IN SITU BIODIESEL PRODUCTION FROM MUNICIPAL WASTE WATER TREATMENT PLANT CLARIFIER EFFLUENT STREAM

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ABSTRACT: The natural occurrence of micro-algal species in water treatment plants introduces many operational problems. If one, however, considers the high lipid, protein and carbohydrate content, micro-algae become attractive as feedstock for biofuels production. The aim of this study was to produce in situ biodiesel by means of hydrothermal and in situ thermochemical liquefaction under supercritical methanol conditions using micro-algae from a water treatment plant as feedstock.
Keywords: biodiesel, liquefaction, wastewater

1 INTRODUCTION

The current increase in the production of environmentally friendly biofuels will not only relieve the pressure on fossil fuels, but also promote sustainable development [1, 2, 3]. Biomass remains one of the most feasible sources to substitute conventional hydrocarbon based fuels [4].

One very promising biomass feedstock for renewable fuel production is micro-algae. Micro-algae form part of the third generation energy crops that do not compete for the available arable land and do not impact food security. Micro-algae species are also known to have a high lipid, protein and carbohydrate content, which are favourable components for the production of biofuels [5, 6].

It is further stated that micro-algae are the fastest growing plants in the world with roughly 500 g oil per kg biomass, thus making it an energy dense feedstock [1]. Algae technologies could provide a key tool for reducing greenhouse gas emissions from coal fired power plants and other carbon intensive industrial processes [7].

Initial processes proposed for the production of biofuels from micro-algae comprises five processing steps, namely cultivation, harvesting, extraction of oils, conversion of oils via transesterification, separation and purification [7, 3]. Many of these processing steps were found to be too costly making large scale production economically infeasible.

In situ processing for micro-algae and utilization of naturally occurring micro-algae species found in sewage handling and water treatment plants can alleviate some of the operating and capital expenditure required for large scale production plants. The effluent water from water treatment plants provides a nitrogen rich environment in which certain algae species can flourish, thus eliminating the need for extra cultivation.

In situ production methods proposed include thermochemical liquefaction, ultrasonication and microwave assisted transesterification. High biodiesel yields of up to 800 $g.kg^{-1}$ biomass have been obtained by means of in situ processing of micro-algae [8]. Hydrothermal liquefaction of micro-algae, on the other hand, has shown even higher bio-oil yields of 360 to 829 $g.kg^{-1}$ biomass [9, 10, 11, 12, 13, 14].

Thermochemical liquefaction is thus an attractive production route. Not only is little or no pretreatment of the feedstock required, but high amounts of biomass can be converted and transesterfied by means of thermochemical liquefaction [8, 15, 16, 17, 18, 19].

2 MATERIALS AND METHODS

2.1 Feedstock

The algae feedstock was obtained from a municipal waste water treatment plant situated in Bethal, Mpumalanga Province, South Africa (S 26° 29' 19.362" E 29° 27' 11.552"). At this plant the algae grow in an open pond after which the algae-containing water overflows into an evaporation pond for disposal of the algae. The feedstock was harvested downstream of the main sewage clarifier at the entry point of the evaporation pond.

The feedstock was classified at the Centre for Bioprocess Engineering (CeBER) at the University of Cape Town (UCT). During classification a diverse range of species were found to be present in the feedstock, including micro-algae (*Nostoc* sp. and *Chlamydomonas*), some macro-algae species, as well as other bacterial species.

The ash, volatile matter and inherent moisture content of the dried feedstock were determined using thermogravimetric analysis (TGA). The fixed carbon was calculated according to the ASTM D3172 standard. The compositional analysis of the biomass feedstock, shown in Table I, was done by the Irene laboratories of the Agricultural Research Council (ARC).

