SUPPORTING INFORMATION

SYNTHESIS OF SULFUR-DOPED POROUS CARBON FROM HEAVY COKER GAS OIL AND ITS APPLICATION IN CO2 CAPTURE

Yi Du[*], Bradley Wooler, Stuart E. Smith, Brenda Raich,
Clarence E. Chase, Lesheng Wang, Chris Kliewer, and Kanmi Mao

ExxonMobil Research and Engineering

Experimental detail - synthesis:

SD-Carbon-1: Physically mix together 0.400g elemental sulfur and 0.800g heavy coker gas oil (HKGO) using a spatula. Heat the mixture without stirring and under nitrogen gas purge at 160°C, with a ramp rate of 5°C/min and a hold time of 6 hours, then cool to room temperature under nitrogen. This heating cycle was performed twice to give a total of 12 hours at 160°C under MCRT (micro carbon residue testing). Weigh the resulting tar-like product, then mix in a 1:1 weight equivalent of KOH powder using a spatula while applying low heat to reduce viscosity for easier mixing. Heat resulting mixture under nitrogen purge to 500°C, with a ramp rate of 5°C/min and a hold time of 2 hours. Heat again under nitrogen purge to 750°C, with a ramp rate of 3°C/min and a hold time of 2 hours, then cool to room temperature under nitrogen. Recover the solid product and wash thoroughly with water to remove excess KOH. Filter product and dry overnight in air at 100°C. The surface area of this sample is measured to be between 1714-1885 m^2/g. This sample is the sulfur-doped carbon used in gas sorption studies in main manuscript and in the supporting information, marked as **SD-Carbon-1** in the manuscript and this SI.

SD-Carbon-2: Physically mix together 0.400g elemental sulfur, 0.200g dicyclopentadiene (DCPD), and 1.200g HKGO using a spatula. Heat the mixture without stirring and under nitrogen gas purge at 160°C, with a ramp rate of 5°C/min and a hold time of 6 hours, then cool to room temperature under nitrogen under MCRT (micro carbon residue testing). This heating cycle was performed twice to give a total of 12 hours at 160°C. Weigh the resulting tar-like product, then mix in a 1:1 weight equivalent of KOH powder using a spatula while applying low heat to reduce viscosity for easier mixing. Heat resulting mixture under nitrogen purge to 500°C, with a ramp rate of 5°C/min and a hold time of 2 hours. Heat again under nitrogen purge to 750°C, with a ramp rate of 3°C/min and a hold

time of 2 hours, then cool to room temperature under nitrogen. Recover the solid product and wash thoroughly with water to remove excess KOH. Filter product and dry overnight in air at 100°C.

SD-Carbon-3: Physically mix together 0.400g elemental sulfur, 0.200g DCPD, and 0.600g HKGO using a spatula. Heat the mixture without stirring and under nitrogen gas purge at 160°C, with a ramp rate of 5°C/min and a hold time of 6 hours, then cool to room temperature under nitrogen under MCRT (micro carbon residue testing). This heating cycle was performed twice to give a total of 12 hours at 160°C. Weigh the resulting tar-like product, then mix in a 1:1 weight equivalent of KOH powder using a spatula while applying low heat to reduce viscosity for easier mixing. Heat resulting mixture under nitrogen purge to 500°C, with a ramp rate of 5°C/min and a hold time of 2 hours. Heat again under nitrogen purge to 750°C, with a ramp rate of 3°C/min and a hold time of 2 hours, then cool to room temperature under nitrogen. Recover the solid product and wash thoroughly with water to remove excess KOH. Filter product and dry overnight in air at 100°C.

SD-Carbon-4: Physically mix together 0.400g elemental sulfur and 0.800g steam cracker tar (SCT) using a spatula. Heat the mixture without stirring and under nitrogen gas purge at 160°C, with a ramp rate of 5°C/min and a hold time of 6 hours, then cool to room temperature under nitrogen under MCRT (micro carbon residue testing). This heating cycle was performed twice to give a total of 12 hours at 160°C. Weigh the resulting tar-like product, then mix in a 1:1 weight equivalent of KOH powder using a spatula while applying low heat to reduce viscosity for easier mixing. Heat resulting mixture under nitrogen purge to 500°C, with a ramp rate of 5°C/min and a hold time of 2 hours. Heat again under nitrogen purge to 750°C, with a ramp rate of 3°C/min and a hold time of 2 hours, then cool to room temperature under nitrogen. Recover the solid product and wash thoroughly with water to remove excess KOH. Filter product and dry overnight in air at 100°C.

Experimental detail - characterization:

NMR: ^{13}C MAS NMR spectra were recorded on an 9.4 T Varian Infinity Plus 400 spectrometer corresponding to Larmor frequencies of 100 MHz, with ^1H decoupling and a pulse delay of 30 seconds. The samples were loaded in a 3.2 mm (o.d.) MAS rotor spinning at 14 kHz. ^1H NMR spectra were recorded at 11.7 T Varian 500 spectrometer corresponding to Larmor frequencies of 500 MHz. Samples were dissolved as 5-15% w/w solution in $CDCl_3$. ^1H chemical shifts are referenced with respect to internal TMS with chemical shift of 0 ppm.

GPC: Instrument: Waters Alliance 2690 with 2410 Refractive Index (RI) Detector and 2998 Photodiode Array Detector (190 - 800 nm). Test Conditions: Solvent (THF), Column Set (2 x Agilent PLgel Mixed D), Flow Rate (0.5 ml/min), Injection Volume (50 ul), Detector

Temp (~ 23 C), Column Temp (~23 C). Process Method: Conventional Calibration based on RI detector signals with Polystyrene standards from Agilent Technologies.

Sorption: All samples were degassed to get rid of any contaminants adsorbed on the surface by evacuating it to 10^{-5} torr dynamic vacuum and simultaneously heating to 120°C for 16 hours in Autosorb-1-C Analyzer of Quantachrome Instruments. A 77 K nitrogen isotherm was then performed on this sample from 0 to 1 atm (1 atm = P0). The Brunauer, Emmett and Teller (BET) model was applied to 5 points of the isotherm for P/P0 between 0.01 to 0.1. CO_2, N_2, H_2 sorption study were then carried out at corresponding temperatures from 0 to 1atm.

Heat of adsorption calculation[1]: Heat of adsorption (Qst) for SD Carbon-1 can be calculated from its CO2 sorption isotherms collected at different temperatures (298K, 303K and 313K) using Clausius-Clapeyron equation Qst=R dlnP/ d(1/T). In order to do so, a plot of lnP against 1/T at constant loading needs to be constructed based on adsorption isotherms. The slope of that lnP vs 1/T plot will be Qst. By examine a few loadings, we can get a trend of Qst as a function of loading (Figure S1b), which indicated it levels to 20 kJ/mol for SD Carbon -1. We applied similar calculation for SD Carbon -2, -3, and -4, and obtained heat of adsorption 20kJ/mol, 19 kJ/mol, and 22kJ/mol, respectively.
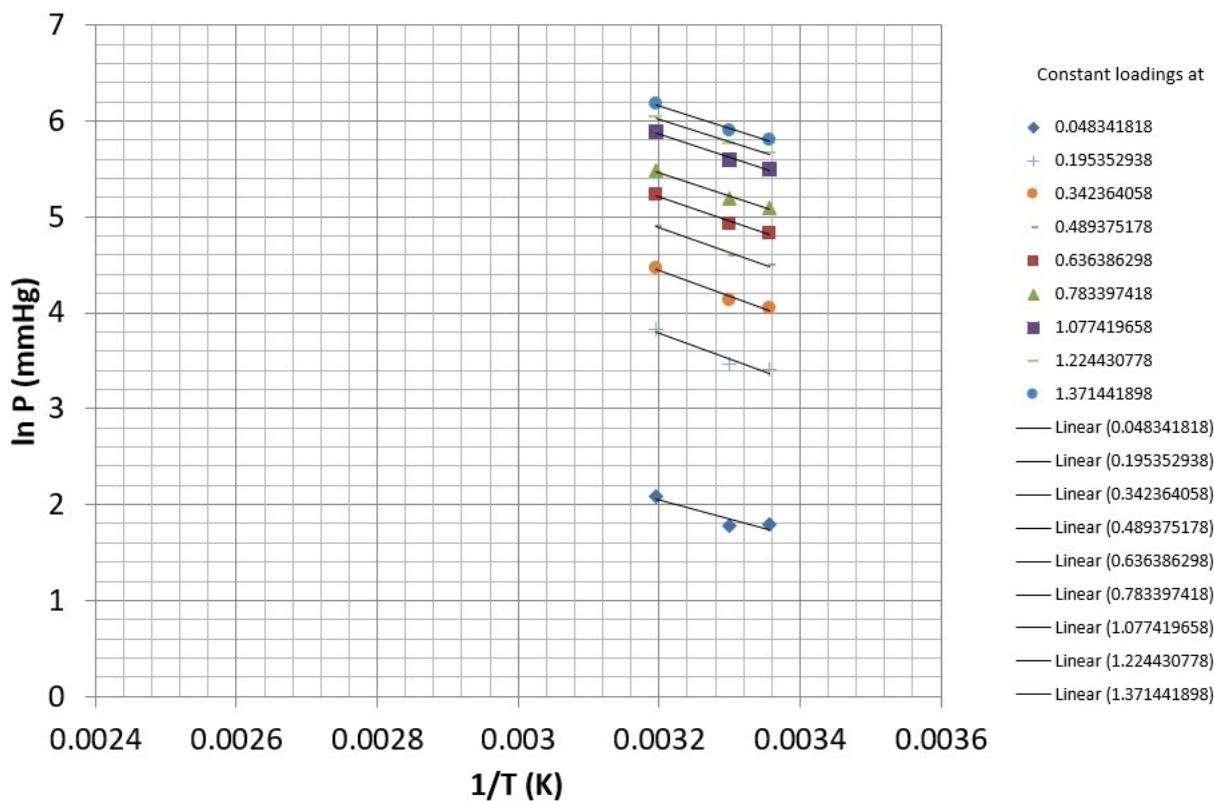
For SD Carbon -1, as an example, first step is to plot adsorption isotherm and fit the data. Choose a loading that can intercept real data at all measured temperatures across the loading levels to form a table below.

