In Situ Biodiesel Production by non-Catalytic Supercritical Reactive Extraction of Low Grade Sunflower Seeds

L.W. Fick, R.J. Venter, S Marx and C.J. Schabort

Abstract—In search of environmentally friendly alternative fuels, development of biodiesel production processes is being intensified. Supercritical Reactive Extraction (SRE) as method for *in situ* biodiesel production is still relatively unexplored. This study aims to shed light on this process by providing insight on the characteristics of bio-oil and biochar produced from low grade sunflower seed in the absence of a catalyst. A bio-oil yield of 275 g/kg with 95% FAME content was obtained at a temperature of 280°C. The bio-oil has a gross calorific value of 37.62 MJ/kg indicating upgrading of the feedstock as fuel and substantial energy densification.

Index Terms— In-situ, liquefaction, Sunflower seeds, supercritical, biodiesel

I. INTRODUCTION

Keeping sustainability in mind, the continuous use of fossil fuel as major fuel source is no longer feasible and alternative fuel sources must be utilised [1].

Alternative fuels are increasingly being developed of which biodiesel is proving very promising with substantial topical research already conducted up to date. Biodiesel is characteristically similar to petro-diesel and can be used in a blend or to completely replace it [2]. Benefits offered by biodiesel are numerous and include being renewable, non-toxic, biodegradable and having low particulate matter and SO_x content [3]. Generally speaking, biodiesel is a liquid fuel consisting of alkyl esters of long-chain fatty acids derived from plant oils and/or animal fat. Biodiesel is produced by transesterification of triglycerides or esterification of fatty acids with short-chain alcohols. The diesel can be produced either by transesterification of triglycerides or esterification of fatty acids with short-chain alcohols acting as acyl acceptors [4].

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The most well-known and commercially established method of biodiesel production is a two-step batch process using a homogeneous basic catalyst and methanol as reagent. First generation (edible) feedstock is mostly used with sodium hydroxide or potassium hydroxide as catalyst [4]. High moisture and free fatty acid (FFA) content can yield unwanted side-reactions e.g. saponification which is detrimental for biodiesel yield, making this method sensitive to water and requiring high-grade feedstock. This in turn raises an economic issue as the raw material in processes utilising first generation feedstock can amount to 70-95% of the total biodiesel production cost [5]. The first step of the two-step method comprises of costly and energy intensive pre-extraction to produce the oil that converted to biodiesel through esterification and/or transesterification. Catalyst recovery from the product mixture is another factor requiring extensive energy and thus incurring additional cost [4]. Economic feasibility must be of priority for biodiesel to compete with and eventually replace its fossil fuel counterpart.

Supercritical Reactive Extraction (SRE) is a relatively unexplored technology showing potential for great economic improvement on traditional biodiesel production. This incentive is based on the efficiency and flexibility of the process in controlling the properties of the final biodiesel product as well as by-products [4]. SRE is an in situ biodiesel production process where a supercritical solvent and co-solvent is used in direct contact with the lipid-bearing biomass, facilitating extraction (by liquefaction/solvolysis) and transesterification in a single step.

Processes for biodiesel production can be categorised into subcritical (120-280 °C) and supercritical (T > 280 °C) conditions. A supercritical fluid is any substance at conditions higher than its critical temperature and pressure and is in an intermediate state between a liquid and a gas. Supercritical processes such as SRE are associated with better solubility, higher reaction rate, and no catalyst requirement, but more severe process conditions. The increase in reaction temperature and pressure (especially so in the supercritical state) exhibits a two-fold positive effect as it not only assists in the overcoming of the activation energy barrier, but also increases the mutual solubility of reactants in the solvent. Characteristics such as low viscosity, high diffusion coefficients, variation of density and lowering of the dielectric constant as a function of pressure are attributed to this state and aids in the increase in solubility between the reagents and the solvent [6]. Methanol has a low boiling point (64.9°C) and can easily be recovered from the product mixture to be used again. It is also found that the use of

non-catalytic SCFs are superior when compared to conventional biodiesel processing concerning reaction time, product separation, FAME yield, and process simplicity. SRE is insensitive to moisture and FFA proving advantageous in the wide range of feedstock now applicable for biodiesel production [7][8].

Temperature was shown to be the parameter with the highest significance in the SRE process by [9] and was accordingly chosen for the process variable of this study. The reason for temperature being so influential is the increase in reaction rate under supercritical conditions. The high temperatures also enabled more effective extraction of oil from the JCL seeds according to [7][10].

