Synthesis and Characterization of Novel Corncob-Based Solid Acid Catalyst for Biodiesel Production

Zakir Hussain, Rakesh Kumar*

Department of Chemical Engineering,

Rajiv Gandhi Institute of Petroleum Technology, Jais, Amethi 229304, India.

*Corresponding Author: Tel.: +91-9450352043. E-mail: rkumar@rgipt.ac.in.

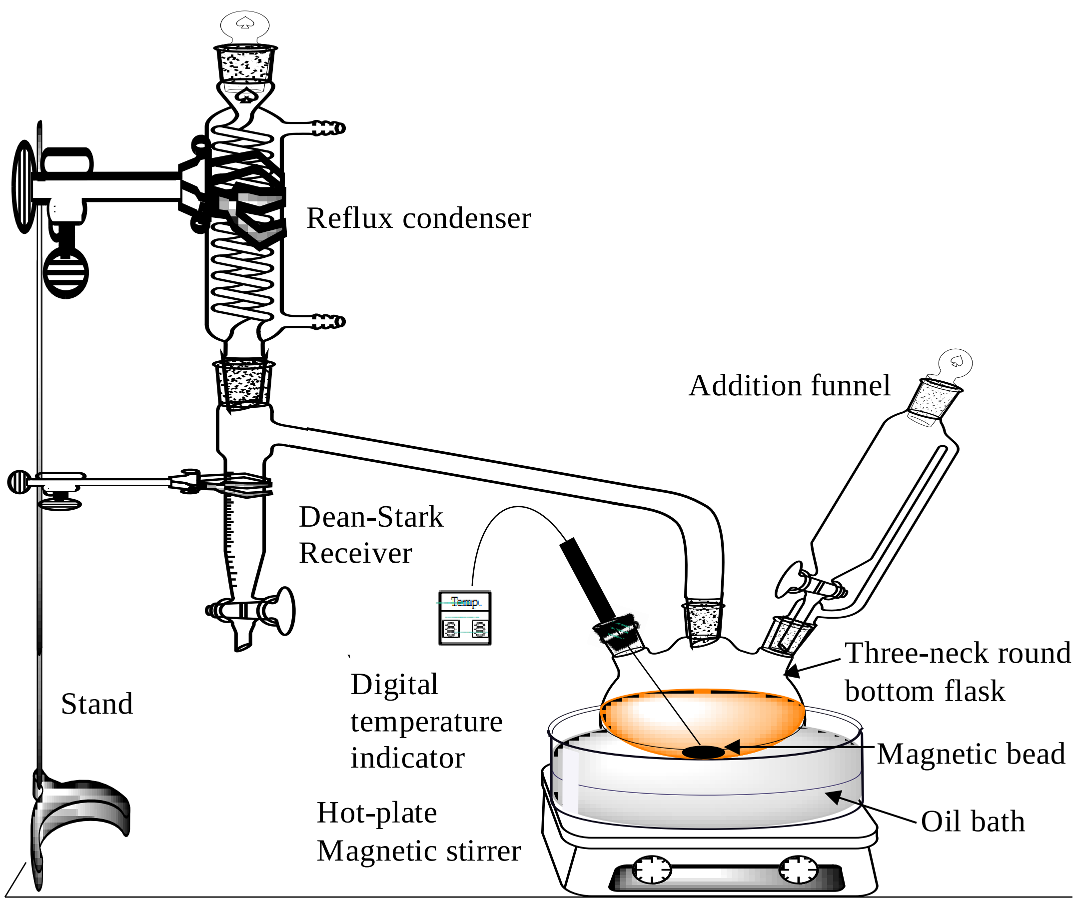

Figure S1. Schematic of the experimental setup

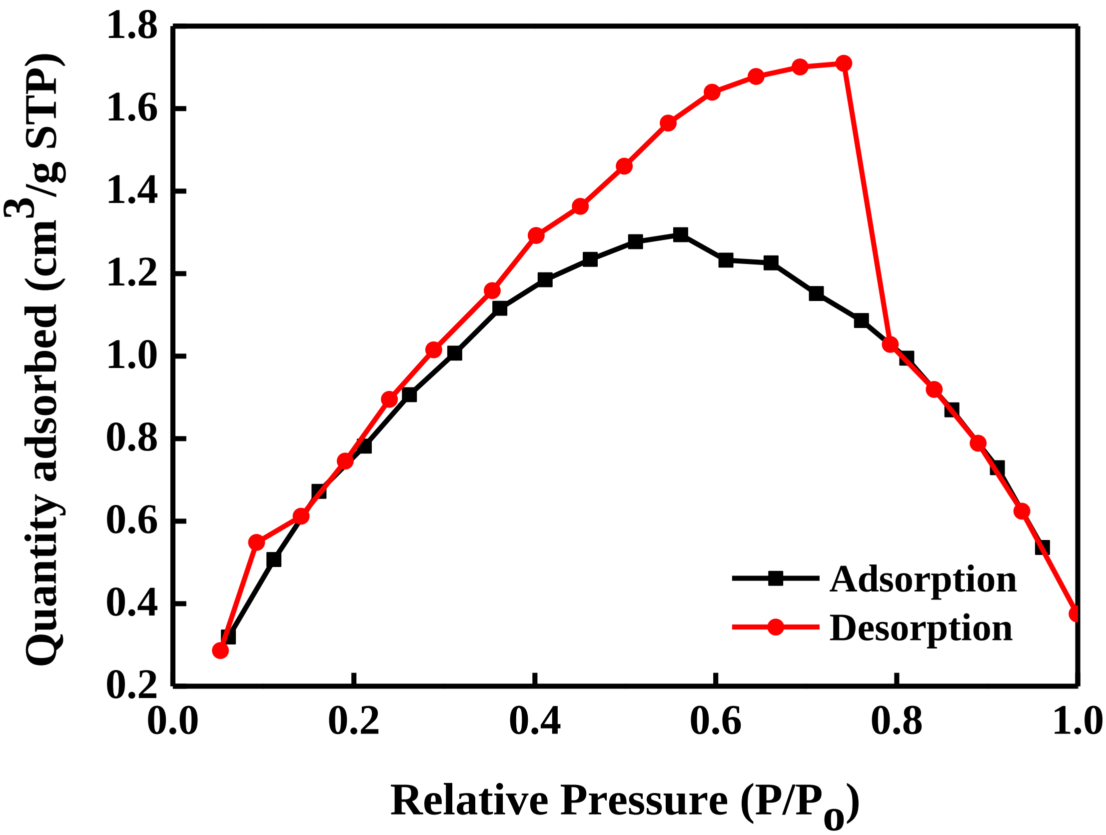

Figure S2. The N_2 adsorption-desorption isotherm of corncob (precursor)

