Thermocatalytic Decarboxylation and Aromatization of Oleic Acid to Aromatics Using Mo/HZSM-5

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Supporting Information

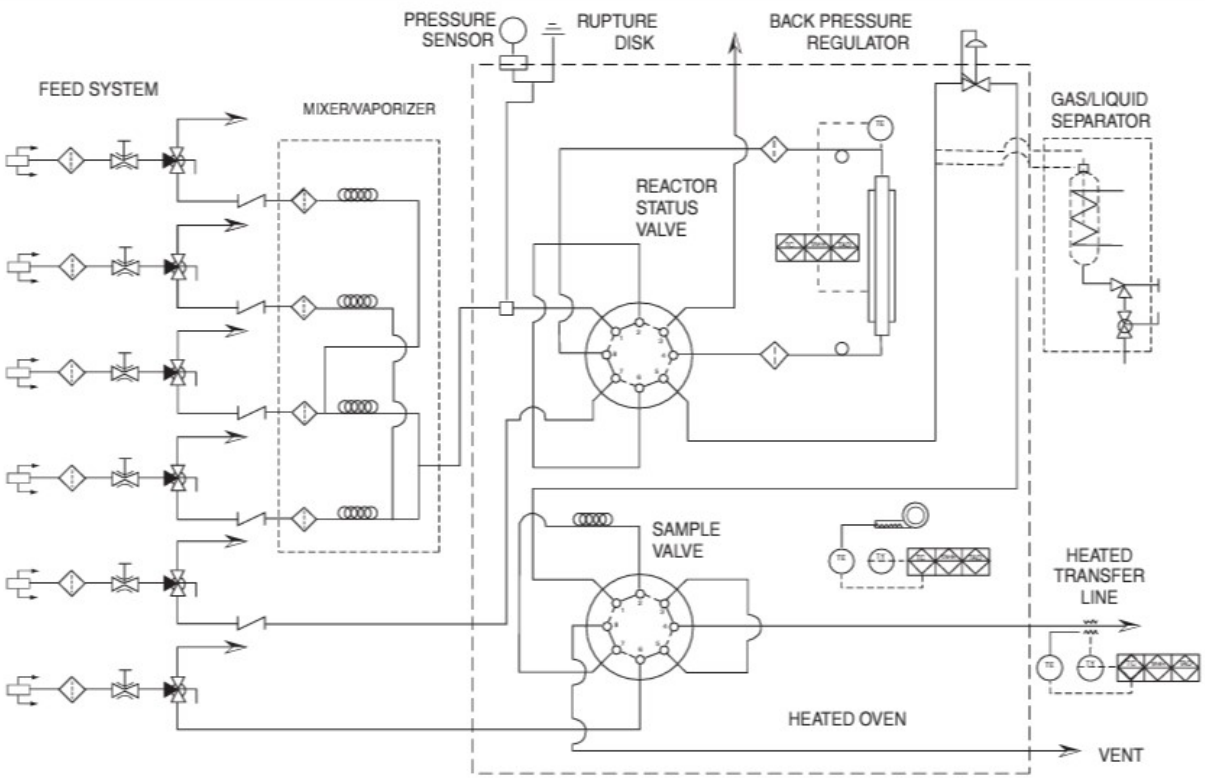


Figure S1 Schematic of the continuous Bench-top Reactor System. (Autoclave Engineers LLC)