T	1/T (K)	loadings at 0.048342 P (mm Hg)	0.195353 P (mm Hg)	0.342364 P (mm Hg)	0.489375 P (mm Hg)	0.636386 P (mm Hg)	0.783397 P (mm Hg)	0.930409 P (mm Hg)	1.07742 P (mm Hg)	1.224431 P (mm Hg)	1.371442 P (mm Hg)
298	0.003356	6.01249	30.10983	57.73707	90.06567	125.7744	163.4811	203.0434	244.9514	288.0747	333.1696
303	0.0033	5.891828	31.84609	62.2233	98.16741	137.3712	179.1953	222.9796	268.6658	316.8793	367.3759
313	0.003195	8.008421	45.59961	87.1495	134.9817	186.7267	239.4022	298.0319	359.4054	419.307	480.995

Next is to plot the lnP vs 1/T at each constant loading, and by applying linear fitting for each data, the slope is the Qst.

[1] Y. Wang, *Ind. Eng. Chem. Res.,* 2020, **59 (17),** 8304-8314

Isostere

Constant loadings at
- 0.048341818
- 0.195352938
- 0.342364058
- 0.489375178
- 0.636386298
- 0.783397418
- 1.077419658
- 1.224430778
- 1.371441898
- Linear (0.048341818)
- Linear (0.195352938)
- Linear (0.342364058)
- Linear (0.489375178)
- Linear (0.636386298)
- Linear (0.783397418)
- Linear (1.077419658)
- Linear (1.224430778)
- Linear (1.371441898)

We can then extract the slope of each fitting and plot that against loading to form the heat of adsorption data as a function of loading. The slope*R/1000 is Qst in unit of kJ/mol. Figure is shown in Figure S1b.

MCRT: Microcarbon residue testing

MCRT heat treatment at 160 ºC:

　　　　The HKGO/sulfur blend is prepared in the desired ratio, and placed in a glass vial (~ 2 g). A PAC Micro Carbon Residue Tester is used to heat treat the sample. The sample is heated to 100 ºC using a 5 ºC/min ramp rate under a flow of nitrogen (600 mL/min). Immediately following 100 ºC, the nitrogen flow rate is decreased to 150 mL/min, and heating to 160 ºC is continued at the 5 ºC/min ramp rate. The sample is held at 160 ºC for 6 h with a continuous nitrogen flow of 150 mL/min. After this heat soak, the sample is cooled to ambient temperature under nitrogen at a 600 mL/min flow rate over the course of about an hour. This heat treating protocol is repeated two more times to ultimately yield the 18 h heat treated sample.

MCRT heat treatment at 500 ºC:

The heat treated HKGO/sulfur sampled is blended with KOH in the desired ratio, and placed in a glass vial (~ 2 g). A PAC Micro Carbon Residue Tester is used to heat treat the sample. The sample is heated to 100 °C using a 5 °C/min ramp rate under a flow of nitrogen (600 mL/min). Immediately following 100 °C, the nitrogen flow rate is decreased to 150 mL/min, and heating to 500 °C is continued at the 5 °C/min ramp rate. The sample is held at 500 °C for 2 h with a continuous nitrogen flow of 150 mL/min. After this heat soak, the sample is cooled to ambient temperature under nitrogen at a 600 mL/min flow rate over the course of 3–4 h.
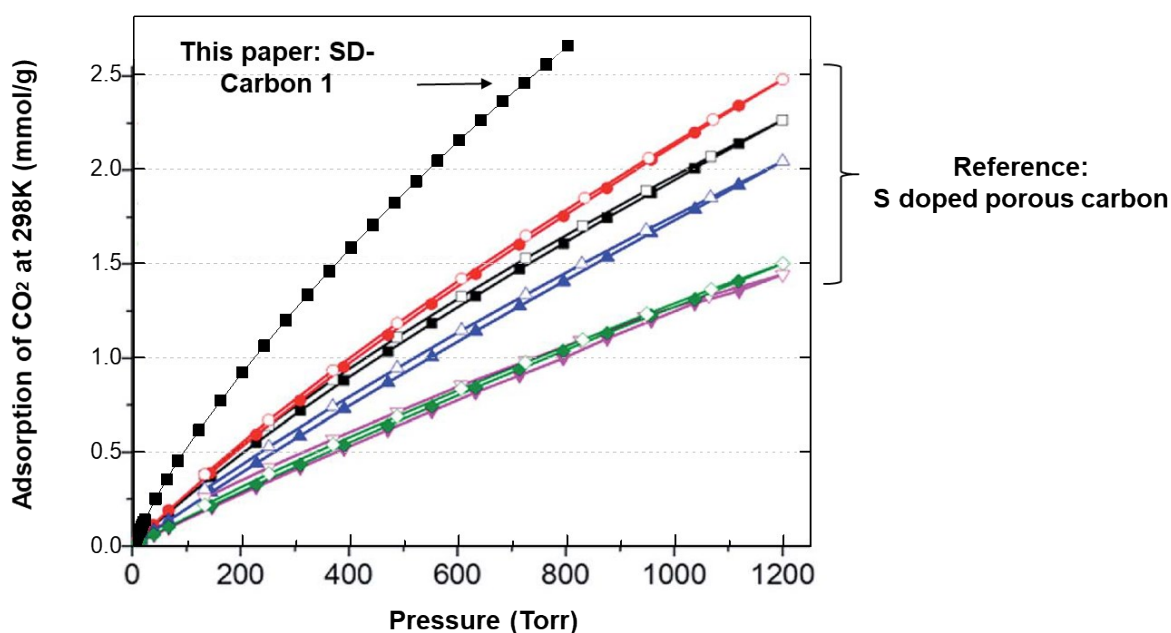
Figure S1a: Comparison of SD-Carbon-1 to Hasell's published results in ref 1[2]. Our sorption capacity is at 2.6 mmol/g (1714 m^2/g) vs. ~ 1.9 mmol/g (2216 m^2/g) for Hasell's carbon. If we calculate the sorption per s.a. our material is 15.2 X 10^{-4} mmol/m^2 vs. Hasell's is at 8.5 X 10^{-4} mmol/m^2, confirming a 78% increase per m^2 surface area.

1   [2].S. Lee, D.J. Parker, A. I. Cooper, T. Hasell, *J. Mater. Chem. A*, 2017,**5**, 18603
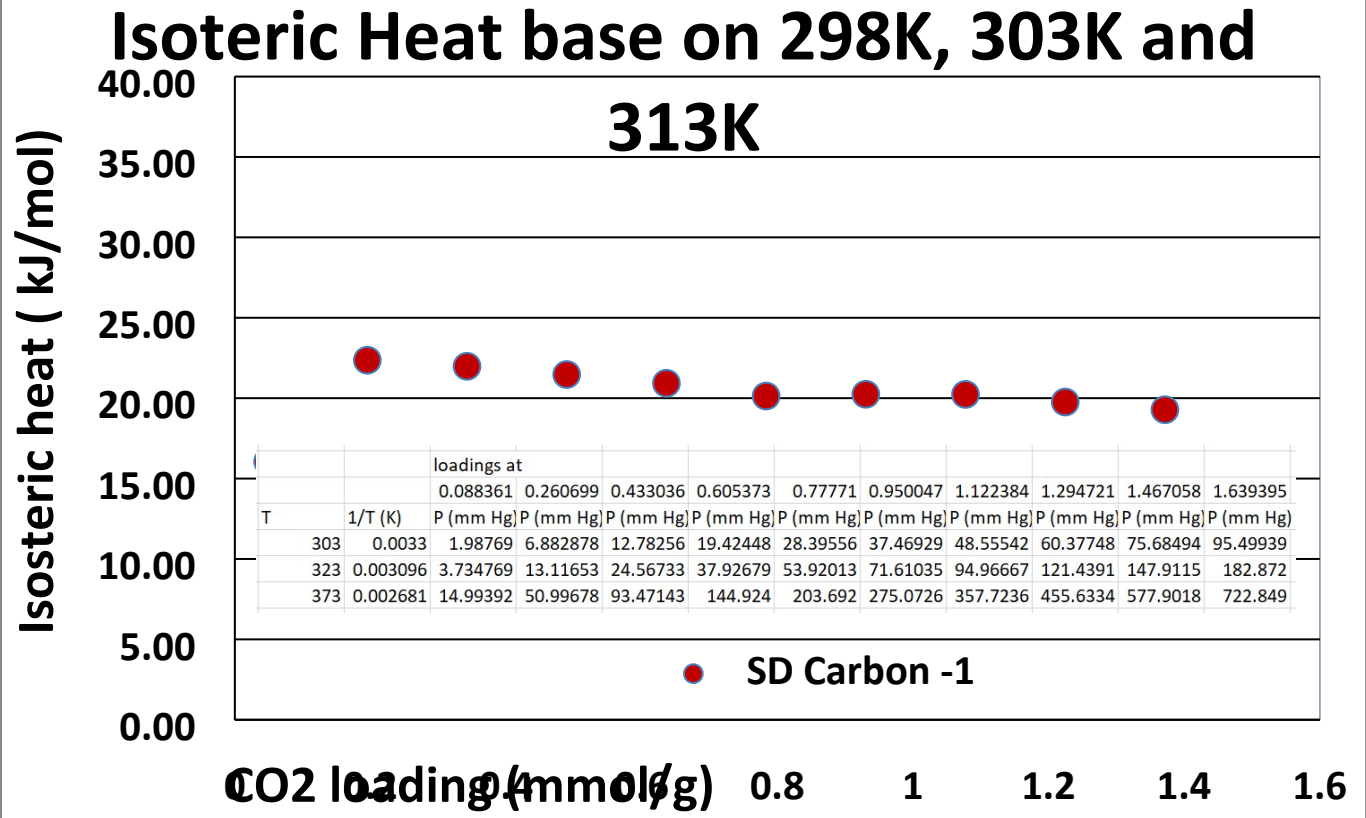
Isoteric Heat base on 298K, 303K and 313K