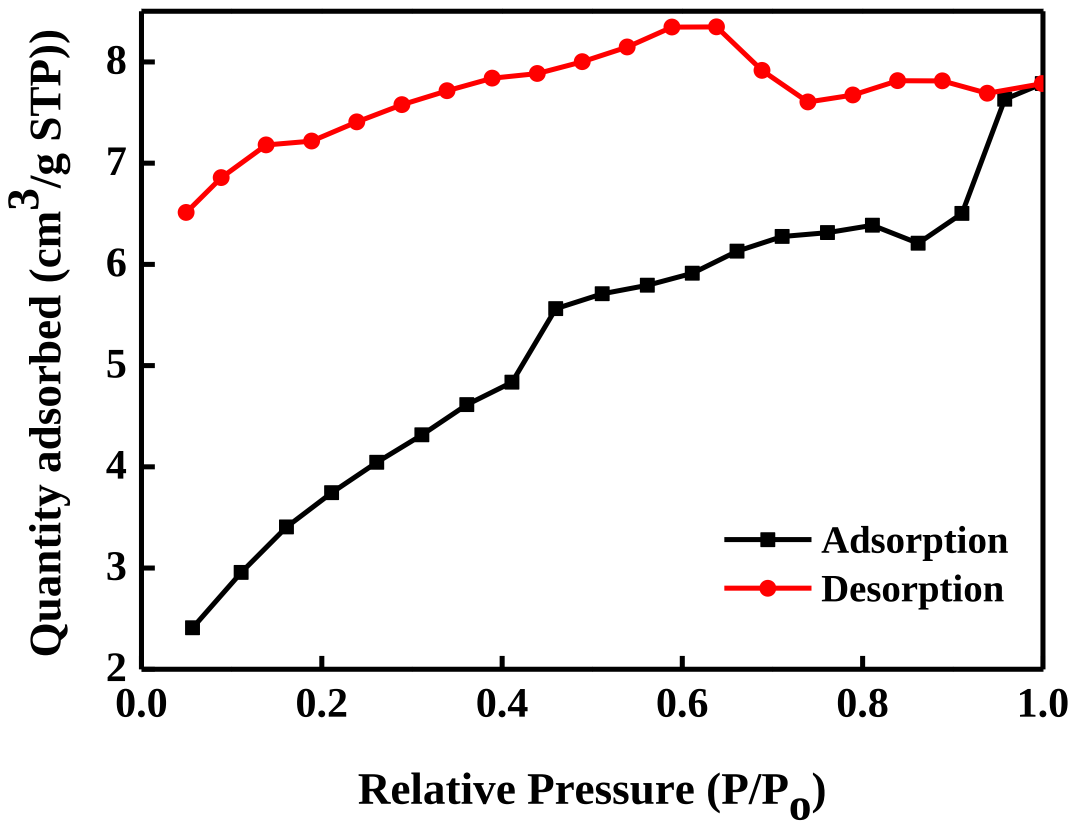

Figure S3. The N_2 adsorption-desorption isotherm of C-corncob (C_T=723K-C_t=8h)

