Electronic Supplementary Information (ESI)

Towards cost-competitive middle distillate fuels from ethanol within a market-flexible biorefinery concept

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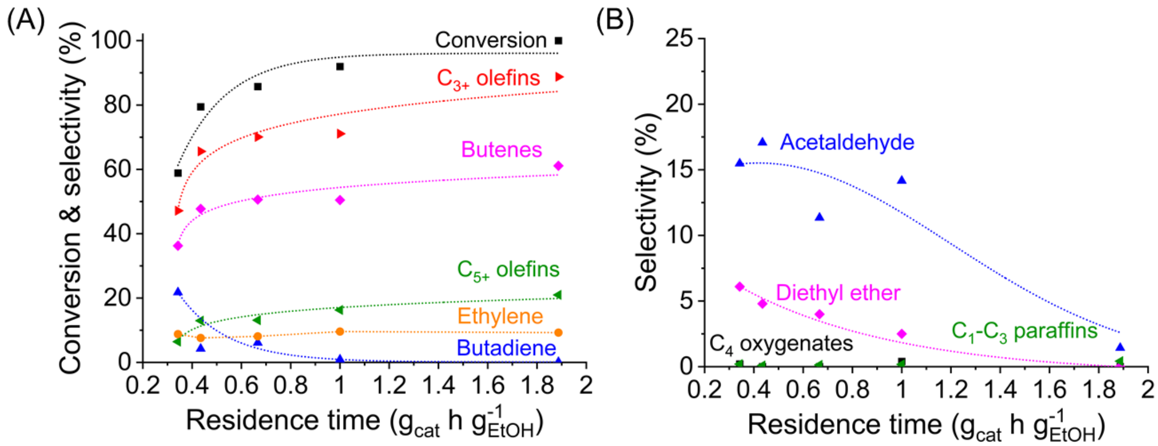


Figure S1. (A) Ethanol conversion and olefin selectivities; and (B) oxygenate selectivities over Cu-Zn-Y/Beta at different residence time. Reaction conditions: 0.054-0.19 g Cu-Zn-Y/Beta catalyst diluted in 0.8 g SiC, 623 K, 7.4-8.4 kPa ethanol, 99.4-113.5 kPa H_2 (variation caused by pressure drop through the catalyst bed at different flow rates). Data is collected at TOS 1.1 h. C_4 oxygenates include 1-butanol, crotyl alcohol, butyraldehyde, and 2-butanone, etc.

