produces large amounts of by-products, such as coffee husks, which have limited applications such as fertilizer, livestock feed, compost and such others.

- Biotechnological applications in the field of industrial residues management promote sustainable development of a country's economy, with production of by-products, via chemical and biotechnological processes. With the background of high crop production in the upcoming years, there is an imperative need to counterpart this production with some utilization and industrial application of coffee by-products.

- Coffee is one of the most important products, its subsequent processes such as cultivation, processing, trading, transportation, and marketing, provide employment and is a huge business worldwide. With the high crop production projected in the future, there is a vital need to counterpart this production with proper utilization and industrial application of coffee by-products.

- From the coffee fractions analysed, only the husks have sufficient amounts of lignocellulosic sugars to justify their processing in hydrolysis biorefineries.

- Also, the coffee husks present a large range of variation for all parameters due to the husks coming from different locations and different crop varieties.

- The leaves presented very low sugars content, not enough for use in biorefineries.

- The bean is not a resource that can practically be used in biorefining since it is used in industry for coffee production.

Table 49: Composition of coffee samples analysed by UNICAMP as part of the DIBANET project.

Plant Fraction	Extr.	Ash	Mois.	Ara.	Gal.	Rha.	Glu.	Xyl.	Man.	Total Sugars	AIR	KL	ASL	AIA	TOTAL	Calor. Value
Average																
Husks	4.21	0.71	8.03	2.99	3.7	0.73	20.88	5.85	2.75	36.55	23.00	22.32	2.12	0.05	92.00	18.06
Toasted coffee	27.54	1.18	3.73	2.88	12.45	0.21	10.03	0.48	5.24	23.00	15.36	15.36	4.42	0.02	72.00	-
Leaves	16.69	1.92	5.66	2.95	2.72	0.69	14.77	5.28	0.58	22.50	18.65	18.54	1.36	0.38	61.00	-
Bean	24.5	0.84	9.95	3.20	8.21	0.45	17.65	6.01	21.12	43.00	12.05	12.00	3.32	0.02	84.00	-
Max																
Husks	30.04	3.35	15.64	6.79	8.95	1.03	37.00	22.85	7.68	65.30	29.05	29.0	5.45	0.13	-	-
Toasted	27.91	1.62	3.73	2.97	12.71	0.22	10.69	0.72	5.66	32.96	21.30	21.26	6.18	0.04	-	-
Leaves	20.96	2.72	7.74	5.55	3.55	0.98	23.36	6.81	0.88	40.62	30.82	30.71	1.88	0.40	-	-
Bean	24.50	0.84	9.95	3.53	8.95	0.47	18.70	6.14	23.14	60.84	16.50	16.50	4.66	0.05	-	-
Min																
Husks	4.12	1.06	2.80	2.87	2.99	0.43	13.12	2.16	1.75	25.74	14.61	14.61	1.55	0.00	-	-
Toasted	23.37	1.12	2.80	2.78	12.19	0.20	9.37	0.25	4.83	29.63	21.14	21.14	5.94	0.00	-	-
Leaves	15.82	1.92	5.45	4.12	3.07	0.80	22.46	6.61	0.74	38.16	22.40	22.00	1.63	0.36	-	-
Bean	20.00	0.63	7.40	2.87	7.47	0.43	16.60	5.87	19.10	52.50	15.22	15.26	4.17	0.00	-	-
Range																
Husks	25.92	2.29	12.84	3.92	5.96	0.6	23.88	20.69	5.93	39.60	14.44	14.39	3.9	0.13	-	-
Toasted	4.54	0.5	0.93	0.19	0.52	0.02	1.32	0.50	0.83	3.33	0.16	8.7	0.24	0.04	-	-
Leaves	5.14	0.8	2.29	1.43	0.48	0.18	0.9	0.21	0.15	2.47	8.4	8.7	0.25	0.04	-	-
Bean	4.5	0.20	2.55	0.66	1.48	0.05	2.1	0.30	4.04	8.34	1.30	1.24	0.49	0.05	-	-
Standard Deviation																
Husks	0.24	0.03	0.12	0.26	0.40	0.10	0.43	0.46	0.23	1.10	0.23	0.20	0.06	0.02	-	-
Toasted coffee	0.52	0.11	0.00	0.14	0.36	0.01	0.94	0.33	0.59	2.00	0.11	0.09	0.11	0.02	-	-
Leaves	0.21	0.07	0.09	0.05	0.06	0.01	1.20	0.94	0.01	2.00	0.35	0.36	0.01	0.02	-	-
Bean	0.25	0.00	0.00	0.47	1.00	0.03	1.30	0.20	1.00	2.00	0.91	0.88	0.33	0.03	-	-
Husks	0.24	0.03	0.12	0.26	0.40	0.10	0.43	0.46	0.23	1.10	0.23	0.20	0.06	0.02	-	-

