Carbon forms of lignocellulosic biofuel residues

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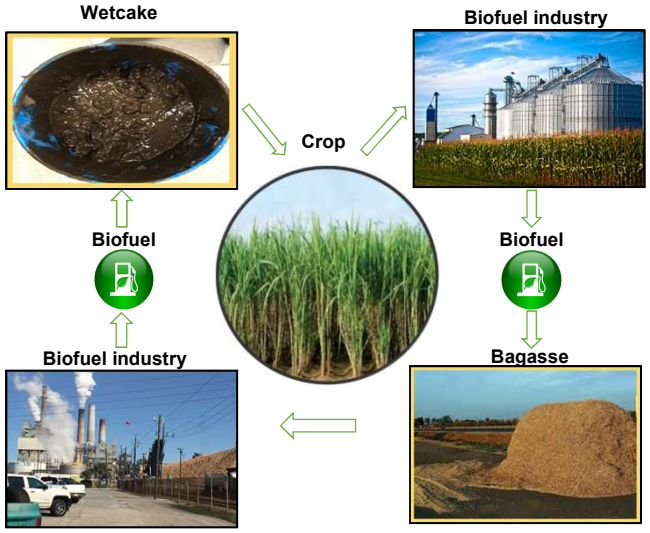
INTRODUCTION

Biofuel production results in vast amounts of residue that can be beneficial as a soil amendment.



Objectives:

- Determine the influence of various drying treatments of wetcake – a second-generation biofuel residue on carbon forms.
- Comparative analysis of physico-chemical properties of first (bagasse) and second (wetcake) generation lignocellulosic biofuel residues.

We hypothesize that bagasse will be composed of large proportion of labile (o-alkyl) carbon whereas wetcake will have more non-labile aromatic/aryl-C.

MATERIALS AND METHODS

Biofuel residues were obtained from the Stan Mayfield Biorefinery in Perry, FL.
Various drying pretreatments have been applied to fresh wetcake samples to evaluate their impact on carbon (C) content and quality.
The fresh wetcake was homogenized and dried at different temperatures as described below:

- Air-dried at 25°C
- Oven-dried at 70°C
- Freeze-dried
- Centrifuged, residue freeze-dried

All pretreated samples were analyzed for operationally defined C pools using a sequential fractionation method.
^{13}C solid-state NMR analysis was conducted on wetcake and bagasse samples to identify organic carbon functional groups.

All samples have also been analyzed for physico-chemical parameters such as pH, LOI, TC, TN, TP and fiber analyzes.

Acknowledgements

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RESULTS

Table 1. Carbon fractions of a sequential extraction procedure including cold water extractable C (CWC), hot water extractable C (HWC), acid extractable C (AEC) and residual C (RSC) of biofuel residues. WC = Wetcake, AD=aired dried, FD=freeze dried, OD=oven dried, CFD=centrifuged freeze fried, BG=bagasse.

Treatment	Total C	CWC	HWC	AEC	CWC+HWC +AEC	RSC
	g kg^{-1}					
WC-AD	520±5b	56±1b	11±1a	38±1b	104±1b	410±9a
WC-FD	527±4ab	67±1a	7±2b	37±2b	112±3a	416±19a
WC-OD	541±7a	48±1c	11±0.3a	40±2b	99±2c	421±14a
WC-CFD	539±4a	50±1c	9±1a	53±2ab	113±2a	430±44a
BG	450±1c	5.3±1d	9±1a	61±1a	76±1d	368±29b

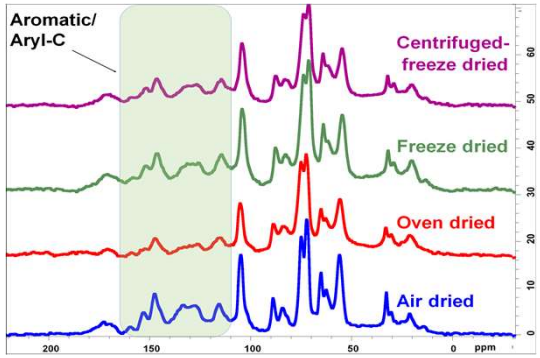

Figure 1. ^{13}C-NMR spectra of differently pretreated wetcake samples.

Table 2. Organic carbon functional groups of various pretreated wetcake samples determined by ^{13}C-NMR .

