Effect of Co-Hydro Processing of Lignocellulosic Biomass on Liquid Product Yield and Distribution

Zandré Broodryk, Roelf Venter, and Sanette Marx

***Abstract*— ** The effect of dry biomass addition to the hydrotreating of bio-oil was studied. Dry cottonseed was used as biomass while cottonseed oil and i-octane were used as solvents. The investigated parameters were the biomass loading, temperature and solvent; biomass loading seems to have an upper bound depending on solvent, while the temperature effects seem to be the most dominant parameter affecting diesel yield. All other parameters were kept constant (pressure= 9MPa, catalyst weight =6g, residence time = 1 hour, heating rate = 6°C/min and total feed weight = 49g). It was observed that char yields decrease with increase in temperature.Aromatic and cyclic compounds were found in the liquid product, and as suspected to be a result of the lignocellulosic biomass in the cottonseed hull. Increasing temperature increased the aromatisation of the cyclic compounds. The optimal temperature was found to be 390°C for maximum liquid yields.

***Index Terms*—** in situ hydrotreating, cottonseed oil, liquefaction, renewable diesel.

I. INTRODUCTION

The characteristics of bio oils that limits usage as fuels are low volatility, high viscosity and thermal instability, which are due to high molecular weight and oxygen atoms being part of the molecule [1-3]. Therefore in order to utilize these oils as transportation fuels, it will have to be upgraded [1]. Three main methods used to upgrade bio-oils are: Hydro deoxygenation/Hydrotreating, zeolite upgrading, forming emulsions with diesel fuel and conversion to fatty acid methyl esters (FAMEs) [2]. The hydrotreating process, or the hydrodesulphurization process was originally used to remove contaminants from crude oil, such as sulphur, nitrogen, oxygen and metals[4]. This process has also been found to be an alternative method of producing biodiesel from triglyceride based oil, the products from this process are straight chain hydro carbons of length $C_{12} – C_{18}$, unlike the Fatty Acid Methyl Esters (FAME) produced by the trans-esterification of triglyceride based oils [2, 5]. The advantage Hydrotreating has over trans-esterification is that the product contains no oxygen atoms, and therefore has a longer storage life and higher energy density than traditional FAME production [5]. Stumborg, et al. [6] claims that hydrotreating has a processing cost of roughly 50% of that of FAME, compatibility with current infrastructure and the method has better feedstock flexibility. During this method H_2 reacts with oxygen atoms and carbon double bonds to produce water and saturated C-C bonds in the product molecule.

In previous studies cottonseed oil has been successfully hydrotreated to produce renewable diesel of proper quality.

This study aims to determine if liquefaction can be done in situ with the hydrotreating process, therefore possibly reducing the cost of renewable diesel production. Since water deactivates the sulphided catalyst, other solvents will have to be considered as the liquefaction solvent. In this study cottonseed oil and i-octane was used as solvents. The reactions were run in a batch reactor. The renewable diesel yield was determined using simulated distillation. The composition of the liquid product was determined which includes n-alkanes, i-alkanes, olefins, cyclic alkanes, aromatics and oxygenates. The gas product was also determined, including n-alkanes, carbon monoxide and carbon dioxide. The reaction mechanisms leading to the product formation found is also presented.

II. EXPERIMENTAL METHODS

A. Materials

Crude cottonseed oil and i-octane was used as solvents, while dried cottonseed was used as the dry biomass feedstock. Hydrogen (purity 99.999), H_2S in Argon (purity 14.9% H_2S) and Nitrogen (purity 99.999%) was purchased from Afrox South Africa. A commercial $NiMo-\gamma Al_2O_3$ catalyst was used.

B. Apparatus

The experiments were conducted in a custom build batch autoclave reactor. The reaction vessel is rated at a maximum pressure of 200 bar, and maximum operating temperature of 420°C, and has a volume of $350\ cm^3$. The reactor has a stirrer mounted on top of the reactor and cooled by a combination of cooling water and pressurized air in order to avoid overheating of the stirrer motor. A heating Jacket was used to heat the reactor.

C. Procedure

1) Reactor preparation

The clean reactor was loaded with a set amount of catalyst (6 grams for this study) and oven dried at 105°C for 1 hour in order to ensure that the catalyst is dry inside the reactor. The dried reactor is then placed inside a heating jacket, the stirrer is mounted and pressure tested.

