

## BIO-OIL AND BIO-CHAR PRODUCTION FROM SUNFLOWER HULLS

Percy van der Gryp\*, Ulrich Baumgarten, Sanette Marx, Corneels Schabort

School of Chemical and Mineral Engineering, North-West University.

Hoffman Street, Potchefstroom, 2522, South Africa.

E-mail: Percy.vandergryp@nwu.ac.za Tel.: +27 18 299 1953 Fax: +27 18 299 1535

**ABSTRACT:** In this paper, the hydrothermal liquefaction of sunflower hulls into bio-oil and bio-char is presented. The main manipulated variables that were studied were biomass load, catalyst type and temperature. The experimental results show that an increase in temperature, increases bio-oil yield and decreases bio-char yield. An increase in biomass load decreases bio-oil yield. The highest bio-oil yield was observed when sodium carbonate was used as catalyst. The bio-oil yield was low in all instances with a maximum oil yield of 4.7 wt% at 340 °C and 30 wt% biomass load. The bio-char yield showed very high yields with a maximum yield of 62 wt% at 280 °C and 30 wt% biomass load. This study shows that liquefaction of sunflower hulls is a viable option for the production of bio-char.

**Keywords:** Liquefaction, Sunflower, Bio-char.

### 1 INTRODUCTION

The continuous depletion of fossil fuel and crude oil recourses with the increasing demand of energy creates a need for alternative energy resources [1-3].

Environmental and sustainable energy resource awareness and an increase in the price of transportation fuel have started to steer researchers towards alternative renewable energy resources such as biofuels [4-8].

Currently, 63% of renewable energy is produced from biomass [1]. Biomass has the potential of producing a wide range of energy related products over the whole range of gaseous, liquid and solid fuels which gives biomass the advantage of diversity [6]. A future added advantage is that the CO<sub>2</sub> emitted while producing energy from biomass is justified by the CO<sub>2</sub> it consumes during photosynthesis [9].

The wide debate on food versus fuel is guiding research in utilizing non-edible resources such as algae, agricultural and forest residues for the production of energy [10-11]. Crop residue can be defined as the non-edible parts of the plants that are left after the edible parts are harvested [2]. The production of bio-fuels and food products such as sunflower oil generally has lignocellulosic waste as by-products (sunflower hulls and stems) and often the assumption is made that these by-products are of no use [7]. Sunflower (*Helianthus annuus*) is planted annually, can be cultivated in any area with limited water supply and can grow in various soil types [2]. Sunflower hulls is currently mainly used for landfills and animal feed. The abundance of sunflower hulls and the fact that it is considered a waste product makes it an ideal feedstock for the production of energy.

Different processes exist for converting biomass to energy and these processes like liquefaction, gasification and combustion have been widely studied [6,12]. One particular interesting process, liquefaction, makes out one of three regions of hydrothermal processing and occurs in the liquid phase between 200-370 °C [13]. A huge amount of experimental work [6,9-10,14-17] has previously been done on liquefaction to convert various biomass feeds (including oil shale, sunflower stalk, Indonesian biomass residues, wood, algae, etc.) to bio-oil, bio-char and bio-gas. However, the bio-oil and bio-char yield that could be obtained through the liquefaction of sunflower hulls has not been investigated previously. It is therefore the objective of this paper to present the

possibility of extracting valuable bio-oil and bio-char from sunflower hulls through hydrothermal liquefaction.

### 2 EXPERIMENTAL

#### 2.1 Biomass and chemicals used

Sunflower hulls cultivated in South Africa (North-West province) were obtained from a local sunflower oil press and used as supplied without any alteration in moisture content or grinding. The sunflower hulls were coned and quartered for representative samples. Distilled water was used as liquefaction solvent and reaction media. Chloroform (Sigma-Aldrich, 99%) was used for extraction. Sodium carbonate (99.5%), sodium hydroxide (98.5%), potassium carbonate (98%) and potassium hydroxide (85%) obtained from Associated Chemical Enterprises were used as catalyst. Ultra high purity nitrogen from Afrox was used for pressurizing the autoclave.