Sample Pretreat.	Alkyl	O-alkyl			Aryl		Carboxyl
	Aliphatic C, methyl C, (–CH_3, -CH_2)	Methoxyl (-OCH_3)	C–O of carbohydrate and cellulose	Anomeric C, Cellulose C-1	aromatic-C; Aromatic lignins	Lignins, phenols Aromatic ethers	Carboxyl-C, Amidic-C esters
WC-CFD	15.0	10.6	35.1	10.3	15.3	9.4	4.3
WC-FD	14.4	10.8	34.8	10.1	15.5	9.5	4.8
WC-OD	14.9	15.2	41.2	9.2	10.3	5.3	4.0
WC-AD	11.2	11.9	33.8	10.3	18.8	10.3	3.7

Table 3. Physicochemical properties of biofuel residues.

Properties	Units	Wetcake	Bagasse
Total C	g kg^{-1}	520 ± 5	450 ± 1
Total N	g kg^{-1}	23.8 ± 1	9.07 ± 1
Total P	g kg^{-1}	0.22 ±1	0.29 ±1
LOI	%	95±0.5	94±1
Cellulose	%	26.5±0.1	48.6±1
Lignin	%	35.4±2	20.2±0.7
-δ 13C	‰	15.1	13.3

Figure 2. Chemical shift region of ^{13}C-NMR spectra of biofuel residues and assignment to the corresponding organic domains.

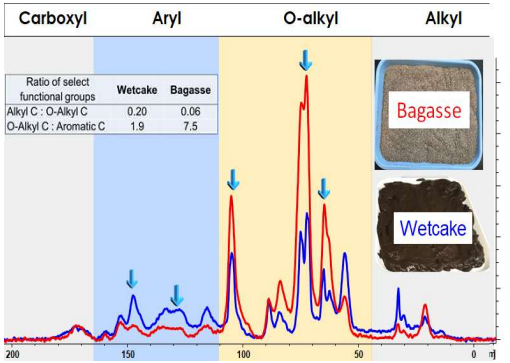

Table 4. Organic carbon functional groups of biofuel residues determined by ^{13}C-NMR .

Sample Treatment		Alkyl	O-alkyl			Aryl		Carboxyl	Total
		Chemical shift region (ppm)							
		0–45	45–60	60–90	90–110	110–140	140–165	165–220	220-0
		Aliphatic C, methyl C, (–CH_3, -CH_2)	Methoxyl (-OCH_3)	C–O of carbohydrate and cellulose	Anomeric C, cellulose C-1	aromatic-C; Aromatic lignins	Lignins, phenols Aromatic ethers	Carboxyl -C, Amidic-C esters	
WC	%	11.2	11.9	33.8	10.3	18.8	10.3	3.7	100
	g kg^{-1}	58.2	61.9	175.8	53.6	97.8	53.6	19.2	520
BG	%	4.6	20.3	46.7	15.4	6.5	4.1	2.5	100
	g kg^{-1}	21.7	96.3	221.7	73.3	30.7	19.5	11.7	475

DISCUSSION AND CONCLUSIONS

- Approximately 75% of the C in wetcake is present in non-labile pool, as determined by fractionation scheme (Table 1). Labile C pools includes acid hydrolysable fraction comprised of proteins, nucleic acids, polysaccharides and carboxyl C and the stable residue includes non-hydrolysable residue typically contains mainly lignin, fats, waxes and resins.
- Air-dried and freeze-dried wetcake samples showed no difference from each other, while oven-dried wetcake sample had higher O-alkyl/aryl ratio of 4.2, as compared to 1.9-2.3 in other pretreated samples (Table 4).
- We assumed that during the oven drying some part of the aryl-C, which consists of the aromatic lignins, phenols and ethers were converted to more labile O-alkyl groups, specifically to methoxyl C, carbohydrate, and cellulose.
- Total extractable C in wetcake showed a positive linear correlation with Alkyl-C (R^2=0.99) and Carboxyl-C (R^2=0.81) whereas it had strong negative correlation with Aryl-C (R^2=0.97) .
- Approximately 82% of total carbon was in O-alkyl-C forms (carbohydrate-derived structures) in bagasse, as compared to 56% in wetcake. Alkyl-C (recalcitrant substances) was 2 times higher in wetcake, showing higher humification degree (alkyl-C/O-alkyl-C ratio) compared to bagasse.

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