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2) *Catalyst activation*

Once the reactor is ready the dry catalyst is purged with nitrogen gas for 30 min, in order to remove any oxygen in the reactor. The reactor is then pressurized with H_2S gas to 5 MPa and heated to 400°C at approximately 6°C/min and kept there for 1 h.

3) *Reaction*

Once the reactor is cooled down and depressurized, the solvent was added to the reactor followed by the addition of the dry biomass (oven dried at 105°C for 1 hour). The addition of the biomass was done by opening the reactor, therefore in order to ensure the catalyst does not deactivate due to exposure to oxygen, the solvent is added before opening via a syringe to submerge the activated catalyst. The reactor is closed and purged with Nitrogen gas for at least 30 min in order to ensure no oxygen remains inside the reactor or solvent. The reactor is then pressurized to 9MPa and heated to the set temp at a heating rate of 6°C and kept at the set point for 1 hour. The contents of the reactor were continuously stirred during this step.

D. *Product analysis*

Once the reactor has cooled to room temperature the gas product is collected and analysed using a gas chromatograph (GC). The reactor was then opened to collect the liquid and solid product. The liquid product was then separated from the solids and analysed. The Liquid was separated from the solids by means of a filter ($.45\,\mu m$ passing), the solids remaining (catalyst and char mixture) was then weighed, while the filtered liquid product was analysed using a gas chromatograph mass-spectrometer (GC-MS).

The efficiency of the bio oil upgrading was calculated as the percentage of the feed that has been converted into a liquid product, with boiling point lower than 370°C by weight.

$$Conversion\ (\%) = \frac{M_{Liquid\ product}^{370-}}{M_{Feed}} \times 100 \qquad 1$$

The liquid yield was calculated as the percentage of the feed that has successfully been converted into liquids.

$$Liquid\ Yield\ (\%) = \frac{M_{Liquid\ product}}{M_{Feed}} \times 100 \qquad 2$$

The diesel yield was calculated as the fraction of liquid product with a boiling point between 240°C and 370°C.

$$Diesel\ yield\ (\%) = \frac{x_{240°-370°C} \times M_{Liquid\ product}}{M_{Feed}} \times 100 \qquad 3$$

Selectivity of diesel was calculated as

$$Y_{diesel} = \frac{Diesel\ yield}{naphta\ yield + kerosene\ yield} \qquad 4$$

Where $M_{Liquid\ product}^{370-}$ is the mass of liquid product with a boiling point lower than 370°C,$M_{Liquid\ product}$is the total mass of liquids produced, M_{Feed} is the total mass of the feed (solvent and biomass), $x_{240°-370°C}$ is the fraction of liquids with boiling point in the range of 240°C – 370°C.1

III. RESULTS AND DISCUSSION

A. *Temperature and pressure profiles*

The co treatment of cottonseeds with various solvents during hydrotreatment was studied and compared with the ideal case of the hydrotreatment of pure triglyceride oil.

Conditions used for comparison were 9MPa, 410°C and 1-hour residence time at reaction temperature. Fishows the temperature and pressure changes with time as the reaction took place for pure cottonseed oil. Figshows the pressure and temperature profiles for cottonseeds in cottonseed oil, andFig shows the pressure and temperature profiles of biomass and i-octane.

Hydrotreating consists of various possible reaction pathways, happening parallel or consecutively [5]. It can be seen at around 275 - 380°C there is a drop in pressure.

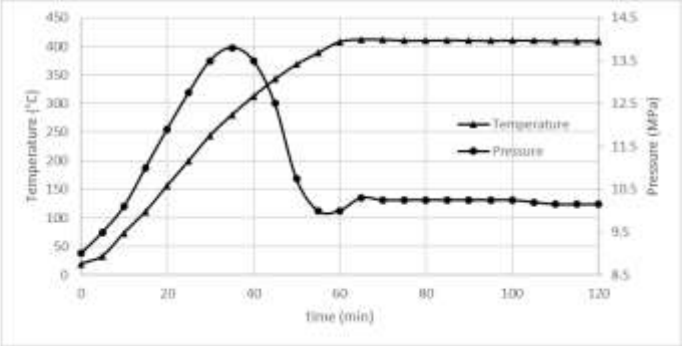


Fig. 1 Typical Pure cottonseed oil run

Whenever cottonseed oil is present in the reactor it can be seen that a slight increase in pressure is observed after the initial pressure drop as can be seen in FigandFig, of the 3 main reaction pathways, decarboxylation and decarbonylation produces more gasses than it consumes. Since the pressure increases with time, it can be concluded that the presence of cottonseed oil, within these operating conditions, has shown that a preference for decarboxylation, and decarbonylation was followed above that of hydrodeoxygenation.

