IN-SITU BIODIESEL PRODUCTION FROM SUNFLOWER SEEDS USING LIQUEFACTION

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ABSTRACT: One of the most expensive steps in the bio-diesel value chain is the extraction of oil from the seeds. Simultaneous extraction and transesterification will lower the overall capital costs of the process while enhancing FAME conversion. In this study, the extraction of oil with supercritical CO_2 was combined with the liquefaction of sunflower seeds and transesterification with sub-critical methanol to enhance biodiesel yield from sunflower seed oil. Supercritical CO_2 was used as a reaction atmosphere at elevated pressures to extract oil from the seeds while continuously reacting the oil with methanol. Reaction temperature, biomass loading, catalyst loading and methanol to biomass loading were varied and the oil and fatty acid methyl acid (FAME) yields were determined using GC-MS. Biodiesel quality was assessed using FTIR and gas chromatography. All variables investigated had an effect on the FAME yield with 330°C, 2wt% $CaCO_3$ as catalyst and a reaction time of 15 minutes resulting in the highest product (550 $g.kg^{-1}$) and FAME (900 $g.kg^{-1}$) yields. The FAME yields obtained indicated that both the oil originally present in the seeds and some of the lignocellulose parts of the seeds were converted to biodiesel. This result shows the potential of in-situ biodiesel production to increase production yields while lowering the overall capital cost and separation cost of the value chain.
Keywords: biodiesel, in-situ, supercritical, liquefaction, transesterification

1 INTRODUCTION

Global urbanisation, industrialisation and rumours of dwindling fossil fuel stocks triggered an uncontrollable increase in the demand for fuel, contributing to skyrocketing fuel prices. Combine these factors with an environmentally concerned green revolution and the end result is a global outcry for an alternative fuel source.

Despite the sources being finite and located in restricted locations around the world more than 85% of world energy originates from fossil fuels [1]. Diesel (a mixture of organic compounds with a boiling point of between 240°C and 370°C) is the driving force behind modern industrialisation. Fossil based diesel can be replaced by biodiesel, which is a mixture of fatty ester esters that can be produced from vegetables oil and animal fats [2].

Extraction of oils from plant materials is still one of the most expensive steps in the biodiesel value chain [3]. *In-situ* trans-esterification of oil containing feedstock is done with simultaneous oil extraction to circumvent the need to process biomass to get the oils beforehand, and it is believed that some financial and production gains can made by this [4, 5]. In the presence of an inorganic acid or base the *in-situ* trans-esterification reaction can occur at moderate temperature and atmospheric pressure, but with lack of prior processing a higher alcohol to oil molar ratio and catalyst loading is needed to overcome interference from contaminating particles from the biomass [6]. The presence of water in the feedstock will initiate unwanted hydrolysis that produces soap as a by-product and thus the feedstock used should not contain more than 3wt% moisture [7].

The major drawback of *in-situ* transesterification for biodiesel production is an increased alcohol to oil molar ratio that is required to compensate for contaminating particles that inhibits the diesel reaction. A too high alcohol to molar will increase the operating cost of the process thus nullifying the advantages gained by combining the extraction and reaction processes [6]. Thermochemical processing of biomass is the treatment of material at high temperatures and pressures in the presence of a working fluid and reaction gas. During hydrothermal liquefaction, biomass material is broken down break down to smaller molecules in the presence of water as solvent to form biochar, bio-oil and biogas [8]. During thermochemical treatment the carbon and hydrogen content of the material is increased and the oxygen content is decreased by a complex series of dehydrogenating, decarboxylating and hydro-deoxy-carbonylation reactions [9]. Supercritical fluids such as carbon dioxide can extract non-polar solutes and enhance solubilisation of more polar moieties by the addition of ethanol or methanol [10]. Supercritical carbon dioxide has been successfully implemented in the trans-esterification of triglycerides with the use of lipases (novozyme SP 435) as catalyst and also to facilitate the upgrading of bio-oil/biodiesel by facilitating the full hydrogenation of methyl esters formed from vegetable oils.

