Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Production of drop-in biodiesel blendstocks via competitive acid-catalyzed dehydration reactions using ethanol oligomerization products

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Index

SI – 1 Feedstock compositions

Table SI 1. Simulated guerbet feedstocks from ethanol, post distillation of aldehydes and ketones. Data obtained from simulations from Restrepo-Flórez and coworkers[1].

Etherification feed code	**SG – 12**	**SG – 44**	**SG – 67**	**SG - 69**
Ethanol conversion (%)	12.26	44.16	66.51	68.9
Compounds		**Mol%**		
Alcohols				
1-butanol	91.09	80.40	62.88	54.26
2-pentanol	0.16	0.54	1.74	5.66
1-hexanol	5.44	9.15	13.28	11.16
2-ethyl-1-butanol	1.59	2.68	4.67	4.83
2-heptanol	0	0.86	1.16	3.25
1-octanol	0.60	1.26	3.27	2.50
2-ethyl-1-hexanol	0.20	0.59	2.02	1.73
4-nonanol	0	0.15	0.69	1.92
1-decanol	0	0.20	0.75	0.55
2-ethyl-1-octanol	0	0.20	0.56	0.55
4-undecanol	0	0.06	0.17	0.63
1-dodecanol	0	0.06	0.36	0.35
2-ethyl-1-decanol	0	0	0.42	0.29
4-tridecanol	0	0	0.19	0.42
1-tetradecanol	0	0	0.09	0.05
2-ethyl-1-dodecanol	0	0	0.04	0.10
2-pentadecanol	0	0	0.12	0.23
2-heptadecanol	0	0	0	0.08
esters				
Isopropyl acetate	0	0	0	0
Ethyl butanoate	0.14	0.10	0	0
Butyl acetate	0.59	0.28	0	0
Isopropyl butyrate	0	0	0.09	0.10
Butyl butanoate	0	1.09	1.95	3.62
Ethyl hexanoate	0.20	0.92	1.09	1.73
Hexyl acetate	0	0.59	0.70	0.95
Butyl hexanoate	0	0	1.62	2.49
Hexyl butanoate	0	0.60	0.19	0.35
Octyl acetate	0	0.07	0.12	0.21
Octyl butanoate	0	0	0.10	0.17
Butyl octanoate	0	0.17	0.05	0.98
Ethyl decanoate	0	0	0.73	0
Decyl acetate	0	0.05	0.05	0.06
Hexyl hexanoate	0	0	0.10	0.12
Hexyl octanoate	0	0	0.58	0.49
Ethyl dodecanoate	0	0	0.04	0.05
Dodecyl acetate	0	0	0.04	0.05
Octyl octanoate	0	0	0.12	0.09

Table SI 2. Model feedstock composition, assuming 100% ester hydrogenolysis and removal of light compounds < C_4. For alcohols that could not be purchased, the mol lumping method was used to maintain the alcohol structure composition of feedstocks. 'L/B' represents the linear to branched alcohol ratio. 'L/S' represents the linear to secondary alcohol ratio.

Etherification feed code	**MG – 12**	**MG – 44**	**MG – 67**	**MG - 69**
Ethanol conversion (%)	12.26	44.16	66.51	68.9
Compounds		**Mol%**		
Alcohols				
1-butanol	91.81	82.20	67.88	60.53
2-pentanol	0.16	0.53	1.78	5.22
1-hexanol	5.64	11.06	15.16	16.05
2-ethyl-1-butanol	1.59	2.63	4.77	4.46
2-heptanol	0	0.85	1.18	3.00
1-octanol	0.60	1.46	3.69	4.18
2-ethyl-1-hexanol	0.20	0.77	3.11	2.46
4-nonanol	0	0.15	0.71	1.77
1-decanol	0	0.25	0.82	0.61
2-undecanol	0	0.06	0.37	1.26
1-dodecanol	0	0.05	0.42	0.41
1-tetradecanol	0	0	0	0.05
Alcohol structure				
Linear **(L)**	98.05	95.02	88.74	81.82
Branched **(B)**	1.79	3.40	7.36	6.92
Secondary **(S)**	0.16	1.58	3.89	11.26
Alcohol ratios				
L/B	55	28	12	12
L/S	617	60	23	7

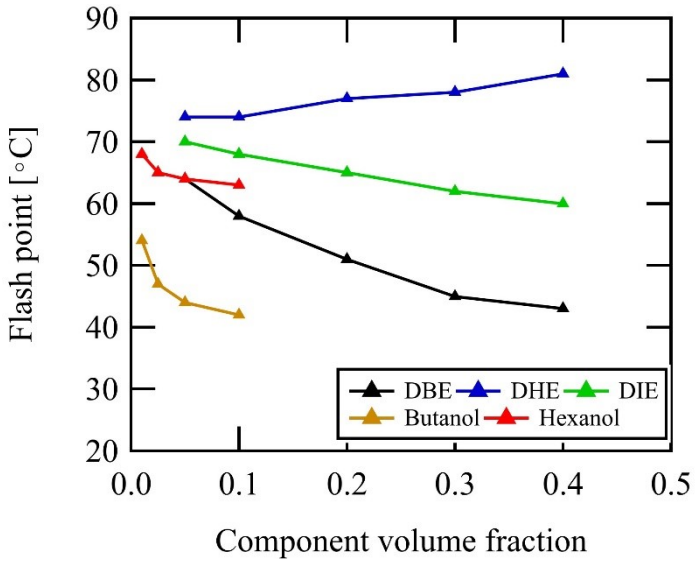

Figure SI 1. flashpoint temperature as a function of volume blending fractions of alcohols and ethers with fossil diesel. For fossil diesel, the baseline flashpoint temperature was 75 °C. DBE represents dibutyl ether, DHE represents dihexyl ether, and DIE represents di-isoamyl ether.

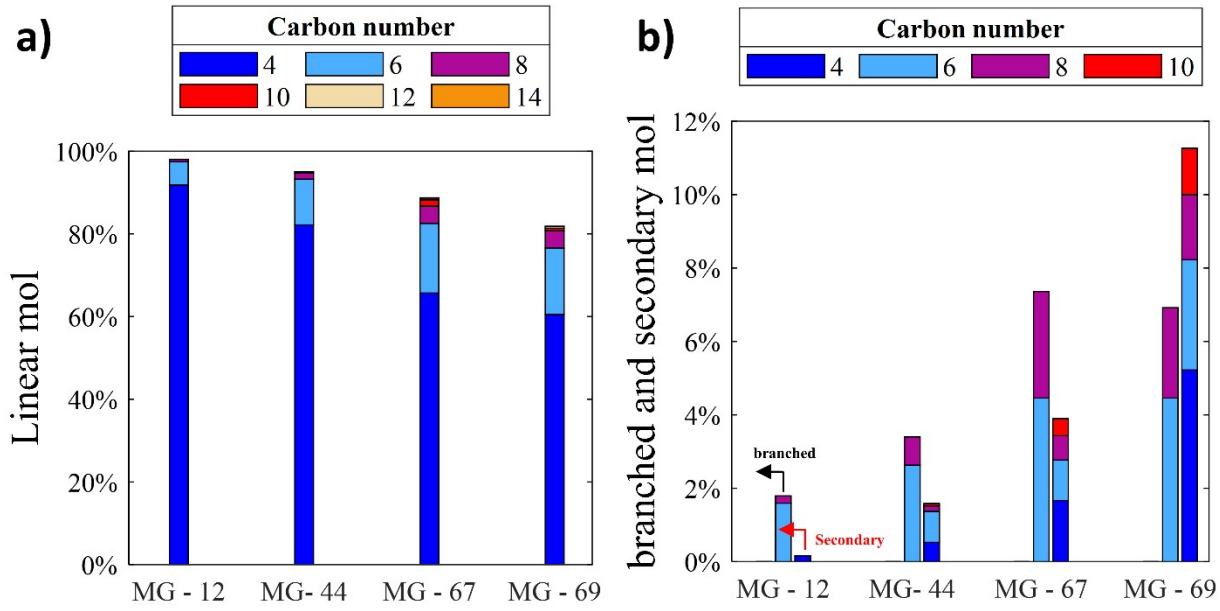

Figure SI 2. Alcohol distribution of products from ethanol oligomerization as a function of ethanol conversion, assuming 100% ester hydrogenolysis. These products will be used as model feedstocks for the etherification experiments in this paper. The conversion was varied by changing the weight hourly space velocity in the ethanol oligomerization reactor. The conversion is shown after the dash. **A)** represents the linear alcohol distribution and **B)** represents the branched and secondary alcohol distributions. For secondary alcohols, the numbering is defined by 'n+1'. Colors not visibly shown for compounds are present in low amounts (< 1.0%).

Table SI 3. Feedstock of SG – 12, where the esters are cut to a total mass of 0.15 wt%. All esters are assumed to be removed equally on a mass basis.

