

EVALUATION OF COTTONSEED OIL AS CO-FEEDSTOCK FOR THE HYDROPROCESSING OF PETROLEUM MIDDLE DISTILLATES FOR DIESEL FUEL PRODUCTION

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ABSTRACT: Mandatory blending of biodiesel into petroleum diesel came to effect in 2015 in South Africa. The availability of biodiesel to implement this mandate however poses a challenge for local biodiesel producers and petroleum refineries. One alternative that could contribute to the solution of this problem is upstream blending of triglyceride oil into the hydrotreater feed of existing refining facilities. Cottonseed oil, a by-product from the cotton wool industry could be considered a co-feed candidate for diesel fuel production. In this study, the effect of catalysts and reaction conditions on the composition and yield of renewable bio-hydrocarbon fuels from cottonseed oil and hybrid diesel fuel from atmospheric gas oil/ cottonseed oil blends were evaluated. Experiments were conducted using a cylindrical bench-scale batch reactor with a volume of 350 cm³ and a maximum pressure rating of 20 MPa. For cottonseed oil the conversion performance order was found to be NiMo-Al₂O₃ (99.86%) > sulphided CoMo-Al₂O₃ (98.9%) > reduced Ni/SiO₂-Al₂O₃ (96.8%). The highest diesel yield obtained at 390°C reaction temperature and initial hydrogen pressure of 9 MPa were 493g.kg⁻¹ for the CoMo-Al₂O₃ catalyst, 492g.kg⁻¹ for the NiMo-Al₂O₃ catalyst and 444g.kg⁻¹ for the NiSiO₂-Al₂O₃ catalyst. For cottonseed oil/gas oil blends up to 20% cottonseed oil, no negative effect was observed on the hydrodesulphurisation of gas oil. Simulated distillation data showed that cracking is promoted with the addition of cottonseed oil and the diesel yield increases with an increase in cottonseed oil concentration.

Keywords: Hydrotreatment, co-processing, cottonseed oil, atmospheric gasoil, hydrodesulphurisation

1 INTRODUCTION

The ever-increasing demand for transportation fuel and the decrease in oil reserves necessitate the effort to find alternative fuel sources. It is estimated that peak oil will occur between 2008 and 2040 depending on the usage rate, the economy and technology development [1]

The most common alternative transportation fuel in use at present in the world is FAME-based (fatty acid methyl ester) biodiesel and ethanol. FAME-based biodiesel is produced from triglycerides via transesterification. Alkaline homogeneous catalysis is the conventional process most often used in industry. More than 95% of the biodiesel produced in the world at present uses edible oil as feedstock [2]. This raises social implications, as it is associated with the food versus fuel debate. Although biodiesel has many advantages compared to petroleum diesel, such as biodegradability, it is a cleaner burning fuel due to the presence of oxygen in the ester molecule, it is renewable, contains low sulphur, has a 90% reduction in cancer risk due to the lower reactive hydrocarbon species and emissions of poly aromatic hydrocarbons and is a non-toxic fuel [3], biodiesel also has a few drawbacks. Compared to petroleum diesel, FAME-based biodiesel has a lower energy content, it has undesired cold flow properties, a lower cetane number, and has lower storage stability. [4, 5].

Although facing the same challenges from a feedstock availability point of view, renewable diesel produced through hydrotreatment, could be a promising alternative to FAME-based biodiesel.

Catalytic hydroprocessing of vegetable oils and animal fats produces paraffinic products without acidic and metallic compounds [1] Paraffinic mixtures that are produced have higher cetane number, and good cold flow properties, which are fully comparable with petroleum diesel properties [6]. Renewable diesel can be blended with petroleum diesel either upstream or downstream to create a biodiesel blend [7].

Authorities promote biofuels by means of specific

action plans setting targets for the blending of biofuels in conventional fuels. The European Commission put forth the Renewable Energy Directive (2009/28/EC) in 2009 with the objective to achieve an overall 20% GHG emission reduction by 2020 [1]. The South African Department of Energy has announced that all gasoline and diesel sold in the country will include the addition of biofuels [10]. Availability of biodiesel to implement this mandate however poses a challenge for local biodiesel producers and petroleum refineries. One alternative that could contribute to the solution of this problem is upstream blending of triglyceride oil into the hydrotreater feed of existing refining facilities.