In this study the in-situ production of biodiesel from sunflower seeds in the presence of methanol with supercritical carbon dioxide was investigated. The effectiveness of alkaline and acid catalyst in methanol to enhance the FAME content of the produced oil were investigated at different temperatures. The bio-oils obtained were characterised in terms of FAME content and compliance to the SANS1935 biodiesel standard of South Africa.

2 MATERIALS AND METHODS

2.1 Feedstock

Sunflower seed from a draught resistant strain with low oil content was acquired from a local farmer in the North West Province, South Africa. The seeds were collected from a harvester in a 50 kg grain pack and transported by car to the University premises. The seeds where milled with a hammer mill to a seed size of 0.8 mm-15 mm before drying at 100°C overnight. The biomass was then quartered and sealed in plastic airtight containers until used. Compositional analysis of dried, milled seeds was done by the Agricultural Research Council, Irene, South Africa and is given in Table I.

Table I: Compositional analysis of sunflower seeds used in this study (wt% on a dry basis)

Component	Wt% (dry basis)
Dry matter	92.21
Moisture	7.79
Ash	3.21
Crude Protein	16.12
Fat (ether extract)	37.66
Neutral detergent fiber (NDF)	30.27
Acid detergent fiber (ADF)	25.85
Acid detergent lignin (ADL)	12.58
Cellulose (ADF-ADL)	13.27
Hemicellulose (NDF-ADF)	4.42
Lignin (ADL)	12.58

2.2 Experimental method

A schematic diagram of the experimental setup used in this study is given in Figure 1.

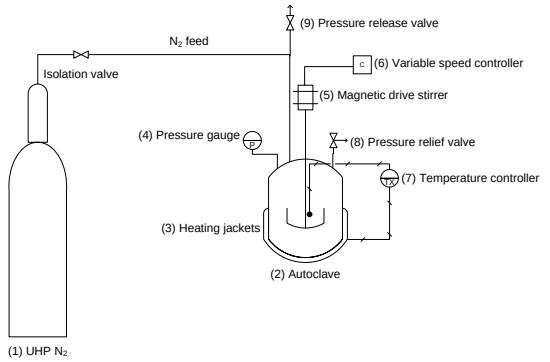

Figure 1: Liquefaction reactor setup used in this study

Liquefaction was done according to standard methods [11, 12]. A stainless steel 316 autoclave with a volume of 954 mL was used for all experiments. The influence of temperature (320°C to 360°), type of catalysts (potassium hydroxide (KOH), sulfuric acid (H_2SO_4) and calcium carbonate ($CaCO_3$)) and biomass loading (150 $g.kg^{-1}$ to 250 $g.kg^{-1}$ in solvent) on the oil and biodiesel yield were investigated. In a typical experiment the reactor was loaded with the desired amount of biomass in 100 mL of methanol and 20 $g.kg^{-1}$ of the desired catalyst. After sealing, the reactor was purged for 10 min with CO_2 gas to remove residual air. The pressure was then raised to 5 bar and left for 15 min to check for gas leaks, before the temperature was increased to the desired holding temperature. Once the reaction temperature was reached the stirrer (300 rpm) was switched on and left for the holding time of 15 min. The temperature was controlled through a standard temperature controller and a set of thermocouples that measured the temperature of the heating jacket and the center of the reactor. After completion of the reaction, the reactor was cooled down to room temperature using forced air.

