

# Composition of Herbaceous Biomass Feedstocks







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DoKyoung Lee  
Vance N. Owens  
Arvid Boe  
Peter Jeranyama  
Plant Science Department  
South Dakota State University

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Sun Grant Initiative  
North Central Center  
South Dakota State University

**Prepared by:**  
North Central Sun Grant Center  
South Dakota State University  
Box 2140C  
Brookings, SD 57007

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## Summary

This report summarizes published information about the chemical composition of potential herbaceous biomass feedstocks for biorefineries in the north-central United States. The specific usefulness of this report varies according to conversion process; thus, values are intended only for exploratory calculations and preliminary estimates about the feasibility and economics of a particular feedstock. More detailed feedstock compositional information will become available as further research is completed at various locations throughout the country.

## 1. Introduction

National energy security and global climate change will require large-scale substitution of petroleum-based fuels by other sources of energy. One source of renewable energy will be biomass for use in transportation fuels.

The U.S. Department of Energy (USDOE) and the U.S. Department of Agriculture (USDA) are strongly committed to expanding the role of lignocellulosic feedstocks as an energy source to reduce oil and gas imports. A goal set forth in “The United States Bioenergy Vision and Sustainable Feedstock Supply” by the Biomass R&D Technical Advisory Committee is that, by year 2030, 30% of current U.S. petroleum-based fuels will be replaced by biofuels. It has been estimated that an annual production of at least 1 billion dry tons of lignocellulosic feedstock will be required to meet this goal [1, 2].

The USDOE and USDA have estimated that more than 1.3 billion dry tons of biomass (368 million dry tons of biomass from forestlands and 998 million dry tons from agricultural lands) can be produced per year in the U.S. [2]. Biomass from agricultural lands would include 428 million dry tons of annual crop residues, 377 million dry tons of perennial crops, 87 million dry tons of grains, and 106 million dry tons of animal manure, process residues, and other miscellaneous sources.

Biomass is defined as consisting of all plant and plant-derived materials including livestock manures. Lignocellulosic biomass is the nonstarch, fibrous part of plant material and is an attractive resource because it is renewable and abundant [2].

Chemical composition of lignocellulosic feedstocks is a key factor affecting efficiency of biofuel production during conversion processes [3, 4]. The structural and chemical composition of lignocellulosic feedstocks is highly variable because of genetic and environmental influences and their interactions.

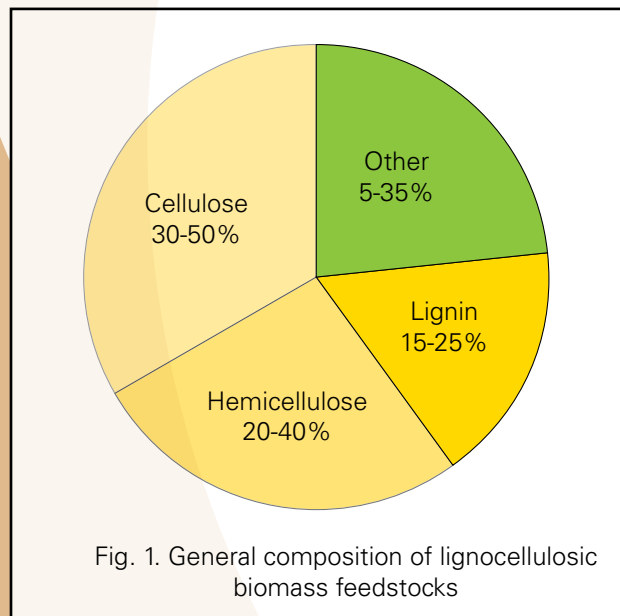


Switchgrass being harvested for biomass feedstock near Bristol, S.D. Photo by Jerry Roitsch.

## 2. General Characteristics of Lignocellulosic Feedstocks

Lignocellulosic feedstocks are composed primarily of carbohydrate polymers (cellulose and hemicellulose) and phenolic polymers (lignin). Lower concentrations of various other compounds, such as proteins, acids, salts, and minerals, are also present.

Cellulose and hemicellulose, which typically make up two-thirds of cell wall dry matter (dry matter: the portion of biomass that is not water), are polysaccharides that can be hydrolyzed to sugars and then fermented to ethanol. Process performance, in this case ethanol yield from biomass, is directly related to cellulose, hemicellulose, and individual sugar concentration in the feedstock. Lignin cannot be used in fermentation processes; however, it may be useful for other purposes.



