Synthesis of Ti-based Hydrotreating Catalyst from Demilitarized $TiCl_4$

J.G. Booysen, S. Marx, and R. Venter

Abstract—Titanium tetrachloride from absolute military mortars was introduced into the aqueous phase during hydrothermal liquefaction of Amaranth biomass with the objective to evaluate the solid reactor product formed during liquefaction as hydrotreating catalysts for the production of biofuels from cottonseed oil.

Absolute military ammunition needs to be recycled as waste products from this ammunition could have negative effect on the environment and human health.

An increasing demand for alternative fuel sources exists which has led to the development of new technologies for the production of bio-fuels. One such technology involves the hydrotreatment of vegetable oils such as cottonseed oil to produce bio-hydrocarbons. The catalyst plays an important role in the hydrotreatment process and also forms a significant part of the cost of hydrotreatment. The utilization of waste titanium tetrachloride in the production of hydrotreating catalysts could result in a situation where a waste material is transformed into useful product.

Biochar from the liquefaction process was tested as catalysts during hydrotreatment of cottonseed oil. Five catalysts prepared as follows were tested: biochar produced at 260 ˚C, iochar produced at 320 ˚C, ash of the 260 ˚C biochar, ash of the 320 ˚C biochar and the 260 ˚C biochar heated to 900˚C under nitrogen atmosphere.

Hydrotreatment of cottonseed oil in a 350 ml batch reactor using the 5 different catalysts was done under hydrogen atmosphere with an initial pressure of 9 MPa, a retention time of 1 hour at a reaction temperature of 410˚C.

The 320 ˚C biochar under nitrogen produced biofuel with the highest paraffin content while the ash from the 320 ˚C biochar produced the highest diesel yield.

Index Terms— Biochar, Catalyst, Hydrotreatment, Renewable Fuels.

I. INTRODUCTION

Ammunition is produced in large quantities for training and combat purposes resulting in military ammunition depots filling up when military activities are not needed, often resulting in ammunition that is kept in the depots till the end of their service life.

Ammunition of this type is then classified as redundant or absolute and should be disposed of in safe and environmental friendly manner [1]. Careful consideration of the disposing of absolute ammunition is needed, as incorrect disposing methods could have a negative effect on human and environmental safety and health. The disposing of absolute ammunition can be done by dismantling/recycling or by physical disposal. Physical disposal includes methods such as open flame detonation, which could have devastating effects on human and environmental health [2] - [4]. Research therefore needs to be done on the dismantling and recycling of absolute ammunition once the servicing of serviceable ammunition is not possible any more [5]. Dismantling and recycling holds great potential as this will insure a safe and environmental friendly way of disposing absolute ammunition, while it is also cost effective as the recycled equipment and material holds capital value.

According to model prediction done on fossil fuels in 2008, that can be classified as crude oil, coal and gas are to be depleted 35, 107 and 37 years respectively [14]. This shows that development of alternative sources of fuels is of upmost importance if we are keep on diminishing non-renewable fossil fuels. Hydrotreatment of vegetable oils and animal fats is one such method of producing alternative fuel. The hydrotreatment process is done when triglyceride based feedstock is converted to a product consisting of a high concentration of n-alkanes. This involves the saturation of unsaturated bonds in the triglyceride feedstock (that are found in animals fats and vegetable oils) through hydrogenation followed by cracking where fatty acids are broken loose from the glycerol backbone, after this selective deoxygenation takes place through one or more of three different pathways namely, hydrodeoxygenation, decarboxylation and decarbonylation to produce n-alkanes. The different reactions take place under typical hydrotreating conditions of 300 – 450 ˚C and 6 – 11 MPa in the presence of a hydrotreating catalyst depending on the desired liquid product composition [14], [15].