After cooling down, the pressure was released and 20 mL of acetone was added to the oil and stirred for 15 min to allow all oil substances to dissolve [13]. The end product was filtered under vacuum through a Whatman no.40 filter paper. The residue (biochar) was dried overnight at 105°C. The bio-oil was water washed using warm water (95°C). After settling, the water phase was decanted and discarded. The washing procedure was repeated three times. An improved washing technique used later utilized n-hexane as oil recovery step before the water washing cycle. An n-hexane ratio of 1 to 2 volumes of crude oil was used for n-hexane washing. The end product was then placed on a hotplate and stirred for an hour at 80°C to remove all n-hexane before being oven dried overnight at 105°C. Oil yields were calculated as the mass of bio-oil product over the mass of sunflower seeds used and expressed as grams bio-oil per kilogram of biomass ($g.kg^{-1}$). Fatty acid methyl esters (FAME) yields were calculated as the weight fraction of bio-oil consisting of fatty acid esters and expressed as gram FAME per kilogram of biomass ($g.kg^{-1}$).

2.3 Analysis

Biodiesel samples were analyzed using gas chromatography (Agilent 7820A, fitted with an HP-66 (100m) column and a flame ionization detector (FID)). Methyl nonanoate was used as internal standard and FAME content was quantified using a set of calibration curves.

Gas chromatography coupled mass spectrometry (GC-MS) analysis (Agilent 7890A, fitted with an HP-5 (30 m) column and an FID detector) was used to identify the residual components in the bio-oil The MS was equipped with an MSD Triple axis detector.

Fourier transform infrared spectroscopy (FTIR) was done using an Eralytics Eraspec fully automated fuel analyser to identify the functional groups present in crude oil. The samples were scanned and the absorbance plotted against wavelength ranged from 600 cm^{-1} to 3000 cm^{-1}. The lowest absorption peaks were used to as transmittance peaks to identify functional groups. This device also measured the density with an oscillating U-tube and calculated the cetane value and aromatic content.

Karl Fischer Coulometry was used to determine the water content of the diesel or oil using the coulometric method with a cell diaphragm (Metrohm Karl Fischer coulometer). The cell was dried until a constant drift of less than 10ppm was maintained. A dry syringe was purged 3 times with the sample before 1g of sample was added to the titration cell and analyzed.

Ultimate analysis was done using a C-440 Elemental analyzer with a CE 490 interface (EAT Exeter analytical, Inc.). Acetaldehyde with a composition of 71.09 wt% C, 6.71 wt% H, 10.36 wt% N and 11.84 wt% O was used as a standard for calibration.

The calorific value (HHV) of biochar and bio-oil was measure using a Bomb-type calorimeter (IKA C5003) with a KV600 water cooling system. C5000 control package and cotton thread flint (C710.4). Benzoic acid (IKA C723) was used as calibration standard.

3 RESULTS AND DISCUSSION

3.1 Effect of catalyst type and temperature

The effect of catalyst type on oil and FAME yield was investigated with a constant catalyst loading of 20 $g.kg^{-1}$ in methanol and a solid loading of 200 $g.kg^{-1}$ in methanol. The effect of the different catalysts on the oil, FAME and biochar yields is shown in Figure 2 to 4. The experimental error for this set of data was calculated as 9.08 % for a 95% confidence level.

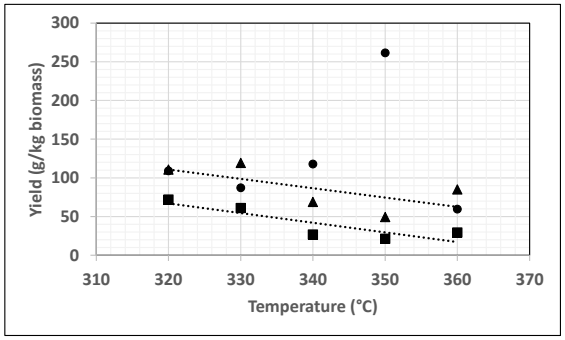

Figure 2: Effect of temperature on bio-oil (▲), biochar (●) and FAME (■) yields in the presence of a KOH catalyst