Etherification feed code	SG – 12@0.15wt%
Compounds	
Alcohols	
1-butanol	91.85
2-pentanol	0.16
1-hexanol	5.49
2-ethyl-1-butanol	1.61
2-heptanol	0.00
1-octanol	0.60
2-ethyl-1-hexanol	0.20
Esters	
Ethyl butanoate	0.01
Butyl acetate	0.06
Ethyl hexanoate	0.02

Table SI 4. Feedstock of EtOH/ButOH oligomerization products used for the n-butanol recycling unit analysis. 'L/B' represents the linear to branched alcohol ratio. 'L/S' represents the linear to secondary alcohol ratio.

Alcohol	Mol%
1-butanol	34.73
2-butanol	1.33
2-methyl-1-butanol	3.62
1-hexanol	40.35
2-ethyl-1-butanol	8.36
2-heptanol	3.42
2-ethyl-1-hexanol	3.60
1-octanol	4.26
2-octanol	0.11
2-nonanol	0.22
Alcohol ratios	
L/B	5
L/S	16

SI – 2 Results

Table SI 5. Linear alcohol results at 100 psig**.** WHSV = 0.54 h^{-1} over HY, flowrate = 0.02 mL/min. The coke selectivity is defined as carbon not detected in the liquid or gas phase.

Alcohol feed	1-butanol	1-hexanol	1-octanol
Liquid and gas carbon balance (%)	96.60	91.15	86.1
Carbon conversion (%)	73.41	84.66	91.21
Ether selectivity (%)	91.60	82.66	73.41
Olefin selectivity (%)	3.40	4.03	8.26
Unknown selectivity (%)	0.37	2.85	3.38
Total coke selectivity (%)	4.63	10.46	14.96

Table SI 6. Linear alcohol results at 100 psig. Adjusted to 100% carbon balance by considering carbon obtained from solid phase TOC analysis. WHSV = 0.54 h^{-1} over HY, flowrate = 0.02 mL/min.

Alcohol feed	**1-butanol**	**1-hexanol**	**1-octanol**
Liquid and gas carbon balance (%)	100	100	100
Carbon conversion (%)	73.41	84.66	91.21
Ether selectivity (%)	91.60	82.66	73.41
Olefin selectivity (%)	3.40	4.03	8.26
Unknown selectivity (%)	0.37	2.85	3.38
Coke on catalyst surface (%)	1.53	5.45	8.95
Coke in liquid phase (%)	3.11	5.01	6.01

Table SI 7. Comparison between esters in stream and effects of pressure on etherification. Leftover carbon not detected in the liquid or gas phase was assumed to go to coke products.

Etherification feed code		1-butanol	1-butanol	SG-12	MG-12	MG-12
Pressure (psig)		0	100	100	0	100
Overall carbon conversion (%)		69.24	73.41	78.33	72.24	73.17
Liquid and gas carbon balance (%)		102.72	96.6	88.26	93.78	96.15
Compound	**Carbon #**					
Alcohols						
Ethanol	2	-	-	0.09	-	-
Ethers						
Ethyl butyl ether	6	-	-	0.30	-	-
Butyl ether	8	86.60	91.60	63.50	46.48	70.40
Butyl ethyl-butane ether	10	-	-	0.81	0.11	0.77
C_{10} linear ethers	10	-	-	9.08	5.25	13.51
Butyl ethyl-hexane ether	12	-	-	-	-	0.12
C_{12} linear ethers	12	-	-	1.37	0.44	0.23
Olefins						
C_4 olefins	4	11.39	3.40	3.53	24.70	3.l4
C_5 olefins	5	-	-	0.18	0.41	0.26
C_6 olefins	6	-	-	2.99	6.75	3.19
C_8 olefins	8	-	-	0.48	1.63	1.21
Other products						
Unknown gas and liquid products	-	5.94	0.37	1.86	5.63	1.91
Coke	-	-	4.63	14.99	8.61	5.26
Esters						
Butyl butanoate	8	-	-	0.25	-	-
C_{10} ester	10	-	-	0.56	-	-

Table SI 8. Comparison between esters in stream and effects of pressure on etherification. Adjusted to 100% carbon balance by considering carbon obtained from solid phase TOC analysis.

Etherification feed code		1-butanol	1-butanol	SG-12	MG-12	MG-12
Pressure (psig)		0	100	100	0	100
Overall carbon conversion (%)		70.78	73.41	78.33	72.26	73.17
Total carbon balance (%)		100.00	100.00	100.00	100.00	100.00
Compound	**Carbon #**					
Alcohols						
Ethanol	2	-	-	0.09	-	-
Ethers						
Ethyl butyl ether	6	-	-	0.30	-	-
Butyl ether	8	80.45	91.60	63.50	46.44	70.40
Butyl ethyl-butane ether	10	-	-	0.81	0.11	0.77
C_{10} linear ethers	10	-	-	9.08	5.25	13.51
Butyl ethyl-hexane ether	12	-	-	-	-	0.12
C_{12} linear ethers	12	-	-	1.37	0.44	0.23
Olefins						
C_4 olefins	4	10.58	3.40	3.53	24.68	3.14
C_5 olefins	5	-	-	0.18	0.41	0.26
C_6 olefins	6	-	-	2.99	6.74	3.19
C_8 olefins	8	-	-	0.48	1.63	1.21
Other products						
Unknown gas and liquid products	-	5.52	0.37	1.86	5.62	1.91
Coke on catalyst surface	-	3.45	1.53	1.62	8.68	3.15
Coke in liquid phase	-	-	3.11	13.38	-	2.11
Esters						
Butyl butanoate	8	-	-	0.25	-	-
C_{10} ester	10	-	-	0.56	-	-

Table SI 9. Product feedstock composition of the ester cut using SG -12. Leftover carbon not detected in the liquid or gas phase was assumed to go to coke products.

Etherification feed code		**SG – 12@0.15wt%**
Pressure (psig)		100
Overall carbon conversion (%)		76.05
Liquid and gas carbon balance (%)		90.14
Compound	**Carbon #**	
Ethers		
Butyl ether	8	64.39
Butyl ethyl-butane ether	10	0.66
C_{10} linear ethers	10	11.17
Butyl ethyl-hexane ether	12	0.06
Olefins		
C_4 olefins	4	5.40
C_5 olefins	5	0.32
C_6 olefins	6	2.94
C_8 olefins	8	1.13
Unknown gas and liquid products	-	0.90
Coke	-	12.97
Esters		
C_{10} ester	10	0.05

Table SI 10. Product feedstock composition of the ester cut using SG -12. Adjusted to 100% carbon balance by considering carbon obtained from solid phase TOC analysis.

Etherification feed code		**SG – 12@0.15wt%**
Pressure (psig)		100
Overall carbon conversion (%)		76.05
Total carbon balance (%)		100
Compound	**Carbon #**	
Ethers		
Butyl ether	8	64.39
Butyl ethyl-butane ether	10	0.66
C_{10} linear ethers	10	11.17
Butyl ethyl-hexane ether	12	0.06
Olefins		
C_4 olefins	4	5.40
C_5 olefins	5	0.32
C_6 olefins	6	2.94
C_8 olefins	8	1.13
Unknown gas and liquid products	-	0.90
Coke on catalyst surface	-	4.34
Coke in liquid phase	-	8.63
Esters		
C_{10} ester	10	0.05

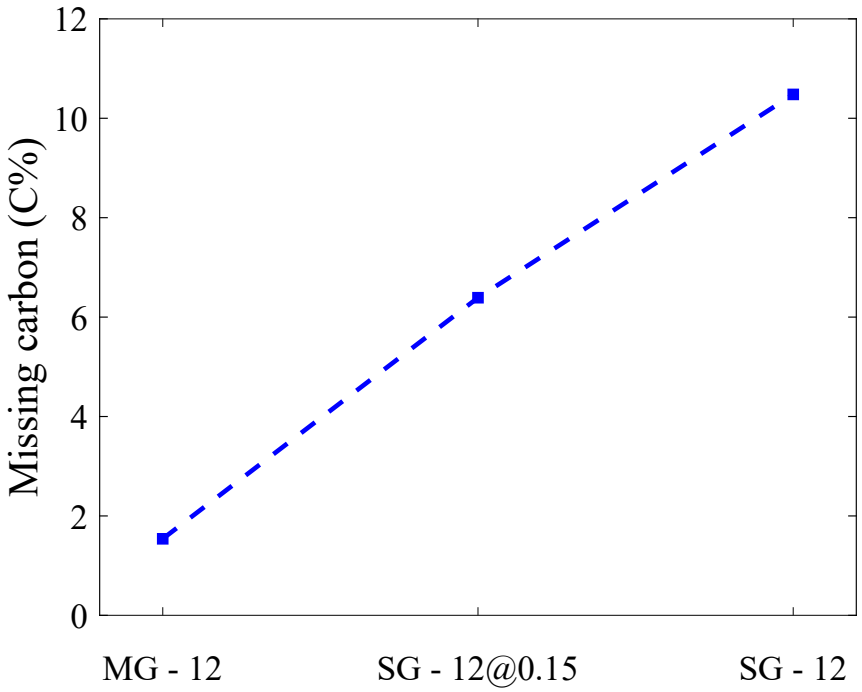

Figure SI 3. Missing carbon as a function of ester concentration. The R^2 value obtained is 0.9969. The missing carbon is defined as carbon that was not detected in the liquid, gas, and solid coke phases. Reaction conditions: T = 170 °C, P = 100 psig, WHSV = 0.54 h^{-1}.

