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Research Article

Chemical and Enzymatic Valorisation of Confectionery Waste into Biofuel: An Application of Circular Economy

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ABSTRACT

Waste oil was extracted from lollipop effluent stream using a mixture of organic solvents *viz.* n-hexane and ethyl acetate. Lollipop effluent samples found to contain ~ 10-18 wt.% oil. Subsequently, the oil was subjected to biodiesel synthesis under solvent free condition using chemical and enzymatic catalysts. Among the base catalysts used, KOH catalyzed reaction gave highest biodiesel yield (99 %) in 20 minutes. Furthermore, nine different lipases were screened as catalysts for biodiesel preparation from lollipop effluent oil. The screening experiments revealed that Novozyme-435 was best among the lipases which gave 94 % biodiesel in 18 h at 40 ^{0}C.

Keywords: sustainability, circular economy, lollipop effluent, catalysts, biodiesel

INTRODUCTION

Confectionery industries contribute immensely towards global food supply (Henricus, 1980). These industries are major enterprises across the world and still expanding rapidly. Liquid and solid wastes generated from confectionery industries contain substantial amount of lipids and carbohydrates. These are non-edible in nature and needs to be managed from the circular economy perspective (Karmee, 2016a, 2016b, 2017, 2018a, 2018b; Karmee et al., 2015, 2018). Thus, these wastes can be valorised for biofuel production. In this context, majority of the world's energy needs are met by burning natural gas, petroleum based fuels and coal. This is leading to depletion of fossil fuels and simultaneously causing environmental degradation. Therefore, there is a need for development of alternative energy resources. In addition, energy starved nations are also exploring renewable energy sources as an option to become energy independent. Along this line, biofuels are extensively researched and recognized as a potential source of energy.

In the above context, biodiesel is a commercially available fuel primarily synthesized from fats, oils and greases. Thus far, industrial biodiesel production is largely focussed on use of many edible feedstocks. However, use of edible feedstocks is creating several challenges including food *vs* fuel debate. In addition, feedstocks are also increasing the biodiesel cost. To circumvent these limitations, non-edible waste feedstocks viz. food waste, sewage sludge and organic waste are currently employed as low-cost or no-value resources for biofuel production (Karmee and Chadha, 2005; Karmee and Lin, 2014). In line with this, confectionery products and their wastes contain oils, syrups, nuts, candied fruits and colour powders. Confectionery industrial effluent streams containing oils and carbohydrates can be directly valorised for bioenergy production (**Figure 1**).

In this paper, biodiesel was prepared from a lollipop effluent stream. In the initial stage, oil from lollipop effluent stream was extracted using *n*-hexane and ethyl acetate. Approximately, 10-18 wt.% oil was recovered from lollipop effluent streams. Moisture from the obtained oil was removed using sodium sulphate (Na_2SO_4). Subsequently, for biodiesel production chemical (KOH, CaO and $Ca(OH)_2$) and biocatalysts (lipases) were used under solvent free condition. Biodiesel preparation *via* lipase catalysis is advantageous since it is substrate specific, moisture tolerant, recyclable and operates under mild experimental conditions (Karmee 2015, 2016a, 2016b, 2017). Initially, a series of commercially available lipases were screened for biodiesel production from confectionery waste oil. Immobilized lipase from *Candida antartica* lipase-B (CAL-B) was found to be suitable. Further optimization of reaction parameters were carried out using CAL-B. Key parameters including feedstock to alcohol molar ratio, temperature, and time course of reaction were optimised. Finally, reusability experiments for the Novozyme-435 was performed.

