Biocatalytic Production of Biodiesel from Spent Coffee Grounds

Wian Swanepoel, Sanjib Kumar Karmee, Sanette Marx

***Abstract*—**Production of biodiesel was carried out by transesterification of spent coffee oil with methanol, using lipases as catalysts. The conversion of spent coffee oil to fatty acid methyl esters (FAME) were investigated by screening different lipases, *Candida rugose, Porcine pancreas, Pseudomonas fluorescens* and *Candida antarctica* lipase-B. Optimal reaction conditions were obtained by varying the oil to methanol molar ratio, temperature and reaction time. Maximum conversion (96.33 %) of spent coffee oil to FAME was found when using *Candida antarctica* lipase-B as catalyst, at 1:4 oil to methanol molar ratio and a temperature of 40 ºC for 12 h. Total coffee waste produced at the North-West University (Potchefstroom Campus) could result in 162 kg of biodiesel that could be added to annual fuel supply for the campus.

***Index Terms*—** Spent coffee grounds, Transesterification, Lipase, Biodiesel.

I. Introduction

The demand for energy is rapidly increasing, putting more pressure on already dwindling non-renewable fossil energy resources [1]. At present, the main concern is exhausting fossil oil reserves, which is expected to deplete in the years to come, and the world is still largely dependent on fossil fuels for power generation and transportation [1]. Thus, focus has shifted towards finding new renewable energy sources to decrease the dependency on fossil fuels and also because of the awareness of the negative impact that burning fossil fuels has on the environment [1, 2].

Biomass resources supplies approximately 10% of the global primary energy demand, making it the largest renewable energy source [1, 3]. There is a diverse range of biomass that can be used as feedstock for biofuel production [2, 3]. The challenge is to find a suitable biomass feedstock that will be sustainable, satisfy demand, such that it does not compete with the food supply and is environmentally acceptable [1, 2, 3].

Biodiesel has been receiving increasing attention as a potential alternative to fossil fuels. Biodiesel is seen as an environmental friendly fuel as it holds some advantages over fossil diesel fuel [4]. These advantages include that biodiesel is a renewable fuel, biodegradable, non-toxic and can be blended with fossil diesel fuel.

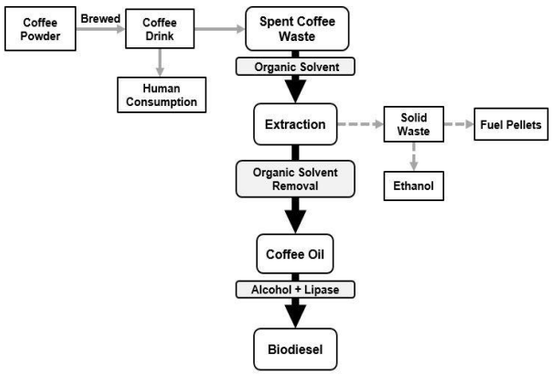

Fig. 1 Schematic of lipase catalysed biodiesel production from spent coffee grounds.

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Wian Swanepoel is an honours student in Chemical Engineering at the North-West University, Potchefstroom, South Africa (e-mail: wiannwu@gmail.com).

Sanjib Kumar Karmee is a post-doctoral fellow within the NRF Research Chair for Biodiesel at the School of Chemical and Minerals Engineering, North-West University, Potchefstroom, South Africa

Sanette Marx is an associated professor and holder of the NRF Research Chair for Biofuels within the School of Chemical and Mineral Engineering, North-West University, Potchefstroom, South Africa

Obstacles biodiesel production faces is the long term commercial viability because of the sustainability and high cost of feedstocks. Ethical issues can influence sustainability of biodiesel as it competes with food production if edible oils are used in the process [1]. Feedstock accounts for 70-80% of the final biodiesel costs [1]. To overcome these obstacles and compete with fossil diesel fuel the feedstock cost must be reduced. In this regard, waste material and non-edible oil are viable alternatives in the production of biodiesel.

Spent coffee grounds (Fig. 1) as raw material can be an alternate feedstock to biodiesel production. Eight million tons of coffee beans were produced word wide in 2010 [1]. The oil that can be recovered from spent coffee grounds is approximately 15 wt% [5]. With a high conversion to biodiesel through transesterification processes, it could add 1 million tons of biodiesel to the transportation fuel supply [1, 4]. Due to its high antioxidant content, biodiesel produced from spent coffee grounds has better stability compared to other sources as feedstock [5].