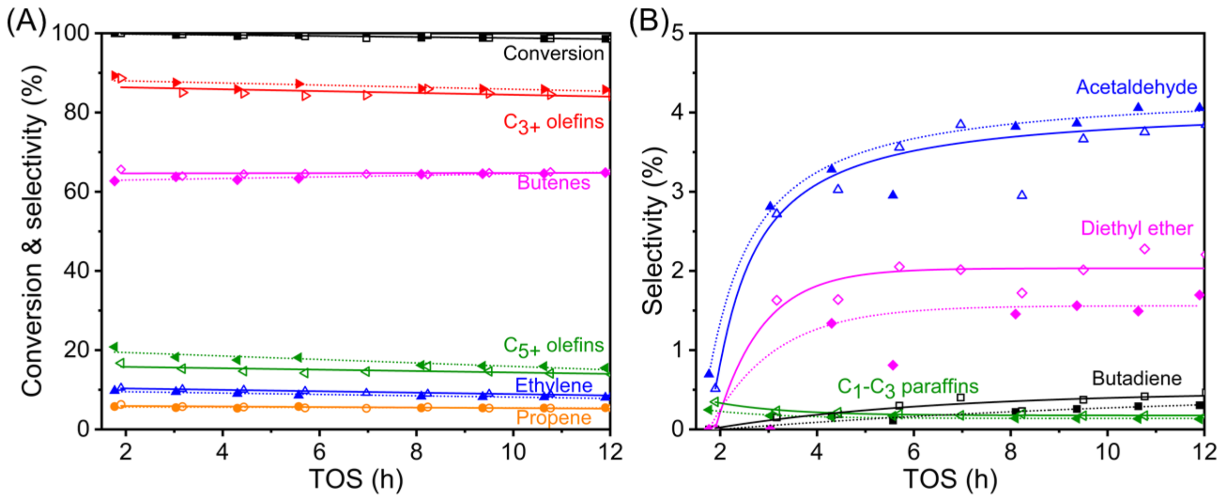


Figure S2. Water impact on ethanol conversion and product selectivity (Reaction conditions: ~0.3 g Cu-Zn-Y/Beta catalyst, 0.52 h^{-1} WHSV, total pressure 109.6 kPa, 6.0 kPa ethanol, 80.6 kPa hydrogen balanced with Ar). Solid and open symbols represent with (2.3 kPa water) or without water cofeeding, respectively. The lines are used to guide the eye.

Table S1. Ethanol conversion and product selectivities for literature reported ethanol to olefin conversion catalysts.

Type of pathway	Catalyst	T (K)	Pressure (MPa)	Ethanol Partial Pressure (kPa)	Conversion	Selectivity						Reference
						C_{3+} olefins	Ethylene	CO_2	Butenes	Butene/C_{3+} olefins	Light paraffins	
Lewis acid zeolites catalyzed with butyraldehyde as intermediate	Cu-Zn-Y/Beta	623	0.1	7.3	100	88	9.1	<0.1	66	75	0.5	This work
Brønsted acid zeolites catalyzed with ethylene as intermediate	5.0 Ce-nano-H-ZSM-5	673	0.1	6.2	99	39	41	N/A*	21	54	N/A	[1]
	MFI-40 (Si/Al = 80)	683	0.1	19	100	51	26	N/A	17	33	7.8	[2]
	In_2O_3-Beta	733	0.1	10	100	56	N/A	N/A	6.0	11	5.0	[3]
	P modified H-ZSM-5	773	0.1	91	100	38	15	N/A	12	32	N/A	[4]
	H-ZSM-5/SAPO-34 composite	773	0.1	20	100	46	22	N/A	21	46	N/A	[5]
	H-ZSM-5 (SAR 50)	773	0.1	51	100	41	33	N/A	16	39	12	[6]
Oxides catalyzed with acetone as intermediate	$Zn_1Zr_{10}O_x$ ($Zn(NO_3)_2$)	723	0.1	0.6	100	58	3.9	16	55	95	5.4	[7]
	$Zn_1Zr_{10}O_x$ ($Zn(NO_3)_2$)	723	0.1	1.8	100	37	2.7	23	52	94	N/A	[7]
	$Zn_1Zr_{10}O_x$ ($Zn(Ac)_2$)	723	0.1	1.5	100	53	2.5	23	49	92	N/A	[8]
	$Zn_1Zr_{10}O_x$ ($ZnCl_2$)	723	0.1	1.5	100	29	2.2	26	26	90	N/A	[8]
	Nb_{10}/CeO_2	673	0.1	30	100	42	17	N/A	10	24	N/A	[9]
	Ti_{10}/CeO_2	673	0.1	30	100	39	15	N/A	12	31	N/A	[9]
	CeO_2	693	0.1	30	100	15	31	N/A	2.3	15	N/A	[9]
	Y_{20}/CeO_2	703	0.1	30	100	31	37	N/A	0.2	0.6	N/A	[9]
	ZrO_2	723	1.1	34	89	46	5.6	N/A	0.6	1.3	N/A	[10]
	Mg_1/ZrO_2	723	1.1	34	93	39	47	10	0.8	2.1	N/A	[10]
	Ca_5/ZrO_2	723	1.1	34	86	39	44	8.8	0.8	2.1	N/A	[10]
	Sr_5/ZrO_2	723	1.1	34	99	39	43	9.9	0.4	1.0	N/A	[10]
	Ba_5/ZrO_2	723	1.1	34	91	39	46	11	0.8	2.1	N/A	[10]
	In_2O_3	723	0.1	30	100	39	N/A	N/A	16.1	41	N/A	[11]
	Sc_3/In_2O_3	823	0.1	30	100	51	N/A	N/A	9.8	19	N/A	[11]
	$Ag-ZrO_2/SiO_2$	598	0.7	77	93.9	60.7	25.7	<0.3	57.7	95	6.5	[12]