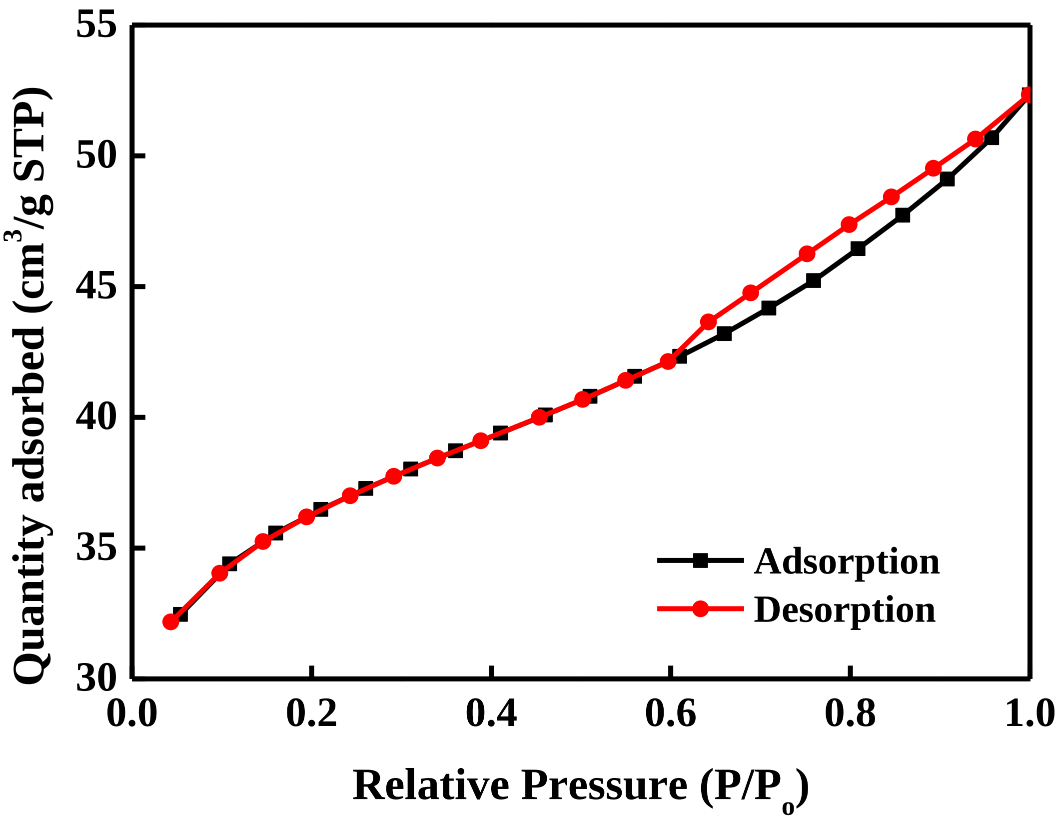

Figure S4. The N_2 adsorption-desorption isotherm of I-C-corncob (I_R=1-I_T=5h-C_t=8h-C_T=523K)

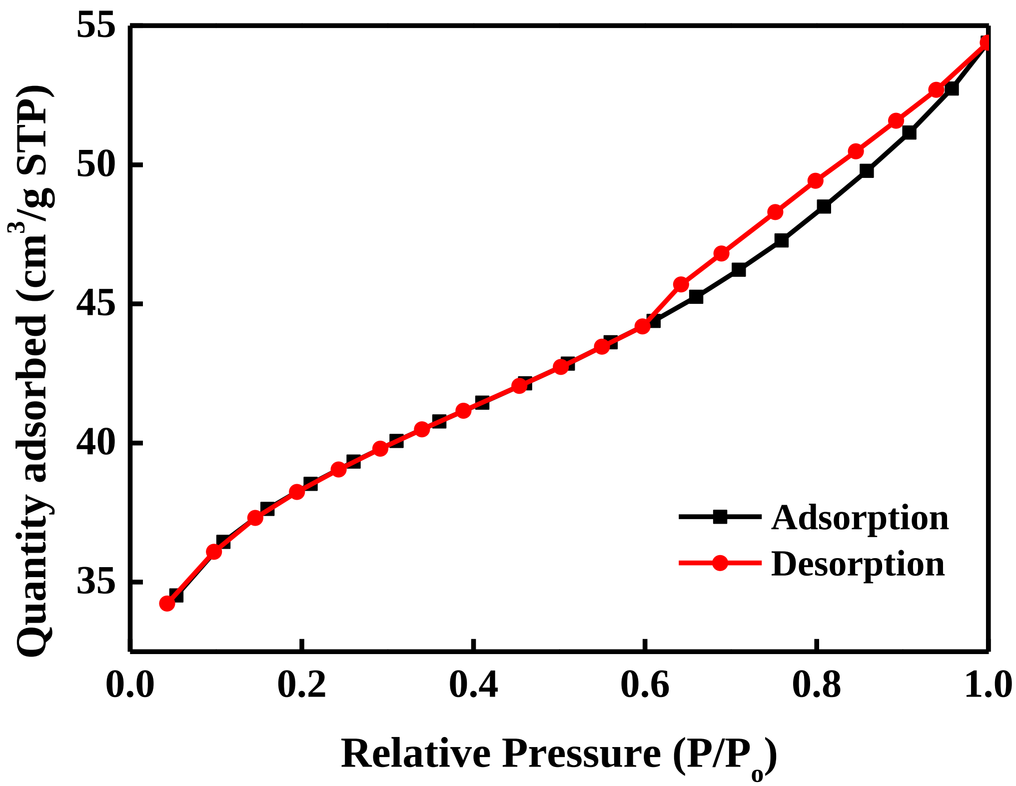

Figure S5. The N_2 adsorption-desorption isotherms of I-C-corncob (I_R=1-I_T=5h-C_t=8h-C_T=623K)

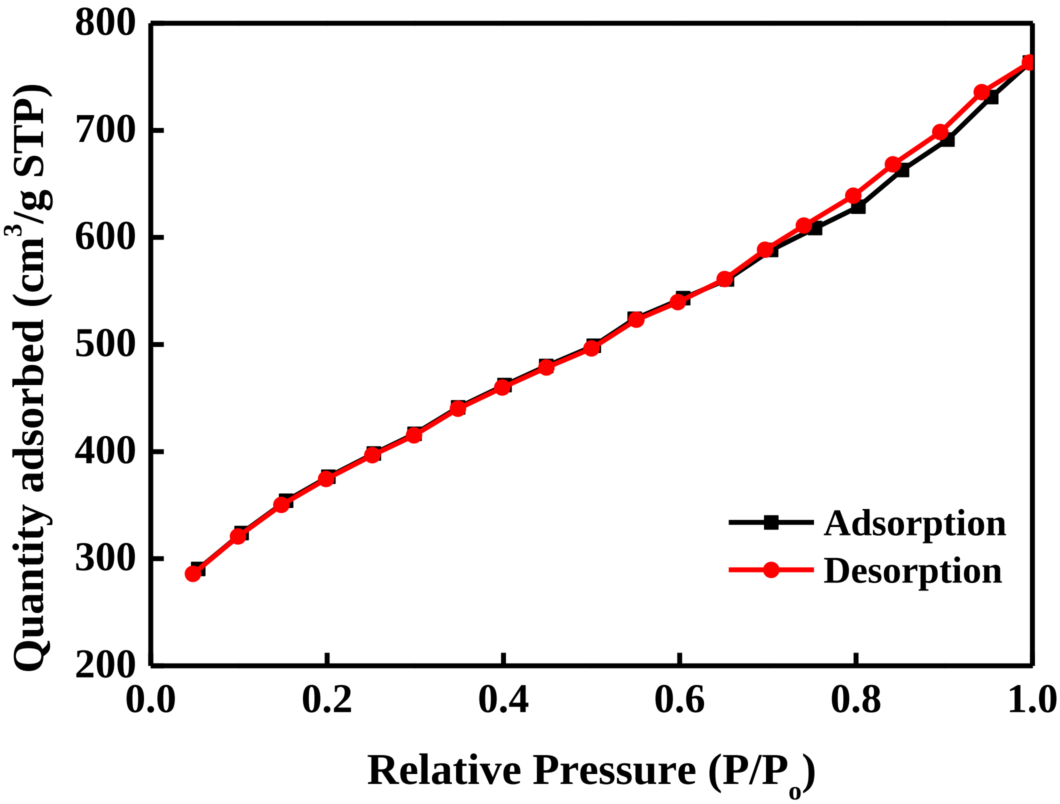

Figure S6. The N_2 adsorption-desorption isotherm of I-C-corncob (I_R=1-I_T=5h-C_t=8h-C_T=673K)

