
Recovering valuable biobased products from thin stillage (CDS) in corn ethanol plants



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Contents

Abstract.....	2
Materials and Methods.....	3
Results and Discussions	6
Conclusion.....	7
Literature Cited	8
Tables	9

Executive Summary

- HTC (Hydrothermal Carbonization) processing of condensed distiller's solubles (CDS) or thin stillage opens new avenues of cash flow generation for corn ethanol plants.
- CDS can be converted to new products such as activated hydrochars with utility as adsorbents for a variety of organic chemicals, phosphate as a fertilizer component, and fatty acids that can be converted to biodiesel.
- The filtrate by-product of HTC processing of CDS has potential as a fertilizer for corn. Initial exploratory experiments have been encouraging. As a result a new project, "Investigate the impact of hydrothermal carbonization filtrate as a fertilizer for corn" has been funded by the Minnesota Corn Research & Promotion Council.
- Continued research to develop specialty absorbents from CDS hydrochar appears to be warranted.

Introduction

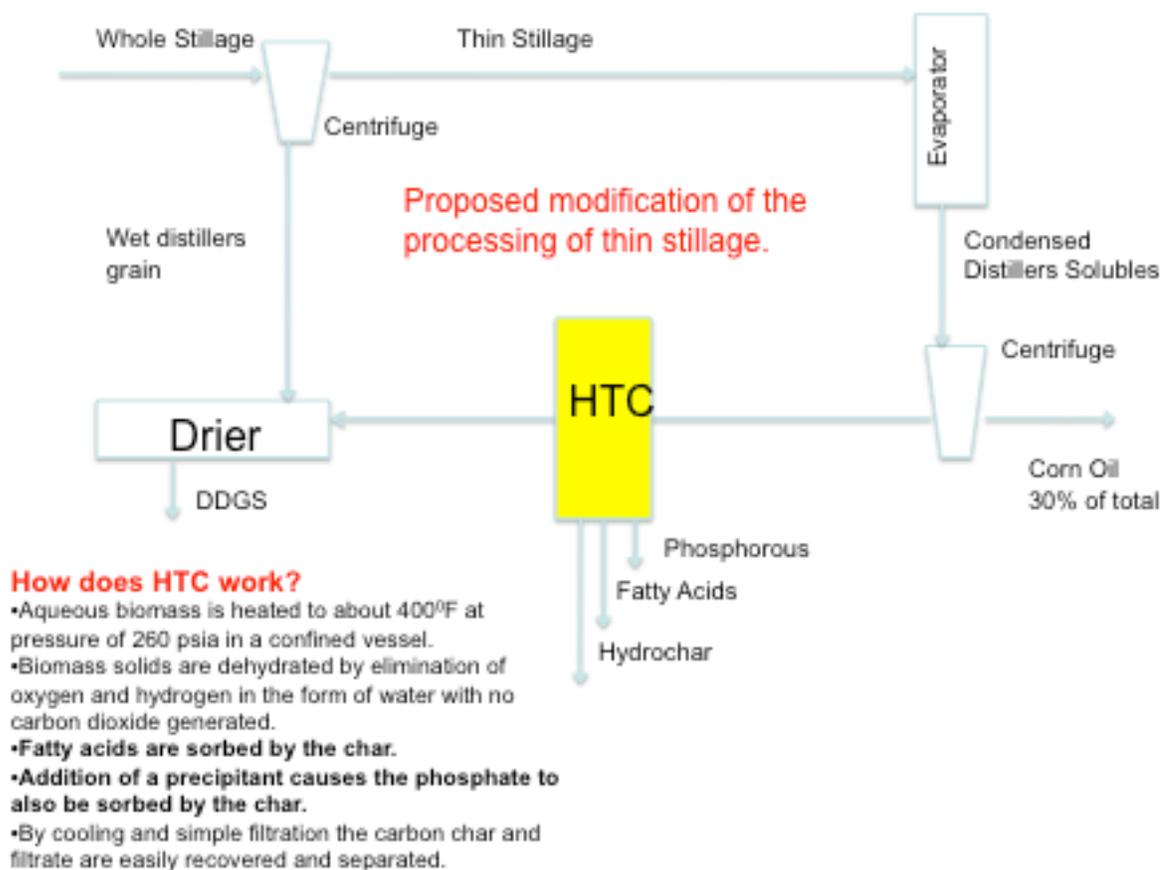
Thin stillage from corn ethanol plants is currently utilized by adding it to DDG and subsequently drying the blended streams to yield DDGS. This is convenient since it avoids treating the thin stillage as a waste stream. The profitability of a corn ethanol plant is driven by the price of ethanol and DDGS balanced by the cost of corn. Corn prices can vary substantially from year to year and this can result in a "feast or famine" economic environment in corn ethanol plants. Generating new value-added products from the thin stillage stream offers an opportunity to add more positive cash flow to the equation independent of corn prices.

Thin stillage is a potential source for several value-added biobased products that include phosphorous, fatty acids, and hydrochar that are produced by a process called Hydrothermal Carbonization (HTC). Hydrochar porosity and structure can be modified by post chemical and thermal treatment for applications such as activated carbons, polymer strengthening additives, and electric double layer capacitors.

The HTC processing unit would be inserted in the process flow to receive the condensed distillers solubles (CDS) from the oil recovery centrifuge as indicated in the schematic below. HTC will remove about a portion of the solids present in the concentrated thin stillage in the form of a hydrochar to which phosphorous that was dissolved in the thin

stillage and the remaining corn oil (in form of fatty acids) are sorbed by the hydrochar. The hydrochar with sorbed components is recovered by conventional filtration. The filtrate from the HTC unit that still contains 70%+ of the original solids is then could be combined with the wet DDG's and dried to a stable moisture content in the normal manner or alternately utilized a fertilizer for corn.

The actual value of hydrochar either in native form or post treated to enhance porosity, surface area and pore volume will be determining by its performance in various applications such as adsorption, strengthening of polymers or as supercapacitors.