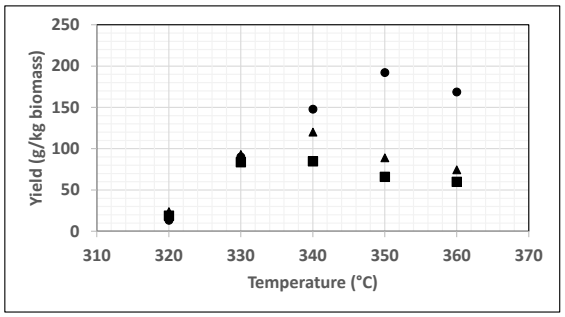

Figure 3: Effect of temperature on bio-oil (▲), biochar (●) and FAME (■) yields in the presence of a $CaCO_3$ catalyst

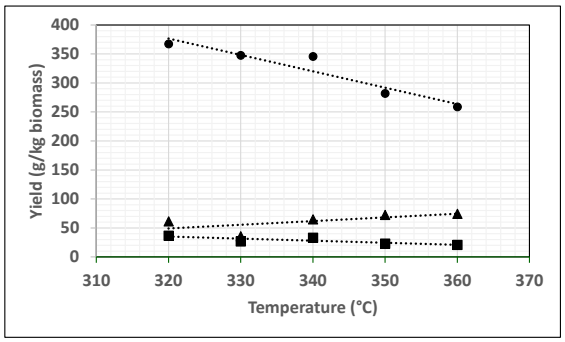

Figure 4: Effect of temperature on bio-oil (▲), biochar (●) and FAME (■) yields in the presence of a H_2SO_4 catalyst

From Figure 2 and 3 it can be seen that the highest bio-oil yield (110.55 $g.kg^{-1}$) and FAME yield (71.72 $g.kg^{-1}$) was obtained when KOH was used as alkaline catalyst at 320°C. The primary product formation led to an initial increase in bio-oil yield from 320°C to 330°C, followed by the primary breakdown of bio-oil from 330°C to 360°C and reformation of bio-oil from 350°C to 360°C. The first increase in bio-oil yield between 320°C and 330°C when KOH is used as catalyst, is attributed to thermal breakdown of the basic biological components of the cell and formation of bio-oil. The primary breakdown between 330°C and 350°C is brought about by cracking of the bio-oil product to smaller compounds through isomerization, dehydration and fragmentation reactions [14]. The increase in of bio-oil yield between 350°C and 360°C is caused by condensation through cyclization, hydration and repolymerization reactions triggered by high temperature and pressure [14]. Alkaline catalysts are especially effective against cellulose and lignin biomolecules during liquefaction by hydrolyzing the intra- and inter-molecular hydrogen bonds which causes swelling of the biomass and an increases the surface of exposure of the cellulose to reactants [15]. The catalyst inhibits the formation of stable bonds such as carbon-carbon bonds which lead to the formation of gas products [16]. KOH promotes the water-gas shift reaction ($CO + H_2O = CO_2 + H_2$) that leads to the production of H_2 and the consumption of H_2O [17]. The H_2 from the water-gas shift reaction and potassium (alkali metal with one electron to donate) stabilize free radicals to promote the formation of bio-oil. KOH is a base catalyst that increases the pH of the solution, resulting in compound ionization or dissociation of biomolecules, and leading to an abundance of charge particles. The latter causes a reduction in the di-electric constant of the solution and increases the solubility of different compounds. The high number of molecules present increases the possibility of dehydration reactions when temperature is increases and the production of water molecules leads to soaps and favors solubility of organics in the aqueous phase [8]. The low and constant char yield obtained when using KOH as catalyst supports the notion that alkali salts do not favor the formation of biochars and are conducive to the formation of gasses and to a lesser extent bio-oil [18, 19].

