

# ACTIVATED CARBON FROM CORN-TO-ETHANOL BY-PRODUCTS FOR AUTOMOTIVE EMISSIONS CONTROL

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## Introduction

A wood-based activated carbon is used in over 90% of the cars in the U.S. for gasoline vapor emissions control. Due to more stringent environmental regulations on the horizon and less and less available space in engine compartments, carbons with higher adsorption capacities and lower cost are needed. The objective of this study [1] was to develop a high capacity, low cost activated carbon from a by-product of the corn-to-ethanol conversion process. Illinois produces 685 million gallons of ethanol from corn annually, making it the largest ethanol producer in the U.S. In the process of doing that, Illinois ethanol producers also generate about 1.7 million tons/year of a solid by-product, referred to here as corn stillage (CS). The conversion of this CS, which is now sold as animal feed for \$0.10/lb, into activated carbon would enable ethanol producers to offset some of their ethanol production costs and make their process more economical.

## Experimental

Table 1 presents the proximate/ultimate analyses of CS, a bituminous coal, and corn kernels. Note that: 1), fixed carbon of CS is one fifth that of coal, 2) CS contains less ash than coal, but more ash than pure corn, 3) sulfur content of CS is less than that of coal, and 4) CS has relatively high nitrogen content. Activated carbons were prepared from CS and IBC-102 coal by physical (CO<sub>2</sub>) activation and/or chemical (KOH, ZnCl<sub>2</sub>, or H<sub>3</sub>PO<sub>4</sub>) activation. Single point N<sub>2</sub> BET surface areas were measured using a Monosorb apparatus (Quantachrome Corporation). Pore size distributions (PSD) were determined from N<sub>2</sub> (77 K) adsorption isotherms (P/P<sub>0</sub> = 0.0001 - 0.98) using an Autosorb-1 apparatus (Quantachrome Corporation) and a model based on a modified DR equation [2]. Butane working capacities were measured at 25 or 68°C (100 or 10% n-butane diluted in UHP N<sub>2</sub>, 150 cm<sup>3</sup>/min) using a thermogravimetric analyzer (TGA-131, Cahn). The carbon samples were first heated in UHP N<sub>2</sub> to 120°C to remove moisture. Flowing N<sub>2</sub> was used to desorb the adsorbed butane. The butane adsorption capacity (BAC) and butane working capacity (BWC) refer to the respective amounts of butane (g/g) adsorbed and desorbed in the first adsorption/desorption cycle (see, for example, Figure 1).

## Results and Discussion

Table 2 lists N<sub>2</sub> BET surface areas of the CS and coal chars produced by pyrolysis and physical activation. CS char made by pyrolysis alone had surface areas of 35 m<sup>2</sup>/g or less. Surface areas of chars activated in 1 atm CO<sub>2</sub> increased from 240 to 446 m<sup>2</sup>/g with increasing conversion. The maximum surface area of 446 m<sup>2</sup>/g obtained at 70% conversion was

considerably less than that achieved by Venkatraman [3] using corn kernels and a two stage method. Figure 2 shows the surface area and yields obtained by activating CS with varying amounts of ZnCl<sub>2</sub> while keeping KOH constant (ZnCl<sub>2</sub>/KOH ratio varied between 0 and 2). The objective here was to achieve higher yields for comparable surface areas by adding small amounts of ZnCl<sub>2</sub> to the KOH/CS mixture. Figure 3 shows the high fixed carbon content in the ZnCl<sub>2</sub> activated CS carbon. Recent literature also indicates that relatively high yields can be obtained for ZnCl<sub>2</sub> activation of biomass materials. To the best of our knowledge, no one has reported using a combination of KOH and ZnCl<sub>2</sub> to increase both yield and surface area of chemically activated biomass derived carbon. Table 2 lists the BACs and BWCs of selected carbons. At 25°C, our best CS carbon (KOH activated), having a surface area of 1846 m<sup>2</sup>/g, had a BWC slightly less than that of the automotive carbon. Butane capacities were also measured at 68°C and 10% n-butane. The BWC of our best KOH activated CS carbon at these conditions was 30% greater than that of the automotive carbon. Micropore size distributions of selected carbons are shown in Figure 4. Note these carbons all have bimodal distributions. The KOH activated chars from CS and coal have comparable micropore size distributions. The automotive carbon has an average micropore size larger than that of the KOH activated carbons (Table 5). The larger micropore size may be why butane is more easily desorbed from the automotive carbon (Figure 1).

## Conclusions

Activated carbons were produced from by-products of the corn-to-ethanol conversion process. The BWC of one KOH activated CS carbon determined at 68°C, 10% butane was 30% greater than that of a carbon used by the automotive industry. ZnCl<sub>2</sub> was added in small amounts to the CS/KOH mixture to increase yield and maintain relatively high surface area. Further work is needed to optimize and scale up this chemical activation process. A PSD model based on a modified DR equation was used to gain further insight into butane adsorption by activated carbon.

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## References

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Table 1. Proximate and Ultimate Analyses of Corn Stillage, IBC-102 Coal, and Corn Kernels.

	Corn Stillage	IBC-102 Coal	Corn Kernels
Proximate analysis (as received wt%)			
Moisture	8.0	14.4	--
Ash	4.3	6.9	1.5
Volatile matter	78.4	39.8	--
Fixed Carbon	9.3	53.3	--
Ultimate analysis (as received wt %)			
Carbon	46.4	74.1	48.4
Hydrogen	7.3	5.3	7.2
Nitrogen	3.8	1.5	0.1
Oxygen	37.8	9.0	43.1
Total sulfur	0.3	3.3	--

(-- unvariable)

Table 2. Surface Areas of Pyrolyzed and Physically Activated Corn Stillage and Coal Chars.