Table SI 11. Vapor pressure of alcohols at 170 °C. Parameters were taken from NIST[2], where values were then extrapolated using Antoine's equation.

Compound	Vapor pressure (psi)
linear	
1-butanol	69.0
1-hexanol	14.5
1-octanol	7.00
branched	
2-methyl-1-butanol	47.9
2-ethyl-1-hexanol	9.7
secondary	
2-butanol	114.6
2-octanol	18.1

Table SI 12. Product feedstock composition post-etherification. Leftover carbon not detected in the liquid or gas phase was assumed to go to coke products.

Etherification feed code		MG-12	MG-44	MG-67	MG-69
Ethanol conversion (%)		12.26	44.16	66.51	68.90
Overall C_{4+} alcohol conversion (%)		73.17	74.76	64.72	78.58
Liquid and gas carbon balance (%)		96.15	88.70	93.32	90.69
Compound	**Carbon #**	**Selectivity %**			
Ethers					
Butyl ether	8	70.40	45.29	21.38	22.42
Butyl ethyl-butane ether	10	0.77	1.16	2.07	1.36
C_{10} linear ethers	10	13.51	18.97	21.76	20.14
Butyl ethyl-hexane ether	12	0.12	0.18	1.43	0.53
Hexyl ethyl-butane ether	12	-	0.16	1.11	0.56
C_{12} linear ethers	12	0.23	3.35	11.62	9.26
Hexyl ethyl-hexane ether	14	-	0.03	0.81	0.25
Octyl ethyl-butane ether	14	-	0.00	0.40	0.24
C_{14} linear ethers	14	-	0.44	5.84	2.99
Decyl ethyl-butane ether	16	-	-	0.23	-
C_{16} linear ethers	16	-	0.06	2.88	1.45
Decyl ethyl-hexane ether	18	-	-	0.14	-
Dodecyl ethyl-butane ether	18	-	-	0.06	-
C_{18} linear ethers	18	-	-	1.11	0.51
Dodecyl ethyl-hexane ether	18	-	-	0.04	-
C_{20} linear ethers	20	-	-	0.36	0.16
Olefins					
C_4 olefins	4	3.14	3.31	1.35	1.87
C_5 olefins	5	0.26	1.40	1.49	5.77
C_6 olefins	6	3.19	4.17	3.63	4.61
C_7 olefins	7	1.21	1.92	2.16	4.66
C_8 olefins	8	-	1.83	3.74	3.17
C_9 olefins	9	-	0.19	0.68	1.47
C_{10} olefins	10	-	0.21	0.30	0.15
C_{11} olefins	11	-	0.14	0.98	1.64
C_{12} olefins	12	-	0.02	0.05	0.04
Other products					
Unknown gas and liquid products	-	1.91	2.05	4.05	4.93
Coke	-	5.26	15.12	10.32	11.85

Table SI 13. Product feedstock composition post-etherification. Leftover carbon not detected in the liquid or gas phase was assumed to go to coke products. Adjusted to 100% carbon balance by considering carbon obtained from solid phase TOC analysis.

Etherification feed code		MG-12	MG-44	MG-67	MG-69
Ethanol conversion (%)		12.26	44.16	66.51	68.90
Overall C_{4+} alcohol conversion (%)		73.17	74.76	64.72	78.58
Total carbon balance (%)		100	100	100	100
Compound	**Carbon #**	**Selectivity %**			
Ethers					
Butyl ether		70.40	45.29	21.38	22.42
Butyl ethyl-butane ether		0.77	1.16	2.07	1.36
C_{10} linear ethers		13.51	18.97	21.76	20.14
Butyl ethyl-hexane ether		0.12	0.18	1.43	0.53
Hexyl ethyl-butane ether		-	0.16	1.11	0.56
C_{12} linear ethers	12	0.23	3.35	11.62	9.26
Hexyl ethyl-hexane ether	14	-	0.03	0.81	0.25
Octyl ethyl-butane ether	14	-	-	0.40	0.24
C_{14} linear ethers	14	-	0.44	5.84	2.99
Decyl ethyl-butane ether	16	-	-	0.23	-
C_{16} linear ethers	16	-	0.06	2.88	1.45
Decyl ethyl-hexane ether	18	-	-	0.14	-
Dodecyl ethyl-butane ether	18	-	-	0.06	-
C_{18} linear ethers	18	-	-	1.11	0.51
Dodecyl ethyl-hexane ether	18	-	-	0.04	-
C_{20} linear ethers	20	-	-	0.36	0.16
Olefins					
C_4 olefins	4	3.14	3.31	1.35	1.87
C_5 olefins	5	0.26	1.40	1.49	5.77
C_6 olefins	6	3.19	4.17	3.63	4.61
C_7 olefins	7	-	1.92	2.16	4.66
C_8 olefins	8	1.21	1.83	3.74	3.17
C_9 olefins	9	-	0.19	0.68	1.47
C_{10} olefins	10	-	0.21	0.30	0.15
C_{11} olefins	11	-	0.14	0.98	1.64
C_{12} olefins	12	-	0.02	0.05	0.04
Other products					
Unknown gas and liquid products	-	1.91	2.05	4.05	4.93
Coke on catalyst surface	-	3.15	10.47	5.65	9.57
Coke in liquid phase	-	2.11	4.65	4.67	2.28
Final ether yields					
C_8 ether yield	-	51.51	33.86	13.84	17.62
C_{10+} ether yield	-	0.71	18.20	32.27	29.41

Table SI 14. Final dehydration product distribution of EtOH/ButOH oligomerization products at varying WHSV. Leftover carbon not detected in the liquid or gas phase was assumed to go to coke products (non-adjusted). The final coke distribution was adjusted to 100% carbon balance by considering carbon obtained from solid phase TOC analysis. The final ether yields shown are based on the adjustment of the carbon balance.

Etherification feed code		EtOH/ButOH	EtOH/ButOH
WHSV (h^{-1})		0.54	1.00
Overall C_{4+} alcohol conversion (%)		81.23	71.13
Liquid and gas carbon balance (%)		85.00	86.53
Compound	**Carbon #**	**Selectivity %**	
Ethers			
Butyl ether	8	4.77	5.27
Butyl ethyl-butane ether	10	0.94	1.56
C_{10} linear ethers	10	19.29	20.94
Butyl ethyl-hexane ether	12	0.38	0.85
Hexyl ethyl-butane ether	12	1.91	3.17
C_{12} linear ethers	12	20.03	22.10
Hexyl ethyl-hexane ether	14	0.78	1.71
Octyl ethyl-butane ether	14	0.31	0.47
C_{14} linear ethers	14	4.45	4.78
C_{16} linear ethers	16	0.48	0.30
Olefins			
C_4 olefins	4	2.56	1.69
C_5 olefins	5	1.12	0.62
C_6 olefins	6	8.37	5.05
C_7 olefins	7	4.47	4.40
C_8 olefins	8	3.64	2.75
C_9 olefins	9	0.29	0.26
Other products			
Unknown liquid and gas products	-	7.75	5.14
Coke selectivity (non-adjusted)	-	18.47	18.94
Coke on catalyst surface	-	4.63	9.44
Coke in liquid phase	-	13.84	9.50
Final Ether yields			
C_8 ether yield	-	3.88	3.75
C_{10+} ether yield	-	39.06	39.74

SI – 3 Coke quantification and analysis

The catalyst beds were a mixture of zeolite HY in its powder form, and the addition of inert silica chips between 30 – 80 mesh. The chips were added to minimize pressure drop across the reactor. The bed mixture was made at a 2:1 inert chip to catalyst ratio, using 1.6 – 1.8 g of catalyst. As the catalyst beds cannot be assumed to be uniform, mainly because of the particle size differences between the catalyst and chips used, total organic carbon (TOC) analysis was conducted 12 times for each individual bed using 4 different mass weights. If one were to consider the coke flowrate for each catalyst bed studied, carbon balances improve by 5 – 10%, leading to carbon balances over 90+%. Here, the flowrates were offset by the startup time of reactor, typically between 13 – 20 hours. The reasoning for long start-up times is due to the low flow rates used (0.02 mL/min) and minimal pressure buildup that may occur across the reactor. We assume that the startup time of reaction does not have a significant impact on the amount of carbon found on the catalyst bed and is set to 13 hours for all beds studied. 13-hour start-up times were chosen as this was usually when mass balances would stabilize for the reaction. Coke flowrates were then calculated for each bed and normalized by the total reaction time. The calculated flowrates were then used to adjust the final carbon balances for all beds studied. For runs that didn't fully add up to 100% carbon balance after the addition of TOC experiments, it is assumed that the missing carbon is due to the formation of heavy oligomers[3, 4] in the final product that are soluble in the organic liquid phase. This assumption is more evident with runs using esters, as the amount of undetected carbon increases linearly with increasing ester concentration (See Figure SI3). Therefore, it is reasonable to assume that carbon not detected in the liquid or gas phase is in the form of coke products that cannot be detected by conventional gas chromatography methods. Tables SI 15 – 17 summarize the results obtained for all beds studied. TGA of MG – 12, MG – 67 and MG – 69 were analyzed to determine the carbon uptake profile. In all cases, the weight change primarily lied between 25 – 400 ^{o}C. The TGA data for these experiments can be found in Figure SI4.