Table I: Compositional analysis of feedstock on a dry basis

Analysis	Method	Unit	Value
Ash	ASM 048	wt%	20.03
Fat (ether extraction)	ASM 044	wt%	4.50
Neutral detergent fibre	ASM 060	wt%	26.13
Acid detergent fibre[a]		wt%	24.57
Acid detergent lignin[a]		wt%	13.06
Cellulose[b]		wt%	11.51
Hemicellulose[c]		wt%	1.56

[a]Not SANAS accredited
[b]Cellulose = ADF – ADL
[c]Hemicellulose = NDF – ADF

2.2 Algal biomass preparation

The harvested feedstock was initially sieved using a 0.5 mm mesh to remove all excess moisture before drying commenced. The filter cake was oven dried overnight at 105°C to remove all surface moisture. The surface moisture content was determined to be 827.2 $g.kg^{-1}$ of biomass with a total moisture content of 944.5 $g.kg^{-1}$ of biomass.

2.3 Experimental procedure

The experimental setup for the liquefaction [3, 8, 12, 17, 20] included an autoclave that was constructed from 316 stainless steel with a design pressure of 200 bar. First the biomass was weighed and then loaded into the autoclave along with water, methanol or acid catalyst depending on the experimental set. The autoclave was closed and bolted shut with the bolts torqued to 70 N.m. The autoclave was then pressurised to 20 bar with ultra-high purity (UHP) nitrogen gas and slowly depressurised in order to purge the system. The system was purged 5 times in total.

After the system had been purged the heating jackets were put on the autoclave and the magnetic stirrer and the temperature controllers switched on. Once the temperature inside the autoclave reached the predetermined set point the temperature was kept constant for 30 minutes. The autoclave was then allowed to cool down to room temperature. An electrical fan was used to cool down the autoclave.

Once the autoclave had reached room temperature the gas was vented from the autoclave. 100 ml of chloroform was added to the autoclave, after which the autoclave was closed again and the magnetic stirrer switched on for 10 minutes. This was done to dissolve any residual organic matter that might have been suspended in the autoclave. The operating pressure and temperatures for a typical set is shown in Table II.

Table II: Temperature and pressure profile for a typical run

Time (minutes)	Pressure (MPa)	Temperature (°C)
0	1	25
80	6	180
120	7.9	245
140	9.8	305
160	11	300
190	11	300
220	7	255
250	5	188
280	1	28

2.4 Analysis of liquefaction products

GC analysis was used to determine the composition of the bio-oil and biodiesel samples. An Agilent 7890 GC was used with an Agilent auto injector, a HP-5MS (100m) capillary column and a flame ionization detector (FID). GC-MS was used to qualitatively determine other hydrocarbons present in the oil sample. The GC-MS used in this study was an AGILENT 5975 µs. A bomb calorie meter was used to determine the higher heating value of the products obtained. The bomb calorie meter used was a MC-1000, Mk 2 Modular Calorimeter.

3 RESULTS AND DISCUSSION

3.1 Hydrothermal liquefaction

Hydrothermal liquefaction was performed on the feedstock as a control set. The influence of temperature on product distribution is shown in Figure 1.

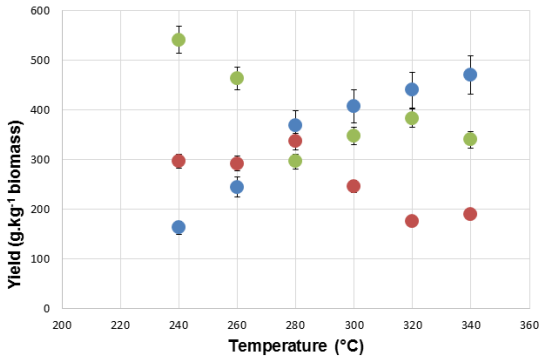

Figure 1: Influence of temperature product distribution for hydrothermal liquefaction at a biomass loading of 500 g.kg^{-1} and residence time of 30 min (● Biochar ● Bio-oil ● Biogas)

The bio-oil yield increases with an increase in temperature, resulting in the highest bio-oil yield of 470.7 g.kg^{-1} biomass achieved at 340°C in the temperature range of 240 – 360°C. The bio-char yield initially increases with an increase in temperature, after which the yield decreases. The highest bio-char yield found at 280°C is 363.2 g.kg^{-1} biomass. The bio-gas yield initially declines as the bio-oil and bio-char yields increase after which the bio-gas yield increases. These trends coincide with the findings of previous studies on hydrothermal liquefaction [6, 21, 22, 23].

