THE HYDROTREATMENT OF AN UNSATURATED FATTY ACID VEGETABLE OIL TO HYDROCARBONS OVER NI/SIO$_2$ – AL$_2$O$_3$

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ABSTRACT: In this study, sunflower oil was hydrotreated in the presence of a nickel catalyst with the objective to evaluate the effect of reaction parameters on the characteristics of the reaction product. The effect of reaction temperature, reaction time and initial hydrogen pressure on the conversion of the triglyceride feedstock, the naphtha, kerosene and diesel yield and the liquid product yield was investigated. The reaction product during hydroprocessing is influenced by the type of catalyst used, the reaction conditions as well as the nature of the feedstock. Experiments were conducted using a cylindrical bench scale batch reactor with an inside volume of 350 cm^3. Reactions were carried out at temperatures of 390°C to 420°C and initial hydrogen pressures of 5 MPa – 11MPa. The effect of using a catalyst versus no catalyst during hydroprocessing was also compared. The gas product was analysed using gas chromatography with FID and TCD detectors while the liquid product was analysed using GC-MS. It was found that temperature and reaction time has a significant effect on the composition of the liquid product. At a temperature of 390°C with a reaction time of 30 minutes, the diesel yield was found to be 68% to be reduced to 29.6% at a reaction temperature of 420°C with a reaction time of 60 minutes. At more harsh conditions the concentration of lower boiling compounds were found to increase due to the effect of side reactions such as cracking, aromatization and cyclization. It was also found that liquid yield decreased with an increase in reaction temperature due to gas formation. Ni/SiO$_2$-Al$_2$O$_3$ was found to be a promising catalyst for the hydrotreatment of triglyceride-based feedstock due to its relatively low cost and no need for sulfidation. A disadvantage of this catalyst is the formation of methane during the reaction which could have a negative effect on optimal hydrogen consumption.
Keywords: renewable diesel, nickel catalyst, hydrotreatment, deoxygenation.

1. INTRODUCTION

As concerns about global climate change increases and petroleum reserves further depletes, the search for alternative fuel sources and production technologies are growing. One such commercially produced alternative fuel is biodiesel consisting of fatty acid methyl esters (FAME) which partially replaces petroleum diesel in industry. Compared to fossil-derived diesel, fatty acid methyl esters have a lower energy content, lower storage stability and undesired low temperature properties [1].

Paraffin-rich hydrocarbons produced by heterogeneous catalytic hydrotreatment of vegetable oils and animal fats received considerable attention the last couple of years as a promising alternative to FAME-based biodiesel. This alternative named renewable diesel shows similar fuel properties to their petroleum counterpart. Conventional hydrotreatment technology as developed by the petroleum industry for the hydrodesulfurisation , hydrodenitogeration and hydrodemetaliasation of middle distillates showed to be effective for the hydrodeoxygenation of bio-oils. Cobalt-molibdenum, nickel-molibdenum and nickel-tungstan catalysts are regarded as the conventional catalysts for this purpose [2].

The conversion of triglyceride molecules to bio gasoil takes place through the following parallel and/or consecutive reactions: [3]
- Saturation of the double bonds in the triglyceride molecule
- Heteroatom removal which includes the removal of oxygen, sulphur, nitrogen, phosphorous and metals. Oxygen removal can take place through hydrodeoxygenation, hydrodecarbonylation or hydrodecarboxylation
- Side reactions such as the hydrocracking of longer fatty acid chains to shorter chains which also could result in gaseous fractions, water-gas shift-reaction, methanisation, cyclisation and aromatisation.
- Isomerisation of n-paraffins

Supported sulfided metal caytalysts, supported noble metal catalysts and supported reduced metal catalysts are the typical catalysts used in the hydrodeoxygenation of bio-oils [4]. Noble metal catalysts are not favoured due to their high cost and sulfided catalysts are being de-activated by low sulphur containing feedstock. Therefore non-sulfided transition metal catalysts such as the Ni/SiO$_2$-Al$_2$O$_3$ catalyst should receive more attention as a catalyst to replace the conventional sulfided metal catalysts.

In this study, neat sunflower oil was hydrotreated in the presence of a nickel catalyst supported on silica-alumina. The effect of temperature, residence time and initial hydrogen pressure on the composition of the resulting liquid product was evaluated. The energy value of the feedstock was also compared with that of the hydrotreated product.

2 EXPERIMENTAL

2.1 Materials, apparatus and methods

The feedstock used was pure sunflower oil procured from a local grocery store. The fatty acid composition of the sunflower oil is shown in Table I. The hydrotreatment was done in the presence of a Ni/SiO$_2$-Al$_2$O$_3$ catalyst purchased from Alfa-Aesar (MA,USA). The Nickel content of the catalyst was 66±5 %. Hydrogen (99.999%) and nitrogen (99.999%) used in the experiments supplied by Afrox South Africa.