#### 2.2 Liquefaction experiments

A standard high pressure autoclave [16-17] constructed from grade 316 stainless steel was used as reaction vessel. The autoclave has an inside diameter of 90 mm and height of 150 mm with a volume capacity of 0.954 L. The inside air was purged with ultra high purity nitrogen gas. In a typical liquefaction experiment, the desired sample of sunflower hulls (range between 20 to 50 wt%) was loaded into the reactor with water and the selected catalyst (NaOH, Na<sub>2</sub>CO<sub>3</sub>, KOH or K<sub>2</sub>CO<sub>3</sub>). The reactor was then closed and heated to the required temperature (260 to 340°C) with electric heating jackets. The heating time was approximately one and a half hour to the set temperature and the reaction time was held constant for 45 minutes. After the completion of the reaction, the autoclave was cooled down to room temperature with a fan.

The gaseous products were vented. Chloroform was added to the solid and liquid reaction mixture and stirred inside the autoclave to ensure that any oil that may be fixed to the inside of the autoclave was dissolved. The mixture was then filtered under vacuum with Whatman No. 31 filter paper to separate the solid bio-char from the liquid bio-oil. The bio-char was dried and weighed to calculate the bio-char yields. The diluted filtrate liquid bio-oil mixture with chloroform was then poured into a separation funnel to allow the mixture to settle out into an

aqueous and an organic layer. The organic layer, which contained the dissolved bio-oil, obtained from decantation was subjected to vacuum distillation in order to obtain pure oil. The vacuum distillation was carried out at a temperature of 70 °C to ensure total evaporation of the chloroform.

The purified bio-oil was weight and the bio-oil yields were calculated. Bio-oil compositions were determined through gaschromatography (GC) using an Agilent 7890 GC equipped with an Agilent 7683B auto injector, HP-5 capillary column (30m x 320 µm x 0.25 µm) and a flame ionization detector. The GC analysis conditions were: inlet temperature of 275 °C; injection volume of 0.2 µL (auto injection); oven programming of 90 °C for 4 min, 90 to 300 °C at 10 °C.min<sup>-1</sup>, 300 °C for 20 min; FID detector at 350 °C; H<sub>2</sub> flow rate of 40 mL.min<sup>-1</sup>, make-up He flow rate of 10 mL.min<sup>-1</sup> and air flow rate of 400 mL.min<sup>-1</sup>. Chloroform and deconoic acid was used as solvent and internal standard with a calibration curve to quantify the triglycerides present in the oil samples.

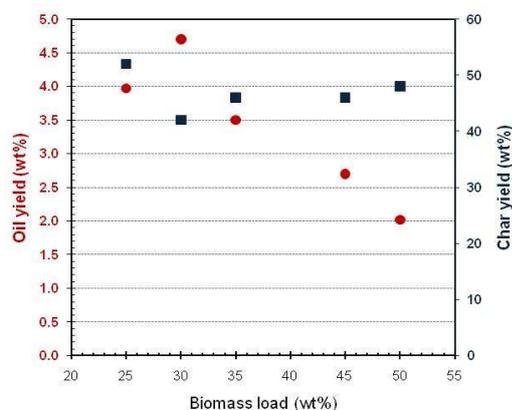
Trimethyl Sulfonium Hydroxide (TMSH) was set as derivatization agent for all GC analyses. Elemental composition of the raw sunflower hulls and products were analyzed with a FLASH 2000 Organic Elemental Analyzer.

### 3 RESULTS AND DISCUSSION

The effects of biomass load (20 to 50 wt%), catalyst type (NaOH, Na<sub>2</sub>CO<sub>3</sub>, KOH or K<sub>2</sub>CO<sub>3</sub>) and temperature (260 to 340°C) on the bio-oil and bio-char yields were investigated for the liquefaction of sunflower hulls. The overall experimental error calculated at a 95% confidence level was 10.6% for the bio-oil yields and 4.9% for the bio-char yields.