Figure 2 presents the triglyceride content present in the bio-oil (the yield shown was derivitised before GC analysis).

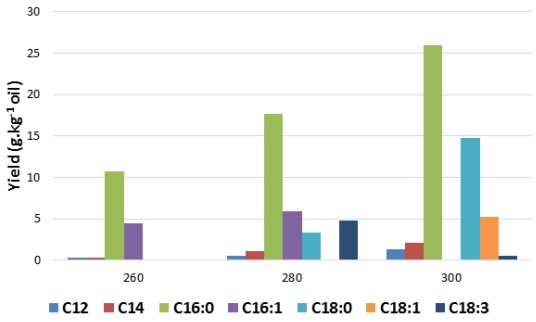

Figure 2: Influence of temperature on the FAME yield and triglyceride yields at 260°C, 280°C and 300°C (— C12 — C14 — C16:0 — C16:1 — C18:0 — C18:1 — C18:2)

At 260°C the bio-oil consists mainly of C16, which comes from the algae oil [24], as well as some C16:1. At 280°C the bio-oil contains a higher amount of C16:0, a slightly higher amount of C16:1, with C18:0 and C18:3 also present, showing an overall increase in the FAME yield. The increase in bio-oil yield between 260°C and 280°C can be attributed to the recovery of the oil content present in the feedstock, as well as to the condensation of the bio-gas present to form longer chain hydrocarbons (C18:0 and C18:3).

From 280°C to 300°C it can be seen that there is an increase in the C16 and C18 yield, with no C16:1 chains present. A possible explanation is that some carbon groups attached to the C16:1 chains to form C18:0 and C18:1. The sharp decline in the C18:3 FAME yield is the

result of the breaking of the double bonds due to hydrogenation. There is also an increase in C12 and C14 FAME yields, which can be explained by decarboxylation and decarbonylation taking place during liquefaction [6, 16, 21]. The combined FAME yields are 15.82 g.kg^{-1} at 260°C, 33.49 g.kg^{-1} at 280°C and 53.68 g.kg^{-1} at 300°C.

3.2 In situ biodiesel production

The bio-oil yield for thermochemical liquefaction (with supercritical methanol) and for hydrothermal liquefaction is presented in Figure 3. The bio-oil yield is shown for a temperature of 240°C to 300°C in intervals of 20°C for the three different methanol to dry biomass mass ratios (1:1, 3:1, 6:1).

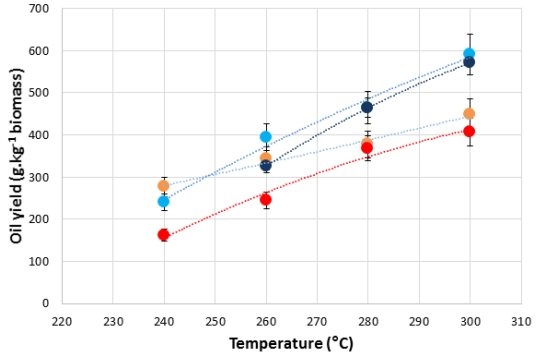

Figure 3: Influence of temperature and methanol to dry biomass ratio on the bio-oil during liquefaction with supercritical methanol at a biomass loading of 500 g.kg^{-1} and residence time of 30 min (● Hydrothermal liquefaction ● 6:1 methanol ratio ● 3:1 methanol ratio ● 1:1 methanol ratio)

From Figure 3 it can be seen that with an increase in temperature there is a linear increase in the bio-oil yield. The increase in yield with an increase in temperature is similar to that found in literature [6, 21, 22, 23]. The highest yield of 591 g.kg^{-1} was achieved with a 3:1 methanol to dry biomass ratio at 300°C.