Biochar is a carbon rich material that is produced by hydrothermal liquefaction of biomass, that has a large internal and external surface area, therefore biochar can serve as perfect catalyst support [7]-[9]. Catalyst support is the physical material to which transition metals like Nickel, Molybdenum and Platinum are bounded. The transition metal then serves as the active site on the catalyst surface, where the active site is the location on the catalyst surface where the actual reaction that the catalyst is designed to improve, will take place [10]. The introduction of the transition metal to the active sites on the catalyst surface can be described by two main preparation methods, namely wet catalyst preparation and dry catalyst preparation [11]. Wet catalyst preparation consist of nine subdivisions that include for example ion exchange and adsorption where metal cations and anions in a dissolved aqueous solution attach to charged sites on the catalyst support

Manuscript received November 7, 2016. This work was supported in part by the North-West University (NWU) Potchefstroom Campus Faculty of Engineering

J.G. Booysen Is a final year chemical engineering student at the NWU

S. Marx is NRF Research Chair in Biofuels, School of Chemical and Minirals Engineering NWU

R. Venter is with the chemical engineering department, NWU Potchefstroom campus.

http://doi.org/10.15242/IAE.IAE1116444

[12]. Dry catalyst preparation consist of five subdivisions that include the fusing method for example where a magnetite precursor is fused with promoter’s silica, alumina and calcium oxide at a high temperature of 1400^0C [12]. In this study hydrothermal liquefaction will be used to introduce the active metals by a combination of wet and dry catalyst preparation techniques to the catalyst support as done by Q. Liu, F. Yang, Z. Liu, G. Li in [13]. Hydrothermal liquefaction is a process where high temperatures and pressures are used to convert the biomass and liquid feed to biochar, bio-oil and bio-gas [20]. A study done by B. Veriansyah et al. shows that type of catalyst plays a crucial role in the composition and quality of the liquid product that is formed by hydrotreatment as one catalyst can promote the formation of bio-diesel while another can promote the formation of kerosene. In the production of bio-diesel molybdenum and nickel combinations on an alumina support is the most used catalyst for the hydrotreatment of vegetable oils to a bio-diesel product [15], [17] and [18]. The formation of different product by the use of different catalyst can be explained by referring to the different reaction pathways that certain catalyst promote or accelerate [15]. Intensive research and testing should therefore be done to determine the main product that a certain catalyst promotes and also at what operating conditions the catalyst is most effective to produce the specific product.

In this study Amaranth biomass will be liquefied in the presence of titanium obtained from the TiCl4 in smoke mortars. The resulting char and its ash were evaluated as hydrotreating catalysts for the hydrotreatment of cottonseed oil to produce renewable biofuel.

II. EXPERIMENTAL

A. Materials

The biomass feed that was used for the hydrothermal liquefaction process was amaranth plants, a plant that grow in warmer and tropical regions, together with a C4 photosynthetic pathway which means high yield and quality biomass [19]. The specific amaranth biomass that was used was milled and dried at a temperature of a 105^oC for 24 hours, after drying the inherent moisture content was 7.44 %. Proximate analysis results on the amaranth biomass showed a 64.38 % volatile matter, 14.56 % ash matter and a 13.63 % fixed carbon matter. The higher heating value (HHV) for the biomass that was used is 13.75 ± 0.11 MJ/kg. Based on elemental analysis that was done on the amaranth biomass that was used an H: C ratio of 1.6 and an O: C ratio of 2.02 was calculated.

The liquid feed that that was used for the hydrothermal liquefaction process consisted out of a 20 wt % $TiCl_4$ and an 80 wt % HNO_3 and H_2O solution that was reacted in a 1:1 weight ratio of HNO_3:H_2O. ICP-OES result done on the liquid feed solution showed an 814.73 ppm titanium amount.

The oil feed that was used in the hydrotreatment process was cotton seed oil with an oil content of 138 g/kg and a water content of 1.5 g/kg, further the saturated C 16 acid content is 289 g/kg and the saturated C 18 acid content is 2 g/kg.

B. Methods

1) Hydrothermal liquefaction

The hydrothermal liquefaction process to produce biochar based catalyst was done in a 950 ml batch autoclave reactor with a stirrer with a constant speed of 500 rpm. The average heating rate was 3.66 ± 0.57 ^{0}C/min and was insured by the fixed heating mantel. The autoclave was loaded with a 50 wt % biomass and 50 wt % liquid that made up 400 ml of the autoclave. After the autoclave was sealed the rest of the reactor volume was purged with nitrogen gas to insure an inert atmosphere. The two different operating temperatures was 260^oC and 320^oC with a residence time of 30 min.

