

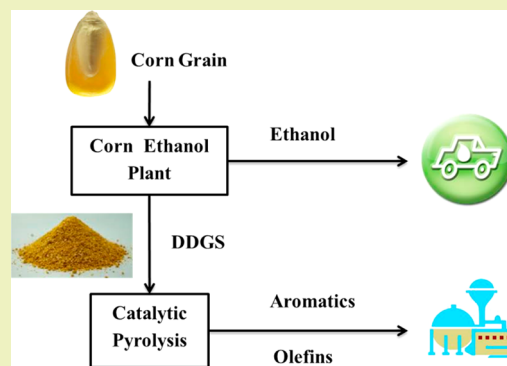
Catalytic Pyrolysis of Corn Dried Distillers Grains with Solubles to Produce Hydrocarbons

Kaige Wang and Robert C. Brown*

Center for Sustainable Environmental Technologies and Department of Mechanical Engineering, Iowa State University, 1140E Biorenewables Research Lab, Ames, Iowa 50011, United States

ABSTRACT: This paper explores dried distillers grains with solubles (DDGS) from corn ethanol production as a potential feedstock for production of hydrocarbons from catalytic pyrolysis. We found substantially higher yield of aromatics and olefins from DDGS compared with lignocellulosic biomass for pyrolysis over HZSM-5. Experiments on individual components of DDGS showed that protein and lipid account for these enhanced yields. We also found that lipids had a positive synergistic effect with other components in the DDGS, enhancing the yield of aromatics. Product distributions for HZSM-5 catalysts with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios were evaluated. The highest carbon yields of aromatics and olefins (44.5% and 12.3%, respectively) occurred for a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 30 for in-situ catalytic pyrolysis at 600 °C. Ex-situ catalytic pyrolysis using the same HZSM-5 catalyst produced lower overall yields of hydrocarbons, but the relative yields of aromatics and olefins were reversed (17.6% and 24.5%, respectively) compared to in-situ catalytic pyrolysis.

KEYWORDS: Catalytic pyrolysis, Pyrolysis, DDGS, HZSM-5, Green aromatics, Green olefins



INTRODUCTION

Production of ethanol from corn has become a major industry in the United States over the past decade, during which corn ethanol production increased 8-fold between 2000 and 2012.^{1–3} With nearly 14 billion gallons of production in 2012, corn ethanol is now 10% percent of fuel supply and 25% of all the transportation fuel produced from domestic resources in the United States.⁴ The production of corn ethanol utilizes the starch present in corn, leaving behind protein, crude fat and fibers as byproducts, which are called dried distillers grains with solubles (DDGS). For every gallon of ethanol produced, approximately 2.6 kg of DDGS are produced.⁴ The U.S. ethanol industry produced 36 million metric tons of DDGS in 2012, which is an increase of nearly 32 million metric tons over the past decade.^{1,4} Due to the expanding export opportunity on the world market, especially for Canada and the European Union,³ the U.S. corn ethanol industry is likely to grow continuously, but not necessarily at as high rates as observed in the past decade.

Currently, DDGS is primarily used as feed supplement for livestock.⁵ The supply of DDGS is likely to increase as the corn ethanol industry grows. However, the demand for DDGS by the livestock industry would be constrained by deleterious effects associated with overfeeding DDGS to cattle, including growth depression and undesirable meat quality.⁵ Moreover, price of DDGS has varied violently in the past decades, which makes the economic feasibility of corn ethanol production vulnerable.³ A previous study has also shown that feeding DDGS to beef cattle results in net increase in greenhouse gas

emissions.⁶ All of the factors combining together may have negative effect on the economic prospect of corn ethanol industry.

Various process technologies have been explored to convert DDGS into value-added bioproducts including energy, biofuel or biobased chemicals.⁴ DDGS has relatively high energy content, making it a potential feedstock for heat and power production. For example, several researchers have investigated gasification of DDGS.^{7–9} They found that the resulting syngas was produced at higher yield with higher heating value than syngas from lignocellulosic biomass. Davies et al.⁹ also demonstrated electricity generation by burning the syngas in a steam power cycle. Pyrolysis has also been well explored as a potential route for converting DDGS into biofuels or biobased materials.¹⁰ Wood et al.^{1,2} showed that yield of bio-oil produced from DDGS was comparable to that from lignocellulosic biomass. GC/MS analysis indicated that the bio-oil from microwave pyrolysis of DDGS contained both aliphatic and aromatic hydrocarbons.¹¹ Boateng's group^{12,13} pyrolyzed barley-derived DDGS, pennycress press cake and other proteinaceous biomass in a fluidized bed reactor and reported relatively higher yield of bio-oil with high-energy content compared with bio-oil from lignocellulosic biomass. They also found that bio-oil from high-protein biomass exhibited better thermal stability than bio-oil from low-protein biomass. In spite

Received: May 25, 2014

Revised: July 26, 2014

Published: August 1, 2014

Table 1. Characterization of DDGS (Oven Dry Basis)

feedstock	elemental analysis/wt %				biochemical analysis/wt %			
	C	H	N	O ^a	carbohydrates	protein	lipid	lignin
DDGS	48.8	6.6	5.4	34.1	37.3	33.5	11.3	10.4

^aCalculated by difference (100 – C – H – N – ash).

of these appealing advantages, bio-oil from proteinaceous DDGS contains substantial high content of nitrogen, which can poison catalysts during bio-oil upgrading and produce unacceptable nitrogen oxide emissions during combustion.^{1,11,14–16} A means to eliminate nitrogen from bio-oil must be devised if transportation fuels are the final products from DDGS.