At lower temperatures only carbonisation reactions will occur during which the biomass constituents are broken down into smaller fragments [6, 21]. The decomposition of hemicellulose and cellulose start at temperatures higher than 250°C [16]. The initial increase in oil would thus be due to the recovery of the lipids present in the biomass after which the increase can be attributed to the degradation of the biomass constituents. The gas yields decline initially with the increase in temperature which could indicate that the H_2 and N_2 content present are used to aid in the reactions taking place.

Above 280°C the increase in bio-oil yield can be attributed to the decomposition of the protein [6]. The compositional analysis of the feedstock showed that the feedstock is high in protein and low in lignin (see Table I). The biomass constituents degrade by means of deoxygenation, decarboxylation and decarbonylation. As the temperature increases the intermolecular forces start to decrease, which then allow for quicker degradation of the feedstock. The compounds formed from the decomposition are stabilised by the free radicals present, resulting in the formation of bio-oil. At higher temperatures higher quantities of free radicals (H^+ ions) are expected as the hydrogen bonds in the solvents become weaker [6, 16].

Another possible explanation is the critical properties of the solvent [6, 16]. In the case of water and methanol, an increase in temperature leads to a decrease in the permittivity, which increases the solubility. A higher temperature also bring about a decrease in the hydrogen bond strength and a higher availability of H^+ and OH^- ions, which will take part in the hydrolysis reactions [6, 21, 22, 23].

From Figure 3 it can further be seen that a higher methanol to dry biomass mass ratio results in a higher bio-oil yield. The highest bio-oil yields of 448 g.kg^{-1}, 592 g.kg^{-1} and 571 g.kg^{-1} were obtained at a temperature of 300°C for the 1:1, 3:1 and 6:1 methanol to dry biomass ratio, respectively. The maximum operating temperature of 300°C was used due to the properties of methanol resulting in very high pressures at temperatures above 300°C. If the bio-oil yields at a 3:1 and a 6:1 methanol to dry biomass ratio are compared at higher temperatures, the difference with regards to total bio-oil yield is negligible, but as will be seen later, the quality of these two oils differ quite considerably.

The increased yield with the increase of solvent can be explained by the hydrogen bonds present in methanol (polar protic solvent).The resulting free hydrogen radicals (H^+) aid in hydrocracking of the proteins and lipids [16, 23, 25]. The hydrogen donation essentially results in higher bio-oil yields. Methanol would also aid in the decomposition of the glycosidic bonds present in cellulose. The interactions between the polar protic solvent and the biomass constituents would explain why higher yields are obtained compared to normal hydrothermal liquefaction. The increased temperatures which aid in the decomposition of biomass constituents as stated earlier could explain the difference between the 1:1, 3:1 and 6:1 mass ratio yields. As an increase in the temperature aid in the decomposition of the biomass constituents (reducing the strength of the intermolecular forces) the amount of hydrogen available to aid in hydrolysis and hydrocracking can induce a higher rate of decomposition. Above 260°C the higher methanol mass ratios (3:1 and 6:1) show a higher rate of conversion, while with the 1:1 ratio the rate of conversion slightly starts to decline [16, 25].

The higher bio-oil yields for certain ratios at lower temperatures for the 1:1 ratio might be explained by the temperatures being below the point of decomposition. So at 240°C it will be expected that the effect of methanol ratios will be negligible as the temperature is still too low for liquefaction to take place [6, 16, 21]. As stated earlier up until 280°C it is expected that mainly carbonisation reactions occur along with the recovery of the lipid content with only small amounts of degradation of biomass constituents taking place.

The rate of biomass conversion for the 6:1 ratio between 280°C and 300°C is slightly higher than the rate of conversion for the 3:1 ratio. This would indicate that the additional amount of methanol allow for quicker decomposition of the biomass constituent. The difference in bio-oil yields formed of the 3:1 and 6:1 ratio become smaller as the temperature increases, suggesting that there is a saturation point where the amount of solvent present does not have an effect on the bio-oil yield anymore. The 6:1 ratio would however have a large effect on the composition of the bio-oil.

Figure 4 shows the compositional analysis of the bio-oil obtained at 300°C for the three different methanol ratios.