Table SI 15. Average wt% detected by TOC for the linear alcohol feeds. A 95% confidence interval is implemented using a two-tailed test. Reaction temperature = 170 ^{o}C.

Etherification feed code	1-butanol	1-butanol	1-hexanol	1-octanol
Pressure	0	100	100	100
WHSV (h^{-1})	0.54	0.54	0.54	0.54
Number of samples	12	12	12	12
Average wt% of carbon detected	2.80	4.29	24.88	27.85
Uncertainty interval (+/-)	0.26	0.53	1.94	1.63
Total reaction time (hr)	22.33	46.33	70.65	46.92

Table SI 16. Average wt% detected by TOC for the model feedstocks. A 95% confidence interval is implemented using a two-tailed test. Reaction temperature = 170 ^{o}C.

Etherification feed code	MG – 12	MG - 12	MG – 44	MG - 67	MG - 69
Pressure	0	100	100	100	100
WHSV (h^{-1})	0.54	0.54	0.54	0.61	0.54
Number of samples	12	12	12	12	12
Average wt% of carbon detected	18.97	8.55	25.8	19.87	26.4
Uncertainty interval (+/-)	1.32	0.53	0.97	0.96	1.52
Total reaction time (hr)	45.63	46.67	50.08	66.05	50.25

Table SI 17. Average wt% detected by TOC for the model feedstocks. A 95% confidence interval is implemented using a two-tailed test. *signifies that the start-up time was set to 26 hrs as the reactor was restarted once. Reaction temperature = 170 °C.

Etherification feed code	SG – 12	SG – 12@15wt%	EtOH/ButOH*	EtOH/ButOH
Pressure	100	100	100	100
WHSV (h^{-1})	0.54	0.54	0.54	1
Number of samples	12	12	12	12
Average wt% of carbon detected	5.65	18.42	24.39	8.36
Uncertainty interval (+/-)	0.86	1.74	2.28	1.40
Total reaction time (hr)	50.50	72.88	92.7	20.97

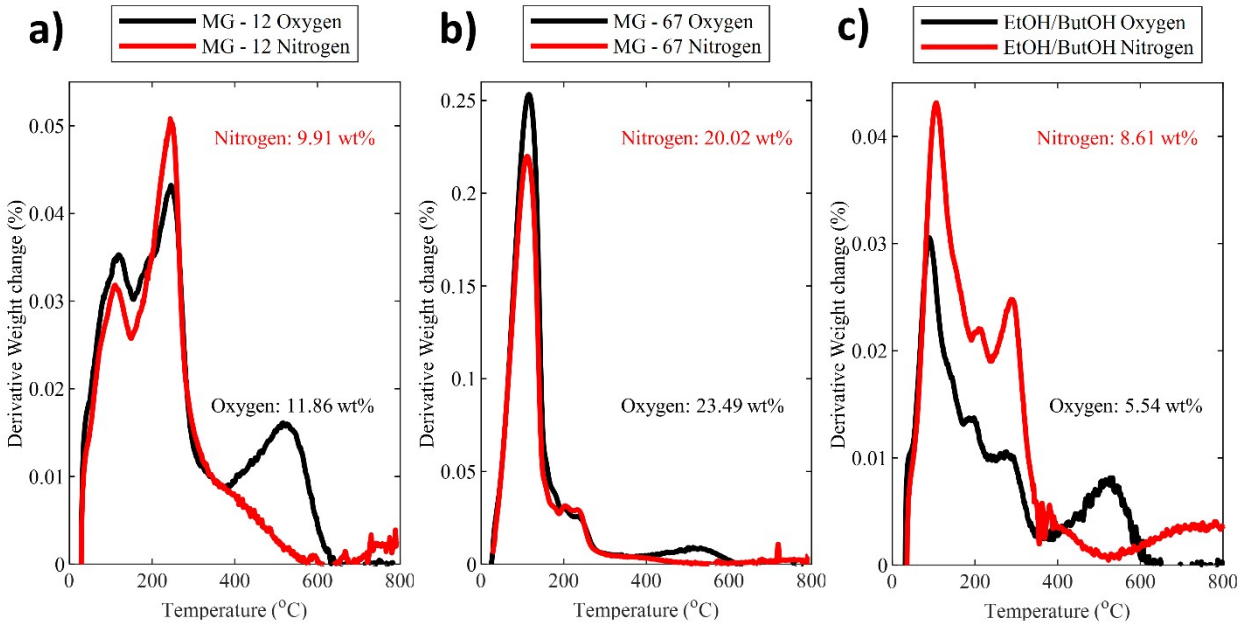

Figure SI 4. A) TGA of spent catalyst using feedstock MG – 12, B) TGA of spent catalyst using feedstock MG – 67 and C) TGA of spent catalyst using EtOH/ButOH oligomerization products at WHSV = 1.0 h^{-1}. Red represents a TGA analysis using nitrogen as the flow gas. Black represents a TGA analysis using oxygen as the flow gas. The wt% values represent the total loss of coke products from the initial sample mass.

SI – 4 Qualitative analysis of cross-etherification products and olefins

Due to the complexity of the model/real guerbet feedstocks, standards for cross-ethers are not commercially available. Furthermore, the GC-MS is limited by suggesting wrong oxygenate compounds being formed (i.e oxalic acids) and being unable to further separate ether species of the same carbon number, a phenomenon also observed in the liquid gas-chromatography FID. Therefore, a qualitative analysis of cross-etherification products is needed to assess both the retention time and carbon number of the unidentified cross ethers formed. Response factors for these species were then estimated using effective carbon number theory[5] by linking the response factors to commercially available standards.

For cross-etherification, an equimolar reaction mixture of two alcohols was analyzed. Then, the chromatograms for single feed alcohol reactions overlapped with the equimolar chromatograms to determine where self-etherification products landed. If one alcohol is removed from the reaction feed, then two peaks must collapse, the first being the self-etherification product of the removed alcohol and the second being the cross-etherification product between the two alcohols in the reaction mixture. Therefore,

the major peak that is not observed in both single alcohol chromatograms must be the cross-etherification peak. Figure SI5 provides an example of the overall procedure to determine cross-etherification products between linear-linear and linear-branched feeds. 2-ethyl-1-butanol was used to assess the retention time of the self-etherification product. The same procedure was done with 1-butanol. Then, the equimolar mixture chromatogram overlapped with the single-feed alcohols to determine the unknown peak. Retention times of olefins were also determined using the same methodology when appropriate.