Isoteric heat (kJ/mol)

	loadings at									
		0.088361	0.260699	0.433036	0.605373	0.77771	0.950047	1.122384	1.294721	1.467058	1.639395
T	1/T (K)	P (mm Hg)	P (mm Hg)	P (mm Hg)	P (mm Hg)	P (mm Hg)	P (mm Hg)	P (mm Hg)	P (mm Hg)	P (mm Hg)	P (mm Hg)
303	0.0033	1.98769	6.882878	12.78256	19.42448	28.39556	37.46929	48.55542	60.37748	75.68494	95.49939
323	0.003096	3.734769	13.11653	24.56733	37.92679	53.92013	71.61035	94.96667	121.4391	147.9115	182.872
373	0.002681	14.99392	50.99678	93.47143	144.924	203.692	275.0726	357.7236	455.6334	577.9018	722.849

● SD Carbon -1

CO2 loading (mmol/g)

x-axis values: 0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.4, 1.6

y-axis values: 0.00, 5.00, 10.00, 15.00, 20.00, 25.00, 30.00, 35.00, 40.00

Figure S1b: Heat of adsorption based on CO_2 isotherms obtained at 298K, 303K and 313K, as illustrated in Figure 1 in the main manuscript. Heat of adsorption is calculated to be 20kj/mol. The pressure obtained at constant loading at the three temperature were obtained from intercepts on fitted CO_2 isotherms to provide accuracy. Slope of each lnP vs 1/T is obtained at each loading and further used to construct Figure S1b. Details of calculation and theory can be referred to ref 1 in SI.
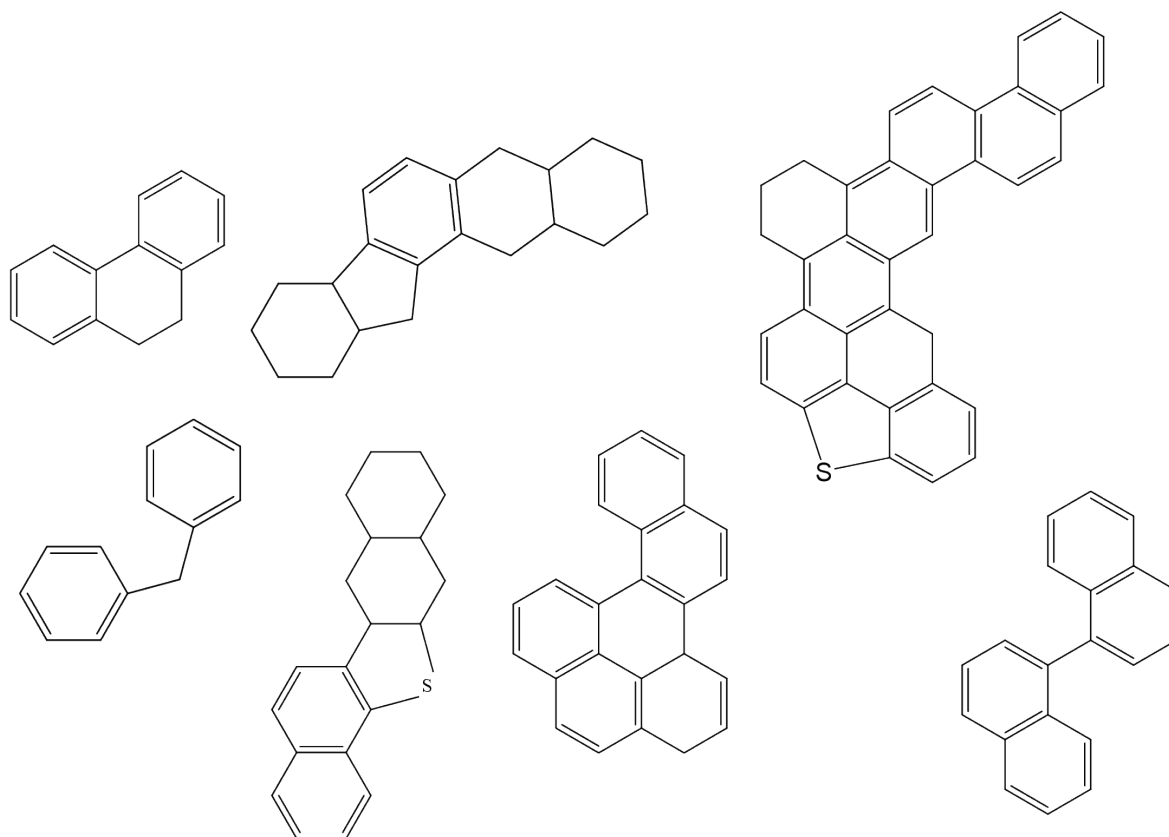
Figure S2: Representative model compound in heavy coker gas oil (HKGO). This is based on distillation and high resolution GC-MS study of representative feedstock to ensure accuracy of C to H ratio, 1 ring, 2 ring or 3+ ring aromatic content, details of which will not be disclosed in this manuscript. Use this plot to explain in heavy coker gas oil, it was not expected the crosslink chemistry will occur especially when NMR in main manuscript do not support change of aromaticity. This is in contrast to the steamed cracked tar (SCT) in Figure S17, S18 where an apparently loss of aliphatic chains was seen.

(a) SD-Carbon 1 (also in main manuscript)
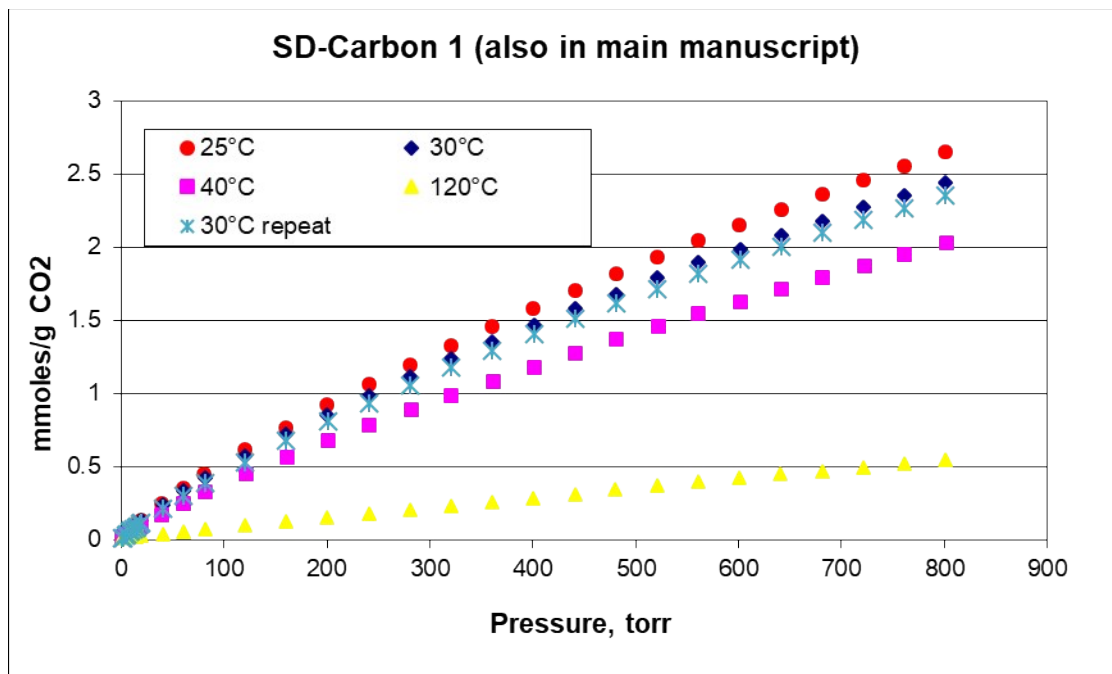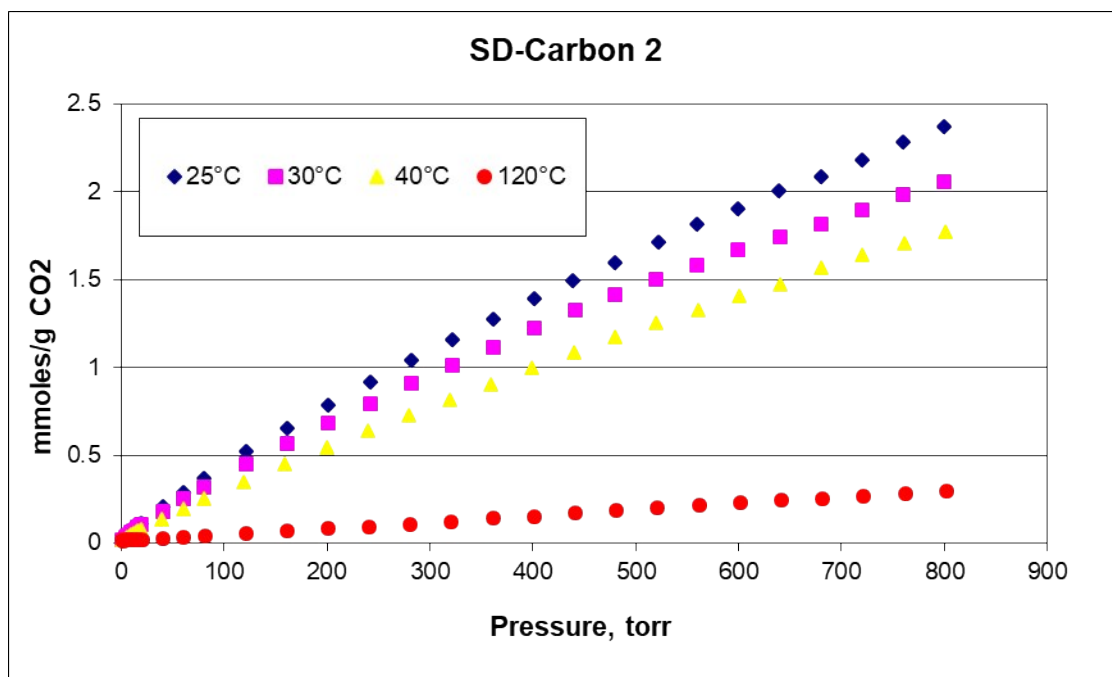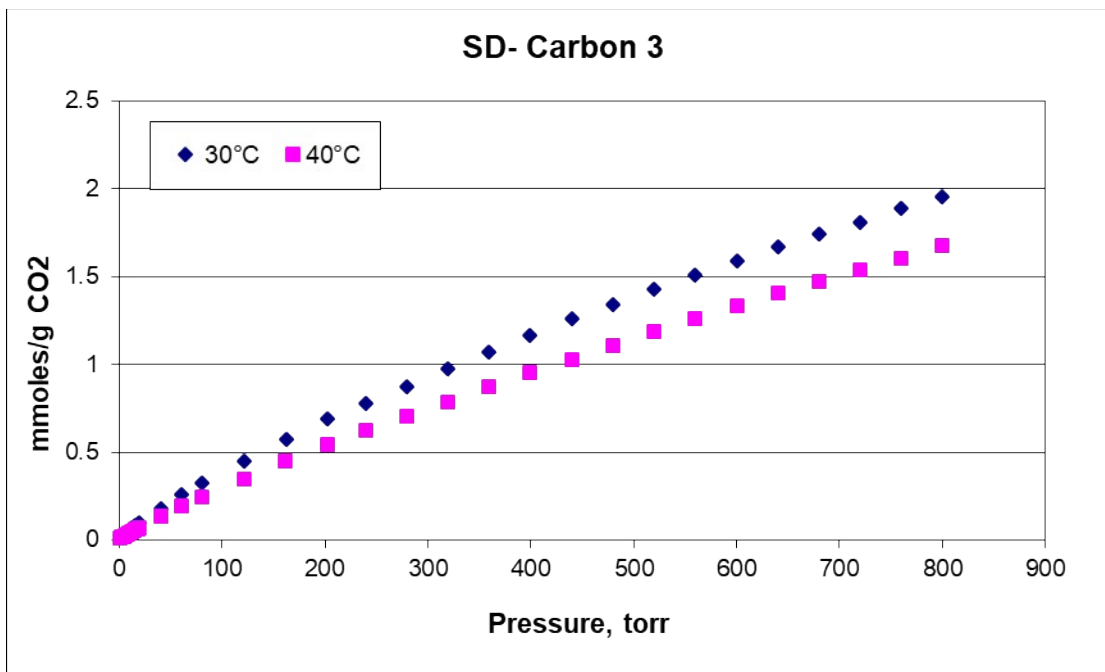
(b) SD-Carbon 2