Hydroprocessing technology has been utilized in the petroleum industry for many years. Petroleum feedstock comprises a complex mixture of hydrocarbons with relative low concentrations of sulphur, nitrogen, oxygen and metals, and therefore its need for hydroprocessing [8]. Catalytic hydroprocessing is employed by petroleum refineries for the removal of heteroatoms and cracking of heavy molecules into lighter compounds. This process can also be applied to triglyceride-based feedstock to produce a diesel biofuel with cetane number, heating value, oxidation stability comparable to or better than petroleum diesel [9].

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. Hydrotreatment is done at elevated temperature and pressure in the presence of a hydrotreating or hydrocracking catalyst. Reaction conditions and catalyst type play a major role in the composition and yield of the liquid product produced.

In this study, crude cottonseed oil, a by-product from the local cotton industry was evaluated as a feedstock for the co-processing with atmospheric gas oil. The effect of the blending of cottonseed oil into the gas oil on the desulphurisation of the gas oil was investigated at two

different reactor temperatures. The effect of 3 different hydrotreating catalysts on the conversion and liquid product composition of hydrotreated cottonseed oil has been compared.

2 EXPERIMENTAL

2.1 Materials, apparatus and methods

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 deacidification. Some properties of crude cottonseed oil are shown in Table I.

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

Figure 1 represents the simulated distillation curve for atmospheric gasoil.

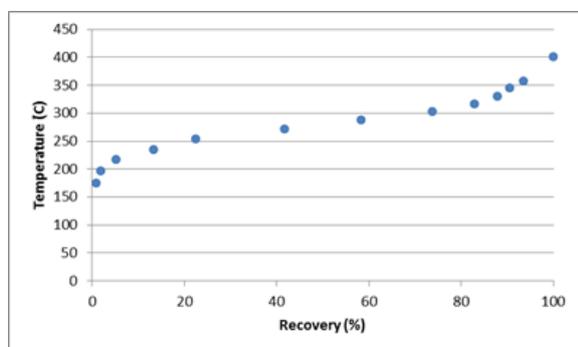


Figure 1: Simulated distillation curve for atmospheric gas oil

Hydrotreatment of crude cottonseed oil in the presence of 3 different catalysts were compared. The CoMo/Al₂O₃ catalyst was purchased from Strem Chemicals (USA), the Ni-SiO₂/Al₂O₃ catalyst was purchased from Alfa-Aesar (MA, USA) and the NiMo/Al₂O₃ catalyst was obtained from a commercial catalyst supplier. Hydrogen (99.999%), 14.9% H₂S in argon and nitrogen (99.999%) used in the experiments were supplied by Afrox South Africa.

The hydrotreatment experiments were conducted in a cylindrical custom-build high-pressure batch reactor with an inside volume of 350 cm³. The contents of the reactor were extensively stirred during the reaction using a magnetic stirrer driven by a variable speed DC motor. The CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts were activated at 2.9 MPa with 14.9% H₂S in argon at 400°C for 1 hour. For the Ni-SiO₂/Al₂O₃ catalyst, hydrogen at

2.9MPa was used in the activation step. 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% H₂S in argon for the NiMo and CoMo catalysts, and with hydrogen for the Ni-SiO₂/Al₂O₃ catalyst. 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 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 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 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 calorific value (HHV) of the liquid product was measured using a Bomb-type calorimeter (IKA C5003) with a KV600 water cooling system and C5000 control package and cotton thread flint (C710.4).

3 RESULTS AND DISCUSSION

3.1 Comparison of catalysts

The effect of temperature and initial hydrogen pressure on the conversion of crude cottonseed oil in the presence of a Ni/SiO₂-Al₂O₃ is shown in figure 2.