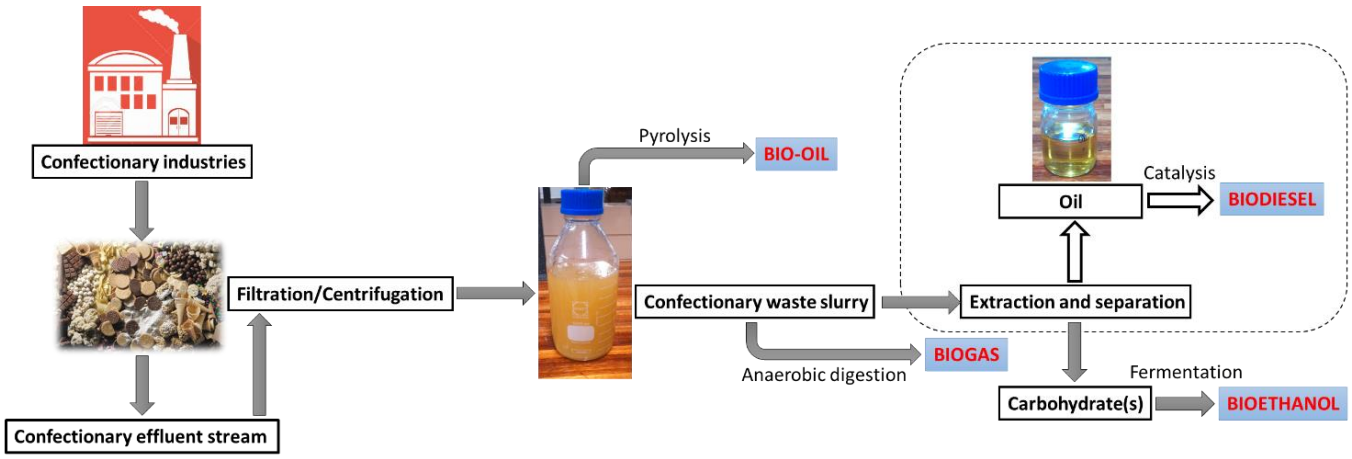

Figure 1. Plausible pathways for biofuel production from confectionery wastes

METHODOLOGY

Enzymes, Chemicals and Instruments

Feedstock used in this experiment was procured from a local lollipop unit located in North-West province, South Africa. KOH, CaO, $Ca(OH)_2$, methanol, diethyl ether and deuterated chloroform ($CDCl_3$) of analytical grades were purchased from Sigma-Aldrich and Associated Chemical Enterprises (ACE), Johannesburg, South Africa. *Mucor miehei*, *Pseudomonas cepacia*, *Rhizopus delemar*, *Geotrichum candidum*, *Candida rugosa, Caprica papaya, Porcine pancreas*-II, *Pseudomonas fluorescence* and *Candida antarctica* lipase-B (Novozyme-435) lipases were obtained from Sigma-Aldrich, Amano Enzyme Inc., Nagoya, Japan and from local enzyme suppliers of South Africa. Waste oil to biodiesel conversion (%) was calculated from ^{1}H NMR (Nuclear Magnetic Resonance) using a Bruker instrument (600 MHz) located at the Faculty of Natural Sciences, Laboratory for Analytical Services, North West University, Potchefstroom, South Africa.

Preparation of Biodiesel from Lollipop Effluent Using Base Catalysts (KOH, CaO and $Ca(OH)_2$)

A reaction mixture containing waste oil (1 g) and methanol (480 µl) was prepared in a round bottom flask. To this mixture base catalyst (1 wt.%) was added at 60^{0}C. The reaction was performed at 1:10 molar ratio of waste oil to methanol for 90 min. The reaction was monitored using ^{1}H NMR.

Screening of Different Lipases for Biodiesel Production from Lollipop Effluent

Nine lipases as stated in the earlier section were used during the screening experiments. For the screening experiments a molar ratio 1: 4 (oil to methanol) was used. The reaction mixture comprising methanol (189 µl), oil (1 g) and lipase (0.1 g, 10 wt%) was stirred at 40^{0}C for 6 h. After that, the mixture was diluted using diethyl ether (2 ml x 2). Subsequently, lipase was filtered and air dried. The biodiesel was placed in a 50 ml round bottomed flask and dried at 70^{0}C for 30 min under vacuum. The product was analyzed using ^{1}H NMR.