Catalytic pyrolysis has been investigated to improve quality of bio-oil and zeolite catalyst has been intensively investigated due to their ability to form gasoline-range hydrocarbons.^{17–20} While many catalytic pyrolysis studies have been conducted using lignocellulosic biomass, there are few that have explored catalytic pyrolysis of protein-rich biomass. We have demonstrated that catalytic pyrolysis of microalgal biomass yields pure hydrocarbons while most of the nitrogen in the biomass is rejected as ammonia.¹⁵ A recent study by Liu et al.²¹ explored catalytic pyrolysis of DDGS using nickel-based catalyst in a fixed bed reactor. Bio-oil with high-energy content was obtained and hydrogen concentration in the gaseous products reached to 55.6 vol % using Ni–Pd– γ -Al₂O₃ as a catalyst.

The goal of this research is to explore the potential of catalytic pyrolysis of DDGS using zeolite catalyst. Catalytic pyrolysis of individual components, namely protein, lipid, and carbohydrates were also performed to investigate the contribution of each component and the interactions among the components. Different methods including adjusting the SiO₂/Al₂O₃ ratio (SAR) of the HZSM-5 catalyst and changing the contacting method of catalyst and biomass were explored to improve the product yield and distribution from catalytic pyrolysis of DDGS.

EXPERIMENTAL SECTION

Materials. DDGS samples were obtained from a local corn ethanol plant (Lincolnway Energy LLC, Nevada, IA). Oven-dried DDGS samples were grounded in a ball miller and sieved down to 200 meshes before analysis. Composition of the DDGS sample were determined and summarized in Table 1. The main components of the DDGS samples were carbohydrates, protein and crude fat, contents of which were 37.3, 33.5, and 11.3 wt %. The DDGS also contained 10.4 wt % lignin. The elemental analysis shows that DDGS contained 48.8 wt % C, 6.6 wt % H, 5.4 wt % N, and 34.1 wt % O. Protein extracted from maize and palmitic acid purchased from Sigma-Aldrich were used as model compounds for protein and lipid in DDGS. Zeolite catalysts were purchased from Zeolyst with SAR of 23, 30, and 80. Zeolite catalysts were calcined under air at 550 °C for 5 h before use.

Pyrolysis Experiments. Pyrolysis experiment was performed in a Tandem microscale reactor system from Frontier Laboratories (Rx-3050 TR). The detailed description of the reactor can be found in a previous study.²² Except where otherwise indicated, all experiments were in-situ catalytic pyrolysis (that is, the zeolite was mixed directly with the catalyst). Catalyst was mixed with DDGS samples in a ratio of 20:1 for these tests. Approximately 5 mg biomass/catalyst mixture was used in a typical in-situ test. Although no catalysts were used in the quartz tube of the second furnace of the tandem system, the temperature of the interface and second reactor were maintained at 350 °C to prevent condensation of pyrolysis products. For ex-situ catalytic pyrolysis, approximately 0.5 mg biomass sample was pyrolyzed in the first reactor and the pyrolysis vapors transported to

the second reactor, which contained 10 mg of catalyst particles. These were obtained by pelletizing the zeolite powder and sieving to 50–70 mesh. Pyrolysis products were identified by GC/MS and quantified by GC/FID/TCD. The injector temperature was 250 °C, and the total helium flow passing through the reactor was 90 mL/min. The calculated retention time was approximately 0.15 s.

For ex-situ CP, the yield of pyrolysis char generated in the first reactor and catalytic coke deposited on the catalyst in the second reactor were analyzed separately. Carbon in the char and coke product were quantified by combustion analysis using an elemental analyzer (vario MICRO cube, Elementar, USA). Since the biomass and catalyst were mixed together for in-situ CP, distinguishing between pyrolysis-derived char and catalysis-derived coke was not possible. Thus, amount of total carbonaceous residue in the mixture after reaction were quantified by combustion analysis using the elemental analyzer. Nitrogen compounds were analyzed using method described in the literature.¹⁵ The final product distribution was reported as molar carbon yield, defined as the molar ratio of carbon in a specific product to the carbon in the feedstock. Nitrogen yield was defined accordingly. All measurements were performed at least in duplicate to check the reproducibility of the data. Average data were reported with standard deviation.

RESULTS AND DISCUSSION

Effect of Reaction Temperature for Catalytic Pyrolysis of DDGS. Temperatures of 400, 500, 600, and 700 °C were tested to investigate the influence of reaction temperature on product distributions for catalytic pyrolysis of DDGS. HZSM-5 catalyst with SAR of 23 was used for this series of experiments. Carbon yields of aromatic, gaseous products, and carbonaceous residue under these reaction temperatures are compared in Figure 1.

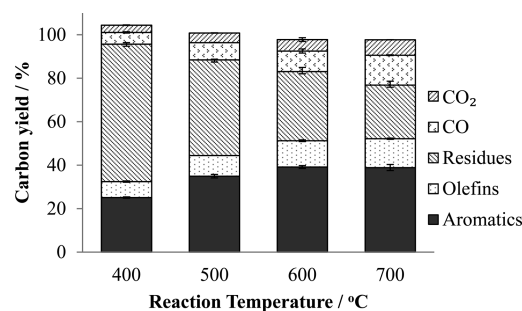


Figure 1. Product distribution from catalytic pyrolysis of DDGS using HZSM-5 under different reaction temperatures (in-situ catalysis; SiO₂/Al₂O₃ ratio = 23; catalyst to biomass ratio = 20).

