Supporting Information

Adsorptive Denitrogenation of Model Fuel with Silica Gel

Peipei Wang[a], Jian Liu[a], Difan Zhang[a], Daniel Chambers[b], Shuyun Li[a], Daniel Santosa[a]

[a]. Pacific Northwest National Laboratory, Richland, WA 99354, USA. *E-mail: daniel.santosa@pnnl.gov

[b]. Northeastern University, Boston, MA 02115, USA

1. Chemicals and Materials

Pyridine, Indole, Decane, and Methanol were all bought from Sigma Aldrich and used without further purification. The Zeolite Y and Zeolite Beta, both 12 x 30 mesh, were procured from Guild. Zeolite 4A in 4-8 mesh form was sourced from Sigma Aldrich. Activated carbon pellets were acquired from Calgon. Amberlyst 15, 16, 36 and 45, all with approximately 50 % moisture content (in H+ form), were obtained from Sigma Aldrich. Silica Gel S736-1 (grade 636, 35-60 mesh) and S745-1 (grade 645, 60-100 mesh) were purchased from Fisher Scientific. Prior to use, all adsorbents underwent a drying process in a 110 °C vacuum oven for two days and were subsequently stored in a desiccator. The jet fraction (150 °C-250 °C) obtained from the distillation of biocrude was collected and subjected to testing.

2. Characterization of NCC

GC-FID Samples were analyzed using an Agilent 6890GC equipped with a flame ionizing detector. The column was an Agilent HP-5MS 30m x 0.25mm x 0.25um film thickness with a carrier gas of helium at 1.0 mL/min. Oven temperature was initially held for 1 min at 40 °C, ramped at 10 °C/min to 180 °C, then ramped at 20 °C/min with a final temperature of 230 °C. The inlet was heated at 260 °C and 1uL of sample was injected using a 5:1 split. Trace N was analyzed on Elementar trace SN combustion analyzer. Nitrogen adsorption–desorption isotherms and pore structure were analyzed by N_2 physisorption at 77 K with an automatic gas sorption system: Quadrasorb EVO/SI Gas Sorption System from Quantachrome Instruments. NH_3-TPD measurements were carried out on a conventional flow-type apparatus with a TCD detector. The supported samples (about 100 mg) were added into a U-utilizes quartz tube reactor, blown out under 30 ml/min helium at 10 C/min heating rate until to 200 ℃, treated in the helium stream at 200 ℃ for 2 h.