Optimization of Feedstock to Alcohol Molar Ratio

All experiments were started by addition of oil (1 g) to Novozyme-435 (0.1 g, 10 wt.%). Then methanol of required molar ratios were added (1:1 (47 µl), 1:3 (146 µl), 1:4 (189 µl), 1:5 (240 µl), 1:6 (285 µl), 1:8 (379 µl), 1:10 (480 µl) for optimization purpose at 40^{0}C. Each reactions were carried out for 6 h. Downstream processing and ^{1}H NMR analysis were carried out as mentioned in the earlier section.

Optimization of Reaction Temperature

A moral ratio of 1:4 (oil to methanol) was used for the experiments, which consists of a mixture of methanol (1:4,189 µl), feedstock (1g) and biocatalyst (Novozyme-435) (0.1 g, 10 wt.%). Reactions were performed at 30^{0}C, 40^{0}C, 50^{0}C and 60^{0}C to determine the maximum biodiesel yield. Each of these experiments was carried out for 6 h.

Two-step Methanol Addition Process for Biodiesel Production

A two-step methanol addition process was followed to maximize the yield of biodiesel. The mixture was comprised of methanol (1:4, 189 µl), oil (1 g) and biocatalyst (0.1 g, 10 wt. %). The initial time duration was 6 h at 40^{0}C. Subsequently, after 6 h of duration an additional amount of methanol (47 µl) was added to the reaction flask through septum. Further, the reaction was allowed to continue until 36 h. All the obtained samples were analyzed using ^{1}H NMR to quantify the biodiesel.

RESULTS AND DISCUSSION

Confectionary Waste Utilization

Different solid and liquid effluents are generated in confectionery industries, which are known to contain organic substances (Beal and Raj, 2000; Das et al., 2013; El-Kassas et al., 2015; Lafitte-Trouque and Forster, 2000). These wastes are generally composed of biodegradable materials such as sugar, sweetener, casein, oil, milk, food colouring and flavouring agents. These are considered no-value resources as these are discarded without any further applications. Confectionery wastes can be converted into aquatic feeds, carbon rich-sources, bioenergy and value added products (Beal and Raj

Table 1. Value added products from confectionery waste as compiled and reported by Johnstone-Robertson (2017)

Solid waste		
Source	**Treatment technologies**	**Product (s)**
Confectionery waste	Biogas integrated gasification fuel cell	Electricity
Confectionery waste	Microbial cultivation	Single cell protein (SCP)
Confectionery waste products	Two-stage anaerobic digestion (AD)	Acetic acid, lactic acid, Ethanol and CO_2
Flour waste streams	Batch fermentation	Bacterial cellulose
Flour rich waste stream	Batch fermentation	Poly hydroxyl butyrate (PHB)
Flour rich waste	Fed-Batch fermentation	Microbial lipid
Sweets waste	Fuel cell	Electricity
Waste wafer material	AD	Biogas and digestate
Liquid waste		
Source	Treatment technologies	Product (s)
Confectionery factory effluent	Shake flask	Algal biomass
Confectionery waste water	Sludge waste water treatment plant	Water for irrigation
Confectionery waste water	Aerobic conditions	Xanthan gum
Confectionery waste water	Anaerobic digestion (AD) with enrich H_2 producing bacteria (Methanogens inactive)	H_2
Chocolate waste water	Microbial fuel cells	Electricity
Chocolate waste water	AD	Electricity
Chocolate soup	AD	Electricity
Candied jujube waste water	Batch fermentation	Bacterial cellulose
Confectionery waste water	Fermentation	Bioflocculant
Confectionery waste water	Sloping pilot plant	Microalgae biomass, enzymatic and non-enzymatic antioxidant
Chocolate waste water	AD	Electricity
(Containing sugar syrups)	Dual anaerobic co-digestion	CH_4
Chocolate waste water	AD	Biogas and COD reduction
Confectionery waste water	Anaerobic pretreatment and aerobic treatment	CH_4 and reduced COD levels and water for irrigation
Confectionery waste water	Sequential two-stage anaerobic treatment	Decrease in COD levels
Confectionery waste water	Fermentation	Clean water with reduced COD, BOD, FOG, TSS, and odors.
Confectionery waste water	Aerobic treatment using trickling filter	Decrease in COD levels