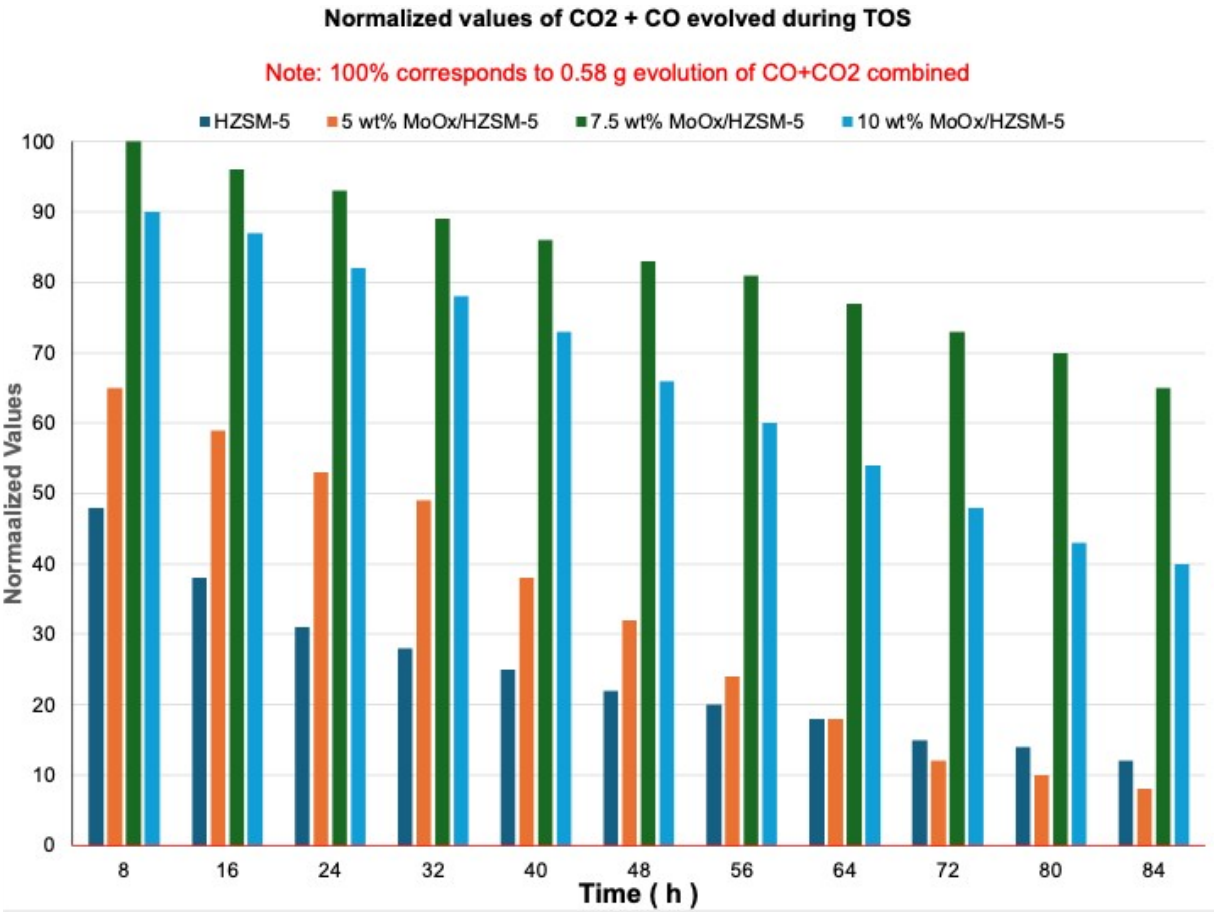


Figure S2 Normalized values of concentrations of CO and CO_2 detected by GC-FID as a function of time. A normalized value of 100 refers to near-complete decarboxylation (~99%) of oleic acid, as obtained with 7.5 wt% MoO_x/HZSM-5.

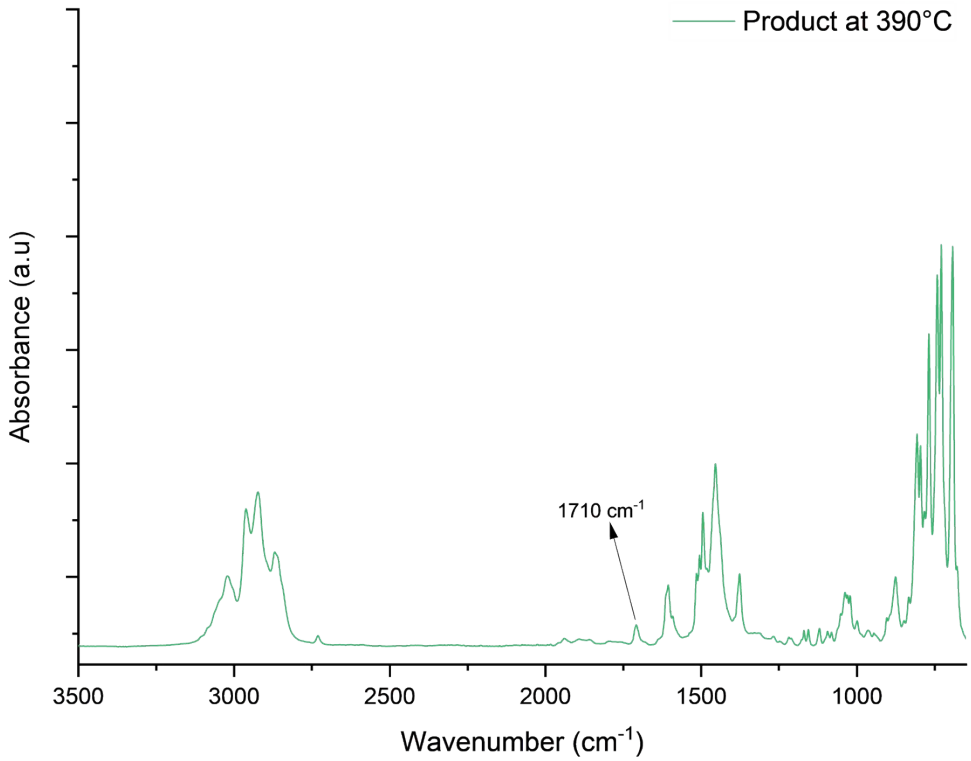


Figure S3 IR spectra of liquid product obtained at T = 390 °C , 7.5 wt% MoO_x/HZSM-5, τ = 4h, water: feed = 4:1.

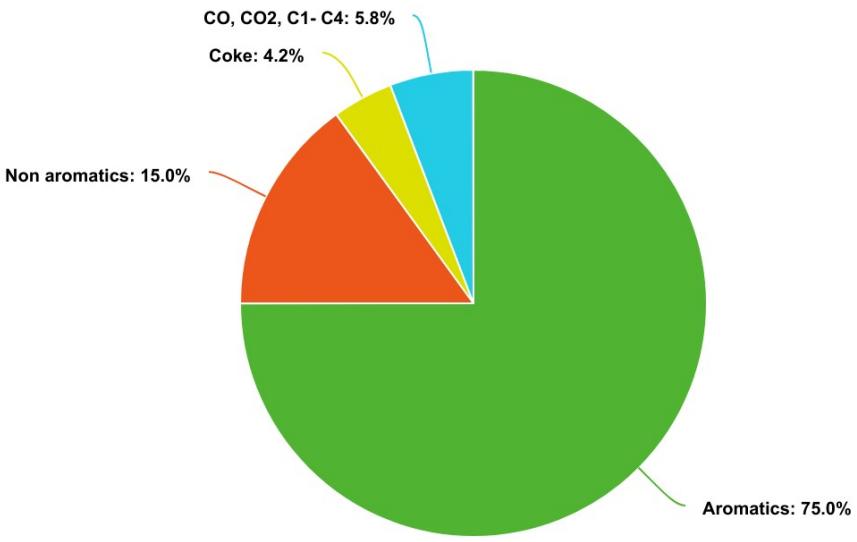


Figure S4 Product distribution for conversion of oleic acid over 7.5 wt% MoO_x/HZSM-5.

