

Renewable Fuel Production by in Situ Hydrotreatment of Spent Coffee Grounds

C. Truter, R. Venter, and S. Marx

Abstract— Renewable diesel production from bio-oils is more expensive in comparison to petroleum diesel, with the production of bio-oils from pyrolysis and liquefaction being significant contributors. The aim of this project is to assess the liquid yield obtainable by the in-situ hydrotreatment of spent coffee grounds through hydrotreatment. The spent coffee grounds are covered with a solvent and hydrotreated in a low or zero oxygen environment within a batch reactor loaded with catalyst. At certain conditions a significant increase in liquid product yield is observed, indicating that not only does hydrotreatment take place, but liquefaction forming bio-oils. These bio-oils are also then hydrotreated increasing the liquid yield obtained from the reactor.

Keywords— in situ hydrotreatment, liquefaction, renewable fuel, spent coffee grounds.

I. INTRODUCTION

Due to the large volumes of fossil fuels required to supply the global demand for fuel, the confirmed reserves of fossil resources are being exhausted [1]. Additionally, the consumption of fossil fuels is leading to an increase in carbon dioxide emitted into the atmosphere, with the global transportation industry playing a substantial part [2]. Alternative energy sources for fossil fuels, such as biodiesel, renewable diesel and bio-ethanol may be the key to the reduction of the global dependence on fossil resources. Most commonly these alternative fuels are produced from edible feedstock for instance rapeseed oil, sunflower oil, palm oil or soybean oil [3]. The use of edible feedstock is leading to an imbalance of the global food supply in a world that is already facing food insecurity [3]. Therefore, a waste to energy concept is more widely acceptable in which waste and non-edible feedstock are used for the production of alternative fuels.

Spent coffee grounds (SCG) are the fine residue obtained when coffee grounds have been milled and infused with hot water to produce various beverages. On a dry weight basis, SCG contain between 11 wt.% - 20 wt.% of fatty acids that

can be converted into bio-oil [3].

Renewable diesel is preferred to bio-diesel due to the difference in fuel properties, specifically considering the cold flow properties and oxygen content [4]. The composition of renewable diesel is very similar to the composition of petroleum diesel, resulting in an alternative fuel that can be used as a 100% blend [4]. Three main methods are used for the upgrading of bio-oil subsequently used in the production of renewable diesel; hydrodeoxygenation/hydrotreating, zeolite upgrading or emulsion formation [5]. The hydrotreatment process has also been used for the production of C_{12} - C_{18} n-alkanes from triglyceride based oils [5]. The major advantage hydrotreatment has over trans-esterification is the zero-oxygen content within the liquid fuel product, resulting in an increased storage life and higher energy density [6]. During hydrotreatment, hydrogen reacts with both the oxygen atoms and unsaturated carbon bonds to produce saturated C-C bonds and water.

Renewable diesel produced by means of the hydrotreatment of biomass is a costly procedure due to the fact that multiple stages are essential for suitable oil extraction to be used as feedstock. In order to reduce the cost of production, in situ hydrotreatment is considered for the production of renewable diesel as alternative to more traditional approaches such as liquefaction and pyrolysis for oil production to be used as feedstock for hydrotreatment. In this study, spent coffee grounds were directly hydrotreated using typical hydrotreating conditions to assess the feasibility of in situ renewable fuel production.

II. EXPERIMENTAL METHODS

A. Materials

Spent coffee grounds were used as feedstock in this study, procured from a local coffee brewery, Toro®. Additionally, isooctane (99 %), 1-methylnaphthalene (95 %) and ethylene glycol (99 %) were used as solvents. The isooctane and 1-methylnaphthalene were procured from Sigma – Aldrich. The ethylene glycol was procured from ACE and the ethanol from Rochelle Chemicals. Nitrogen (99.999 %), Hydrogen (99.999 %) and H_2S in Argon (14.9 %) was purchased from Afrox Potchefstroom. $NiMo/\gamma-Al_2O_3$ commercial catalyst was obtained from a commercial catalyst supplier.

The feedstock, spent coffee grounds, were analyzed by Irene Analytical Services based in Pretoria. The analysis results are shown in Table I.