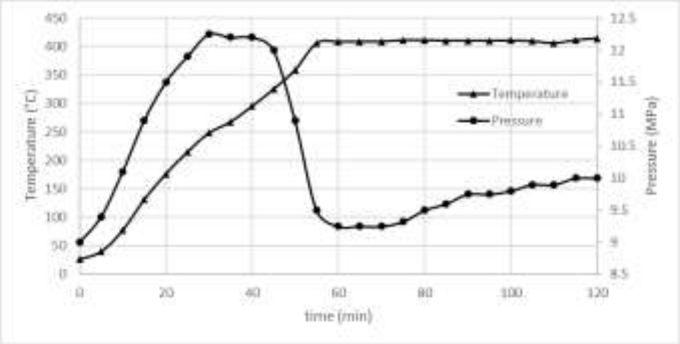


Fig. 2 Typical cottonseed oil solvent run

This drop in pressure is due to saturation of double bonds and the cracking of the triglycerides into free fatty acids using the hydrogen in the reactor. The presence of dry cottonseed inhibits hydrogen consumption, as can be seen in the higher pressure's reached before the pressure drop starts. This is verified by the presence of unsaturated hydrocarbons in the liquid product when dry cottonseed is present as can be seen in Fig. The rapid consumption does not occur when i-octane is used as solvent as there are no unsaturated fatty acids present in the solvent, therefore, the fatty acid (from biomass) to hydrogen molar ratio is lower when compared to the runs with a tri-glyceride based solvent. As can be seen, the preferred route of the NiMo catalyst is followed, at a reduced rate with the i-octane solvent, as hydrogen is gradually consumed, reducing the pressure.

TABLE I
EFFECT OF TEMPERATURE AND SOLVENT ON LIQUID PRODUCT CHARACTERISTICS

Temperature	Solvent	$\frac{C_{18}}{C_{17}}$	$\frac{C_{16}}{C_{15}}$	% isomerization	Aromatics	Cyclic alkanes	Olefins	Oxygenates
350	CSO	0.86	0.98	1.16%	0	0.68	16.23	0.21
390	CSO	0.70	1.04	0.32%	0	0.09	1.10	0.17
410	CSO	0.49	0.56	0.89%	0.28	0.81	6.79	0.73
350	Octane	1.73	1.86	0.00%	0	0	0	0
370	Octane	1.71	1.79	1.34%	0	0	0	0
390	Octane	1.75	1.83	1.57%	1.43	3.81	0	0
410	Octane	1.79	1.95	2.20%	7.06	2.15	0.71	0

TABLE II
COMPOSITION OF COTTONSEEDS USED

Analysis	Dry matter	Moisture	Ash	Protein	Fat	Neutral detergent fibre	Acid detergent fibre	Acid detergent lignin	Carbohydrates
Composition (wt.%)	92.59	7.41	3.15	16.19	19.23	41.09	32.79	8.49	54.02

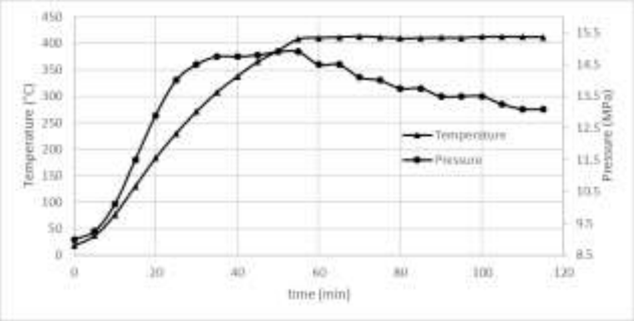


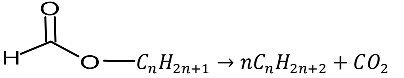
Fig. 3 Typical i-octane solvent run

In Figit can be seen that the pressure is constantly decreasing, therefore hydrodeoxygenation is the dominant reaction pathway when no cottonseed oil is present in the reactor. This is also confirmed in

Table , where the $\frac{C_{n+1}}{C_n}$ ratio for n = 15 and 17 is larger than 1 for the liquid product with an i-octane solvent as compared to the lower than 1 ratio for the diesel product of the cottonseed oil solvent. The slow rate of pressure change during these runs is due to the fact that the bio oilneeds to be released from the raw biomass before it can be upgraded to saturated n-alkanes.