This study provides insight on biodiesel and biochar produced by SRE over an extensive temperature range using low grade sunflower seeds as feedstock. Other parameters (biomass loading, solvent to solid ratio, reaction atmosphere, stirring rate, and holding time) were kept constant. The energy content of the biodiesel and biochar product gave an indication of its applicability to be used as fuel, while extraction efficiency and FAME yield obtained at the optimal temperature was compared to results from existing literature. As raw material cost comprises a large fraction of the total biodiesel production cost; this study also aimed to better understand the SRE process for further use in studies using low cost feedstock or feedstock regarded as waste for in situ biodiesel production.

II. MATERIALS AND METHODS

A. Reagents and Materials

The sunflower seed used in this study was kindly provided by a local farmer in Sasolburg (-26.793614, 27.820412), South Africa. Methanol (99.5%) used as analytical reagent was obtained from Rochelle Chemicals. N-hexane (95%) was obtained from ACE chemicals. Carbon dioxide (CO_2, instrument grade N3.0) was used as reaction atmosphere and was obtained from AFROX. For the dilution of the crude oil and sunflower oil prior to analysis 2,2,4-trimethylpentane and dichloromethane were used respectively. The 2,2,4-trimethylpentane ($\geq$ 99%) was obtained from Sigma-Aldrich Chemical Company while the dichloromethane (99%) was obtained from ACE chemicals. For biomass characterization methyl-nonanoate was used as internal standard as obtained from Sigma-Aldrich ($\geq$ 97%).

B. Analysis

Gas analysis was done using an Agilent 6890 plus gas chromatograph (GC) equipped with a TCD and FID detector coupled in series, with a split/splitless inlet at a temperature of 200°C at 100.87 kPa. A 60m GS-GasPRO column was used with a diameter of 0.32mm. The oven program was as follows: Initial temperature of 30°C held for 3min, ramping to 175°C at 20°C/min held for 2min and ramping to 250°C at 20°C/min and holding for 8min. The TCD was operated at 155°C with a reference flow of 20ml/min and make-up helium flow of 10ml/min. The FID detector was operated at 300°C with H_2 flow rate of 40ml/min, air flow rate of 450ml/min, and make-up helium flow rate of 5ml/min.

The FAME in the crude bio-oil product was quantified using an Agilent Technologies 7890A GC coupled with a 5975C mass spectrometer (MS). Injection volume was 1µl with a split/splitless injector at 250°C and 29.7kPa with a split ratio of 5:1. A 30m HP-S MS column with a diameter of 0.25mm and film thickness of 0.25µm was used. The oven program was as follows: Initial temperature of 35°C held for 2min ramping to 320°C at 5°C/min held for 10min. The detector was operated at MS source of 230°C with a 4.5min solvent delay and MS quad at 250°C.

For FAME analysis, quantification, and oil characterization an Agilent technologies 7280 GC with FID detector was used. The inlet was split/splitless operated at 250°C and 413kPa with a split ratio of 150:1 and injection volume of 1µl. A 100m HP-88 column with 0.25mm diameter and 0.2µm film thickness was used. The oven program was as follows: Initial temperature at 100°C held for 5min ramping to 120°C at 10°C/min held for 1min, ramping to 175°C at 10/min held for 5min, ramping to 210°C at 5°C/min held for 5 min, and ramping to 230°C at 5°C/min held for 5min. The detector was operated at 350°C with a H_2 flow rate of 40ml/min, air flow rate of 450ml/min, and make-up helium flow rate of 1ml/min.

For all (Fourier Transform Infrared Spectroscopy) FT-IR analysis a Shimadzu IRAffinity - 1 Infrared Spectrometer was used. Solids were analysed in a KBr matrix using an EasiDiff Diffuse Reflectance accessory by Pike technologies. Liquids were analysed as is using a HATR Horizontal ATR accessory by pike technologies.

Proximate analysis was done using a U-THERM proximate analyser. Moisture was determined by holding at 110°C for 30min. Elemental analysis was done using an EAI Exeter Analytical Inc. CE-440 elemental analyser set in NCH mode

Calorific values were determined (as HHV) using a IKA C5003 calorific meter, set to DIN/IKA and operated in dynamic mode.