### Important Constituents of Lignocellulosic Feedstocks

**Lignocellulose** is the term used to describe the three-dimensional polymeric composites formed by plants as structural material. It consists of variable amounts of cellulose, hemicellulose, and lignin [5].

**Cellulose** (30–50% of total feedstock dry matter) is a glucose polymer linked by  $\beta$ -1,4 glycosidic bonds. The basic building block of this linear polymer is cellobiose, a glucose-glucose dimer (dimer: two simpler molecules—monomers—combined to form a polymer). Hydrolysis of cellulose results in individual glucose monomers. This process is also known as saccharification.

**Hemicellulose** (20–40% of total feedstock dry matter) is a short, highly branched polymer of five-carbon (C5) and six-carbon (C6) sugars. Specifically, hemicellulose contains xylose and arabinose (C5 sugars) and galactose, glucose, and mannose (C6 sugars). Hemicellulose is more readily hydrolyzed compared to cellulose because of its branched, amorphous nature. A major product of hemicellulose hydrolysis is the C5 sugar xylose.

**Lignin** (15–25% of total feedstock dry matter), a polyphenolic structural constituent of plants, is the largest non-carbohydrate fraction of lignocellulose. Unlike cellulose and hemicellulose, lignin cannot be utilized in fermentation processes.

**Ash** (3–10% of total feedstock dry matter) is the residue remaining after ignition (dry oxidation at  $575 \pm 25^\circ\text{C}$ ) of herbaceous biomass. It is composed of minerals such as silicon, aluminum, calcium, magnesium, potassium, and sodium.

**Other compounds** present in lignocellulosic feedstocks are known as extractives. These include resins, fats and fatty acids, phenolics, phytosterols, salts, minerals, and other compounds.

### 3. Composition of Lignocellulosic Biomass Feedstock Resources

An ideal biomass resource will be high yielding, have low production costs, be readily available, and have consistent desirable chemical concentrations. The feasibility of a new energy crop will depend largely on its production costs, cost of converting the biomass to usable energy, and cost of competing fuels.

Agriculture-derived biomass, specifically crop residues from corn and small grains and dedicated perennial grasses such as switchgrass, are emphasized in this report. Table 1 lists general characteristics of these and other potential biomass resources.

#### 3.1. Corn Stover, Wheat Straw, and Switchgrass

The most probable feedstocks for initial processing facilities would be low-cost agricultural residues because of their abundance and proximity to existing grain-to-ethanol conversion facilities.

On the other hand, it is assumed that significant amounts of land could be shifted to production of perennial energy crops if a large market for bioenergy and biobased products emerges. Characteristics which make perennial grasses attractive for biomass production are yield potential, high concentration of lignocellulose, and generally positive environmental impact.

The chemical composition of switchgrass, corn stover, and wheat straw is relatively similar when harvested to maximize the lignocellulosic component (Fig 2). However, when grown in different environments, considerable variation in feedstock composition may occur, as demonstrated by the range of data reported for these crops in the literature (Table 2). In addition to the range in genetics, environmental effects on feedstock composition also are significant.

Corn stover-to-grain ratios are about 1:1 on a dry matter basis, and corn stover is about 38% cellulose, 26% hemicellulose, and 19% lignin.

Wheat straw yields, dry matter basis, are about 1.3–1.4 lb straw per 1 lb grain. Wheat straw is about 38% cellulose, 29% hemicellulose, and 15% lignin.

Similarly, switchgrass biomass on a dry matter basis is about 37% cellulose, 29% hemicellulose, and 19% lignin during late autumn.

