Slow Pyrolysis of De-Oiled Rapeseed Cake: Influence of Pyrolysis Parameters on the Yield and Characteristics of the Liquid Obtained

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Experimental section

Characterization and analysis

TGA is performed on a NETZSCH STA 449 F5 coupled with QMS 403 D mass detector, where parameters were set as followed: with a flow rate of 80 ml·min^{-1} (N$_2$), a heating rate of 5 °C·min^{-1} up to the final temperature of 800 °C. The elemental composition (CHNS) of feedstock, bio-oil and bio-char fractions were determined using EA flash 1112 elemental analyzer (Thermo Electron Corporation), while the O content is calculated by mass difference. The higher heating value (HHV) is calculated according to ultimate analysis using Equation (S1) [1]:

HHV = 3.55·C^2 - 232·C - 2230·H + 51.2·C·H + 131·N + 20600, kJ·kg^{-1}, $\qquad$ (S1)

where C, H, O and N refer to the mass fraction of the elements.

After two successive Soxhlet extractions (24 h) with 95% ethanol (VWR) and hot water, respectively, a component analysis is performed on the de-oiled rapeseed cake (DRC) according to an adapted method of Van Soest and Wine, as described by Faithfull et al and Qi et al [2, 3]. To tackle the problem of interference by proteins, the results of each step of the component analysis is corrected by determination of its protein content via elemental analysis (N content multiplied by a protein factor of 6.25), thus corresponding crude protein content (N × 6.25) is also determined. The constitutes in the pyrolysis liquids are qualitatively identified using GC-MS (Agilent, 6890N) equipped with a HP-INNOWAX column. Water contents of the liquids are determined by Karl Fisher titration according to ASTM D1744. The total acid number (TAN) is determined by the ASTM D664-04 method, where end-point of the titration

is set at pH 11 using an aqueous buffer solution as prescribed in the ASTM method. pH values of the pyrolysis liquids were measured using a digital pH meter (Mettler Delta 340), corresponding values were obtained after 10 min stabilization of the mechanically stirred liquids. The viscosity of pyrolysis liquids is determined using rheometer type ARS TA and temperature is set at 25 and 60 °C. Density was determined based on ASTM D1298.

The raw rapeseed oil cake was characterized by using proximate and ultimate analysis. Moisture, volatile, fixed carbon and ash content was established according to ASTM standards D 2016 74, D3174 89 and D1102 84, respectively. The ultimate analysis was performed to determine the content of carbon, hydrogen, nitrogen, sulfur and oxygen, using an EA flash 1112 elemental analyzer according to ASTM D 5373 and composition was established according to ASTM D 3176. The higher heating value (HHV) was determined according to ASTM D240-02 and calculated using Equation (S1). The lower heating value (LHV) was calculated using equation as followed[4]:

$$LHV = 0.126*CO + 0.108*H_2 + 0.358*CH_4 + 0.665*C_nH_m, \text{ MJ / Nm}^3, \tag{S2}$$

where CO, H_2, CH_4 and C_nH_m (n=2, m=2, 4 and 6) represents the molar fractions of the species.

Acetone was added into chars to separate any heavy hydrocarbons. Product yield was calculated using the following Equations (S3)–(S5):

$$\text{Bio-char Yield } (wt\%) = Y_{Bio\text{-}char} = (W_{Bio\text{-}char} / W_{Feedstock}) \times 100\% \tag{S3}$$

$$\text{Bio-oil Yield } (wt\%) = Y_{Bio\text{-}oil} = (W_{Bio\text{-}oil} / W_{Feedstock}) \times 100\% \tag{S4}$$