Project Objectives

1. Establish efficacy of HTC for phosphorous sorbing from thin stillage.
2. Confirm performance and cost for phosphorous recovery by aid washing and conversion to phosphoric acid.
3. In collaboration with colleagues from Chemical Engineering and Chemistry, evaluate performance of native and modified hydrochars as;

- Functional activated carbon in chemical processes and fuel production,
 - Strengthening additives in polymer systems and
 - Electric double layer capacitors and similar applications.
4. Assess suitability of fatty acids for conversion to jet fuel and/or biodiesel.
 5. Estimate capital and operating costs for HTC processing of thin stillage.
 6. Perform in vitro genotoxicity screening on HTC filtrate to confirm suitability as an animal feed/
 7. Investigate market size for various hydrochar products.

Objective 1. Establish efficacy of the HTC process for recovery of phosphorous from thin stillage as well as processes for recovery from the HTC filtrate.

Our earlier experiments indicate that phosphorous will bind to hydrochars made from manures and municipal sludge because metals such as calcium, aluminum, iron, magnesium and zinc are present when the hydrochar is formed through HTC. With manures, recovery of phosphorous by the hydrochar ranges from 81-89% and is almost quantitative with sludge. While CDS contains a relatively high level of phosphorous it does not contain sufficient concentration of any of the necessary metals needed to bind the phosphate to the hydrochar as effectively as with manures and sludge. Initial experiments with CDS indicate that only about 50% (MNK 62) of the phosphorous is bound to the char after HTC. The mechanism for phosphorous binding is unclear since we can postulate two possible binding routes. In the HTC process phosphorous binds to di or trivalent cations from metals that are in the feedstock along with the phosphorous. As the hydrochar is formed there are two possible explanations for the binding. The first is ligand binding of the metal-phosphorous complex to carboxyl groups on the hydrochar. The second is a physical occlusion of the metal-phosphorous complex as the hydrochar is forming. It is possible that both mechanisms could be responsible for the binding.

To confirm the importance of metals in the binding, experiments with iron and magnesium added prior to HTC were conducted with CDS. Phosphorous binding was increased to about 84% (MNK 87) with iron added and to 74% with magnesium added (MNK 86). All of the phosphorous binding values are measured prior to any washing of the hydrochar. It is recognized that washing of the char removes residual interstitial and surface liquor or filtrate, which contains some phosphorous. In addition some of the bound phosphorous is also desorbed from the char. Desorption will be a function of the binding forces for a particular metal-phosphate complex (i.e. magnesium, calcium, iron, etc.).

4. Desorption experiments were performed on a CDS hydrochar, with added magnesium and iron (MNK86 & 87) and without added metals, (MNK 62) that had all been washed prior to desorption. In the case of hydrochar without added metals the phosphorous was essentially desorbed and biologically available within 24 hours. This was also the case with hydrochar with added magnesium. However, for the hydrochar with added iron, desorption and bioavailability was considerably less. This would have implications for use of the hydrochar as a fertilizer or additive for soil improvement. Phosphorous would be readily available to the plants for the hydrochars either with magnesium added or with no metals added. For the iron containing hydrochar phosphorous would be essentially unavailable for plants.

Objective 2. Cost for phosphorous recovery by acid washing and conversion to phosphoric acid

When applying a hydrothermal carbonization (HTC) process to CDS, a portion of the phosphorous contained in the CDS will be retained as phosphate with the hydrochar formed during the HTC process. The most prevalent phosphate salts in the hydrochar are expected to be calcium phosphate, magnesium phosphate, and iron phosphate.

Phosphate rock, phosphorite, mined commercially for phosphoric acid production, typically contains 14.5-19% P by weight. By comparison, unwashed CDS char contains 2.5 to 3.5% phosphorus. We expect that this percentage can be further increased to about 7% by adding calcium or iron salts to the CDS prior to the HTC process.

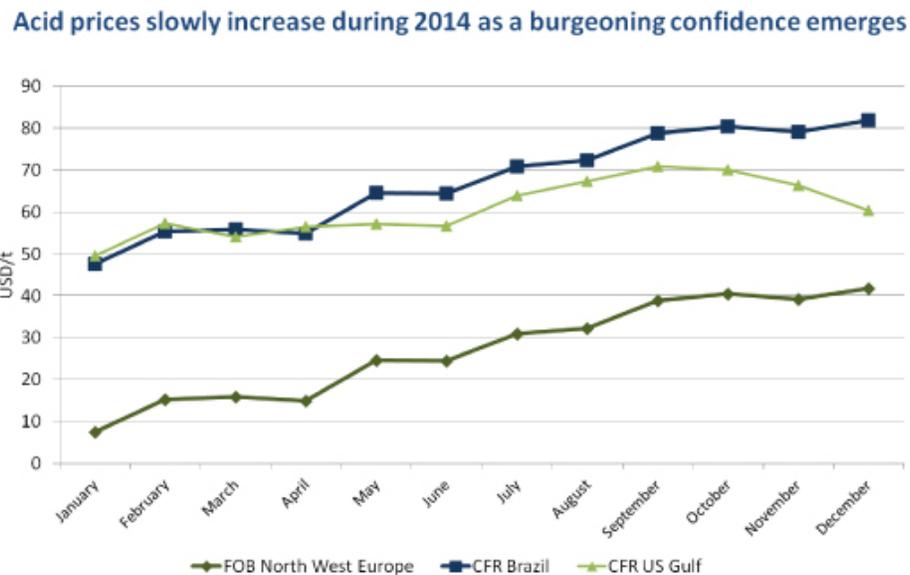
The phosphates in the char can be solubilized by washing the char with a strong acid, e.g. sulfuric acid, resulting in the formation of phosphoric acid as well as insoluble sulfates (calcium sulfate, magnesium sulfate and iron sulfate). The phosphoric acid containing solution can be separated from the char by simple belt filtration. Subsequent micro- or nanofiltration will remove any insoluble sulfates that were not retained by the first filtration step. The dilute phosphoric acid solution can then be concentrated by evaporation of water to produce commercial- or merchant-grade phosphoric acid, which contains about 54–62% P_2O_5 (75–85% H_3PO_4). This process is analogous to the “wet process” used to produce phosphoric acid from phosphate rock. However, if the goal is to only make simple fertilizer, such a mono or dicalcium phosphate concentration may not be necessary.