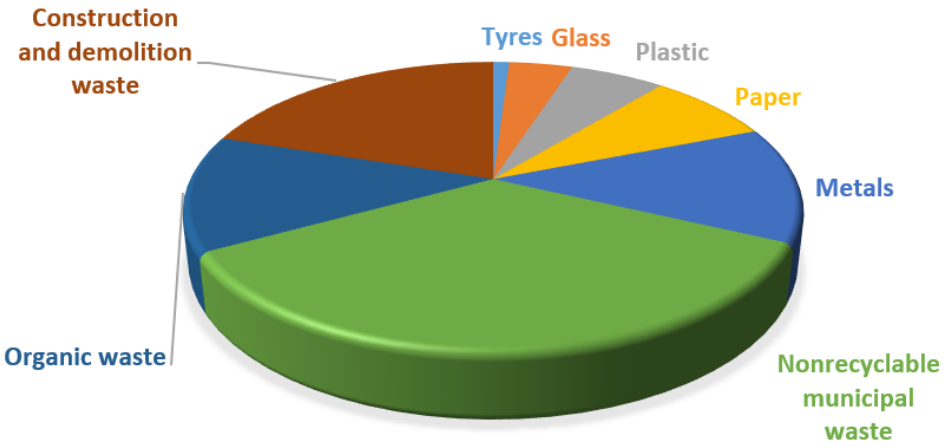

Figure 2. Distribution of different types of wastes generated in South Africa (Ekelund and Nyström, 2007; Environment outlook, 2013; NOWCS South Africa, 2013)

2000; Das et al., 2013; El-Kassas et al., 2015; Lafitte-Trouque and Forster, 2000). In this context, South Africa, has many confectionery industries such as lollipop factories that produce sizeable quantities of wastes, which can be valorised into biofuels, chemicals and biopolymer (García et al., 2011; Genc and Ozbay, 2015; Gough et al., 2013; Johnstone-Robertson, 2017; Lunghi and Burzacca, 2004; Pilarska et al., 2019; Ranade et al., 1989; Ruggeri et al., 2013; Tsakona et al., 2016) (**Table 1**). Similarly, using advanced valorisation technologies the ~ 13% organic waste generated in South Africa can be converted into biofuels, chemicals, materials and other high value products (Ekelund and Nyström 2007; NOWCS South Africa 2013; Environment outlook 2013). (**Figure 2**). Environmental friendly management of confectionery wastes is significant from waste management and circular economy context (Miah et al., 2018) (**Figure 3**).

Biodiesel Production from Lollipop Effluent *via* Base Catalysis

Food industries generate significant amounts of waste during processing, production, packaging, and storage (Sohair et al., 2008). South Africa generates large quantities of organic food wastes which needs technical valorisation (Greben and Oelofse, 2009; Oelofse and Nahman, 2013). During the course

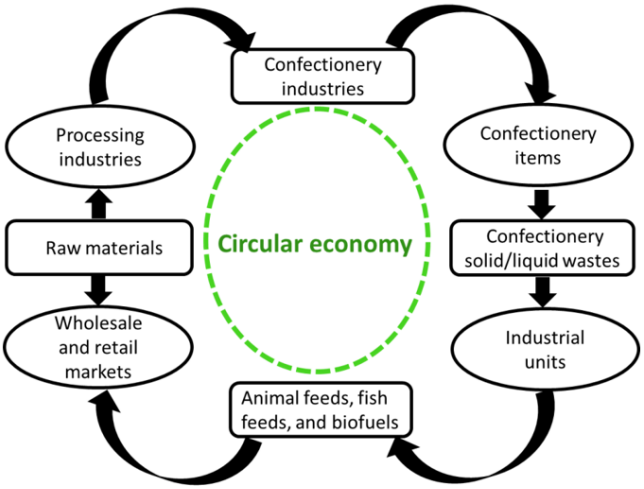

Figure 3. A circular economy approach for valorisation of confectionary waste into biofuels and value added products