Biodiesel is produced by the transesterification (Fig. 2) of vegetable oils and animal fats. An acid, alkali or enzyme catalyst can be used in the process [2]. The transesterification process converts an ester (triglyceride), present in the oil, to another form of ester (fatty acid alkyl ester) and glycerol [9].

Disadvantages of acid- and alkali-catalyzed reactions are: high energy requirements, difficult recovery of catalyst and glycerol, it is toxic and corrosive [4, 10]. As an alternative

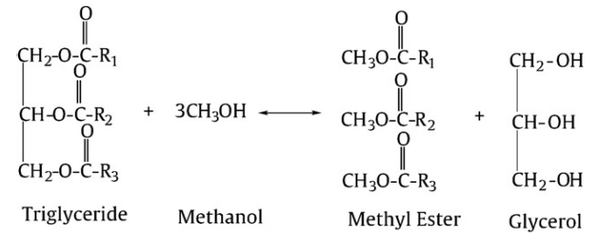

Fig. 2 General transesterification method.

lipase can be used for biodiesel production to overcome the limitations of chemical catalysts: since lipases can be used under moderate conditions, easy to recover, moisture and free fatty acid tolerant [2].

Due to the high cost of biocatalysts, lipases are immobilized on acrylic resin to improve lipase stability and catalytic activity [10]. Therefore, in this project *Candida antarctica* lipase-B immobilized on an acrylic resin was used as catalyst for biodiesel production. In addition, to expand the lipase toolbox several other lipases namely *Candida rugose, Pseudomonas fluorescens and Porcine pancreas* were tested under similar reaction conditions.

II. Materials and Methods

A. Materials and apparatus

Spent coffee ground oil was obtained from the North West University, Department of Chemical and Mineral Engineering. The lipases from *Candida rugose, Pseudomonas fluorescens, Porcine pancreas* and *Candida antarctica* lipase-B and deuterated chloroform ($CDCl_3$) were purchased from Sigma Aldrich, Kempton Park, Gauteng, South Africa. Methanol and diethyl ether were purchased from ACE Chemicals, Johannesburg, South Africa. The conversion of coffee oil to fatty acid methyl esters was calculated using ^{1}H Nuclear Magnetic Resonance (NMR) spectrometry. A Bruker 600 MHz instrument was used to record ^{1}H NMR spectra at the Laboratory for Analytical Services (LAS), Faculty of Natural Sciences, North-West University, Potchefstroom, South Africa. The reactions were carried out in 50ml pear shaped flasks. An

oil bath was used to maintain constant temperature of the reaction. The reaction mixture was stirred using a magnetic stirrer.

B. Methods

1) Screening of lipases

Spent coffee oil (1 g), methanol (135 µl) and different lipases (0.1 g, 10 wt.%) viz. *Candida rugose, Pseudomonas fluorescens, Porcine pancreas* and *Candida antarctica* lipase-B were added to different reaction flasks. Methanol was added according to the stoichiometric molar ratio (1:3) of oil to methanol. The reactions were carried out at 40 ºC for 6 h. After the reactions were completed, the lipases were separated from the samples by centrifugation. The remaining organic phase was dried under vacuum at 70 ºC. The obtained mixture was analyzed by ^{1}H NMR to quantify the biodiesel.

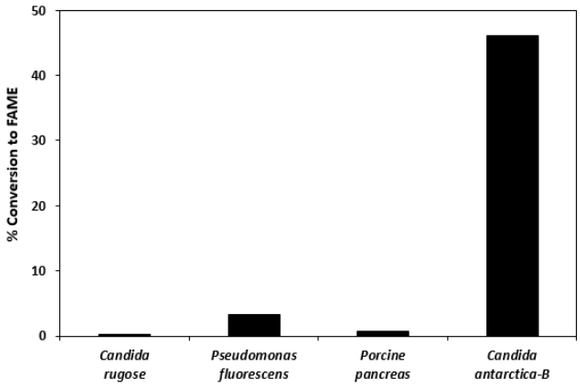

Fig. 3 FAME conversion obtained from different lipases.

