EVALUATION OF BIO-CHAR BASED PRODUCTS AS HYDROTREATING CATALYSTS FOR THE PRODUCTION OF RENEWABLE FUEL

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ABSTRACT: Increasing demand for alternative fuel from fossil fuel 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 makes up 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. Products from the hydrothermal liquefaction process was tested as catalysts during hydrotreatment of cottonseed oil. Five catalysts were prepared and tested as follows: 1) biochar produced at 260 ˚C, 2) Biochar produced at 320 ˚C, 3) ash of the 260 ˚C biochar, 4) ash of the 350 ˚C biochar and 5) the 320 ˚C biochar heated to 900˚C under nitrogen atmosphere. Cottonseed oil was hydrotreatment in a 350 ml batch reactor using the 5 different catalysts. This was done under hydrogen atmosphere with an initial hydrogen pressure of 9 MPa, a retention time of 1 hour at a reaction temperature of 410˚C. The liquid product produced using the 5 catalysts was compared with the liquid product produced with a commercial NiMo hydrotreating catalyst. The 320 ˚C biochar yielded the highest n-alkane content with a liquid product composition similar to that of the commercial NiMo hydrotreating catalyst as well as the fuel with the highest energy value of all 5 catalysts of 45.47 MJ/kg. The conversion of cottonseed oil for the 5 catalysts was lower compared to that of the commercial catalyst showing that direct co-liquefaction of the biomass with the metal does not result in a hydrotreating catalyst with high enough catalyst activity.

Keywords: Bio-char, Catalyst, Hydrotreatment, Carbon, Catalyst support, Renewable Fuel, De-oxygenation, Crude cottonseed oil.

1 INTRODUCTION

Fossil fuels classified as crude oil, coal and gas are to be depleted in 35, 107 and 37 years respectively according to model predictions done in 2008 [1].This emphasizes the urgency for the development of alternative fuels as replacement.

The hydrotreatment of vegetable oils and animal fats to produce renewable diesel is one alternative way to produce a replacement for petroleum diesel. The conversion of triglyceride molecules to renewable hydrocarbons takes place through a number of parallel and/or consecutive reactions, which include hydrogenation, cracking, heteroatom removal, oxygen removal through decarboxylation, decarbonylation, hydrodeoxygenation and side reactions such as isomerisation and cyclisation. 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 [1], [2].

Reaction conditions and catalyst type play a major role in the composition and yield of the liquid product produced. The role of the catalyst is to increase the reaction rate by decreasing the activation energy and to allow control over the selectivity of products.

Hydrotreating catalysts are comprised of an inert catalyst support and an active component which can be transition metals such as Cobalt, Molybdenum, Tungsten and Nickel. In the petroleum industry, the catalyst support used in hydrotreatment catalysts is often aluminium oxide. A well-developed pore structure and high surface area, which are likely to favour the uniform dispersion of active components and to stabilise these against sintering is essential for an effective catalyst support [3].

Biochar is a carbon rich material produced by means of hydrothermal liquefaction of biomass, could have a large internal and external surface area, therefore biochar can serve as perfect catalyst support [4]-[6]. Transition metals dispersed on the surface of the support serves as the active sites of the catalyst where the actual reaction the catalyst is designed to catalyze, will take place [7]. The method of introduction of the transition metals onto the catalyst surface can be described by two main preparation methods, namely wet catalyst preparation and dry catalyst preparation [8]. Wet catalyst preparation consist of nine subdivisions that include for example ion exchange and adsorption where metal in a dissolved aqueous solution attach to charged sites on the catalyst support [9]. 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 temperature of 1400^0C [9].

Biochar as carbon based catalyst supports is an environmentally attractive alternative to oxide supports due to the low sulphur and metal content, stability in acidic and basic environments and its carbon neutrality [10]. Biochar is a competitive material for catalyst support compared to conventional oxide supports due to the polar groups detected on the surface of the biochar which makes it an attractive candidate because of its adsorption applications [10]. Due to the acidity of the supports, the neutrality of carbon supported catalysts allow the support to be less prone to coking than the oxide alternatives [12]. Carbon supported catalysts were found to be more active than analogous alumina supported catalysts (Farag, et al., 1999)

In this study titanium was introduced into biochar by means of co-liquefaction of biomass at two different liquefaction temperatures in a batch type hydrothermal liquefaction reactor. The resulting bio-char was further used to prepare different catalysts to be tested in the hydrotreatment of cottonseed oil. Titanium as $TiCl_4$ was obtained from absolute or redundant ammunition which needs to be disposed of or recycled in an environmentally friendly manner. If successful this can be a way of converting a waste material to a high value product.