C. Preparation of Feedstock

Sunflower seeds (shells still intact) were milled with a hammer mill to a particle size of approximately 5mm before drying at 105 ˚C for 12 hours in a Scientific Series 2000 oven. The dried seeds as biomass feedstock were quartered and sealed in airtight bags until used. Quartering was done to obtain representative subsamples (30g $\pm$ 2 g) of the entirety.

D. Seed Characterisation

The oil content in the milled and dried seeds was determined by conventional n-hexane Soxhlet extraction and characterized by GC analysis after derivatization to identify the fatty acid profile. Three seed samples of ±11g were subjected to extraction by 250ml n-hexane for 6 hours each. The oil content was calculated by equation 1. This amount was used as the theoretical oil yield of the SRE process.

$$\text{oil content (wt.\%)} = \frac{\text{weight of oil from soxhlet extraction } (g)}{\text{weight of seed sample } (g)} \times 100 \quad (1)$$

Ultimate and proximate analysis were done for seed characterization. In addition, analysis was also done by ARC-Irene Analytical Services in Irene (Pretoria, South Africa) to characterize the seed for dry matter, moisture, ash,

protein, fat/oil, total carbohydrates, neutral-detergent fibre (NDF), acid-detergent fibre (ADF), and acid-detergent lignin (ADL) content. The fat/oil content was determined by ether extraction.

E. Supercritical Reactive Extraction Process

Temperature was varied from 280°C to 360°C in increments of 20°C. Other process parameters were kept constant as follows (based on the intensification study by [7]):

- Biomass loading: 30g seed.
- Solvent to solid ratio (SSR) at 5 ml solvent/g biomass
- Stirring rate: 300rpm.
- Holding time: 30min
- Methanol as solvent and CO_2 as reaction atmosphere and co-solvent.

Supercritical reactive extraction was done in a high pressure batch reactor described by [11]. In a typical experiment the autoclave was loaded with the specified amount of milled and dried biomass and methanol as solvent. The reactor was then sealed/closed and bolted shut, and purged with CO_2 gas three times. After purging, the pressure was increased to 0.5MPa to check for leaks, after which the stirrer was switched on and the temperature increased to the desired temperature using heating jackets at a heating rate of 5.4°C/min. Once the desired temperature was reached, the temperature was kept constant for 30min after which the heating jackets were switched off and removed and the reactor was allowed to cool down to room temperature using a fan. After cool down, the change in reactor pressure was noted and the gas was purged to a GC for analysis. Once the product has cooled and the gas inside the reactor purged, the reactor content was decanted and the autoclave was washed with 40ml n-hexane, to ensure removal of all the oil. The total product was filtered three times to remove all solid residues from the oil, each time washing the solid residue with 20 ml n-hexane to ensure optimum extraction of oil from the solids (biochar). The biochar was dried overnight at 105 ˚C before being weighed and stored in air-tight bags prior to analysis.

The liquid product was washed three times using 100ml n-hexane in a separation funnel to ensure proper separation of the organic and polar layers. The polar layer containing glycerol, unreacted methanol, and other organic-insoluble material was decanted and stored. N-hexane was removed from the organic product at 80 ˚C. The final oil product was weighed and stored prior to analysis. The mass of the final crude oil product was used to calculate the extraction efficiency (E_{eff}) of the process according to Equation 2. The process was repeated 5 times at reaction temperature of 300°C to determine the experimental error as standard deviation.

extraction efficiency (E_{eff}) as % of theoretical yield =

$$\frac{\text{weight of crude oil (g)}}{\text{weight of oil from soxhlet extraction (g)}} \times 100 \qquad (2)$$

F. Product characterisation and analysis

Biochar and crude oil were subjected to ultimate analysis, proximate analysis, and FT-IR analysis. Ultimate analysis of the biochar and crude oil products provided a breakdown of the elemental composition according to weight% C, H, N, S, and O, whereas proximate analysis provided moisture, ash, volatile matter, and fixed carbon content. FT-IR analysis of the char enabled monitoring of the SRE process by the appearing and disappearing of certain peaks related to functional groups according the IR spectra. FT-IR analysis of the crude oil enabled qualification of methyl ester production and glycerol conversion by identification of peaks related to specific functional groups according to the IR spectra. Different methyl esters in the crude oil product were qualified by GC-MS analysis. The FAME content and distribution in the crude oil was also quantified. Quantification of different methyl esters was done using a set of standard calibration curves. The weight% of the FAME was used to calculate FAME yield (F_y) by the SRE process according to Equation 3 whereas biochar yield (Cy) was calculated by Equation 4. Higher heating values (HHV) of both crude oil and biochar were determined by means of a bomb calorimeter. Evaluation of the HHV along with atomic H:C and O:C ratios of both solid and liquid products viewed on a Van Krevelen plot proved the suitability of the products to be used as fuel.