A first approximation of the cost of producing phosphoric acid from CDS hydrochar, is derived from information provided in the Fertilizer Manual (1985) for the sulfuric acid based process using rock phosphate as a starting material.

According to that information, the raw materials (sulfuric acid and phosphate rock) represent over 70% of the cost of phosphoric acid production. However, it is important to keep in mind that a typical fertilizer plant has a production capacity of >200 t P₂O₅ per day, while a single 100 Million gallon per year corn ethanol plant only generates enough hydrochar to extract a maximum of 2.4 t per day, depending on how the hydrochar is being prepared. While the per unit capital cost of plants between 200 t and 800 t per day does not seem to be very sensitive to scale, it is not likely that this holds true if a plant is scaled down to a range of 1-10t per day. Since the scope of this project did not allow us to experimentally develop a phosphoric acid process suitable for hydrochar, capital cost estimates are not included and focus instead is on the key operating cost parameter, which is sulfuric acid supply. Sulfuric acid demand is driven by the amount CaO and CaO equivalents present in the hydrochar. Based on this number, the amount of sulfuric acid required per ton of P₂O₅ produced is 0.81 tons. At a price of \$60 per ton of sulfuric acid this corresponds to an acid cost of \$43 per ton of P₂O₅. The market price of phosphoric acid in 2014 was between \$680 and \$850 per ton of P₂O₅. This price to cost differential looks promising and should warrant a more detailed experimental examination of a scalable phosphorus recovery process from hydrochar.

References:

Fertilizer Manual, edited by Travis P. Hignett, Springer, 1985



Source: <http://www.crugroup.com/about-cru/cruinsight/around-the-world-in-12-months-a-sulphur-and-sulphuric-acid-perspective>

Objective 3. In collaboration with colleagues from Chemical Engineering and Chemistry, evaluate performance of native and modified hydrochars

Functional activated carbon in chemical processes and fuel production

5-Hydroxymethyl furfural (HMF) is considered to be an important precursor in producing a range of biomass-derived chemicals. HMF yield from fructose dehydration in water is low due to its rehydration to levulinic acid and formic acid and parallel reactions of fructose to products other than HMF. Various strategies have been adopted to avoid byproduct formation. One strategy to prevent loss of HMF after it is formed is to remove it from the reaction mixture containing fructose through adsorption by activated carbon. In particular adsorbents such as BP2000 (Cabot, www.cabot-corp.com) and Norit 1240 (Norit, www.norit-america.com) exhibit selectivity for HMF adsorption over fructose in aqueous solution.

In the collaboration with the Tsapatsis group efforts were focused on the effectiveness of HTC hydrochars derived from CDS (condensed distiller's solubles). The starting material in all of these experiments was a hydrochar made from thin stillage supplied by Al-corn with HTC conditions of 2 hrs at 225^oC and post treated for 1 hour in an argon atmosphere at 800^oC.

#1 JM 13.11.15.3 Hydrochar washed with water only.

#2 JM 13.11.11 Hydrochar water, acetone and acid washed

#3 JM 13.11.15-2 Same as #2 but subsequently heated to 800^oC, inert atmosphere

#4 JM 13.15-1 Same as #2 KOH treated and heated to 800^oC, inert atmosphere

All four samples were tested for HMF adsorption from water. The post -treated KOH (Potassium hydroxide) sample (#4) sorbed 0.55g HMF/ g sorbent and the control sample #2 sorbed 0.18 g/g HMF. Samples #1 and 3 had negligible HMF adsorption. HMF concentration in the challenge solution was 0.049 g/ml.

Further examination of the KOH treated char (#4) showed adsorption of HMF at 0.64 g/g sorbent and fructose sorption of 0.33 g/ g sorbent.

While these results are encouraging it was noted that activation with KOH resulted in a 90% loss of the starting hydrochar. To mediate this large mass loss other activators were considered. ZnCl₂ (zinc chloride) was found to be an efficient activator generating considerable microporosity with a reduced mass loss of about 50%. From an economic standpoint this is quite significant.

ZnCl₂ activated char (MNK-1-26) was made with a 0.75:1 Zn:Char ratio and heated at 450°C in an inert Argon atmosphere. HMF and Fructose adsorption isotherms were generated and BET surface area was measured. Results are shown below in Table 1.

Table 1: BET Surface area and pore areas/volumes for MNK-1-26

Absorbent	BET surface area (m ² /g)	Micropore area (m ² /g) t-method	Total pore volume (cm ³ /g)	Micropore volume (cm ³ /g) t-method
BP 2000	1216	678	3.189	0.322
MNK 1-26 (0.5-1mm)	918.8	839.1	0.428	0.323
MNK 1-26 (>1mm)	927.3	839.9	0.416	0.323
MNK 1-46	162.5	124.6	0.074	0.046

BET: The specific surface area of a powder is determined by physical adsorption of a gas on the surface of the solid and by calculating the amount of adsorbate gas corresponding to a monomolecular layer on the surface.

Particle size showed no discernable effect on surface areas or adsorption (table 2).

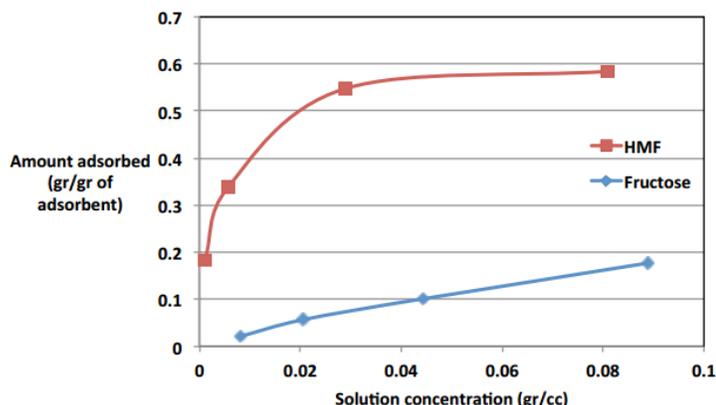
MNK-1-26 underperformed compared to adsorption achieved by BP2000.