Oleic Acid; 1H NMR: δ 0.86 (3H, t, J = 7.0 Hz), 1.17-1.34 (14H, 1.23 (quint, J = 7.0 Hz), 1.23 (quint, J = 7.0 Hz), 1.24 (quint, J = 7.0 Hz), 1.24 (quint, J = 7.0 Hz), 1.25 (tt, J = 7.7, 7.0 Hz), 1.28 (h, J = 7.0 Hz), 1.28 (quint, J = 7.0 Hz)), 1.35-1.62 (6H, 1.42 (tt, J = 7.4, 7.0 Hz), 1.43 (tt, J = 7.4, 7.0 Hz), 1.55 (tt, J = 7.7, 7.4 Hz)), 1.90-2.02 (4H, 1.96 (q, J = 7.4 Hz), 1.97 (q, J = 7.4 Hz)), 2.30 (2H, t, J = 7.4 Hz), 5.30-5.45 (2H, 5.37 (dt, J = 15.6, 7.4 Hz), 5.37 (dt, J = 15.6, 7.4 Hz)).

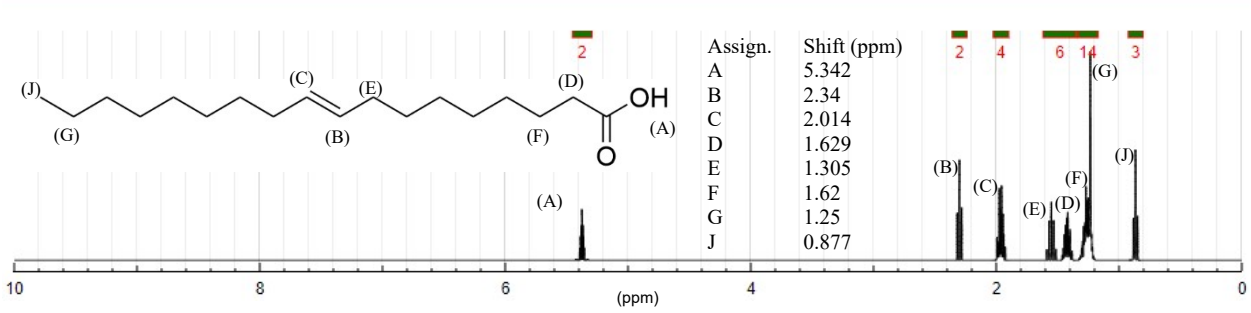


Figure S5 NMR Spectra for a model compound; Different types of protons can be seen in different ppm regions.

Figure S6 Relative ratios of integral area for different chemical shifts and interpretation**.**

Sample	Integral Ratio				Interpretation
	A (Protons associated with aromatic ring)	**B (Protons associated with vinyl group)**	**C (Protons associated with allyl and benzyl group)**	**D (Protons associated with -CH_2- and -CH_3 groups of alkyl chain**	
Oleic Acid	0	2	4 (allylic protons; no benzylic protons)	27	Linear chain aliphatic structure with backbone with an unsaturation (C=C) in the chain
Deoxygenated product under preferred reaction conditions	7.51	Negligible	8.35 (benzylic protons, negligible allylic protons)	3	Substantially aromatic compounds with short-chain alkyl substituents

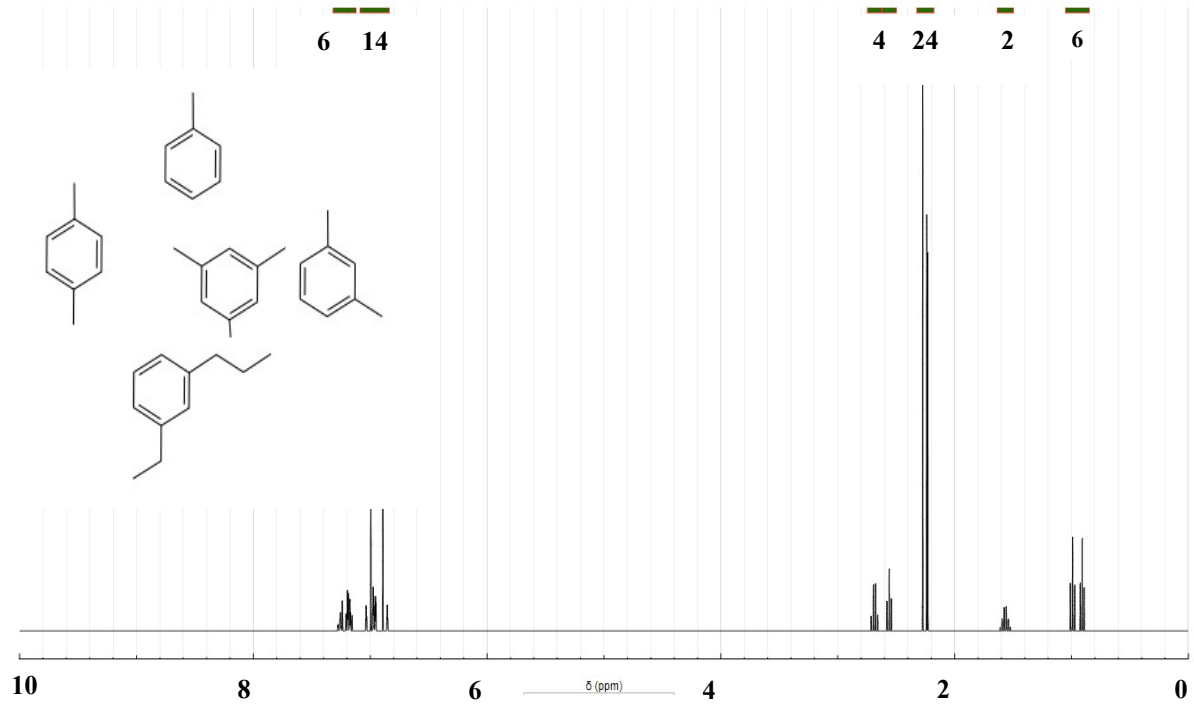


Figure S7 Simulated ^{1}H-NMR spectra of alkyl aromatics; Integral area are as follows: (A) = 20, (B) = 28 & (C) = 8.