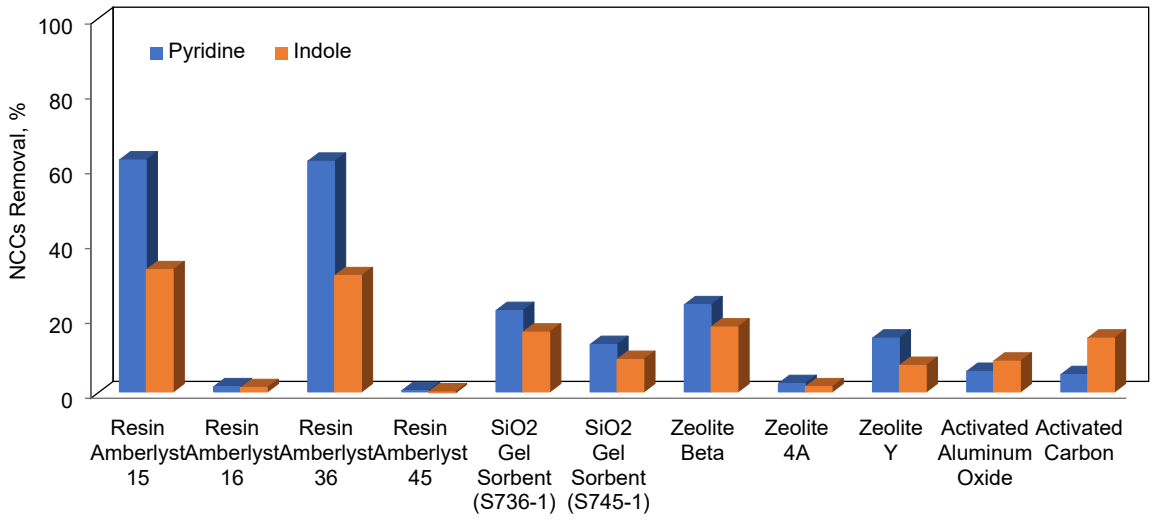
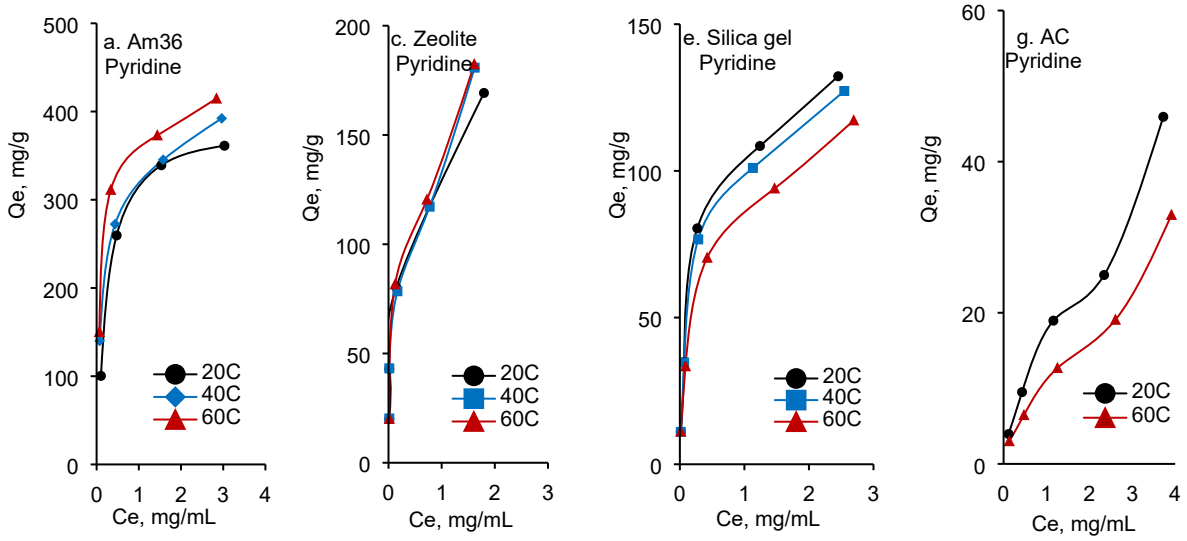


Figure S1. Sorbent screening with 1500 ppm N in Decane as mimic feed, 1000 ppm N from pyridine and 500 ppm N from Indole, fuel/adsorbent 100:1, 40 ℃, 24 h.



