Direct Solvothermal Liquefaction of *Pennisetum purpureum* Biomass to Produce Biocrude Using Ethanol Solvent

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**Abstract.** Direct solvothermal liquefaction was used in converting the lignocellulosic biomass, *Pennisetum purpureum* or Napier grass using ethanol as solvent. Liquefaction of Napier grass resulted in a dark and viscous bio-crude product and exhibited promising yields (34.6377% to 48.6267%). It was determined that the effects of temperature and residence time were statistically significant with the residence time having the greatest positive effect on yield. High yields of bio-crude from Napier grass seem to occur when solvothermal temperature, residence time increased and as solids ratio decreased. However, elemental analysis showed that the bio-crude produced needs to undergo deoxygenation (O: 14.25 – 49.42%) before mixing with petroleum. For the higher heating value (HHV), the parameters observed in the study were statistically insignificant, however, temperature was determined to have the greatest positive effect on HHV. It was observed that high HHV bio-crude were produced at high temperatures, low solids ratio, and low residence times. The acquired averages for the HHV (20.0333 MJ/kg to 29.7744 MJ/kg) were all higher than the HHV of the Napier grass sample used in the study (12.9394 MJ/kg). It was observed in the study, that even though solids ratio has the least effect on both responses, the choice of solids ratio is dependent on its interaction effects with the other parameters as its effects contribute to the observed responses.

1. Introduction
The modern world is highly dependent on energy. About 96.7% of 9425 Mtoe of the total final consumption of the world by fuel in 2014 depends on oil, natural gas, coal, and other non-renewable energy sources and about 98.6% of 13699 Mtoe of the total primary energy supply by fuel in 2014 were non-renewable [1].

The continuous use of non-renewable energy sources may lead to a drastic decrease in supply resulting to different environmental issues. These led to researches on the discovery to use renewable energy sources including the use of chemical, geothermal, hydro, solar, and wind energy.

For the worldwide consumption of 15 TW of power for the year 2004, it was observed that solar energy has a high potential as its energy sources amount to 89000 TW. One means of extracting solar energy is through the indirect use of solar energy sinks such as lignocellulosic biomasses.

Bio-energy is the renewable energy stored in lignocellulosic biomasses in the form of chemical compounds, namely cellulose, hemicellulose, and lignin. Biomass most commonly refers to plant-derived organic matter. It was estimated to contribute about 10 – 14% of the primary energy supply of the globe [2].
One particular lignocellulosic biomass, Pennisetum purpureum, or commonly known as Napier grass, is a robust, reed-like perennial grass. This biomass has caught the attention of many researchers due to its unique characteristics. A specific study mentioned that Napier grass shows promise as a source for the acquisition of new products such as composites, cellulose derivatives, and biofuels [3].

In light of this, several methods to extract energy from the interconnected simple sugars present in cellulose and hemicellulose were developed [4]. Thermochemical conversion is the most used method in upgrading biomass to much more valuable products [5]. Hydrothermal liquefaction involves the use of water and possibly catalysts to directly liquefy pretreated lignocellulosic biomass resulting in the latter converting to liquid oil at temperatures below 400 °C [6].

However, due to the extreme operating conditions of hydrothermal liquefaction, other solvents such as ethanol may be used [7], [8]. Hence, solvothermal liquefaction was utilized in converting Napier grass as this opens up another potential energy source without compromising the environment since the use of renewable fuels from biomass provides for a carbon neutral energy source [7], [9], [4]. The effects of temperature, solids ratio, and residence time on the higher heating value (HHV), yield, and elemental components of the bio-crude were investigated in the study.

2. Materials and methodology

2.1. Preparation of biomass samples
The Napier grass samples collected from the Dairy Training and Research Institute in the University of the Philippines Los Baños were dried, milled, and sieved (Mesh 20-80). The particle size used in the study were the bottoms of the 80-mesh sieve (<0.177 mm). Water displacement method using a 10-mL graduated cylinder was performed to determine the density of the fine Napier grass samples used.

2.2. Effects of parameters
The study focused on three parameters: temperature, solids ratio, and residence time. Using a fractional factorial design of experiment, the low- and high-level of each factor is shown in Table I. From this, necessary calculations for the amounts of biomass and solvent needed were performed based on the allowable volume of 4.5 mL of the reactor, and solids ratio, 10% and 20%, to be used in the study.

2.3. Solvothermal liquefaction
The liquefaction process was done in a sand bath heater with temperature control. The temperature of the reactor was allowed to reach the desired operating temperature, 230°C and 250 °C, before starting the countdown on the residence time, either 30 minutes or 60 minutes.

After the liquefaction process, the reactors were immediately quenched in running water. The product was extracted from the reactors using ethanol and was passed through a filter paper. The excess solvent was then allowed to evaporate before transferring into a vial. Further evaporation of the bio-crude was done until a constant mass was achieved.