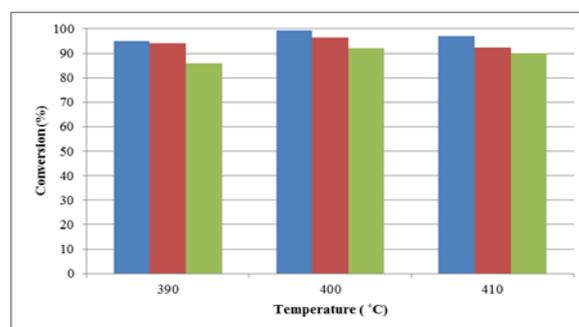


Figure 2: The effect of reaction temperature and initial hydrogen pressure on the conversion of crude cottonseed oil in the presence of a NiSiO₂-Al₂O₃ catalyst (9 MPa ■, 10 MPa ■, 11 MPa ■)

The conversion of cottonseed oil increased from 94.5% to 99.8% with an increase in reaction temperature from 390 °C to 400 °C for all initial hydrogen pressures. The conversion decreased with a further increase to 410 °C. Conversion is defined as the mass percentage of cottonseed oil converted to organic liquid product with a boiling range less than 370 °C. A possible explanation for the increase in conversion is that the endothermic decarboxylation and/or decarbonylation reactions are promoted by an increase in temperature. A decrease in conversion with a further increase in temperature is possibly a result of deactivation of the catalyst due to the formation of water through the water shift reaction [4].

The conversion of cottonseed oil decreased with an increase in initial hydrogen pressure at a constant reaction temperature. For a reaction temperature of 390 °C the conversion decreased from 95% to 86% with an increase in initial hydrogen pressure from 9 MPa to 11 MPa. Side reactions such as methanation and water gas shift reaction consume hydrogen to produce methane. Compositional gas analysis of the gas product showed an increase in methane content with the gas product formed at 10 MPa containing 37 % methane. This confirms the lower conversion with an increase in pressure due to methanation. The endothermic decarboxylation and/or decarbonylation reactions are less favoured at higher pressures where water formation of the hydrodeoxygenation reaction has a deactivation effect on the catalyst [4].

The effect of reaction temperature and initial hydrogen pressure on the conversion of crude cottonseed oil in the presence of a NiMo/Al₂O₃ catalyst is presented in figure 3. For the NiMo catalyst almost complete conversion was observed for all temperature and pressure variations. Complete conversion and although within experimental error, what appears to be higher conversion at higher temperature and pressure, can be explained by the promotion of the endothermic decarboxylation and/or decarbonylation reactions at higher temperatures [4].

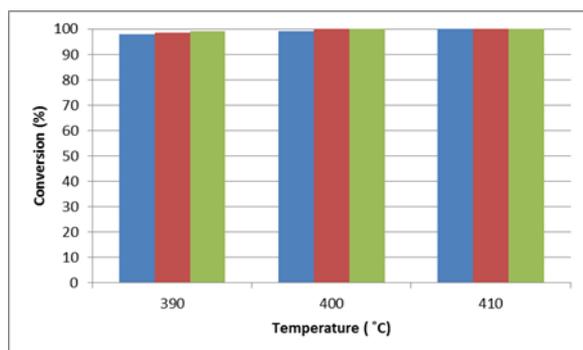


Figure 3: The effect of reaction temperature and initial hydrogen pressure on the conversion of crude cottonseed oil in the presence of a NiMo/Al₂O₃ catalyst (9 MPa ■, 10MPa ■, 11MPa ■)

Compositional gas analysis of the gas product showed an average methane concentration of 2% which decreases with an increase in temperature from 390 °C to 410 °C. Low concentration of methane produced through methanation minimizes hydrogen consumption which makes it available for deoxygenation reactions. The NiMo catalyst is well known for its resistance to methane formation reactions [11].

The effect of reaction temperature and initial hydrogen pressure on the conversion of crude cottonseed oil in the presence of a CoMo/Al₂O₃ catalyst is shown in figure 4.

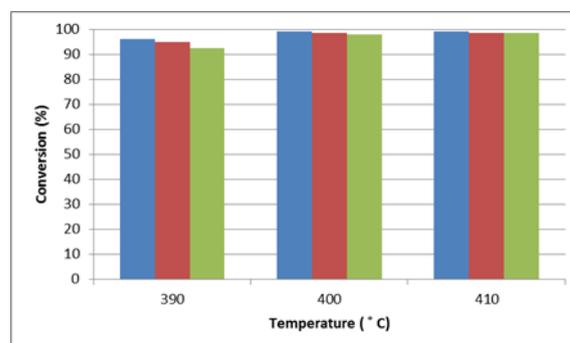


Figure 4: The effect of reaction temperature and initial hydrogen pressure on the conversion of crude cottonseed oil in the presence of a CoMo/Al₂O₃ catalyst (9 MPa ■, 10MPa ■, 11MPa ■)