Transition metal promoted Lewis acid oxide catalyzed with butadiene as intermediate	Ag-ZrO_2/SiO_2	673	0.7	77	99	69	19	N/A	63	91	N/A	[12]

*N/A: not available in the reported work.

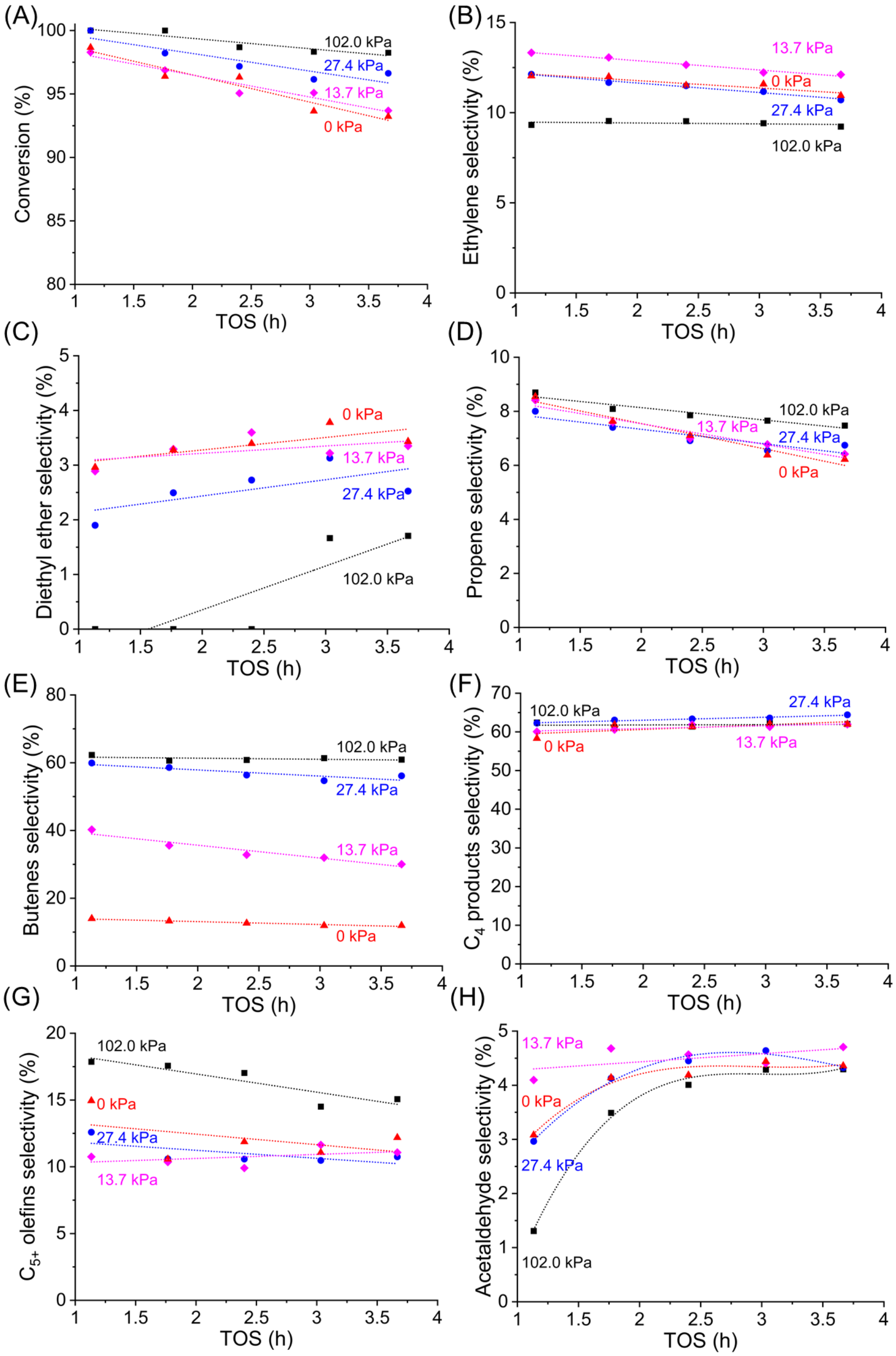