Sample	Temperature (°C)	Conversion	N <sub>2</sub> BET Surface Area (m <sup>2</sup> /g)
Pyrolysis, N <sub>2</sub>			
CS	800	0	35
CS	900	0	4
Coal	900	0	5
Physical Activation, CO <sub>2</sub>			
CS	843	0.21	240
CS	843	0.38	299
CS	843	0.49	401
CS	843	0.70	446
Coal	860	0.22	342
Coal	860	0.46	495
Coal	860	0.71	752

Table 3. Butane Capacities of Selected Corn Stillage, Coal and Automotive Carbons.

Sample	Surface Area (m <sup>2</sup> /g)	Butane Working Capacity		Butane Working Capacity	
		Adsorption (g/g), T=25°C	Capacity (g/g), T=25°C	Adsorption (g/g), T=68°C	Capacity (g/g), T=68°C
CS+KOH (0.25)	1846	0.50	0.44	0.27	0.26
CS+KOH (0.1)	891	0.21	0.14	--	--
CS+ZnCl <sub>2</sub>	986	0.22	0.21	0.09	0.09
CS+KOH+ZnCl <sub>2</sub>	1381	--	--	0.21	0.20
CS, CO <sub>2</sub> , X <sub>c</sub> =0.70	446	0.09	0.08	--	--
IBC-102+KOH	1240	0.27	0.17	0.21	0.18
IBC-102+ZnCl <sub>2</sub>	521	0.128	0.11	--	--
IBC-102, CO <sub>2</sub> , X <sub>c</sub> =0.71	752	0.12	0.08	--	--
Automotive Carbon	1500	0.57	0.53	0.20	0.20

Table 4. Pore Structure Parameters of Selected Activated Carbons.

Sample	Micropore Volume (cm <sup>3</sup> /g)	Total Pore Volume (cm <sup>3</sup> /g)	Average Pore Width (Å)
CS, CO <sub>2</sub> , X <sub>c</sub> =0.70	0.23	0.63	31.41
KOH/CS=0.25	0.84	1.00	13.38
ZnCl <sub>2</sub> /CS=2.0	0.38	0.65	30.20
CS, ZnCl <sub>2</sub> /KOH=0.4	0.43	0.51	15.46
CS, ZnCl <sub>2</sub> /KOH=0.6	0.43	0.52	21.25
IBC-102, KOH	0.58	0.59	8.48
Automotive Carbon	1.02	1.61	22.61

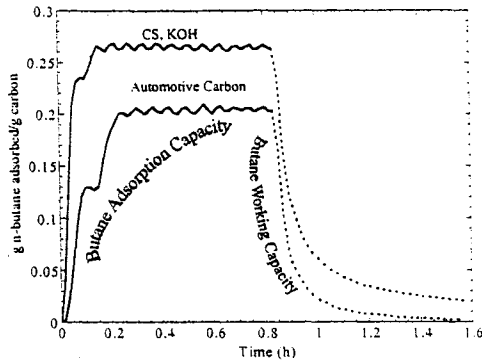


Figure 1. Butane Adsorption/Desorption Profiles at 68°C for CS and Automotive Carbons.

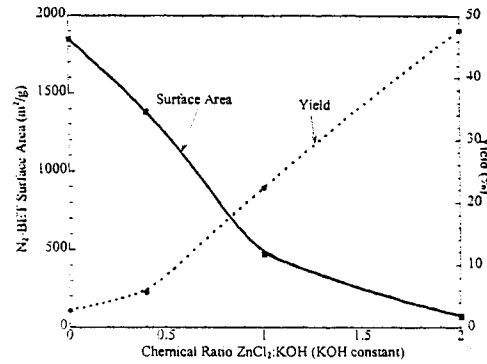


Figure 2. Variation in Surface Area and Yield of KOH/ZnCl<sub>2</sub> Activated Stillage with ZnCl<sub>2</sub>/KOH Ratio.

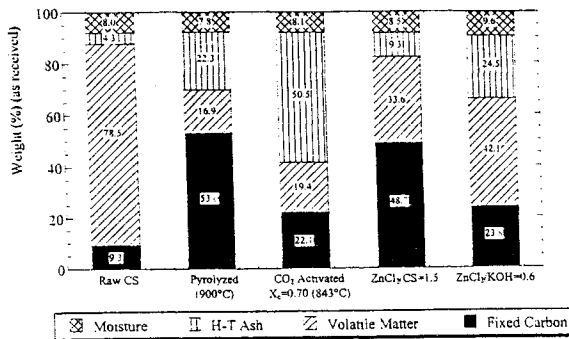


Figure 3. Proximate Analyses of Selected CS Carbons

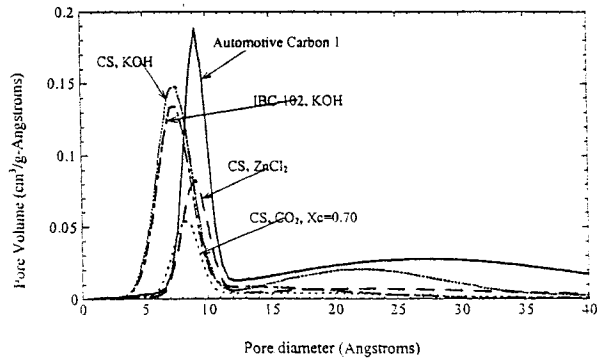


Figure 4. Pore Size Distributions of Selected Carbons Determined by Modified DR Model.