An increase in reaction temperature from 390 °C to 410 °C resulted in an increase in conversion from 96.5% to 99.2%. The highest conversion occurred at the lowest initial hydrogen pressure of 9 MPa and at 410 °C. The increase in conversion when temperature was increased was due to decarbonylation and/or decarboxylation reactions being favoured at higher temperatures. These reactions are endothermic, and therefore the increase in temperature will increase conversion [4], [12]. The conversion of cottonseed oil decreased with an increase in initial hydrogen pressure from 97% at 9 MPa to 93% at 11 MPa at a constant reaction pressure. The reduction in conversion as initial hydrogen pressure increases is due to the decarboxylation and/or decarbonylation reactions being less favoured where hydrodeoxygenation is promoted. Oxygen is removed as water during the hydrodeoxygenation of fatty acids which has a deactivation effect on the catalyst [4], [13].

The reaction product yield for the hydrotreatment of crude cottonseed oil at 390 °C and initial hydrogen pressure of 9 MPa using 3 catalyst types is represented in figure 5.

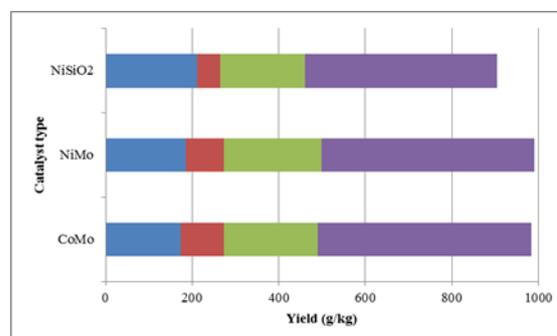


Figure 5: Reaction product yield comparison of crude cottonseed oil at 390 °C and 9 MPa initial hydrogen pressure for the 3 catalyst types (gas yield ■, naphtha yield ■, kerosene yield ■, diesel yield ■)

The highest diesel yield obtained at 390°C reaction temperature and initial hydrogen pressure of 9 MPa is

493g.kg-1 for the CoMo-Al₂O₃ catalyst, 492g.kg-1 for the NiMo-Al₂O₃ catalyst and 444g.kg-1 for the NiSiO₂-Al₂O₃ catalyst. The highest conversion was obtained for the NiMo-Al₂O₃ and CoMo-Al₂O₃ catalysts which are 98.5% and 99.7%, respectively, at 410°C reaction temperature and initial hydrogen pressure of 11 MPa. In terms of conversion performance, the order was found to be NiMo-Al₂O₃ (99.86%) > sulphided CoMo-Al₂O₃ (98.9%) > reduced Ni/SiO₂-Al₂O₃ (96.8%).

The NiSiO₂ catalyst has the highest gas yield of 211.5 g/kg. This can be attributed to the formation of methane amongst other as Ni catalysts are known for catalyzing the methanation reaction. The CoMo catalyst showed the highest naphtha content as well as a high kerosene content which could be attributed to its relatively higher tendency to crack longer alkane chains to lighter compounds.

Figure 6 represents the liquid product composition of crude cottonseed oil at different reaction temperature and pressure in the presence of a Ni-SiO₂/Al₂O₃ catalyst. Marginal decrease in n-alkanes has been observed with an increase in temperature and an increase in pressure. This is attributed to cracking of longer chain compounds under more severe reaction conditions. A slight increase of iso alkanes was observed at more severe conditions which is a desired side reaction to improve the cold flow properties of a fuel. The formation of olefins decreased significantly with temperature and pressure. This could be attributed to the activity of the hydrocracking catalyst which improves at more severe reaction conditions as well as the increase in hydrogen partial pressure [19].