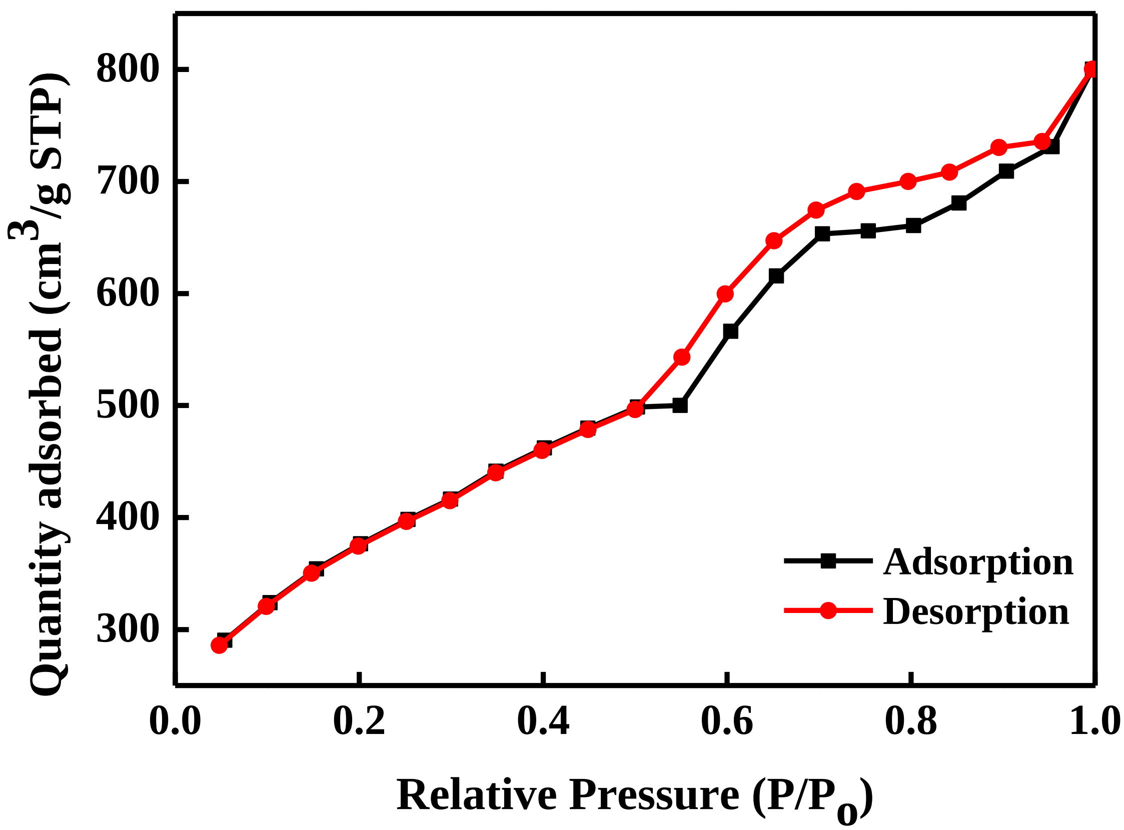

Figure S7. The N_2 adsorption-desorption isotherm of I-C-corncob (I_R=1-I_T=5h-C_t=8h-C_T=723K)