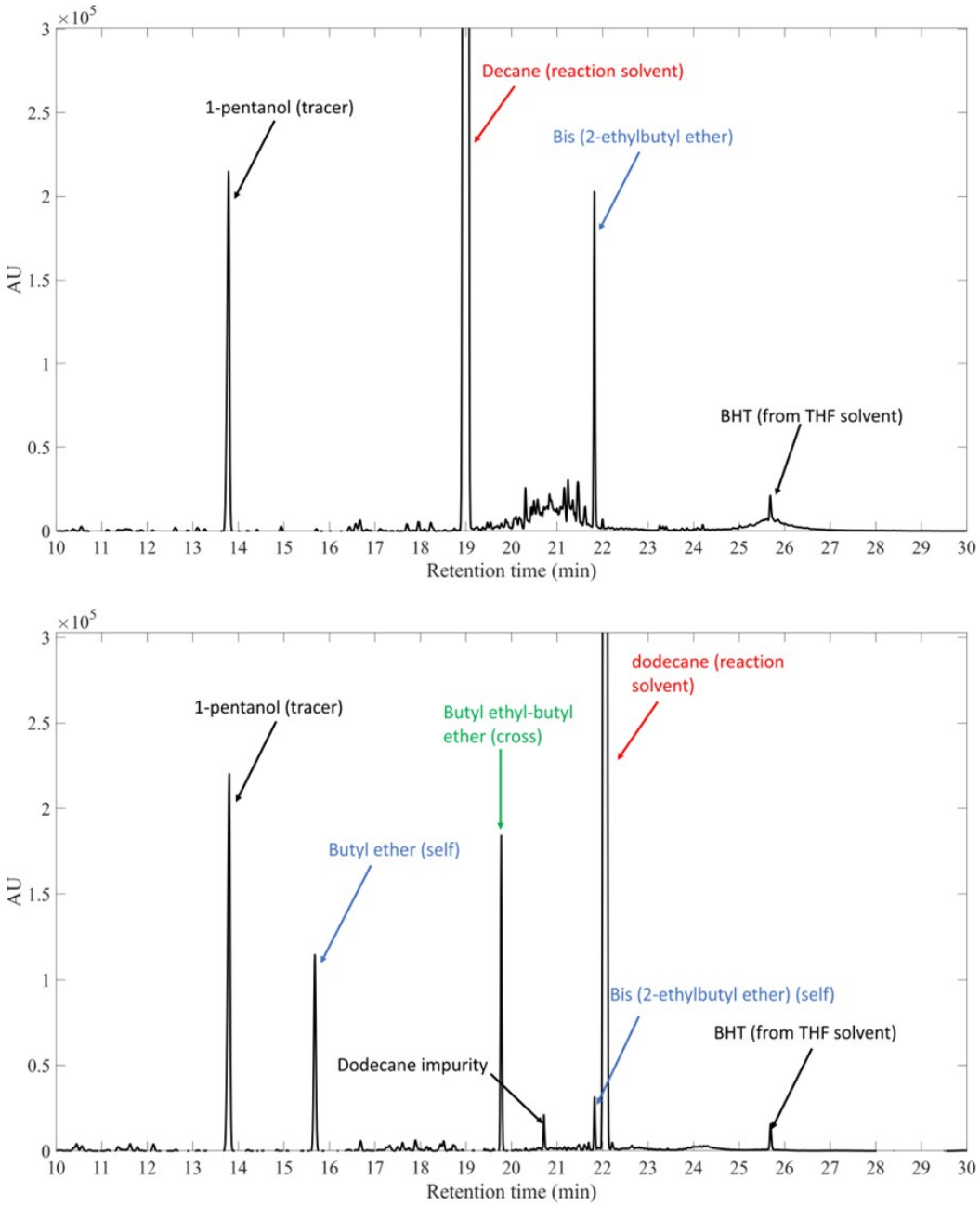

Figure SI 5. Identification of cross etherification products of 2-ethyl-1-butanol and 1-butanol. **Top:** etherification products of 2-ethyl-1-butanol. **Bottom:** Etherification products of equimolar butanol and 2-ethyl-1-butanol. Reaction conditions: 170 ^{o}C, stirrate = 550 rpm in a silicon oil bath.

SI - 5 TOS runs

Table SI 18. Conversion of 1-butanol at data points (hr) obtained at atmospheric pressure.

Compound	18.4 TOS	21.2 TOS	**Average conversion (C%)**
1-butanol	69.1	69.4	69.2

Table SI 19. Conversion of 1-butanol at data points (hr) obtained at 100 psig.

Compound	25.6 TOS	35.3 TOS	44.9 TOS	**Average conversion (C%)**
1-butanol	73.5	73.7	73.1	73.4

Table SI 20. Conversion of feedstock MG – 12 at data points (hr) obtained at atmospheric pressure.

Compound	21.6 TOS	43.3 TOS	45.6 TOS	**Average conversion (C%)**
1-butanol	74.0	67.6	65.8	69.6
2-pentanol	100.0	100.0	100.0	100.0
1-hexanol	91.7	89.5	89.4	90.4
2-ethyl-1-butanol	100.0	100.0	100.0	100.0
1-octanol	80.5	82.4	80.8	81.5
2-ethyl-1-hexanol	100.0	100.0	100.0	100.0
Overall (C%)	76.3	70.4	68.9	71.9

Table SI 21. Conversion of feedstock MG – 12 at data points (hr) obtained at 100 psig.

Compound	19.2 TOS	21.9 TOS	36.2 TOS	**Average conversion (C%)**
1-butanol	71.9	71.2	70.2	71.1
2-pentanol	100.0	100.0	100.0	100.0
1-hexanol	84.7	85.4	86.7	85.6
2-ethyl-1-butanol	97.0	96.9	96.8	96.9
1-octanol	91.8	88.9	79.2	86.6
2-ethyl-1-hexanol	95.6	95.5	97.2	96.1
Overall (C%)	73.8	73.3	72.4	73.2

Table SI 22. Conversion of feedstock MG – 44 at data points (hr) obtained at 100 psig.

Compound	25.7 TOS	35.0 TOS	44.4 TOS	48.1 TOS	**Average conversion (C%)**
1-butanol	69.4	68.2	68.2	69.5	68.8
2-pentanol	100.0	100.0	100.0	100.0	100.0
1-hexanol	89.1	88.6	88.3	88.5	88.6
2-ethyl-1-butanol	96.1	95.4	95.3	95.6	95.6
2-heptanol	100.0	100.0	100.0	100.0	100.0
1-octanol	92.7	91.5	91.3	91.4	91.7
2-ethyl-1-hexanol	100.0	100.0	100.0	100.0	100.0
4-nonanol	100.0	100.0	100.0	100.0	100.0
1-decanol	100.0	100.0	100.0	100.0	100.0
2-undecanol	100.0	100.0	100.0	100.0	100.0
1-dodecanol	100.0	100.0	100.0	100.0	100.0
Overall (C%)	75.3	74.3	74.2	75.3	74.8

Table SI 23. Conversion of feedstock MG – 67 at data points (hr) obtained at 100 psig.

Compound	21.4 TOS	31.8 TOS	43.0 TOS	**Average conversion (C%)**
1-butanol	48.6	44.3	46.1	46.4
2-pentanol	100.0	100.0	100.0	100.0
1-hexanol	79.0	79.1	77.0	77.6
2-ethyl-1-butanol	82.0	79.1	79.4	80.2
2-heptanol	100.0	100.0	100.0	100.0
1-octanol	89.1	88.5	88.1	88.6
2-ethyl-1-hexanol	95.5	94.6	94.1	94.7
4-nonanol	100.0	100.0	100.0	100.0
1-decanol	94.4	95.9	94.3	94.8
2-undecanol	100.0	100.0	100.0	100.0
1-dodecanol	94.9	98.6	90.6	94.7
1-tetradecanol	96.3	100.0	92.3	96.2
Overall (C%)	66.4	63.5	64.3	64.7

Table SI 24. Conversion of feedstock MG – 69 at data points (hr) obtained at 100 psig.

Compound	26.5 TOS	36.7 TOS	**Average conversion (C%)**
1-butanol	63.0	63.4	63.2
2-pentanol	100.0	100.0	100.0
1-hexanol	86.0	86.1	86.0
2-ethyl-1-butanol	93.7	93.9	93.8
2-heptanol	100.0	100.0	100.0
1-octanol	90.4	90.2	90.3
2-ethyl-1-hexanol	98.4	98.5	98.5
4-nonanol	100.0	100.0	100.0
1-decanol	84.9	91.5	88.2
2-undecanol	100.0	100.0	100.0
1-dodecanol	95.5	94.6	95.1
1-tetradecanol	100.0	100.0	100.0
Overall (C%)	78.5	78.7	78.6

Table SI 25. Conversion of feedstock SG – 12 at data points (hr) obtained at 100 psig.

Compound	25.1 TOS	37.8 TOS	49.5 TOS	**Average conversion (C%)**
1-butanol	77.6	77.3	75.7	76.9
2-pentanol	100.0	100.0	100.0	100.0
1-hexanol	90.9	90.9	90.3	90.7
2-ethyl-1-butanol	98.4	98.4	98.1	98.3
1-octanol	91.1	91.5	90.5	91.0
2-ethyl-1-hexanol	100.0	100.0	100.0	100.0
Ethyl butanoate	100.0	100.0	100.0	100.0
Butyl acetate	22.8	23.3	17.3	21.1
Ethyl hexanoate	100.0	100.0	100.0	100.0
Overall (C%)	79.0	78.8	77.3	78.3

Table SI 26. Conversion of feedstock SG – 12@0.15wt% at data points (hr) obtained at 100 psig.

Compound	23.5 TOS	35.1 TOS	46.7 TOS	48.8 TOS	**Average conversion (C%)**
1-butanol	73.8	74.7	73.8	74.4	74.2
2-pentanol	100.0	100.0	100.0	100.0	100.0
1-hexanol	86.3	87.8	88.3	87.3	87.4
2-ethyl-1-butanol	98.1	97.9	97.7	97.7	97.9
1-octanol	94.4	89.1	87.9	83.5	88.7
2-ethyl-1-hexanol	100.0	100.0	100.0	100.0	100.0
Ethyl butanoate	100.0	100.0	100.0	100.0	100.0
Butyl acetate	17.1	0.7	0.6	0.5	4.72
Ethyl hexanoate	100.0	100.0	100.0	100.0	100.0
Overall (C%)	75.7	76.6	75.8	76.2	76.1

Table SI 27. Conversion of 1-hexanol at data points (hr) obtained at 100 psig.

