

# Organic compounds profiling in bioethanol samples of different nature and the related fractions

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Table S 1. Limits of quantification (LOQ) determined according to the  $10(\text{SNR})/\text{sensitivity}$ .

Analyte	LOQ (mg L <sup>-1</sup> )
Acetaldehyde	65
methanol	103
Acetone	44
2-propanol	90
1-propanol	157
2-butanol	135
i-butanol	192
1-butanol	178
1,1-diethoxyethane	118
Isoamyl alcohol	126

Table S 2. Alcohols found by GC-MS in the bioethanol samples.

ALCOHOLS (23)	Retention times (min)	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10	B11	B12	B13	B14	B15	B16	B17	B18	B19	B20	B21	B22	B23	B24	B25	B26	B27	B28	B29	B30	B31-B34	B35-B38	B39	B40	B41	B42			
2-propanol	5.437	X							X								X		X									X	X	X										
2-propen-1-ol	7.590																		X																					
1-propanol	7.878	X	X	X			X	X	X	X	X	X	X	X	X	X	X	X	X	X		X									X	X				X				
2-Butanol	11.750						X				X	X				X			X			X								X	X									
Isobutanol	12.044	X	X	X			X		X	X	X	X	X	X	X	X	X	X	X	X																X				
1-Butanol	13.707	X	X	X							X	X			X				X			X								X	X			X						
2-methyl-2-propen-1-ol	14.380																																	X						
2-Pentanol	14.780																X			X										X			X							
Isoamyl alcohol	16.336	X	X	X			X	X	X		X	X	X	X	X			X	X	X		X								X	X		X	X	X	X				
Amyl alcohol	16.423	X	X	X			X	X	X		X	X	X	X	X			X	X	X		X								X	X		X	X	X	X				
2-hexanol	16.880																X																							
Diethylenglicol	18.247																			X																				
1,3-butanediol	18.540																																					X		
2,3-butanediol	18.700			X																																		X		
3-ethoxy-1-propanol	18.900																																					X		
1-hexanol	19.327			X											X				X																		X			
Cyclohexanol	19.730																X																							
2-Furanmethanol	19.563			X																X																				
Guaiacol	22.578																			X																				
benzene etanol	22.974			X											X					X																	X			
1-undecanol	23.811						X																																	
Tetradecanol	24.074				X																																			
3,5-dimethyl	25.260				X																									X										



Table S 4. Esters found by GC-MS in the bioethanol samples.

ESTERS (24)	Retention times (min)	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10	B11	B12	B13	B14	B15	B16	B17	B18	B19	B20	B21	B22	B23	B24	B25	B26	B27	B28	B29	B30	B31-B34	B35-B38	B39	B40	B41	B42		
Ethyl acetate	8.905	X	X	X			X	X	X	X	X	X	X	X	X	X	X	X	X	X		X	X	X	X	X						X			X				
Ethyl propionate	14.369	X		X			X	X	X		X	X	X				X	X	X	X		X	X	X	X	X	X					X			X				
n-Propyl acetate	14.585																		X																				
Ethyl isobutirate	16.094																		X																				
Isobutyl acetate	16.785																X																						
Isoamyl formate	17.260																																						
Ethyl butirate	17.379	X		X			X	X	X	X	X	X	X	X			X	X	X			X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X		
Ethyl (S)-(-)-lactate	18.249			X															X	X			X																
ethyl 3-methylbutanoate	18.557																		X												X								
Isobutyl propionate	18.910																																						
isoamyl acetate	19.043	X	X	X			X		X		X	X	X		X		X	X	X	X		X								X	X	X	X	X	X				
amyl acetate	19.110																													X									
2-methylbutyl acetate	19.113																		X																				
Ethyl valerate	19.424			X			X	X			X	X	X				X	X												X	X								
isobutyl isobutyrate	19.690																																						
Methyl caproate	19.841																		X																				
Ethyl caproate	20.871		X	X			X	X			X	X	X				X	X				X								X	X								
Methyl furoate	21.039																			X																			
isobutyl isopentanoic acid ester	31.080																																						
Ethyl heptanoate	22.059			X																																			
Ethyl caprylate	23.047			X															X	X										X	X								
ethyl nonanoate	24.057																			X																			
Phenylethyl acetate	24.180			X																																			
Ethyl caprate	25.185			X															X	X										X	X								

Table S 5. Ethers found by GC-MS in the bioethanol samples.

ETHERS (16)	Retention times (min)	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10	B11	B12	B13	B14	B15	B16	B17	B18	B19	B20	B21	B22	B23	B24	B25	B26	B27	B28	B29	B30	B31-B34	B35-B38	B39	B40	B41	B42			
		2-ethoxy-2-methylpropane	8.905																X																					
1-ethoxy-1-methoxyethane	14.369																		X																					
1,1-dimethoxyethane	14.585																		X																					
1,1-diethoxyethane	16.094	X	X	X			X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			X	X			X				
2,4,5-trimethyl-1,3-dioxolane	16.785																					X																		
2,2-diethoxypropane	17.260	X								X																														
3,3-diethoxy-1-propene	17.379																X																							
1-ethoxy-1-propoxyethane	18.249																		X																			X		
1,1-diethoxy-2-methylpropane	18.557						X	X	X		X	X		X				X	X			X			X	X	X			X	X			X		X				
1,1-diethoxybutane	18.910			X													X						X						X											
1,1-diethoxy isopentane	19.043							X											X																					
1,1-diethoxy-3-methylbutane	19.110						X	X									X																							
1-ethoxy-1-pentoxyethane	19.113																		X																X					
Diisobutylacetal	19.424																																				X			
1,1,3-triethoxypropane	19.690																			X																				
1,1-diethoxyhexane	19.841																			X																				

Table S 6. Hydrocarbons found by GC-MS in the bioethanol samples.