(c)
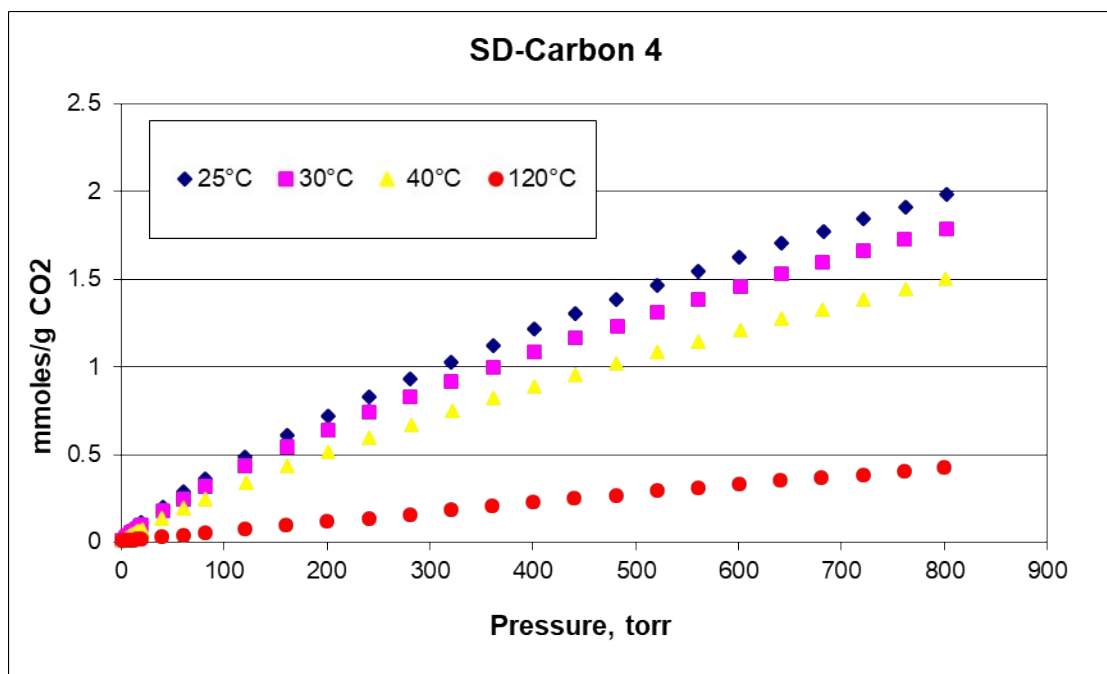
(d)

Figure S3: CO_2 adsorption isotherms at various temperature for sample (a) SD-Carbon 1, (b) SD-Carbon 2, (c) SD-Carbon 3, and (d) SD-Carbon 4. CO2 adsorption isotherms reflect the equilibrium adsorption at 2.44mmol/g, 2.05 mmol/g, 1.95mmol/g, and 1.79 mmol/g at 30 ^{o}C, respectively. SD – Carbon 1 has an isosteric heat of adsorption at 22.3 kJ/mol at low loading and close to 19.8 kJ/mol at high loading. SD – Carbon 2 has an isosteric heat of adsorption at 24.6 kJ/mol at low loading and close to 20.1 kJ/mol at high loading. SD – Carbon 3 has an isosteric heat of adsorption at
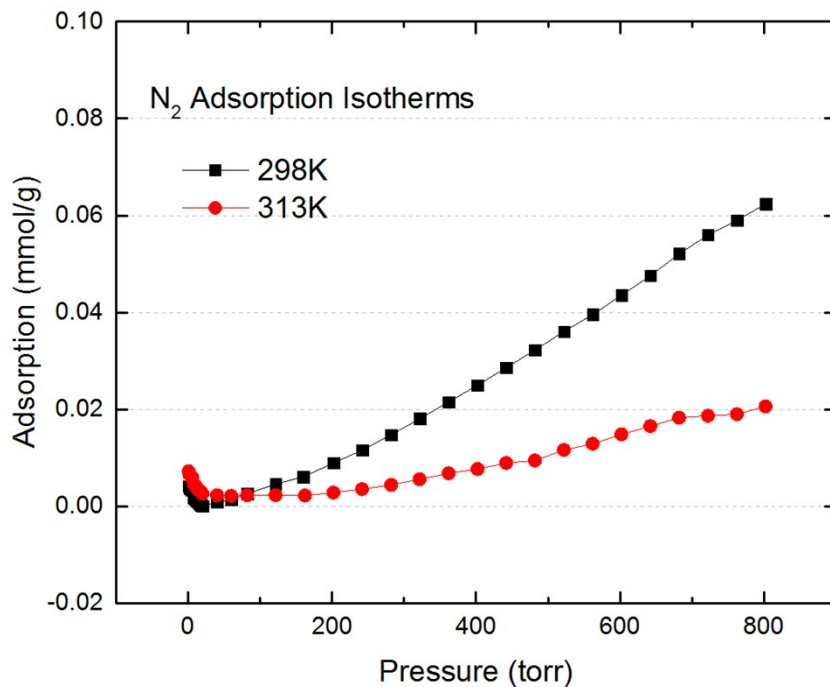
26.6 kJ/mol at low loading and close to 19.4 kJ/mol at high loading. SD – Carbon 4 has an isosteric heat of adsorption at 25.1 kJ/mol at low loading and close to 21.4 kJ/mol at high loading.

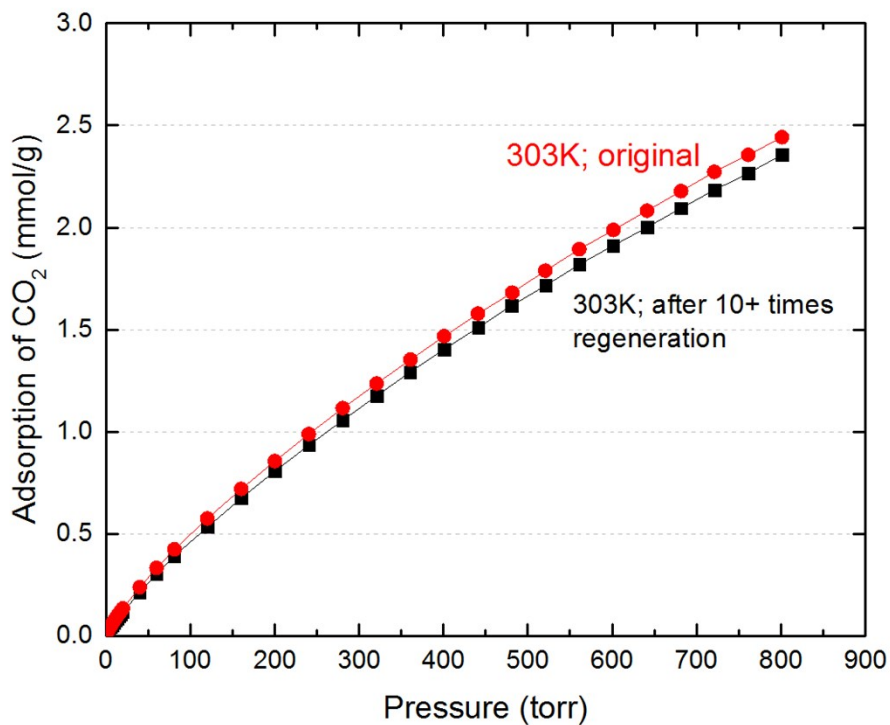**Figure S4:** N_2 adsorption isotherms of SD-Carbon 1.

