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ORIGINAL PAPER

Valorization of coffee byproducts for bioethanol production using lignocellulosic yeast fermentation and pervaporation

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Abstract Industrial residue management is a critical element of sustainable development. The aim of this research was to investigate the potential of different coffee waste fractions for bioethanol fermentation and its purification by pervaporation; these fractions and the role of pervaporation in this application have not been studied before. Bioethanol production from different coffee waste fractions has now been studied by acid or acid and enzymatic hydrolysis. The fermentation was conducted using two different yeasts (baker's yeast and lignocellulosic yeast). By using the cellulolytic enzymes and lignocellulosic yeast, a higher bioethanol yield was achieved. Further purification of the fermented filtrate was carried out by an alcohol selective pervaporation membrane at four temperatures (23, 30, 40 and 50 °C). Hydrolysis of the samples using cellulose complex and β-glucosidase enzymes and fermentation with lignocellulosic yeast, followed by purification using pervaporation resulted a superior bioethanol yield of 51.7 ± 7.4 g/l for spent coffee and 132.2 ± 40 g/l for husk. Husk hydrolysis using cellulolytic enzymes and fermentation with lignocellulosic yeast, followed by product recovery through pervaporation membrane, was found to be the optimal procedure, producing ethanol at a concentration of 132.2 ± 40 g/l. In general, husk hydrolysis using acid and cellulolytic hydrolysis and fermentation with lignocellulosic yeast GSE16-T18 followed by pervaporation was found to be the best process for producing the highest ethanol yield compared to the other fractions of coffee waste samples.

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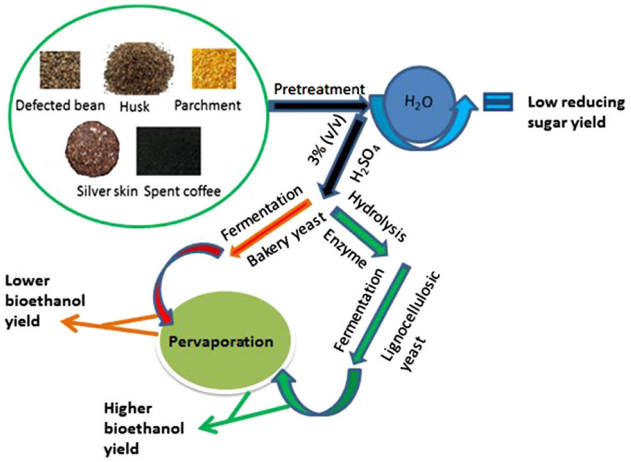
Graphical Abstract



Keywords Coffee waste · Enzymatic hydrolysis · Pervaporation membrane · Pretreatment · Purification

Introduction

The global high energy demand has exerted an excessive stress on the use of non-renewable resources such as fossil fuels and various minerals (Loow et al. 2016b). The population growth (Gerland et al. 2014) and predictable depletion of the finite natural resources pose a great threat to long-term economic development and environmental safety. New renewable and environment-friendly sources of energy have been explored because of the depletion of fossil fuel reserves and concerns about climate change (Choudhary et al. 2016). The recent paradigm of sustainable development has resulted in a large amount of research on socially beneficial, economically viable and environmentally benign production technologies. As a result, agricultural waste has become a critical element of sustainable development, closely linking production and consumption. To support this goal, this research focuses on the possibilities of resource recovery by extraction of disposed coffee waste fractions for bioethanol production.

Energy demand is mainly fulfilled with conventional fossil fuels (66.2%), while biofuels from waste and other sources have only a minor contribution (12.7%) (International Energy Agency I 2012). However, burning fossil fuels releases CO_2 from historical stockpiles and accounts for about 70% of total climate harmful emissions (Balat et al. 2008).

Lignocellulosic biomass is plant-derived matter that is being considered as a renewable carbon resource for the production of reducing sugar, which can be used as an alternative source for biofuels and chemicals (Loow et al. 2017). The development of second-generation biofuels from lignocellulosic biomass has many advantages from an energy and environmental point of view. The potential environmental benefits that can be obtained by replacing petroleum fuels with biofuels, derived from renewable sources of biomass, are the main driving forces for promoting the production and use of biofuels (Tiwari et al. 2015). Lignocellulosic biomass can be used for instance as a sustainable and cheap feedstock for the production of bioethanol, which will not only facilitate agricultural residue management, but also provides fuel mainly for the transport sector (Rehman et al. 2014). Plant biomass is the most abundant renewable source of energy. However, it is largely wasted either by burning or by disposal in landfill sites, which results in huge production of greenhouse gases (Choudhary et al. 2016).

Biofuels appear to be one of the most viable and green alternatives among various renewable energy sources (Nigam and Singh 2011). Production of biofuels, such as bioethanol, is a highly efficient pathway for reduction of crude oil demand and for environmental compliance (Achinas and Euverink 2016). The main environmental advantage of fuel ethanol is its sustainability in using a renewable resource as a feedstock, thus promoting independence of fossil fuel and maintaining a constant level of CO_2 (Tiwari et al. 2015). Bioethanol is a clean energy source that can be produced by fermentation of biomass (Verhoef et al. 2008). Bioethanol cannot only be used as fuel for energy generation, but also as chemical in various industrial applications. Because of this broad potential, world bioethanol production has increased tremendously over the past decade (Chovau et al. 2013).