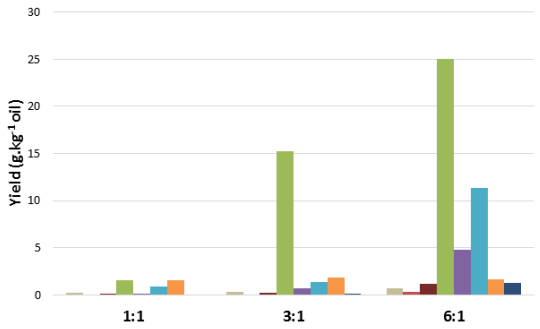

Figure 4: Influence of methanol to dry biomass ratio on the FAME yield and triglyceride yields at 300°C (C12 C14 C14:1 C16:0 C16:1 C18:0 C18:1 C18:2)

From Figure 4 it can be seen that as the methanol to biomass mass ratio increase the amount of FAME formed also increase. It can also be noted that compared to the control hydrothermal set and the fatty acids present, the amount converted for the 6:1 biomass mass ratio was close to the amount extracted in the control set which would indicate that almost complete in situ biodiesel production was achieved. The highest quality biodiesel was obtained at the 3:1 methanol ratio due to low yields of unsaturated FAME with a value of 15.2 $g.kg^{-1}$ biomass. As the methanol ratio is increased from 3:1 to 6:1 the amount of unsaturated fatty acids (C16:1, C18:2) increases drastically, as well as the quantity of C18 formed. The higher quantities of C16:1 to C18:2 would indicate that some carbon groups attached to C16 to form the C18 chains.

The higher yield with the addition of methanol might be due to the excess amounts of methanol present to aid in the transesterification of the triglycerides [26, 27]. The change in properties would then be ascribed to the extra hydrogen present and the different reactions taking place during liquefaction. The hydrogen will aid in the stabilisation of the components formed [6, 21, 22, 23].

Figure 5 shows the effect of temperature on the FAME yield. The result shown is for the 3:1 methanol to biomass mass ratio.

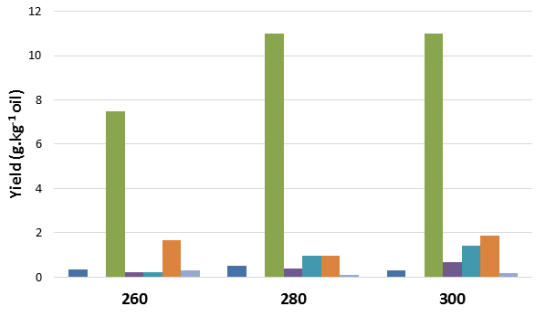

Figure 5: Influence of temperature on the FAME yields for the 3:1 methanol to dry biomass ratio (C12 C14 C16:0 C16:1 C18:0 C18:1 C18:2)

From Figure 5 it can be seen that with an increase in temperature the FAME yields increase due to the carbonization reactions as mentioned earlier up until 280°C. The highest FAME yield present is C16:0 which comes primarily from the algal oils [24].

The higher yield of FAME at higher temperatures can be explained by the fact that at a higher temperature (above methanol's critical point) the oils and the methanol would mix into one miscible fluid [15, 28]. According to Arrhenius law, as temperature increases the reaction rate would increase [15]. Thus if the increased reaction rate is combined with the fact that at higher temperatures higher amounts of oil is produced it would explain the higher yields of FAME at higher temperatures.

At 260°C the primary FAME present is C16:0. From 260°C to 280°C there is a decrease in the C18:2 but an increase in C18:0, which could indicate that some of the double bonds broke or two carbons were removed and is in the higher C16:0 yields or evaporated into the gas phase. The decrease in C16:0 between 280°C and 300°C may be attributed to the condensation of carboxylic components from the biogas that would also explain the increase in C18:0.

4 CONCLUSIONS

The results in this study have shown that stable in situ biodiesel can successfully be produced with thermochemical liquefaction and supercritical methanol conditions. The use of an algal based feedstock that occurs naturally proves to have many advantages as it reduces the capital and operating expenditure for large scale production plants in terms of the large capital investment needed into cultivation units.

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7 LOGO SPACE