Hydrothermal Carbonization of Stillage Products Generated from Corn Ethanol Production

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Abstract

Hydrothermal carbonization (HTC) is a platform thermochemical technology that heats wet biomass in a closed vessel at moderate temperatures (175-250°C) and pressure. The process produces a carbonized (improved C:O ratio) charcoal-like material (char) along with a liquid fraction, which can easily be separated by filtration. Additionally, previous research on microalgae has shown that fatty acids present in the system are principally absorbed on the char product [1].

HTC of whole and thin stillage from the corn ethanol industry presents an opportunity to:

- Diversify Value-added Products
  1. Char – Chemical absorbent, Low ash/sulfur solid fuel, Soil amendment
  2. Liquid Fraction – Reduce water usage by improving back-set, Liquid fertilizer
  3. Fatty Acids – Liquid transportation fuels
- Reduce Energy Usage
  - HTC uses ~80% less energy to turn thin stillage into a shelf stable product

Product diversity is important because there is concern that the DDGS (dried distillers grains and solubles) market will become saturated by industry expansion [2]. The goal of this research is to provide the corn ethanol industry with efficient and economic options.

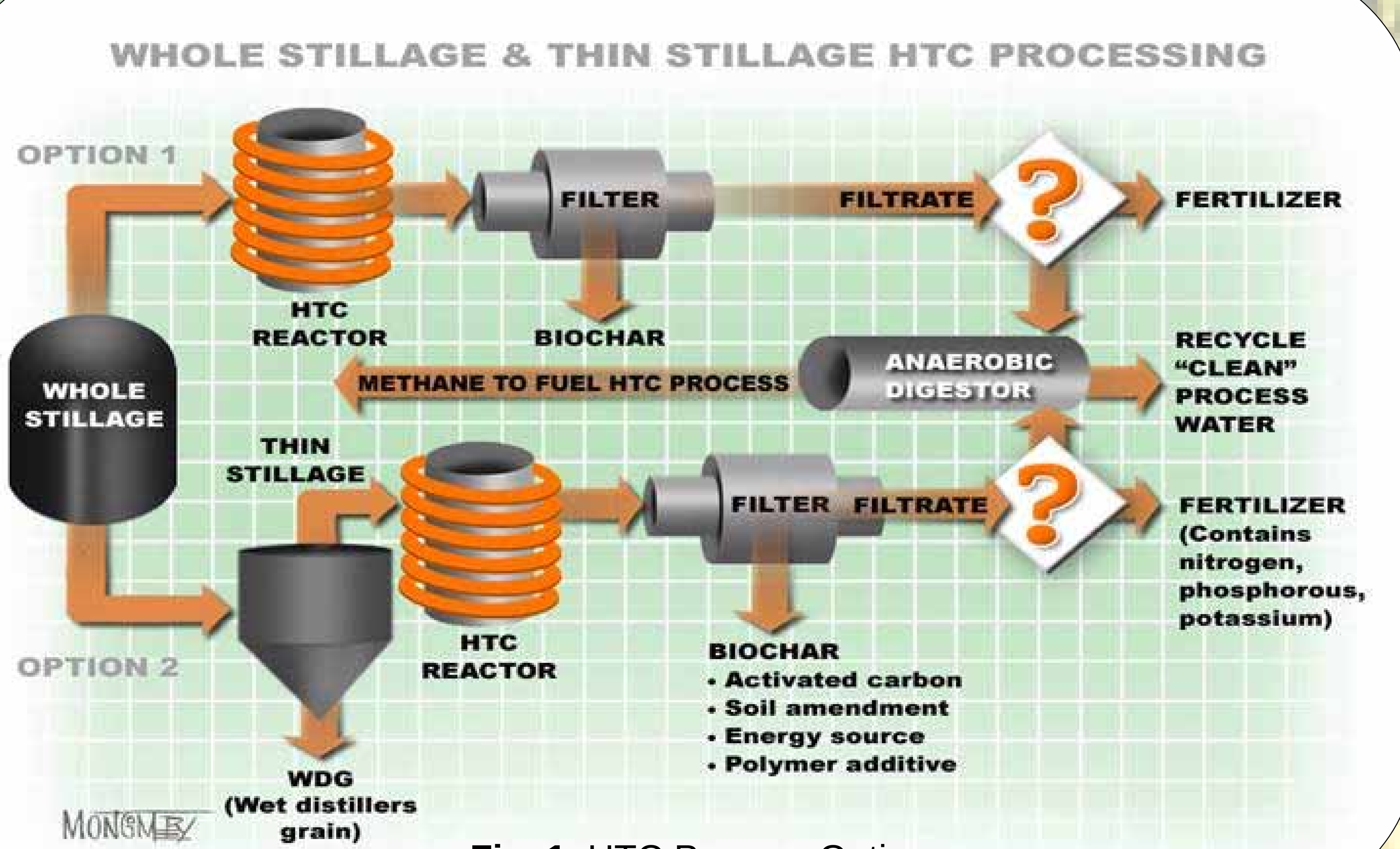


Fig. 1. HTC Process Options

Materials and methods