Table 2: HMF and Furfural(FF) adsorption data as compared to BP2000 for MNK-1-26

	BP 2000		MNK 1-26 (<0.5 mm)		MNK 1-26 (0.5-1mm)		MNK 1-26 (>1 mm)	
	Soln Conc. (g/ml)	Ads (g/gr)	Soln Conc. (g/ml)	Ads (g/gr)	Soln Conc (g/ml)	Ads (g/gr)	Soln Conc (g/ml)	Ads (g/gr)
HMF	0.07	0.78	0.1	0.6	0.01	0.62	0.1	0.6
FF	0.06	0.9	0.1	0.6	0.01	0.58	0.1	0.58

While adsorption was not as high as BP2000, MNK-1-26 did show significant efficacy in selectively binding HMF over furfural, figure 1.

Fig. 1. HMF and fructose adsorption from water on MNK 1-26 char.



A replication of MNK-1-26 was made with MNK-1-46. MNK-1-46 showed significantly lowered surface area and porosity (see table 1). It was determined that the poor results of MNK-1-46 could be due to experimental error in some capacity and a series of replications of MNK-26 and MNK-46 were carried out. The three replicates are MNK-76-PTT2, MNK-76-PTT3, and MNK-76-PTT4. MNK-76-PTT1 was post-thermally treated at 800°C compared to 450°C for the other samples. The MNK-76 series shows high reproducibility with regards to surface area, porosity, and sugar adsorption.

Table 3: Surface area and porosity for MNK-76 series hydrochars

Adsorbent	BET surface area (m ² /g)	Micropore area (m ² /g) t-method	Total pore volume (cm ³ /g)	Micropore Volume (cm ³ /g) t-method
MNK-76-PPT1	747	646.3	0.319	0.23
MNK-76-PPT2	874	679.3	0.387	0.245
MNK-76-PPT3	753	581.1	0.385	0.21
MNK-76-PPT4	805	628.6	0.365	0.227

While the surface areas are higher (avg. 810 m²/g) than MNK-1-46 (162.5 m²/g) they are still lower than MNK-1-26 (~920 m²/g). Total pore volume is also lower with an average of 0.379 cm³/g compared with ~0.420 cm³/g for MNK-1-46. These differences may explain the lower adsorption observed for the MNK-76 series as compared with MNK-26. Max g/g adsorption on MNK-26 was about 0.58 gHMF/gChar for a 0.1 molar HMF solution (see Fig. 1.) and 0.2 g HMF/g Char. There are some differences between the

starting materials (CDS) for the MNK series and the MNK 76 series. The MNK 26 and 46 series were made from CDS provided by Al-Corn Ethanol. The 76 series are from CDS provided by CVEC (Chippewa Valley Ethanol Corp). CDS is a product of a fermentation process to produce ethanol. As such one can expect differences between plants operating under different conditions with corn sourced from different locations. HTC processing of somewhat different starting materials can be expected to result in hydrochars with varying carbon content and number of functional groups. Additionally the 76 series of hydrochars was size reduced to a finer and narrower granulation range than the 46 series. In the post treating process the hydrochar is placed in crucibles filled to a fixed depth within the inert atmosphere oven. A smaller granulation will result in a larger mass being placed in each crucible. Since the crucibles are not of a flow through design one can expect a diminished treatment impact if more mass is treated for a fixed time at fixed temperature. This could lead to smaller BTE area as well as less pore volume.

What can one conclude from these experiments?

- HTC hydrochars can be effective adsorbents for HMF as well as furfural
- Sorption of HMF appears to be a non-linear function of BET area and pore volume
- The batch post treatment oven should be converted to a flow through configuration to eliminate loading and gas flow issues. The batch crucible configuration is not scale able whereas the flow through design would be
- Hydrochars need to be characterized before and after post treatment for carbon content and number of carboxyl groups present
- Starting materials need to be characterized for variation in composition and subsequently processed under HTC conditions that will yield a chemically consistent hydrochar from one source to another

Strengthening additives in polymer systems.

The major objective of this research was to provide an additive in the form of native or modified hydrochars for strengthening polylactide polymer systems at reduced cost compared to activated carbons (> \$10/kg).

Despite the comparable mechanical properties that polylactide exhibits with respect to petroleum-based materials (e.g., tensile strength and modulus), it has a low elongation at break and heat resistance that limits its applications (Auras, 2010). Our working hypothesis is that hydrochars, which are reported (Li et al., 2010) to possess relatively high surface concentrations of carboxylic acid functional groups [or can be post-

thermally modified to further increase them (Chen et al., 2011)] can function as reinforcing additives through hydrogen bonding and dipole-dipole interactions that can increase intermolecular interactions, potentially providing improvement in one or more of these deficiencies. This validity of this hypothesis was demonstrated by the addition of a commercially available activated carbon material [Cabot BP 2000 that is reported to possess relatively high levels of carboxylic acid groups (Oickle et al. 2010)]. By the addition of 3-wt% of BP 2000 to polylactide, the material exhibited increased crystallinity, and increased its tensile strength and heat deformation temperature. Unfortunately, BP2000 is priced significantly higher than \$10/kg.

This work was conducted in collaboration with the laboratory of Prof. Marc Hillmyer of the department of Chemistry at the University of Minnesota. The most significant result achieved in the initial stage of the project was the observation that BP 2000, which is a commercial activated carbon derived from petroleum residues, was the first additive examined with polylactides that did result in improved thermal performance. At 3 weight percent BP 2000 in PLLA, the tensile strength increased to 88.3 MPa from 77.2 MPa in non-reinforced PLLA.

The Hillmyer laboratory was provided with CDS hydrochars that have been treated with phosphoric acid, followed by post-thermal treatment to 450 °C under argon. This post-thermal treatment is purported to retain overall particle macrostructure but to also increase surface area and provide high surface concentrations of carboxylic and hydroxyl functional groups. The control, BP2000, has also been heat treated to provide for a two- way comparison.

