OIL PRODUCTION FROM CATALYTIC HYDROTHERMAL LIQUEFACTION OF CORN STOVER WITH AQUEOUS PHASE RECYCLING

Chris Ian L. Avendaño[1], Rowena B. Carpio[2] , Gino Apollo M. Guerrero[3], Monet Concepcion M. Detras[4], Manolito E. Bambase, Jr.[5]
Department of Chemical Engineering, University of the Philippines Los Baños, College, Batong Malake, Los Baños Laguna, 4031, Philippines.
[1]clavendano@up.edu.ph, [2]rbcarpio@up.edu.ph, [3]gmguerrero@up.edu.ph, [4]mmdetras@up.edu.ph, [5]mebambase@up.edu.ph

INTRODUCTION

Hydrothermal liquefaction (HTL) is a thermochemical process that can convert biomass feedstock to liquid biofuel. Unlike other methods, HTL uses water as the reaction medium, thus, making it suitable for wet feedstocks, such as agricultural residuals. Lignocellulosic (LC) biomasses are an inexpensive, abundant, and renewable source for biofuel production. Under typical HTL conditions, the oil production of high-lignin-containing biomass is suppressed by high solid formation. However, using an alkali catalyst such as K_2CO_3 was reported to enhance the oil yield and reduce the solid/char formation during HTL of some LC biomass such as barley straw [1]. Furthermore, recycling of aqueous phase (AP) into the HTL process was successfully demonstrated using barley straw [1]. This process will be crucial for the industrial scale of HTL to achieve environmental and economic sustainability.

Maize (or corn) is a major crop in the Philippines, with 7.8 MMT production in 2018 (PSA, 2019), which generates tremendous amounts of waste that are underutilized. For the first time, this study explored the oil production from HTL of corn stover (CS) from our locally-grown corn plant with K_2CO_3 as a catalyst and recycled AP as part of the reaction medium.

A survey of the performance of different LC biomass of different ecotypes and planting origins is crucial in developing a scale-up of this technology to efficiently convert different types of biomass into biofuel.

METHODOLOGY

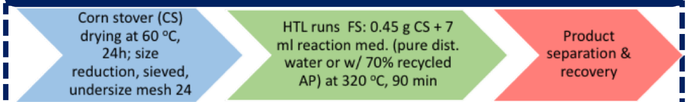

Fig. 1. Ground corn stover (L) & HTL reactors (R)

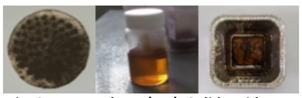

Fig. 2. HTL products (L-R): Solid residue, Aqueous phase, & Biocrude oil

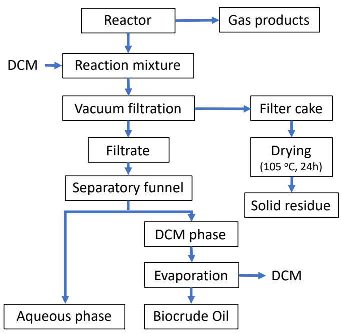

Fig. 3. Product separation procedure

Table 1. Experimental factors and levels

Factors	Levels
Aqueous phase recycling	0 up to 3rd level
K_2CO_3 catalyst (% w/w dried CS)	0 or 5%

Notes: **Corn stover (CS)** from locally-grown variant waxy corn Macapuno, National Seed Found., UPLB; **Reactor**: 316 SS Swagelok union and caps, 8.5 ml cap; **Oil extrac. solvent**: Dichloromethane (DCM), 30 ml; **Oil and solid residue yield**: estimated by gravimetry; **Stat. analysis**: ANOVA and Duncan's multiple range test, $p \leq 0.05$; **Oil quality**: GC-MS

References:
1. Zhu, Z., Rosendahl, L., Sohail, S., Yu, D., Chen, G., 2015. Hydrothermal liquefaction of barley straw to bio-crude oil : Effects of reaction temperature and aqueous phase recirculation. Appl. Energy 137, 183–192.
2. Yin, S., Tan, Z., 2012. Hydrothermal liquefaction of cellulose to bio-oil under acidic, neutral and alkaline conditions. Appl. Energy 92, 234–239.
3. Álvarez-Flórez, J., Egusquiza, E., 2015. Analysis of damage caused by siloxanes in stationary reciprocating internal combustion engines operating with landfill gas. Eng. Fail. Anal. 50, 29–38

RESULTS AND DISCUSSIONS

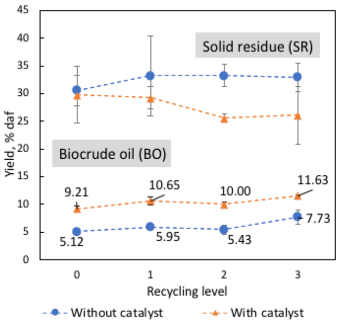

Fig. 4. Effect of catalyst and aqueous phase (AP) recycling on biocrude oil and solid residue yields

- Significant factor(s) affecting SR yield: catalyst only
- Significant factor(s) affecting BO yield: both catalyst and aqueous phase recycling
- SR yield: decreased with cat.; improved conversion with cat.; K^+ catalyzes biomass decomp. under hydrothermal conditions
- BO yield: general increased after 3rd recycling; 50-80% higher w/ cat. than w/o cat. at the same levels of recycling
- Reaction medium: Cat. pH = 11.3; Non-Cat pH = 3.85 – 6.61;

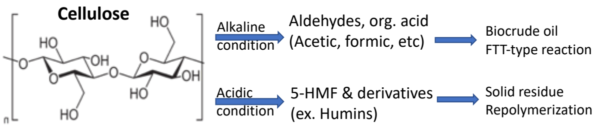

Fig. 5. Degradation of cellulose under alkali and acidic conditions [2]

- Oil yield obtained is lower than the values reported for most LC biomasses (including corn stover) in the literature; limitation of reactor – no mixing, no purging air, no charging of initial pressure

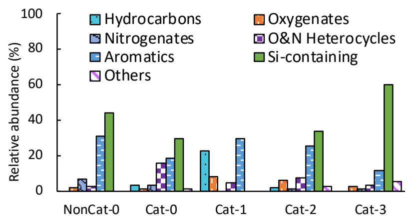

Fig. 6. Analysis of biocrude oil

- Oil is generally rich in aromatic and Si-containing compds (mainly silanes and siloxanes); Corn plant is considered a Si accumulator

- After 3rd recycling, oil is mainly Si-containing compounds - with long-chain hydrocarbon and several benzene rings; less polar, partition to organic solvent (DCM) during oil extraction
- Si-containing compounds can provide high thermal stability and good lubricating property in oil; Siloxanes may damage internal combustion engines upon combustion [3]; other applications: as inert fluid, functional fluid, coatings membranes, and geopolymer coupling agent.

CONCLUSIONS

The study successfully demonstrated the benefits of K_2CO_3 catalyst and aqueous phase recycling on oil production of corn stover derived from our locally-grown corn plant variant via HTL. However, the oil produced could be detrimental for fuel applications due to its rich Si-containing compounds. Future directions of this project include 1) performing a screening experiment using different alkali catalysts for better oil yield and quality; (2) conducting a more comprehensive parametric and optimization study; (3) investigating the effect of lignin content and its relative ratio to cellulose and hemicellulose on oil production of LC biomass; (4) investigating the limit of the number of sequential aqueous phase recycling that will not produce inhibitory compounds in oil formation or harm the HTL process.

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