Microwave-assisted conversion of carbohydrates to levulinic acid: an essential step in biomass conversion

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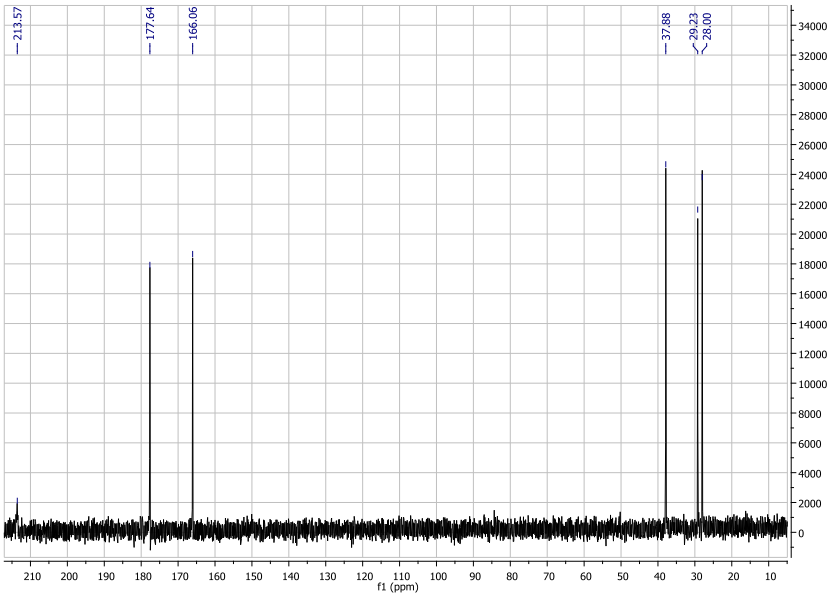
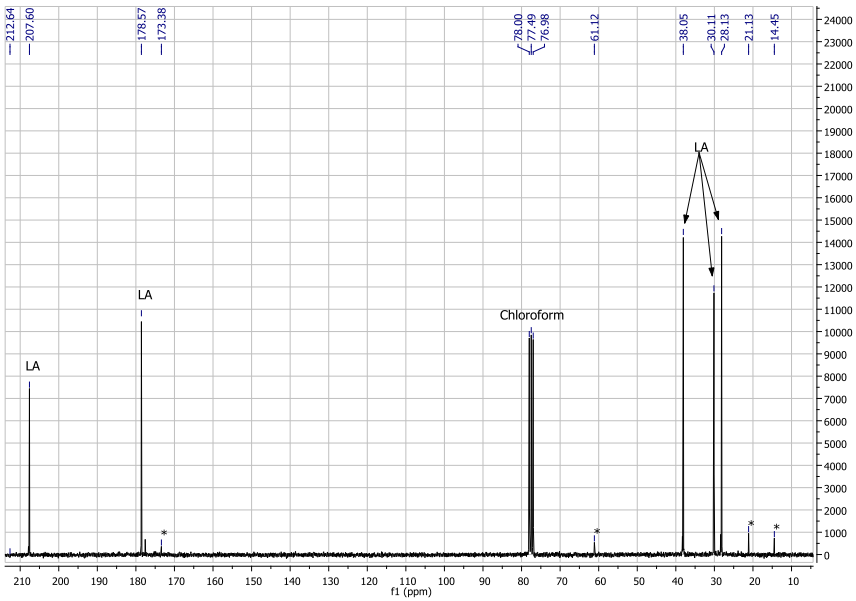
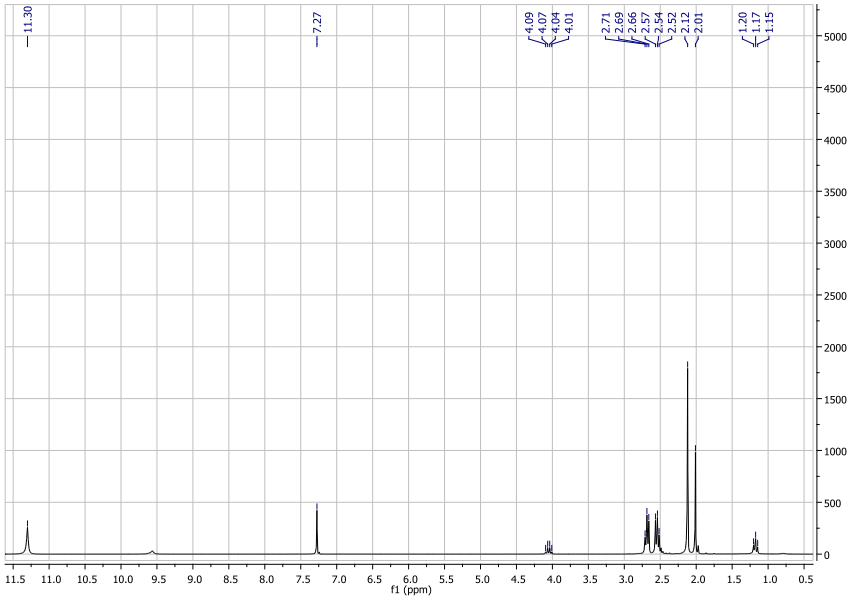
Electronic Supplementary Information (ESI)