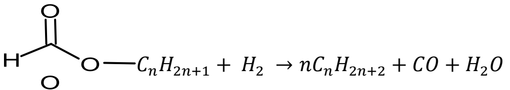
B. *Liquid product composition*

From the free fatty acids 3 main reaction pathways are possible, namely decarboxylation (5), decarbonylation (6) and hydrodeoxygenation (7).



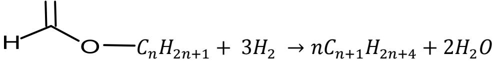
$$\mathrm{HC(=O)O}—C_nH_{2n+1} \rightarrow nC_nH_{2n+2} + CO_2$$

5



$$\mathrm{HC(=O)O}—C_nH_{2n+1} + H_2 \rightarrow nC_nH_{2n+2} + CO + H_2O$$

6



$$\mathrm{HC(=O)O}—C_nH_{2n+1} + 3H_2 \rightarrow nC_{n+1}H_{2n+4} + 2H_2O$$

7

With n being an odd number (15 or 17 in the case of cottonseed oil). From the n-alkanes various reactions can occur, such as cyclization, isomerization and cracking, of which cracking is undesirable, since it produces lighter hydrocarbons which are gasses at atmospheric conditions. Isomerization is desirable since it improves the cold flow properties of the renewable diesel product. The increase in pressure observed with the biomass in a cottonseed oil solvent is not attributed to excessive cracking since the liquid yield is comparable to that of pure cottonseed oil. Fig shows the liquid product composition of pure cottonseed oil, biomass in a cottonseed oil solvent and biomass in a i-octane solvent. All of these experiments were done at 410°C 9MPa and 1-hour residence time. The presence of isomers is reduced in both experiments with biomass present, while cottonseed oil as solvent promotes the formation of unsaturated olefins, which is undesirable as a lower H/C ratio decreases energy values of the product, however the i-octane solvent allowed for the formation of a significant portion of aromatics, which are most likely a result of the hydrotreating of lignocellulose present in the cottonseed hull. Unfortunately, these aromatic compounds have not been saturated to their corresponding cyclic alkanes at 410°C. The aromatic compounds add up to 7.06 wt.% of the liquid product of the i-octane run at 410°C, while lignin amounts to 8.49 wt.%, shown in TABLE of the cottonseeds used in these experiments. Bio-oil compounds such as benzene, 1-ethyl-2-methyl-, it corresponding cyclic compound cyclohexane, 1-ethyl-2-methyl- and naphthalene compounds such as naphthalene, 2,3-dimethyl- was detected in the liquid products of the i0octane runs using the GC-MS. The same compounds was found by Wang, et al. [7], when hydrotreating liquefied bio-oil, indicating bio-oil extraction as well as upgrading of said bio oils did occur with the cotton seeds. Oxygenates are not present in the liquid product of pure cottonseed oil or when i-octane was used as a solvent and is present in very low concentrations, therefore showing that heteroatom removal was very efficient under the specified reaction conditions.