Table I: Fatty acid composition of sunflower oil feedstock used in this study

Fatty acid	wt%
Palmitic acid (C16:0)	9.3
Oleic acid (C18:1)	14.0
Linoleic acid (C18:2)	73.5
Linolenic acid (C18:3)	3.3

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.

The nickel catalyst was activated at 2.9 MPa with hydrogen at 400°C for 1 hour. 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 hydrogen. After the activation step, the reactor was allowed to cool down to 35°C followed by reducing the pressure to almost atmospheric when 63 grams of the oil sample 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 the desired pressure for the reaction. 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. The gas composition 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 Product analysis

The liquid product was analyzed using a GC-MS (Agilent 7890A GC system, 5975C inert MSD with triple-axis detector) fitted with a HP5-MS column. Hydrotreatment conversion was determined and hydrocarbon distributions was evaluated and simulated distillation curves were compiled using a method based on the ASTM D-7213 procedure with data obtained from the GC-MS. The GC-MS was calibrated with an alkane calibration standard obtained from Supelco, Pennsylvania, USA. The composition of the gaseous product was analyzed using a gas chromatograph (HP 6890 Series) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The GC was fitted with a GasPro column from Agilent.

3   RESULTS AND DISCUSSION

3.1 Temperature and pressure profile

The temperature and pressure changes versus time during the hydrotreatment of sunflower oil in the presence of a Ni/SiO$_2$-Al$_2$O$_3$ catalys is shown in Figure 1. The conversion of triglycerides by means of hydrotreatment consists of parallel and/or consecutive reaction steps including saturation, cracking, decarboxylation, decarbonylation and/or hydrodeoxygenation. As shown in Figure 1, the first temperature drop occurs between 100 and 130°C. This pressure drop represents the saturation step where the unsaturated bonds in the oleic acid, linoleic acid and linolenic acid are saturated via hydrogenation to form saturated palmitic acid and stearic acid. Hydrogen consumption results in the pressure drop.
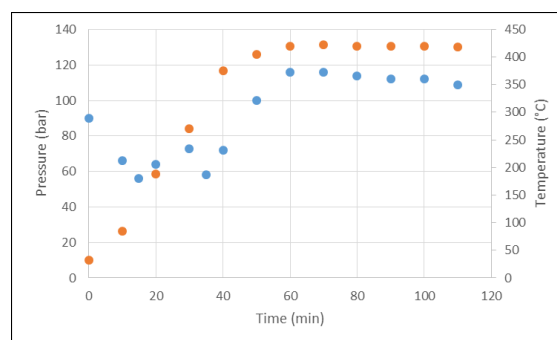

Figure 1: Temperature and pressure profile during hydrotreatment of sunflower oil in the presence of a Ni/SiO$_2$-Al$_2$O$_3$ catalyst

A second pressure drop was observed at temperatures in the range of 270 – 330°C, which is an indication of the cracking of the triglycerides, resulting in the formation of intermediates such as free fatty acids, mono- and di-glycerides where the fatty acids are broken loose from the glycerol backbone. The equable drop in pressure between 60 and 120 minutes is caused by the taking of samples every 10 minutes during the reaction.

3.2 Effect of reaction temperature

Simulated distillation curves for the hydroteatment of sunflower oil are shown in Figure 2. Four of the hydrotreatment runs (390°C, 410°C, 420°C and 390°C without a catalyst) were conducted for 1 hour after the reactor has reached the desired temperature followed by leaving the reactor to cool down to 30°C. One run at 390°C was conducted for 30 minutes after the reaction reached the desired temperature and a sample taken before cooling down. All runs were conducted at an initial pressure of 9 MPa pressurised with hydrogen.
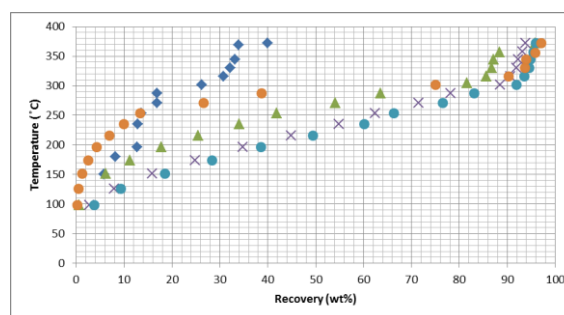

Figure 2: Simulated distillation curves (◆ - 390°C without catalyst, ● - 390°C with 30 minutes reaction time, ▲ - 390°C with 60 minutes reaction time, ✕ - 410°C with 60 minutes reaction time, ● and 420 ° C with 60 minutes reaction time

From Figure 2 it can be seen that the hydrotreatment run at 390°C without a catalyst resulted in a low low conversion of the feedstock and low concentrations of the desired products. A higher diesel yield was obtained at shorter retention times where a sample was taken after 30 minutes. As the temperature of the reaction was raised at longer retention times the fraction recovered at lower temperatures (below 270°C) increased which is an indication of side reactions taking place such as cracking of longer chains to form increased lighter fractions.