Figure S3. Hydrogen partial pressure impact on ethanol conversion and product distributions. C_4 products include butenes and butadiene.

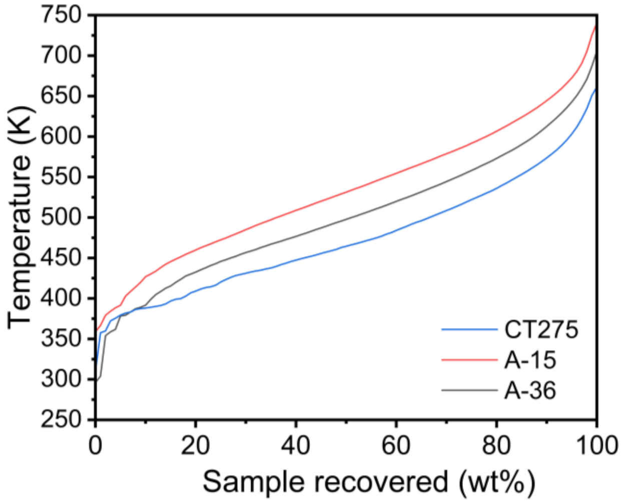
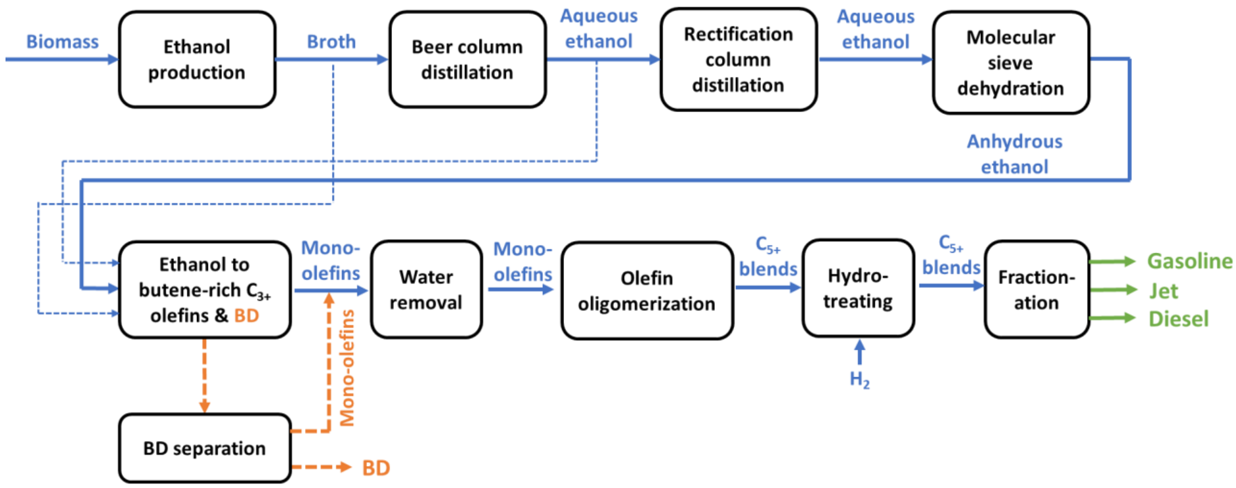