#### 3.1 Effect of biomass load

The biomass load (weight percentage biomass to water) was varied from 25 to 50 wt%. Sodium carbonate (5 wt% based on biomass) was used as catalyst and the reaction temperature was kept constant at 340 °C. The effect of biomass load on the bio-oil and bio-char yield is shown in Figure 1.



**Figure 1:** Biomass load dependence of the oil and char yields. (● - Oil yield and ■ - Char yield)

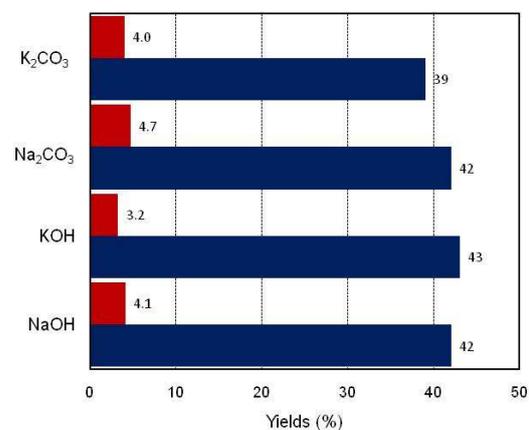
It can be seen from Figure 1 that the maximum bio-oil yield occurs at 30 wt% biomass load with a relative low yield of 4.7 wt%. Furthermore the bio-oil yield mainly decreases with an increase in biomass load. That

is, the bio-oil yield increase with an increase in solvent (water) to biomass ratio. The decrease in bio-oil yield as biomass load increases could be explained by the decrease in solving ability of low water content and because more water have the ability to donate more hydrogen for destruction of molecular structure and thus more monomers can be solved. In a similar study, Akhtar *et al.* [12] liquefied empty palm fruit bunch biomass in water at 270°C with different biomass loads ranging from 10 to 45 wt%. These results showed the same trend as in this study and it was suggested that the decrease in bio-oil yield could be due to the stronger alkali media (K<sub>2</sub>CO<sub>3</sub> was used as catalyst) creating more free radicals to enhance re-polymerization rather than dissolution at lower solvent concentrations. The decrease in bio-oil yield with an increase in biomass load is a disadvantage for industrial production of bio-oil because of the larger amount of water that will be needed and the associate increase in reactor costs. Furthermore, GC analyses showed that only approximately 10 wt% of the bio-oil produced contained components with carbon length of between C14 and C20, while the remaining 90 wt% was components with carbon lengths larger than C20. The bio-oil produced from sunflower hulls in this study would thus not be suitable for biodiesel production.

#### 3.2 Effect of catalyst type

It is important to identify and test different types of catalysts that are cheap, demonstrate enhance yields and can be implemented commercially with relative ease.

Previous studies have shown that homogeneous based catalysts gave better catalytic activity towards liquefaction than heterogeneous based catalysts such as the Raney-Nickel catalyst [18-19]. Salts, such as sodium hydroxide [10], sodium carbonate [9] and potassium carbonate [6] have demonstrated relative good catalytic activities during liquefaction. In this study, the catalytic effect of four different salts (sodium carbonate, potassium carbonate, sodium hydroxide and potassium hydroxide) on the bio-oil and bio-char yield was investigated. The temperature and biomass load were kept constant at 340 °C and 30 wt% respectively. The main results obtained are summarised in Figure 2.



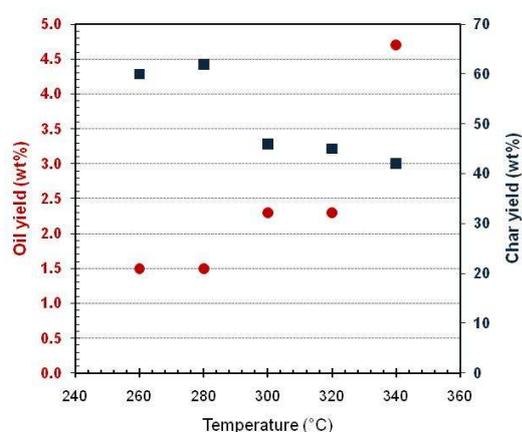
**Figure 2:** Char and oil yields with different catalyst types. (■ - Oil yield and ■ - Char yield)