The recovery of liquid product as shown in the simulated distillation curves are defined as the fraction of the liquid product that has a certain boiling point. The liquid yield is defined as the amount of sunflower oil that was converted to liquid product. The yield for the different fractions was calculated using the simulated distillation curves and the amount of the liquid product as weighed after each run. The cut-off points used in this study are shown in Table II.

Table II: Cut-off points used for determining naphtha, kerosene and diesel yields from simulated distillation curves

Product	Boiling range
Naphtha	C5 to 160°C
Kerosene	160 to 240°C
Diesel	240 to 370°C

The effect of reaction temperature on the liquid product yield, naphtha yield, kerosene yield and the diesel yield is shown in Figure 3.
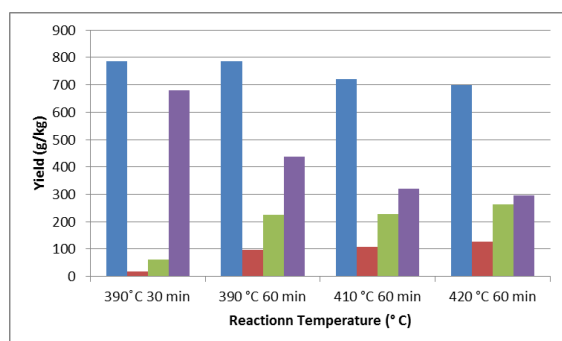

Figure 3: Effect of reaction temperature on liquid yield (■), naphtha yield (■), kerosene yield (■), and diesel yield (■) at different reaction temperature and reaction times.

With an increase in reaction temperature it is observed that the liquid yield decreased from 786.2 g.kg^{-1} feedstock at 390°C to 700 g.kg^{-1} feedstock at a temperature of 420°C. This can be explained by the conversion of feedstock to gas product at more severe reaction conditions. The liquid yield for the run conducted at 390°C with a reaction time of 30 minutes produced about the same amount of liquid product compared to the run at a longer reaction time of 1 hour.

The naphtha yield increased from 98.3 g.kg^{-1} feedstock to 126 g.kg^{-1} with an increase in temperature from 390°C to 420°C. The naphtha yield was much lower (16.7 g.kg^{-1} feedstock) for the run at 390°C with a reaction time of 30 minutes. The kerosene yield showed the same behavior where the yield increased from 224.1 g.kg^{-1} feedstock to 263.9 g.kg^{-1} feedstock with an increase in temperature from 390°C to 420°C. The kerosene yield for the run at 390°C with a shorter reaction time of 30 minutes was also much lower (62.5 g.kg^{-1} feedstock). The diesel yield decreased from 436.3 g.kg^{-1} feedstock to 296.1 g.kg^{-1} feedstock with an increase in temperature while for the run at 390 °C with 30 minutes reaction time the diesel yield was much higher at 679.7 g.kg^{-1} feedstock. This could be explained by the occurrence of the side reactions such as cracking, cyclization and aromatization of the longer carbon chains

at more severe reaction conditions to form lighter fraction compounds. Therefore the diesel fraction is being reduced with an increase in kerosene and naphtha fractions at higher temperatures and longer reaction time.

3.3 Effect of reaction time

The effect of reaction time on product yield was evaluated by using the sampling system where samples were taken during the reaction under high pressure and temperature. As shown in Figure 4, the optimum diesel yield was obtained after 30 minutes reaction time.
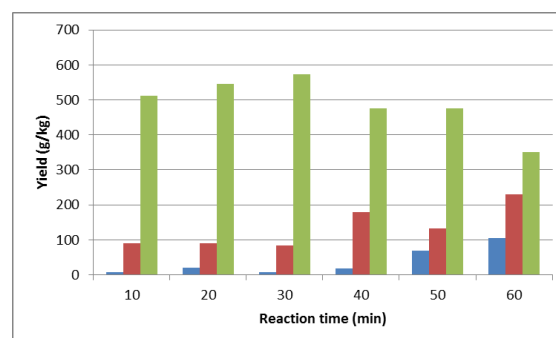

Figure 4: Effect of reaction time on naphtha yield (■), kerosene yield (■) and diesel yield (■) during the hydrotreatment of sunflower oil in the presence of a Ni/SiO$_2$-Al$_2$O$_3$ catalyst at 410°C

During the first 30 minutes the diesel yield increases as the conversion is expected to increase. The decrease in diesel yield after 30 minutes is as a result of the increasing of lighter hydrocarbons with increasing residence time. After 30 minutes the diesel selectivity is decreasing as the naphtha and kerosene fractions are increasing, probably due side reactions like cracking, cyclization and aromatization.