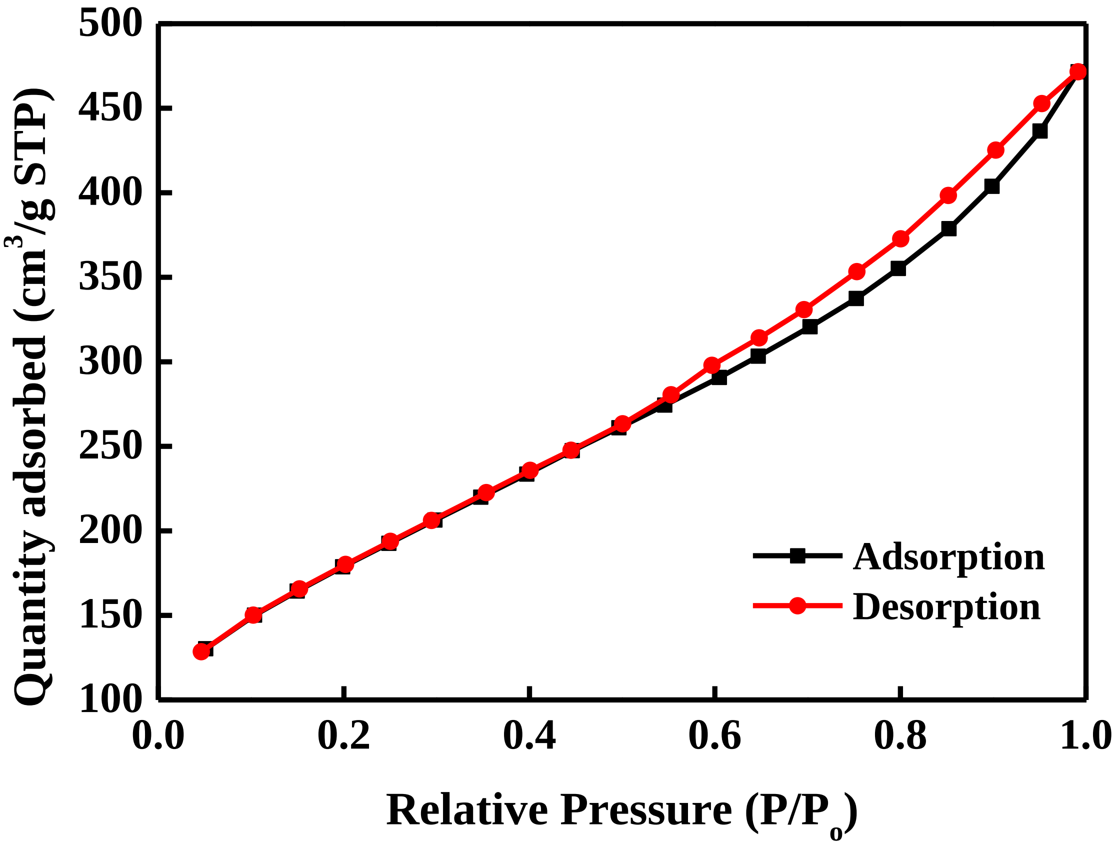

Figure S8. The N_2 adsorption-desorption isotherms of I-C-corncob (I_R=1-I_T=5h-C_t=8h-C_T=773K)

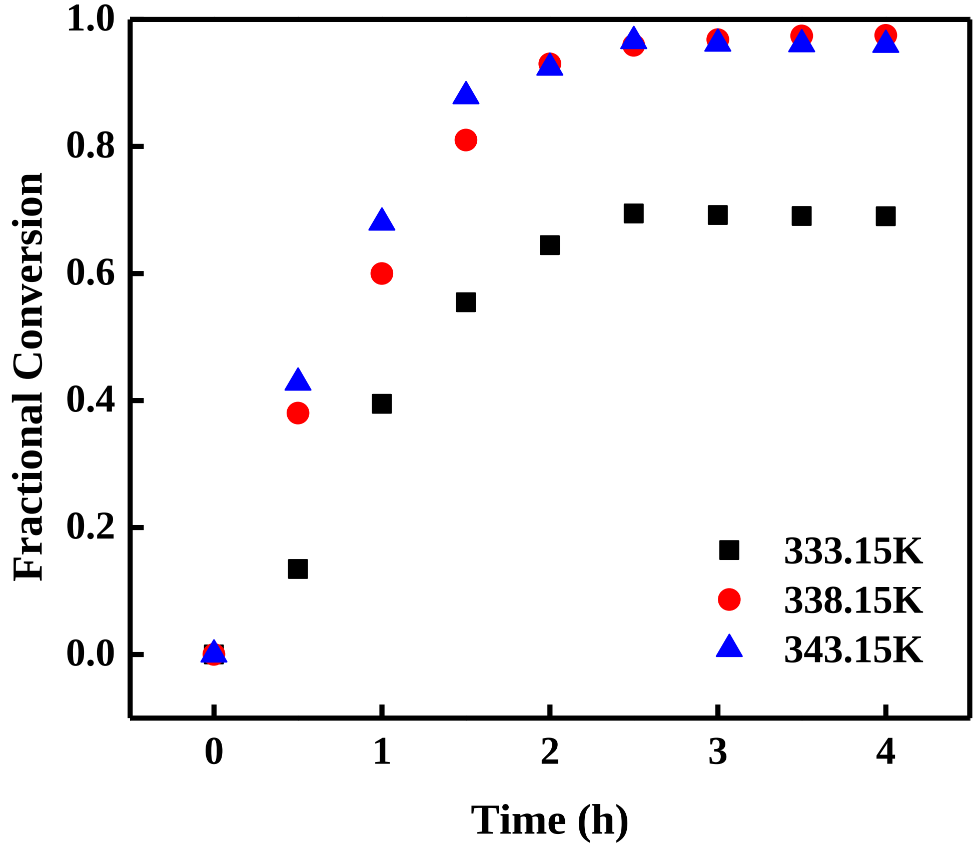

Figure S9. Effect of reaction temperature at various intervals on palmitic acid conversion (R=1:9 and W = 8 wt %)