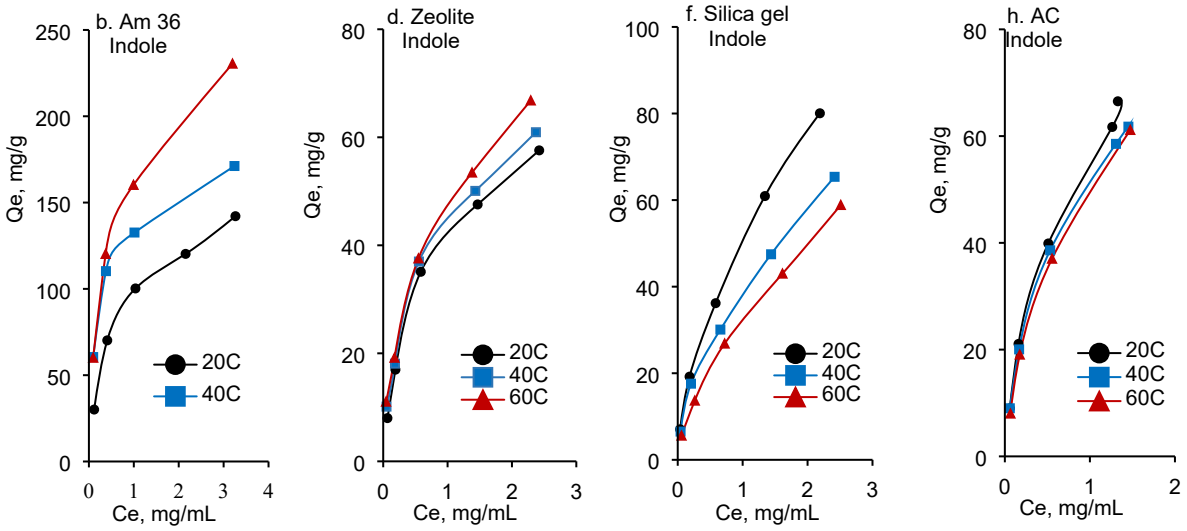


Figure S2. Equilibrium adsorption isotherms of Pyridine and Indole adsorption over Amberlyst 36 (a, b), Zeolite (c, d), Silica gel (e, f) and Activated Carbon (g, h).

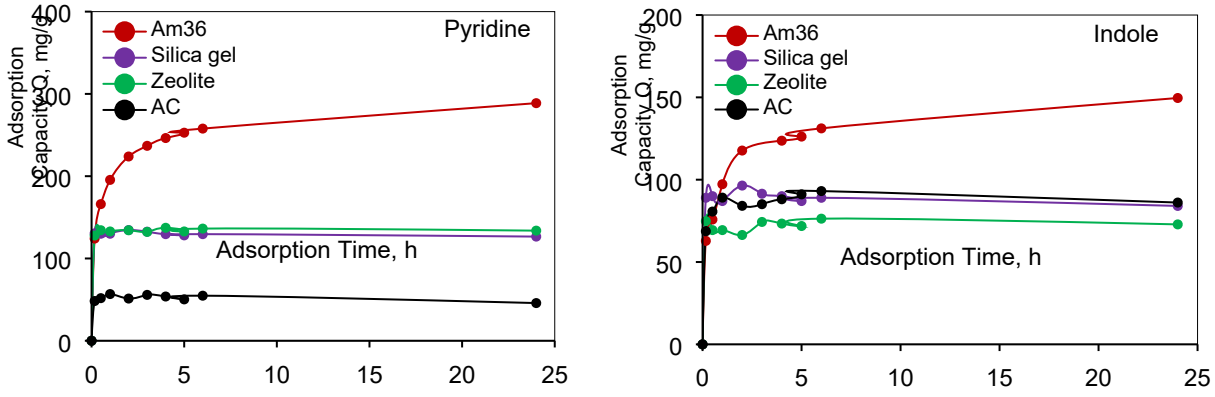


Figure S3. Effect of adsorption time on the adsorbed amounts of Pyridine and Indole. The initial concentration of pyridine and indole in mimic fuel was 1000 ppm N from pyridine, 500 ppm N from indole, Surrogate Fuel/Adsorbent = 50:1, 20 ℃.