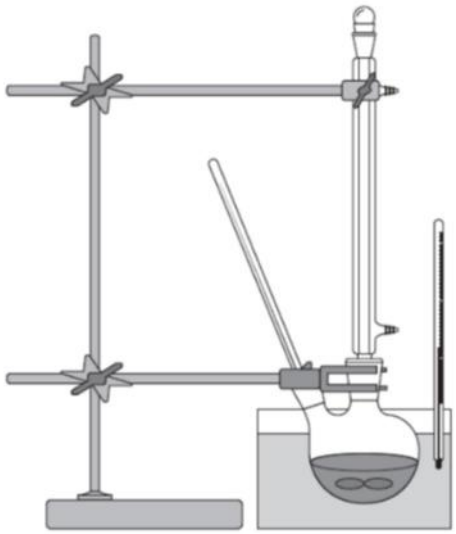

Figure 4. Experimental set-up for biodiesel preparation from confectionery waste

of this work, lollipop industry waste stream was valorised for biofuel production. Initially oil from the lollipop effluent was extracted using *n*-hexane and ethyl acetate (95v: 5v) as a solvent. Up to 10-18 wt.% of oil was recovered from confectionery waste samples. After extraction, the recovered oily portions were combined and concentrated via a roatary evaporator. To remove trace amount of moisture in the oily fraction it was dried over sodium sulphate and stored for further use.

The waste oil isolated from the lollipop effluent was subjected to base catalysed biodiesel preparation. The KOH, CaO and $Ca(OH)_2$ catalysed (1 wt. %) reactions were performed at 1:10 molar ratio of waste oil to alcohol at 60 ^{0}C in a two necked round bottom flask equipped with heating bath, condenser and magnetic stirrer (**Figure 4**). Among all base catalysts, high conversion (99%) of biodiesel was observed in 20 min during KOH catalysed reaction (**Figure 5**).

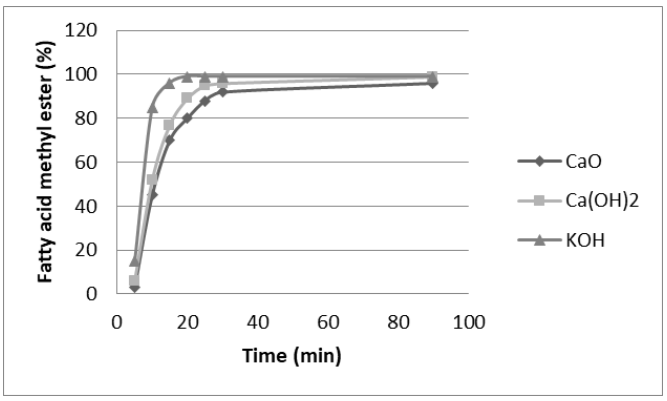

Figure 5. Base catalysed production of biodiesel from confectionery waste

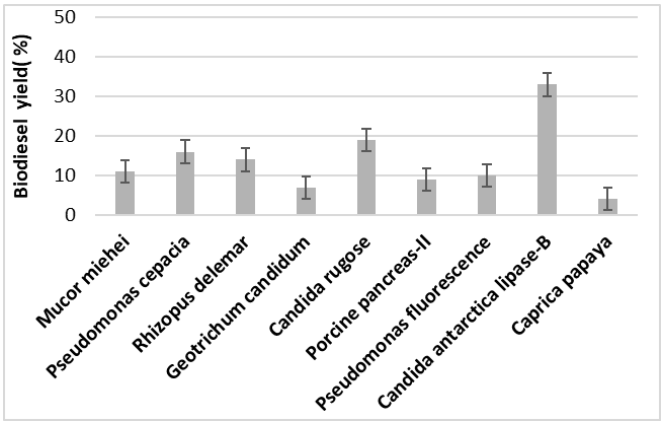

Figure 6. Potential of lipases for biodiesel production from confectionery waste oil