**Table 1. Composition of potential lignocellulosic biomass resources.<sup>a</sup>**

	<i>Cellulose<sup>c</sup></i>	<i>Hemi-cellulose<sup>c</sup></i>	<i>Lignin<sup>d</sup></i>	<i>Acid detergent lignin<sup>e</sup></i>	<i>Crude protein<sup>f</sup></i>	<i>Ash</i>	<i>References</i>
	% of dry matter						
<b>Crop residues</b>							
Corn stover	38	26	19	4	5	6	6, 7-20
Soybean	33	14	-	14	5	6	48, 49
Wheat straw	38	29	15	9	4	6	7, 9, 11, 21-26
Rye straw	31	25	-	3	3	6	38, 39
Barley straw	42	28	-	7	7	11	11
<b>Warm-season grasses</b>							
Switchgrass	37	29	19	6	3	6	6, 7, 11, 27-37
Big bluestem	37	28	18	6	6	6	32, 33, 37
Indiangrass	39	29	-	6	3	8	32, 37
Little bluestem	35	31	-	-	-	7	37
Prairie cordgrass	41	33	-	6	3	6	46
Miscanthus	43	24	19	-	3	2	42-45
<b>Cool-season grasses</b>							
Intermediate wheatgrass	35	29	-	6	3	6	33
Reed canarygrass <sup>b</sup>	24	36	-	2	10	8	47, 48
Smooth brome <sup>b</sup>	32	36	-	6	14	8	47, 48
Timothy <sup>b</sup>	28	30	-	5	7	6	40, 41
Tall fescue	25	25	14	-	13	11	7
<b>Other crops</b>							
Alfalfa <sup>b</sup>	27	12	-	8	17	9	40
Forage sorghum	34	17	16	-	-	5	7
Sweet sorghum	23	14	11	-	-	5	7
Pearl millet <sup>b</sup>	25	35	-	3	10	9	47, 48
Sudangrass	33	27	-	8	12	12	47, 48

<sup>a</sup>Values in table are means or values obtained from cited references.

<sup>b</sup>Data for these species were available for hay only. All other species harvested for biomass.

<sup>c</sup>Reported directly from literature, calculated from individual sugars (Cellulose = Glucan; Hemicellulose = Xylan + Arabinan + Galactan + Mannose), or based on fiber analysis (Cellulose = ADF - ADL; Hemicellulose = NDF - ADF).

<sup>d</sup>Lignin is total lignin (acid soluble lignin + acid insoluble lignin), which is measured using ASTM standard method.

<sup>e</sup>Acid detergent lignin (ADL) is commonly used for forage. In general, acid insoluble lignin is 30% higher than ADL for legumes and 2 to 4 times greater than ADL for grasses [50].

<sup>f</sup>Reported directly from literature or calculated from total nitrogen (crude protein = % total N \* 6.25).