In a typical experiment ~250ml of stillage was added to a 450ml Parr reactor. The reactor was heated using an induction heating system. After cooling, the mixture was separated using vacuum filtration. The liquid filtrate was bottled and stored in a 4°C fridge and solid char was freeze dried. The freeze dried char was extracted by re-suspending in 8 parts methyl t-butyl ether (MTBE), shaking for 30mins, and vacuum filtering. MTBE was removed from the liquid fraction by rotary evaporation. MTBE was further removed from the char by drying at 40°C overnight.

Table 1 - Designed experiment examining the effects of reaction temperature, time, and thin stillage concentration

Temp (°C)	Time (h)	% Solids	% Mass Yield Unextracted	% Mass Yield Extracted	% Carbon of Extracted Char
200	0.5	5.3	14.16	4.15	60.45
200	0.5	9.1	15.77	6.38	61.48
200	2	5.3	19.9	6.04	66.11
200	2	9.1	16.85	7.63	65.86
240	0.5	5.3	13.81	4.38	59.68
240	0.5	9.1	17.52	6.68	59.6
240	2	5.3	10.86	4.14	48.66
240	2	9.1	20.53	7.1	51.45
220	1.25	7.2	18.73	6.08	65.28
220	1.25	7.2	16.04	6.09	62.5
220	1.25	7.2	16.95	6.08	63.98

Extracted Char HHV - 11366 BTU/lb
Fatty Acids HHV - 16461 BTU/lb

Results

In order to investigate the effects multiple variables have on process outputs, a full factorial experiment was conducted on thin stillage. Results are shown in Table 1. Linear regression models were generated for important outputs from the designed experiment.