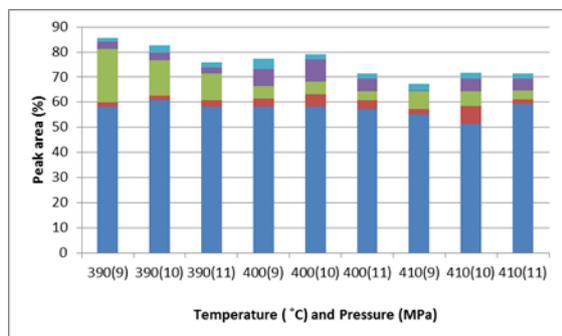


Figure 6: Liquid product composition of crude cottonseed oil hydrotreated at different temperature and pressure in the presence of a Ni-SiO₂/Al₂O₃ catalyst (n-alkanes ■, iso-alkanes ■, olefins ■, aromatics ■, cyclic compounds ■)

The liquid product composition of hydrotreated crude cottonseed oil in the presence of a NiMo/Al₂O₃ hydrotreating catalyst is shown in figure 7. The n-alkane concentration decreases with an increase in reaction temperature from 390 °C to 410 °C with the increase in iso alkanes indicating that isomerization of n-alkanes are taking place. The decrease in n-alkanes is also as a result of cracking reactions.

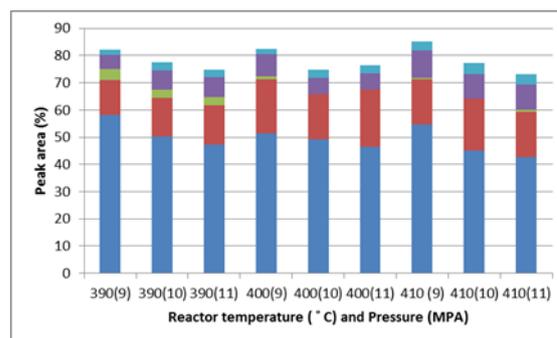


Figure 7: Liquid product composition of crude cottonseed oil hydrotreated at different temperature and pressure in the presence of a NiMo/Al₂O₃ hydrotreating catalyst (n-alkanes ■, iso-alkanes ■, olefins ■, aromatics ■, cyclic compounds ■)

The decrease of iso-alkanes at temperatures above 400°C is mainly due to the cracking of iso-alkanes which are less stable at higher temperatures [14]. Furthermore, an increase in pressure from 9 to 11 MPa resulted in a significant decrease in n-alkanes, while the iso-alkanes increased slightly. The decrease in n-alkanes with an increase in reaction pressure is as a result of the cracking of n-alkanes. Changes in the liquid product composition due to the changes in reaction pressure are promoted by cracking reactions where pressure has a minimal effect on isomerisation [15]. Olefins are decreasing at higher temperature and pressure. As for molybdenum catalysts, hydrogenation takes place at higher temperatures. At higher initial hydrogen pressure, it is also observed that the olefin concentration in the liquid product decreases. The olefin content decreased from 3.4% to 2.4% when the pressure was increased from 9 to 11 MPa. A possible explanation is the saturation of double bonds at higher hydrogen supply [7].

Aromatic and cyclic compounds increased with an increase in both the temperature and pressure. An increase in temperature from 390 to 410°C at a constant initial hydrogen pressure resulted in an increase in aromatic content from 4% to 8.1%. Cyclisation of the aliphatic hydrocarbons are promoted at severe conditions such as high reaction temperatures and long residence time [16].

The liquid product composition of crude cottonseed oil hydrotreated in the presence of a CoMo/Al₂O₃ catalyst is shown in figure 8. As shown, there is a reduction of n-alkanes as temperature was increased from 390 to 410°C. Additionally, there was a slight increase in iso-alkanes with increase in temperature. These changes are due to n-alkanes undergoing isomerisation to form isomers and also cracked into lighter molecules of which some are gas at room temperature. Increasing temperature increases the amount of isomers of straight-chain alkanes in the liquid [17], [18].

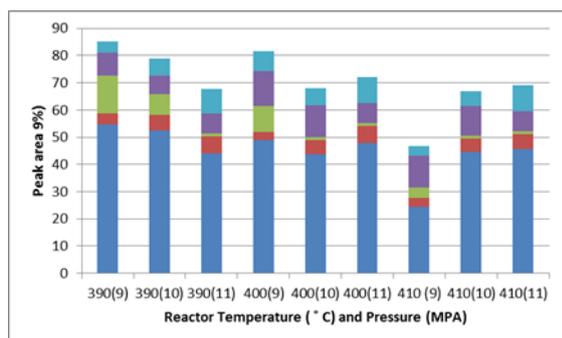


Figure 8: Liquid product composition of crude cottonseed oil hydrotreated at different temperature and pressure in the presence of a CoMo/Al₂O₃ hydrotreating catalyst (n-alkanes ■, iso-alkanes ■, olefins ■, aromatics ■, cyclic compounds ■)

A slight insignificant reduction in n-alkanes was observed when the pressure was increased from 9 to 11 MPa at 390°C. At a temperature of 410 °C the n-alkane concentration increased with an increase in initial hydrogen pressure.