The composition, functionality, particle size and surface area of hydrochars were characterized by elemental analysis, FT-IR spectroscopy, SEM, and nitrogen adsorption techniques, respectively. These materials were blended at 3-wt% in commercial polylactide. The resulting composites presented similar brittle behavior as neat polylactide. However, hydrochars effectively accelerated the crystallization process of the polylactide resulting in stiffer and more thermally stable composite materials. Subsequently a zinc chloride heat- treated hydrochar was tested. This material is closer in physical structure to BP2000 having a similar micropore area and a surface area about 50% of the BP2000 level. However, the results Experiments with a zinc-hydrochar material were disappointing in that there was no improvement in polymer strength.

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Electric double layer capacitors and similar applications

This project was conducted in collaboration with Prof. Fiona Doyle of the Material Science Department at the University of California, Berkeley and her doctoral student, Mr. Brandon M. Wood. Brandon evaluated two modified hydrochars. The first was processed with KOH (Potassium Hydroxide) and post heat treated in our inert gas oven. The second sample was processed with zinc chloride and post heat treated similarly to the KOH sample. Characterization of the zinc chloride construct showed it to have a significant amount of microporosity which is believed to be beneficial in the supercapacitor application.

A testing device, commonly referred to as a pouch cell, was developed for electrode material testing in electrochemical capacitors. Pouch cells utilize 12 cm² electrodes, NKK cellulose based separator, and Tetraethylammonium tetrafluoroborate (TEA-BF₄) dissolved in Propylene carbonate (PC) as electrolyte. All indications show that the device provides a suitable environment for industrially relevant electrochemical testing. The last steps before testing CDS hydrochar materials were milling the samples to give a reasonable particle size, and formulating the correct ratio of binder to active material for film casting.

The hydrochars were milled down to an average particle diameter in the 5-15µm range, which is useful for casting thin electrode films. Average particle diameter was measured using a number of different techniques including light diffraction, optical microscopy, and SEM. With accuracy and time constraints in mind optical microscopy was taken as the default measurement. It should be noted that although the average particle diameter is within the desired range a more thorough statistical analysis is needed to comment of the distribution of particle sizes. Observations indicated that there were a

lot of small particles and a number of large particles without much in between (a bimodal particle size distribution). A possible explanation is that during ball milling small pieces are broken off the larger particles. This could have an effect on the electrochemical performance of the electrode. Other characterization included surface area measurements and pore distribution. The low BET surface area for the hydrochar activated with KOH might be attributed to the particle size distribution. After characterization, the ZnCl₂ activated hydrochar was used successfully to cast a 150 μm film.

Hydrochar thermally activated with ZnCl₂ and Kuraray Chemical YP-50 9 were evaluated as electrode materials in symmetric electrochemical double layer capacitors. YP-50 carbon is an industry standard high surface area carbon used as a control. The carbon materials were mixed with an aqueous styrene butadiene rubber (SBR) type binder and coated on an aluminum current collector. Electrodes were cut from the laminate, and assembled in a pouch cell. Pouch cells were filled, in an argon glove box, with 1M tetraethylammonium tetrafluoroborate (TEABF₄) dissolved in propylene carbonate (PC), and sealed. Cyclic voltammetry (CV) was performed on the cells at a number of different scan rates. Both cells were stable over ~30 cycles, however the specific capacitance of the hydrochar carbon was two orders of magnitude lower than YP-50. Capacitance is proportional to surface area, and as a result it was expected the hydrochar carbon (400 m²/g) would have a lower capacitance than YP-50 (1500 m²/g), but not the dramatically reduced capacitance we observe. Additionally, the hydrochar laminate was brittle compared to that of YP-50 at the same binder/active mass ratio. It is hypothesized that the wide particle size distribution of the hydrochar carbon resulted in a lower quality laminate. More replicates are necessary to confirm these results. Looking forward, to obtain a hydrochar carbon with high double layer capacitance the activation process would have to be altered to result in higher surface area, post processing methods tuned to generate a narrow particle size distribution, and the optimal ratio of binder to active material would need to be determined.

Objective 4. Assess suitability of fatty acids for conversion to jet fuel and/or biodiesel.

This objective has been accomplished in collaboration with an outside company, Revolution Fuels, LLC (Fairfield, CT). Employing their proprietary

process, conversion of fatty acids extracted from stillage hydrochars into fatty acid methyl esters was accomplished in > 99% yield.

Objective 5. Estimate capital and operating costs for HTC processing of thin stillage.

Analysis of cost and potential value of HTC processing of CDS

We wanted to determine the potential economic benefits of processing CDS via the hydrothermal carbonization process. We started with establishing a mass balance for the process based on CDS production at a 100 Million gallon per year corn ethanol plant. The primary products from the process are hydrochar and a nutrient-rich filtrate. Associated with and “bound” to the hydrochar are fatty acids and phosphate, which can be extracted, leaving an “extracted hydrochar” as a product for sale. The mass balance based on experimental data is summarized in Table 1.

Table 1:

Mass balance for HTC processing of CDS from 100 MM GPY Ethanol Plant

	lbs/year	gal/year	tons/year
Thin stillage liquid (pre HTC):	145,084,746	17,480,090	
Dry solids in Thin stillage:	42,800,000		21,400
Hydrochar (wet weight):	27,156,528		13,578
Hydrochar (dry weight):	11,984,000		5,992
Extracted hydrochar (dry weight):	8,388,800		4,194
Fatty Acid recoverable from hydrochar:	1,797,600		899
P recoverable from hydrochar (as P2O5):	773,903		387.0
Water discharged as steam due to flash cooling of HTC reactor	24,649,305	2,969,796	
Final filtrate volume	93,278,913	11,238,423	
Dry solids in filtrate	26,504,793		13,252
Potassium as K2O	1,112,604		556
Total NH4	3,371,527		1,686
Phosphorus as P2O5	1,046,703		455

Additionally, the filtrate represents a valuable material as a liquid fertilizer containing nearly all the potassium, about 50% of the phosphate, and over 80% of the nitrogen of the starting material. The filtrate also still has a significant organic load, which can be

converted into biogas. Previous experiments have shown that 83% of the organic load in CDS HTC filtrate can be converted to biogas. This amount would likely be sufficient to cover the gas needs for heating the HTC process. Since most of the nutrients pass through an anaerobic digester, the fertilizer value of the anaerobic digester effluent is assumed to be similar to that of the incoming filtrate.