Test Parameter	Method Reference	Percentage in CDO	Percentage in UCO
Free Fatty Acid (as Oleic Acid)	AOCS Ca 5a-40	12.87%	14.0%
Unsaponifiable Matter	AOCS Ca 6a-40	1.26%	1.8%
Moisture and Volatility	AOCS Ca 2b-38	0.46%	0.8%
Palmitic Acid (C16:0)	AOAC 963.22 & 991.39	14.30%	29.0%
Palmitoleic Acid (C16:1)	AOAC 963.22 & 991.39	0.10%	0.8%
Heptadecanoic Acid (C17:0)	AOAC 963.22 & 991.39	0.10%	0.2%
Stearic Acid (C18:0)	AOAC 963.22 & 991.39	1.80%	4.0%
Oleic Acid (C18:1)	AOAC 963.22 & 991.39	24.40%	35.0%
Vaccenoic Acid (C18:1w9)	AOAC 963.22 & 991.39	0.70%	1.5%
Linoleic Acid (C18:2)	AOAC 963.22 & 991.39	55.80%	12.0%
Linolenic Acid (C18:3w3)	AOAC 963.22 & 991.39	1.30%	0.6%
Arachidic Acid (C20:0)	AOAC 963.22 & 991.39	0.40%	0.5%
Behenic Acid (C22:0)	AOAC 963.22 & 991.39	0.20%	0.3%
Eicosenoic Acid (C20:1)	AOAC 963.22 & 991.39	0.30%	0.7%
Eicosadienoic Acid (C20:2)	AOAC 963.22 & 991.39	0.10%	0.2%
Lignoceric Acid (C24:0)	AOAC 963.22 & 991.39	0.50%	0.8%

Figure S8 Total Fatty Acid (TFA) Composition of Corn Distiller's Oil (CDO) and Used Cooking Oil (UCO)

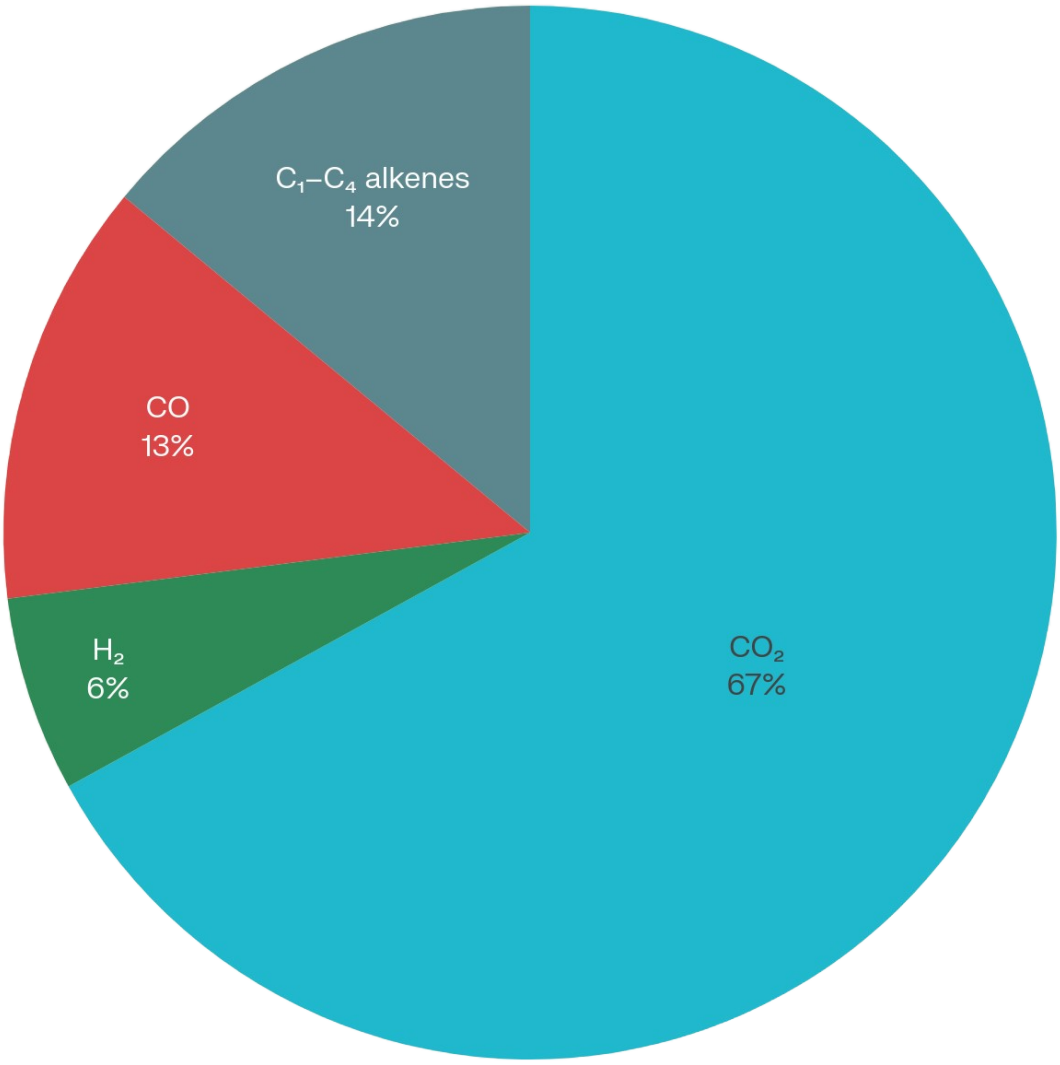
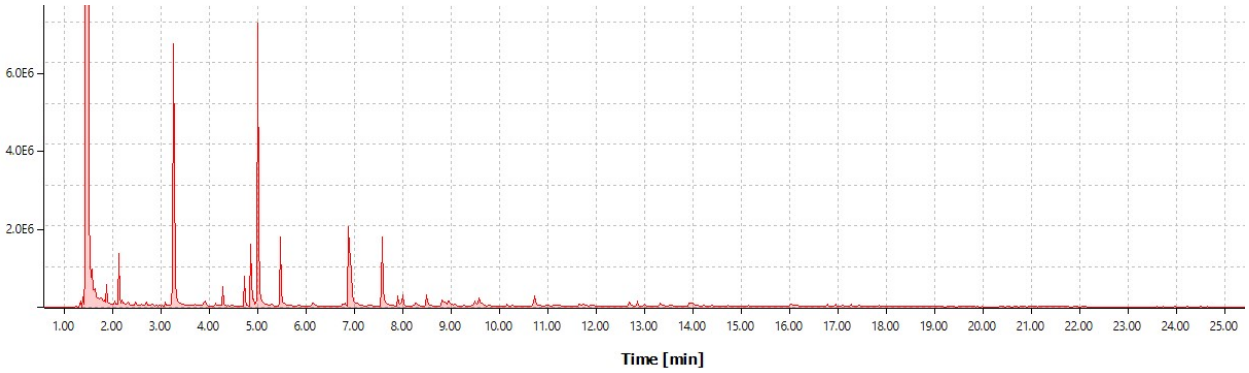