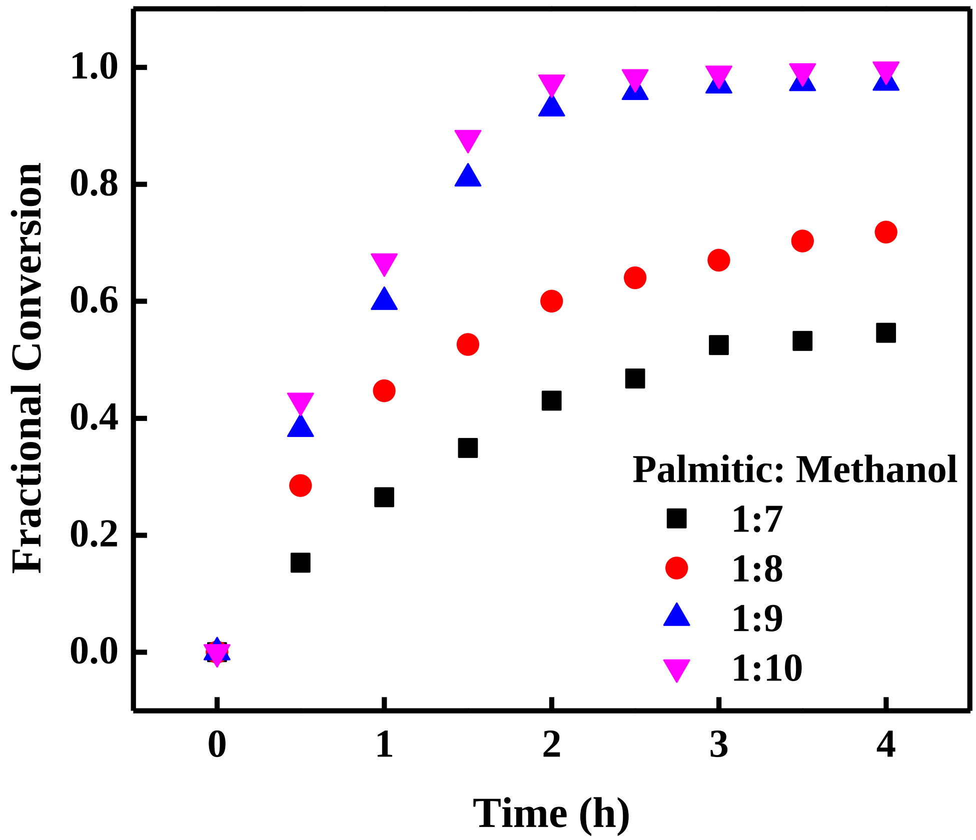

Figure S10. Effect of palmitic acid to methanol ratio on palmitic acid conversion (W= 8 wt % and T=338K)

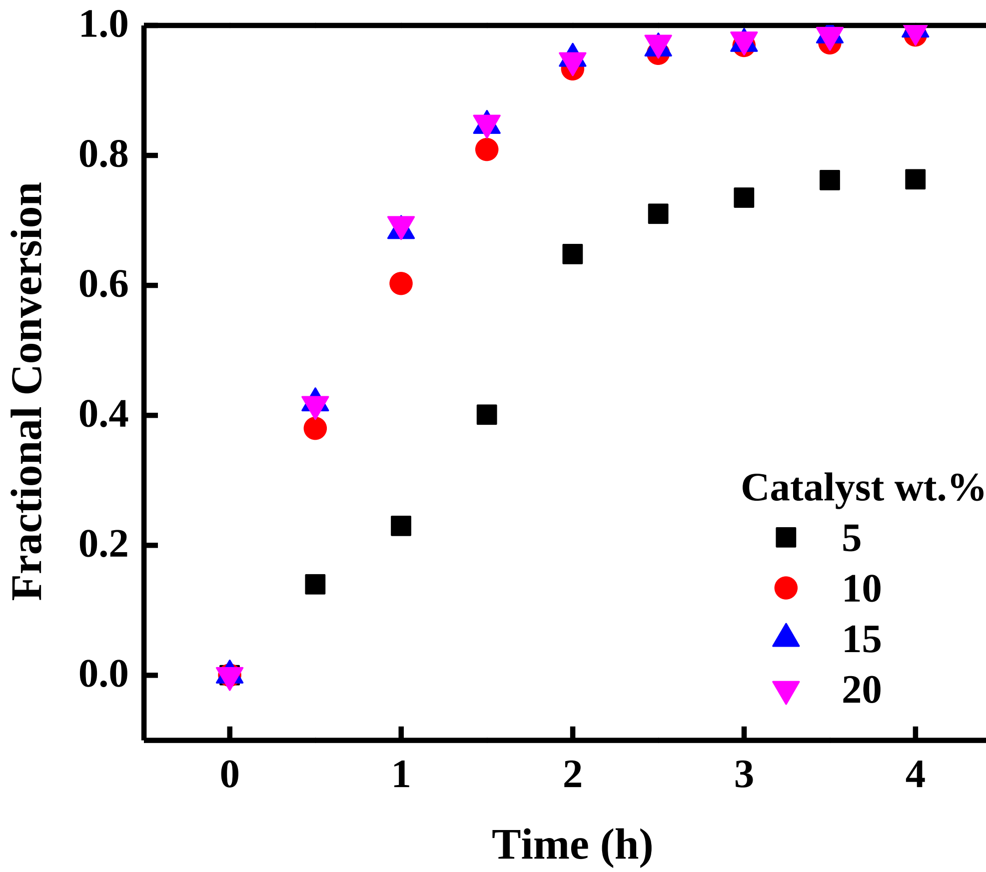

Figure S11. Effect of catalyst loading (wt %) on palmitic acid conversion (R=1:10 and T=338K)