Aromatics and olefins were the two major hydrocarbon products from catalytic pyrolysis of DDGS. For the reaction conditions used, aromatic hydrocarbons prevailed over olefins. Increasing reaction temperature increased yields of both hydrocarbon products. Carbon yield of aromatic hydrocarbons was 25.1% at 400 °C, increasing to 38.8% at 700 °C. Yield of olefins increased from 7.3% to 13.2% as temperature increased from 400 to 700 °C. This suggests that high reaction temperature enhanced the reaction rate of formation of hydrocarbons. Additionally, faster approach to thermodynamic

Table 2. Structures of Individual Components of Biomass

Components	H/C _{eff} ^a	Structure
Cellulose	0	
Xylan	0	
Lignin	0.3	
Corn protein	0.23	
Palmitic acid	1.75	

$$^a\text{H/C}_{\text{eff}} = (\text{H} - 2\text{O} - 3\text{N} - 2\text{S})/\text{C}$$

equilibrium as a result of higher diffusion rates with increasing temperature may also contribute to the increasing yield.²³ However, no further significant changes occurred above 600 °C. At 600 °C, yield of olefins and aromatics were 39.2% and 12.1%, respectively. Compared to lignocellulosic biomass, DDGS produced substantially higher yield of aromatics and olefins. With identical reaction conditions, yields of aromatics and olefins from switchgrass at 600 °C were only 21.1% and 5.7%, respectively.²⁴ Much of the difference in hydrocarbon yields for these two feedstocks is due to the much larger fraction of lignin in the lignocellulosic feedstock, which primarily produces solid carbonaceous residue, including char and coke, during catalytic pyrolysis.²⁴ The relatively low lignin content and higher content of fat and protein in the DDGS is expected to produce higher yields of aromatics and olefins. As subsequently described, catalytic pyrolysis of individual components found in DDGS confirm this hypothesis.

Increasing temperature also enhanced decarbonylation and decarboxylation of biomass components to form carbon oxides, especially CO as the reaction temperature becomes very high. Carbon yields of CO increased from 5.4% to 13.7% in increasing temperature from 400 to 700 °C. Carbonaceous residue decreased dramatically over this same temperature range. Alkanes such as methane, ethane and propane were also detected although the yields were very low.

A previous study has shown that nitrogen in protein is released as ammonia during catalytic pyrolysis of microalgal biomass.¹⁵ Catalytic pyrolysis of DDGS showed similar nitrogen conversion. At 400 °C, 16.2% of the nitrogen in DDGS was rejected as ammonia. The nitrogen yield of ammonia increased dramatically to 45.1% and 51.0% at 600 and 700 °C, respectively. This indicates the potential of recycling the ammonia as fertilizer for crop growth. Nitrogen also appeared in the gaseous products as hydrogen cyanide (HCN) and within the carbonaceous residue. At 400 °C, 72% of the nitrogen in the DDGS was retained in the carbonaceous residue as nitrogenous compounds. As pyrolysis temperature increased, nitrogen in the residue decreased rapidly until only 21% of the original nitrogen remained in the residue. Nitrogen compounds have been reported to increase the rate of zeolite deactivation.²⁵ Thus, a relatively higher catalyst regeneration rate is required to maintain catalyst activity when pyrolyzing DDGS compared to lignocellulose biomass, which has negligible nitrogen content. As temperature increased, nitrogen yield of HCN increased from 2% to 6% at 700 °C. This indicates that methods must be devised to remove this toxic compound from the product stream.

Catalytic Pyrolysis of Individual Components. The major components of DDGS are protein, lipid, and carbohydrates, while those for lignocellulosic biomass are cellulose, hemicellulose, and lignin. Structures of these

components are shown in Table 2. H/C_{eff} ratios of these feedstocks are also listed in Table 2. In a previous study we showed that product distributions from catalytic pyrolysis of lignocellulosic biomass depends on the composition of the biomass.²⁴ Previous studies suggest that, with the exception of lignin, feedstocks with higher H/C_{eff} ratios will produce higher yields of hydrocarbons. Thus, DDGS with its high contents of lipid and protein, should yield relatively more hydrocarbons during catalytic pyrolysis.

To investigate the contribution of protein and lipid to hydrocarbon yields from DDGS, in-situ catalytic pyrolysis was performed on corn protein and palmitic acid as model compounds. Product distributions and aromatic selectivity are summarized in Figures 2 and 3, respectively, along with results obtained in a previous study for cellulose, hemicellulose, and lignin pyrolyzed under identical reaction conditions.²⁴

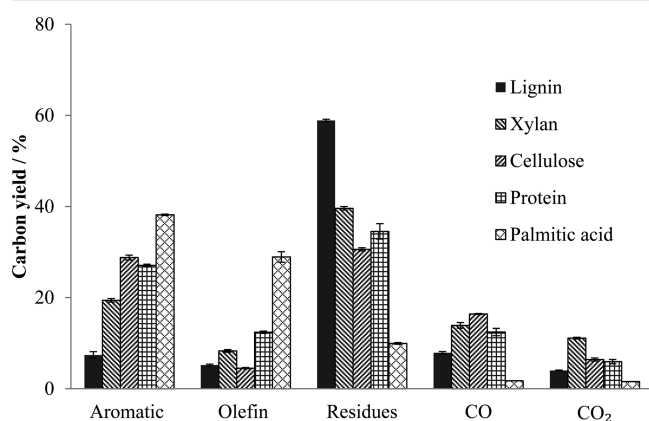


Figure 2. Product distributions for catalytic pyrolysis of individual components using HZSM-5 catalyst (in-situ catalysis; reaction temperature 600 °C; $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio = 23; catalyst to biomass ratio = 20).