The liquefaction product was then filtered using a Büchner funnel and the biochar was washed with dichloromethane to remove any residual oil. The biochar was then further dried in an oven at 105^0C and the oil was separated from the dichloromethane by means of a separating funnel and the residual dichloromethane was then evaporated using a hot plate and magnetic stirrer at a temperature of 40^0C. The biochar and oil was then weighed and the amount of gas that formed was calculated taking into account the final temperature and pressure inside the reactor using the ideal gas law.

2) Preparation of catalysts

In total five catalyst where prepared, two of these where the biochar products that were produced at 260^0C and 320^oC. The next two catalyst where prepared by burning the 260^oC and 320^oC biochars in an oxygen atmosphere at 900^oC for 2 hours to form the 260^oC biochar ash catalyst and 320^oC biochar ash catalysts. The fifth and final catalyst was prepared by heating the 260^oC biochar at 900^oC in a nitrogen atmosphere for 2 hours to form the 260^oC biochar in N_2 catalyst. Two other products were also produced by washing the 260^0C and 320^oC biochars with a 5% HCl solution, but where not used in the hydrotreatment process as catalysts as they were too amorphous.

3) Hydrotreatment of cotton seed oil

The hydrotreatment process was carried out in a 350ml batch reactor. The activation of the catalyst was carried out by inserting 5.8g of catalyst into the reactor, where after the reactor was then sealed and purged with nitrogen for 20 min and hydrogen for 10 min, after which the hydrogen pressure was increased to 5MPa and the reactor was heated to 400^oC and maintained at 400 ˚C for 1 hour. After activation the reactor was cooled down to room temperature. After the reactor has cooled down 63g cotton seed oil is added to the reactor through a valve, as the valve comes into contact with atmospheric air the valve is closed and the reactor is once again purged for 20 min with nitrogen and 10 min with hydrogen. The reactor pressure is then taken to 9MPa with hydrogen and heated to 410^oC while the oil and catalyst is stirred continuously inside the reactor, when the reactor reached the 410^oC mark it is kept there for a residence time of one hour. The average heating rate of the reactor mantel is 6.437 ± 0.633^oC/min. The product is then taken out of the reactor, weighed and then stored after being filtered through a 2µm syringe filter.

C. Analysis methods

In order to determine the inherent moisture, volatile, ash and fixed carbon content proximate analysis was done. This was done by weighing of ± 1g of sample in a crucible and then drying the samples for 24 hours in a vacuum oven at 105^oC and then weighing the samples again to determine the inherent moisture content. The samples where then heated for 7 min at 900^0C in a oven and weighed once again after cooling down to determine the volatile content after the samples where heated to 900^0C for 4 hours and weighed after cooling down to determine the ash content. The fixed carbon content was then calculated as the residual weight inside the crucible.

All of the catalyst, biomass and hydrotreatment products where analysed using a Bomb-type calorimeter (IKA C5003) to determine their HHV in MJ/kg.

In order to determine the percentage carbon, hydrogen and nitrogen elemental/ultimate analysis was done on the biomass and all seven of the catalysts by the use of an Elemental Analyser (CE-440).

As all of the catalyst are solids that are not easily dissolved in water or acids, X-ray fluorescence (PANalytical X'Pert Pro) is therefore used to determine the amount of different elements in the seven biochars.

X-ray diffraction (PANalytical Axios Max) was used to determine the nature of the crystallinity and type of molecules where formed and are present in the seven biochars. The types of crystals and molecules in the catalyst can help understand why certain catalyst produce certain products and other catalysts other products.

The hydrotreatment oil products was analyzed using a GC-MS (Agilent 7890A GC system, 5975 C inert MSD with triple-axis detector) to determine the liquid product composition of the liquid product formed in the reactor. The results from the GC-MS was used to construct simulated distillation graphs that are used to determine the fuel properties.

III. RESULTS AND DISCUSSION

A. The effect of the addition of titanium solution to hydrothermal liquefaction process

In figure 1 run 1 represents the run of amaranth as biomass and water as liquid feed at a reaction temperature of 260^0C, run 2 represents the run of amaranth as biomass and water as liquid feed at a reaction temperature of 320^0C, run 3 represents the run of amaranth as biomass and $TiCl_4/H_2O$ solution as liquid feed at a reaction temperature of 260^0C and run 4 represents the run of amaranth as biomass and $TiCl_4/H_2O$ solution as liquid feed at a reaction temperature of 320^0C.