Bio-gas Yield ($wt\%$) = $Y_{Bio\text{-}gas}$ = 100 - $Y_{Bio\text{-}char}$ - $Y_{Bio\text{-}oil}$ (S5)
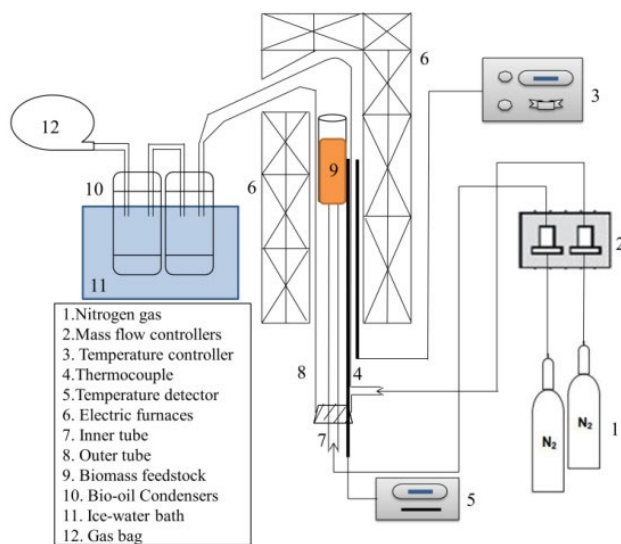

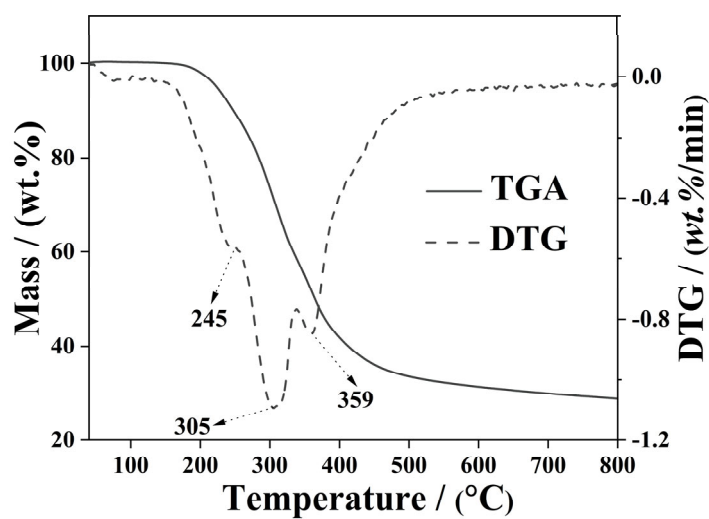**Figure S1.** Frame diagram of pyrolysis process.

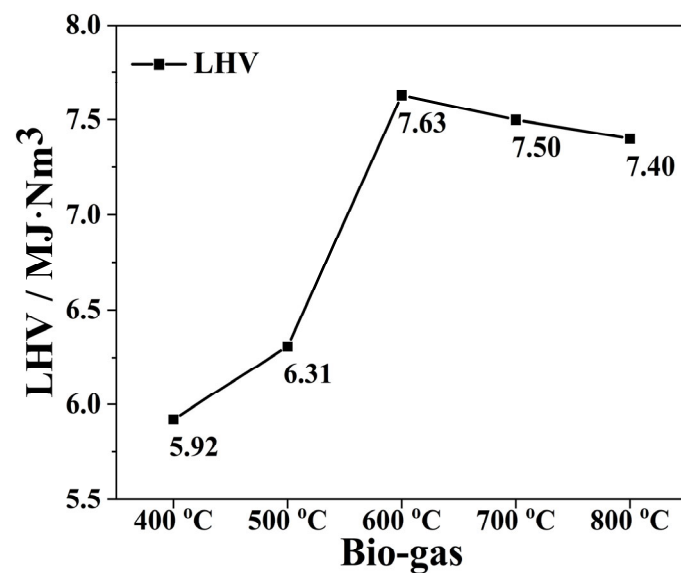**Figure S2.** The TGA and DTG curves of de-oiled rapeseed cake.