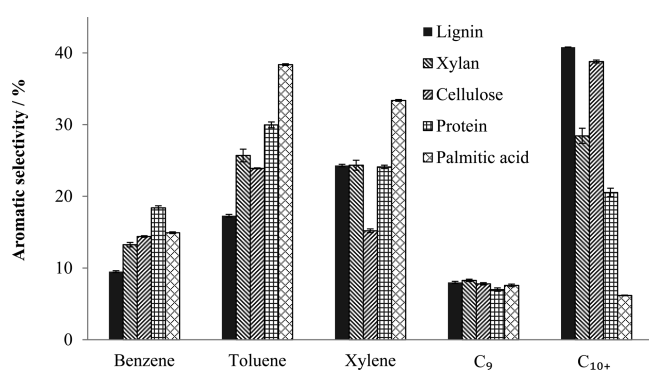


Figure 3. Aromatic selectivity for catalytic pyrolysis of individual components using HZSM-5 (in-situ catalysis; reaction temperatures 600 °C; $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio = 23; catalyst to biomass ratio = 20; C₉ includes indanes, indenenes, and alkylbenzene; C₁₀₊ includes naphthalenes and higher polyaromatics).

As shown in Figure 2, yields of aromatics and olefins from catalytic pyrolysis of palmitic acid were 38.2% and 28.9%, respectively. High yields of olefin and aromatic products obtained from palmitic acids in this study are in accordance with previous studies.^{26–28} Compared with other components of biomass, triglyceride or fatty acid in biomass has much less oxygen content and more effective hydrogen content available to form hydrocarbon over zeolite catalyst. Among all the

components, catalytic pyrolysis of palmitic acid produced the lowest carbonaceous residue yield, which was less than 10%.

Catalytic pyrolysis of protein produced a very high carbon yield of olefin: 12.4% compared with 4.5%, 8.3%, and 5.2% for pyrolysis of cellulose, hemicellulose, and lignin, respectively. The difference can be explained by the unique composition of proteins compared to the other components. Proteins are macromolecules composed of various amino acids. Non-catalytic pyrolysis of some aliphatic protein amino acids, such as valine and isoleucine, generate substantial amounts of olefins.^{29–31} In this study, we also performed noncatalytic pyrolysis of those individual components at 600 °C. Carbon yield of olefins from noncatalytic pyrolysis of corn protein was 3.4%. In comparison, olefin yields from noncatalytic pyrolysis of cellulose, hemicellulose, and lignin were 0.34%, 0.45%, and 0.24%, respectively, under identical reaction conditions. The large amounts of thermally derived olefins from corn protein may also contribute to the total olefins from catalytic pyrolysis. Moreover, compared to the components of lignocellulose, corn protein and amino acids have relatively high H/C_{eff} ratio, which is an index of the relative abundance of hydrogen in feedstocks.^{32–34} The H/C_{eff} ratio for corn protein and its major amino acids, leucine and valine, are 0.23, 1.17, and 0.80, respectively, while it is zero for both cellulose and xylan. The high H/C_{eff} ratio for corn protein and its amino acids may also account for the high yields of aromatics and olefins.

The yield of aromatics from catalytic pyrolysis of protein was 27.1%, which was comparable to the yield from cellulose. The high yield of aromatics from protein can also be explained by the structure of protein as previously described. In addition, corn protein contains large amounts of aromatic amino acids, from which noncatalytic pyrolysis can produce substantial amounts of toluene, styrene, and other aromatic hydrocarbons.^{4,31} These thermally derived aromatic hydrocarbons may also contribute to the aromatics from catalytic pyrolysis of protein.

As indicated in Figure 3, the distribution of aromatic hydrocarbons from catalytic pyrolysis of individual components also varied dramatically. DDGS components, especially lipid, showed the highest selectivity toward lower molecular weight aromatic products such as benzene, toluene, and xylene (BTX). The total selectivity for BTX was 72.5% and 86.7% for corn protein and palmitic acid, respectively, while that for cellulose, hemicellulose, and lignin was 53.5%, 63.2%, and 51.1%, respectively. In contrast, lignocellulosic components, especially lignin, were more selective toward larger aromatic compounds including naphthalenes and higher polyaromatic hydrocarbons. The selectivity difference may also be explained by the higher H/C_{eff} ratio for protein and lipid.