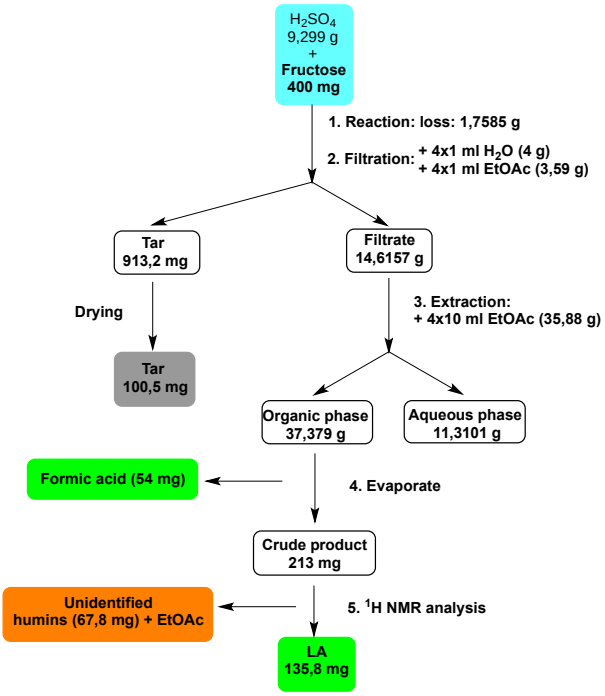
ESI-FIG 1. ^{13}C-NMR of the neat reaction mixture of sulfuric acid dehydrated fructose (400 mg in 8 mL 2M H_2SO_4).



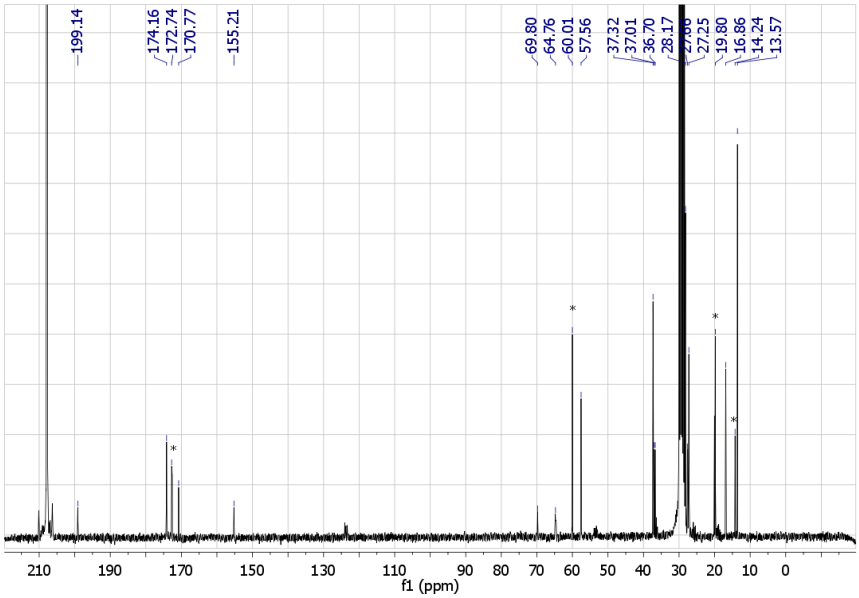
ESI-FIG 2. ^{13}C-NMR of the product of the reaction mixture of sulfuric acid dehydrated fructose after workup procedure. *: Ethyl-acetate residue from extraction