During $CaCO_3$ catalyzed liquefaction there is a complex set of reactions taking place simultaneously. The Ca-ion is an alkali earth metal with the potential to donate two electrons and can act as a simple Bronsted base catalyst. The Ca-ion is believed to participate via Lewis acid complexation to the carbonyl group of the triglyceride [20]. The latter, combined with the fact that the carbonate ion is a strong base, results in increased alkoxide-intermediate formation which serves as a catalyst for trans-esterification. The carbonate ion can also break down to form CO and CO_2, which leaves a stable atmosphere [20, 21, 22]. This explains the higher FAME yield obtained with $CaCO_3$ as a catalyst compared to KOH at higher temperatures.

During an ion exchange reaction, weak organic acids are produced from the interaction between the Ca-ion and carboxylic acids (originates from triglyceride degradation). These acids can contribute to catalysis of trans-esterification or with harsh conditions may reduce yield via dehydration reaction producing Ca-containing emulsifying agents [22]. Murakami and co-workers [23] showed that most of the carboxylic acid ends up as CO_2, suggesting multiple potential Ca-ion exchange reactions. The combinations of these reactions accelerate the degradation of feedstock and favor gasification [23], which explains the decrease in bio-oil and FAME yield at higher temperatures.

Both alkaline catalysts produced relatively low biochar yields. According to Zhou and co-workers [19] alkaline catalysts suppress biochar formation and increase gas formation. This is in agreement with the low char and oil yields obtained in the presence of alkaline catalysts in this study.

Figure 4 show that the highest yields in the presence of H_2SO_4 were 36.61 $g.kg^{-1}$ FAME, 61.15 $g.kg^{-1}$ bio-oil and 367.25 $g.kg^{-1}$ biochar at a temperature of 320°C. The breakdown of bio-oil occurred from 320°C to 330°C and the formation of bio-oil occurred from 330°C to 360°C.

The breakdown of biomass occurred due to the acidic

catalyst hydrolyzing and breaking down carbohydrates to polar water soluble compounds [24]. The increase in bio-oil yield was caused by reactive intermediates from the mixture produced during the decomposition of biomass depolymerizing, recombining and repolymerizing to form bio-oil [15]. Sulfur is detrimental to lignin gasification, slowing down and even halting the gasification process and is considered a poison in coal and biomass gasification [25]. Sulfur binds aromatics such as benzene and toluene (both present in abundance) to form tars. Sulfur also binds to trace elements, especially metals, forming metal sulfide complexes on any surface. These sulfur containing species bind and form inactive sulfur masses [26]. This was evident in this study in the high biochar yields obtained due to the formation of lignosulfonates, a causative agent of gumming. Sulfuric acid is also a strong diprotic acid. A single molecule will donate two protons to the solution, decreasing the pH and triggering the binding of hydrogen atoms by biomolecules and the reduction of charged particles in solution. This will result in desorption of complexes that will contribute to biochar formation and decrease bio-oil formation.

Sulfuric acid as catalyst resulted in the highest char production (367.25 $g.kg^{-1}$) at a temperature of 320°C and the yield gradually reduced in a linear fashion as temperature increased.

Results of the elemental analysis showed little change in the H/C, O/C and HHV of the oils and chars with a change in temperature, but the O/C ratio and HHV did differ slightly for the different catalysts. The H/C and O/C ratios of the oils were slightly higher than that of the seeds and the HHV of the oils were significantly higher than that of the sunflower seeds. The HHV of the chars did not change much from that of the seeds, but the H/C ratio for the chars were lower and the O/C ratio significantly higher than that of the seeds. The average values for the elemental analysis and HHV of the oils and chars are compared to that of South African high grade coal, crude oil and the raw feedstock in Table II.