Synergetic Effect among Components during Catalytic Pyrolysis. Previous studies on catalytic pyrolysis indicate that a positive synergetic effect occurred when cofeeding biomass and plastics.^{35–37} Presence of hydrogen-rich plastics enhanced the yield of aromatics, which may be attributed to the interactions of abundant olefins produced from plastics and biomass-derived oxygen compounds over zeolite catalyst.³⁵ Synergetic yield benefits were also obtained from catalytic pyrolysis when biomass was coprocessed with alcohol of high H/C_{eff} ratio.^{38,39} Since plastics and fatty acids both contain long chain hydrocarbons and higher H/C_{eff} ratios, lipid compounds in DDGS might also have a positive synergetic effect on catalytic pyrolysis. To test this hypothesis, the observed carbon yields of gaseous products and aromatic hydrocarbons from

DDGS were compared with calculated yields obtained from the weighted sum of yields for the individual components of DDGS, which assumes no interactions between lipid and other components during catalytic pyrolysis

As shown in Figure 4a, the observed yield of aromatic hydrocarbons from DDGS was 52.1% higher than the

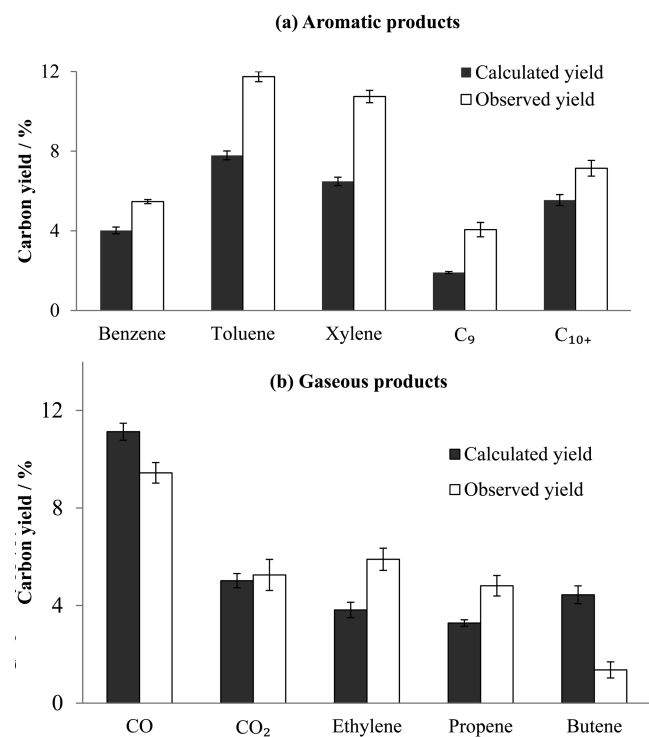


Figure 4. Comparison of observed and calculated yields of (a) aromatic hydrocarbons and (b) gaseous products from catalytic pyrolysis of DDGS using HZSM-5 (in-situ catalysis; reaction temperatures 600 °C; SiO₂/Al₂O₃ ratio = 23; catalyst to biomass ratio = 20; C₉ includes indanes, indenenes, and alkylbenzene; C₁₀₊ includes naphthalenes and higher polyaromatics; calculated yields assume no interactions among components of DDGS).

calculated yield. The enhanced aromatic yield indicates a prominent synergistic effect among the components of DDGS. Observed yields of benzene, toluene, and xylene from DDGS were 36–65% higher than the calculated yields. The observed yield of C₁₀₊ aromatics was only 10.9% higher than the predicted yield, suggesting that the synergistic effect among components favors light aromatics (BTX). These results are consistent with the recent study by Li et al. and Dorado et al.^{35,36} who have shown that cofeeding polyethylene (PE) with lignocellulosic biomass improved aromatic production from catalytic pyrolysis. A recent study showed that cofeeding hydrogen-rich propylene or higher olefins with furanic compounds over HZSM-5 increased the rate of toluene and xylene production through Diels–Alder reactions.³²

The abundant olefins produced from lipids in DDGS are expected to account for much of the enhanced selectivity toward toluene and xylene.

As shown in Figure 4b, observed and calculated yields of CO were 9.4% and 11.1% respectively. The slight decrease is expected because lipid-derived olefins increase the rate of Diels–Alder reactions, thus shifting deoxygenation from carbon monoxide-producing decarbonylation reactions to water-

producing dehydration reactions.³² Only a small difference between observed and calculated CO₂ yield was found. Observed yield of total olefins from DDGS was 12.1%, which was similar to the calculated yield 11.5%. However, the olefins yield varied between the observed and calculated values. Observed yields of ethylene and propene were higher than the calculated yields while the observed yield of butene was lower than the calculated yield.

Effect of SiO₂/Al₂O₃ Ratio of Zeolite. Changing the SiO₂/Al₂O₃ ratio (SAR) of zeolite catalyst will impact the strength of acid sites as well as the density of Brønsted acid sites. An optimum SAR of zeolite catalyst may exist for catalytic pyrolysis. Experiments were conducted using HZSM-5 with three different SAR (i.e., 23, 30, and 80) to study its effect on catalytic pyrolysis of DDGS. The product distributions for the products of the three samples are summarized in Figure 5.

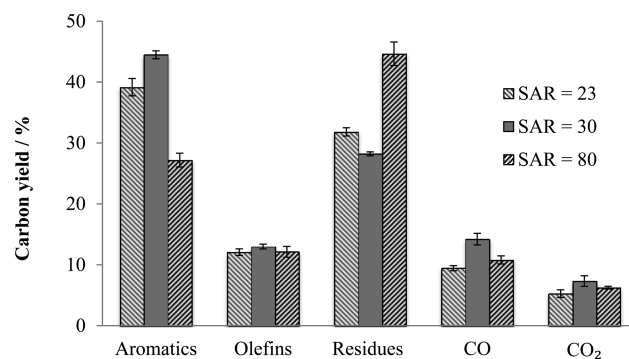


Figure 5. Product distribution from catalytic pyrolysis of DDGS using HZSM-5 with varying SAR (in-situ catalysis; reaction temperatures 600 °C; catalyst to biomass ratio = 20).