Figure S4. Simulated distillation of the liquid hydrocarbons obtained from oligomerization of C_{3+} olefins over Amberlyst-36 (A-36), Amberlyst-15 (A-15) and CT275. Olefin conversions: for A-36, 100% propene conversion, 99% butenes conversion, 93% 2-pentene conversion and 96% 2-hexene conversion; for A-15, 100% conversion of propene, butenes and 2-hexene, and 96% 2-pentene conversion; for CT275, 100% propene conversion, 95% butenes conversion, 90% 2-pentene conversion and 77% 2-hexene conversion. Mass balance of the reaction is 95-101%.

Table S2. Carbon conversion efficiency for ethanol to liquid hydrocarbons

Step	Carbon Efficiency (mol C in product/mol C in feed)
Ethanol to C_{3+} olefins	0.89
Oligomerization to C_{5+}	0.94
Oligomerization to middle distillate	0.84
Hydrotreating	0.99*
Overall (to liquid hydrocarbons)	0.85
Overall (to middle distillate)	0.74

* Estimated based on the NREL 2018 Biochemical Design Case report[13].



Scheme S1. Process scheme of biomass conversion to hydrocarbon fuels and butadiene. The orange dashed arrows indicate the ethanol-to-middle-distillate-and-butadiene operation mode. Ethanol production includes feedstock handling, pretreatment, saccharification (or enzymatic hydrolysis) and fermentation.

Table S3. Process parameters for the base case and sensitivity analysis

Process Parameters	Base Values	Parameter Changes	% Change in Parameter
Inlet ethanol concentration (wt.%)	100%	13-100%	-87
Oligomerization catalyst WHSV (h^{-1})	1	0.25–5	-75 and +400
Liquid hydrocarbon yield (GGE/gallon EtOH)	0.58	0.43	-26
Ethanol upgrading catalyst WHSV (h^{-1})	1	0.25-3	-75 and +200
Oligomerization catalyst replacement (year)	1	0.5-2	-50 and +100
Oligomerization catalyst cost ($/kg)	154	77-231	-50 and +50
Ethanol upgrading catalyst replacement (year)	1	0.5-2	-50 and +100
Ethanol upgrading catalyst cost ($/kg)	60	30-90	-50 and +50
Upgrading reaction temperature (°C)	350	250-450	-29 and +29

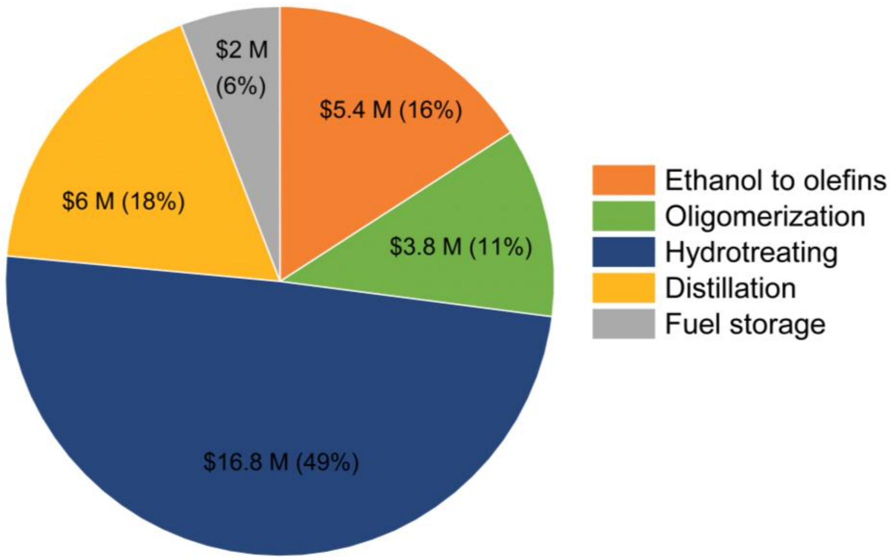


Figure S5. Total installed equipment cost for ethanol upgrading, separation and fuel storage (unit: million USD)