Figure S5: CO_2 adsorption isotherm before and after 10 regenerations for SD-Carbon-1. This indicated a good regenerabilty of the materials without degradation of performance.
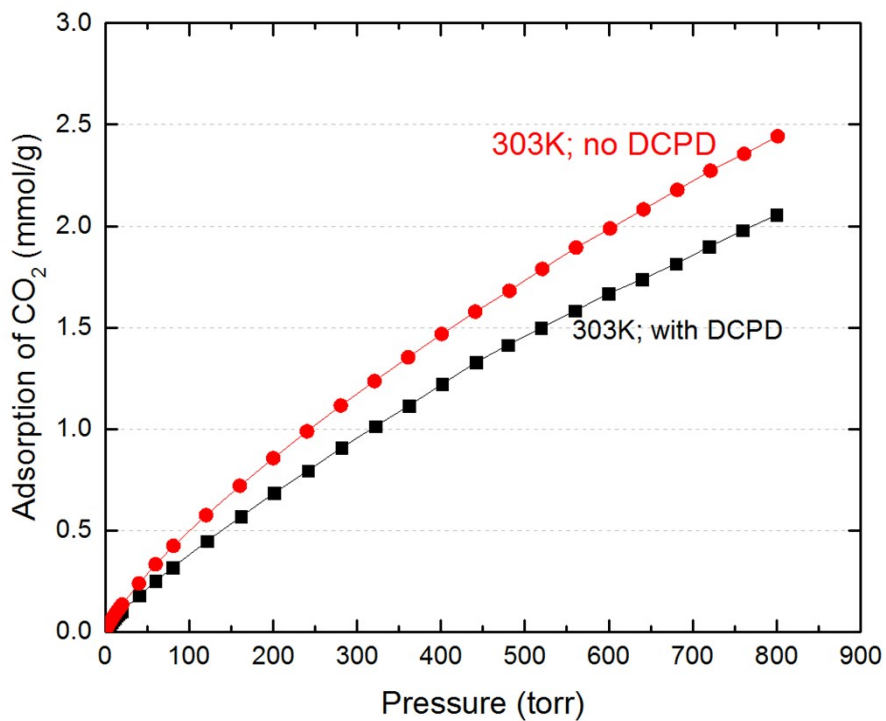
Figure S6: CO_2 isotherm of SD-Carbon-1 (without DCPD), and SD-Carbon-2 (with DCPD). This reveals presence of DCPD in our synthesis condition did not provide any positive outcome.
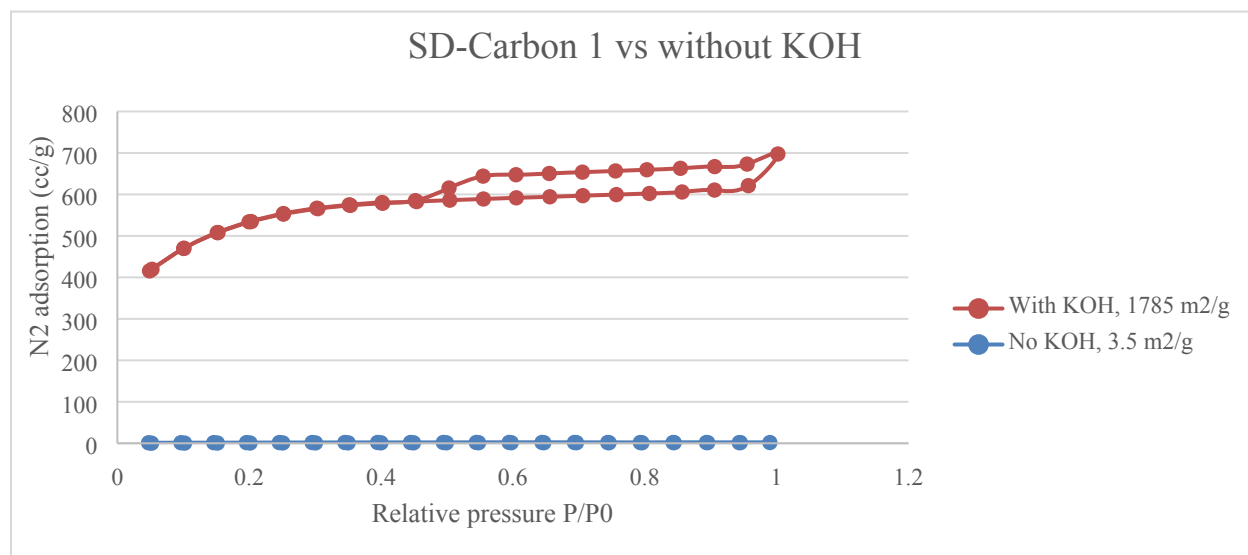

SD-Carbon 1 vs without KOH

- With KOH, 1785 m2/g
- No KOH, 3.5 m2/g

Figure S7: N_2 adsorption data at 77K for SD-Carbon 1 with or with KOH. (Raw data for BET surface area analysis).

Impact of Sulfur content

- SD-Carbon 1, 1785m2/g
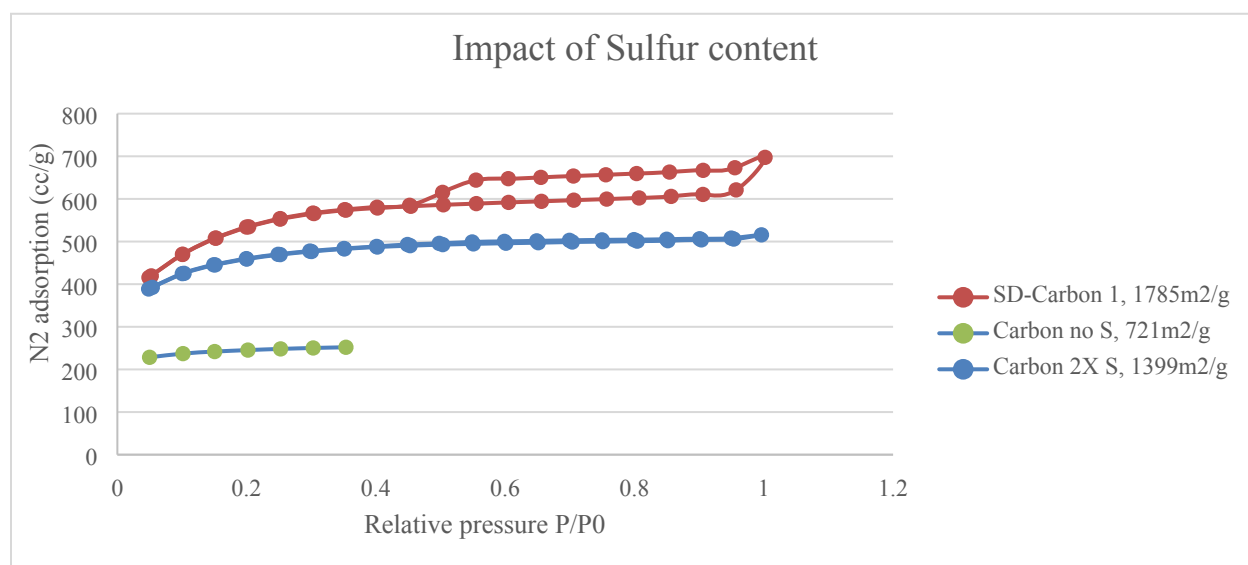- Carbon no S, 721m2/g
- Carbon 2X S, 1399m2/g

Figure S8: N_2 adsorption data at 77K for SD-Carbon 1 with extra or without S. (Raw data for BET surface area analysis).
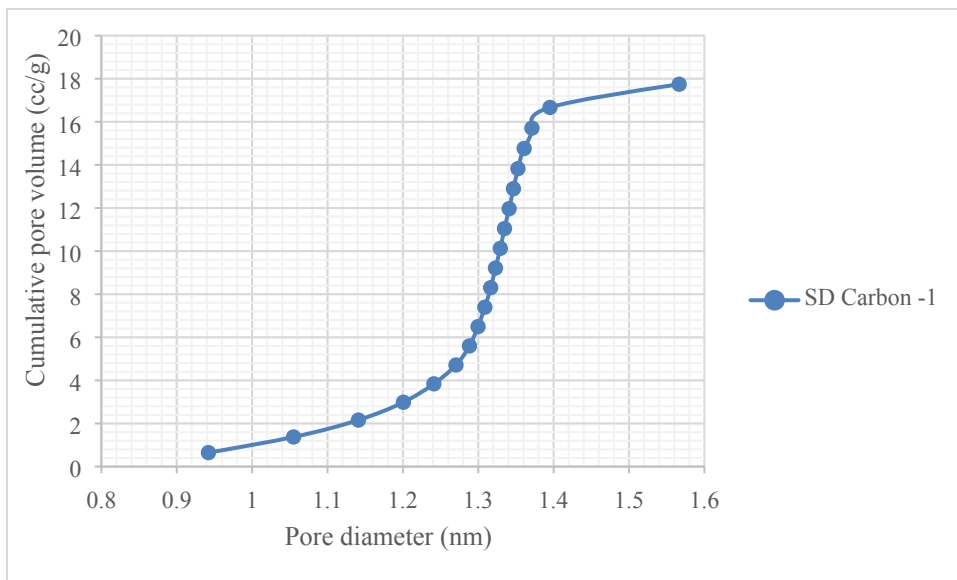
Figure S9: N_2 adsorption data at 77K for SD-Carbon 1 derived cumulative pore volume with pore diameter plot.
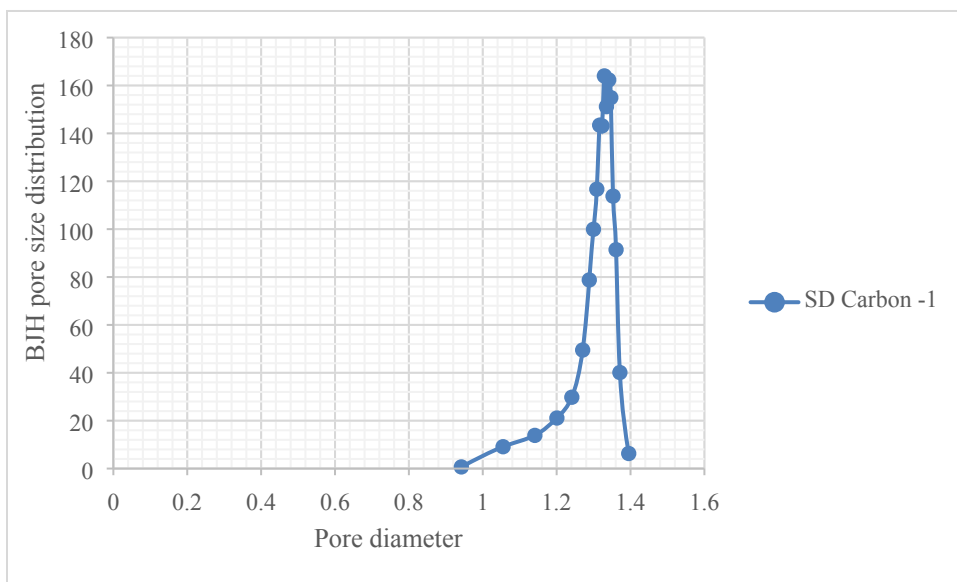