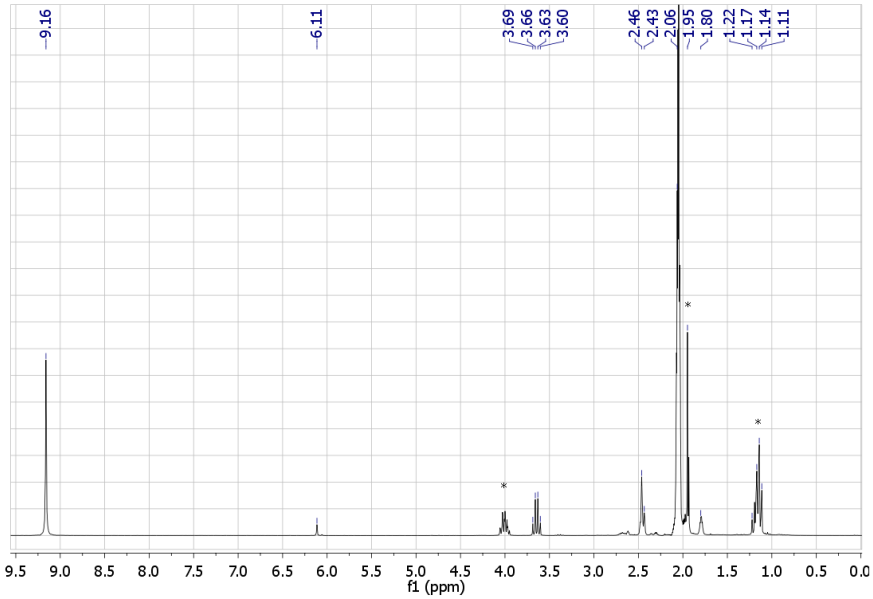
ESI-FIG 3. Typical ^{1}H-NMR spectrum of the product mixture of sulfuric acid dehydrated fructose after addition of benzene (10 μL) as internal standard.



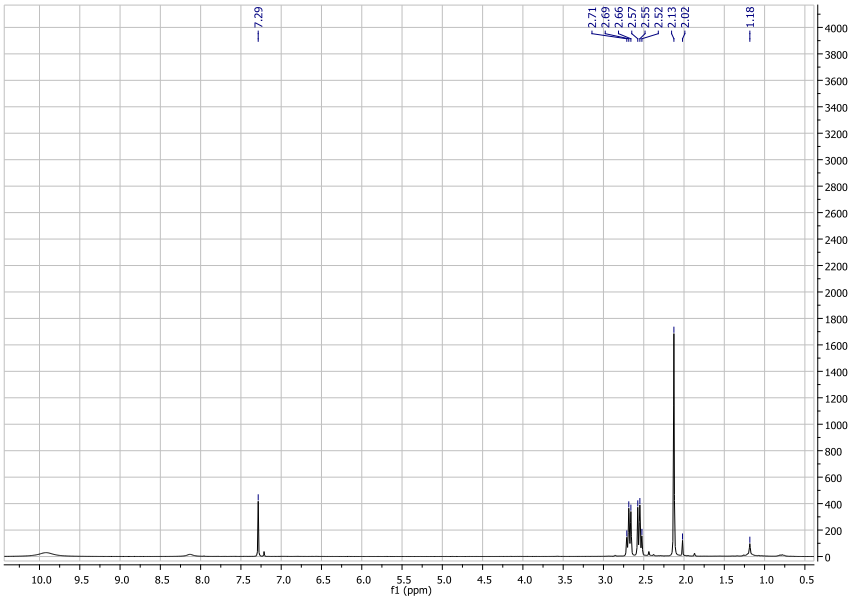
ESI-FIG 4. Mass balance of the process of the sulfuric acid catalyzed dehydration of 400 mg fructose.



