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Utilizing lipid-extracted microalgae biomass residues for maltodextrin production

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HIGHLIGHTS

- Recovering valuable carbohydrate compounds from microalgae biomass residues.
- Optimization of hydrolysis conditions to obtain low-molecular-weight maltodextrin.
- Maltodextrin obtained was resistant to enzymatic hydrolysis.
- Maltodextrin obtained was found similar as commercial-grade maltodextrin.

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ABSTRACT

Cultivation of microalgae biomass for biodiesel production has been placed as one of the forefront research fields that gained wide interest from researchers across the world. Nevertheless, after extracting the lipid from the microalgae biomass, little attention is given on the possibility to convert the microalgae biomass residues to other value-added co-products. In the present study, the microalgae biomass residues were utilized by recovering valuable carbohydrate compound remaining in the biomass after lipid extraction. Parametric study on the carbohydrate hydrolysis conditions was performed to obtain low-molecular-weight maltodextrin from the microalgae carbohydrate. It was found that the highest maltodextrin yield (90%) could be attained by using 3 vol.% of H_2SO_4 (or 0.56 M) at operating temperature of 90 °C after 1 h of hydrolysis time. In addition, the maltodextrin obtained from the microalgae biomass residues was resistant to enzymatic hydrolysis, in which this form of maltodextrin is usually denoted as resistant maltodextrin.

1. Introduction

In these recent years, renewable and sustainable energy production from photosynthetic microalgae has attracted considerable interest by the bioenergy and biotechnology sectors [1]. There are enormous advantages of cultivating microalgae for biofuels production, such as: (1) exceptional fast growth rate, which is 100 times faster than terrestrial plants [2]; (2) high lipid and carbohydrate productivity [3,4]; (3) high photosynthetic rate which makes them superior in CO_2 bio-mitigation [5–9]; (4) does not trigger in any debate on food versus fuel feud [4,10]; and (5) can be cultivated under extreme environment such as using industrial wastewater as nutrients source [11]. Unfortunately, several recent life cycle assessments (LCA) on microalgae biofuels have proven that massive energy input are required to produce the biofuels (e.g. biodiesel), especially during cultivation stage and harvesting of microalgae biomass [12–16]. In fact, a negative energy balance was observed in these LCA studies, indicating that the sustainability of microalgae biofuels as the fuel of the future is still questionable [1,4,8,17–19].

One of the plausible solutions to improve the sustainability of microalgae biofuel is through integrated biorefinery concept, by producing different range of products from microalgae biomass. At the moment, after extracting lipids from microalgae biomass for biodiesel production, the leftover biomass residues are not effectively utilized but instead being discarded as waste. Although there are some scattered researches being carried out to utilize the leftover biomass but more concrete findings are urgently needed to address the possibility of integrated biorefinery approach. In addition to that, utilizing the lipid-extracted microalgae biomass residues are challenging because during the lipid extraction process, other compounds (e.g. carbohydrate and protein) in the microalgae biomass that can be used to produce high value-added products might be decomposed, depending on the extraction methods and conditions [20]. Thus, in the present study, attempt was made to extract microalgae lipid at room temperature in order

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to retain as much carbohydrate as possible in the microalgae biomass. The lipid-extracted microalgae residues were then recovered after lipid extraction to further explore the potential of utilizing the retained carbohydrate. Hydrolysis experiments were carried out to hydrolyze the carbohydrate into low-molecular-weight compound such as maltodextrin as one of the co-products in microalgae biodiesel refinery. Maltodextrin is an oligosaccharide which is usually produced during partial-hydrolysis of potato and corn starch. There is a wide range commercial applications for maltodextrin, such as being used as water soluble glues, thickening agents in food processing, and binding agents in the pharmaceutical industry [21]. However, not all forms of maltodextrin are digestible, and indigestible or resistant dextrin is sometimes used as fiber supplements [21]. Through this approach, the main aim of the present study is to clearly illustrate the integrated biorefinery concept by simultaneously producing biodiesel and maltodextrin from microalgae biomass.

2. Materials and methods

2.1. Materials

Sodium nitrate ($NaNO_3$), calcium chloride dihydrate ($CaCl_2{\cdot}2H_2O$), magnesium sulfate heptahydrate ($MgSO_4{\cdot}7H_2O$), dipotassium hydrogen phosphate (K_2HPO_4), monopotassium hydrogen phosphate (KH_2PO_4), sodium chloride (NaCl), ethylenediaminetetraacetic acid (EDTA) anhydrous, potassium hydroxide (KOH), iron(II) sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$), sulfuric acid (H_2SO_4), boric acid (H_3BO_3), zinc sulfate heptahydrate ($ZnSO_4{\cdot}7H_2O$), manganese(II) chloride tetrahydrade ($MnCl_2{\cdot}4H_2O$), molybdenum trioxide (MoO_3), copper (II) sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$), cobalt(II) nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), methanol (CH_3OH), chloroform ($CHCl_3$), hydrochloric acid (HCl), sodium hydroxide (NaOH) were purchased from Fisher Scientific, Malaysia. Enzyme α-amylase from *Aspergillus oryzae* (aqueous solution, ⩾800 FAU/g), enzyme amyloglucosidase from *Aspergillus niger* (aqueous solution, ⩾300 U/mL), commercial-grade starch and maltodextrin were purchased from Sigma–Aldrich, Malaysia. Organic fertilizer (Baja Serbajadi Humus 27) which was used as the main nutrient source for the 5 L cultivation of microalgae was purchased from a local market.