$$F_y(wt\%) = \frac{\text{total mass of FAME in sample (g)}}{\text{mass of crude oil sample (g)}} \times 100 \qquad (3)$$

$$C_y(wt\%) = \frac{\text{mass of biochar (g)}}{\text{mass of initial biomass sample (g)}} \times 100 \qquad (4)$$

III. RESULTS AND DISCUSSION

A. Feedstock characterization

The total amount of oil extracted from the sunflower seeds with conventional Soxhlet extraction using n-hexane was found to be 10.67 ± 0.37 wt%, which is in quantitative agreement with fat content of 7.33 wt% as found by ARC-Irene analytical services (Pretoria, South Africa) through ether extraction. This value was used as reference when calculating E_{eff}. The fatty acid profile of the sunflower oil is 6% palmitic acid, 6% stearic acid, 18% oleic acid, and 70% linoleic acid as determined by GC analysis Additional seed characterization as done by ARC is shown in Table I.

TABLE I
COMPOSITIONAL ANALYSIS OF SEEDS ON DRY BASIS (WT%)

Component	Method	Value
Dry matter	ASM 013	96.34
Moisture	ASM 013	3.66
Ash	ASM 048	2.59
Protein[a]	ASM 078	13.41
Fat	ASM 044	7.33
Carbohydrates	ASM 075	73.01
Neutral detergent Fibre (NDF)	ASM 060	45.25
Acid detergent fibre (ADF)	n/a	42.60
Acid detergent lignin	n/a	20.92
Cellulose content[b]	Calculated	21.68
Hemicellulose content[c]	Calculated	2.65

a. Conversion factor used for nitrogen to protein = 6.25
b. Cellulose = ADF-ADL
c. Hemicellulose = NDF-ADF

B. Product yields

Crude oil, char, and gas yields as obtained by the in situ process are shown in Fig. 1. The error bars on the figure represents the experimental error at a 95% confidence level.
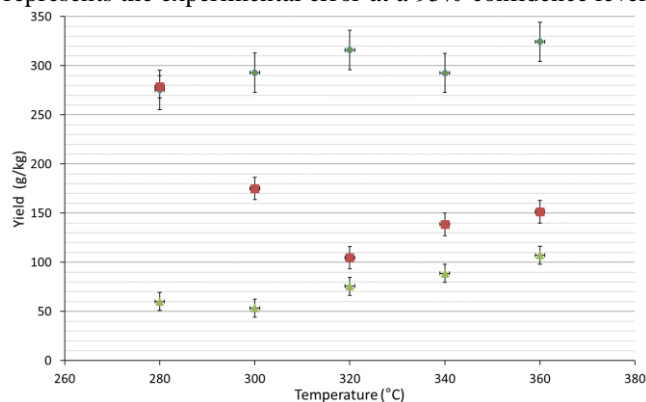

Fig. 1 Effect of temperature on crude oil (♦), char (■), and gas (▲) yield

In the current study an E_{eff} of 258% at 280°C increasing to 303% at 360°C with an average of 281% ± 16% over the entire temperature range was observed. This result indicates a dependence of E_{eff} on temperature as the maximum and minimum efficiencies differ by a factor of 1.174. This can be explained by supercritical conditions prevailing over the entire operating range, unlike the cases reported by [9] and [7], where the transition from sub-critical to super-critical regimes can clearly be seen in the variation of E_{eff}. The advantage of operating in the supercritical regime is thus still utilised in the study. The extraction efficiency greatly exceeds 100% of the theoretically predicted value. This is due to the theoretical extraction being based on conventional Soxhlet extraction, while some of the biomass was converted to oil and FAME in the supercritical state [7].

Seeing that the oil yield is a direct result of the E_{eff} the exact same trend was observed with the minimum oil yield of 275 g/kg at 280°C increasing to 324 g/kg at 360°C (here differing by a factor of only 1.177) with an average of 300 g/kg ± 20 g/kg over the entire operating range. High bio-oil yields as a result of high extraction efficiencies is because oil is not only produced by the lipid content, but also from protein and carbohydrate constituents [12].