Figure S3. LHV of gaseous products at different temperatures.
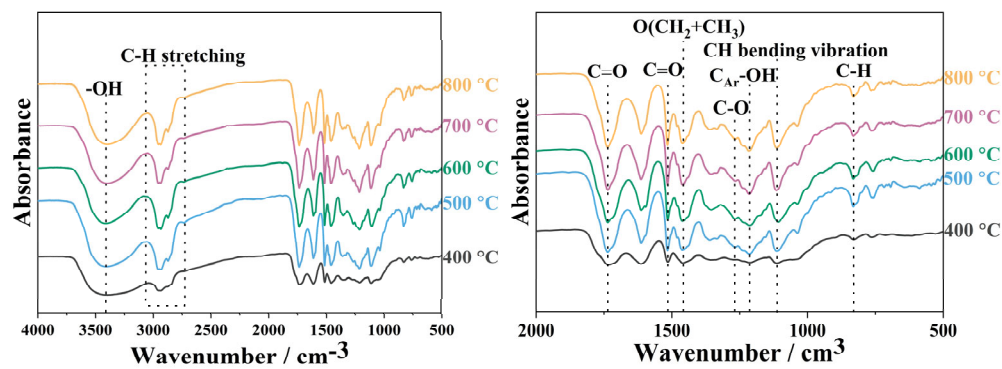

Figure S4. FT-IR spectra of bio-oils from different pyrolysis temperatures. Left panel shows the whole spectra ranging from 4000-500 cm^{-1}, right panel indicates the specific spectra ranging from 2000-500 cm^{-1}.

FT-IR spectra were introduced to identify the functional groups existed in the bio-oils obtained from different pyrolysis temperatures, and these are presented in Figure S6. Characteristic absorbance of the bio-oil remained almost unchanged with pyrolysis temperature above 400°C.

Table S1. Products Distribution via different pyrolysis temperatures.

	Pyrolysis temperature (°C)				
	400	500	600	700	800
Yield ($wt\%$)					
Liquid	40.4	48.9	51.6	47.5	45.4
Solid	41.8	33.6	31.4	29.9	28.8
Gas	17.8	17.5	17	22.6	25.8

The conversion and yields ($wt.\%$) were based on the initial weight of rapeseed oil cake.

Table S2. Ultimate, Proximate and HHV of DRC and bio-chars investigated by temperatures.

Solids	Ultimate Analysis (wt% dry basis)					Proximate Analysis (wt% dry basis)			H/C ratio	O/C ratio	HHV (MJ·kg⁻¹)
	C	H	N	Oᵃ	S	VM	FC	Ash			
DRC	46.96	6.98	6.67	38.36	1.03	70.32	12.29	0.38	1.77	0.61	19.62
400	73.65	3.85	2.51	19.36	0.63				0.62	0.20	29.03
500	75.32	3.67	2.47	18.03	0.51				0.58	0.18	29.56
600	76.97	3.51	2.43	16.66	0.43				0.54	0.16	30.10
700	77.13	3.47	2.38	16.51	0.41				0.54	0.16	30.10
800	77.42	3.41	2.36	16.42	0.39				0.52	0.16	30.14

ᵃO=100-C-H-N (*wt.%*)

$$\frac{H}{C} molar\ ratio = \frac{Weight\ Percent\ Hydrogen/Atomic\ Weight\ Hydrogen}{Weight\ Percent\ Carbon/Atomic\ Weight\ Carbon}$$

$$\frac{O}{C} molar\ ratio = \frac{Weight\ Percent\ Oxygen/Atomic\ Weight\ Oxygen}{Weight\ Percent\ Carbon/Atomic\ Weight\ Carbon}$$

Table S3. Composition of gaseous products obtained at different temperature.

	Temperatures (°C)				
	400	500	600	700	800
Composition (*vol.%*)					
CO / vol.%	12.48	13.25	19.09	17.55	16.53
CO_2 / vol.%	77.44	75.98	68.76	70.12	71.07
CH_4 / vol.%	5.75	6.15	6.97	7.07	7.11
C_2H_6 / vol.%	3.27	3.48	3.89	3.93	3.95
H_2 / vol.%	1.06	1.14	1.29	1.33	1.34
LHV / $MJ·Nm^{-3}$	5.92	6.31	7.63	7.50	7.40

Table S4. Products Distribution via different flow gas rates.

