Hydrothermal Liquefaction of Coffee Pulp Wastes: Effect of Ozonolysis Pretreatment and Operating Conditions on Biocrude Yield

ORAL
Ph.D. Student: N
Journal: NONE

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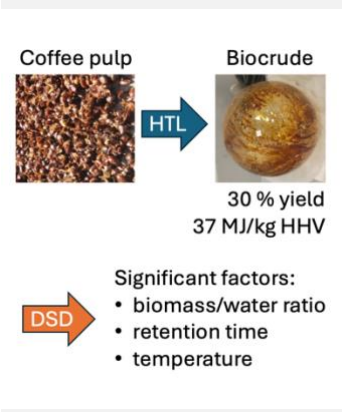

Hydrothermal liquefaction of agricultural wastes is a promising technology to produce sustainable fuels. This research aimed to evaluate the effect of ozonolysis pretreatment and some operating conditions (particle size, biomass/water ratio, retention time, pH, and temperature) on the biocrude yield obtained from the hydrothermal liquefaction of coffee pulp wastes. The evaluation was done using a definitive screening design which revealed that, under the studied conditions, only the biomass/water ratio, the retention time, and the reaction temperature have a significant effect on the biocrude yield. The ozonolysis pretreatment produced low delignification of the biomass (6-13 %) and therefore, its impact on biocrude yield was low. It is hypothesized that larger ozonolysis pretreatment times are required to generate a significant impact on the biocrude yield. This research provides a valuable reference for using ozone in alternative applications such as biomass waste valorization.

Introduction

One of today's most significant engineering challenges is to provide our society with sustainable fuels produced by low-carbon footprint processes. One potential technology is hydrothermal liquefaction (HTL) of biomass. HTL is a thermochemical process that utilizes water and moderate temperatures (250-550 ºC) and pressures (5-15 MPa) to transform biomass into a biocrude that can later be upgraded to traditional liquid fuels. Biocrude yield and properties depend on many variables, e.g., the operating conditions, nature of the biomass, and use of pretreatments or catalysts. In the case of lignocellulosic materials, higher biocrude yields are obtained from biomasses with high cellulose and hemicellulose content. Lignin tends to hinder the process performance because it is considered one of the major obstacles to an energy-efficient biomass deconstruction process [1]. However, lignin is highly reactive toward ozone [2]; consequently, ozonolysis pretreatment of the biomass can potentially reduce its lignin content leading to better biocrude yields and properties.

The main objective of this research was to determine the effect of ozonolysis pretreatment and some HTL operating conditions (particle size, biomass/water ratio, retention time, pH, and temperature) on the biocrude yield obtained from the hydrothermal liquefaction of coffee pulp wastes, one of the most abundant agriculture wastes generated worldwide.

Material and Methods

HTL of coffee pulp wastes from a coffee mill in Costa Rica was carried out in a 300 mL mini reactor (Parr 4560). The statistical analysis was performed following a definitive screening design (DSD) where six factors at three different levels were studied (ozonolysis pretreatment time: 0, 10, 20 min; particle size: 1, 2, 3 mm, HTL biomass/water ratio: 0.30, 0.45, 0.60; HTL retention time: 60, 90, 120 min; HTL pH: 4, 7, 10; HTL temperature: 200, 250, 300 ◦C). Seventeen experiments were carried out, and the optimization response variable was the biocrude yield. Lignin degradation due to ozonolysis was determined for experiments where ozone was applied. Ozonation experiments were carried out in a 5 L reactor with constant gas flow rate (5 L/min), ozone generation (4.8 g/h), agitation (200 rpm), and biomass/water load ratio (30/70). Coffee pulp wastes were characterized (HHV, moisture, cellulose, hemicellulose, lignin, and ash content) as the obtained biocrude (GC/MS, RMN, CHONS, TGA, and HHV).