The olefin content of the liquid product decreased with both an increase in pressure and temperature. The hydrogenation activity of the CoMo-Al₂O₃ takes place at higher temperatures of around 400°C resulting in reduced olefin content. The olefin content also decreased with an increase in initial hydrogen pressure. The olefin content decreased from 3.5 peak area % to 0.3 peak area % with an increase in initial hydrogen pressure from 9 MPa to 11 MPa. At higher initial hydrogen pressure more hydrogen is available for hydrogenation [4].

The aromatic content increased with an increase in temperature and initial hydrogen pressure. Intermediates containing double bonds undergo cyclisation and dehydrogenation to form aromatic compounds [14].

3.2 Co-processing of atmospheric gas oil and crude cottonseed oil

Figure 9 shows the sulphur removal efficiency of the hydrotreatment of light gas oil containing different concentrations of crude cottonseed oil. Sulphur removal efficiency was calculated using equation 1

$$\text{Sulphur}_{\text{removal}} = \frac{\text{Sulphur}_{\text{feed}} - \text{Sulphur}_{\text{product}}}{\text{Sulphur}_{\text{feed}}} \times 100\% \quad 1$$

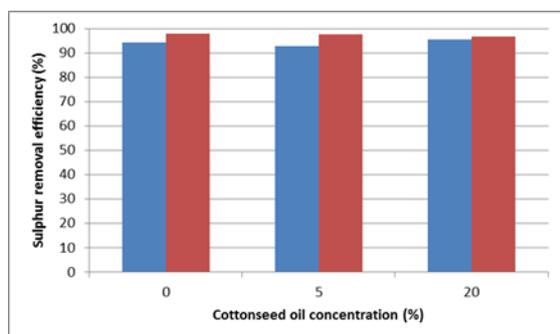


Figure 9: Sulphur removal efficiency during hydrotreatment of atmospheric gasoil containing 0%, 5% and 20% crude cottonseed oil (390°C ■, 410°C ■)

The removal of sulphur as heteroatom is high and increases with hydrotreatment temperature. The sulphur concentration in the feedstock was reduced from 7100 ppm by means of hydrotreatment to 410 ppm at 390 °C and 150 ppm at 410 °C where no cottonseed oil was added. For a 5% cottonseed oil concentration the sulphur concentration was reduced to 520 ppm at 390 °C hydrotreatment temperature and to 160 ppm at 410 °C. For 20 % cottonseed oil concentration the sulphur level reduced to 320 ppm at 390 °C and to 240 ppm at 410 °C.

Figure 10 represents the simulated distillation curves for hydrotreated gas oil containing different concentrations of cottonseed oil.

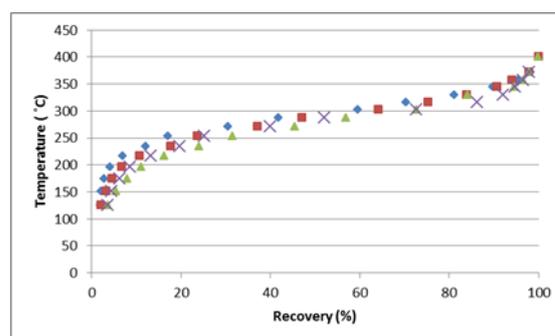


Figure 10: Simulated distillation curves for the hydrotreatment of gas oil containing different concentrations of crude cottonseed oil (untreated gas oil ◆, 0% ■, 5% ▲ and 20% × cottonseed oil)

As shown in figure 10 cracking seems to be promoted with the addition of cottonseed oil to the gas oil. More liquid product is recovered at lower distillation temperature compared to the hydrotreatment of neat gas oil. Heavier molecules are cracked to form shorter chain compounds which boil at lower temperatures. Figure 11 represents the diesel yield calculated using the simulated distillation curves shown in figure 10.