	N_2 flow rate (mL·min^{-1})				
	30+40	40+60	50+80	60+100	70+120
Yield (*wt*%)					
Liquid	45.7	49.4	51.6	49.1	46.3
Solid	39.1	34.8	31.4	30.3	29.6
Gas	15.2	15.8	17	20.6	24.1

The conversion and yields (*wt.*%) were based on the initial weight of de-oiled rapeseed cake.

Table S5. Products Distribution via different flow retention time.

	Retention time (h)				
	0	0.5	1	1.5	2.0
Yield (*wt.*%)					
Liquid	49.7	51.6	51.7	51.9	51.9
Solid	33.1	31.4	31.6	31.9	32.0
Gas	17.2	17	16.7	16.2	16.1

The conversion and yields (*wt.*%) were based on the initial weight of rapeseed oil cake.

Table S6. Products Distribution via different volume of condensers.

	Volume of condenser (cm^3)		
	15+15	**15+210**	**210+210**
Yield (*wt.%*)			
Liquid	47.3	49.1	51.6
Solid	34.2	32.8	31.4
Gas	18.5	18.1	17.0

The conversion and yields (*wt.%*) were based on the initial weight of rapeseed oil cake.

Table S7. Physical chemical characteristics of the bio-oils obtained from DRC pyrolysis temperature at 5 intervals (400-800 °C, 50 and 80 mL·min^{-1} for inner and outer tubes, retention time of 0.5 h, volumes of condensers with 210+210 cm^3).

Ultimate Analysis / *wt.%*	Pyrolysis temperature / °C				
	400	500	600	700	800
C	65.15	66.72	67.41	67.63	67.69
H	8.43	8.56	8.64	8.65	8.67
N	8.46	8.71	8.99	9.05	9.07
S	0.50	0.52	0.55	0.58	0.60
O^a	17.46	15.49	14.41	14.09	13.97
H/C atomic ratio	1.54	1.53	1.53	1.52	1.52
O/C atomic ratio	0.20	0.17	0.16	0.16	0.15
Moisture / *wt.%*	5.18	4.96	4.87	4.83	4.80
Viscosity (40 °C, mm^2.s^{-1})	406.50	406.50	413.22	416.67	416.67
TAN (mg KOH / g)	44.76	44.68	44.51	44.37	44.34
Density (g / mL)	1.23	1.23	1.21	1.20	1.20
Surface tension(25°C mN·m^{-1})	25.74	25.61	24.10	24.08	24.07

HHV (MJ·kg⁻¹)	30.98	32.22	32.82	32.99	33.06

Limited variation of carbon, hydrogen content could be observed over 400 ℃, as well as corresponding molar ratios and HHV value. The moisture content declined from 5.18 *wt*% to 4.80 *wt*% with increase in temperatures from 400 to 800 ℃. Thermal physical properties of pyrolysis liquid were getting better with increase in temperature, while limited optimization could be observed over 600℃.

Table S8. Physical chemical characteristics of the bio-oils obtained from DRC pyrolysis at 5 flow gas rates (30+40-70+120 mL·min^{-1}, 50 plus 80 mL·min^{-1} for inner and outer tubes, retention time of 0.5 h, volumes of condensers with 210+210 cm^3).