Results and Discussion

Biocrude yields obtained in the DSD experiments ranged from 10 % to 28 %, as shown in Figure 1. These yields represent good results according to other reports found in the literature [3]. The first step in the statistical analysis was to determine the factors that significantly affected the response variable. The initial analysis of variance (ANOVA) for the biocrude yield, including all the factors, revealed that none of the factors were significant ($p \leq 0.05$). To increase the degrees of freedom for the error sum of squares, the sums of squares of the less critical factors were pooled into the error term. Table 1 shows the final ANOVA, including only the significant factors ($p \leq 0.05$). The biomass/water ratio, the retention time, and the reaction temperature

resulted in a substantial effect on the biocrude yield. The ozonolysis pretreatment, the particle size, and the pH showed no significant influence on the process performance. The validation experiment carried out under the optimal conditions (2 mm particle size, no ozonolysis pretreatment, 30 % biomass/water ratio, 90 min retention time, pH=7, and 250 °C reaction temperature) gave 30 % biocrude yield. This result confirmed the optimization process.

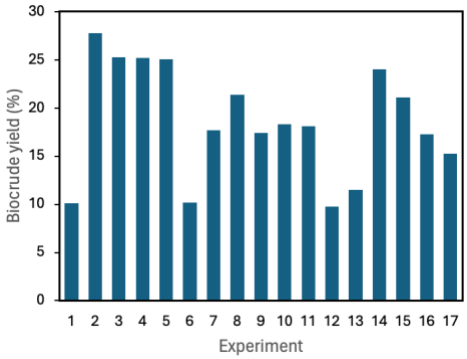

Figure 1. Biocrude yield obtained under the DSD conditions.

Table 1. Final ANOVA after pooling the sum of squares of minor factor variances.

Source of variation	Sum of squares	Mean square	p-value
Biomass/water ratio	0.0147	0.0074	0.0130
Retention time	0.0129	0.0064	0.0194
Reaction temperature	0.0156	0.0078	0.0113
Error (pooled)	0.0107	0.0010	

The delignification produced by the ozonolysis pretreatment was no larger than 13 % (see Figure 2). This result might explain why this factor was not statistically significant on the biocrude yield. Larger ozonolysis pretreatment times might be required to observe an important effect of this factor on HTL biocrude yield. Other researchers [4-5] have obtained biomass delignification of 30-60 % by applying ozone for approximately two hours.

The following properties were obtained for the coffee pulp wastes: 88 % moisture, 19 % cellulose, 24 % hemicellulose, 18 % lignin, and 23.13 MJ/kg HHV. The obtained biocrude presented 39 % carbon content and was comprised mainly of aromatic, phenolic, and fatty acid compounds with an HHV of 37.10 MJ/kg.

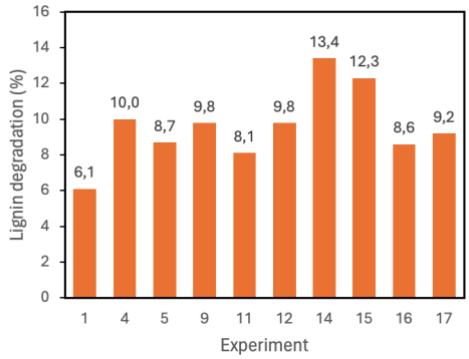

Figure 2. Lignin degradation obtained in the experiments with ozonolysis pretreatment.

Conclusions

Biocrude with a 30 % yield and 37.10 MJ/kg HHV was obtained from the HTL of coffee pulp wastes. DSD experimental design revealed that the biomass/water ratio, retention time, and reaction temperature significantly affected the biocrude yield. The ozonolysis pretreatment showed no important effect on the HTL process; larger ozonolysis pretreatment times are probably required to delignificate the pulp waste and produce higher biocrude yields.

Acknowledgments

The authors acknowledge the School of Chemical Engineering and the Vicerrectory of Research of the University of Costa Rica for their financial support.

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