Compound	20.7 TOS	23.2 TOS	25.8 TOS	37.9 TOS	50.0 TOS	**Average conversion (C%)**
1-hexanol	84.7	84.7	84.5	85.1	84.2	84.7

Table SI 28. Conversion of 1-octanol at data points (hr) obtained at 100 psig.

Compound	19.4 TOS	22.5 TOS	34.4 TOS	46.9 TOS	**Average conversion (C%)**
1-hexanol	90.4	91.5	91.6	91.4	91.2

Table SI 29. Conversion of EtOH/ButOH oligomerization products at data points (hr) obtained at 100 psig and WHSV = 0.54 h^{-1}.

Compound	20.9 TOS	23.1 TOS	25.2 TOS	**Average conversion (C%)**
1-butanol	61.2	63.9	62.2	62.4
2-butanol	100.0	100.0	100.0	100.0
2-methyl-1-butanol	72.1	74.6	74.2	73.6
1-hexanol	84.1	85.1	84.7	84.6
2-ethyl-1-butanol	92.4	93.5	93.6	93.2
2-heptanol	100.0	100.0	100.0	100.0
2-ethyl-1-hexanol	97.3	97.7	97.5	97.5
1-octanol	91.9	89.4	88.1	89.8
2-octanol	100.0	100.0	100.0	100.0
2-nonanol	100.0	100.0	100.0	100.0
Overall (C%)	80.7	81.9	81.2	81.2

Table SI 30. Conversion of EtOH/ButOH oligomerization products at data points (hr) obtained at 100 psig and WHSV = 1.0 h^{-1}.

Compound	15.9 TOS	17.9 TOS	20.0 TOS	**Average conversion (C%)**
1-butanol	55.9	58.2	48.3	54.1
2-butanol	100.0	100.0	100.0	100.0
2-methyl-1-butanol	57.3	59.3	49.1	55.2
1-hexanol	76.4	77.8	70.6	74.9
2-ethyl-1-butanol	79.7	81.4	73.1	78.1
2-heptanol	100.0	100.0	100.0	100.0
2-ethyl-1-hexanol	91.1	91.7	85.8	89.5
1-octanol	81.7	83.2	75.0	80.0
2-octanol	100.0	100.0	100.0	100.0
2-nonanol	100.0	100.0	100.0	100.0
Overall (C%)	72.7	74.3	66.5	71.1

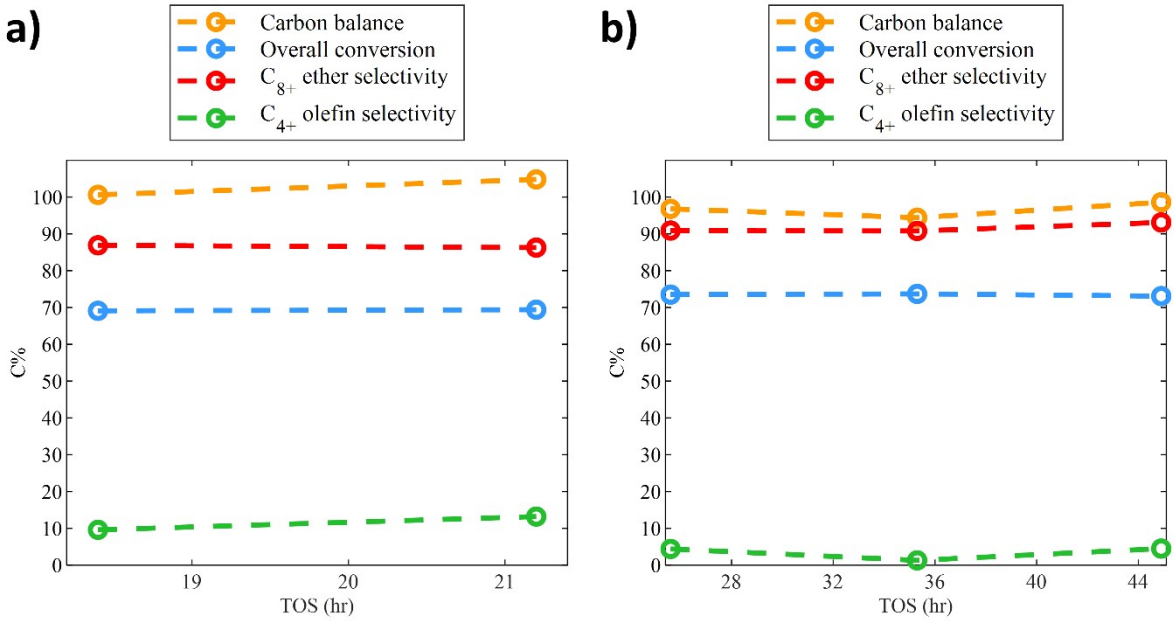

Figure SI 6. TOS data of 1-butanol at a) atmospheric pressure and b) 105 psig. Reaction conditions: T = 170°C, feedstock flowrate = 0.020 mL/min, Ar flowrate = 10 mL/min, WHSV = 0.539 – 0.540 h^{-1}.

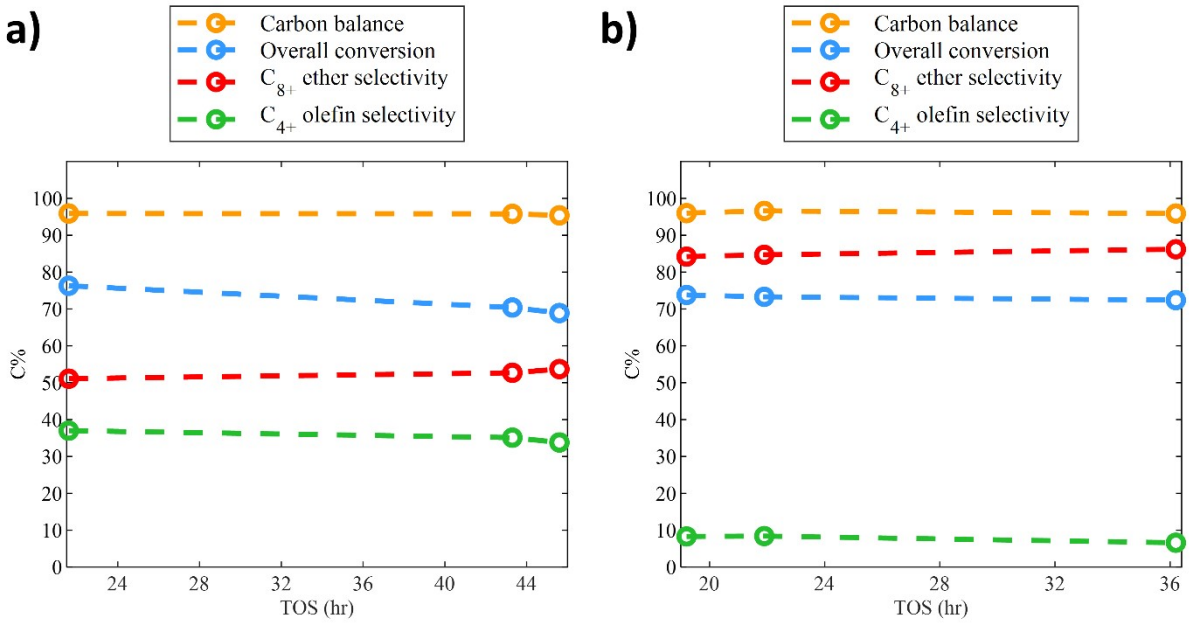

Figure SI 7. TOS data of the 12.3% model feedstock at a) atmospheric pressure and b) 95 psig. Reaction conditions: T = 170 °C, feedstock flowrate = 0.020 mL/min, Ar flowrate = 10 mL/min, WHSV = 0.539 – 0.540 h^{-1}.