% Mass Yield - Extracted Char
$Y1 = 5.89 – 0.24X1 + 0.42X2 + 1.14X3$

% Carbon - Extracted Char
$Y2 = 60.46 – 4.31X1 – 1.14X2 + 0.44X3$

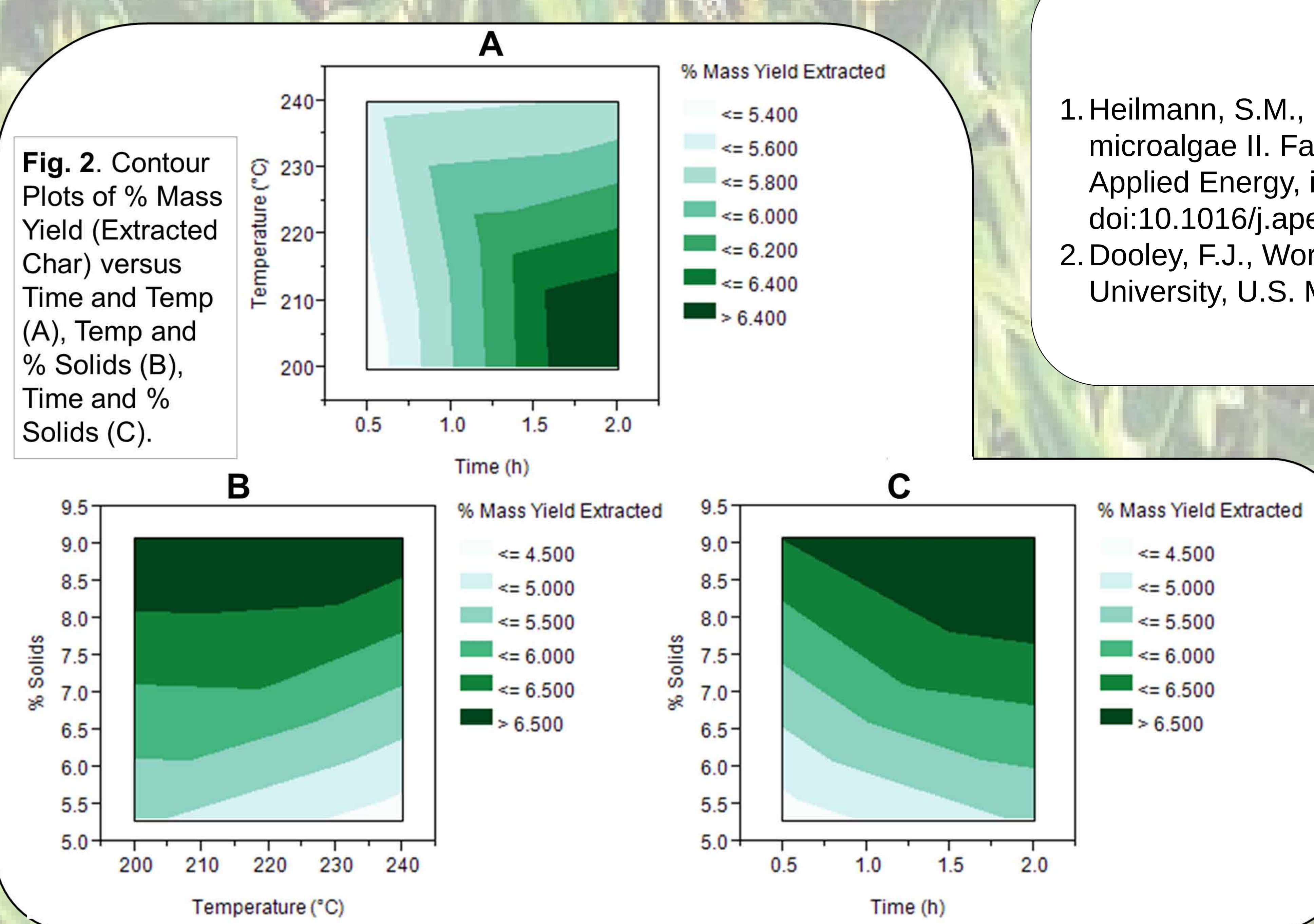
X1 = dimensionless temperature X2 = dimensionless time X3 = dimensionless % solids

Analysis of variance (ANOVA) for % mass yield model:
- % Solids, Time, Time*Temperature were statistically significant (99,98,97% confidence)

Analysis of variance (ANOVA) for % Carbon model:
- Temperature was the only significant variable (97% confidence)

Contour plots are shown in Fig. 2 to visualize the variables effects on % mass yield (extracted char). Dark green regions represent conditions that maximize extracted char yield.

Fig. 2. Contour Plots of % Mass Yield (Extracted Char) versus Time and Temp (A), Temp and % Solids (B), Time and % Solids (C).



Conclusions

- Temperature did not significantly affect % mass yield (extracted char), illustrating the potential to operate at lower temperatures (200-210°C).
- Increasing temperature had a negative effect on % carbon of extracted char, once again reinforcing the use of lower temperatures.

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Future Directions

- Designed experiment with whole stillage
- Fermentation trials with liquid filtrate back-set
- Anaerobic digestion of liquid filtrate
- Char absorption studies

References

1. Heilmann, S.M., et al., Hydrothermal carbonization of microalgae II. Fatty acid, char, and algal nutrient products. Applied Energy, in press. doi:10.1016/j.apenergy.2010.12.041.
2. Dooley, F.J., Working Paper #08-12, Dec. 2008, Purdue University, U.S. Market Potential for DDGS.

Acknowledgments

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