Table 2 shows the revenue potential of the different product streams generated in the HTC process.

Table 2:
Annual Value of HTC Products produced from 100 MM GPY Ethanol plant

Char	
Production in tons	4,194
Price per ton	\$350
Char Sales	\$1,468,040
Fatty Acids	
Production in lbs	1,797,600
Price per lbs	\$0.25
Fatty Acid Sales	\$449,400
Phosphorus as phosphoric acid	
Production in tons (as P2O5)	387
Price per ton (priced as P2O5)	\$650.00
Phosphoric Acid Sales	\$251,518
Filtrate as Fertilizer	
Potassium ¹⁾	\$200,269
Nitrogen ²⁾	\$1,011,458
Phosphate ³⁾	\$181,838
Filtrate Fertilizer Value	\$1,393,564
TOTAL VALUE	\$3,562,523

1) based on value of K2O at \$360/ton, 2) based on value of NH4 at \$600/ton

3) based on value of P2O5 at \$400/ton, Numbers were derived from Farm futures (<http://farmfutures.com/story-weekly-fertilizer-review-0-30765>)

Pairing these potential revenue numbers with the cost numbers presented in Table 3, we were able to prepare a simple net present value analysis for adding an HTC system to a 100 MM GPY ethanol plant. The cost numbers were derived from a more detailed capital cost analysis and detailed process cost calculations, which are included as an appendix. The HTC system design consists of two 6,500 gal pressure vessels with external gas-fired heaters in which the CDS is heated from 190F to 437F and kept at that temperature for two hours. The cool down of the reactors to 212F is achieved by evaporative cooling, which results in a volume reduction of the filtrate by nearly 25% with the benefit of providing a more concentrated fertilizer solution. The energy content of the low pressure steam generated during the evaporative cooling may be used for heating requirements in the ethanol plant, especially if used in conjunction with vapor recompression. However, for the purpose of this analysis, we did not give any credit for the heating value of this steam.

Table 3: Cost structure for CDS HTC system

Variable Cost Assumptions		
Gas Cost	\$/MM BTU	\$5.00
Electricity	\$/kWh	\$0.05
Value of CDS	\$/ton (dry)	\$120
Annual Variable Cost		
Gas		\$224,230
Electricity		\$1,286
CDS		\$2,140,000
Annual O&M Cost		
Labor (including benefits & taxes)		\$150,000
Maintenance (5% of Capital)		\$77,301.80
G&A		\$50,000
Processing Cost Assumptions		
Fatty Acid Extraction	\$/ton	\$250
Phosphoric Acid Recovery	\$/ton P2O5	\$200
Annual Processing Cost		

Fatty Acid Extraction		\$224,700
Phosphoric Acid Recovery		\$77,390
Capital Cost		
HTC Reactor		\$1,396,036
Filter Press		\$100,000.00
Filtrate Storage Tank		\$50,000.00
Total Capital Cost		\$1,546,036

The results for the base case of the NPV analysis are shown in Table 4. Under the given conditions the NPV is slightly positive for a 15% discount rate. The greatest uncertainty in the analysis is the value to be put on the extracted char. The \$350 per ton used for this analysis was essentially the minimum required to achieve a positive NPV at a 15% discount rate. However, at this time we have not yet identified an application for the hydrochar that will support this price level. Upgrading the hydrochar to an activated carbon can potentially push into a price range of greater than \$500/ton, but the activation process reduces yield, while adding additional processing cost. For example with a yield of 50% for activation of the hydrochar a price of \$700/ton for the activated char would yield the same NPV. Prices upwards of \$700/ton would accordingly increase the NPV. The market overview section of this report indicates retail prices for activated carbon in the range of \$4500-\$9000/ton. Obviously there is considerable opportunity to be realized by developing activated carbon products from the CDS hydrochar. The greatest driver on the cost side of the NPV analysis is the CDS feedstock, representing more than two thirds of the non-capital cost of the process. Since the value of CDS is determined by the market price of DDGS, there is very little that can be done to control this cost.

Table 4: Net Present Value Analysis

Year	1	2 - 10
Total Income	\$3,562,523	\$3,562,523
Total Cost without Capital	\$(2,944,907)	\$(2,944,907)
Capital Cost	\$(1,546,036)	
Depreciation	\$(154,604)	\$(154,604)
Earnings before taxes	\$463,012	\$463,012
Profit after taxes	\$282,437	\$282,437
Present Value	\$282,437	\$245,598

Net Present Value	\$84,074	

Assumptions: 15% Discount Rate, 10 year straight line Depreciation, 39% Tax Rat

Appendix I: HTC Process Calculations for 100 MM GPY Ethanol Plant

ASSUMPTIONS:			
BATCH PROCESS			
USE CP (BTU/LB/F)=	1		
USE MATERIAL WT (LB/GAL)=	8.3		
OPERATING HOURS/DAY=	24		
OPERATING DAYS/YEAR=	250		
STARTING TEMP (F)=	190		
FLOW GPD=	70,000		
DISCHARGE TEMP (F)=	180		
PROCESSING VESSELS=	2		
COOK TIME (MIN)=	30		
COOK TEMP (F)=	437		
COOK PRESSURE (PSIA)=	370		
HEATING EFFICIENCY of NAT GAS BURNER	0.8		
BATCH SIZE (GAL)			
FEED STOCK(GAL/BATCH)	5,104		
TANK DESIGN SIZE AT 80%=	6,380		
<u>DESIGN CYCLE (MIN);</u>			
FILL	15	340	GPM pump speed
HEAT	30	20.9	MBTU/HR
COOK	120		
COOL	30		
DRAIN	15	258	GPM pump speed
TOTAL CYCLE TIME=	210		
BATCHS PER DAY/COOKER=	6.9		
BATCH SIZE (GAL)=	5,104		
ENERGY CONSIDERATIONS-			
ENTHALPY OF HOT WATER 437F(BTU/LB)=	415.7		
ENTHALPY OF HOT WATER 212F(BTU/LB)=	180.2		
DELTA ENTHALPY(BTU/LB)=	235.5		
% EVAP AS STEAM=	24.3		
STEAM EVAPORATED(LBS)=	10,282		
GAL WATER EVAPORATED=	1,239		
<u>HEATUP</u>			