Table S4. MFSP based on ethanol feed with different ethanol concentrations

	Ethanol Prices ($/gal)	Ethanol Prices ($/GGE)	Upgrading Costs ($/GGE)	MFSP ($/GGE)
100% Ethanol*	$1.79	$2.72	$0.60	$3.68
50% Ethanol	$1.70	$2.58	$0.64	$3.57
13% Ethanol	$1.59	$2.42	$0.87	$3.61

*Corn ethanol price of $1.79 is used for the 100% ethanol case. We assume similar liquid hydrocarbon yield from different ethanol feeds.

Figure S6. Historical ethanol selling price in 2010-2020.

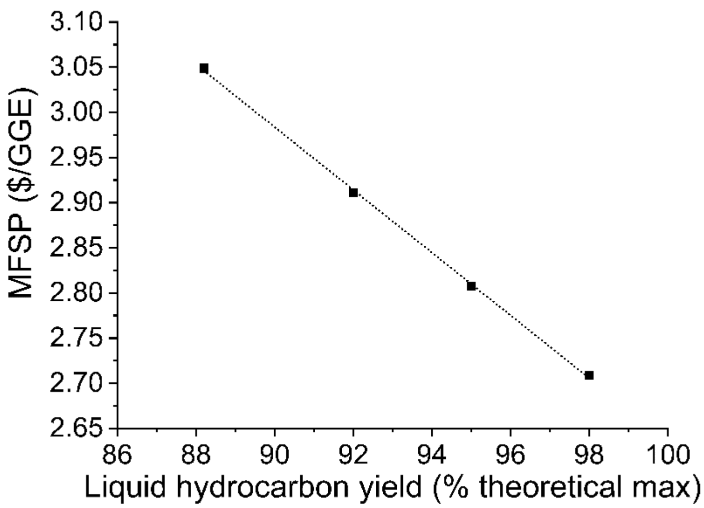


Figure S7. MFSP vs liquid hydrocarbon yield with corn stover as feedstock. Projected corn stover ethanol price ($1.42/gal) is used here.

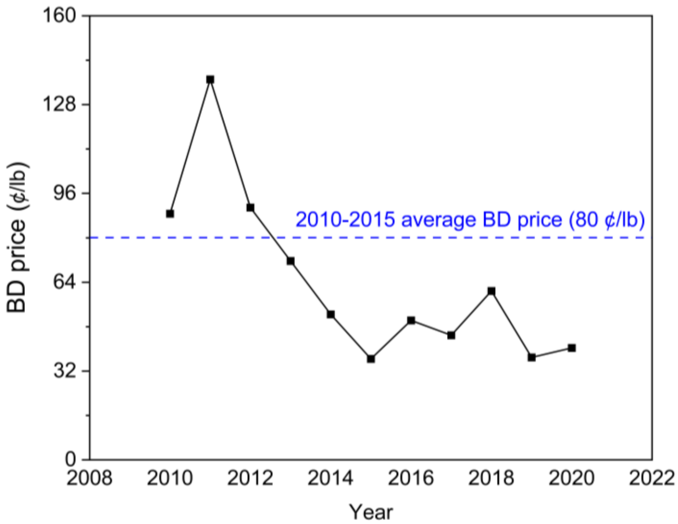


Figure S8. Butadiene historical price in 2010-2020.