Biodiesel Production from Lollipop Effluent Using Lipases

Lipases are widely used enzymes for applications in energy, food, beverage, detergent, leather, pharmaceutical and paper industries. Under physiological conditions, lipases catalyse hydrolysis of triglycerides to glycerol and free fatty acids. However, in non-conventional media lipase catalyses esterification and transesterification reaction. As mentioned in **Figure 6**, nine different lipases were screened for biodiesel production from waste oil derived from lollipop effluent stream. The biodiesel yield was in the range of 4-34% (**Figure 6**). During screening it was observed that *Candida antarctica* lipase-B (Novozyme-435) gave 34% biodiesel yield (**Figure 6**).

Novozyme-435 was applied for further optimization of reaction conditions. The time course study of biocatalytic biodiesel production was carried out for 36 h. However, at 18 h, a maximum 94% biodiesel yield was achieved (**Figure 7**). Therefore, 18 h is considered to be the optimum reaction time. The reusability of the biocatalyst (Novozyme-435) was studied at 1:5 molar ratio and 40 ^{0}C. It was found that, after 14th reaction cycle, 72 % biodiesel yield was obtained. Around 24% decrease in biodiesel yield was observed after the 14th reaction cycle (**Figure 8**).

Base catalysed reaction is faster as compared to the enzyme catalysed reactions. During base catalysis methoxide is formed; whereas, during lipase catalysed reaction enzyme-

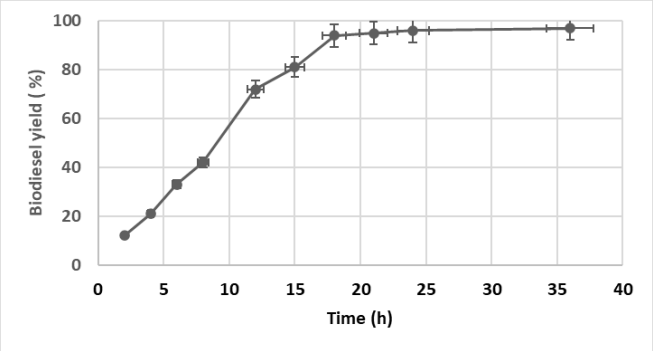

Figure 7. Reaction kinetics of Novozyme-435 catalysed biodiesel production from confectionery waste

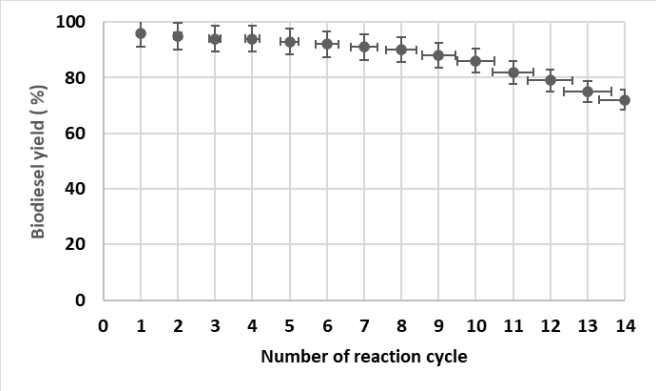

Figure 8. The reusability of Novozyme-435 during biodiesel preparation

substrate complex is formed. For the base catalysed reaction optimum conditions are: 1:10 molar ratio (substrate to alcohol), 60 ^{0}C and 20 min (reaction time). In contrast, for the lipase catalysed reaction, optimum conditions are: 1:5 molar ratio (substrate to alcohol), 40 ^{0}C and 18 h.

CONCLUSIONS

Liquid effluents from confectionery industries are potential feedstocks for biofuel production. In this work, both chemical (base) and biocatalysts (lipases) were used for biodiesel preparation from confectionery waste oil. KOH gave 99% biodiesel yield in 20 min; whereas, Novozyme-435 catalyzed reaction produced 94% biodiesel in 18 h.

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