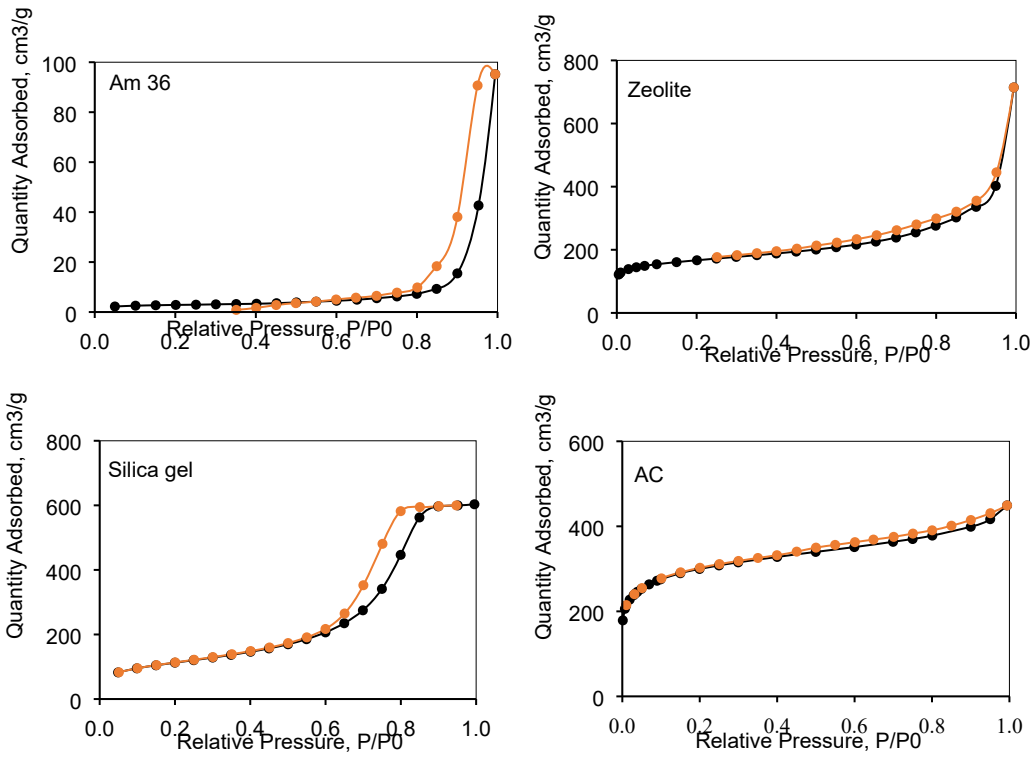


Figure S4. N_2 adsorption isotherms for Amberlyst 36, Zeolite, Silica gel and Activated carbon. Black curve represents adsorption, yellow curve represents desorption.

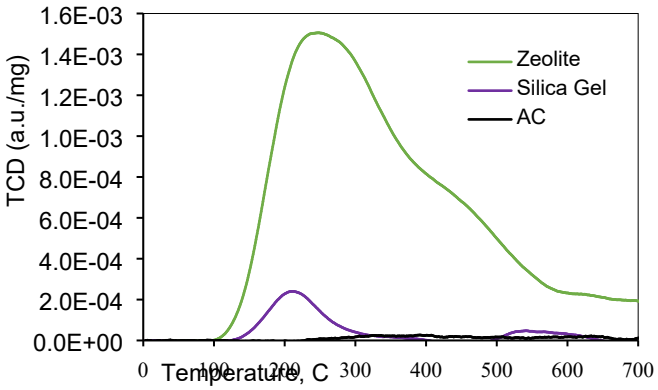


Figure S5. NH_3-TPD curves of Zeolite, silica gel and activated carbon.

Table S1.1 Kinetic fitting (Pyridine) for Silica gel

Kinetic Models	Parameters	Amberlyst 36	Silica gel	Zeolite Beta	Activated Carbon
Pseudo- first - order	K_1 (min^{-1})	0.08	0.12	0.21	0.14
	R^2	0.79	0.92	0.98	0.92
Pseudo-second-order	K_2 (g mg^{-1} min^{-1})	1×10^{-6}	9×10^{-6}	3×10^{-6}	2×10^{-6}
	R^2	0.86	0.98	0.99	0.84