2) Molar ratio optimization

The reactions were carried out at oil to methanol molar ratios of 1:1, 1:4, 1:5, 1:6, 1:8, and 1:10. Different amounts of methanol (44 µl, 175 µl, 220 µl, 265 µl, 350 µl and 440 µl) were added to the mixture of 1 g spent coffee oil and 0.1 g (10 wt.%) *Candida antarctica* lipase-B. The reactions were carried out at 40 ºC. After 6 h the samples were centrifuged, to remove the lipase, and dried. The samples were analyzed by ^{1}H NMR.

3) Temperature optimization

To a mixture of spent coffee oil (1 g) and *Candida antarctica* lipase-B (0.1 g, 10 wt.%), a known amount of methanol (1:4, 175 µl) was added to the reaction flasks. The reactions were carried out at different temperatures (30 ºC, 50 ºC and 60 ºC). After 6 h of reaction, the lipase was separated from each sample. The samples were then dried and analyzed by ^{1}H NMR.

4) Reaction time optimization

The mixture consisted of spent coffee oil (1 g), *Candida antarctica* lipase-B (0.1 g, 10 wt.%) and methanol (175 µl, 1:4). The reactions were carried out at different reaction times (0.5 h, 1 h, 2 h, 3 h, 4 h, 6 h, 8h, and 12 h) and at a constant temperature of 40 ºC. The lipases were then separated from each sample. The samples were dried under vacuum and analyzed by ^{1}H NMR.

III. Results and Discussion

A. Screening of lipases for biodiesel production from spent coffee oil.

Four different lipases were screened for biodiesel production, namely the lipases from *Candida rugose, Pseudomonas fluorescence, Porcine pancreas* and *Candida antarctica* lipase-B. Methanol was added (135 µl) to the reaction mixture according to the oil to methanol molar ratio of the reaction stoichiometry (1:3). The reactions were carried out at a temperature of 40 ºC for 6 hours. The efficiency of each lipase as catalyst in the transesterification process of spent coffee oil conversion to FAME is shown in Fig. 3.

The results show that the lipase from *Candida antarctica* lipase-B delivered the highest conversion of spent coffee oil to FAME (46.08 %), outperforming all other lipases. Lipase from *Candida Antarctica-B* was found to be the best catalyst for biodiesel production from spent coffee oil and was used in all further experiments unless otherwise stated.

B. Optimization of molar ratio on biodiesel production.

In the previous experiment the stoichiometric oil to methanol molar ratio was used (1:3). It has been reported that an excess methanol is needed for higher conversion to FAME [1]. The oil to methanol molar ratio was thus varied to obtain the optimal molar ratio. The reaction was performed at a temperature of 40 ºC and reaction time of 6 hours. The results of various oil to methanol molar ratios are presented in Fig. 4. The conversion to FAME increased from the molar ratio of 1:1 to 1:4. Further increase in the molar ratio resulted in a decrease in FAME yield. A molar ratio of 1:4 gave the highest

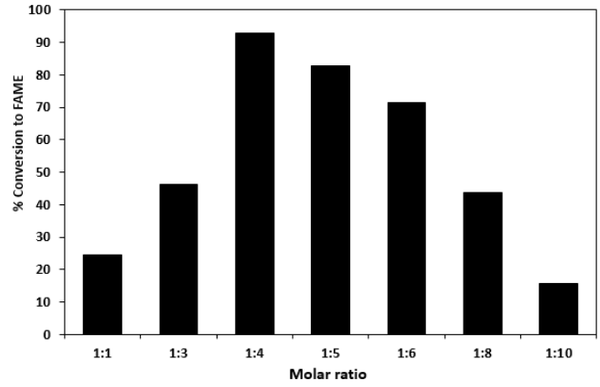

Fig. 4: Effect of molar ratio on % oil conversion to FAME.

FAME yield (92.83 %), whereas at a molar ratio of 1:5 the conversion was 82.66 %.

Although the conversion at 1:5 molar ratio is high, the effects of excess methanol is starting to decrease the lipase catalyst activity. This is due to excess methanol not dissolving in the oil and not taking part in the transesterification reaction. The excess methanol formed droplets and adhered to the surface of the catalyst [14]. Thus, the interfacial area of the catalyst coming in contact with the reaction medium decreased, decreasing catalyst activity and inhibiting the reaction. For all further experiments an oil to methanol molar ratio of 1:4 was used.