ESI-FIG 5. ^{13}C-NMR spectrum of the humins obtained from ethyl-acetate extraction. The dark brown residue (67.8 mg) was dissolved in acetone-d_6 after EtOAc removal by vacuum.



ESI-FIG 6. ^{1}H-NMR spectrum of the humins obtained from ethyl-acetate extraction. The dark brown residue (67.8 mg) was dissolved in acetone-d_6 after EtOAc removal by vacuum.



ESI-FIG 7. Typical ^{1}H-NMR spectrum of the product mixture of sulfuric acid dehydrated glucosamine after addition of benzene (10 μL) as internal standard.

Method of calculation for LA

Benzene was used as internal standard for quantitative analysis of levulinic acid (LA) formed.

Int.stand.	M (g/mol)	m (g)	d (g/ml)	V (ml)	n (mol)
benzene	78	0,008786	0,8786	0,01	0,000113

The formula used to calculate amount of LA:

$$n_{LA} = \frac{2 \cdot n_B \cdot I_{LA}}{I_B} = 2 \cdot n_B \cdot I_{LA} = 0.000226 \cdot I_{LA}$$

n_B = mol of benzene added as internal standard
n_{LA} = mol of levulinic acid formed
I_B = ^{1}H-NMR integral of benzene (6H). Value was set to 1.
I_{LA} = ^{1}H-NMR integral of peak of levulinic acid at 2.1 ppm (-CH_3; 3H)

The table of yields and the corresponding integrals:

substrate	$c_{substrate}$/mol/dm^3	catalyst	t/min	Yield/%	m/m%	Integral(I_{LA})
cellulose	0,6175	H_2SO_4	30	21,4	15,4	2,35
cellulose	0,6175	HCl	50	46,0	31,0	4,74
cellulose	0,6175	H_2SO_4	50	34,2	23,0	3,53
glucose	0,5550	HCl	30	48,6	31,4	4,80
glucose	0,5550	H_2SO_4	30	40,5	26,1	4,00
fructose	0,5550	HCl	30	49,4	31,8	4,87
fructose	0,5550	H_2SO_4	30	42,7	27,5	4,21
cellobiose	0,2925	HCl	30	44,0	29,9	4,57
cellobiose	0,2925	H_2SO_4	30	41,3	28,0	4,29
chitin	0,4925	HCl	30	32,7	18,7	2,86
chitin	0,3700	H_2SO_4	30	37,8	21,6	2,48
l-chitosane	0,4125	HCl	20	31,9	22,7	2,60
l-chitosane	0,4175	H_2SO_4	20	19,3	13,7	1,57
M-chitosane	0,4175	HCl	20	37,0	26,3	3,02
M-chitosane	0,4125	H_2SO_4	20	32,1	22,8	2,62
glucosamine	0,4175	HCl	10	36,4	19,6	2,25
glucosamine	0,4175	H_2SO_4	10	25,6	13,8	1,58
N-acetyl-glucosamine	0,3400	HCl	10	22,4	11,8	1,35
N-acetyl-glucosamine	0,3400	H_2SO_4	10	20,6	10,8	1,24