Table II: Average values of elemental analysis for chars and oils (the average values is for all the temperatures)

Catalyst	H/C	O/C	HHV
		Bio-oils	
KOH	1.7	0.1	42.6
H_2SO_4	1.7	0.1	42.1
$CaCO_3$	1.6	0.2	39.2
		Biochars	
KOH	1.0	0.5	28.6
H_2SO_4	1.1	0.3	30.2
$CaCO_3$	1.1	0.5	27.6
		Comparison	
SA Coal	0.7	0.09	
Crude oil	1.0	0.05	37.4
Sunflower seeds	1.5	0.03	29.6

* HHV= (0.3361C+1.419H-(0.1532-0.0007O) [3]

The effect of catalyst on in-situ FAME yield is dependent on the type of catalyst, as shown by these results, where none of the three selected catalysts delivered the same trends regarding biochar production. Catalysts precipitate in char, increasing the mineral content and lowering quality. Catalysts tend to lower char quality, decrease the gas yield and increased the oil yield [8, 19].

3.2 Effect of solid loading

The effect of biomass loading on FAME, oil and biochar yield was investigated with a 20 $g.kg^{-1}$ $CaCO_3$ catalyst at a constant temperature of 330°C. The effect of biomass loading on biochar, bio-oil and FAME yields are given in Figure 5.

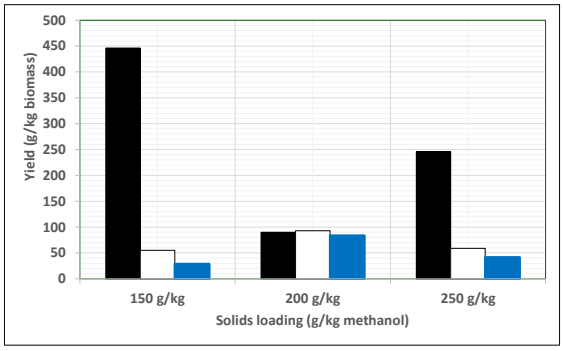

Figure 5: Effect of solid loading on biochar (■), bio-oil (□) and FAME (■) yields in the presence of a $CaCO_3$ catalyst at a temperature of 330°C

Lower biomass loadings should yield lower levels of solid residue due to the fact that there is more solvent available for solvolysis (higher alcohol to oil molar ratio) [27]. However, several studies, including this one have identified that higher biomass loadings yield lower char contents compared to lower biomass loadings [18, 8, 17, 27].

The supercritical point of the reactant/product mixture was reduced when the surface of exposure was increased [28, 3, 29]. Optimum yields are achieved when the solvent solute mixture is in supercritical state because the (pseudo) critical point removes the interface layer between phases of the optimum mixing and maximum exposure levels [29]. The methanol under supercritical conditions breaks down intermolecular hydrogen bonding resulting in polarity and dielectric constant of methanol to reduce, allowing it to function as a free monomer [3]. This allows methanol to act as a solvent and a hydrogen donor that stabilize radical production to promote the formation of oil, inhibiting secondary decomposition of oil and repolymerization [30]. Higher alcohol volumes can also inhibit polymerization and thermal degradations by diluting reactants and free radical production [31]. Exceeding the critical temperature can also lead to the breakdown of bio-oil and FAME [28, 3 32]. With a too high biomass loading the opposite occurs and the reaction becomes obstructed at high loadings [28].

This explains the low bio-oil yields at low biomass loadings of 150 $g.kg^{-1}$ where the sample was diluted to such an extent that biomass only partially degraded, leading to high biochar yields. At high biomass loadings, the reaction chamber became constricted and un-stabilized free radical formation led to excess gas production. This is confirmed by the elemental analyses that show low carbon and high oxygen content.

Elemental analysis of the oils and chars obtained at different solid loadings is presented in Table III. It can be seen from Table 3 that biomass loading appeared to have a major influence on the elemental compositions of both bio-oil and biochar. All three biomass loadings, when compared to the raw biomass, resulted in an increase in carbon, hydrogen and oxygen content as well as HHV and reduced the nitrogen content of the bio-oil

and biochar. C, H, N, O and HHV is thus influenced by biomass loading as was also reported in literature [19, 30, 24, 32]. Results contradict findings by Jazrawi *et al.* [17] that biomass loading should not have an adverse effect on bio-oil quality.