Figure S10: N_2 adsorption data at 77K for SD-Carbon 1 derived pore size distribution as a function of pore diameter plot. This indicated the mesoporosity natured of SD-Carbon 1.
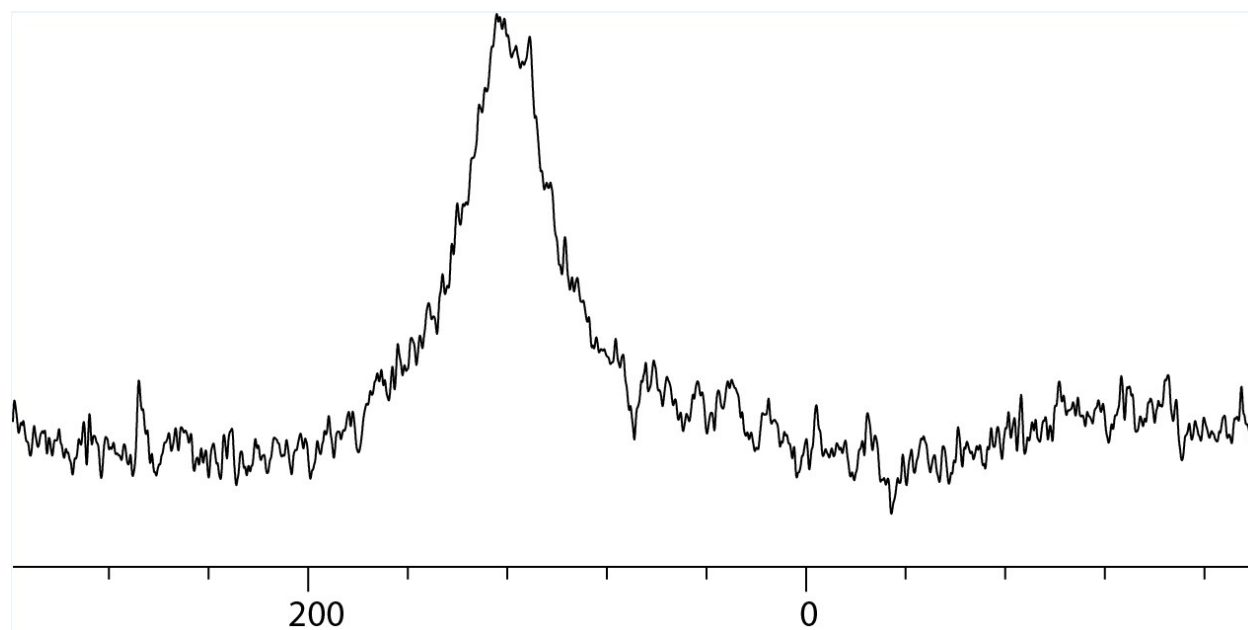
Figure S11: ^{13}C NMR of the sulfur-doped porous carbon product as SD-Carbon-1. The broad feature of ^{13}C NMR proving the graphitic nature of the carbon.
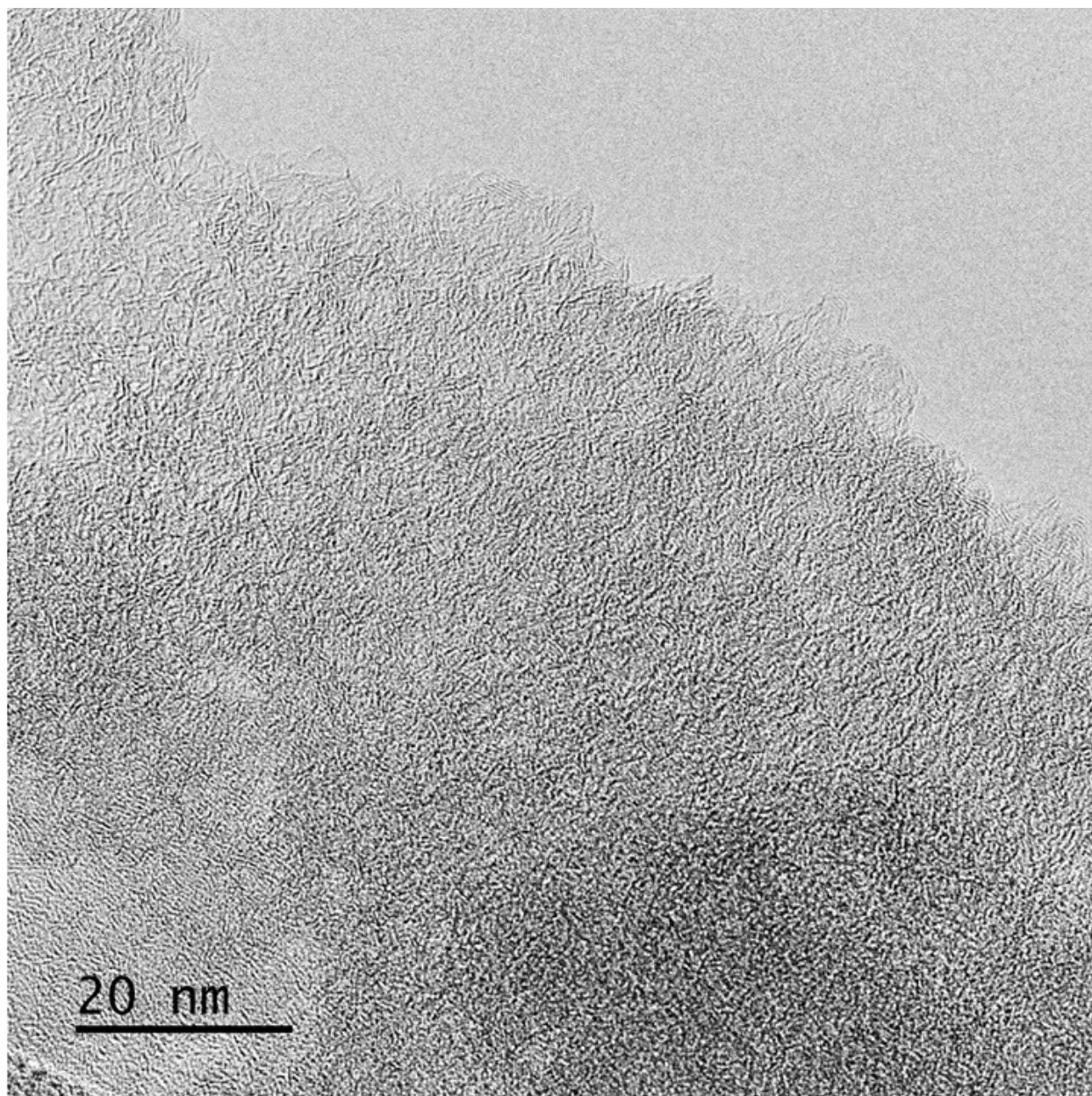
Figure S12: TEM images of the sulfur doped porous carbon, revealing its graphic nature. There is also no ordered microporosity observed throughout the TEM measurement.