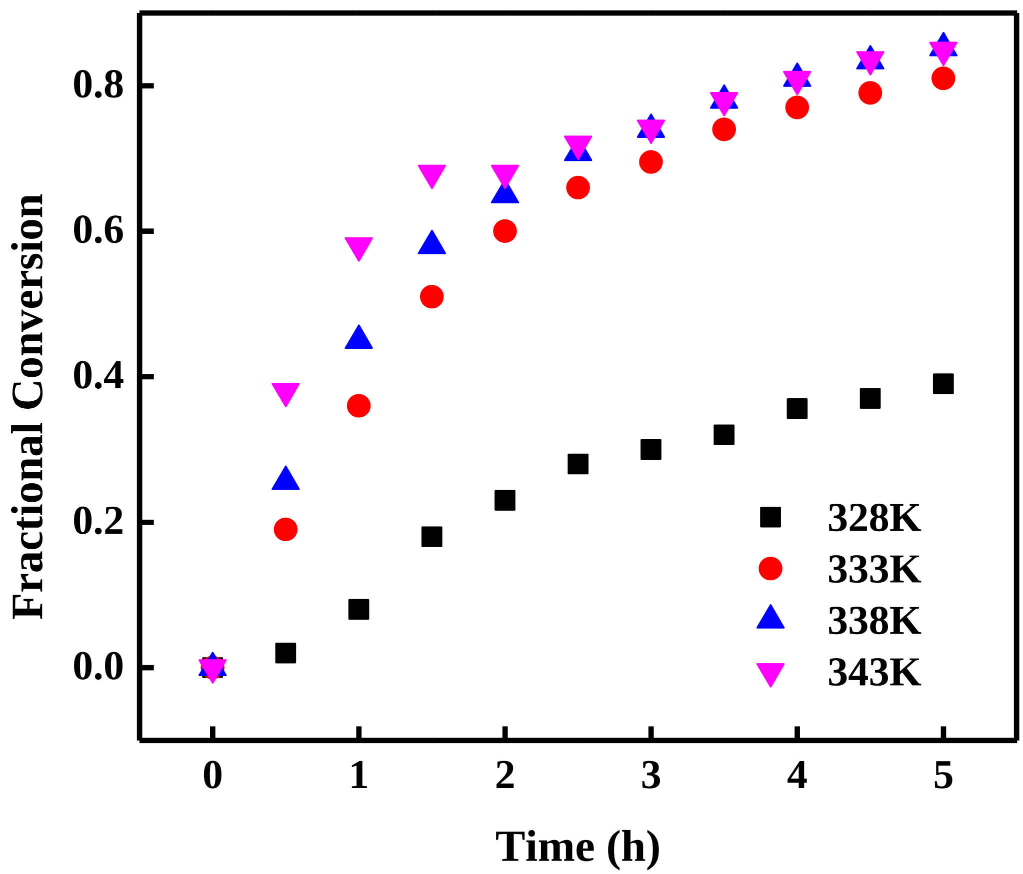

Figure S12. Effect of reaction temperature on Karanja oil free fatty acid conversion (R=1:10 and W= 10 wt %)

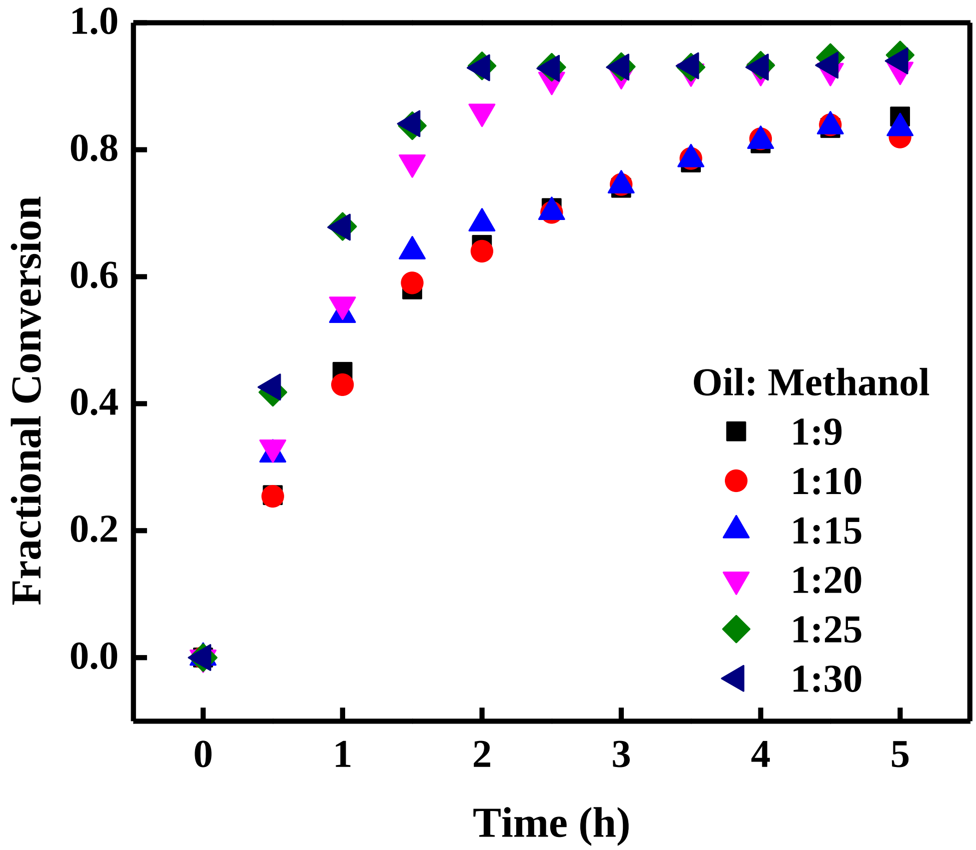

Figure S13. Effect of Karanja oil to methanol ratio on free fatty acid conversion (W= 10 wt % and T=338K)