3.4 Effect of initial hydrogen pressure

The effect of initial hydrogen pressure on the batch mode hydrotreatment of sunflower oil at two different temperatures is shown in Figure 5.
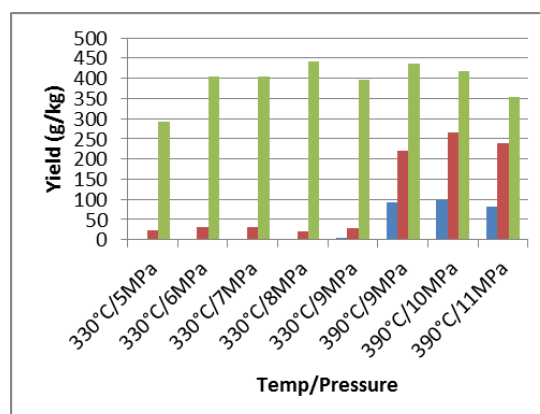

Figure 5: The effect of initial hydrogen pressure at two different temperatures on the composition of the liquid product (■ - Naphtha, ■ - Kerosene, ■ - Diesel)

At the milder reaction temperature of 330°C and an initial hydrogen pressure of 5 MPa, a diesel yield of 292 g.kg^{-1} feedstock was obtained which increased to 405

g.kg^{-1} at an initial pressure of 6 MPa. Hydrogen plays an important role during hydrotreatment with reactions such as hydrogenation, hydrogenolysis and hydrodeoxygenation. Given the relatively milder reaction conditions, the formation of lighter compounds as a result of side reactions such as cracking is limited which explains the low occurrence of kerosene and naphtha fractions in the liquid product at these conditions. The relatively low diesel yield could be attributed to the incomplete conversion of the feedstock to hydrocarbons. At more harsh conditions of 390°C, the naphtha and kerosene fractions increased drastically as a result of side reactions taking place. This increase in lighter fractions takes place to the expense of the heavier diesel fractions, explaining the relatively low diesel yield of between 350 and 440g.kg^{-1} feedstock at these harsh conditions. As shown in Figure 3, a diesel yield of 680 g.kg^{-1} feedstock was obtained at a reaction temperature of 390°C and much shorter reaction time of 30 minutes.

The gas product composition that formed during hydrotreatment of sunflower oil at 410°C at an initial hydrogen pressure of 9 MPa is shown in Table III.

Table III: Gaseous product composition for the hydrotreatment of sunflower oil at 410°C and 9 MPa

Gas component	Mole %
Methane (CH_4)	40.83
Ethane (C_2H_6)	2.9
Propane (C_3H_8)	0.8
Butane (C_4H_{10})	0.1
Nitrogen/Oxygen (N_2/O_2)	0.03
Carbon monoxide (CO)	0.4
Carbon dioxide (CO_2)	21.5
Hydrogen sulfide (H_2S)	0
Other	28.37
Total	100

The CO_2 concentration (21.5 mole%) corresponds with the suggestion that the decarboxylation/ decarbonylation reaction pathways dominate. The methane concentration is also very high as a result of the methanation reaction taking place.

The energy value of the hydrotreated product was compared with that of the feedstock and commercially available petroleum diesel as shown in Table IV.

Table IV: Gross calorific values for sunflower oil and hydrotreated product

Product	Higher heating value (HHV) (MJ.kg^{-1})
Neat sunflower oil	39.6
Hydrotreated sunflower oil	46.9
Commercial petroleum diesel	41.0

The higher heating value of the hydrotreated product shows that the removal of oxygen from the feedstock during hydrotreatment was done effectively.

4 CONCLUSIONS

Reaction conditions have a significant effect on the reaction product during the hydrotreatment of sunflower oil in the presence of a Ni/SiO$_2$-Al$_2$O$_3$ catalyst. More severe conditions such as higher reaction temperatures and longer residence time has a negative effect on diesel selectivity and a positive effect on naphtha and kerosene selectivity as side reactions such as cracking, aromatization and cyclization are responsible for the formation of lighter fractions.

The relatively low cost of the Ni/SiO$_2$-Al$_2$O$_3$ catalyst and the fact that it can be activated by means of reduction where feedstock with low sulfur content does not deactivate the catalyst make it an attractive option as a hydrotreatment catalyst for triglyceride based feedstock.

5 REFERENCES

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6 ACKNOWLEDGEMENTS

7 LOGO SPACE