The maximum yield of aromatics occurred at SAR of 30, while no significant changes were observed for the yield of olefins for different SARs. The lowest yield of residue was also obtained for SAR of 30. A previous study of catalytic pyrolysis of glucose over HZSM-5 also showed that SAR of 30 produced the highest aromatic yield.³⁴ With increasing SAR, the density of Brønsted acid sites in the HZSM-5 crystal decreases, whereas the strength of the individual acid sites will increase. A methanol-to-olefins study showed that increased Brønsted acid site density facilitates the formation of larger coke species and enhances their rate of formation.²³ The incorporation of excessive Brønsted acid sites may promote secondary reactions responsible for converting aromatic species to coke within the micropores of zeolite. SAR of 30 may represent an optimal Brønsted acidity and density, providing maximum availability of acid site and simultaneously minimizing coke formation. The highest yield of carbonaceous residue obtained for SAR of 80. This indicates the low reactivity of pyrolysis-derived oxygenates over zeolite with low Brønsted acidity. The amount of CO produced is at maximum for the sample of SAR of 30. This agrees with our previous study of catalytic pyrolysis in which the formation of aromatic and olefins correlated with the formation of CO by decarbonylation.²⁴

Comparison of in-situ and ex-situ Catalytic Pyrolysis.

Depending upon the method of contacting catalyst and pyrolysis vapors, catalytic pyrolysis is classified as either in-situ or ex-situ. In a previous study on catalytic pyrolysis of lignocellulosic biomass we showed that ex-situ catalytic pyrolysis has the potential to produce predominantly olefins

while in-situ catalytic pyrolysis produces predominately aromatics.²² A comparison of in-situ and ex-situ catalytic pyrolysis of DDGS as feedstock is shown in Table 3 using HZSM-5 with SiO₂/Al₂O₃ ratio of 30.

Table 3. Distribution of Products for ex-situ and in-situ Catalytic Pyrolysis (CP) of DDGS^a

methods	in-situ CP	ex-situ CP
	Overall Yield/C %	
CO	14.2 ± 0.95	9.05 ± 0.13
CO ₂	7.33 ± 0.86	9.74 ± 0.75
total carbonaceous residue	28.2 ± 0.33	42.2 ± 2.19
aromatic hydrocarbons	44.5 ± 0.66	17.6 ± 0.39
olefins	12.3 ± 0.41	24.5 ± 0.65
total carbon balance	107.2 ± 3.20	103.1 ± 4.11
aromatic selectivity/%		
benzene	13.2 ± 0.14	20.6 ± 0.31
toluene	28 ± 0.62	38.2 ± 0.46
xylene	30 ± 0.11	16.1 ± 0.18
C ₉ aromatics	13.3 ± 0.71	11.3 ± 0.46
C ₁₀₊ aromatics	15.7 ± 0.15	14.1 ± 0.14
olefin selectivity		
ethylene	48.1 ± 0.64	36.6 ± 1.28
propene	39.6 ± 0.82	45.8 ± 0.55
butene	12.3 ± 0.18	17.6 ± 1.84

^aPyrolysis temperature 600 °C; HZSM-5 SiO₂/Al₂O₃ ratio = 30; catalyst bed temperature for ex-situ method 600 °C; catalyst-to-biomass ratio = 20; total carbonaceous residue is the sum of pyrolysis char and catalytic coke; C₉ includes indanes, indenenes, and alkylbenzene; C₁₀₊ includes naphthalenes and higher polyaromatics).

As shown in Table 3, the yield of aromatics by the in-situ method was 44.5%, which was much higher than the 17.6% yield using ex-situ catalytic pyrolysis. In comparison, the yield of olefins by the ex-situ method was 24.5%, which was substantially higher than for the in-situ method. Distribution of aromatic hydrocarbons showed differences between the in-situ and ex-situ methods. Selectivities of benzene and toluene for the ex-situ method were 20.6% and 38.2%, respectively, compared with 13.2% and 28% for the in-situ method. The olefin selectivity also varied for these two methods. Ethylene was the predominate olefin product for in-situ catalytic pyrolysis while propene was the predominate olefin for the ex-situ method. Differences in heat and mass transfer for the two methods may explain the differences in product distributions.²² The results suggest some flexibility in controlling product yields by changing reactor configurations.

CONCLUSION

This study found that DDGS is an attractive feedstock for producing aromatic and olefin hydrocarbons via catalytic pyrolysis, producing significantly higher yields and selectivity of desired products compared to lignocellulosic biomass. Both the protein and lipid content of DDGS contribute to this advantage, especially compared to lignin. The observed synergistic effect among the components of DDGS is likely due to the lipid content, which produces significantly higher yields of hydrogen-rich olefins compared to the other components. The optimum SiO₂/Al₂O₃ ratio for the zeolite catalyst for hydrocarbon production appears to be about 30. Olefins have previously been observed to enhance yields of hydrocarbons during copyrolysis of biomass and plastics. Both

ex-situ and in-situ catalytic pyrolysis were explored, with the former producing predominately olefins and the latter producing predominately aromatics.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +1 515 294 7934. Fax: +1 515 294 3091. E-mail address: rcbrown3@iastate.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors greatly acknowledge financial support from Iowa Energy Center (Grant No. 10-02). The authors are also grateful to Lincolnway Energy for providing the DDGS sample and Dr. Zhiyou Wen of Iowa State University for performing fatty acid analysis.