2.2. Microalgae biomass cultivation

2.2.1. Inoculums cultivation

A wild-type *Chlorella vulgaris* was isolated from local freshwater located at Penang, Malaysia. The microalgae was preserved and grown in Bold's Basal Medium (BBM), consisting of: (1) 10 mL per liter of culture medium using the following chemicals: $NaNO_3$ (25 g/L), $CaCl_2{\cdot}2H_2O$ (2.5 g/L), $MgSO_4{\cdot}7H_2O$ (7.5 g/L), K_2HPO_4 (7.5 g/L), KH_2PO_4 (17.5 g/L), NaCl (2.5 g/L) and, (2) 1 mL per liter of culture medium using the following chemicals: EDTA anhydrous (50 g/L), KOH (31 g/L), $FeSO_4{\cdot}7H_2O$ (4.98 g/L), H_2SO_4 (1 mL), H_3BO_3 (11.4 g/L), $ZnSO_4{\cdot}7H_2O$ (8.82 g/L), $MnCl_2{\cdot}4H_2O$ (1.44 g/L), MoO_3 (0.71 g/L), $CuSO_4{\cdot}5H_2O$ (1.57 g/L), $Co(NO_3)_2{\cdot}6H_2O$ (0.49 g/L). The initial pH of the medium was adjusted to 6.8. The culture was grown in a 100 mL Erlenmeyer flask containing 50 mL of medium, aerated with compressed air, surrounding temperature of 25–28 °C and illuminated continuously with cool-white fluorescent light (Philip TL-D 36W/865, light intensity of 60–70 μmol m^{-2} s^{-1}).

2.2.2. Mass cultivation

Organic fertilizer derived from compost was used as the main nutrients source to cultivate the microalgae in a larger scale. 10 g organic fertilizer (Baja Serbajadi Humus 27) was immersed in 600 mL tap water and stirred for 24 h using a magnetic stirrer. After the stirring process, non-soluble particulate solids were separated using filter paper (Double Rings 101). The resulting organic fertilizer medium was dark-brown in color and the characteristics are shown in Table 1. Subsequently, 100 mL of organic fertilizer medium was loaded into a photobioreactor with 5 L tap water (without sterilization) and the pH of the medium was adjusted to 5. Then, 10 mL inoculums culture with cell concentration of 0.3×10^6 cells was introduced into the photobioreactor. The photobioreactor was aerated with compressed air continuously and illuminated 24 h with cool-white fluorescent light (Philip TL-D 36W/865, light intensity of 60–70 μmol m^{-2} s^{-1}) for 14 days. The microalgae biomass yield attained on day-14 was 0.5–0.55 g/L [22].

2.3. Biomass harvesting process

After 14 days of cultivation, air aeration to the photobioreactor was stopped. The microalgae cells were allowed to settle naturally to the bottom of the photobioreactor for two days. Two distinct layers were observed, in which the upper layer consisted of water with suspended microalgae cells and the bottom layer consisted of microalgae biomass. The water in the upper layer was slowly decanted, leaving behind the microalgae biomass which was further dried in an oven at 100 °C for 24 h. The dried microalgae biomass was collected and kept in a sealed empty container for lipid extraction.

2.4. Microalgae lipid extraction

50 g of dried *C. vulgaris* biomass was placed in a 500 mL conical flask together with 300 mL of methanol–chloroform solution (volume ratio of 2:1). The mixture was stirred at 400 rpm for 24 h at room temperature. After that, the biomass was filtered using filter paper and the filtrate was evaporated in a rotary evaporator at 100 °C. The leftover microalgae lipid was collected after all the solvent was evaporated. The filtered microalgae biomass was then mixed with the recovered solvent for second cycle of lipid extraction. A total of 20% lipid was extracted from the microalgae biomass.

Table 1
Characteristics of organic fertilizer medium.

Parameter	Unit	Concentration
Chemical oxygen demand (COD)[a]	ppm	1729.9
Biochemical oxygen demand (BOD) – 5 days test at 20 °C[b]	ppm	576.0
Nitrogen[c]	ppm	1323.2
Phosphorus[d]	ppm	213.6
Potassium[e]	ppm	634.4
Calcium[f]	ppm	269.9
Magnesium[g]	ppm	54.5
Manganese[h]	ppm	1.0
Boron[i]	ppm	4.1
Iron[j]	ppm	1.3

Testing method:
[a] APHA 5220 B (2005).
[b] APHA 5210 B (2005).
[c] APHA 4500-NH_3 F.
[d] APHA 4500-P E (2005).
[e] APHA 3111 B (2005).
[f] APHA 3111 B (2005).
[g] APHA 3111 B (2005).
[h] APHA 3111 B (2005).
[i] APHA 4500-B C (2005).
[j] APHA 3111 B (2005).