Table III: Elemental analysis of oils and chars obtained at different solids loadings in the presence of a $CaCO_3$ catalyst

Catalyst	Loading	H/C	O/C	HHV
	$g.kg^{-1}$		**Bio-oils**	
$CaCO_3$	150	1.6	0.14	39.4
	200	1.7	0.19	42.1
	250	0.9	0.08	23.9
			Biochars	
$CaCO_3$	150	1.2	0.49	28.5
	200	1.0	0.35	29.4
	250	1.2	0.32	29.7
			Comparison	
SA Coal		0.7	0.09	
Crude oil		1.0	0.05	37.4
Seeds		1.5	0.03	29.6

The increase in carbon and hydrogen content is due to the promotion of denitrification, hydrogenation and deoxygenation as evident by increasing HHVs [17]. A loss of carbon at a biomass loading of 250 $g.kg^{-1}$ is attributed to gasification in the form of CO and CO_2 [33]. Lower biomass loadings favour hydrogenation of bio-oil as indicated by the high hydrogen content [32]. Oxygen content is reduced due to reduction in carbonyl content by formation of CO and CO_2 gas products, as well as H_2O [34]. Nitrogen concentrations (7-9 wt%), is indicative of protein contribution to oil and the reduction of nitrogen compared to biomass is due to denitrification to NH_4 and other water soluble compounds [32, 33, 30]. The reduction in the C/H ratio in chars at a biomass loading of 200 $g.kg^{-1}$ is partly due to the formation of benzenes and phenols as confirmed by GC-MS.

The most prominent peaks obtained from an FTIR analysis of the oils is listed in Table IV.

Table IV: Prominent peaks of FTIR spectra of bio-oils

Wavelength (cm^{-1})	Assignment
1600-1800	Carbonyl Groups (C=O Vibrations)
1705-1725	Acyclic Ketones
1705-1850	Cyclic Ketones
1735-1750[1]	Esters (C=O Vibrations)
1377, 1456	Esters (C-H Bending)
1735-1750	Carboxylic Acids (C=O Vibrations)
1377	Aromatics (C-O Stretching)
650-900	Aromatics(C-H Bending)
700-850, 1450-1600	Aromatics(C=C Stretching)
1000-1100	Alcohols(C-O Stretch)
1400-1600	Amines(C-N Stretch)
1515-1560	Nitro- Compounds(N-O Stretch

The components in the oil identified by GC-MS analysis is listed in Table V.

Table V: Components in bio-oils identified by GC-MS

Components
Toluene
Hexanal
Pentanoic acid, 2,4-dimethyl-,methyl ester
Octanoic acid,2-methyl-,methyl ester
Nonanoic acid methyl ester
Nonanoic acid
Benzenepropanoic acid methyl ester
Benzenepropanoic acid
Pentadecanoic acid,14 methyl, methyl ester
Hexadecanoic acid, 14-methyl, methyl ester
Hexadecanoic acid
8,11-octadecadienoic acid, methyl ester
9,12-octadecadienoic acid,(Z,Z)-, methyl ester
8-octadecenoic acid, methyl ester E
9-octadeccenoic acid, methyl ester Z
6-octadeccenoic acid, methyl ester Z
9,12-octaddecadien-1-ol,(Z,Z)-9-eicosyne
Octadecanoic acid
7,10-octadecadienoic acid, methylester
9,12-octadecadienoic acid (Z,Z)-,methyl ester
10,13-Octadecadienoic, methyl ester
6,9-Octadecadienoic, methyl ester
5-nonadecen-1-ol
9,15-Octadecadienoic, methyl ester
9,11-Octadecadienoic, methyl ester
5-dodecyne
9-octadecenoic acid (Z) methyl ester
10-octadecenoic acid methyl ester
7-octadecenoic acid methyl ester
Hexadecanoic acid,16-methyl, methyl ester
Hexadecanoic acid, 15-mthyl, methyl ester
Heptadecanoic acid,16-methyl, methyl ester
Cyclopentanetridecanoic acid, methyl ester
Decanoic acid methyl ester
Phenol, 4-ethyl-2methoxy-
Phenol, 2-methoxy-4-propyl
10-undenoic acid methyl ester
Methyl tetra decanoate