2.4. Response and analysis
Once the bio-crude inside the vial achieved constant mass, the yield was calculated based on the amount of dried biomass used in the liquefaction process and the final mass of the bio-crude product.

For the HHV, around 0.2 g of each bio-crude product was added with ethylene glycol making sure that the total mass did not exceed 2 g. This was then subjected to bomb calorimetry in the Chemical Engineering Analytical Laboratory of the University of the Philippines – Diliman. One sample for each run was sent for elemental analysis at the Department of Science and Technology to determine its hydrogen to carbon and oxygen to carbon ratios.

Statistical analysis was performed to determine the main effects with the aid of a statistical software, Minitab 17. The necessary statistics plots were also generated to determine the significance of the effects of each parameter on the response with a significance level $\alpha$ of 5%.
Table 1. Value of Low- and High-Level for each Factor

| Factor                        | Variation Interval |
|-------------------------------|--------------------|
|                               | Low Level | Basic Level | High Level |
| Temperature (°C), x1          | 230        | 240         | 250        |
| Solids Ratio (%), x2          | 10         | 15          | 20         |
| Residence Time (min), x3      | 30         | 45          | 60         |

3. Results and discussion

3.1. Biocrude synthesis
The study was successful in producing bio-crude by directly subjecting Napier grass to solvothermal liquefaction. Directly subjecting refers to liquefaction of the biomass without any chemical pretreatment performed. This was a concern in the study due to Napier grass having high lignin content, 30.40% [3] From this, it can be inferred that solvothermal liquefaction is capable of converting lignocellulosic biomass without pretreatment or catalyst. This also showed that Napier grass is indeed a promising lignocellulosic biomass for the production of different valuable materials as mentioned by [3].

3.2. Elemental analysis of biocrude and parameter effects
One way of determining the quality of bio-crude produced is through its elemental components. Results for the Elemental analysis of bio-crude produced along with a comparison of the typical ranges for the elemental components of petroleum are shown in Table II.

The % w/w of O was calculated by difference with the assumption that the % w/w of S is negligible. Determination of the elemental components of bio-crude is essential as bio-crude is used as an amendment to petroleum in refineries to address the demand for conventional fuels [10]. However, Table 2 shows that the elemental components of the crude produced does not fall between the ranges of the typical values for petroleum. This is the reason why direct use of bio-crude as transportation fuels prove to be a challenge, as it requires chemical modifications such as oxygen removal and molecular weight reduction to increase volatility, thermal stability and reduce viscosity [11].

It was observed in the study that increasing the levels of both temperature and solids ratio results in decreased atomic H/C ratio and that the inverse was true for the residence time. As with [11], an increase in temperature lead to an increase in the carbon content of the product resulting to a decrease in the atomic H/C ratio.

It was also observed through a Pareto Chart that the solids ratio had the greatest (0.2811) on the atomic H/C ratio, followed by temperature (0.2613), and then the residence time (0.2464). However, all parameters were insignificant to the response.

Table 2. Elemental Analysis of Bio-crude per run in % w/w Dry Basis

| Run | Run | Run | Run | Petroleum (Speight, 2006) |
|-----|-----|-----|-----|--------------------------|
|     | 1.1 | 2.1 | 3.1 | 4.1                       |
| C   | 41.8| 55.4| 62.0| 74.6| 83.0 – 87.0               |
| H   | 7.42| 7.49| 8.28| 9.87| 10.0 – 14.0               |
| N   | 1.36| 2.40| 1.05| 1.28| 0.10 – 2.00               |
| O   | 49.4| 34.7| 28.7| 14.3| 0.05 – 1.50               |
| H/C | 2.13| 1.62| 1.60| 1.59| -                         |
| O/C | 0.887| 0.470| 0.347| 0.143| -                         |
3.3. Higher heating value of biocrude produced and parameter effects

Another measure of the quality of bio-crude is its HHV. Table III shows the acquired HHV of each sample from bomb calorimetry.

It can be seen that the acquired average for the HHV ranges from around 20 to 30 MJ/kg, which is higher than the HHV of the Napier grass sample used, 12.9394 MJ/kg. This shows an increase of 54.82% for the lowest average, and an increase of 130.11% for the highest average. As a comparison, the acquired HHV in the study has a wider range (12.71 to 35.34 MJ/kg) compared to other studies: 28 to 34 MJ/kg [12], 27.9 to 33.8 MJ/kg [13], 32 to 34.7 MJ/kg [14], 35.9 to 39.6 MJ/kg [10], and 22.74 to 30.68 MJ/kg [11] due to the presence of an outlier.

It was observed in the study that an increase in the level of both temperature and solids ratio results in an increase in HHV, while the opposite was true for the residence time. This follows the work of [9] wherein it was mentioned that “an increase in temperature well above the activation energies for bond cessation causes extensive biomass depolymerization and that increasing the solids ratio allows for more sources of hydrogen and carbon for the final crude product”. For the residence time, this may be explained by the fact that since Napier grass has a high oxygen content, allowing it to fully degrade might result to the final crude product having more oxygen, thus a higher atomic O/C ratio, resulting in low HHV.