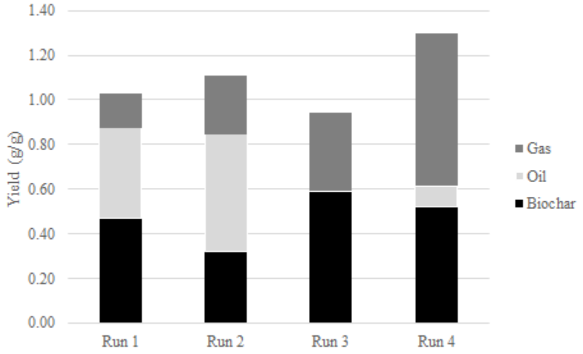

Fig. 1. The effect of the presence of titanium in the aqueous phase during liquefaction on the reactor product yield and composition

As seen from figure 1 at a reaction temperature of 260^0C the biochar and gas yield percentage increase with the addition of $TiCl_4$ to the reaction in the autoclave at the same operating conditions, this could possibly be as a result of the titanium acting as a catalyst for the formation of biochar and gas. On the other hand the oil yield percentage decreases as more biochar and gas is formed.

In figure 1 there can once again be seen that at a reaction temperature of 320^0C that biochar and gas yield percentage increase with the addition of $TiCl_4$ to the reaction in the autoclave at the same operating conditions, and this is also possibly because of the catalytic effect of the titanium. The oil yield percentage also drops as the amount of biochar and gas increases.

It becomes apparent from figure 1 that at higher operating temperatures more oil will form and therefore less biochar and gas.

B. Biochar composition

As shown in figure 2 the volatile matter wt % decreases after hydrothermal liquefaction is done, whilst the ash and fixed carbon wt % increases after hydrothermal liquefaction is done.

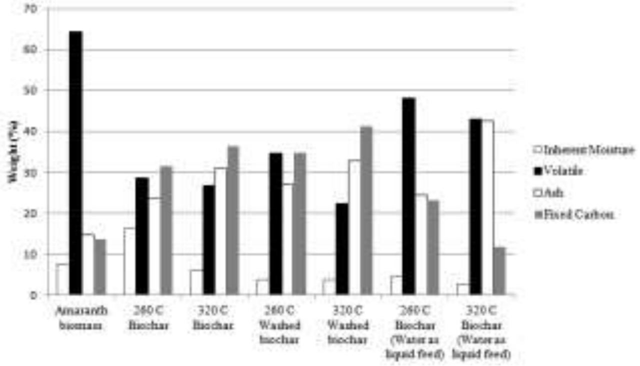

Fig. 2. Biochar composition

This illustrates that hydrothermal liquefaction condenses the biomass to a solid that contains more carbon. The 260^oC biochar ash catalyst, 320^oC biochar ash catalysts and 260^oC biochar in N_2 catalyst had a fixed carbon wt % of 100 and is therefore not illustrated on figure 2.

C. *Energy content of biochars*

In figure 3 it also becomes apparent that the addition of titanium products to the liquid feed decreases the HHV, as all the runs that contain titanium in the liquid feed have lower combustion values than the runs with pure water as feed, this can be explained due to the fact that runs with titanium form crystalline products that are more stable at higher temperatures and do therefore combust in the bomb calorie meter. There can also be seen that the biochars that where washed with a 5% HCl solution have a higher HHV that unwashed biochars, this can be explained due to the fact that components like ash that have a low calorific value are washed away in the process leaving a condensed product.

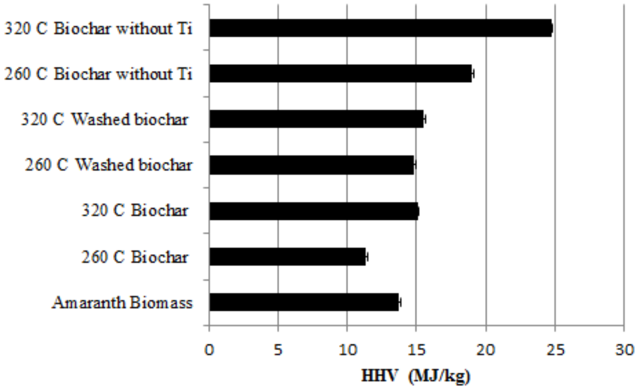

Fig. 3. Calorific values (HHV) of different biochars

Biochars at 260^0C also have a lower HHV than biochars at 320^0C this can be explained due to the densification of carbon atoms in the char and the reduction of oxygen atoms, this will further be illustrated in the elemental/ultimate analysis results. The 260^oC biochar ash catalyst, 320^oC biochar ash catalysts and 260^oC biochar in N_2 catalyst had a HHV of 0 MJ/kg and are therefore not illustrated on figure 3.