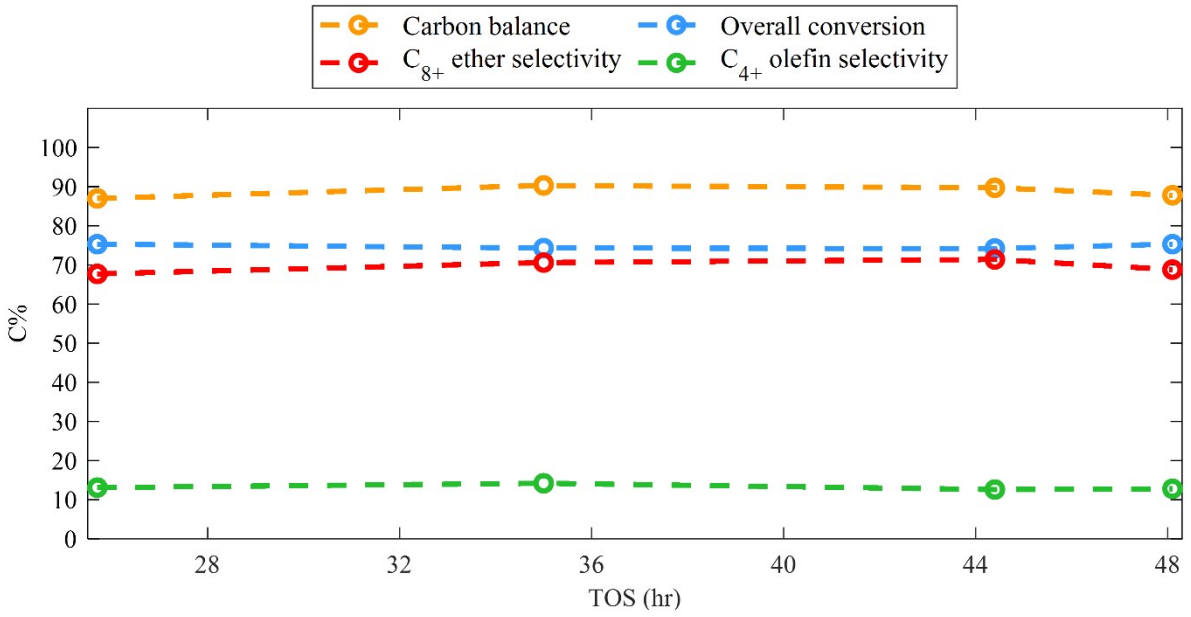

Figure SI 8. TOS of the 44.2% model feedstock. Reaction conditions: T_{avg} = 170.1 °C, P_{avg} = 104 psig, feedstock flowrate =0.020 mL/min, Ar flowrate = 10 mL/min, WHSV = 0.540 h^{-1}.

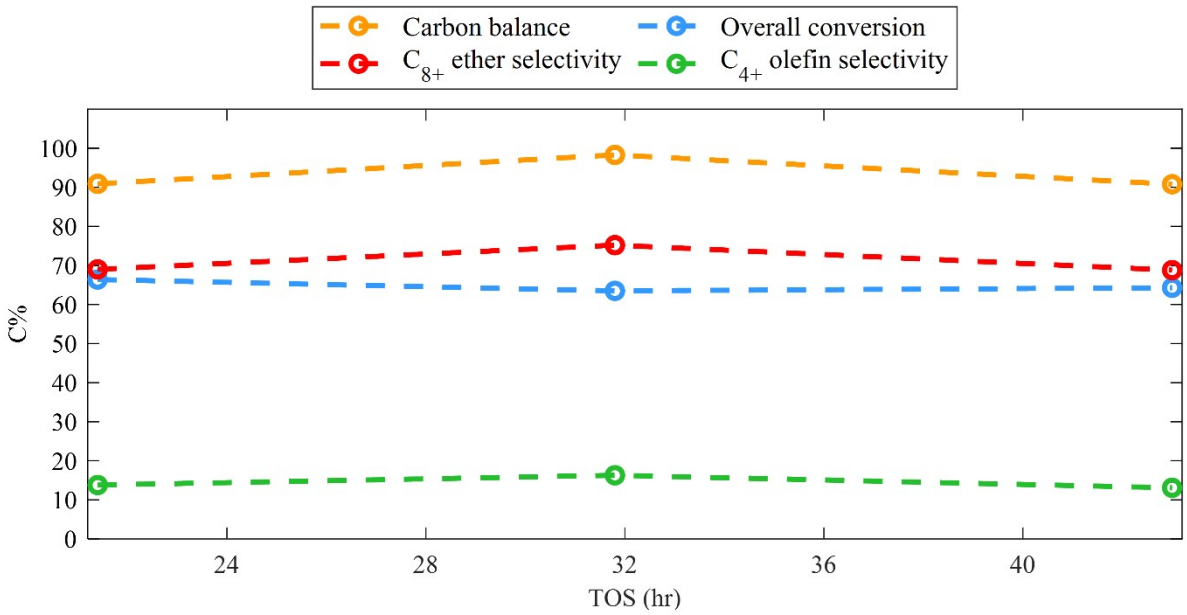

Figure SI 9. TOS of the 66.5% model feedstock. Reaction conditions: T_{avg} = 170.1 °C, P_{avg} = 106 psig, feedstock flowrate =0.020 mL/min, Ar flowrate = 10 mL/min, WHSV = 0.61 h^{-1}.

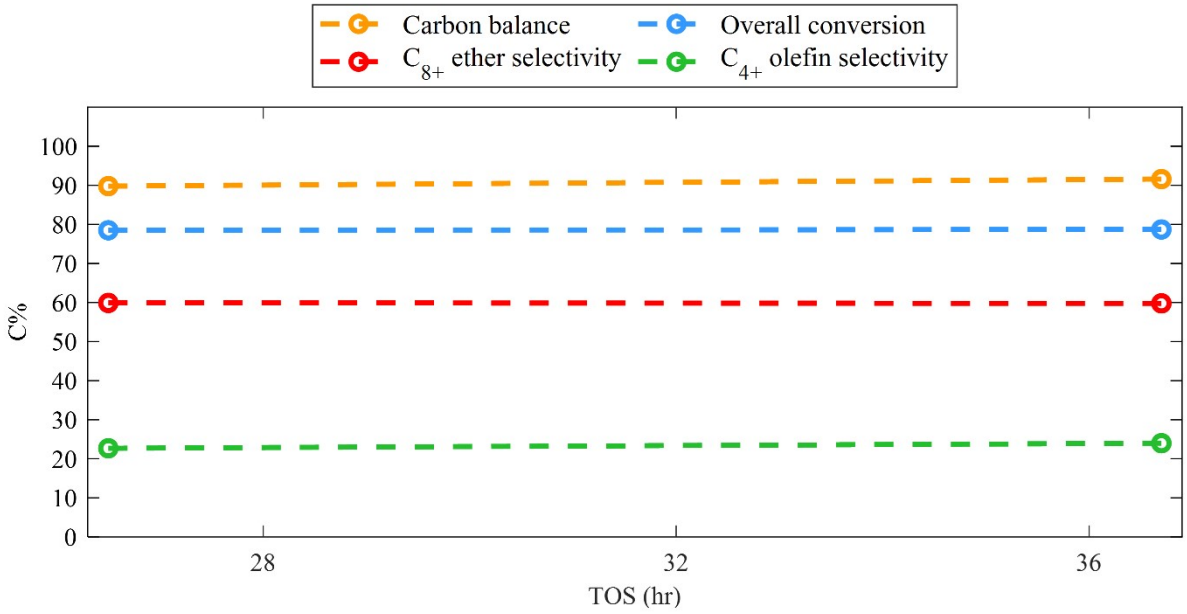

Figure SI 10. TOS of the 68.9% model feedstock. Reaction conditions: T_{avg} = 170.1 °C, P_{avg} = 110 psig, feedstock flowrate =0.020 mL/min, Ar flowrate = 10 mL/min, WHSV = 0.543 h^{-1}.

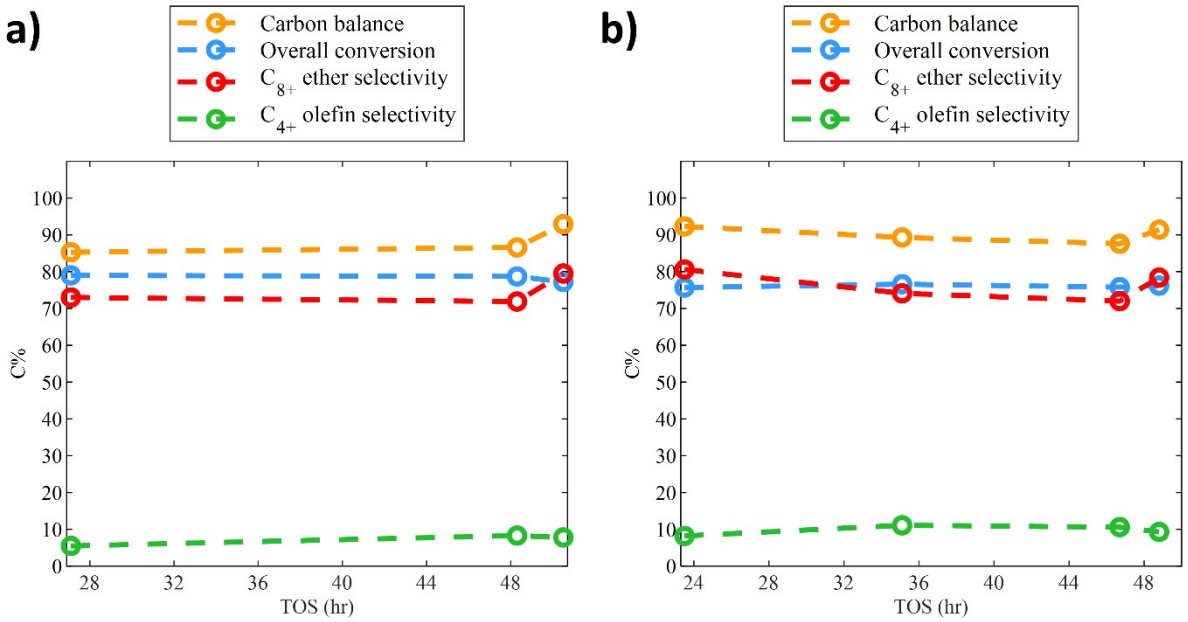

Figure SI 11. TOS of the A) 12.3% simulated feedstock with 1.5 wt% esters and B) 12.3% simulated feedstock with 0.15 wt% esters in the reaction stream. T = 170°C, P = 100 psig, feedstock flowrate =0.020 mL/min, Ar flowrate = 10 mL/min, WHSV = 0.539 -- 0.541 h^{-1}.