**Table 2. Detailed compositional analysis of switchgrass, corn stover, and wheat straw.<sup>a</sup>**

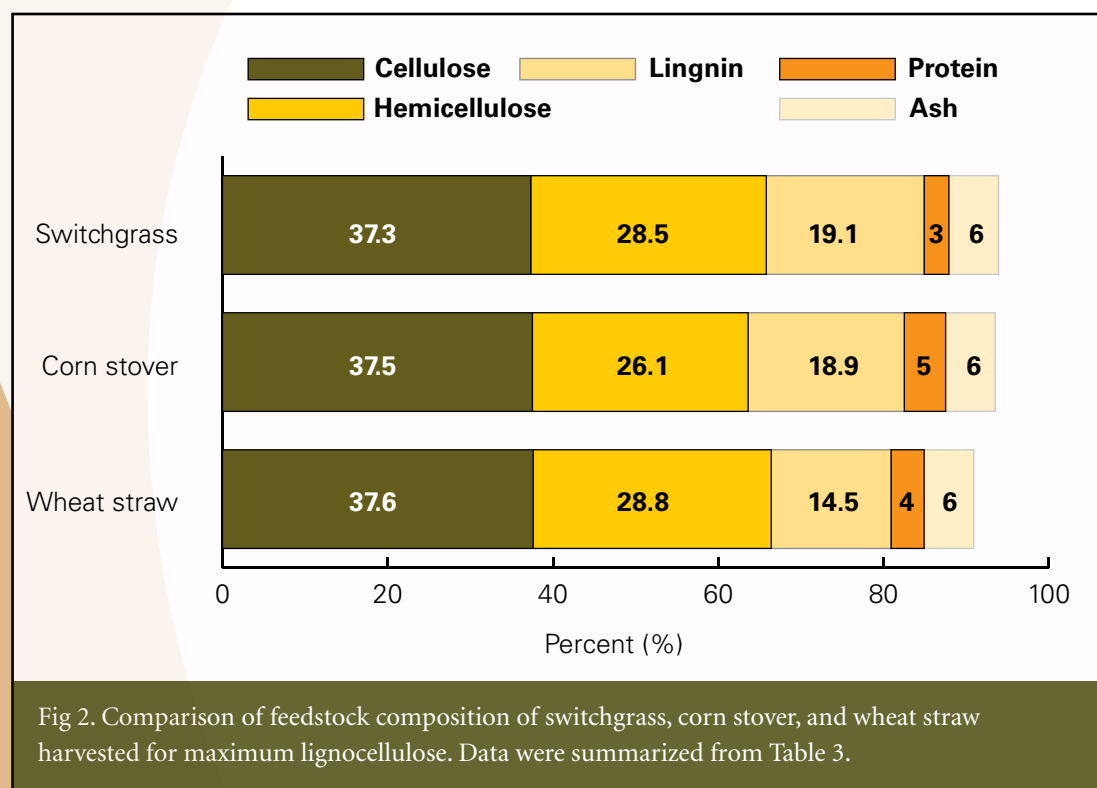
	<i>Minimum</i>	<i>Maximum</i>	<i>Mean</i>	<i>SD</i>
	<i>% of dry matter</i>			
<b>Corn Stover</b>				
Cellulose <sup>b</sup>	31.3	41	37.5	2.8
Structural glucan	33.8	41	37.5	2.2
Hemicellulose	20	34.4	26.1	4.8
Xylan	19.8	25.8	21.7	2.1
Arabinan	1.7	6.1	2.7	1.6
Galactan	0.7	3	1.6	1
Mannan	0.3	1.8	0.6	1.1
Total lignin	15.8	23.1	18.9	2.6
Acid soluble lignin	1.9	3.6	2.9	0.9
Acid insoluble lignin	13.6	19.8	16.4	3.1
Acid detergent lignin	3.1	5	4.1	1.3
Crude protein	3.5	8.7	4.7	2.2
Ash	4.2	7.5	6.3	1.2
Soil	-	-	1.3	-
<b>Wheat Straw</b>				
Cellulose	31.5	48.6	37.6	5.7
Structural glucan	31.5	32.6	32.1	4.5
Hemicellulose	22.6	38.8	28.8	5.7
Xylan	19.2	19.7	19.5	0.3
Arabinan	2.4	3.2	2.8	0.6
Galactan	0.8	1.5	1.1	0.5
Mannan	0.3	0.9	0.6	0.4
Total lignin	5.3	19	14.5	6.2
Acid soluble lignin	-	-	2.5	-
Acid insoluble lignin	5.3	16.5	10.9	7.9
Acid detergent lignin	7.6	11.2	9.2	1.6
Crude protein	1.9	5.7	3.8	1.9
Ash	1.4	10.2	6.4	3.4
Soil	-	-	-	-
<b>Switchgrass</b>				
Cellulose	31.4	45	37.3	4.4
Structural glucan	31.4	38	34.2	2.1
Hemicellulose	22	35.1	28.5	3.5
Xylan	20.2	24	22.8	1
Arabinan	2.7	3.8	3.1	0.5
Galactan	0.7	1.9	1.4	0.5
Mannan	0.3	0.4	0.3	0
Total lignin	17.7	22	19.1	1.7
Acid soluble lignin	3.3	3.7	3.5	0.3
Acid insoluble lignin	15.8	16.5	16.2	0.5
Acid detergent lignin	4	12	6.4	2.7
Crude protein	1.6	3.8	3.1	0.7
Ash	4.4	8.5	5.9	1
Soil	-	-	-	-

<sup>a</sup>Values in table are compiled from references listed in Table 1.

<sup>b</sup>Cellulose and hemicellulose values may not equal the sum of individual sugars because of limited data for individual sugars.

## 3.2 Other Crops

Other potential biomass crops may have levels of lignocellulose comparable to switchgrass, corn stover, and wheat straw at similar stages of maturity (Tables 1 and 2). However, warm-season grasses generally contain higher concentrations of lignocellulose than crop residues and cool-season grasses (Table 1).



## 4. Harvest and Storage Issues

Biomass feedstock composition is affected by time and method of harvest and storage.

Several studies have been published regarding the effect of harvest timing on feedstock composition [50, 34, 20] particularly as harvest timing relates to optimizing lignocellulosic concentrations. There is less published information about storage of biomass resources for biorefineries.

However, since biorefineries will require a consistent supply of product, feedstock storage either at the farm or at the biorefinery will be necessary. Storage examples for round bales of switchgrass and corn stover are discussed in section 4.2.