Table S1.2 Kinetic fitting (Indole) for Silica gel

Kinetic Models	Parameters	Amberlyst 36	Silica gel	Zeolite Beta	Activated Carbon
Pseudo- first - order	K_1(min^{-1})	0.05	0.35	0.47	0.13
	R^2	0.79	0.66	0.85	0.94
Pseudo-second-order	K_2 (g mg^{-1} min^{-1})	1×10^{-5}	6×10^{-5}	2×10^{-5}	1×10^{-5}
	R^2	0.95	1.00	0.99	0.94

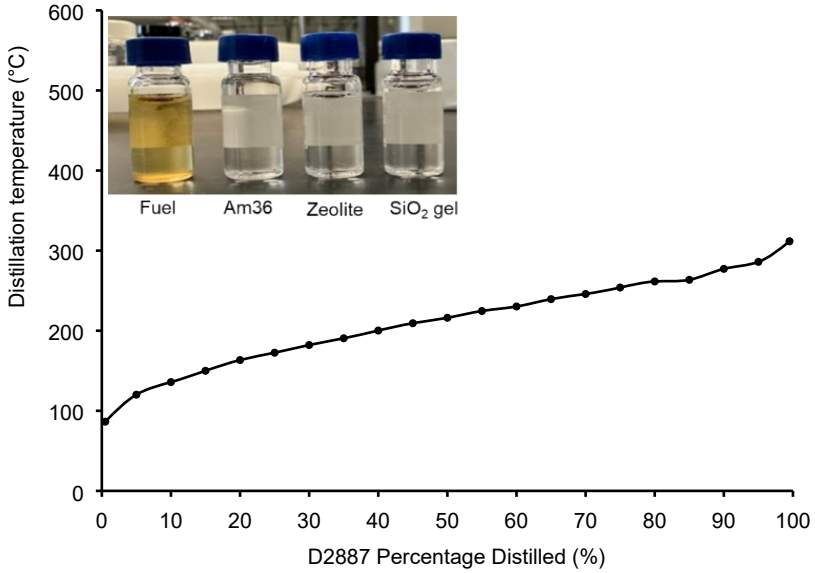


Figure S6. SAF property, inserted with photo of SAF treated with Am36, Zeolite, and Silica gel, SAF/adsorbent at 2:1 by weight, 20 ℃ 24 h.

Table S2. Property of the fuel fraction for adsorption test.

Fuel Fractions	Average N, ppm	Average S, ppm	Density, g/ml
SAF	336	237	0.784

Table S3. N and S concentration and removal after treatment with different adsorbents, surrogate fuel/adsorbent at 2/1, RT for 24 h.

Adsorbents	N after, ppm	N removal, %	S after, ppm	S removal, %
Am36	0.8	99.8	184	22.2
Zeolite	1.2	99.6	132	44.3
Silica gel	2.3	99.3	138	41.7
AC	69.4	79.3	107	54.8

Table S4. BET analysis results for Silica gel after post-calcination.

Calcine T, C	**BET, m^2/g**	**Pore Size, nm**	**Pore Volume, cm^3/g**
SiO_2-fresh	431.6	10.0	0.92
SiO_2-450	432.6	9.51	0.93
SiO_2-500	440.8	9.53	0.95
SiO_2-550	430.9	9.58	0.96
SiO_2-600	394.4	9.43	0.86

Table S5. BET analysis results for Silica gel after post-calcination for 5 cycles.

Calcine T, °C	**BET, m^2/g**	**Pore Size, nm**	**Pore Volume, cm^3/g**	**Pyridine Removal, %**	**Indole Removal, %**
SiO_2-fresh	431.6	10.0	0.92	98.44	81.77
SiO_2-450-1st	437.2	10.0	0.91	97.74	75.54
SiO_2-450-2nd	425.6	10.0	0.91	98.09	75.06
SiO_2-450-3rd	433.9	10.0	0.89	98.26	76.02
SiO_2-450-4th	428.4	9.50	0.89	97.57	71.70

Note: The adsorption process involved treating 1000 ppm N from pyridine and 500 ppm N from indole, with a fuel/adsorbent ratio of 10:1, at 40 °C for 24 h.