Figure S9 Distribution of Gaseous Products for catalytic conversion of fatty acid-derived feedstocks over 7.5 wt% MoO_x/HZSM-5.

Sample CDO

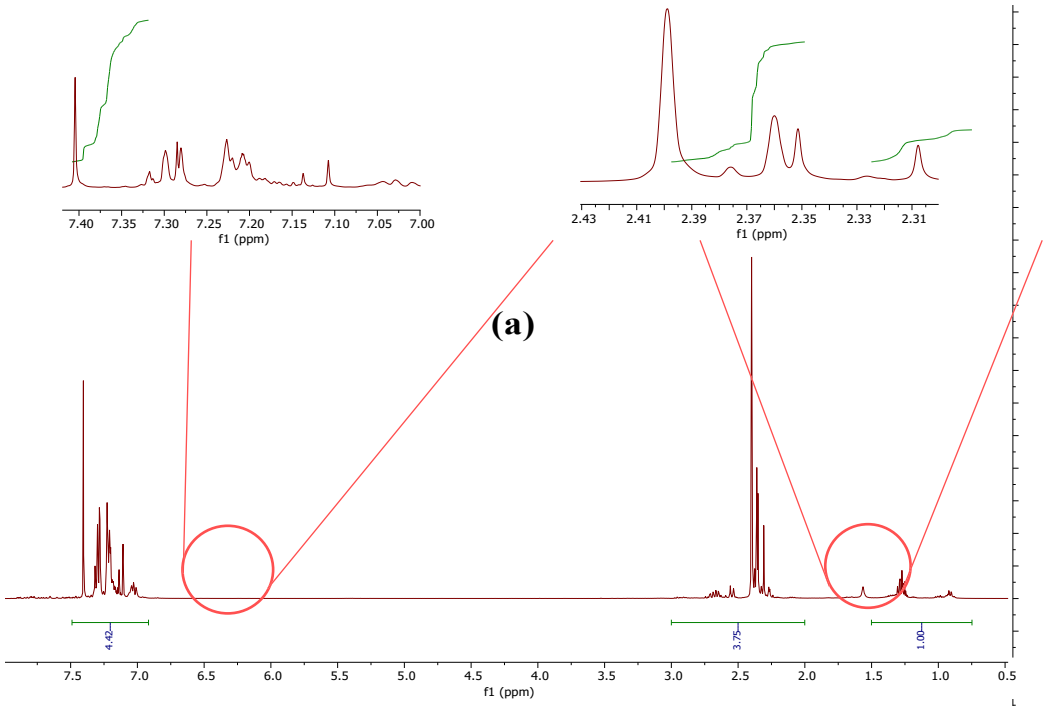


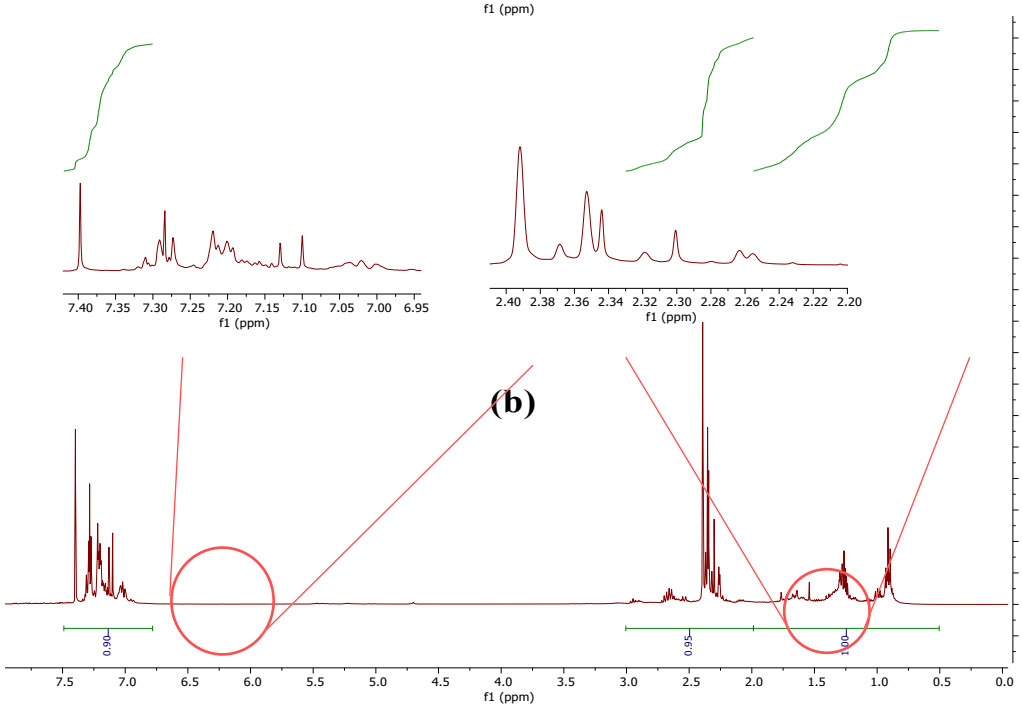
RT (min)	CAS#	Name	wt %
1.8949	000096-37-7	Cyclopentane, methyl-	0.67
2.1425	000071-43-2	Benzene	8.45
3.2568	000108-88-3	Toluene	19.19
4.8662	000100-41-4	Ethylbenzene	4.14
5.0148	000108-38-3	m-Xylene	18.12
	000106-42-3	p-Xylene	
5.4852	000095-47-6	o-Xylene	4.62
6.1538	000098-82-8	Isopropylbenzene	0.28
6.7728	000103-65-1	n-Propylbenzene	0.29
6.8966	000620-14-4	m-Ethyltoluene	7.86
	000622-96-8	p-Ethyltoluene	
7.5652	000095-63-6	Benzene, 1,2,4-trimethyl-	4.27
7.9118	062016-34-6	Octane, 2,3,7-trimethyl-	0.80
7.9861	017302-28-2	Nonane, 2,6-dimethyl-	1.02
8.2585	000099-87-6	p-Cymene	0.58
8.4813	000496-11-7	Indane	1.22
8.828	001074-55-1	Benzene, 1-methyl-4-propyl-	1.03
8.9518	000135-01-3	Benzene, 1,2-diethyl-	1.22
9.4965	000767-58-8	Indan, 1-methyl-	0.59
9.5956	002870-04-4	Benzene, 2-ethyl-1,3-dimethyl-	1.21
10.2641	000095-93-2	Benzene, 1,2,4,5-tetramethyl-	0.29
10.7098	000874-35-1	1H-Indene, 2,3-dihydro-5-methyl-	1.26
11.205	000119-64-2	Naphthalene, 1,2,3,4-tetrahydro-	0.61
11.6507	056253-64-6	Benzene, (2-methyl-1-butenyl)-	0.72
11.9231	016002-93-0	trans-1-Phenyl-1-pentene	0.40