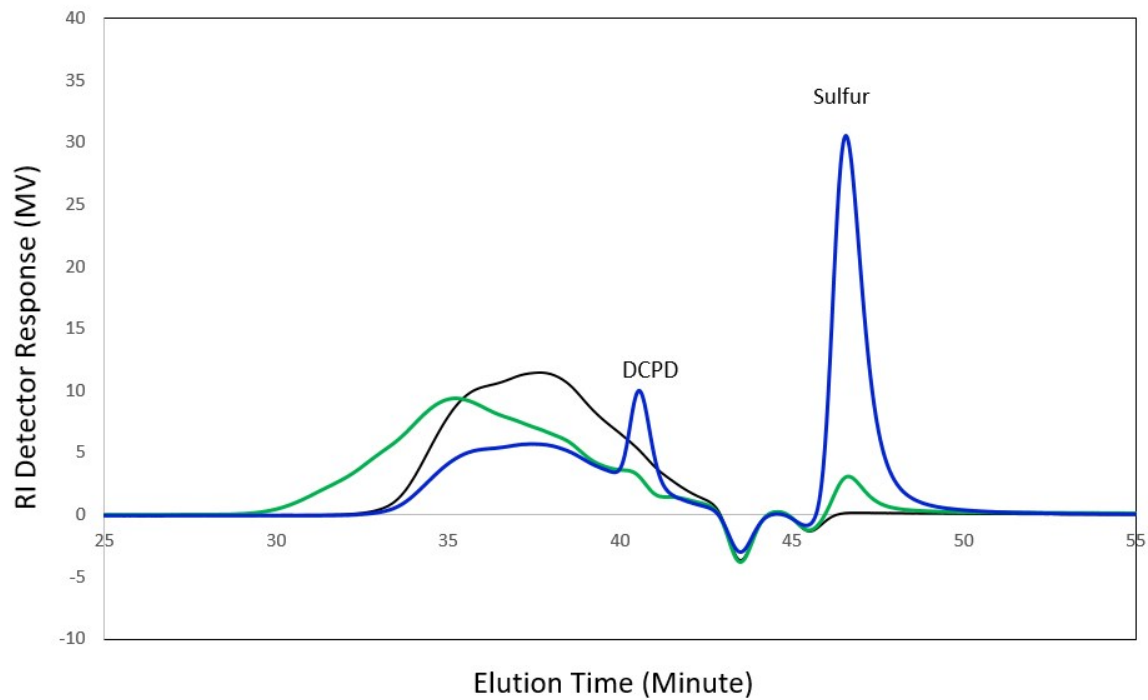**Figure S13:** GPC overlay plot of RI (refractive index) detector for HKGO, precursors of SD-Carbon-2, and crosslinked products of SD-Carbon-2.
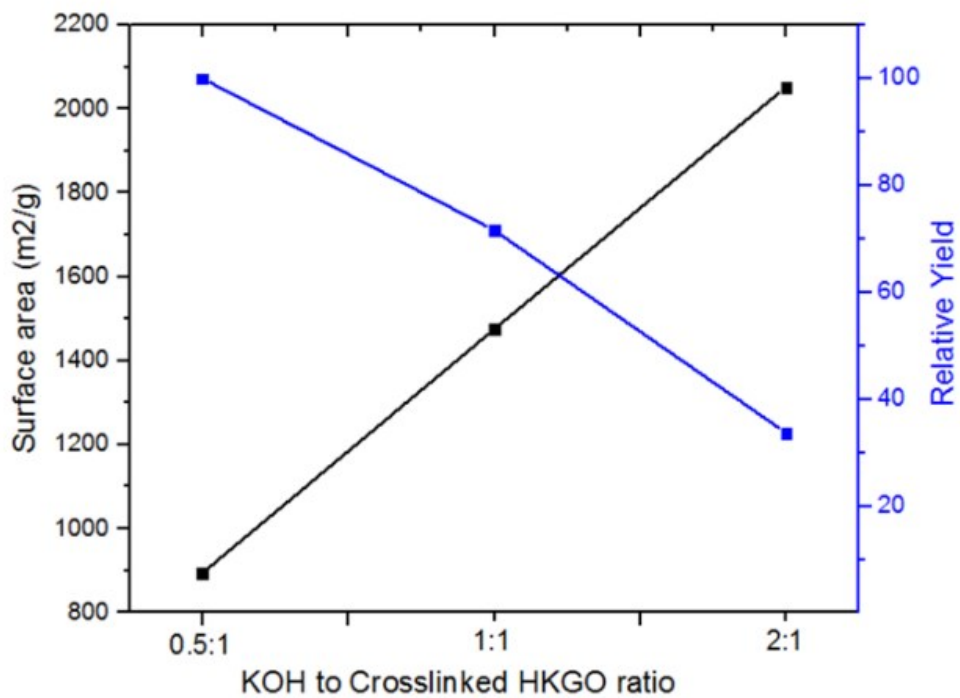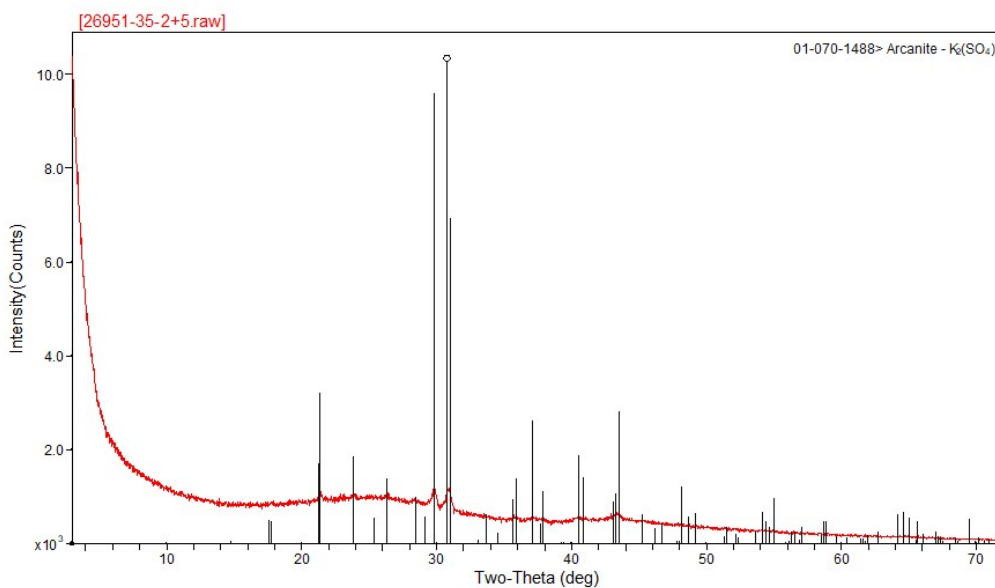
Figure S14. KOH impact on yield and porous carbon's surface area.

(a)
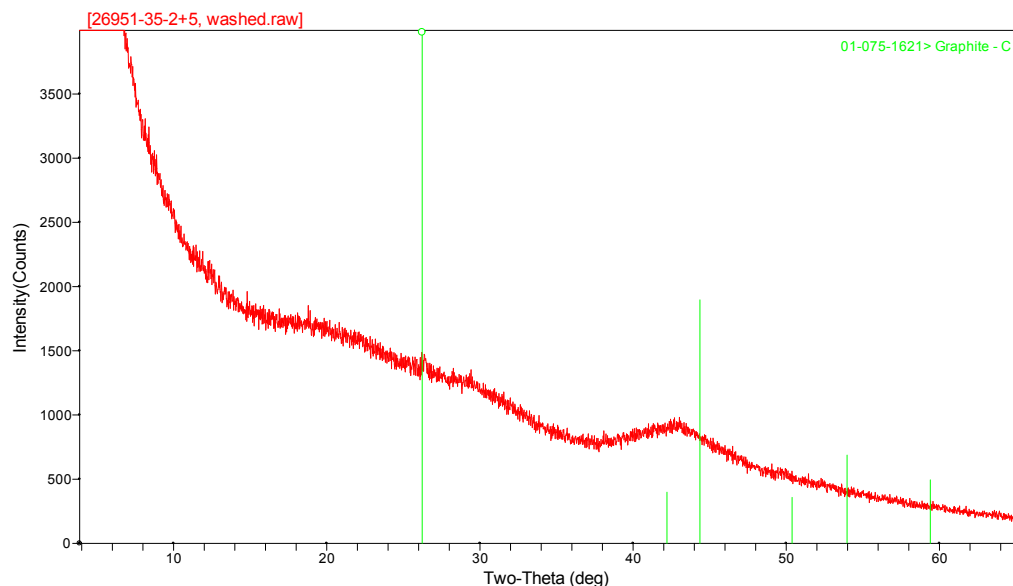
(b)

Figure S15: XRD of (a) gentle washed sulfur doped carbon revealing a trace amount of K2SO4 (b) further wash can generate pure graphite like carbon without any K impurity. The formation of K2SO4 indicate the oxidation of sulfur containing compounds during carbonization. Given the process occurs in inert N2 atmosphere, CO_2 or CO_3^{2-} are speculated to be reduced to carbon, to balance the electrons, with equations written as $4KOH + S + CH_2- \rightarrow K_2SO_4 + 3H_2 + 2K + C$ (in main manuscript also).

Figure S16: ^{1}H NMR for SCT (steam cracker tar), SCT with sulfur before heating, and after heating, as reaction precursors to SD-Carbon-4. Olefin H decrease from 0.17wt% to 0 after heating/crosslink chemistry at 160C/18hr.

Figure S17: ^{13}C NMR Aliphatic region for SCT (steam cracker tar), SCT with sulfur before heating, and after heating, as reaction precursors to SD-Carbon-4. The heating process changes structure/composition of SCT. After heating, SCT becomes heavier, less aliphatics. Very few sharp peaks of heated sample, indicates molecules are less soluble, and becomes bigger molecules

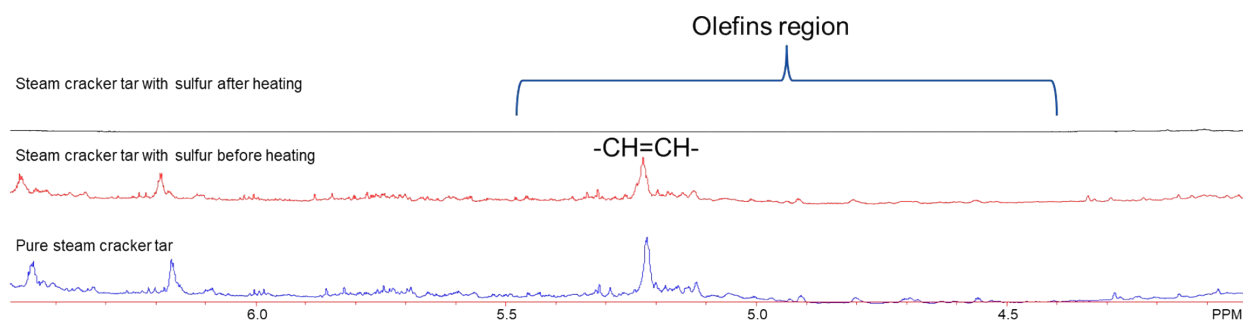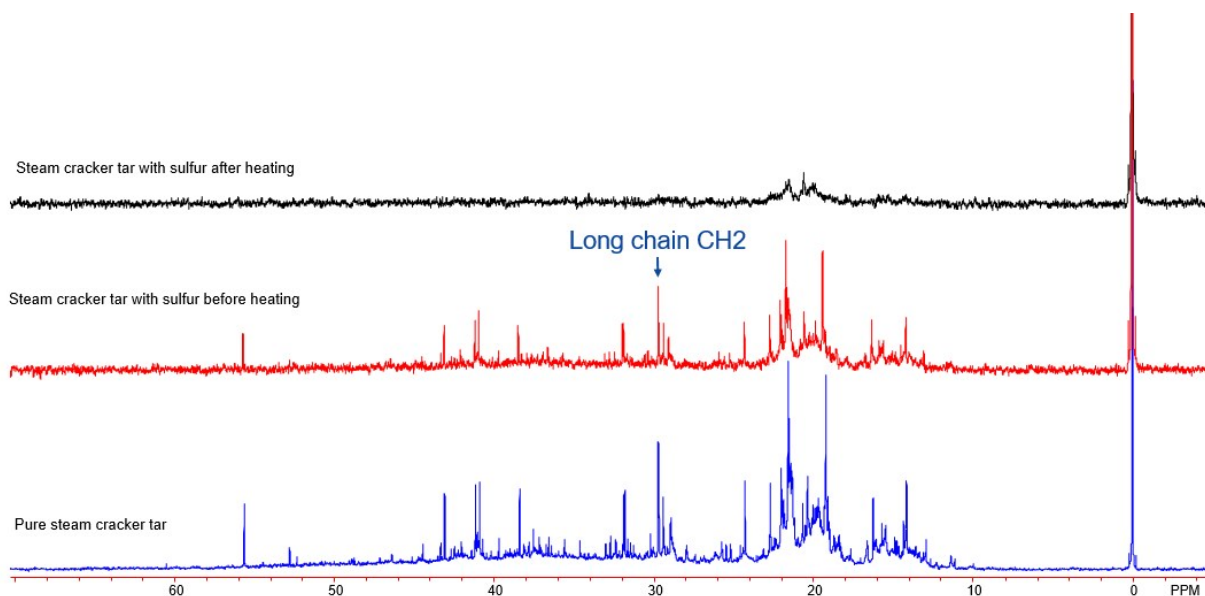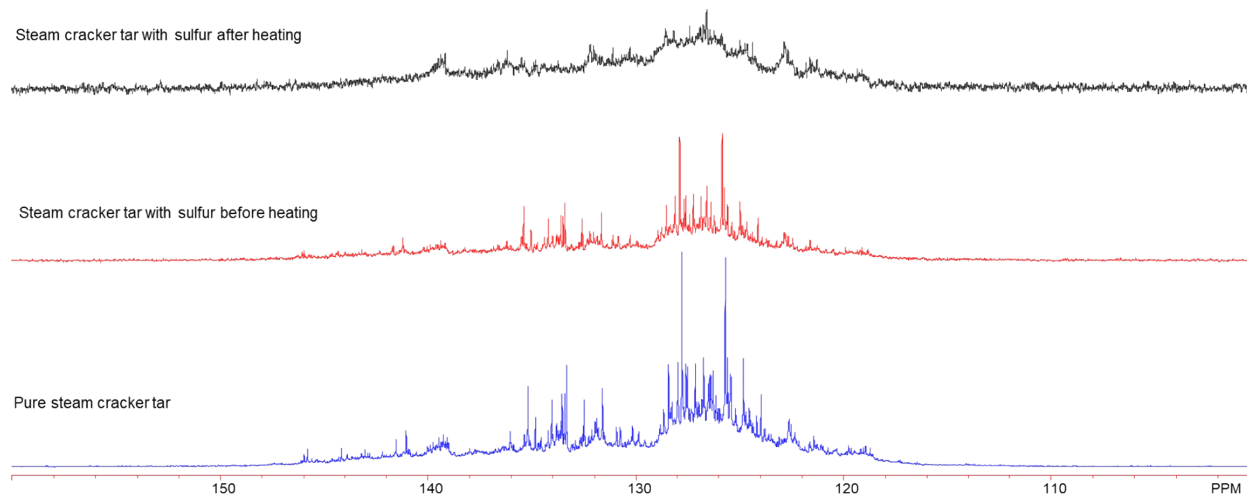**Figure S18:** ^{13}C NMR aromatic region for SCT (steam cracker tar), SCT with sulfur before heating, and after heating, as reaction precursors to SD-Carbon-4. The heating process changes structure/composition of SCT. After heating, SCT becomes heavier, more aromatics. Very few sharp peaks of heated sample, indicates molecules are less soluble, and becomes bigger molecules