## 4.1 Harvest Timing

Feedstock composition varies with crop maturity. Maximum lignocellulosic yield for corn is obtained when corn stover fractions are harvested at physiological maturity. For switchgrass, maximum yield is obtained when harvested around anthesis; however, stand health and longevity will decrease as a result of harvesting annually at anthesis. Therefore, harvesting around a killing frost in the fall is recommended for switchgrass grown for biomass. A reduction in certain chemical elements that reduce process performance is an added benefit of harvesting later in the season.

In corn, soluble solids rapidly decrease and lignin and xylan increase shortly after grain physiological maturity (Table 3) [12]. In switchgrass, cellulose, hemicellulose, and lignin concentrations increase while total nitrogen and ash content decreases when harvest is delayed from anthesis to a killing frost (Table 4) [33]. In switchgrass biomass, total potassium (K) and water extractable chlorine (Cl) decrease 60% and 70%, respectively, when harvest is delayed from green stem to late winter (Table 5) [27]. Other warm-season perennial grasses would likely behave similarly; however, research with individual species is required to verify this assertion.

**Table 3. Changes in composition of corn stalk and leaf with crop maturity.**

	<i>Late dent (110d<sup>a</sup>)</i>	<i>Physiological maturity (153d) % of dry matter</i>	<i>Post physiological maturity (220d)</i>
<b>Corn stalk</b>			
Structural glucan	35	35	35
Xylan	16	22	23
Lignin	15	20	19
Protein	3	4	4
Soluble solids	15	4	4
<b>Corn Leaf</b>			
Structural glucan	18	23	32
Xylan	2	17	22
Lignin	4	13	16
Protein	8	8	4
Soluble solids	35	8	6

Source: [12]  
<sup>a</sup>Days after planting

**Table 4. Changes in composition of 'Nebraska 28' switchgrass with crop maturity.**

	<i>Harvest Time<sup>a</sup></i>		
	<i>Anthesis<sup>a</sup></i>	<i>Post physiological maturity</i>	<i>Overwintered</i>
	<i>% of dry matter</i>		
Cellulose	33.0	35.2	41.8
Hemicellulose	31.0	31.1	33.7
Acid detergent lignin	3.8	4.6	6.2
Protein	5.3	2.3	1.8
Ash	6.5	5.8	5.2

Source: [33]

<sup>a</sup>Harvest time: Anthesis, early August; post physiological maturity, November; and overwintered, spring of following year near Brookings, S.D.**Table 5. Changes in potassium and chloride in switchgrass biomass with crop maturity.**

	<i>Harvest Time<sup>a</sup></i>		
	<i>Green stem</i>	<i>Dead stem</i>	<i>Late winter</i>
	<i>ppm of dry matter</i>		
Total potassium	5580	2555	1961
Water extractable chloride	3283	1412	972

Source: [27]

<sup>a</sup>Harvest time: Green stem, after anthesis; Dead stem, post physiological maturity.

## 4.2. Storage

Any large-scale biofuel production facility needs the capacity to store biomass feedstocks for 6–12 months to ensure continuous availability during the year. Quantity and time of feedstock in storage will depend on size and requirements of the biorefinery, available storage capacity, distance from producer fields to the biorefinery, and other issues.

Covered storage for bales of lignocellulosic feedstocks is unlikely to be economical or practical considering the quantities involved. However, unprotected outside storage results in feedstock losses that can cause potential economic and efficiency losses in any energy conversion process.

Feedstock losses can be categorized in terms of loss of dry matter and in compositional changes. In a 2-year trial, loss of extractives was greater for switchgrass stored outside than inside, particularly during the first year when total precipitation was 69% higher than in the second year (Table 6) [6, 20]. However, in the same study, little or no change was observed for cellulose, hemicellulose, and lignin in either switchgrass or corn stover bales (Tables 6 and 7) [6, 20].