The usefulness of the char product produced by means of hydrothermal liquefaction directly used as a hydrotreating catalyst was evaluated avoiding complex and expensive catalyst preparation procedure.

2 EXPERIMENTAL

2.1 Materials

Amaranth was used as feedstock in the hydrothermal liquefaction process which is a plant that grows in warm and tropical regions, together with a C4 photosynthetic pathway which means high yield and quality biomass [19]. The amaranth biomass was milled and dried at a temperature of a 105^{o}C for 24 hours and after drying the inherent moisture content was 7.4 %. Proximate analysis results on the amaranth biomass showed a 64.4 % volatile matter, 14.6% ash matter and a 13.6 % fixed carbon matter. The higher heating value (HHV) of the biomass was is 13.753 ± 0.114 MJ/kg. Based on elemental analysis data the amaranth biomass had a calculated hydrogen to carbon ratio of 1.604 and an oxygen to carbon ratio of 2.022.

The aqueous phase used in the hydrothermal liquefaction process consisted of a mixture of $TiCl_4$ and HNO_3 with a titanium concentration of 814.731 ppm.

Crude cottonseed oil was obtained from the agricultural industry and the oil was taken from an oil press prior to any refining such as degumming and de-acidification. Some properties of crude cottonseed oil are shown in table 2.1.

Table I: Some properties of crude cottonseed oil used in this study (wt %)

Property	**Value**
Palmitic acid (C16:0)	28.9
Stearic acid (C18:0)	0.2
Palmitoleic acid C16:1)	0.7
Oleic acid (C18:1)	21.3
Linoleic acid (C18:2)	45.4
Linolenic acid (C18:3)	0.3
FFA	13.8
Water content*	0.15

*Cottonseed oil was dried to a moisture content of 0.001% prior to hydrotreatment

2.2 Methods

2.2.1 Hydrothermal liquefaction

The hydrothermal liquefaction process for the production of biochar based catalysts was done in a 950 ml batch autoclave fitted with a stirrer with a constant stirring speed of 500 rpm. The average heating rate was 3.657 ± 0.570 ^{0}C/min which was insured by a heating mantel. The autoclave was loaded with a 50 wt % biomass loading in the titanium containing liquid occupying 400 ml of the 950 ml autoclave. After the autoclave was sealed the reactor volume was purged with nitrogen gas to insure an inert atmosphere. The liquefaction was done at two different operating temperatures of 260^{o}C and 320^{o}C at a residence time of 30 min. The liquefaction product was then filtered using a Büchner funnel and the biochar was washed with dichloromethane for the removal of any residual oil. The biochar was then dried in an oven at 105^{0}C. The oil phase was separated from the aqueous phase by means of a separating funnel and the residual dichloromethane was then evaporated. The biochar and oil was then weighed and the gas formed during the reaction was calculated taking into account the final temperature and pressure inside the reactor using the ideal gas law.

2.2.2 Preparation of catalysts

The following five catalysts were prepared and tested in this study:

1) Biochar product produced at 260^{0}C
2) Biochar product produced at 320^{o}C.
3) Ash from biochar produced at 260˚C
4) Ash from biochar produced at 320˚C
5) Biochar product produced at 260˚C heated to 900˚C in a nitrogen atmosphere for 2 hours

These five catalysts were compared with a commercial NiMo hydrotreating catalysts in terms of the liquid product produced during hydrotreatment.

2.2.3 Hydrotreatment of cottonseed oil

The hydrotreatment experiments were conducted in a cylindrical custom-build high-pressure batch reactor with an inside volume of 350 cm^3. The contents of the reactor were extensively stirred during the reaction using a magnetic stirrer driven by a variable speed DC motor. in argon at 400°C for 1 hour. During activation 5.8 grams of the catalyst was loaded into the reactor, purged with nitrogen for 30 minutes followed by purging with hydrogen for 10 minutes after which the pressure was increased to 2.9 MPa with 14.9% H_2S in argon. After the activation step, the reactor was allowed to cool down to 30°C followed by reducing the pressure to almost atmospheric when 63 grams of the cottonseed oil was introduced into the reactor. This was done by means of a syringe through a rubber septum preventing oxygen from entering the reactor. The reactor was then purged with nitrogen for 20 minutes, followed by hydrogen purging for 10 minutes, after which the reactor was pressurised with hydrogen to 9 MPa. The reactor was then heated for about 1 hour to reach the desired temperature after which it was kept at this temperature for the duration of the reaction of 1 hour. After the reaction, the reactor was cooled down to room temperature using a fan as well as compressed air. The composition of the gas in the reactor was analysed using an online-connected gas chromatograph. The reactor was depressurised to atmospheric pressure after which the contents of the reactor was quantitatively removed and weighed followed by analysis of the liquid product.