D. Elemental Carbon, Hydrogen, Nitrogen and R group elements composition for different biochar products

TABLE I
ELEMENTAL COMPOSITION OF PRODUCED BIOCHARS AND BIOMASS FEEDSTOCK

Detail	H:C	R:C
Amaranth biomass	1.604	2.022
260 C Biochar	1.326	3.417
320 C Biochar	1.277	2.664
260 C Washed Biochar	0.582	1.779
320 C Washed Biochar	0.623	2.246
260 C Amaranth + water	1.169	1.194
320 C Amaranth + water	0.985	0.677
260 C Biochar in N2	0.085	2.177

Table I illustrates the change in elemental composition as the products are treated in different ways. It is clear from the diagram that there is an increase in the carbon element for all of the different products, with the increase of the carbon element as follows amaranth biomass < biochar 260^0C < biochar 320^0C < amaranth and water 260^0C < amaranth and water 320^0C < washed biochar 260^0C < washed biochar 320^0C < biochar 260^0C in N_2 at 900^0C. This increase in the carbon element correlates to the increase in HHV. Table I also illustrates that there is a decrease in the R group of elements from the biomass to the amaranth and water runs at 260^0C and 320^0C, while there is an increase in the amount of the R group elements in the runs where titanium was added to the liquid feed in the hydrothermal liquefaction process in the following order washed biochar 260^0C < washed biochar 320^0C < biochar 260^0C in N_2 at 900^0C < biochar 320^0C < biochar 260^0C. This also correlates to the statement made in the HHV results that more stable components are form in runs where titanium was added to the liquid feed as the R group elements contain titanium. Elemental/ultimate analysis was also done on the 260^0C biochar in O_2 at 900^0C and 320^0C biochar in O_2 at 900^0C runs, but both only had R group elements, indicating that all of the carbon, hydrogen and nitrogen elements in the 260^0C and 320^0C runs reacted with the oxygen atmosphere to form gasses like CO_2,NO_2 and H_2O (g).

Catalysts 260^0C Biochar ash and 320^0C Biochar ash consisted out of a 100 % R group elements and are therefore not illustrated in table I.

E. Catalyst crystalline structure and titanium distribution

XRF is an X-ray technique used to determine the amount of an element present in a sample, while XRD is an X-ray technique used to determine the type of crystals in the sample. Metals that are incorporated in the support framework could only contribute to the charge of the support framework depending on the other metals present and the nature of the structure.

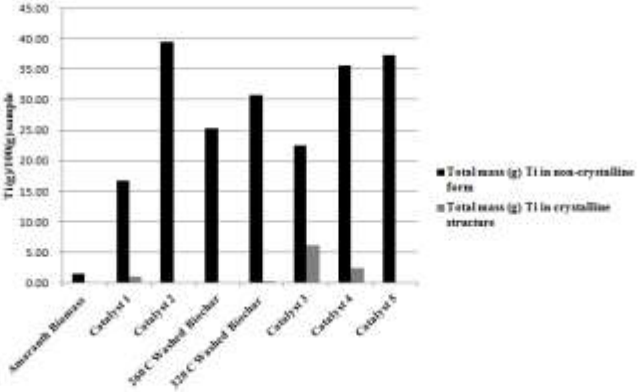

Fig. 4. Titanium (Ti) distribution diagram

This charge needs to be compensated by a cation which means that the acidity of the support could contribute to catalytic activity. Active metals deposited on the support surface act as active catalytic sites. XRD and XRF analysis where therefore used to construct the titanium distribution diagram by determining the amount of titanium in the crystalline structure and then subtracting it from the total amount of titanium in a 100g sample that was calculated by XRF method. Figure 4 shows that the mass of titanium elements per 100g sample that are in a crystalline form as well as the mass of titanium that is in a non-crystalline form per 100g of sample. Titanium that is in a non-crystalline form are able to form a metal under reducing conditions, that is then able to form active metal sites on the catalyst support or in the amorphous state. The increasing probability that a specific catalyst is able to produce a metal under reducing conditions is as follows, 260^0C Biochar < 260^0C Biochar ash < 260^0C Washed Biochar < 320^0C Washed Biochar < 320^0C Biochar ash < 260^oC biochar in N_2 < 320^0C Biochar. The effect of the different catalysts on the hydrotreatment process is shown in figure 5.