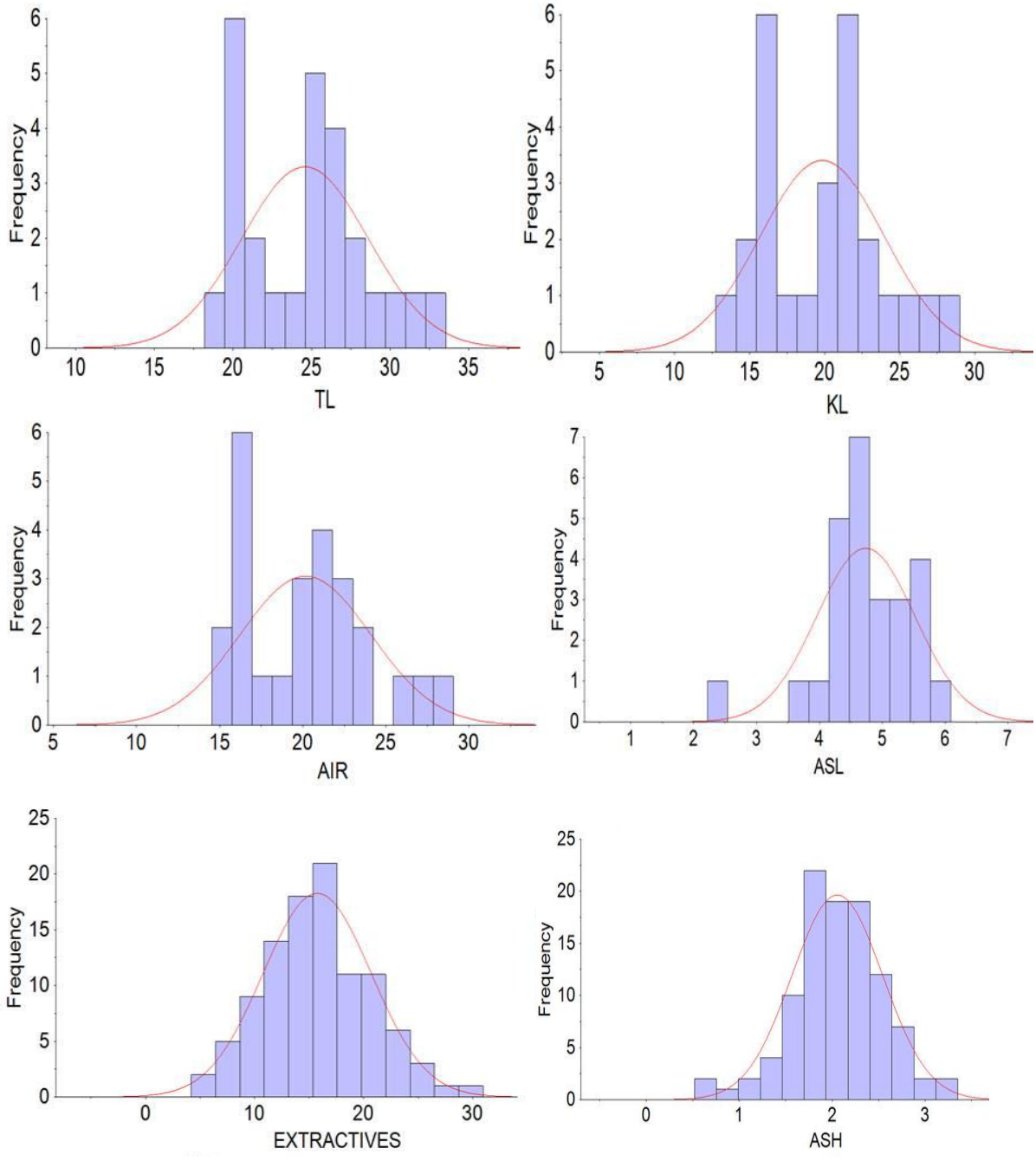


Figure 52: Histograms for extractives, lignin total, Klason lignin, acid soluble lignin, acid insoluble residue, and ash for the coffee samples analysed via wet-chemical means.

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