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TABLE I - SPENT COFFEE GROUND COMPOSITION OBTAINED FROM EXTERNAL ANALYSIS AT ARC - IRENE ANALYTICAL SERVICES

Content	Value
Dry Matter (%)	94.5
Ash (%)	1.34
Protein (Nx6.25) (%)	12.71
Fat (Ether extraction) (%)	12.86
Carbohydrates (calculated) (%)	67.62
Neutral detergent fibre (%)	66.11
Acid detergent fibre (%)	31.14
Acid detergent lignin (%)	11.88
Hemicellulose (%)	34.97
Cellulose (%)	19.26
Lignin (%)	10.54

B. Methods

1) Apparatus

All the experiments were done in a batch autoclave reactor. The vessel of the reactor has a volume of 350 cm³, a maximum operating temperature of 420°C and a maximum pressure of 200 bar, however the release valve of the vessel is set at a pressure of 150 bar. A heating jacket was used to heat the reactor and a magnetic coupled stirrer is fitted at the top of the reactor. Compressed air and cooling water was used to protect the magnetic coupled stirrer from overheating during the reaction.

2) Catalyst Preparation and Activation

A catalyst to reagent weight ratio of 1:10 was used in this study. The catalyst is dried over an hour at 100°C and placed inside an aluminum cup fitted in the reactor. The reactor is closed off and purged with nitrogen for 30 min, removing any unwanted air inside the reactor. The reactor is pressurized with H₂S and heated to 400°C. The reactor is held at these operating conditions for 1 hr. after being cooled with compressed air and a fan to 35°C.

3) Reaction

After the reactor system is depressurized into the chemical hood, the reactor is purged with hydrogen for 5 min. displacing all the remaining H₂S in the reactor. The solvent is introduced into the reactor by injection through a rubber septum. The biomass is added into the reactor by re-opening the reactor while purging with nitrogen, introducing the biomass and closing the reactor off again. The reactor is purged with hydrogen for 3 min displacing the nitrogen and then pressurized with hydrogen to 8 MPa (initial operating pressure). The magnetic stirrer is switched on together with the heating oven. The reactor is heated to the operating temperature of 390°C and kept there for 1 hr. The reacting system is allowed to cool to 35°C before the content of the reactor is removed and analyzed.

C. Liquid Product Analysis

The liquid and solid product is removed from the reactor after the cooling process has been completed. The content of both the aluminum cup and the reactor is separated from the solid product by using a Buchner funnel. The liquid product

accumulated within the Buchner funnel is then analyzed using a gas chromatograph mass spectrometer (GC-MS).

In order to ensure that all the liquid is recovered from the aluminum cup and the reactor, it was rinsed using dichloromethane and filtered through the filter paper in the Buchner funnel. The dichloromethane was then evaporated leaving the liquid product behind. The solids (catalyst and char mixture) which remain on the filter paper is dried and weighed.

The total liquid yield of the run is calculated as the percentage of the feed that has been converted into liquids using equation 1.

$$\text{Liquid yield (\%)} = \frac{M_{LP}}{M_F} * 100 \quad (1)$$

M_{LP} represents the mass of the liquid product and M_F the mass of the feedstock. The diesel yield is then calculated using equation 2 as the fraction of the total liquid product with a boiling point within the 240°C to 370°C diesel fraction range.

$$\text{Diesel yield (\%)} = \frac{x * M_{LP}}{M_F} * 100 \quad (2)$$

x Represents the fraction of the liquid product falling in the diesel boiling range. The diesel selectivity is further calculated using equation 3:

$$Y_D = \frac{\text{Diesel yield}}{\text{Naptha yield} + \text{Kerosene yield}} \quad (3)$$

Finally, the yield for the diesel, kerosene and naphtha from the SCG is calculated as illustrated in equation 4.

$$\text{Yield} \left(\frac{g}{kg \text{ SCG}} \right) = \frac{\text{yield}_i * \text{SCG} (g)}{\text{SCG} (kg)} \quad (4)$$

i Represents the different fractions within the liquid product.

The sample for the GC-MS (Agilent 7890A, 5975C inert MSD, with triple axis detector) is diluted in a vial and consists of 0.02 g sample and 1.3 g DCM. The DCM is added as diluent into the vial. The calibration standard for the GC-MS pertaining to the simulated distillation was obtained from Supelco, Pennsylvania, USA and contains normal alkanes from C8 to C40 (Bachler, et al., 2010). The data obtained from the analysis completed using the GC-MS is further processed and simulated distillation curves are drawn up using a modified method in order to determine the boiling ranges for the liquid product obtained.

After separation of the contents of both the reactor and the aluminum cup the higher heating value of the liquid product was tested using a bomb calorific meter (IKA® C500). The sample is prepared according to the calibration of the meter used. The sample is weighed and the weight transferred to the calorific meter. The sample is loaded into the bomb together with a cotton thread that is ignited in the presence of pure oxygen. The increase in temperature of the water in the calorific meter is noted and used to determine the higher heating value of the sample in the bomb.