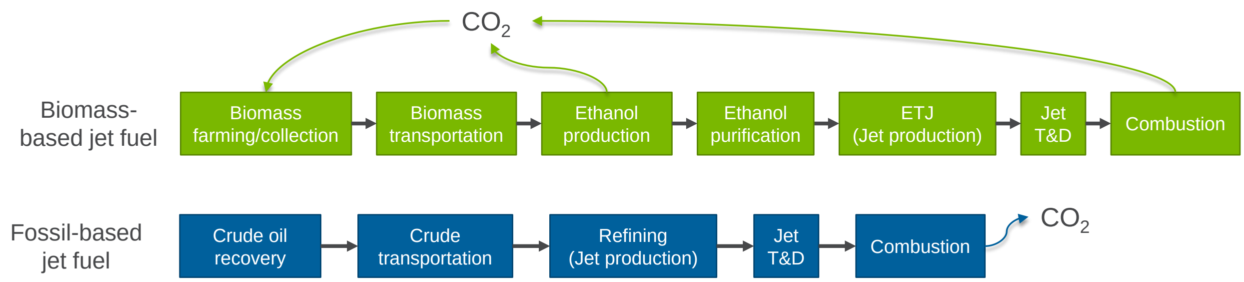


Figure S9. Well-to-wake pathways of biomass-based and fossil-based jet fuel (ETJ: ethanol to jet, T&D: transportation and distribution, NG: natural gas, FT: Fischer Tropsch)

Table S5. Major parameters and key assumptions of the life cycle analysis of ethanol supply chain

	Corn starch			**Corn stover**	**Miscanthus**
	Dry milling w/o corn oil extraction	**Dry milling w/ corn oil extraction**	**Wet milling**		
Ethanol yield	2.93 (gal per bushel of corn)	2.95 (gal per bushel of corn)	2.74 (gal per bushel of corn)	93.7 (gal per dry MT)	93.7 (gal per dry MT)
Share of Corn Ethanol Plant Types (corn starch)	18.2%	72.9%	8.9%		
Co-product *	DDGS, soybean mill, urea			Co-generated electricity	
Land-use change ** (grams CO_2 per gal ethanol)	594			-50	-1,607
Energy inputs for ethanol production * (MJ/gal ethanol)**					
Natural gas	9.1	8.7	21.8		
Coal	2.1	2.0	13.8		
Electricity	2.7	2.6			
Diesel				0.19	0.19
Biomass				58.6	61.7

* We considered credits for displacing distiller's dried grains with solubles (DDGS), soybean mill, urea, and electricity, which are co-products in the ethanol production process.

** Domestic and foreign CO_2 emissions from land-use change (LUC) are included. Miscanthus has large negative GHG emissions from LUC due to its high crop yield[14] .

*** Energy inputs for producing 13% concentration of ethanol. Heat demand for ethanol purification (14.5 MJ of NG/biomass per gal ethanol) was adjusted.

Table S6. Input materials for ethanol purification and downstream ethanol upgrading process for 1 MJ liquid hydrocarbon fuel produced

	0.58 GGE/gal EtOH			0.43 GGE/gal EtOH	Unit
	100% EtOH	50% EtOH	13% EtOH	100% EtOH	
Ethanol	0.042	0.044	0.046	0.059	kg/MJ
Water in ethanol feed	-	0.041	0.293	-	kg/MJ
Hydrogen *	0.035	0.027	0.027	0.059	MJ/MJ
Catalyst-ETO	5.4	5.6	5.9	7.5	mg/MJ
Catalyst-Oligomerization	3.2	3.5	3.6	5.5	mg/MJ
NG/biomass (for purification) **	0.205	0.174	-	0.287	MJ/MJ
NG (for ETO)	0.025	0.052	0.452	0.035	MJ/MJ

* Hydrogen required for ETO is assumed to be imported from natural gas steam methane reforming plants transported 150 miles via pipeline.

** For ethanol purification, corn starch feedstock uses natural gas, and corn stover/miscanthus uses biomass as heat source.