2.2.4 Product analysis

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

The calorific value of all catalyst and original biomass and the hydrotreatment products were determined using a Bomb-type calorimeter (IKA C5003). Ultimate analysis was performed on all catalysts to determine the oxygen, carbon, hydrogen and nitrogen content using an Elemental Analyser (CE-440).

X-ray fluorescence analysis using a PANalytical X'Pert Pro) instrument was used to quantify the elemental composition of the catalysts and X-ray diffraction (PANalytical Axios Max) was used to determine the crystallinity of the catalysts.

The liquid product produced by means of hydrotreatment using the different catalysts was analysed using a GC-MS (Agilent 7890A GC system, 5975 C inert MSD with triple-axis detector). Simulated distillation curves were compiled using the data to throw more light on the fuel properties of the produced products from the hydrotreatment processes.

3 RESULTS AND DISCUSSION

3.1 The effect of adding titanium to the hydrothermal liquefaction process

As shown in figure 1, run 1 and run 2 represent the product composition of amaranth biomass and water liquefied at 260 ˚C and 320 ˚C respectively. Run 3 and run 4 shows the reaction product at 260 ˚C and 320 ˚C with titanium added to the liquefaction process. It can be seen from run 1 and 2 that liquefaction at a higher reaction temperature yields more oil and less char.

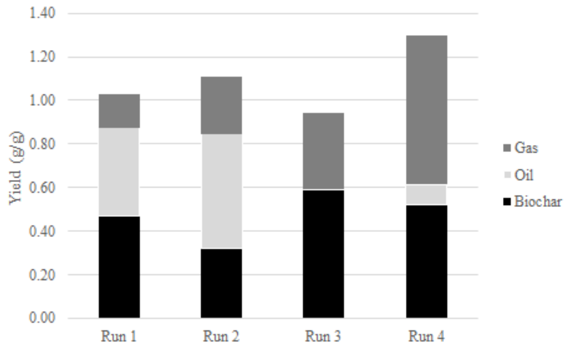

Figure 1: The effect of the presence of titanium in the aqueous phase during liquefaction on the reactor product yield and composition

Comparing the results from run 1 with run 3, it is clear that the addition of titanium to the aqueous phase reduced the oil yield with an increase in the gas and char yield. The same trend can be seen at a reaction temperature of 320 ˚C but the oil yield is relatively higher compared to the 260 ˚C runs due to higher oil yields obtained at higher reaction temperatures. The higher char and gas yield with the addition of titanium to the liquefaction process could possibly be attributed to a catalytic effect of the titanium.

3.2 Catalyst crystalline structure and titanium distribution

Figure 2 shows the amount of titanium per 100 grams of sample in crystalline form versus the amount of titanium in non-crystalline form that formed during hydrothermal liquefaction. For catalyst 3 and 4 the highest concentration of crystalline titanium was observed. It can also be expected that non-crystalline titanium could act as an unsupported catalyst when activated.

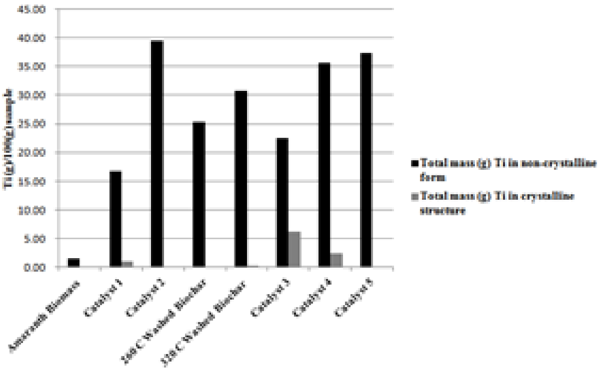

Figure 2: Distribution of titanium in crystalline form versus non-crystalline form during co-liquefaction

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

The liquid product composition of the hydrotreated cottonseed oil was determined using GC-MS analysis and is shown in figure 3.