C. Optimization of temperature on biodiesel production.

In Fig. 5 the effect of temperature on spent coffee oil conversion to FAME is shown. The reactions were carried out at four different temperatures: 30, 40, 50, and 60 ºC with a reaction time of 6 hours. The optimal temperature was found to be at 40 ºC with a conversion of 92.83 %. The conversion increased from 30 to 40 ºC and then started to decrease for any further increase in temperature. Denaturation of the lipase starts to take place at temperatures higher than 40 ºC, decreasing the activity and subsequently decreasing oil conversion to FAME [10]. Further optimization experiments were carried out at 40 ºC.

D. Optimization of reaction time on biodiesel production.

To optimize reaction time, reactions were carried out at 0.5 to 12 hrs and at 40 ºC. The reaction reaches equilibrium after 3 hours with conversions to FAME of 90 % (Fig. 7.). Lipase catalyzed biodiesel production normally has slow reaction times for high FAME yields.

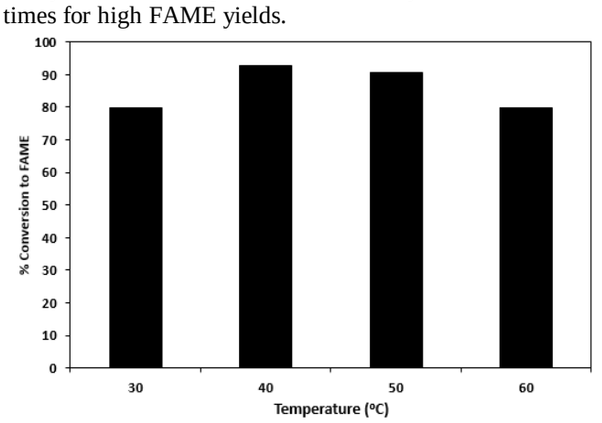

Fig. 5 Effect of temperature on FAME conversion

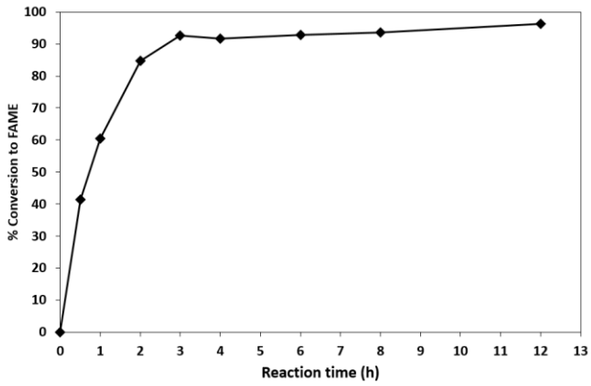

Fig. 6 Effect of reaction time on % oil conversion to FAME.

Thus, a reaction time of 3 h with a high FAME yield is fast and is not yet reported. Further investigation will be needed. The highest FAME yield was obtained after 12 h (96.33 %).

IV. Coffee waste production

Data collected on the total coffee usage per month on Potchefstroom Campus of the North-West University is shown in Table I. Taking into account the university is active for approximately 10 months, the total coffee usage annually is 1504 kg. The mass lost during the brewing process is between 18 and 22%. Working on an average of 20%, 1203 kg coffee waste is produced annually on campus. The oil that can be retrieved is 15 wt% of the total coffee waste, resulting in 180 kg coffee oil. Spent coffee oil to FAME conversions of 90 % and above was obtained in this study. Thus, a total of 162 kg of biodiesel can be produced from spent coffee grounds on campus to augment the transportation fuel supply for the campus.

TABLE I
NWU PC Coffee usage

Department	Coffee usage (kg/month)
Faculty of Arts	6.0
Faculty of Natural Sciences	28.5
Faculty of Theology	0.6
Faculty of Educational Sciences	1.0
Faculty of Economic and Management Sciences	0.0
Faculty of Law	6.7
Faculty of Engineering	17.0
Faculty of Health Sciences	10.7
Klipoog Cafeteria and food courts	80.0
TOTAL	150.4

V. Conclusion

The production of biodiesel from spent coffee grounds using a lipase as catalyst was successful with conversions to FAME over 90%. This result confirms lipase-catalyzed biodiesel production from non-edible low grade waste oils is very promising. The cost of biocatalyst together with up-scaling from laboratory experiment remains a major challenge. However, this can be overcome by reusing the lipases for many reaction cycles. The reusability of lipases will be studied in the future.

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