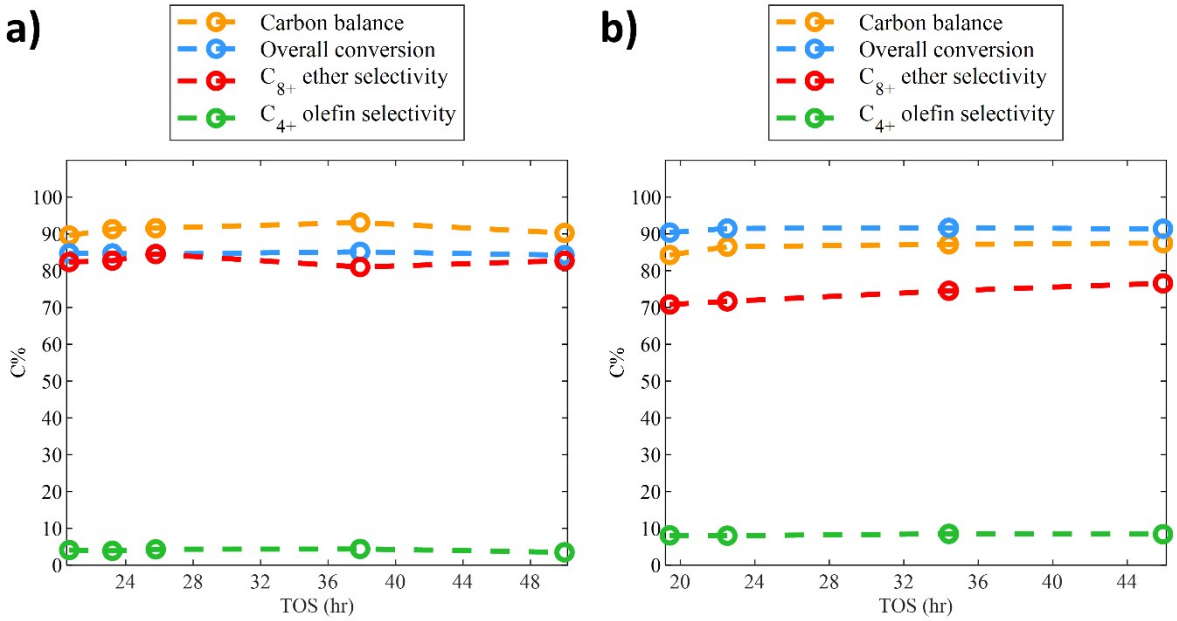

Figure SI 12. TOS of a pure A) 1-hexanol feed and B) 1-octanol feed. T = 171 °C, P = 115 psig, feedstock flowrate =0.020 mL/min, Ar flowrate = 10 mL/min, WHSV = 0.543 h^{-1}.

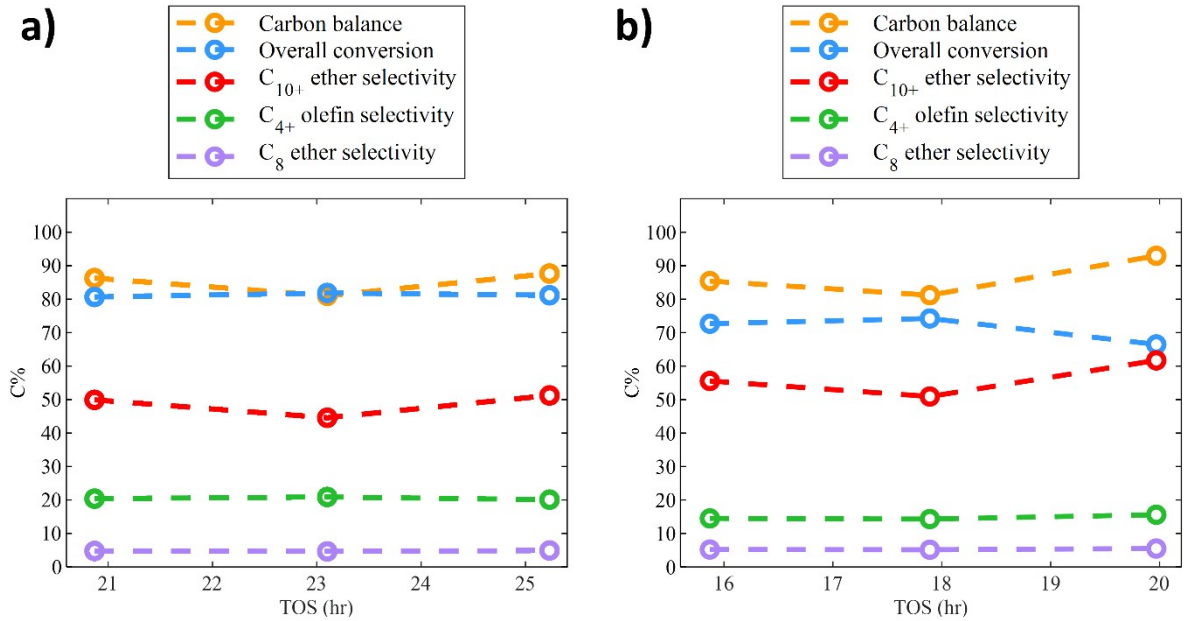

Figure SI 13. TOS data of EtOH/oligomerization dehydration products at A) WHSV = 0.54 h^{-1} and B) WHSV = 1.0 h^{-1}. T = 170 °C, P = 100 psig, feedstock flowrate = 0.02 – 0.04 mL/min, Ar flowrate =10 mL/min. For run A, an in-situ regeneration procedure was attempted at 500 °C using 100 mL/min of Air; however, there were no signs of reaction improvement after > 25 hr TOS.

SI – 6 Final diesel #2 composition

Table SI 31. Final diesel #2 composition obtained from the overall process. C% represents the product carbon fraction with respect to the initial ethanol flowrate. Data was taken from Restrepo-Flórez and coworkers[1].

Compounds	Carbon #	Flowrate (kmol/hr)		C%
Olefins				
1-nonene	9	0.266		0.26
8-methyl-4-nonene	10	0.383		0.42
2- methyl-2-undecene	12	0.960		1.26
2-methyl-2-tridecene	14	0.570		0.87
2-methyl-1-tetradecene	15	0.029		0.05
2-methyl-1-pentadecene	16	0.304		0.53
9-methyl-8-heptadecene	18	0.68		0.13
2-methyl-1-nonadecene	20	0.013		0.03
7-hexyl-7-pentadecene	21	0.042		0.10
1-tetracosene	24	0.013		0.03
Alcohols				
1-hexanol	6	0.537		0.35
2-ethyl-1-butanol	6	0.246		0.16
2-heptanol	7	0.206		0.16
1-octanol	8	0.713		0.62
2-ethyl-1-hexanol	8	1.918		1.68
4-nonanol	9	0.188		0.19
1-decanol	10	1.970		2.16
4-undecanol	11	0.256		0.31
1-dodecanol	12	0.547		0.72
2-butyl-1-octanol	12	0.626		0.82
4-tridecanol	13	0.289		0.41
1-tetradecanol	14	0.134		0.21
4,10-dimethyl-1-dodecanol	14	0.067		0.10
1-pentadecanol	15	0.188		0.31
Esters				
Butyl butyrate	8	2.873		2.52
Ethyl caproate	8	1.635		1.43
Hexyl acetate	8	1.053		0.92
Butyl caproate	10	2.440		2.67
Hexyl butyrate	10	0.282		0.31
Octyl acetate	10	0.188		0.21
Octyl butyrate	12	0.156		0.21
Butyl capyrlate	12	0.078		0.10
Ethyl caprate	12	1.095		1.44
Decyl acetate	12	0.078		0.10
Hexyl hexanoate	12	0.156		0.21
Hexyl caprylate	14	0.871		1.34
Ethyl laurate	14	0.067		0.10
Dodecyl acetate	14	0.067		0.10
Octyl octanoate	16	0.176		0.31
Ethers				
Butyl ether	8	3.675		3.22
C_{10} ethers	10	12.475		13.66
C_{12} ethers	12	5.105		6.71
C_{14} ethers	14	1.050		1.61
Di-octyl ether	16	0.242		0.40
Feedstock				
Ethanol	2	456.480	**Total C%**	**49.46**

SI – 7 References

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