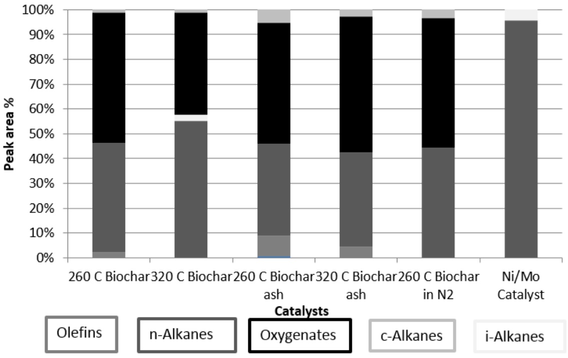

Figure 3: Liquid product composition of hydrotreated cottonseed oil using the 5 produced catalysts compared with a commercial NiMo catalyst

The liquid product composition of the hydrotreatment of cottonseed oil for the 5 catalysts is being compared with the liquid product composition when a commercial NiMo hydrotreating catalyst is used. For the commercial catalyst the liquid product mainly consist of n-alkanes, C15 – C18 with more or less 5% iso-alkanes. The presence of iso-alkanes has a positive effect on the cold flow properties of the fuel.

The liquid product for all 5 catalysts contain significant amounts of oxygenates indicating that for the given reaction conditions and retention time the conversion is incomplete. Catalyst 2 which is the biochar produced at 320 ˚C showed the highest conversion from the 5 catalysts tested. Catalyst 2 also showed the highest yield of n-alkanes. This relatively high concentration of n-alkanes could be an indication that catalyst 2 shows the highest extent of selective deoxygenation. The n-alkane content can possibly be increased using a higher catalyst to oil ratio and by increasing the retention time. This higher catalyst activity can also be attributed to a higher specific surface area of the biochar produced at a higher temperature. It is known that biochar produced at higher temperatures has a higher specific surface area compared to those produced at lower temperatures. Another factor contributing to higher n-alkane content can also be the relatively high concentration of a titanium salt such as TiCl3 that could act as an unsupported catalyst.

The abundance of the different fractions relative to one another of the liquid product produced for the different catalysts are shown in figure 4. These fractions were determined using simulated distillation data.

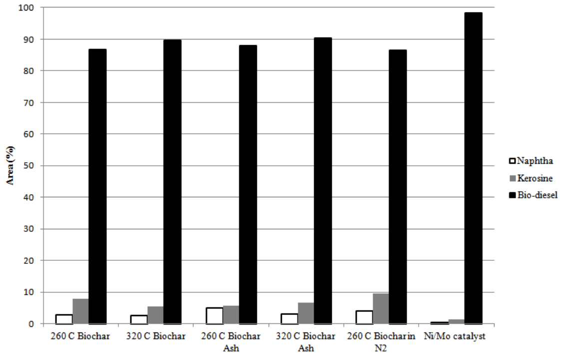

Figure 4: The yield of the different fractions of the liquid product for the 5 catalysts, compared with the commercial catalyst

Comparing the 5 catalysts with the commercial catalyst, all 5 catalysts shown a higher degree of cracking than the commercial catalyst explaining the presence of lighter compounds formed via cracking. Catalysts 3 and 4 shows slightly higher levels of kerosene and naphtha range compounds, possibly due to the presence of more crystalline compounds in the ash but also possibly due to side reactions caused by severe reaction conditions.

3.4 Comparison of energy content of the liquid product

Table 1 shows the energy content of the liquid product produced using the 5 catalysts, compared to the energy content of the liquid product produced using the commercial catalyst.

Table II: Higher heating value (HHV) of the liquid product produced by hydrotreatment of cottonseed oil using the 5 catalysts compared with the commercial catalyst

Detail	HHV (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

The higher heating value of crude cottonseed oil was measured at 39 MJ/kg. Using the commercial NiMo catalyst, increases the energy value to 47.531 MJ/kg. The 320 ˚C biochar was the catalyst closest compared with the commercial catalyst which upgraded the oil to 45.47 MJ/kg indicating that this catalyst performed the best of the 5 catalysts produced. The direct co-liquefaction of the biomass with the metal does not result in a hydrotreating catalyst with high enough catalyst activity.

4 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 observed for the 320^0C Biochar catalyst which could be an indication of the highest degree of selective deoxygenation. This was confirmed by the highest energy value obtained with the 320˚C biochar catalyst.

Although the liquid product composition of the fuel produced using catalyst 2 was to a large extent similar to that produced with the commercial NiMo catalyst, the conversion was not up to standard. This is an indication that the specific surface area of the produced catalysts are too low resulting in inferior catalyst activity and an activation step for the char is needed before the metal loading step.

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