From Figure 1 it can also be seen that the maximum biochar yield was obtained at 280°C (278 g/kg) after which it drastically decreases to 175 g/kg at 300°C and then to a minimum of 105 g/kg at 320°C. The decrease in biochar yield with increasing temperature is due to the gradual conversion of biomass by depolymerisation of hemicellulose, cellulose, and lignin to either bio-oil or bio-gas [13] [14] [15]. As the temperature is increased from 320°C a slight increase in biochar yield is again observed. This can be explained by the decomposition of some oily products and re-polymerisation to biochar at high temperatures [13].

The gas yield steadily increases with increasing temperature. The minimum yield of 53.4 g/kg is found at 300°C, closely comparing to the yield at 280°C, with a maximum yield of 107.2 g/kg at 360°C. The influence of temperature on FAME yield is shown by Fig.2. It is suspected that cracking of FAME compounds to gaseous compounds occur as the FAMEs thermally degrade as shown by Fig. 2. Similar results were found by [16] where a decrease in FAME yield and increase in gas production was observed from 270°C to 370°C. Ester losses above 275°C were also observed by [17] and is attributed to thermal degradation where unsaturated fatty acids can decompose into gaseous products in the presence of alcohols near to and above 300°C. [10] explained that thermal degradation is initiated by the cis/trans isomerisation of C-C double bonds and that trans-esters will break down by autoxidation.
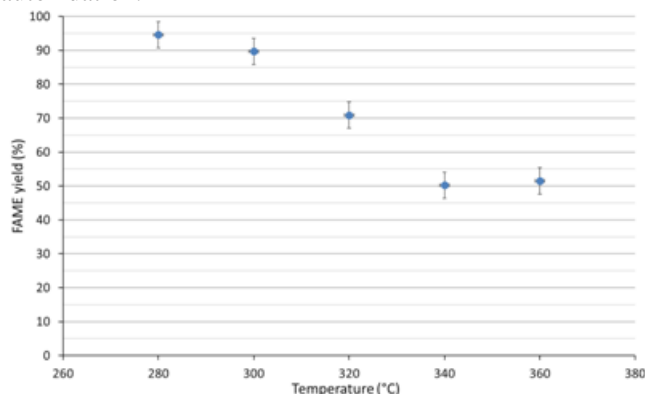

Fig. 2 Effect of temperature on FAME yield (♦)

From Figure 2 it can be deduced that a maximum operating temperature exists, after which a decrease in FAME yield is observed due to thermal degradation of FAMEs. High yields of 95% and 90% are found at 280°C and 300°C respectively. The yield then drops sharply to around 70% at 320°C and again to 50% at 340°C where it remains constant. This is due to thermal degradation of the FAMEs beyond an optimum temperature and is explained by [18] who reported that fuel degradation can occur while the reaction system is in supercritical state. As reaction temperature increases above 325 °C cis/trans isomerisation, hydrogenation, and pyrolysis of FAMEs were detected by [18]. The same phenomenon is seen in results obtained here. As all biodiesel products remained stable below 325 °C and 23 MPa these conditions are to be taken as the maximum limit when opting for high-yield biodiesel production. Different FAMEs present in the liquid oil product as qualified by GC-MS analysis is listed in Table II.

TABLE II
FAMEs PRESENT IN LIQUID OIL PRODUCT

Benzoic acid, methyl ester
Methyl octanoate
2-Octenoic acid, methyl ester
Pentadecanoic acid, methyl ester
Hexadecanoic acid, methyl ester
9-Hexadecenoic acid, methyl ester
Heptadecanoic acid, methyl ester
Methyl stearate
9-Octadecenoic acid, methyl ester
9,12-Octadecadienoic acid, methyl ester
7,10-Octadecadienoic acid, methyl ester
Methyl 10-trans,12-cis-octadecadienoate
Methyl 9-cis,11-trans-octadecadienoate

C. Compositional analysis of products

Proximate, ultimate, and HHV analyses of the sunflower

seeds, biochars and bio-oils are shown in Table III and IV respectively.