12.6907	001559-81-5	Naphthalene, 1,2,3,4-tetrahydro-1-methyl-	0.48
12.8392	017301-30-3	Undecane, 3,8-dimethyl-	0.45
12.9878	017312-65-1	Undecane, 3,3-dimethyl-	0.29
13.3345	006682-71-9	1H-Indene, 2,3-dihydro-4,7-dimethyl-	0.67
13.9535	000091-57-6	Naphthalene, 2-methyl-	1.01
14.3992	007524-63-2	Naphthalene, 1,2,3,4-tetrahydro-2,6-dimethyl-	0.31

16.0334	000581-42-0	Naphthalene, 2,6-dimethyl-	0.90
16.7762	003891-99-4	2,6,10-Trimethyltridecane	0.25
16.9495	025117-32-2	Tetradecane, 5-methyl-	0.25

Note: Chemicals in green background were quantified with standards while others were semi-quantified based on reference m/p-xylene.

Figure S10 A representative GC-MS chromatogram under maximized conditions with CDO as feedstock.


7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00
f1 (ppm)
2.43 2.41 2.39 2.37 2.35 2.33 2.31
f1 (ppm)
(a)
4.42
3.75
1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95
f1 (ppm)
2.40 2.38 2.36 2.34 2.32 2.30 2.28 2.26 2.24 2.22 2.20
f1 (ppm)
(b)
0.90
0.95
1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

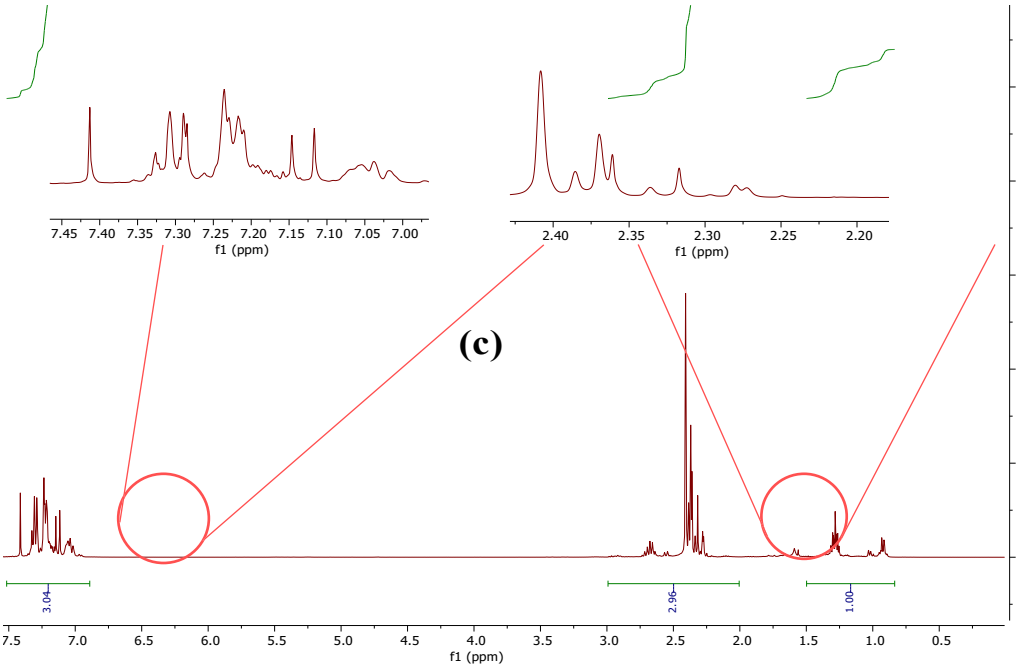


Figure S11 Product distribution for catalytic conversion of oleic acid with (a) Linoleic acid, (b) Used Cooking oil and (c) Corn Distiller's Oil under maximized operating conditions.