REFERENCES

- (1) Wood, C.; Muthukumarappan, K.; Rosentrater, K. A. Pyrolysis of Distillers Grains. Presented at 2012 ASABE Annual International Meeting, Dallas, TX, July, 2012.
- (2) Wood, C.; Muthukumarappan, K.; Rosentrater, K. A. Optimization of the Pyrolysis of Distillers Dried Grains with Solubles. Presented at 2013 ASABE Annual International Meeting, Kansas City, MO, July, 2013.
- (3) Dinneen, B. 2013 Ethanol Industry Outlook; Renewable Fuels Association, 2013.
- (4) Lammens, T. M.; Franssen, M. C. R.; Scott, E. L.; Sanders, J. P. M. Availability of protein-derived amino acids as feedstock for the production of bio-based chemicals. *Biomass. Bioenerg.* **2012**, *44*, 168–181.
- (5) Song, R. Lipid peroxidation in corn dried distillers grains with solubles (DDGS) and effects of feeding a highly oxidized DDGS source to swine. Ph.D. Thesis, The University of Minnesota, 2013.
- (6) Hünerberg, M.; Little, S. M.; Beauchemin, K. A.; McGinn, S. M.; O'Connor, D.; Okine, E. K.; Harstad, O. M.; Kröbel, R.; McAllister, T. A. Feeding high concentrations of corn dried distillers' grains decreases methane, but increases nitrous oxide emissions from beef cattle production. *Agr. Syst.* **2014**, *127*, 19–27.
- (7) Kumar, A.; Eskridge, K.; Jones, D. D.; Hanna, M. A. Steam–air fluidized bed gasification of distillers grains: Effects of steam to biomass ratio, equivalence ratio and gasification temperature. *Bioresour. Technol.* **2009**, *100*, 2062–2068.
- (8) Tavasoli, A.; Ahangari, M. G.; Soni, C.; Dalai, A. K. Production of hydrogen and syngas via gasification of the corn and wheat dry distiller grains (DDGS) in a fixed-bed micro reactor. *Fuel Process. Technol.* **2009**, *90*, 472–482.
- (9) Davies, A.; Soheilian, R.; Zhuo, C.; Levendis, Y. A. Pyrolytic Conversion of Biomass Residues to Gaseous Fuels for Electricity Generation. *J. Energy Resour.* **2013**, *136*, 021101–021101.
- (10) Mohan, D.; Pittman, C. U.; Steele, P. H. Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review. *Energy Fuel.* **2006**, *20*, 848–889.
- (11) Lei, H. W.; Ren, S. J.; Wang, L.; Bu, Q.; Julson, J.; Holladay, J.; Ruan, R. Microwave pyrolysis of distillers dried grain with solubles (DDGS) for biofuel production. *Bioresour. Technol.* **2011**, *102*, 6208–6213.
- (12) Boateng, A. A.; Mullen, C. A.; Goldberg, N. M. Producing Stable Pyrolysis Liquids from the Oil-Seed Presscakes of Mustard Family Plants: Pennycress (*Thlaspi arvense* L.) and Camelina (*Camelina sativa*). *Energy Fuel.* **2010**, *24*, 6624–6632.
- (13) Mullen, C.; Boateng, A. Production and Analysis of Fast Pyrolysis Oils from Proteinaceous Biomass. *BioEnergy Res.* **2011**, *4*, 303–311.
- (14) Mullen, C. A.; Boateng, A. A.; Hicks, K. B.; Goldberg, N. M.; Moreau, R. A. Analysis and Comparison of Bio-Oil Produced by Fast

Pyrolysis from Three Barley Biomass/Byproduct Streams. *Energy Fuel* **2010**, *24*, 699–706.

(15) Wang, K.; Brown, R. C. Catalytic pyrolysis of microalgae for production of aromatics and ammonia. *Green Chem.* **2013**, *15*, 675–681.

(16) Wang, K.; Brown, R. C.; Homsy, S.; Martinez, L.; Sidhu, S. S. Fast pyrolysis of microalgae remnants in a fluidized bed reactor for bio-oil and biochar production. *Bioresour. Technol.* **2013**, *127*, 494–499.

(17) Carlson, T. R.; Jae, J.; Lin, Y.-C.; Tompsett, G. A.; Huber, G. W. Catalytic fast pyrolysis of glucose with HZSM-5: The combined homogeneous and heterogeneous reactions. *J. Catal.* **2010**, *270*, 110–124.

(18) Carlson, T. R.; Tompsett, G.; Conner, W.; Huber, G. Aromatic Production from Catalytic Fast Pyrolysis of Biomass-Derived Feedstocks. *Top. Catal.* **2009**, *52*, 241–252.

(19) Lappas, A. A.; Kalogiannis, K. G.; Iliopoulou, E. F.; Triantafyllidis, K. S.; Stefanidis, S. D. Catalytic pyrolysis of biomass for transportation fuels. *Wiley Interdiscip. Rev.: Energy Environ.* **2012**, *1*, 285–297.