The parameter that had the highest effect according to the Pareto Chart was temperature (1.3976), followed by residence time (1.2882), and then the solids ratio (0.5955). However, all parameters were statistically insignificant to the HHV.

3.4. Yield of biocrude and parameter effects

Another objective of the study is to be able to produce bio-crude with high yields. Table IV shows the yields of bio-crude in the study.

The acquired average for the yield ranges from around 34 to 49%. As a comparison, the yield acquired from the study is the highest (34.64 to 48.63%) when compared to other studies: 3 to 13% [12], ~10 to 15% [13], ~2.5 to 37.5% [14], 9.4 to 32.6% [10], and 21.8 to 36.5% [11]. This enforces the idea that solvothermal liquefaction is capable of producing higher yields of bio-crude compared to hydrothermal liquefaction. However, an appropriate comparison should be done for hydrothermal liquefaction of Napier grass with the same conditions as in the study.

| Run | $y_{u1}$ | $y_{u2}$ | $y_{u3}$ | $y_{u}$ | $\sigma$ |
|-----|---------|---------|---------|---------|---------|
| 1   | 18.7686 | 28.6193 | 12.7121 | 20.0333 | 8.0287  |
| 2   | 20.1542 | 28.3525 | 32.0887 | 26.8651 | 6.1047  |
| 3   | 28.9203 | 27.7182 | 32.6846 | 29.7744 | 2.5910  |
| 4   | 35.3421 | 23.8814 | 22.5624 | 27.2620 | 7.0286  |

Reference [15] observed that the kinetics of esterification of fatty acids in alcohols at critical supercritical conditions were influenced by numerous factors. In the study performed, it was observed that an increase in the response of yield occurs when the level of both temperature and residence time increases, while the opposite is true for the solids ratio. This shows that the yield of bio-crude from solvothermal liquefaction is affected by the physicochemical properties of the alcohol at different operating conditions as with the esterification of fatty acids.

It was observed that higher values of biomass to solvent ratio results in increased formation of solid residues as with [2]. This may have resulted from the decrease in relative interactions between the molecules of biomass and that of ethanol at high biomass to solvent ratios resulting to the suppression of the dissolution of biomass components as explained by [9]. It was also observed in the study that the yield of bio-crude decreased as the solids ratio was decreased. This was also observed by [16]. Thus, it can be concluded that the increase in solids residue and decrease in bio-crude oils are relatively based on the solids ratio, wherein the solids residue and bio-crude produced can be thought
of as a percentage of the solids ratio. It was observed that yield of bio-crude from Napier grass seems to increase as solvothermal temperature, residence time increased and as solids ratio decreased.

It was determined using a Pareto Chart that the residence time has the greatest effect (4.3661) on yield, followed by temperature (2.4604), and then the solids ratio (2.2461). Additionally, the effects of residence time and solids ratio were statistically significant to the yield of bio-crude. This is supported by a study performed by Akhtar and Amin [9] wherein they mentioned that temperature has a synergetic effect on the yield of bio-crude and that the residence time may dictate the overall conversion of biomass.

Table 4. Table of Yield for Each Sample in %

| Run | y_{u1}  | y_{u2}  | y_{u3}  | \bar{y}_u | \sigma |
|-----|---------|---------|---------|----------|-------|
| 1   | 43.4129 | 48.9832 | 52.1662 | 48.1874  | 4.4306|
| 2   | 33.6439 | 34.0373 | 36.2319 | 34.6377  | 1.3946|
| 3   | 41.6446 | 41.9098 | 49.2927 | 44.2824  | 4.3411|
| 4   | 51.0352 | 45.0518 | 49.7930 | 48.6267  | 3.1576|

4. Conclusion
In the study, an energy efficient way for producing bio-crude oil from lignocellulosic biomass, Pennisetum purpureum or Napier grass, by direct solvothermal liquefaction using ethanol as solvent was done and the effects of various parameters on the yield and quality of the biocrude produced was explored.

Elemental analysis shows that the bio-crude produced do not fall the in typical range of components of petroleum, thus renders the product immiscible with the latter. The oxygen content for all products are considerably large, thus a need for deoxygenation arises. This high oxygen content may be explained by the inefficient liquefaction of the biomass used or that equilibrium conversion was not yet achieved.

The acquired averages for the HHV of the bio-crude produced were all higher than the HHV of the Napier grass sample used in the study. It was determined that temperature has the greatest effect on the HHV. Increasing the residence time has a negative effect on the HHV of the bio-crude. However, it was observed that the effects of the parameters were statistically insignificant to the HHV. For yield, however, temperature and residence time were statistically significant. It was observed that residence time has the greatest effect on yield. However, increasing the solids ratio is shown to have a negative contribution on the yield of bio-crude.

It was observed that despite the solids ratio having the least effect on both responses, the choice of solids ratio greatly depends on its interaction with the other parameters observed in the study.

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