HYDROCARBONS (17)	Retention times (min)	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10	B11	B12	B13	B14	B15	B16	B17	B18	B19	B20	B21	B22	B23	B24	B25	B26	B27	B28	B29	B30	B31-B34	B35-B38	B39	B40	B41	B42
n-pentane	3.180																																				
n-hexane	5.940	X														X							X	X	X	X	X	X	X	X						X	
Cyclohexane	9.988	X																					X	X	X	X	X										
1,3-dimethylcyclopentane																	X																				
1,2-dimethylcyclopentane	11.830																X																				
n-heptane	12.332																X					X												X	X		
Bicycle (2.2.1) hepta-2,5-diene	13.200																						X	X	X	X	X	X	X	X							
Methylcyclohexane	13.600																X																				
Ethylcyclopentane	14.120																X																				
Ethylcyclohexane	17.680																																				
1,1,cis 3,5-tetramethylcyclohexane	19.260																						X														
1-Dodecene	22.781	X			X																																
Tridecane	22.782						X																														
Butylcyclohexane	23.476							X																													
Cyclododecane	24.874				X																																
1-tetradecene	24.876					X	X									X																					
11-tricosene	27.726				X																																

Table S 7. Aromatic hydrocarbons found by GC-MS in the bioethanol samples.

AROMATIC HYDROCARBONS (12)	Retention times (min)	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10	B11	B12	B13	B14	B15	B16	B17	B18	B19	B20	B21	B22	B23	B24	B25	B26	B27	B28	B29	B30	B31-B34	B35-B38	B39	B40	B41	B42	
Toluene	16.182	X														X	X					X	X	X	X	X	X	X	X	X					X	X	X	
Ethylbenzene	18.719											X										X															X	
p-xylene	18.869	X			X		X					X		X		X	X					X	X	X	X	X	X	X	X							X	X	X
m-xylene	18.872	X					X					X				X	X					X	X	X	X	X	X	X	X							X	X	X
Stirene	19.423	X																					X	X	X	X	X	X										
o-xylene	19.939																					X															X	
o-methyltoluene	20.490																																			X		
1,2,3-trymethylbenzene	20.950																																		X	X		
1,2,4-trymethylbenzene	20.950																																		X	X		
1,3,5-trimethylbenzene	20.950																																		X	X		
1,2,3,4-tetrahydro-1,1,6-trimethyl-1-napthalene	24.982																			X																		
1,2-dihydro-1,1,6-trimethylnapthalene	25.333																			X																		



Table S 8. Nitrogen compounds found by GC-MS in the bioethanol samples.

NITROGEN COMPOUNDS (10)	Retention times (min)	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10	B11	B12	B13	B14	B15	B16	B17	B18	B19	B20	B21	B22	B23	B24	B25	B26	B27	B28	B29	B30	B31-B34	B35-B38	B39	B40	B41	B42			
		N-ethyl-1,3-dithioisoindoline	17.228	X							X										X																	X		
2-methylazetidine	17.370																																			X				
2-Methylpyridine	18.110																																			X				
Methylpyrazine	18.300																																			X				
2,4,5-trimethyloxazole	19.810																																			X				
2,5-dimethylpirazine	21.120																															X								
2,3,5-trimethylpirazine	22.100																																			X				
tetramethylpyrazine	22.730																															X								
Pyrazole	23.021																			X																				
Tributylamine	17.228	X		X			X						X								X															X	X	X		

Table S 9. Organic acids found by GC-MS in the bioethanol samples.

ORGANIC ACIDS (2)	Retention times (min)	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10	B11	B12	B13	B14	B15	B16	B17	B18	B19	B20	B21	B22	B23	B24	B25	B26	B27	B28	B29	B30	B31-B34	B35-B38	B39	B40	B41	B42			
		Acetic acid	13.623			X																X												X						
Isobutyric acid	17.910																																		X					

Table S 10. Furane derivatives found by GC-MS in the bioethanol samples.

FURANE DERIVATES (8)	Retention times (min)	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10	B11	B12	B13	B14	B15	B16	B17	B18	B19	B20	B21	B22	B23	B24	B25	B26	B27	B28	B29	B30	B31-B34	B35-B38	B39	B40	B41	B42		
		Furfural	18.966		X																	X																	
Furylcarbinol	19.563			X																X																			
Acetylfurane	20.251																			X																			
2-pentylfurane	20.740									X																													
Ethylfurane carbonate	20.905																			X																			
Methyl furoate	21.039																			X																			
2-acetyl-5-methylfurane	21.608																			X																			
1-(2-furyl)-3-butanone	22.268																			X																			

Table S 11. Other organic compounds found by GC-MS in the bioethanol samples.

OTHER COMPOUNDS (6)	Retention times (min)	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10	B11	B12	B13	B14	B15	B16	B17	B18	B19	B20	B21	B22	B23	B24	B25	B26	B27	B28	B29	B30	B31-B34	B35-B38	B39	B40	B41	B42			
		Chloroform	9.544	X																																				
Dimethoxydimethylsilane	15.615	X																																						
Hexamethyl-cyclotrisiloxane	15.824							X	X					X							X																X	X	X	
Myrcene	17.313																					X																		
Limonene	18.560				X		X									X			X		X	X	X	X	X	X	X	X	X	X				X						
alpha ionene	20.610																			X																				