(20) Mihalcik, D. J.; Mullen, C. A.; Boateng, A. A. Screening acidic zeolites for catalytic fast pyrolysis of biomass and its components. *J. Anal. Appl. Pyrol.* **2011**, *92*, 224–232.

(21) Liu, W.-w.; Wang, X.-p.; Hu, C.-w.; Tong, D.-m.; Zhu, L.-f.; Li, G.-y. Catalytic pyrolysis of distillers dried grain with solubles: An attempt towards obtaining value-added products. *Int. J. Hydrogen Energy* **2014**, *39*, 6371–6383.

(22) Wang, K.; Johnston, P. A.; Brown, R. C. Comparison of in-situ and ex-situ catalytic pyrolysis in a micro-reactor system. *ACS Sustainable Chem. Eng.*, accepted for publication.

(23) Mores, D.; Kornatowski, J.; Olsbye, U.; Weckhuysen, B. M. Coke Formation during the Methanol-to-Olefin Conversion: In Situ Microspectroscopy on Individual H-ZSM-5 Crystals with Different Brønsted Acidity. *Chem.–Eur. J.* **2011**, *17*, 2874–2884.

(24) Wang, K.; Kim, K. H.; Brown, R. C. Catalytic pyrolysis of individual components of lignocellulosic biomass. *Green Chem.* **2014**, *16*, 727–735.

(25) Caeiro, G.; Magnoux, P.; Ayrault, P.; Lopes, J. M.; Ribeiro, F. R. Deactivating effect of coke and basic nitrogen compounds during the methylcyclohexane transformation over H-MFI zeolite. *Chem. Eng. J.* **2006**, *120*, 43–54.

(26) Benson, T. J.; Hernandez, R.; White, M. G.; French, W. T.; Alley, E. E.; Holmes, W. E.; Thompson, B. Heterogeneous Cracking of an Unsaturated Fatty Acid and Reaction Intermediates on H+ZSM-5 Catalyst. *Clean Soil, Air, Water* **2008**, *36*, 652–656.

(27) Lestari, S.; Mäki-Arvela, P.; Beltramini, J.; Lu, G. Q. M.; Murzin, D. Y. Transforming Triglycerides and Fatty Acids into Biofuels. *ChemSusChem* **2009**, *2*, 1109–1119.

(28) Weisz, P. B.; Haag, W. O.; Rodewald, P. G. Catalytic Production of High-Grade Fuel (Gasoline) from Biomass Compounds by Shape-Selective Catalysis. *Science* **1979**, *206*, 57–58.

(29) Simmonds, P. G.; Medley, E. E.; Ratcliff, M. A.; Shulman, G. P. Thermal decomposition of aliphatic monoaminomonocarboxylic acids. *Anal. Chem.* **1972**, *44*, 2060–2066.

(30) Ratcliff, M. A.; Medley, E. E.; Simmonds, P. G. Pyrolysis of amino acids. Mechanistic considerations. *J. Org. Chem.* **1974**, *39*, 1481–1490.

(31) Tsuge, S.; Matsubara, H. High-resolution pyrolysis-gas chromatography of proteins and related materials. *J. Anal. Appl. Pyrol.* **1985**, *8*, 49–64.

(32) Cheng, Y.-T.; Huber, G. W. Production of targeted aromatics by using Diels-Alder classes of reactions with furans and olefins over ZSM-5. *Green Chem.* **2012**, *14*, 3114–3125.

(33) Cheng, Y.-T.; Jae, J.; Shi, J.; Fan, W.; Huber, G. W. Production of Renewable Aromatic Compounds by Catalytic Fast Pyrolysis of Lignocellulosic Biomass with Bifunctional Ga/ZSM-5 Catalysts. *Angew. Chem.* **2012**, *124*, 1416–1419.

(34) Foster, A. J.; Jae, J.; Cheng, Y.-T.; Huber, G. W.; Lobo, R. F. Optimizing the aromatic yield and distribution from catalytic fast

pyrolysis of biomass over ZSM-5. *Appl. Catal., A* **2012**, *423–424*, 154–161.

(35) Dorado, C.; Mullen, C. A.; Boateng, A. A. H-ZSM5 Catalyzed Co-Pyrolysis of Biomass and Plastics. *ACS Sustainable Chem. Eng.* **2013**, *2*, 301–311.

(36) Li, X.; Zhang, H.; Li, J.; Su, L.; Zuo, J.; Komarneni, S.; Wang, Y. Improving the aromatic production in catalytic fast pyrolysis of cellulose by co-feeding low-density polyethylene. *Appl. Catal., A* **2013**, *455*, 114–121.

(37) Zhang, H.; Nie, J.; Xiao, R.; Jin, B.; Dong, C.; Xiao, G. Catalytic co-pyrolysis of biomass and different plastics (PE, PP, PS) to improve hydrocarbon yield in a fluidized bed reactor. *Energy Fuels* **2014**, *28*, 1940–1947.

(38) Zhang, H.; Carlson, T. R.; Xiao, R.; Huber, G. W. Catalytic fast pyrolysis of wood and alcohol mixtures in a fluidized bed reactor. *Green Chem.* **2012**, *14*, 98–110.

(39) Chen, N. Y.; Walsh, D. E.; Koenig, L. R. In *Pyrolysis Oils from Biomass*; American Chemical Society: Washington, D.C., 1988; Chapter 24, pp 277–289.