START TEMP(F)=	190		
FINAL COOK TEMP(F)=	437		
DELTA T FOR HEAT TO 437 (F)=	247		
BATCH WT (LBS)=	42,365		
TOTAL ENERGY TO HEAT (BTU)=	10,464,052		
COOL DOWN			
DISCHARGE TEMP AFTER VENTING	212		
BATCH WT (LBS)=	32,082		
TOTAL ENERGY COOL TO 180F(BTU)=	1,026,635		
LB'S OF WATER REQ'D (60 TO 180F)	8,555		
GALS OF WATER REQ'D (60 TO 180F)	1,031		

UTILITIES			
	Per Batch	Per Day	Per Year
BTU required for heating	10,464,052	143,507,000	35,876,750,000
Natural Gas required in MBTU	13,080,065	179,383,750	44,845,937,500
Cost of Natural Gas @ \$5/MBTU	\$65.40	\$896.92	\$224,230
BTU available in low pressure steam	2,421,468	33,208,704	8,302,175,938
Gal of water to cool reactor from 212F to 180F	1,031	14,136	3,534,027
Cost of water @ \$0.001/gal	\$1.03	\$14.14	\$3,534
Electricity for pumps in kWh	7.5	103	25,714
Cost of electricity at \$0.05/kWh	\$0.38	\$5.14	\$1,286

APPENDIX II: HTC REACTOR CAPITAL COST ESTIMATE							
ASSUMPTIONS:							
SKID MOUNTED UNITS							
NO PIPING TO OR FROM UNIT INCLUDED							
NO UTILITIES TO OR FROM UNIT INCLUDED							
NO BUILDING							
PREHEAT BY FLASHING OFF BATCH							
NO COOLING HT-EXCHANGER, FLASH COOLING TO 212F							
	SQ FT	\$/SF	MEN	DAYS	X.X	\$	
	B/C	RATIO	EXP				
2-6,500 GAL PRESSURE VESSELS	\$430,000	2.09	0.65			\$694,499	
2 HEAT EXCHANGERS							
3 PUMPS							
40M BTUGAS FIRED BOILER/HEATER							
LOAD CELLS							
2-SKIDS							
PIPING							
SPECIAL VALVES AND PIPING						\$50,000	
INSULATION			2	5	2		1
ELECTRICAL			2	15	3		1
INSTURMENTATION						\$100,000	
MECHANICAL ASSEMBLY			4	5	1.5		1
PLC/HMI						\$40,000	
PROGRAMING						\$30,000	
-							
	SUBTOTAL						
-						ENGINEERING 10%	
						SUBTOTAL PROJECT	
						CONTINGENCY 25%	
						TOTAL PROJECT	

Objective 6. Perform in vitro genotoxicity screening on HTC filtrate to confirm suitability as an animal feed.

CDS filtrate samples were screened for potential biochemical toxicity as a quick test to determine potential suitability as an animal feed. Tests were performed by Cyprotex US LLC, an independent testing lab. The results indicate that the filtrate exhibits a high level of cellular toxicity for ATP. Results for GST (Glutathione S-transferase) were inconclusive, probably due to interference from the compounds present in the filtrate. Thus the CDS filtrate is unsuitable as an animal feed based on this preliminary test.

An alternative use for the HTC filtrate is to consider it as a fertilizer for corn and other crops. The filtrate contains nitrogen, phosphorous and potassium. However, the major question was whether or not it is in any way detrimental to seed germination or plant growth. Fertilization studies conducted with the filtrate were completed with encouraging results. Corn germination and early growth tests were performed with varying levels of concentration and aging time for the filtrate. At dilution of 1:10, aged filtrate performed as well as commercial fertilizer. While very encouraging, more extensive testing at a larger scale is necessary to fully establish efficacy. To this end, the Minnesota Corn Growers have awarded a grant to pursue green house testing of CDS filtrate as the next step beginning in July 2015.

Objective 7. Investigate market size for various hydrochar products.

Market Overview of Potential Uses for Hydrochar

Hydrochar is the solid carbonaceous product formed during hydrothermal carbonization of liquid and/or solid organic starting materials. Depending on the type of starting material in addition to the carbonaceous material phosphate and fatty acids can be associate with the hydrochar and can be selectively recovered. However, for the purpose of this market overview we are focusing on solid carbonaceous material. Specific product opportunities that were explored are activated carbon, super capacitor carbon, and polymer additives.

1) Activated Carbon

Activated carbon is a highly porous adsorptive material produced by the thermal or chemical activation of either fossil coal or pyrolytic char derived from biological raw materials such as wood or coconut shells.

Market size and pricing:

The market for activated carbon in the US in 2014 was about 600 Million lbs/year. This number is expected to grow by an additional 350-550 Million lbs/yr due to new EPA mercury regulations. Globally, the need for activated carbon to sequester mercury from the smoke stacks of coal-fired power plants is also expected to grow rapidly. In China alone, the expected potential for mercury removal is several times larger than in the US. Besides mercury removal, other target markets include:

- Wastewater Treatment (toxic chemical removal – GAC)
- Drinking Water Treatment (removal of chlorine-by-products)
- Personal protection (respirators)

- Food and Beverage Industry (removal of color and odor from liquids)
- Chemical and petroleum industry
- Metal Recovery (gold and silver, ion exchange)

The key industry players in the US are:

- Calgon (150 Million lbs per year, all from coal)
- Cabot
- Albermarle
- ADA Carbon Solutions

Typical price ranges for bulk activated carbon in quantities of 1 metric ton or more range between \$0.50 for \$2.50 per kg plus shipping, often from China. In the US, online retail prices range from \$5 to \$10 per kg for 55 lbs bags. Ultimately, the exact price will be highly dependent on the quality parameters required for a specific carbon.