Table S1: Pyrolysis temperature and its impact on s.a. Products treated on at 500 °C gives 9 m^2/g product, versus product treated at 750 °C gives 1216.57 m^2/g s.a. product. This high s.a. is likely to come from a combination of sulfur and CO_2 puffing from the system in the presence of KOH and heat.

750C effect	sulfur wt %	HKGO wt%	sulfur weight	DCPD weight	HKGO weight	total weight	MCRT (160C16hr)	KOH (1to1 weight ratio)
S50H50-500C	50	50	0.8	0.00	0.80	1.60	Liquid	mix well
S50H50-750C	50	50	0.4	0.00	0.40	0.80	Liquid	mix well

Table S2: S content variation impact on s.a. Sulfur to HKGO is a key parameter to dial the final product's porosity: We can make porous sulfur dope carbon with surface area ranged from 750-1886 m2/g simply by varying sulfur to HKGO ratio. This can be achieved with or without DCPD present. We believe any unreacted DCPD will be evaporated at the final pyrolysis temperature.

Vary S content	sulfur wt %	HKGO wt%	sulfur weight	DCPD weight	HKGO weight	total wt	MCRT (160C 16hrs)	KOH (1to1 wt ratio)	MCRT (500C 2hr)	Heat (750C 2hr)	BET (m2/g)
S22H67	22.22	66.7	0.4	0.20	1.20	1.80	Liquid	mix well	Yes	Yes	1886
S17H67	16.6 7	66.67	0.4	0.40	1.60	2.40	Liquid	mix well	Yes	Yes	1710
S33H67	33.33	66.7	0.4	0.00	0.80	1.20	Liquid	mix well	SPILL	Yes	1216.6
S33H33	33.3	33.3	0.4	0.40	0.40	1.20	Liquid	mix well	Yes	Yes	751.55
S33H50	33.3	50	0.4	0.20	0.60	1.20	Liquid	mix well	Yes	Yes	1473
S33H50rp	33.3	50	0.4	0.20	0.60	1.20	Liquid	mix well	Yes	Yes	1642

	sulfur wt %	HKGO wt%	sulfur wt	DCPD wt	HKGO weight	total wt	MCRT (160C 12hrs)	KOH (1to1 wt ratio)	MCRT (500C 2hr)	Heat (750C 2hr)	BET (m2/g)
S33H67	33.3	66.7	0.4	0.00	0.80	1.20	Liquid	No KOH	Yes	Yes	3.65
S22H78	21.74	78.3	0.25	0.00	0.90	1.15	Liquid	mix well	Yes	Yes	1807.89
S14H86	14.29	85.7	0.15	0.00	0.90	1.05	Liquid	mix well	Yes	Yes	1399.72
S0H100	0	100.0	0	0.00	1.00	1.00	No	mix well	Yes	Yes	721.23

Table S3: KOH content or mixing and its impact on product s.a. These two parameters were key in making successful high s.a. porous carbon. Without proper mixing, s.a. can change from >1800m^2/g to <30m^2/g. Same applies to the absence of KOH. However, higher KOH content will compromise the yield (Figure 7) and so the ratio is kept at 1:1 to balance yield and high s.a.

Vary KOH or mixing	sulfur wt %	HKGO wt%	sulfur weight	DCPD weight	HKGO weight	total wt	MCRT (160C 16hrs)	KOH (1to1 wt ratio)	MCRT (500C2hr)	Heat (750C 2hr)	BET (m2/g)
no mixing	50	0	0.4	0.40	0.00	0.80	Solid	not mix well	Yes	Yes	26
Referece	33.3	33.3	50	0.4	0.20	0.60	1.20	mix well	Yes	Yes	1642
No KOH	33.3	66.7	0.4	0.00	0.80	1.20	Liquid	No KOH	Yes	Yes	0

Table S4: This same method is successful applied to stream cracker tar to generate 1416 m^2/g porous carbon

	sulfur wt %	HKGO wt%	sulfur wt	DCPD wt	SCT	total wt	MCRT (160C18hrs)	KOH (1to1)	MCRT (500C2hr)	Heat (750C2hr)	BET (m2/g)
SCT-1	33.3	66.7	0.25	0.00	0.500	0.75	Liquid	mix well	Yes	Yes	1149.1
SCT-2	23.07	76.9	0.200	0.00	0.667	0.87	Liquid	mix well	Yes	Yes	649.5
SCT-3	42.31	57.7	0.330	0.00	0.450	0.78	Liquid	mix well	Yes	Yes	653.5
SCT-4	53.85	46.2	0.420	0.00	0.360	0.78	Liquid	mix well	Yes	Yes	1416.2

Table S5: This below is to change KOH to other salt. NaOH works somewhat but KCl or NaCl failed almost completely.

sulfur wt %	HKGO wt%	total weight	HKGO (160C12hrs)	Salt variation [keep alkaline metal molar the same] (Mixwell)	MCRT (500C2hr)	CatPrep (750C3hr)	BET (m2/g)	Yield after washing
33.3	66.7	1.20	as is -12hr tt	KCl 1.59g	Yes	Yes	1.5	0.387
33.3	66.7	1.20	as is -12hr tt	NaOH 0.85g	Yes	Yes	216.5	0.101
33.3	66.7	1.20	as is -12hr tt	NaCl 1.25g	Yes	Yes	0.4	0.382

Table S6: Change of S to SCT ratio to seek the changes in s.a.

sulfur wt %	HKGO wt%	sulfur weight	DCPD weight	SCT	total weight	MCRT (160C18 hrs)	KOH (1to1 weight ratio)	MCRT (500C2 hr)	CatPrep (750C2 hr)	BET (m2/g)	Yield after washing
33.33	66.7	0.250	0.00	0.500	0.75	Liquid	mix well	Yes	Yes	1149.1	0.205
23.07	76.9	0.200	0.00	0.667	0.87	Liquid	mix well	Yes	Yes	649.5	0.274
42.31	57.7	0.330	0.00	0.450	0.78	Liquid	mix well	Yes	Yes	653.5	0.253
53.85	46.2	0.420	0.00	0.360	0.78	Liquid	mix well	Yes	Yes	1416.2	0.108

Table S7: NMR summary of the H or C % in various HKGO source or SCT, before heating, and after heating.

description	H aromatic%	C aromatic%	H Olefins%
Fresh HKGO with sulfur heated	9.9%	41.8%	0%
Fresh HKGO no heat	8.5%	40.0%	0.44%
Aged HKGO with heated	11.0%	47.1%	0%
Aged HKGO	8.6%	39.5%	0.44%
SCT +S heated	44.2%	92.1%	0%
SCT no heat	40.4%	78.0%	0.17%
Pure SCT	40.5%	76.7%	0.17%

Table S8: Change of elemental sulfur in crosslinked S and HKGO products after different crosslink time or heat space gas flow dynamics at constant temperature 160C.

Sample Label	Free Sulfur Fraction RI Detector	Free Sulfur Fraction UV 254 nm
S-Carbon-1 (before heat treatment)	0.35	0.37
S-Carbon-1 (sealed 12hr)	0.27	0.30
S-Carbon-1 (sealed 12hr + flow 6hr)	0.22	0.25

Sample Label	Free Sulfur Fraction RI Detector	Free Sulfur Fraction UV 254 nm
S-Carbon-1 (before heat treatment)	0.35	0.37
S-Carbon-1 (flow 6hrs)	0.23	0.25
S-Carbon-1 (flow 12hrs)	0.04	0.05