It is clear from Figure 2 that the different catalysts species did not have a significant effect on the bio-oil and bio-char yields as these values falls with in the range of experimental errors. However, it appears that the

carbonated catalyst species demonstrated a more enhancing effect for oil-production and a hindering effect for char production compared to the hydroxinated species. The carbonated species probably favours the hydrolyses reaction more and inhibits the dehydration reaction with the weakening of the C-C bonds that decreases the activation energy for the reaction. A similar hypothesis was presented by Sun *et al.* [20].

### 3.3 Effect of temperature

The effect of temperature (260 °C to 340 °C) on bio-oil and bio-char yield was investigated for the liquefaction of sunflower hulls. The biomass load was kept constant at 30 wt% and sodium carbonate was used as catalyst. The main results obtained are summarised in Figure 3.



**Figure 3:** Effect of temperature on bio-oil and bio-char yields. (● - Oil yield and ■ - Char yield)

It is clear from Figure 3 that as the temperature increases bio-oil yield increases and char yield decreases.

These results correlate well with previous studies [2,10,15]. The maximum bio-oil yield of 4.7 wt% occurs at 340°C and the maximum char yield of 62 wt% occurs at 280°C. The increase in temperature increases the dehydration reaction to produce more bio-oil from the lignin and increases gasification of the bio-char to produce bio-gas. Thus, the higher the temperature, the easier the defragmentation of the polymers into a liquid-rich phase.

### 3.4 Element analysis

The elemental composition of the raw sunflower hulls and the bio-char products from the liquefaction was analyzed. The results obtained and the HHV are presented in Table I, compared with that of crude wood and pinewood powder.

**Table I:** Elemental composition of different biomass raw material and bio-char products.

Sample	Elemental composition, wt%					HHV <sup>b</sup>
	C	H	O <sup>a</sup>	S	N	
Sunflower hulls	46.9	5.1	46.2	0.3	1.5	14.91
Char-product	65.9	4.3	29.6	0.2	1.9	23.15
Pinewood <sup>[5]</sup>	49.2	6.2	44.2	0.1	0.3	16.32
Crude wood <sup>[20]</sup>	45.5	6.3	48.1	-	0	15.81
Char-product <sup>[20]</sup>	61.5	4.9	33.5	-	0	21.86

(a) By difference.

(b) Calculated according to the Dulong Formula, i.e., HHV (MJ/kg) = 0.3383C + 1.422(H - O/8).

As can be seen from Table I the elemental compositions of carbon, hydrogen, and oxygen and therefore the HHVs, gave similar values as was reported by Liu *et al.*[5] and Sun *et al.*[20] for the different raw materials and bio-chars. The HHV of the bio-char for this study is around 23 MJ/kg, in comparison with the HHV of 15 MJ/kg for the raw sunflower hulls. The energy density had therefore increased almost by 100%. The calorific value of the bio-char compares to that of high rank coal and can therefore be used as a solid fuel. The liquefaction of residue sunflower hulls in water may thus be a promising technique for upgrading biomass feedstock with low caloric value to a higher caloric value product.

## 4 CONCLUSIONS

In this study sunflower hulls from a local oil press in the North-west province of South Africa was used to produce bio-oil and bio-char through liquefaction. The influence of biomass load, catalyst type and temperature were evaluated. It was found that a small amount of bio-oil (less than 5 wt%) was produced, while around 50 wt% useful bio-char was produced that can be used as a solid fuel. The bio-oil consisted mainly of C20 carbon-chain length components and the energy density of the bio-char had increased up to 100% with comparable calorific value of high rank coal. Different alkali salt catalysts (NaOH, Na<sub>2</sub>CO<sub>3</sub>, KOH and K<sub>2</sub>CO<sub>3</sub>) did not demonstrate any significant effects on the bio-oil and bio-char production. Temperature and biomass, however, showed the classical effects.

## 5 REFERENCES

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