F. Liquid product composition of hydrotreated cottonseed oil

GC-MS analysis was done on all the hydrotreatment products in order to determine the composition of the products to determine what reactions took place.

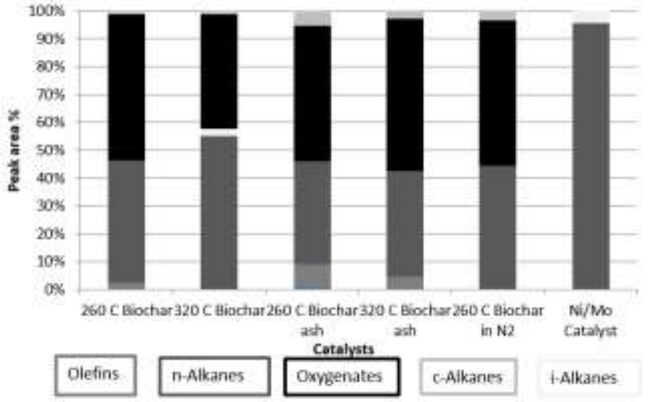

Fig. 5. Liquid product composition of hydrotreated cottonseed oil using the different catalysts

Shown in figure 5 above is the liquid product composition for all the hydrotreatment runs with the different catalysts. As explained earlier cotton seed oil composes mostly of triglycerides that are hydrogenated to form hydrogenated triglycerides which are then cracked to form fatty acids also known as oxygenates. Oxygenates are then converted into n-alkanes, iso-alkanes, aromates, cyclic alkanes and olefins depending on which reaction pathways are followed, with this said it's possible to determine to what extent the reaction has converted the oxygenates to the other oxygen free components. From figure 5 it becomes quite clear that the standard hydrotreatment catalyst Ni/Mo that all of these free fatty acids are converted to oxygen free components with the majority of them are being converted to n-alkanes with 4.3 % peak area iso-alkanes . Based on the amount of n-alkanes to oxygenates shown in figure 5 catalyst 320^0C Biochar converted a higher percentage oxygenates to oxygen free components while the catalysts 260^0C Biochar, 260^0C Biochar ash, 320^0C Biochar ash and 260^oC Biochar in N_2 all have a lower conversion of oxygenates to n-alkanes. For all catalysts deoxygenation took place to a certain extend with the NiMo catalyst the highest.

As shown in figure 5 catalysts 260^0C Biochar ash, 320^0C Biochar ash and 260^oC Biochar in N_2 all have trace amount of cyclic alkanes, the reason for this can possibly be because of the crystalline structure of these catalyst as they were treated under high temperatures. The crystalline structure of these catalysts can then cause catalytic cracking that form cyclic alkanes. Another explanation for the cyclic alkanes that were formed is the possibility of side reactions that take place to form cyclic alkanes [15]. Olefins on the other hand may have formed because of an incomplete hydrogenation reaction that took place.