Activated Carbon Manufacturing Process

Activated carbon is manufactured through two different processes.

Physical Activation

The Physical or Steam Activation Process is known for yielding higher quality activated carbon. However, due to the amount of heat necessary to produce activated carbon using this method, it is more expensive and requires industry manufacturing.

Physical Activation, or Steam Activation, places a carbonaceous source material such as wood, coal, petroleum pitch or even coconut shells in a tank without oxygen, and pyrolyzes them at a high temperature, usually 600° - 900° C, to create a char. Then, the char is oxidized or “activated” at temperatures above 250° C, usually 600° - 1200° C, by blasting it with steam. Through this process, all of the volatile compounds are removed, while enlarging the internal pores and leaving behind a carbon skeleton. By removing carbon from the char, the internal surface area of the material is also increased. After the process is complete, 3 lbs. of source material usually yields 1 lb. of activated carbon.

Chemical Activation

Chemical Activation is often the preferred method due to its shorter production time and lower temperatures required to produce activated carbon.

During chemical activation, the source material is impregnated with certain chemicals, typically an acid, a strong base or a salt (phosphoric acid, potassium hydroxide, calcium chloride and zinc chloride). The chemical solution chews away at the internal structure of the material. Then, the raw material is carbonized at a low temperature, usually 450° – 900° C. It is believed that in this process, the carbonization / activation steps proceed simultaneously.

This process results in a very large surface area, that is about 600 – 1,200 m² per gram, depending on the source material.

Activated Carbon Properties

The quality and use of activated carbon is evaluated on a number of criteria dependent on their intended use. Here are a few of the most common properties important for manufacturers.

Density: The higher the density of a sample of activated carbon, the greater the activity or adsorption per unit volume, indicating a higher quality activated carbon.

Particle Size Distribution: The smaller the particle size of an activated carbon, the greater the access to surface area, and the faster the rate of adsorption by the material.

Mesh Size: The physical size or mesh size of the carbon can significantly impact its resistance to flow within a system. The smaller the mesh, the greater the resistance to flow, and the greater the adsorption.

Iodine Number: Is a measure of the micropore space of activated carbon and is one of the most fundamental parameters to characterize the performance of activated carbon, particularly vis-à-vis the adsorption of small molecules.

Molasses Number: The molasses number is the measure of the mesopore content of the activated carbon, and the degree of decolorization. A high molasses number indicates a high adsorption of big molecules.

Ash Level: The ash level is a measure of the purity of a sample of activated carbon. This is important when the carbon is used as a catalyst in an industrial process.

2) Super Capacitor Carbon

Super capacitor carbon is a premium activated carbon grade, which is purified to reduce ash below 1% and to reduce halogen and iron impurities below 100 ppm to enable extended cycling.

According to a recent study by Lux Research (Power Play: Supercapacitor Innovation for Growth in Transportation and Electronics.), the market for supercapacitors will more than double to \$836 million in 2018, up from \$466 million in 2013. Supercapacitors will grow based mainly on adoption in transportation applications like hybrid buses and micro-hybrids. Consumer electronics and wind turbines make up the other opportunities.

The key material inside supercapacitors is activated carbon, with the standard grade today providing capacitance of 100 F/g and costing around \$28/kg. According to another industry source, the average price for acceptable quality super capacitor carbon is between \$25 and \$40 per kg. For specialty applications requiring very high quality, e.g. aerospace applications, the price can be as high as \$100/kg. The current world market for super capacitor carbon is estimated to be approximately 250 to 350 MT/year. Kuraray of Japan is an important supplier of super capacitor carbon, most of which is being derived from coconut shells.

Material Characteristics of Kurray Super Capacitor Carbons

Test Parameters	Units	YP-50F	YP-80F
Total Surface Area	m ² /g	1500-1800	1900-2200
PH	PH	7-10	7-10
Moisture Content	wt%	3 Max	3 Max
Ash Content	%	Less than 1	Less than 1
Raw Material		Coconut	Coconut
Activation		steam	steam

Cosmin Laslau, Lux Research Analyst and the lead author of the report stated: "To reach the technology's full commercial potential, innovations in electrode materials are needed to drive down cost and improve performance." Graphene and nanostructured carbon are some of the materials developers are pursuing, as a higher capacity alternative to traditional activated carbon. 50F and YP-80F are powdered type activated carbons for electric double-layer capacitors. The

3) Polymer Additive

Carbonaceous materials are added to polymers for a variety of purposes. The most frequently used material is carbon black. Carbon black is virtually pure elemental carbon in the form of colloidal particles that are produced by incomplete combustion or thermal decomposition of gaseous or liquid hydrocarbons under controlled conditions. Its physical appearance is that of a black, finely divided pellet or powder. Its use in tires, rubber and plastic products, printing inks and coatings is related to properties of specific surface area, particle size and structure, conductivity and color. Carbon black is also in the top 50 industrial chemicals manufactured worldwide, based on annual tonnage. Current worldwide production is about 18 billion pounds per year [8.1 million metric tons]. Approximately 90% of carbon black is used in rubber applications, 9% as a pigment, and the remaining 1% as an essential ingredient in hundreds of diverse applications.

The price for carbon black covers a wide range, with several of them being very expensive. One of the carbon black materials we used as reference for polymer additive testing as well as adsorption testing was Cabot's BP2000, which consists of very fine particles and has very high surface area and electric conductivity. The price as quoted by one of their regional distributors was \$28.67/lbs if buying less than 88 lbs. For volumes over 88lbs the price goes down to \$27.55/lbs. Prices are FOB at Chicago. If going to somewhat bigger pearls, e.g. BP1300, the price comes down to about \$20/lbs. Powdered carbon black would be cheaper still.

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