III. RESULTS AND DISCUSSION

A. Hydro-Processing of SCG in the Presence of isooctane

1) The Effect of Solvent Loading on the Boiling Point Distribution Range of the Liquid Product

The hydrotreatment of different solvent loadings with a constant feedstock mass of 5 g was studied and compared. **Error! Reference source not found.** represents the simulated distillation curves for the 55 g and 6 g solvent loadings. The conditions at which the comparison was done, were 8 MPa, 390°C and one-hour of residence time at constant reaction temperature.

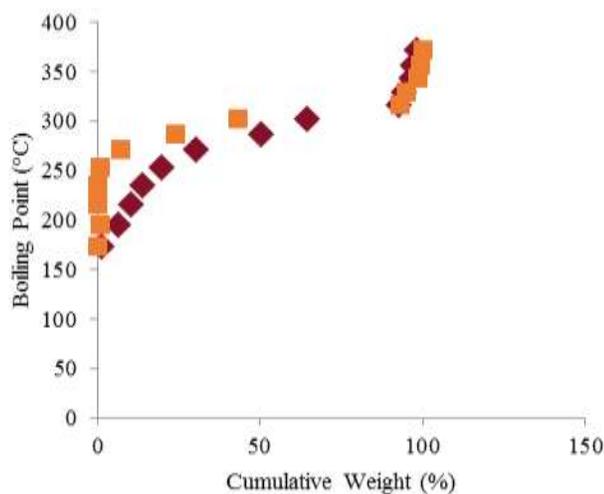


Fig. 1 - The effect of solvent loading on the boiling range distribution for 55 g and 6 g solvent loadings during the hydrotreatment of SCG in the presence of isooctane. (■ 55 g solvent, ◆ 6 g solvent)

The solvent loadings were varied at 55 g and 6 g to 5 g of biomass respectively. The 55 g loading resulted in a diesel fraction of 99 wt.%. A significant increase in kerosene fraction is noted at a fraction of 16.42 wt.% for the 6 g solvent loading as illustrated in **Error! Reference source not found.**. The 55 g solvent loadings resulted in no noteworthy quantities of kerosene formation. A higher solvent to biomass ratio resulted in the formation of kerosene as well as diesel fractions in the liquid product. Moreover, the production of kerosene indicates that not only has the fatty acids in the spent coffee grounds been converted to renewable diesel but additionally the lignocellulose containing cellulose, hemicellulose and lignin and other ingredients such as proteins have undergone liquefaction and hydrotreatment, resulting in the lighter kerosene fraction. The formation of the lighter fractions such as kerosene and naphtha may be attributed to depolymerization of the materials other than fatty acids such as lignocellulose during the hydrotreatment process. Various articles such as reviewed in [7] indicate that a high selectivity and conversion of lignin is obtained through polymerization using super critical fluids. Isooctane has a critical pressure of 25.7 ± 0.2 bar and a critical temperature of 270.75 ± 0.4 °C [8]. Therefore, isooctane is at super critical conditions during the hydrotreatment process and

depolymerization of the lignocellulose may occur leading to the formation of kerosene and naphtha fractions in the liquid product.

In consideration of the boiling range distribution and the liquid product composition comparisons of each solvent loading the low solvent to biomass ratio is more favorable for the production of renewable fuel that may be comparable to petroleum diesel in further studies. Additionally, not only is diesel formed during hydrotreatment but also kerosene as part of the liquid product. Thus, more valuable fuel compounds are extracted from the feedstock although separation is required after the hydrotreatment process.

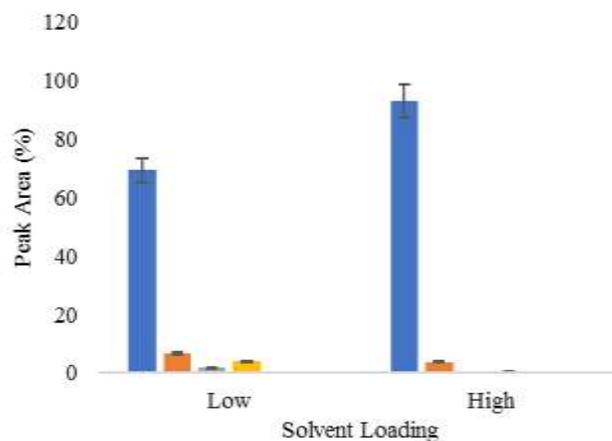


Fig. 2 - The effect of solvent loading on the liquid product composition for the hydrotreatment of SCG in the presence of isooctane. (■ n-Alkanes ■ i-Alkanes ■ Aromatics ■ Cyclic alkanes ■ Olefins ■ Oxygenates)