Table S7. Carbon credit impact on the MFSP

	Corn starch (LCA case 1)	Corn stover (LCA case 5)
GHG emission reduction relative to petroleum reference (g/MJ)	21	72
LCFS credit ($/ton CO_2) *	195	195
LCFS credit ($/GGE)	0.50	1.70
MFSP with LCFS carbon credit ($/GGE)	3.20	3.28
US RFS D6 RIN ($/ton CO_2) *	8.91	
US RFS D3 RIN ($/ton CO_2) *		131
US RFS RIN credit ($/GGE)	0.02	1.14
Total credit ($/GGE)	0.52	2.84
MFSP with total carbon credit ($/GGE)	3.18	2.14

* 2019 Q2 data was used as reported in Hannon et al[15].

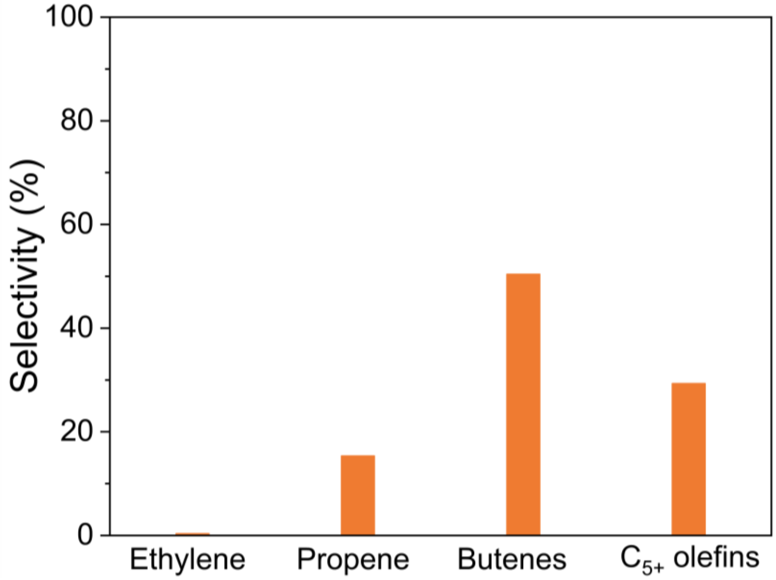


Figure S10. Conversion of acetone-butanol-ethanol mixture (ABE in liquid feeding: 60 wt% 1-butanol, 30 wt% acetone and 10 wt% ethanol) (0.51 h^{-1} WHSV, total pressure 106.8 kPa, 1.3 kPa ethanol, 4.8 kPa 1-butanol and 3.1 kPa acetone balanced with H_2) at 623 K over Cu-Zn-Y/Beta. The total carbon conversion is 99%.

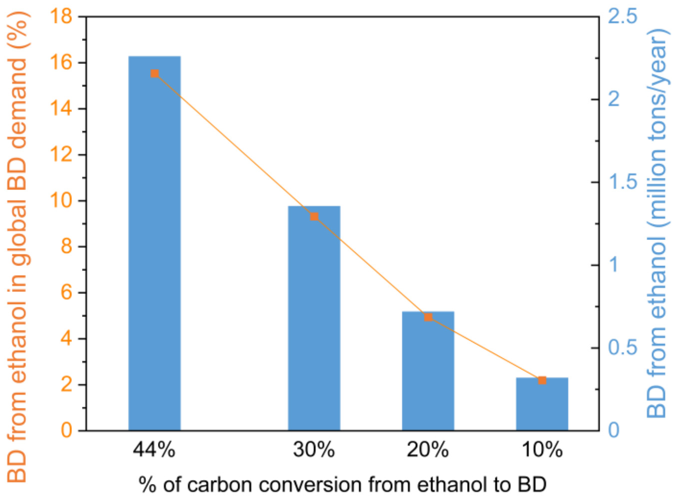


Figure S11. BD production volume and percent BD from ethanol in overall BD demand of 2025 when varying the amount of carbon from ethanol to BD, assuming 10% of the predicted 2025 SAFs (4.76 billion gallon/year[16]) is captured by ethanol to jet.

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