TABLE III
COMPOSITION ANALYSIS OF SUNFLOWER SEEDS AND BIOCHAR (WT%, D.A.F BASIS) (ENERGY CONTENT IN MJ/KG)

Property	Seed	280°C	300°C	320°C	360°C	340°C
C	52.61	58.72	64.73	76.70	86.54	80.44
H	8.05	6.34	6.46	6.59	7.05	6.80
N	2.22	2.02	4.01	3.63	3.59	3.49
S	0.17	0.05	0.05	0.04	0.05	0.03
O[a]	36.95	32.87	24.75	13.04	2.77	9.24
Moisture	0.13	2.04	2.70	1.20	0.30	0.95
Volatiles	86.35	69.13	55.90	41.34	38.58	39.24
Ash	2.31	6.92	12.64	19.38	20.10	19.30
Fixed Carbon	11.21	21.91	29.12	38.08	41.03	40.51
Energy content	21.77	20.72	22.77	25.77	28.88	22.19

a. Oxygen content was determined by difference

TABLE IV
COMPOSITION ANALYSIS OF VIRGIN SUNFLOWER OIL AND CRUDE OIL (WT%, D.A.F BASIS) (ENERGY CONTENT IN MJ/KG)

Property	Oil	280°C	300°C	320°C	340°C	360°C
C	82.69	80.38	82.18	80.93	78.31	78.81
H	12.31	12.20	12.48	12.07	11.61	11.52
N	0.40	0.86	0.83	1.04	1.07	1.05
S	0.23	0.07	0.08	0.10	0.08	0.09
O[a]	4.37	6.49	4.43	5.86	8.93	8.53
Moisture	10.92	6.98	8.66	7.80	6.30	5.31
Volatiles	88.46	92.87	90.60	90.88	92.10	94.68
Ash	0.06	0.00	0.02	0.99	0.01	0.00
Fixed Carbon	0.56	0.12	0.69	0.33	1.59	0.01
Energy content	33.94	37.62	37.64	37.15	37.35	37.38

A decrease in volatile matter and increase in fixed carbon content and ash content with increasing reaction temperature is shown by proximate analysis for the biochar product. The results for volatile matter and fixed carbon values are as expected, because more degradation of biomass will take place at higher temperatures, resulting in the releasing of more volatile matter and condensing of biomass to biochar through carbonization [19]. Similar fixed carbon content was found over a similar temperature range by [19] and [20] performing hydrothermal carbonization of palm empty fruit bunches and pyrolysis of pine wood respectively. The ash content from the feedstock to biochar at 280°C increased by a factor of 3, by a factor of 5.5 to biochar at 300°C, and by a factor of about 8.5 to biochar at 320°C – 360°C. Comparable results were obtained by [11] producing biochar from sunflower husks. The increasing ash content is as result of less combustible products remaining in the biomass as temperature increases [21]. Inspecting the elemental composition of the biochar shows a significant increase of carbon content with increasing temperatures due to carbonization. A substantial decrease of oxygen content and minor decrease of hydrogen content is also observed with increasing temperature. This is also evident as viewed on a Van Krevelen diagram as illustrated by Fig. 3. This diagram offers insight in the chemical transformations occurring in the process [22]. The biochar products move from top right to bottom left from the original feedstock as temperature is increased. This behaviour with increasing temperature can be ascribed to decarboxylation and

dehydration which is expected for the *in situ* process and is promoted by the supercritical CO_2 [22] [23] [24].

The net increase in heating value with increasing temperature seen in the biochar production is indicative of upgrading the fuel quality of the feedstock. A maximum energy densification of 1.33 achieved at 360°C is as expected seeing that dehydration, decarboxylation, and condensation reactions of the coalification process is promoted at higher temperatures [19].

The elemental composition of the crude oil over the entire temperature range remains practically constant. When however, compared to the feedstock a significant increase in carbon content, a notable increase in hydrogen content and a significant decrease in oxygen content is exhibited by the bio-oil and can be clearly seen by Fig. 3. The small increase in hydrogen and decrease in oxygen is as a result of methyl addition to fatty acid molecules and removal of oxygenates by transesterification. The produced bio-oil is thus a superior fuel compared to the feedstock and most of the produced chars concerning oxygen content and is further confirmed by the energy densification factor of 1.72, achieved from feedstock to bio-oil via the *in situ* SRE process.