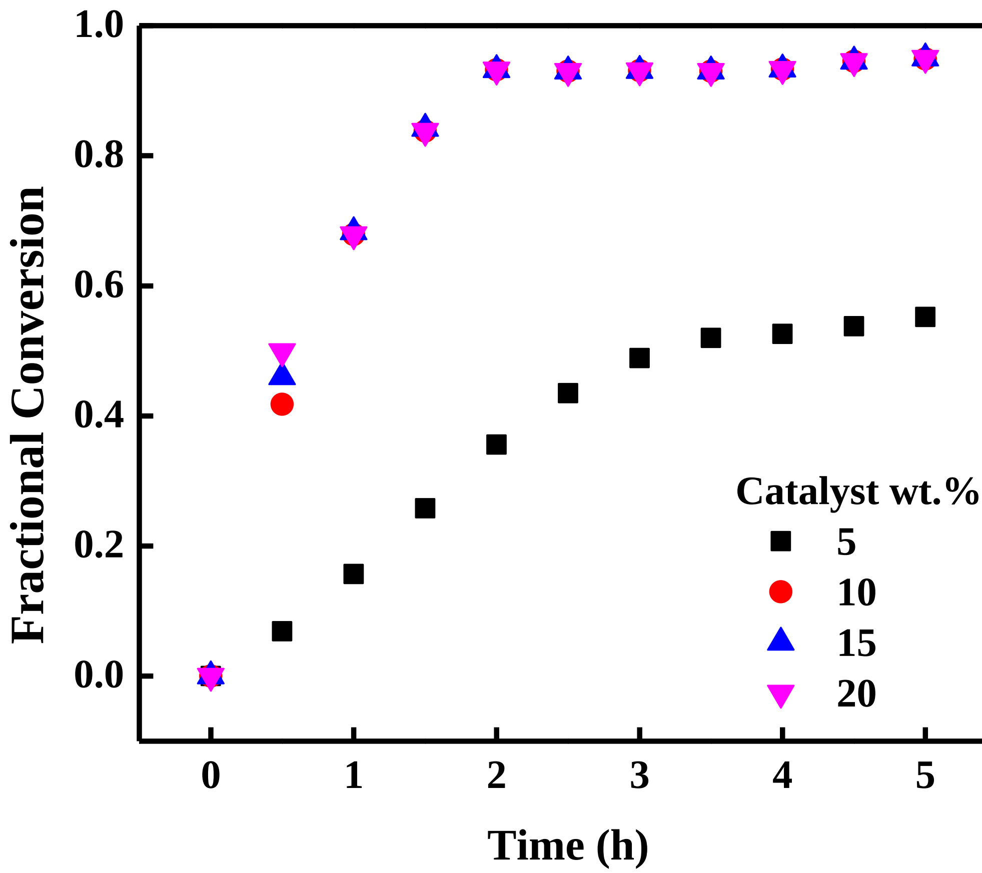

Figure S14. Effect of catalyst loading on Karanja oil free fatty acid conversion (R=1:20 and T=338K)

Table S1. Acid Densities of the Spent Catalysts Washed with Methanol and Ethanol

run no.	acid densities (mmol/g catalyst) of the catalyst: $\mathrm{I}_{R=1}^{t=5}-\mathrm{C}_{T=723}^{t=8}-\mathrm{S}_{T=393}^{t=15}$							
	methanol washing				ethanol washing			
	SO_3H	COOH	OH	Total	SO_3H	COOH	OH	total
1	3.16	2.22	0.18	5.56	3.16	2.22	0.18	5.56
2	3.14	2.22	0.18	5.54	3.11	2.21	0.18	5.5
3	3.14	2.21	0.18	5.53	3.01	2.19	0.18	5.38
4	2.98	2.22	0.18	5.38	2.98	2.16	0.19	5.33
5	2.98	2.22	0.19	5.39	2.98	2.16	0.19	5.33
6	2.98	2.22	0.21	5.41	2.98	2.16	0.19	5.33
7	2.93	2.22	0.22	5.37	2.63	2.15	0.18	4.96
8	2.91	2.19	0.22	5.32	2.63	2.15	0.18	4.96
9	2.83	2.19	0.22	5.24	2.63	2.15	0.18	4.96
10	2.74	2.16	0.22	5.12	2.63	2.15	0.18	4.96
11	2.69	2.15	0.22	5.06	2.12	2.15	0.19	4.46
12	2.63	2.16	0.22	5.01	1.26	2.12	0.19	3.57
13	2.60	2.14	0.22	4.96	1.26	2.12	0.19	3.57
14	2.60	2.13	0.22	4.95	1.26	2.12	0.19	3.57
15	2.60	2.14	0.22	4.96	1.26	2.12	0.19	3.57
16	2.60	2.14	0.22	4.96	1.26	2.12	0.19	3.57
17	2.60	2.13	0.22	4.95	1.26	2.12	0.19	3.57
18	2.60	2.14	0.22	4.96	1.26	2.12	0.19	3.57
19	2.60	2.14	0.22	4.96	1.26	2.12	0.19	3.57
20	2.60	2.14	0.22	4.96	1.26	2.12	0.19	3.57

Table S2. Comparison of Present (I-C-S-Corncob) Catalyst Performance with Other Catalysts for Oleic Acid Esterification

S. no.	catalyst	reaction conditions[a]	reaction time (h)	oleic acid conversion (%)	operational stability (No of runs)	remarks
1	Without catalyst[44]	10:10:353	24	-	-	No product
2	Corncob-derived [Present work]	10:10:338	2	94.4	>12	Mild temperature, high conversion, shorter reaction time, high stability.
3	Concentrated H_2SO_4[44]	10:10:353	2	95.4	NA	High conversion, Homogenous, very short reaction time.
4	Corncob-derived[44]	10:10:353	2	89.2	>8	High temperature, good conversion, shorter reaction time, high stability.

Table S2 (continued)

5	Bagasse-derived[29]	5:10:353	6	95.0	>8	High temperature, high conversion, long reaction time, high stability.
6	Amberlyst-15[29]	5:10:353	12	60.6	1	High temperature, Low conversion, long reaction time, very low stability.
7	Niobic acid[29]	5:10:353	12	13.7	1	High temperature, Very low conversion, very long reaction time, very low stability.
8	Kraft lignin[82]	5:12:353	5	96.1	-	High temperature, high conversion, short reaction time.
9	Glucose-derived[34]	5:10:353	6	94.8	-	High temperature, high conversion, long reaction time.

Table S2 (continued)

10	Starch-derived[34]	5:10:353	3	95.2	>50	High temperature, high conversion, very short reaction time, very high stability & reusability.
11	20%$H_3PW_{12}O_{40}$ /ZrO_2[80]	0.2:6:373	4	88	-	Very high temperature, good conversion, short reaction time.
12	30%SiW_{12}/Hβ[8]	0.2:20:333	10	86	-	Mild temperature, good conversion, very high reaction time.
13	TPA_3/Hβ[81]	0.2:20:333	6	84	-	Mild temperature, good conversion, high reaction time.

[a]Reaction conditions:- amount of catalyst (wt %): mole ratio of methanol to oleic acid: reaction temperature (K)

Table S3: Comparison of Present Catalyst (I-C-S-Corncob) Performance with Other Catalysts for Reduction of FFA

S. no.	catalyst	oil	acid value (mg KOH/g oil)	reaction conditions				conversion of FFA (%)	reference
				t	T	W	R		
1	corncob	Karanja	63.2	2	338	10	1:20	>90	[present]
2	coconut shell	Palm	not reported	6	333	6	1:30	88.95	[35]
3	concentrated H_2SO_4	Jatropha	16.1	1	333	10	1:60	>90	[16]

t= reaction time (h); T= reaction temperature (K); W= catalyst loading (wt %); R= oil to methanol molar ratio.