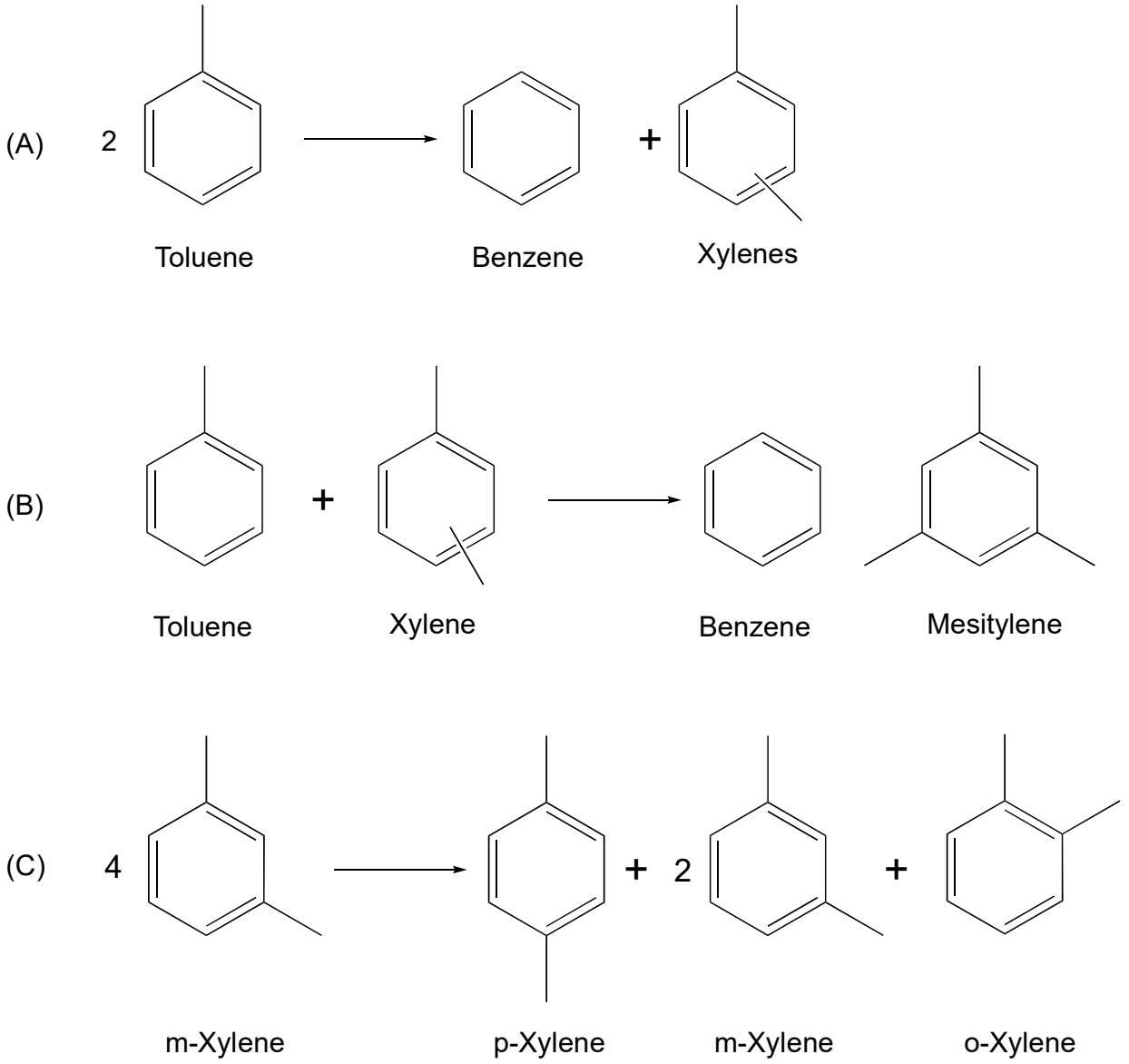


Figure S12 Proposed reaction pathway for formation of benzene and xylene isomers.