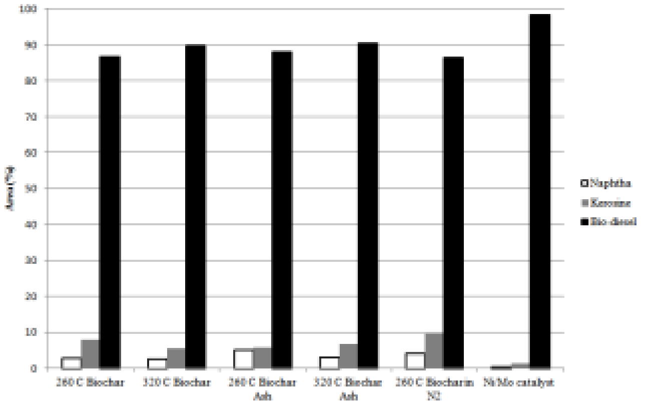

Fig. 6. Liquid product yield

Figure 6 shows that all catalysts produce naphtha, kerosene and bio-diesel. For all of the catalyst a larger bio-diesel content in the liquid product compered to naphtha and kerosene. The bio-diesel area % that is an indication of the amount of bio-diesel in the fuel product ordered from smallest to largest is as follows 260^0C Biochar catalyst = 260^oC Biochar in N_2 catalyst < 260^0C Biochar ash catalyst < 320^0C Biochar catalyst < 320^0C Biochar ash catalyst < Ni/Mo catalyst. The amount of naphtha and kerosene present in the hydrotreatment product if the target is to produce biodiesel can have a negative effect on the usability of the catalyst as this will cause a lower grade biodiesel product, this is said because the naphtha and kerosene should be separated to produce a higher grade bio-diesel by means of separation techniques like distillation. With this said it is shown that the Ni/Mo catalyst run has less naphtha and kerosene in the fuel product than the other catalyst runs. Separation by distillation is an extremely expensive technique and should at all times be minimized, therefore if naphtha and kerosene was classified as contaminants if bio-diesel was to be produced the worst to best catalyst would be as follows 260^oC Biochar in N_2 catalyst < 260^0C Biochar ash catalyst < 260^0C Biochar catalyst < 320^0C Biochar ash catalyst < 320^0C Biochar catalyst < Ni/Mo catalyst.

The above results demonstrate that the catalyst plays an important role in the manipulation of the hydrotreating process to produce a liquid product of specific composition.

G. Energy content of hydrotreatment liquid product

The average calorific value of pure cotton seed oil is 39 MJ/kg, therefore any of the hydrotreatment liquid product with a value higher than that of pure cotton seed oil indicates that deoxygenating took place. This was true for all the runs as shown in table II. The liquid product when the 320^0C Biochar catalyst was used has the highest calorific value as seen in table II.

TABLE II
HHV OF HYDROTREATMENT LIQUID PRODUCT

Detail	H (MJ/kg)
260 C Biochar	41.622
260 C Biochar Ash	42.823
Ni/Mo Catalyst	47.531
320 C Biochar	45.470
320 C Biochar Ash	41.255
260 C Biochar in N2	42.51

Table II also indicates that the Ni/Mo catalyst had the highest calorific value and therefore deoxygenating took place to the largest extent.

IV. CONCLUSION

For all 5 catalysts evaluated in this study, incomplete conversion of the cottonseed oil feedstock during hydrotreatment was observed for the chosen reaction conditions. The highest n-alkane content was observe for 320^0C Biochar catalyst which could be an indication of the highest degree of selective deoxygenation. The highest diesel yield was obtained with 320^0C Biochar ash catalyst. The energy value of the produced liquid product was lower which could be attributed to a lower extend of deoxygenation. Hydrocracking was the highest for 260°C Biochar in N_2 catalyst as can be seen in the higher content of lighter fractions. The titanium content as amorphous material is one of the highest in the 320^0C Biochar catalyst which could be the reason for the higher selectivity.

It is however important to do further research on metal/biochar based hydrotreatment catalysts to determine if for example other metals like Ni or Mo will give improved results in the fuel production.

ACKNOWLEDGMENT

A special thanks to Rheinmetall Denel Munition for the chance to develop a method of re-using absolute ammunition chemicals.

REFERENCES

[1] F. van der Merwe, "Design a process that can safely dispose of titanium tetrachloride ($TiCl_4$)", Project Proposal. Personal communication. 15 Mar. 2016.

[2] S.K.B. Godschalk and C.J. Ferreira. (April 1998). South Africa's Challenge to Manage Obsolete Ammunition. [Online]. pp.1-7. Available: http://www.dfac.mil.za/publications/presentations/papers/Article%20Obsolete%20Ammo.pdf

[3] A.L. Juhasz and R. Naida, *Explosives: Fate, Dynamics and Ecological Impacts in Terrestrial and Marine Environments, Reviews of Environmental Contamination and Toxicology*, 1st ed. New York,: Springer, 2012.

[4] P.D. Sharma, (November 2009). Air Pollution from coal mines. [Online]. Avialable: http://www.sourcewatch.org/index.php/Air_pollution_from_coal_mines

[5] S. Pèzard and H. Anders, *Targeting Ammunition*, 1st ed. Geneva, Switzerland, 2006.