The composition of the liquid product formed for both the high (55:5) and low (6:5) solvent loadings are illustrated in **Error! Reference source not found.**. The high solvent loading hydrotreatment run resulted in mostly n-alkane compounds as part of the liquid product formed during the hydrotreatment of the SCG. Contrary to the high solvent loading run, a lower solvent loading run resulted in more isomers, aromatics and cyclic compounds forming.

2) The effect of biomass loading on the liquid product yield

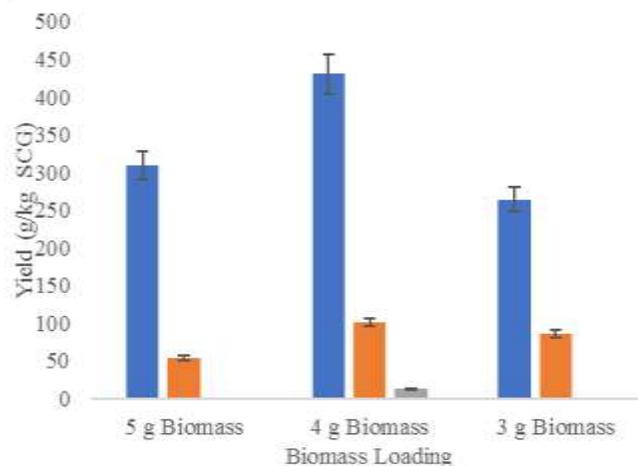


Fig. 3 - The effect of biomass loading on the liquid product yield during hydrotreatment of SCG in the presence of iso-octane (■ Diesel yield ■ Kerosene yield ■ Naphtha yield)

The hydrotreatment of different biomass loadings with a constant iso-octane loading of 6 g was studied and compared. The conditions at which the comparison was done, were 8 MPa, 390°C and one-hour of residence time at constant reaction temperature. After each run the reactor content was filtered using a Buchner funnel and the remaining catalyst on the filter paper was washed with dichloromethane (DCM) extracting all the liquid product from the solids. Fig. 3 shows the diesel, kerosene and naphtha yield obtained for each of the biomass loadings in grams per kilogram SCG.

The diesel yield for the 5 g biomass loading was 309 g/kg SCG. The diesel yield for the 4 g biomass loading was 430 g/kg SCG and 264 g/kg SCG for the 3 g biomass loading. From figure 4-1 it is clear that the highest diesel yield was obtained from the 4 g biomass loading as well as the highest kerosene and naphtha yield is also observed with the 4 g biomass loading. This indicates that for the experimental setup in this study the 4 g biomass loading proves to be the most favorable choice from a biofuel production point of view. Experimental error for this project was determined by repeating the 4 g biomass, 6 g solvent loading experiments and an experimental error of 6.22% was calculated.

The liquid product of the 5 g biomass feed loading comprised of 31 wt.% of diesel and 5 wt.% of kerosene with a total liquid product yield of 36.98 %. The 4 g biomass feed delivered a 43 wt.% of diesel, 10 wt.% of kerosene and 1 wt.% of naphtha with a total liquid yield of 62.60 % and the 3 g loading of biomass contained 26 wt.% diesel and 9 wt.% kerosene with a total liquid yield of 35.01 %. The highest yield was obtained at the biomass loading of 4 g, assuming that a harmonious ratio of biomass to solvent has been reached, resulting in a significantly higher liquid yield attained in comparison to the three and five gram spent coffee ground loadings.

This resulted in a diesel selectivity for the 5 g biomass loading at 5.76, the 4 g loading with 3.77 and the 3 g biomass loading with 3.08. A preference towards the production of diesel is shown for all three cases although a decrease in diesel selectivity is noted with a decrease in the biomass loading.

For the 4 g biomass loading case, the liquid product had an average gross calorific value (CV) of 44.334 MJ/kg. This value is comparable to literature which is 45 MJ/kg for renewable diesel (Anon., 2016). The higher heating value for spent coffee grounds was measured to be 22.14 MJ/kg which was increased with 22.194 MJ/kg to 44.334 MJ/kg by means of in-situ hydrotreatment of the SCG.