Evaluating the results of HHVs of the crude oil it is evident that the energy content of the oil is independent of reaction temperature. [25] found the average HHV of biodiesel from a variety of feedstock to be 39.46 ± 0.67 MJ/kg and the entire range to agree within 3 MJ/kg. This is in quantitative agreement with a HHV of 37.52 ± 0.29 MJ/kg as established over the temperature range of this study.
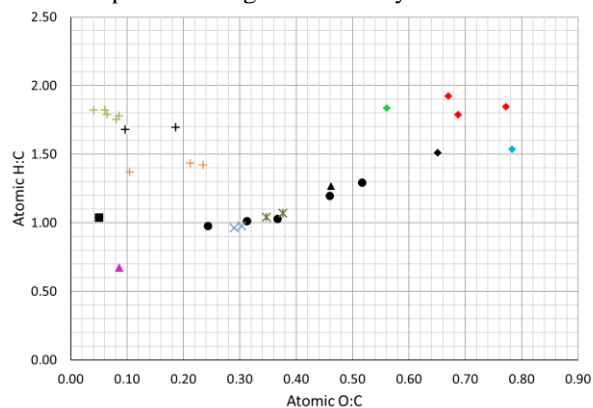

Fig. 1: Van Krevelen diagram for bio-oil and biochar compared to other fuels. ♦ - Feedstock, ● – biochar from this study, + - bio-oil from this study, + - bio-oil [23], + - bio-oil [26], ▲ – SA coal [23], ■ – crude oil [23], × - Bio-char [11], ✳ -Biochar [23], ▲ - low grade coal [19], ♦ - Sunflower husk [11], ♦ - Sunflower seed [23], ♦ - Algal biomass [26]

D. Structural analysis of products

FT-IR analysis of the oil product compared to that of sunflower oil proved informative on the product formation. The sunflower oil was extracted with conventional Soxhlet extraction from the feedstock used in the study. Fig. 4 shows the absorbance of the infrared spectrum as obtained by FT-IR analysis. At wavelength 3460 cm^{-1} O-H stretching can be observed which is indicative of moisture and/or other polymeric hydroxide impurities present in the seed oil. The

peaks present in the seed disappear with increasing temperature indicating possible hydrolysis of triglycerides and shows good separation by liquid-liquid extraction in the processing steps [27]. Formation of methyl esters is confirmed by the appearing of a peak at all reaction temperatures at 1440 cm^{-1} with the presence of CH_3 group indicated by the CH_3 asymmetric bend [28]. Absorption bands in the region 1300 cm^{-1} – 1000 cm^{-1} also shows the presence of methyl esters. There can be differentiated between glycerol esters and methyl esters from absorption due to C-O vibrations. A large peak is exhibited by the seed oil at 1160 cm^{-1} and is split into two distinct peaks at 1200 cm^{-1} and 1170 cm^{-1} respectively for all reaction temperatures. This can show the conversion of glycerol esters to methyl esters by SRE as the peak at 1200 cm^{-1} (O-CH3 vibration) is characteristic of the initial methyl group added from methesterification [28] and the 1170 cm^{-1} peak is characteristic from CH_3 rocking vibration from the methyl group [29]. Another peak appearing at 1020 cm^{-1} after SRE also shows formation of methyl esters from the stretching vibration of the C-O ester group [29]. At wavelength 1100 cm^{-1} a peak is present in the seed oil, but disappears at all reaction temperatures indicating the absence of glycerol, again confirming good liquid-liquid extraction during the processing steps, and the conversion of triglycerides. This is due to O-CH_2-C symmetric stretch and –CH_2-OH stretch vibrations [28]. A collective picture by the FT-IR results shows good liquid-liquid extraction during the processing steps, conversion of triglycerides and forming of methyl esters, and the absence of glycerol in the final oil product.