[6] M. Sun, D. Nicosia and R. Prins, "The effects of fluorine, phosphate and chelating agents onhydrotreating catalysts and catalysis," Catalyst Today, vol. 86, pp. 173-189, Jan. 2003. https://doi.org/10.1016/S0920-5861(03)00410-3

[7] R. Brown, *Biochar Production Technology, Biochar for Environmental management*, 1st ed., EarthScan, London, 2009.

[8] O. Dunisch, V.C. Lima, G. Seehann, J. Donath, V.R. Montoia, T. Schwarz, Retention properties of wood residues and their potential for soil amelioration, Wood Science and Technology 41 (2007) 169-189. https://doi.org/10.1007/s00226-006-0098-1

[9] J. Thies and M. Rillig, *Characteristics of Biochar: Biological Properties – Effects of biochar on the activity of the soil biota. In: In: Lehmann, J., Joseph, S., Biochar for Environmental management*, 1st ed., London, EarthScan, 2009.

[10] H.S. Fogler, *Elements of Chemical Reaction Engineering*, 4th ed., Pearson Education Limited, Pearson Education Limited London, 2014.

[11] J.A. Schwarz, C. Contescu and A. Contescu, "Methods for Preparation of Catalytic Materials," *Chemical Review*, vol. 95 pp. 477-510, Nov. 1995. https://doi.org/10.1021/cr00035a002

[12] G. Busca, *Heterogeneous Catalytic Materials*, 1st ed., London, Elsevier, 2014.

[13] Q. Liu, F. Yang, Z. Liu and G. Li, "Preparation of SnO_2-Co_3O_4/C biochar catalyst as a Lewis acid for the corncob hydrolysis into furfural in water medium," *Journal of Industrial and Engineering Chemistry*, vol. 26, pp. 46-54, Jun. 2015. https://doi.org/10.1016/j.jiec.2014.11.041

[14] G.W. Huber, P. O'Connor and A. Corma, "Processing biomass in conventional oil refineries: Production of high quality diesel by hydrotreating vegetable oils in heavy vacuum oil mixtures," *Applied Catalysis A: General, vol.* 329, pp.120-129, Feb. 2014. https://doi.org/10.1016/j.apcata.2007.07.002

[15] B. Veriansyah, J.Y. Han, S.K. Kim, S, Hong, Y.J. Kim, J.S. Lim, Y. Shu, S. Oh and J. Kim, "Produstion of renewable diesel by hydrotreatment of soybean oil: Effects on catalyst," *Fuel*, vol. 9, pp. 578-585, Jul. 2012. https://doi.org/10.1016/j.fuel.2011.10.057

[16] L.A. Sousa, J.L. Zotin and V. Teixeira da Silva, "Hydrotreatment of sunflower oil using supported molybdenum carbide," *Applied Catalyst A: General*, vol. 449, pp.105-111, Oct. 2012. https://doi.org/10.1016/j.apcata.2012.09.030

[17] G.N. da Rocha Filho, D. Brodzki and G. Djega-Mariadassou, "Formation of alkanes, alkylcycloalkanes and alkylbenzenes during the catalytic hydrocraking of vegetable oils," *Fuels*, vol. 72, pp. 543-549, Nov. 1993. https://doi.org/10.1016/0016-2361(93)90114-H

[18] P. Simacek, D. Kubicka, G. Sebor and M. Pospisil, "Hydroprocessed rapeseed oil as a source of hydrocarbon-based biodiesel," *Fuel*, vol. 88, pp. 456-460, Sep. 2009. https://doi.org/10.1016/j.fuel.2008.10.022

[19] J. Viglasky, I. Andrejcak, J. Huska and J. Suchomel, "Amaranth (Amarantus L.) is a potential source of raw material for biofuels production," *Agronomy Research*, vol. 7, pp. 865-873, Oct. 2009.

[20] S.S. Toor, L. Rosendahl and A. Rodulf, "Hydrothermal liquefaction of biomass: a review of subcritical water technologies," *Energy*, vol. 36 pp. 2328-2342, Jan. 2011. https://doi.org/10.1016/j.energy.2011.03.013

J.G. Booysen, born in Krugersdorp, South Africa on April 12 1994. Educational background include completing a national senior certificate in 2012 in Krugersdorp and is currently busy as a full time Chemical Engineering student at the North-West Universities Potchefstroom campus in South Africa.