Moreover, on a dry weight basis, SCG contains between 11 wt.% – 20 wt.% fatty acid oil (Phimsen, et al., 2016). For all three the biomass loadings in this study a liquid product yield greater than 20 wt.% was obtained, indicating the likelihood of liquefaction and hydrotreatment of the SCG simultaneously taking place during hydrotreatment. The bio-oils produced

through liquefaction are thereafter hydrotreated, resulting in a hydrotreated liquid product.

3) The Effect of Biomass Loading on The Liquid Product Composition

The hydrotreatment of different biomass loadings with a constant iso-octane mass of 6 g was studied and compared. The conditions at which the comparison was done, were 8 MPa, 390°C and one-hour of residence time at constant reaction temperature. All the runs were washed with dichloromethane (DCM) extracting all the liquid product formed. Fig. 4 illustrates the liquid product composition for each biomass loading obtained.

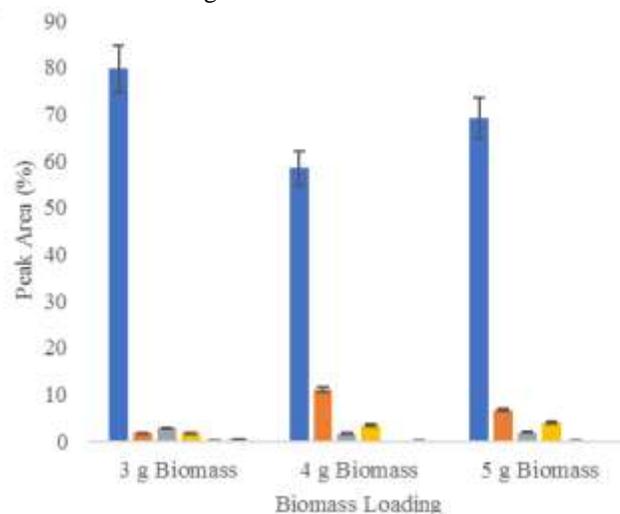


Fig. 4. - The effect of biomass loading on the liquid product composition during hydrotreatment of SCG in the presence of iso-octane. (■ n-Alkanes ■ i-Alkanes ■ Aromatics ■ Cyclic alkanes ■ Olefins ■ Oxygenates)

The largest fraction of all three biomass loadings were n-alkanes. The 4 g biomass loading resulted in the largest fraction of isomers in the liquid product, leading to a decrease in the peak area of the straight alkane chains formed. This may be due to an optimal biomass to solvent ratio for the favoritism of isomers. A higher content of isomers within the liquid product may lead to favorable cold flow properties of the liquid product.

Similar peak areas are seen for the 4 g and 5 g biomass loading in consideration of cyclic component formation, with a small increase in aromatic compounds for the 3 g biomass loading in comparison to the 4 g and 5 g biomass loadings. Insignificant amounts of alkenes and oxygenates were found in all three the compared cases

B. Hydro Processing of SCG In the Presence of Different Solvents

For the optimal biomass and solvent loading ratio determined, the hydrotreatment of varying solvents with a constant feedstock mass of 4 g and constant solvent mass of 6 g was studied and compared. The conditions at which the comparison was done, were 8 MPa, 390°C and one-hour of residence time at constant reaction temperature.

Isooctane as solvent resulted in a diesel fraction of 69 wt.% with a kerosene fraction in the liquid product of 16 wt.%. A diesel fraction of 85 wt.% with a kerosene fraction of 15 wt.% was obtained using the ethylene glycol as solvent. For the methylnaphthalene a much smaller diesel fraction of 38 wt.% is noted, resulting in a kerosene fraction of 62 wt.%. For both these solvents no naphtha or heavy fractions were observed

At the same operating conditions, biomass and solvent loadings, ethylene glycol as solvent resulted in the highest diesel fraction. The largest kerosene fraction was obtained using methylnaphthalene as solvent during the hydrotreatment of SCG.