Ultimate	Flow gas rates / mL·min^{-1}				
Analysis / *wt.%*	30+40	40+60	50+80	60+100	70+120
C	64.07	64.99	67.41	67.53	67.58
H	8.41	8.48	8.64	8.66	8.67
N	8.37	8.69	8.99	9.04	9.06
S	0.49	0.53	0.55	0.56	0.56
O[a]	18.66	17.31	14.41	14.21	14.13
H/C atomic ratio	1.56	1.55	1.53	1.53	1.53
O/C atomic ratio	0.22	0.20	0.16	0.16	0.16
Moisture / *wt.%*	5.01	4.92	4.87	4.95	4.99
Viscosity (40 °C, mm^2.s^{-1})	431.03	420.17	413.22	406.50	403.23
TAN (mg KOH / g)	44.27	44.46	44.51	44.67	44.76
Density (g / mL)	1.16	1.19	1.21	1.23	1.24
Surface tension(25°C mN·m^{-1})	23.4	23.8	24.1	24.7	25.2

HHV (MJ·kg^{-1})	30.24	30.96	32.82	32.94	32.99

Content of carbon and hydrogen increased obviously by 3.34 and 0.23 *wt%*, respectively, when increased flow gas rates from 30+40 to 50+80 mL·min^{-1}, little increasement could be observed with further increase in flow gas rates, HHV value increased from 30.24 to 32.82 MJ·kg^{-1} in the same flow gas rate range, with further increase in flow gas rates, limited variation could be observed. Moreover, properties such as viscosity value was in the negative correlation with the flow gas rates, but in the positive correlation with other characters such as TAN, density and surface tension. Moisture decreased to minimum value of 4.87 *wt%* with gas flow rate of 50+80 mL·min^{-1}.

Table S9. Physical chemical characteristics of the bio-oils obtained from DRC pyrolysis at 5 retention times (0-2h with step of 0.5 h, pyrolysis temperature at 600 °C, 50 plus 80 mL·min^{-1} for inner and outer tubes, respectively, retention time at 0.5 h, volumes of condensers with 210+210 cm^3).

Ultimate Analysis / *wt.%*	Retention time / h				
	0h	0.5h	1h	1.5h	2h
C	64.53	67.41	67.48	67.51	67.52
H	8.41	8.64	8.66	8.69	8.69
N	8.73	8.99	9.04	9.06	9.07
S	0.53	0.55	0.56	0.58	0.58
O[a]	17.8	14.41	14.26	14.16	14.14
H/C atomic ratio	1.55	1.59	1.60	1.60	1.60
O/C atomic ratio	0.21	0.16	0.16	0.16	0.16
Moisture / *wt.%*	5.02	4.87	4.79	4.72	4.69
Viscosity (40 °C, mm^2.s^{-1})	406.50	413.22	416.67	423.73	423.73
TAN (mg KOH / g)	44.45	44.51	44.59	44.64	44.69
Density (g / mL)	1.23	1.21	1.20	1.18	1.18

Surface tension(25°C mN·m^{-1})	24.69	24.1	24.07	24.05	24.04
HHV (MJ·kg^{-1})	30.59	32.82	32.90	32.96	32.97

Composition of bio-oils obtained from different retention time is shown in Table S9. As could be observed, corresponding values for various parameters remained almost unchanged since prolonging the retention time above 0.5 h.

Table S10. Physical chemical characteristics of the bio-oils obtained from DRC pyrolysis at 3 tandem condensers (15+15)-(210+210) cm^3, pyrolysis temperature at 600 ℃, retention time of 0.5 h, 50 plus 80 mL·min^{-1} for inner and outer tubes, respectively).

Ultimate	Volumes of tandem condensers / cm^3		
Analysis / *wt.%*	15+15	15+210	210+210
C	65.12	66.67	67.41
H	8.37	8.56	8.64
N	8.53	8.82	8.99
S	0.53	0.54	0.55
O[a]	17.45	15.41	14.41
H/C atomic ratio	1.53	1.53	1.53
O/C atomic ratio	0.20	0.17	0.16
Moisture / *wt.%*	4.68	4.81	4.87
Viscosity (40 ℃, mm^2.s^{-1})	403.23	409.84	413.22
TAN (mg KOH / g)	44.37	44.43	44.51
Density (g / mL)	1.24	1.22	1.21
Surface tension(25℃ mN·m^{-1})	25.77	25.63	24.1

HHV (MJ·kg^{-1})	30.91	32.20	32.82

With augmented volume of condensers, carbon and hydrogen content reached to 67.41 and 8.64 *wt.%*, respectively, yielding a better H/C molar ratio of liquid with HHV of 32.82 MJ·kg^{-1}. Regarding the other characteristics, it seemed to be in little variation as investigated on other pyrolysis parameters on the composition of bio-oils obtained.