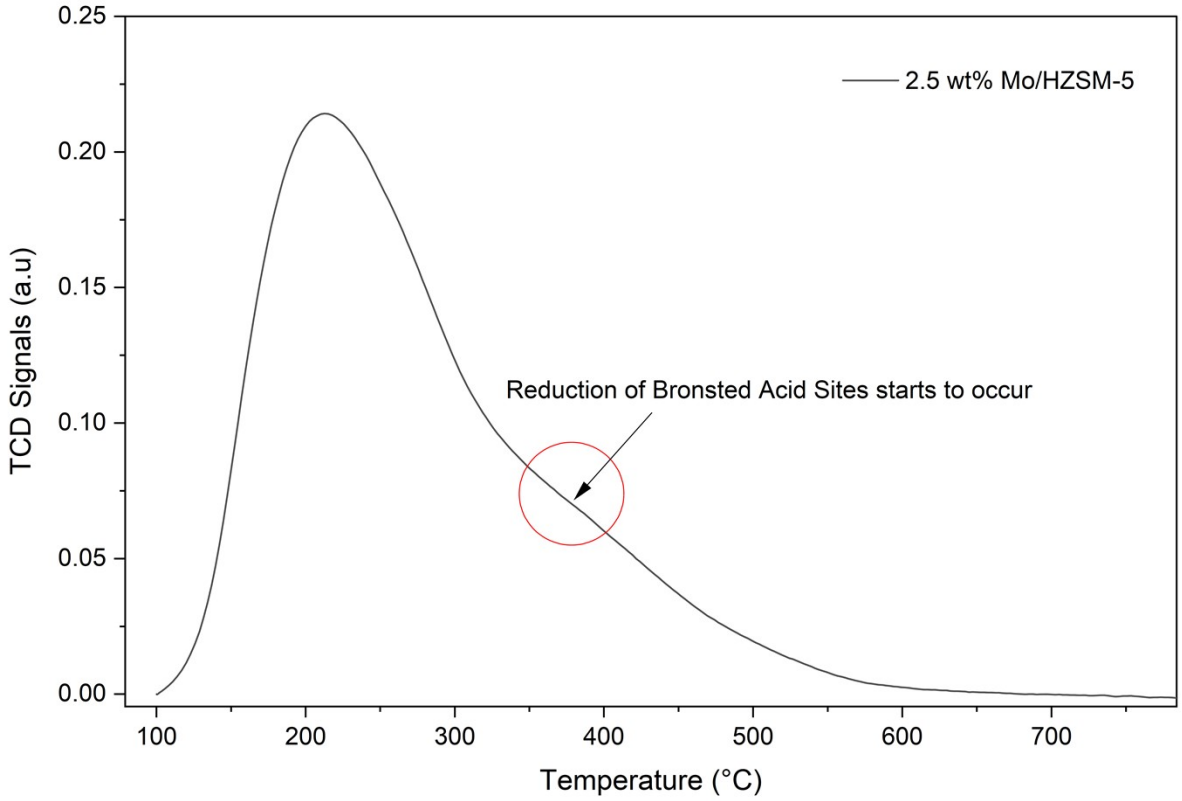


Figure S13 NH_3 TPD of 2.5 wt% Mo/HZSM-5.

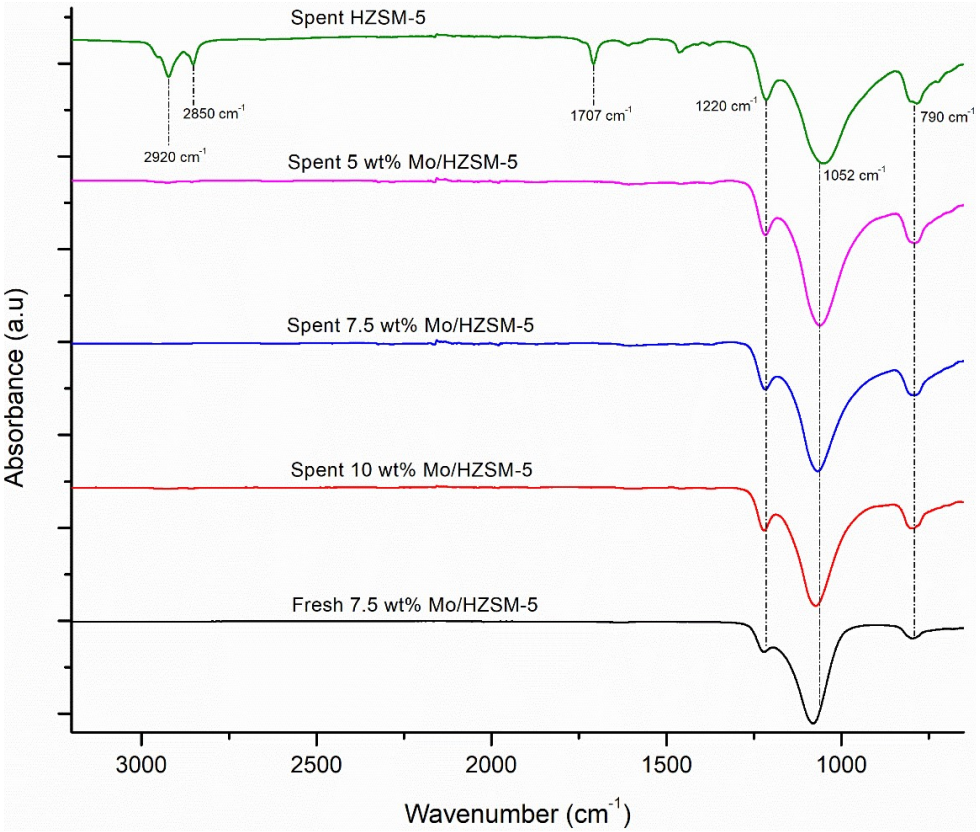


Figure S14 FTIR analysis of the fresh and spent catalysts.

Parameter / Analyte	MRL	Units	7.5% Mo/HZSM-5	10% Mo/HZSM-5	Ref. Method
Barium	0.1	mg/kg	< 0.10	< 0.10	EPA 3050B/6010C
Calcium	3	mg/kg	21	130	EPA 3050B/6010C
Cobalt	0.1	mg/kg	0.18	0.88	EPA 3050B/6010C
Copper	0.1	mg/kg	1.3	1.7	EPA 3050B/6010C
Iron	1	mg/kg	140	140	EPA 3050B/6010C
Molybdenum	0.5	mg/kg	74800	98700	EPA 3050B/6010C
Nickel	1	mg/kg	32	24	EPA 3050B/6010C
Potassium	5	mg/kg	17	80	EPA 3050B/6010C
Sodium	5	mg/kg	120	110	EPA 3050B/6010C
Strontium	0.1	mg/kg	0.24	0.32	EPA 3050B/6010C
Vanadium	0.5	mg/kg	< 0.51	< 0.50	EPA 3050B/6010C

Figure S15 ICP-AES analysis for 7.5 wt% Mo/HZSM-5 and 10 wt% Mo/HZSM-5.