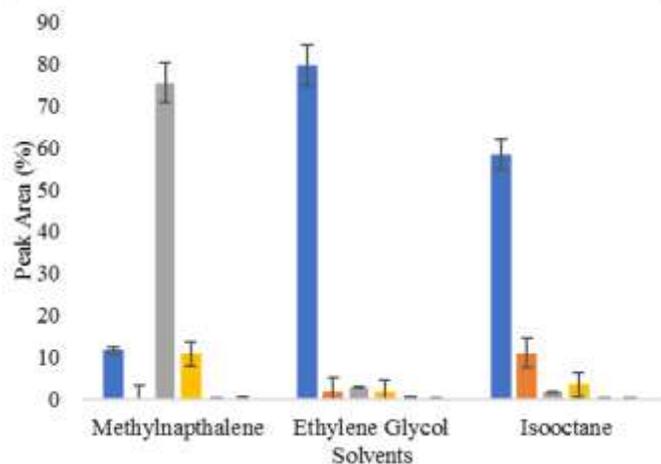


Fig 5. -The effect of solvent on the liquid product composition for the hydrotreatment of SCG. (■ n-Alkanes ■ i-Alkanes ■ Aromatics ■ Cyclic alkanes ■ Olefins ■ Oxygenates)

The liquid product composition for each solvent is illustrated in Fig 5. It can be seen that for the methylnaphthalene solvent the largest contributor to the composition of the liquid product are aromatic compounds, followed by n-alkanes and cyclic components. For both the ethylene glycol and the isooctane, n-alkanes are the largest contributors of the liquid product composition in each case.

Hydrotreatment in the presence of isooctane resulted in the highest isomer content. The NiMo hydrotreating catalyst is known for the isomerization of n-alkanes. Renewable diesel distilled from the liquid product will exhibit improved cold flow properties as a result of its higher isomer content.

The C15-C18 n-alkanes observed in the liquid product are assumed to be formed due to the hydrotreatment of the fatty acids within the SCG. All the components found in the liquid product of an experimental run can either be attributed to the hydrotreatment of fatty acids in the SCG, hydrotreatment of the solvent or hydrotreatment of the other compounds such as the lignocellulose in the SCG as well as cracking of the longer n-alkane chains. The latter two attributions form components which fall in the kerosene boiling range.

A comparison between the liquid product composition of the hydrotreatment of SCG in the presence of 1-methyl-naphthalene with a solvent to biomass ratio of (6:5) and the hydrotreatment of 1-methyl-naphthalene only (6 g) was done. The following components were found in both cases; 1-ethyl-

2-methyl-*cis*-cyclohexane, decahydro-2-methyl-naphthalene, (2-methyl-1-butenyl)-benzene and 1,2,3,4-tetrahydro-5-methyl-naphthalene. For the hydrotreatment of the SCG experimental case in the presence of 1-methyl-naphthalene the components that did not match with a component in the case without the SCG are assumed to be formed from either the lignocellulose that has undergone liquefaction and hydrotreatment or from cracking of the C15-C18 n-alkanes.

After the hydrotreatment of the SCG in the presence of all three solvents investigated during the experimental period, no significant amounts of oxygenates are present in the liquid product of each case. The absence of oxygenates is a clear indication of successful deoxygenation in each case.

IV. CONCLUSION

The effects of varying solvent loadings, varying biomass loadings and different solvents during the hydrotreatment of SCG was examined in a batch reactor system. The solvent to biomass ratio was varied at a high of (55:5) and low of (6:5) individually. The biomass loading was varied at 5 g, 4 g and 3 g respectively. Lastly, three different solvents, namely; isooctane, ethylene glycol and 1-methyl-naphthalene were tested.

The low solvent to biomass ratio of (6:5) resulted in the formation of a higher ratio in the kerosene fraction, whilst maintaining a high diesel ratio of 83.58 wt.% in the presence of isooctane. The low solvent to biomass ratio was thus found not only feasible for the production of renewable diesel from SCG through hydrotreatment but additionally formed kerosene which indicates the possibility of liquefaction of the lignocellulose within the SCG. These two fractions will however have to be separated in an additional step.

The 4 g biomass loading in the presence of isooctane resulted in the highest diesel yield of 430 g/kg SCG and additionally resulted in the formation of higher kerosene and naphtha fractions in the liquid product. As seen for the low solvent to biomass ratio (6:5), the increase in kerosene and naphtha fractions formed may be attributed to the liquefaction of lignocellulose that has simultaneously undergone hydrotreatment.

The different solvents used during the hydrotreatment of SCG, resulted in significant differences in the diesel to kerosene ratio of the liquid product as well as the liquid product composition. Similarities between the liquid product composition for the different solvents may be attributed to the compounds other than fatty acids in the SCG.

For all the experiments conducted complete oxygen removal and saturation of olefins have been observed. The in-situ hydrotreatment of SCG is feasible for the production of renewable diesel and a decrease in cost for the production of renewable fuel is achievable by the implementation of in-situ hydrotreatment of SCG

APPENDIX

Appendices, if needed, appear before the acknowledgment.

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