From the GC-MS analysis, three major types of compounds where identified, i.e. phenols, methyl esters, and carboxylic acids. Higher temperatures and alkali catalysts produced a wider range of molecules. Methyl

ester production of C5-C20 remained consistent with al catalysts, and production of shorter chain components was favored with an increase in temperatures. The methyl ester hydrocarbon chains consisted of even and uneven numbers, straight and branched as well as saturated, mono- and polyunsaturated hydrocarbon chains. The ketones and phenols present are derived from decomposition of lignocellulose. Increasing temperature increased the ketone and phenol content, indicating breakdown of lignocellulose [8]. Lignin is composed of phenyl propane, a rich source of phenolic compounds [35]. Indole, pyrole and phenol derivatives may originate from cyclic amino acids such as phenylalanine and tryptophan [36, 37]. The presence of pyran derivatives is thought to be due to the presence of methanol [35]. Reaction conditions may have contributed to an abundance of smaller molecular weight compounds and aromatics increased with temperature.

The most common compounds were; aromatics such as ethyl/methyl-benzenes (toluene and styrene); aliphatic compounds such as pentadecene, cycloalkanes and oxygenated hydrocarbons (hexanal), C5 - C20 methyl esters and several different amides [8, 38]. The amide content, also identified with FTIR is indicative that part of the oil production stems from non-lipid components such as the protein (various reaction with ammonia after protein deamination) and lignocellulose [36, 8]. Fatty acid esters were produces from fats and waxes, as was identified with FTIR and GC-MS [35]. Biomass derived oil is extremely complex and was found in this study to contain 30% cyclic compounds indicating phenols is the major destination for many constituents. Increased phenol content is promoted by the formation of smaller molecules after primary breakdown, then depolymerisation into unsaturated compounds and cyclic, aromatic and polycyclic compounds [8]. This explains the high cyclic contents which were identified with both GC-MS and FTIR.

GC-MS and FTIR analysis detected and converged in an abundance of aromatic compounds, unsaturated, branched, uneven hydrocarbon chains. The bio-oil can therefore be classified as paraffin, but a high level of methyl esters means that the bio-oil should be classified as low quality diesel oil [39].

Some properties of the diesel produced in the presence of calcium carbonate catalyst is given in Table VI.

Table VI: Comparison of some biodiesel properties to that of the SANS1935 biodiesel standard

Property	**FAME produced in this study**	**SANS1935 Standard**
FAME yield (% mass fraction) (min)	90.1	96.5
Water content (% mass fraction) (min)	0.15	0.005
Cetane number (min)	88.7	51
Density (kg/m^3)	919.9	860-900

4 CONCLUSIONS

The results of this study showed that it is possible to produced relatively high quality biodiesel in-situ from sunflower seeds using liquefaction with supercritical carbon dioxide as reacting atmosphere. The highest bio-oil and FAME yields were obtained using $CaCO_3$ as catalyst. The yields reported were low due to the water washing process employed during recovery of the oil from the char. The use of n-hexane as an additional solvent for separation increased the oil yield to 555 g.kg^{-1} seeds and the FAME yield to 500 g.kg^{-1} seeds. These yields and the quality of FAME produced makes this process an economically viable process route for producing biodiesel cheaper on a large scale.

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6 ACKNOWLEDGEMENTS

This work is based on the research supported by the National Research Foundation. Any opinion, finding and conclusion or recommendation expressed in this material is that of the author(s) and the NRF does not accept any liability in this regard.

7 LOGO SPACE