**Table 6. Changes in composition of switchgrass round bales during storage.**

	<i>Harvest 1 (Oct. 1991)</i>			<i>Harvest 2 (Aug. 1992)</i>		
	<i>Time zero</i>	<i>26 weeks storage</i>		<i>Time Zero</i>	<i>26 weeks storage</i>	
	<i>% of dry matter</i>	<i>Inside</i>	<i>Outside</i>	<i>% of dry matter</i>	<i>Inside</i>	<i>Outside</i>
		<i>% change</i>			<i>% change</i>	
<b>Composition on whole biomass basis</b>						
Extractives	17.0	-7.7	-10.5	14.2	<0.6	-1.8
Ash	5.8	+0.3	+0.2	4.8	<1.0	<1.0
Protein	3.2	+0.6	+0.6	2.8	-0.8	-0.9
<b>Composition on extractive-free basis</b>						
Lignin	21.4	+0.8	+1.5	20.6	-0.5	-0.4
Arabinan	3.4	-0.4	-0.4	3.2	<0.2	<0.2
Xylan	24.9	-1.5	-1.6	25.5	<1.3	<1.3
Mannan	0.4	<0.1	+1.4	0.3	<0.2	<0.2
Galactan	1.1	<0.1	<0.1	1.0	+0.1	<0.1
Glucan	37.8	-2.1	-2.2	40.8	<2.5	<2.5

Source: [6 and 20]

**Table 7. Changes in composition of corn stover square bales during storage.**

	<i>Time zero</i>	<i>26 weeks storage</i>		<i>52 weeks storage</i>	
	<i>% of dry weight</i>	<i>Inside</i>	<i>Outside</i>	<i>Inside</i>	<i>Outside</i>
		<i>% change</i>		<i>% change</i>	
<b>Composition on whole biomass basis</b>					
Extractives	7.6	<1.4	-2.5	-2.9	-2.3
Ash	6.8	-1.3	-1.3	<1.1	<1.1
<b>Composition on extractive-free basis</b>					
Lignin	18.5	+2.7	+0.9	+3.7	+3.0
Arbinan	3.4	-0.7	-0.5	-1.0	-0.8
Xylan	20.1	<0.8	+0.9	+2.0	+2.8
Mannan	0.7	-0.1	-0.1	-0.2	-0.2
Galactan	1.1	-0.1	<0.1	-0.3	+0.1
Glucan	40.7	-1.5	<1.6	-1.6	<0.6

Source: [6 and 20]

## 5. Summary

This review of data from published and electronic sources indicated:

1. When switchgrass was harvested at physiological maturity and corn stover and wheat straw were harvested after grain removal, their chemical compositions were found to be similar.
2. Other potential biomass feedstocks, including other cereal crop residues and annual and perennial warm- and cool-season grasses, may be expected to have comparable levels of lignocellulose as switchgrass, corn stover, and wheat straw when harvested after physiological maturity.

## Glossary

**Acid detergent fiber (ADF):** Organic matter that is not solubilized after 1 hour of refluxing in an acid detergent solution consisting of acetyltrimethylammonium bromide in 1N sulfuric acid. ADF includes cellulose, lignin, and ash. This analytical method is commonly used in the feed and fiber industries.

**Acid detergent lignin (ADL):** Organic matter that is not solubilized after 3 hours of extraction in 72% sulfuric acid.

**Dimer:** Molecules composed of two similar subunits or monomers linked together. Sucrose is a dimer, composed of a glucose molecule and a fructose molecule.

**Dry matter:** Moisture-free biomass, obtained by drying a sample or specimen at high temperature (105° C).

**Extractives:** Any number of different compounds in biomass that are not an integral part of the cellular structure. The compounds can be extracted from biomass by means of polar and non-polar solvents including hot or cold water, ether, benzene, methanol, or other solvents that do not degrade the biomass structure. The types of extractives found in biomass samples are entirely dependent upon the sample itself.

**Genetic:** Pertaining to or concerned with inheritance.

**Glucan:** A glucose polymer, which can be hydrolyzed (split into two parts by adding water) to glucose. Cellulose is a form of glucan.

**Neutral detergent fiber (NDF):** Organic matter that is not solubilized after one hour of refluxing in a neutral detergent solution consisting of sodium lauryl sulfate and EDTA at pH 7. NDF includes hemicellulose, cellulose, lignin, and ash.

**Phenology:** Periodicity in organisms as related to climate events; in plants, the various biological processes that are correlated with the seasons, e.g. flowering, fruiting, dormancy, root or stem elongation, etc.

**Physiological maturity:** The plant maturity stage at which no new dry matter is added to the plant.

**Polymer:** Very large molecules formed by linking together a large number of repeating structural units, or monomers.

**Senescence:** The growth phase in a plant or plant part (as a leaf) from full maturity to death during which time significant drying occurs.

**Xylan:** A xylose polymer and a major portion of hemicellulose. It can be hydrolyzed to xylose.

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