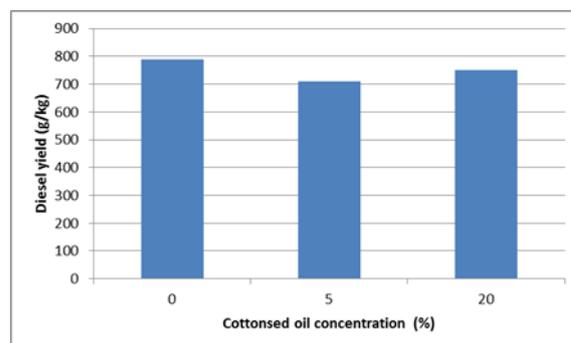


Figure 11: Diesel yield obtained from the hydrotreatment of atmospheric gas oil containing different concentrations of crude cottonseed oil

In Figure 11 it can be seen that the diesel yield decreases from 790 g per kilogram feedstock to 710 g/kg with a 5% cottonseed oil blend and then increased again with a 20 % cottonseed oil blend.

Figure 12 represents the liquid product composition of hydrotreated gas oil and hydrotreated gas oil containing 20% cottonseed oil.

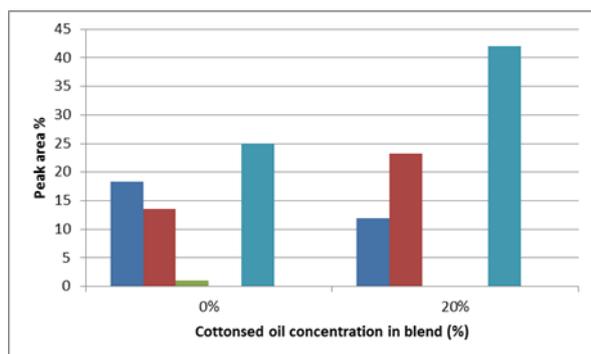


Figure 12: Liquid product composition after hydrotreatment of gas oil and gas oil/cottonseed oil blend in the presence of a NiMo catalyst (iso-alkanes ■, aromatics ■, cyclic compounds ■, olefins ■, n-alkanes ■, oxygenates ■)

The decrease in diesel yield shown in figure 10 could be attributed to cracking of larger molecules to form lower boiling range compounds and the increase in diesel yield with higher cottonseed oil blend concentration is due to the formation of more n-alkanes during hydrotreatment. The formation of n-alkanes from long chain esters present in cottonseed oil confirms the removal of oxygen during hydrotreatment.

4 CONCLUSION

Co-processing of crude cottonseed oil with atmospheric gas oil could be a prominent process for the production of hybrid biofuels. The potential exist for the utilization of existing refinery facilities for co-processing.

The effect of the co-processing of different concentrations of cottonseed oil in gas oil on the desulphurization of light gas oil was evaluated. The addition of cottonseed oil at a ratio of up to 20% did not have a negative effect on the desulphurization process. Higher reaction temperatures showed an increase in sulphur removal efficiency. Simulated distillation data showed that cracking is promoted with the addition of cottonseed oil and the diesel yield increases with an increase in cottonseed oil concentration.

Besides the effect of co-processing of cottonseed oil with gas oil, the effect of different catalyst on the hydrotreatment of crude cottonseed oil was also compared. Catalyst type and reaction conditions are important tools available to manipulate the composition of the liquid product. The highest conversion of crude cottonseed oil was observed for the NiMo catalyst where the conversion increased with an increase in reaction temperature and initial hydrogen pressure. In terms of conversion performance, the order was found to be NiMo-Al₂O₃ (99.86%) > sulphided CoMo-Al₂O₃ (98.9%) > reduced Ni/SiO₂-Al₂O₃ (96.8%). The highest liquid product yield of 811 g.kg⁻¹ was obtained during the hydrotreatment of cottonseed, in the presence of the NiMo catalyst. The reduction in liquid product yield was also insignificant when the NiMo catalyst was used for temperature and pressure ranges of 390 to 410°C and 9 MPa to 11 MPa, respectively. This shows that the NiMo catalyst is more of a hydrotreating catalyst suitable to minimise the liquid product yield reduction.

The highest iso-alkane content was observed when

the NiMo catalyst was used. Olefin content decreased with increasing temperature for all 3 catalyst.

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6 ACKNOWLEDGEMENTS

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7 LOGO SPACE