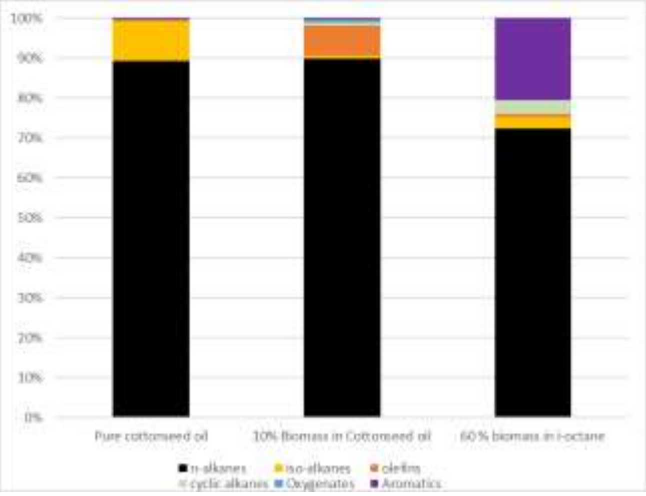


Fig. 4 Liquid compositions of the various solvent runs

C. *Yields*

The liquid yield of pure cottonseed oil was found to be 75 wt.% while the addition of 10 wt.% biomass reduced the liquid yield to 69%. The liquid yield of cottonseeds in i-octane was significantly lower, 47 wt.%, this could likely be due to cracking of the i-octane solvent to lighter gasses. The diesel fraction of all these cases are high, 97 wt.% for pure cottonseed oil, 95.5 wt.% for biomass in cottonseed oil and 86.5 wt.% for i-octane. This shows a very high selectivity towards diesel. Diesel selectivity as calculated using equation 4, reduces with the addition of biomass from 35 for pure cottonseed oil to 22.1 for 10 wt.% biomass in cottonseed oil, and even lower selectivity of 6.4 for i-octane. Indicating a preference towards diesel production rather than lighter fractions, even at the high temperature conditions.

The liquid products of pure cottonseed oil and biomass in an i-octane solvent was a transparent light yellow colour while the liquid product of the cottonseed oil with biomass was an opaque dark brown liquid.

D. *Biomass loading*

The biomass loading reduces isomerization severely as seen in Fig, therefore reducing the cold flow properties of the diesel product. A slight downward trend in n-alkane yield is observed with an increase in biomass loading, shown in

Table .

TABLE III
EFFECT OF BIOMASS LOADING ON ALKANE YIELD

Biomass loading	n-alkanes	iso-alkanes
0%	85.82	9.7
5%	89.34	1.03
10%	82.29	0.73
15%	84.29	0.94

The presence of olefins in the final liquid product indicate deactivation of the catalyst, which may be due to oxygen exposure during the addition of biomass to the reactor or coke formation during the experimental run. Catalyst poisoning due to CO_2 formation could also be a cause of the incomplete saturation of carbon double bonds.

It can be seen in Fig that diesel yield is mostly unaffected until around 10 wt% mass biomass, and sharply decreases at higher biomass loadings. This is due to a significant increase in char production which lead to coking of the catalyst. A 95 wt.% of the liquid product was within the diesel boiling range (240-370°C), which is roughly the same as the diesel percentage of the hydrotreated pure cottonseed oil with 97 wt.%. The simulated distillation curve indicates that all of the liquid product is already vaporized at 370°C indicating a complete conversion.

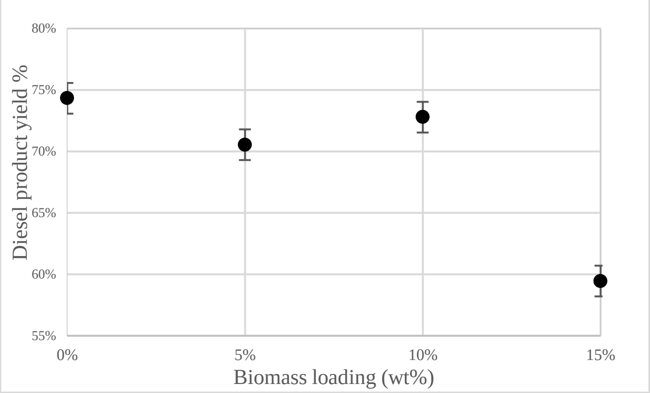


Fig. 5 Effect of biomass loading on liquid yield

E. *Temperature*

1) *Cottonseed oil solvent*

As shown in Figure 1, cottonseed oil and biomass showed an optimal liquid production at 390°C. The solid yield decreases with an increase in temperature, as shown in

Table . Liquid yield has shown to be a maximum at 390°C, decreasing strongly with both higher and lower temperatures. Reaction conditions of 350°C shows a slight increase in liquid yield from 370°C, as well as an increased solids yield, which leads to catalyst deactivation. The catalyst's preference for the hydrodeoxygenation pathway decreases with an increase in temperature, since the $\frac{C_{n+1}}{C_n}$ decreases for n = 17. For n = 15, the ration $\frac{C_{n+1}}{C_n} \approx 1$ for the entire temperature range studied indicating that neither of the 3 dominant reaction pathways are dominant. The olefin composition decreases with an increase in temperature, suggesting that the catalyst might be able to completely saturate the unsaturated C=C double bonds at higher temperatures. A lower quality fuel product is produced when compared to a pure cottonseed oil feedstock. Oxygen removal and isomerization does not change significantly within the temperature range studied.