Upon inspecting the data from the FT-IR analysis shown in Fig. 5 substantial information is obtained concerning biomass breakdown and char formation. The fluctuation of peak height and width at wavelength 3400 cm^{-1} suggests progression of the dehydration of cellulose as temperature increases where -OH stretching is associated with breakage of hydrogen bonds in cellulose [30]. The peak present at 3000 cm^{-1} (signified by -C-H stretching of symmetric aliphatic -CH_x) in the seed disappears at all reaction temperatures is attributed to degradation of the biomass by cracking of longer chains. At wavelength 2360 cm^{-1} a prominent peak exists for 280°C and decreases with increasing temperature. This is typical of the conversion of amorphous cellulose [30] as identified by aliphatic -C-H vibrations and strong C=O stretching in ketone groups [11]. A distinct peak is present in the seed at 1760 cm^{-1}, but decreases drastically with increasing temperature, signifying lignin being broken down [30]. This is identified by -C=O carbonyl groups and -C-O-C- ether bonds associated with lignin. At 1600 cm^{-1} no peak exists with the seed, but exists across the entire temperature range becoming more prominent as temperature increases. This indicates the breaking down of lignin and the forming of aromatic compounds. Appearing of peaks at 1600 cm^{-1} along with disappearing of peaks at 3400 cm^{-1} as temperature increases indicates dehydration and decarboxylation reactions associated with charring [11] (being identified by aromatic skeletal vibrations and stretching of C=C aromatic groups in lignin). A peak exists in the seed at 1160 cm^{-1}, but decreases with increasing temperature until it

disappears at 320°C (-C-O-C- stretching in lignocellulose), showing cellulose decomposing through dehydration and carboxylation [11]. At wavelength 900 cm^{-1} a small peak exists in the seed sample which increases substantially with an increase in temperature. This indicates the formation of polycyclic aromatic structures which can be linked to the decomposing of lignin observed by the disappearance of peaks with increasing temperature observed at 1160cm^{-1}. It can thus be concluded that SRE will result in breaking down of basic biomass constituents as well as charring of the biomass.
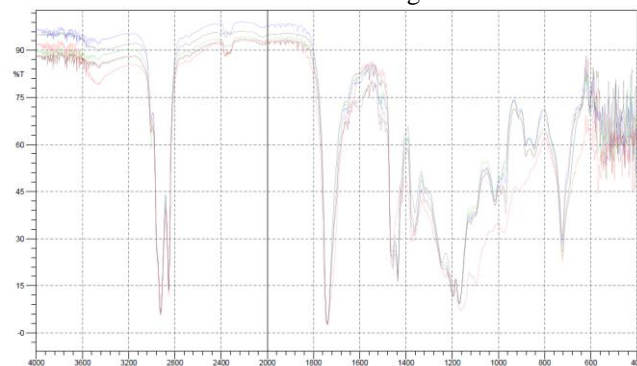

Fig. 4 FTIR analysis of crude oil and sunflower oil. - Sunflower oil, -
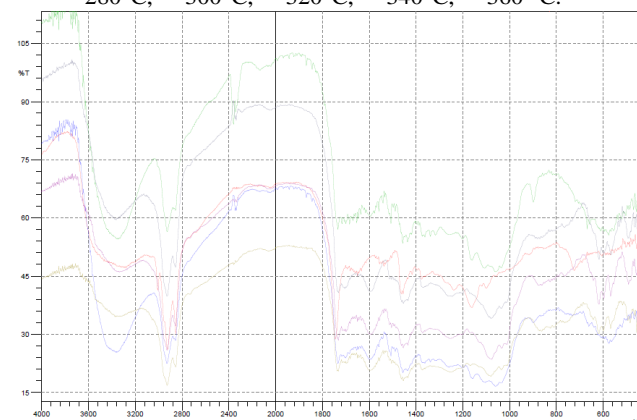280°C, - 300°C, - 320°C, - 340°C, - 360 °C.

Fig. 2: FTIR analysis of char and sunflower seed. - Seed, - 280°C, -
300°C, - 320°C, - 340°C, - 360 °C.

IV. CONCLUSION

Temperature has only a small effect on the extraction efficiency and bio-oil yield once supercritical state is achieved (280°C). The operating point for optimal FAME yield (95%) is 280°C while FAME yield is drastically reduced when operating above 300°C due to thermal degradation. The produced crude oil is superior to the feedstock as fuel source considering the oxygen content and HHV since energy densification by a factor of 1.72 is observed.

Increasing the operating temperature has an adverse in effect on the char yield do to coalification occurring at high temperatures. Evaluating the elemental composition of the produced bio-oils and chars indicates dehydration and decarboxylation reactions which again confirms liquefaction and transesterification.

In situ biodiesel production by SRE of low grade feedstock is thus capable of producing respectable oil yields with high

FAME content even in the absence of catalyst. A suggestion is the use of seed cake produced from the extraction of edible oil as feedstock as done by [28], but to make use of non-catalysed SRE for biodiesel production instead of the ultrasound assisted techniques used.

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