Table S11. The relative content of compounds in the bio-oil under 5 pyrolysis temperatures.

Compounds / area %	Pyrolysis temperature / ℃				
	400	500	600	700	800
Hydrocarbons	**7.13**	**11.04**	**16.41**	**12.31**	**11.43**
Heptadecane	3.86	4.39	6.32	4.83	5.34
Pentadecane	0.53	1.35	2.03	1.53	1.19
2,6,6-Trimethyl-bicyclo[3.1.1]heptane	0.31	0	0.21	0.15	0
Heptadecane, 2-methyl-	0.37	0	0	0.09	0
1-Tetradecene	0.09	0.36	0.92	0.33	0
Octadecane	0.77	1.28	2.35	1.58	2.27
Decane, 3-methyl	0	0.09	0	0.21	0.64
1,3-Cyclopentadiene,5,5-dimethyl-1,2-Dipropyl	0	1.21	0.23	0	0
Cyclohexane, 1,3-dimethyl-2-methylene-, cis-	0.18	0	0	0.33	0

1-Pentadecene	0.29	0.15	0.36	0	0.91
Tetradecane	0.32	1.34	2.39	1.96	0
Naphthalene	0	0.44	0.95	0.27	0.76
Naphthalene, 2-methyl-	0.25	0	0.13	0	0
2-Hexadecene, 3,7,11,15-tetramethyl-,	0.16	0.43	0.52	1.03	0.32
Phenols	**2.06**	**2.89**	**3.53**	**3.81**	**3.98**
Phenol, 2-methoxy-	0.19	0.25	0.36	0.69	0.81
Phenol	0.38	0.56	0.88	1.23	1.16
p-Cresol	0.1	0	0.17	0	0
Phenol, 2,6-dimethoxy-	0.13	0.35	0.56	0.87	1.02
2-Methoxy-5-methylphenol	0.13	0.22	0.31	0.19	0
Phenol, 4-ethyl-2-methoxy-	0.06	0.22	0	0	0
Phenol, 2-methyl-	0.27	0	0.06	0	0
Phenol, 4-ethyl-	0	0.11	0.21	0.36	0
Isoeugenol	0	0	0	0.12	0

Vanillin	0.42	0.29	0	0	0.33
Eugenol	0	0	0	0	0
Catechol	0	0.12	0	0	0
Maltol	0	0	0	0.21	0.37
Phenol, 2,4-dimethyl-	0.09	0.33	0	0.06	0.16
3-Allyl-6-methoxyphenol	0.22	0.36	0.84	0.08	0.13
Butylpyrogallol	0.07	0.08	0.14	0	0
Acids	**68.38**	**62.96**	**56.12**	**59.59**	**60.19**
Docasadienoic acid	0.81	0.57	0.65	0.19	0
Gamolenic acid	0.49	0	0.58	0	0.89
Octadecanedioic acid	1.12	0.86	1.61	0.07	0
n-Hexadecanoic acid	13.53	7.19	18.33	12.92	10.53
Octadecanoic acid	6.88	9.04	4.36	6.74	9.37
Tetradecanoic acid	4.24	4.01	1.08	5.83	8.58
Pentanoic acid, 3-methyl-	0	1.03	0.54	0.31	2.24
Oleic acid	6.07	8.05	5.11	5.47	6.32
Acetic acid	35.24	29.83	20.37	25.49	17.39