2) *I-octane solvent*

Table shows that high char yields are present at temperatures below 390°C. A large drop in char production is observed at 390°C. The Liquid product yield follows a similar trend when compared with the cottonseed oil solvent as seen in Figure 1. A maximum liquid yield of 47.28% was achieved at 390°C, and liquid yield reducing to roughly 30% at temperatures deviating in either direction from the optimal point. With the i-octane solvent oxygen removal was effective, with no oxygenates present in the liquid product. Isomerization is increased as well when compared to the cottonseed oil solvent, although as can be seen in Fig, and increasing with temperature. Aromatics are present in the liquid product at temperatures of 390°C and higher, indicating that lower temperatures are insufficient in extracting the bio oils from the biomass in order to promote cyclization. The presence of cyclic alkanes indicates saturated aromatic compounds, since no aromatics are released from the biomass at the lower temperatures, no cyclization occurs either. The cyclic alkanes to aromatics ratio indicate the degree to which the cyclic compounds in the feed was aromatised. With this ratio being a maximum at 390°C and reducing sharply at higher temperatures it indicates that aromatisation occurs more at higher temperatures. Hydrodeoxygenation stays the dominant pathway with the $\frac{C_{n+1}}{C_n}$ ratio staying larger than 1 for the temperature range studied.

TABLE IV
EFFECT OF TEMPERATURE OF PHASE YIELD

	Cotton seed oil solvent		i-octane solvent	
Temperature	Liquid yield	Solid yield	Liquid yield	Solid yield
350	72%	9%	34%	19%
370	70%	7%	29%	20%
390	82%	2%	47%	7%
410	76%	1%	29%	11%

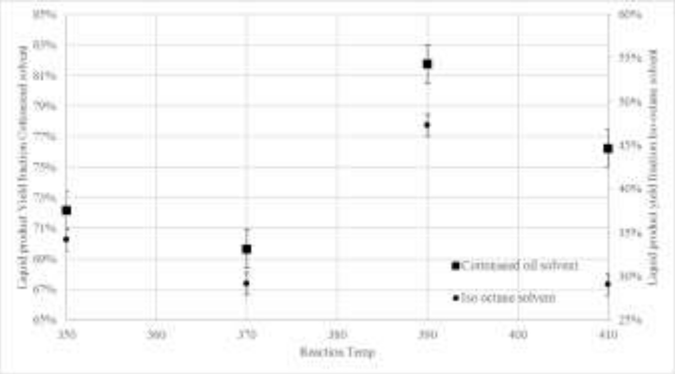


Figure 1: Effect of temperature on liquid yield

IV. CONCLUSIONS

The effects of addition of biomass to the hydrotreating process was examined in a batch reactor system. Two solvents were tested, namely cottonseed oil and i-octane. The addition of biomass was found to be feasible, as it can possibly replace the liquefaction step in the production of renewable diesel at the cost of shorter catalyst lifespan, reducing both the operational cost and the capital investment. The optimum temperature for a batch system was found to be at 390°C regardless of solvent used. The maximum biomass loading using cottonseed oil as solvent was found to be 10 wt.% while the maximum loading for i-octane was not found, while the effect of different biomass loadings should be studied further. An optimal liquid yield of 81 wt.% was found with a cottonseed oil solvent and the optimal liquid yield with the i-octane solvent was found to be 47 wt.%. The n-alkane yield of these liquids was found to be around 80 wt.% for the cottonseed oil solvent and around 70 wt.% for i-octane solvent. Complete oxygen removal was observed in all experiments conducted, though incomplete saturation of olefins was observed. Cyclic and aromatic compounds have been produced from the biomass, with cyclic compounds being converted to their corresponding aromatic compounds at higher temperatures.

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