Butanoic acid (3-methyl-)	0	2.38	3.49	2.57	4.87
Esters (Total)	**9.31**	**8.97**	**8.81**	**8.27**	**7.97**
Trichloroacetic acid, undecyl ester	2.31	2.19	2.27	2.48	2.09
2-Butenedioic acid (Z)-, monododecyl ester	2.14	2.03	1.89	1.35	2.32
Hexadecenoic acid, 9-octadecenyl ester	1.79	1.35	1.46	1.26	1.57
Diethylmalonic acid, ethyl 3-methylbenzyl ester	0.88	1.04	0.91	1.04	0.52
Hexadecenoic acid, 9-octadecenyl ester	1.38	1.66	1.75	1.53	0.7
Docosahexaenoic acid, methyl ester	0.81	0.7	0.53	0.61	0.77
Ketones (Total)	**2.38**	**2.76**	**3.16**	**3.49**	**3.78**
2-Cyclopenten-1-one and derivatives	0.51	0.64	0.83	1.45	1.68
Ethanone and derivatives	0.34	0.4	0.29	0.66	0.84

1-Hydroxy-2-butanone	0	0.13	0	0.32	0.27
1,2-Cyclopentanedione	0.47	0.57	0	0.72	0.49
Propanone and derivatives	0.31	0.61	1.22	0	0.11
3-Octadecanone	0.63	0.25	0.58	0.19	0.28
Nonadecanone	0.12	0.16	0.24	0.15	0.11
Alcohols (Total)	**7.31**	**7.68**	**8.25**	**8.68**	**8.83**
Furanmethanol	2.91	2.32	2.47	2.85	2.09
3,5-Dimethoxy-4-hydroxytoluene	1.85	1.68	1.32	1.77	1.55
Cyclohexaneethanol, 2-methylene-	0.54	0.77	0.91	1.39	1.24
Heptadecyn-1-ol	0.42	0.53	0.63	0.94	1.44
Nonanediol	0.83	0.95	1.14	1.03	0.88
Heptacosanol	0.44	0.82	1.33	0.41	0.97
Hexadien-2-ol	0.32	0.61	0.45	0.29	0.66
N-Compounds	**1.53**	**1.79**	**1.92**	**1.68**	**1.49**
Pentadecanenitrile	0.27	0.33	0.21	0.17	0.09

Octadecanenitrile	0.18	0.26	0.35	0.22	0.44
2-Pentenenitrile	0	0.11	0	0.23	0.19
Hexadecanamide	0.21	0.09	0	0	0.06
Pentanamide, 4-methyl-	0	0.03	0.07	0	0
Hexanamide	0.08	0.05	0	0	0.17
Propanamide	0.05	0	0.22	0	0
4-Pyridinol	0.13	0.22	0	0	0
3-Pyridinol, 6-methyl-	0	0	0.07	0	0.13
3-Pyridinol, 2-methyl-	0	0	0.1	0.21	0.25
Pyridine, 2-methyl-	0	0.12	0.22	0.37	0
2-Aminopyridine	0	0	0.03	0	0
Isoxazole, 3,5-dimethyl-	0	0.11	0	0	0.07
2-Piperidinone	0	0.07	0.11	0.23	0
2,5-Pyrrolidinedione	0	0	0.02	0	0
1H-Imidazole-2-methanol	0.25	0.1	0	0	0
1H-Imidazol-1-yl-ethanone	0	0	0.03	0	0

Imidazole,2-acetamino-5-methyl	0	0	0.08	0.02	0
2-Imidazolidinone, 1,3-diethenyl	0	0.04	0	0.02	0
2-Ethyl-3-methoxypyrazine	0	0.14	0.23	0.12	0.09
2,4,6-Pyrimidinetriamine, 5-t-butoxycarbonylamino-	0.25	0.08	0.18	0.09	0
L-Glutamic acid, diethyl ester	0.11	0.04	0	0	0
LGO	**0.87**	**1.04**	**1.27**	**1.56**	**1.68**
Monoglycerides	**1.03**	**0.87**	**0.54**	**0.61**	**0.65**

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