Agricultural waste contributes significantly to the global yield of lignocellulosic biomass (Loow et al. 2015). For example, the coffee industry generates huge amounts of coffee byproducts, which are rich in carbohydrates (cellulose, hemicellulose), proteins, pectins, bioactive compounds like polyphenols and are cheap renewable resources (Murthy and Naidu 2010). However, direct large-scale utilization of coffee waste around the world remains a challenge due to the presence of caffeine, free phenols and tannins (polyphenols) (Fan et al. 2003). Thus, alternative routes are needed for a feasible coffee waste management (Caetano et al. 2012).

There are challenges to resource recovery from lignocellulosic waste because the structure of lignocellulose is very resistant to degradation. This is due among others to cross-linking between the polysaccharides cellulose and hemicelluloses, and the lignin via ester and ether linkages (Lin and Tanaka 2006). In order to overcome the recalcitrant structure of the biomass for effectively improving

sugar recovery, a pretreatment stage is normally required (Loow et al. 2016b). When biomass is exposed to a pretreatment, several operations, such as the increase in the surface area and porosity, modification of the lignin structure, removal of lignin, partial depolymerization of hemicellulose and reduction of cellulose crystallinity, can be accomplished (Loow et al. 2015).

Various pretreatment technologies have been extensively studied to process different types of biomass for cellulosic bioethanol production. None of those can be declared as optimal, because each pretreatment has its intrinsic advantages and disadvantages. No standalone pretreatment option is available yet for commercial scale applications (Alvira et al. 2010). Acid pretreatment has been extensively and successfully investigated for several lignocellulosic biomass fractions (Yaqoob et al. 2012). Diluted-acid hydrolysis is probably the most commonly employed and most effective method among the chemical pretreatment methods (Loow et al. 2016a). It can be used either as pretreatment to turn the lignocellulose more accessible for the cellulolytic enzymes, or as the sole hydrolysis method to obtain fermentable sugars (Taherzadeh and Karimi 2008). In addition, it is a favorable and cheap method for industrial application (Alvira et al. 2010). Therefore, for this study, dilute acid treatment was used for the production of bioethanol from coffee waste fractions.

Hexoses and pentoses are the main sources of monomeric sugars in the lignocellulosic hydrolysates. Monomeric hexoses are naturally fermented to bioethanol by *S. cerevisiae*, while the fermentation of pentoses is only done by other yeast species or by a few engineered *S. cerevisiae* strains harboring heterologous genes (Choudhary et al. 2016). Since the pentose sugars comprise a high percentage of the available sugars in lignocellulosic materials, its fermentation is essential for economic conversion of lignocellulose to bioethanol (Jun and Jiayi 2012).

The product stream after the fermentation step, often denoted as the beer, consists of bioethanol, lignin, unconverted organic compounds, various inorganic soluble and water. Typical bioethanol concentrations reached after fermentation of lignocellulosic biomass is in the range of 3–6 wt.% (Balat et al. 2008). During purification, usually by distillation, the bioethanol is recovered from the beer to obtain fuel grade bioethanol. The energy requirement rapidly increases when the ethanol concentration in the beer falls below 5 wt.% (Madson and Lococo 2000). Hence, alternative technologies can be considered. Among them, pervaporation is one of the most promising alternatives, due to the simplicity of operation, the absence of extra chemicals, low energy requirements and hence low operational cost (Bowen et al. 2007). Although distillation can achieve very high bioethanol recovery, it has some disadvantages when it comes to the purification of lignocellulosic bioethanol, i.e., a batch mode of operation and high energy requirement. Pervaporation can overcome these drawbacks and could, therefore, potentially replace the first distillation column (beer column) of the purification train (Chovau et al. 2013).

Several recent studies indicate that coffee byproducts (husk, pulp and spent coffee) can be suitable for bioethanol production using fermentation technology (Ayele 2011; Choi et al. 2012; Gouvea et al. 2009; Shenoy et al. 2011; Woldesenbet et al. 2016). However, no research has been carried out to compare different coffee waste fractions (CWFs) as potential substrates, followed by purification of the produced bioethanol via pervaporation. Thus, the current study focuses on both bioethanol production and its quality upgrading by pervaporating the produced bioethanol using alcohol selective membranes. The study was conducted at Department of Chemical Engineering of the University of Leuven (KU Leuven), Belgium from September 2014 to December 2015.

Materials and methods

Coffee waste collection

Coffee waste samples were collected in May and June 2014 from dry coffee processing plants in Jimma zone and Addis Ababa city, Ethiopia. This study included most coffee waste fractions (Fig. 1). They were parchment, husk defected coffee beans (DCB), silver skin (SS) and spent coffee (SC) ground. These fractions are produced when washed coffee is dried and deshelled, coffee berries are processed by the dry method, immature or overripe coffee bean, which is too low in quality is separated, coffee is roasted and as residue of coffee brewing, respectively. The husk and defected coffee beans were collected from Manna, Limmu Kossa and Gomma districts of Jimma zone in Ethiopia. The spent coffee samples were collected from Jimma town residential houses, staff lounge and student cafeterias of Jimma University, Ethiopia. The parchment and silver skin samples were collected from dry coffee processing plants in Addis Ababa, Ethiopia.

Fresh samples of the coffee waste were collected from the chosen locations (coffee processing plants, cafeterias and households). The samples were taken from five parts of the pile (i.e., from the bottom, top, left, right side and interior of the pile) and thoroughly ground and mixed to obtain homogeneous samples. Grinding was carried out with a coffee blender with grinder 'Seven 7 star' (Germany) to obtain particle sizes <0.500 mm. The ground coffee waste samples were sieved with a U.S. standard sieve series mesh (ASTM E11-61, Tyler equivalent 32 inches mesh with 0.5 mm pore size, The W.S Tyler

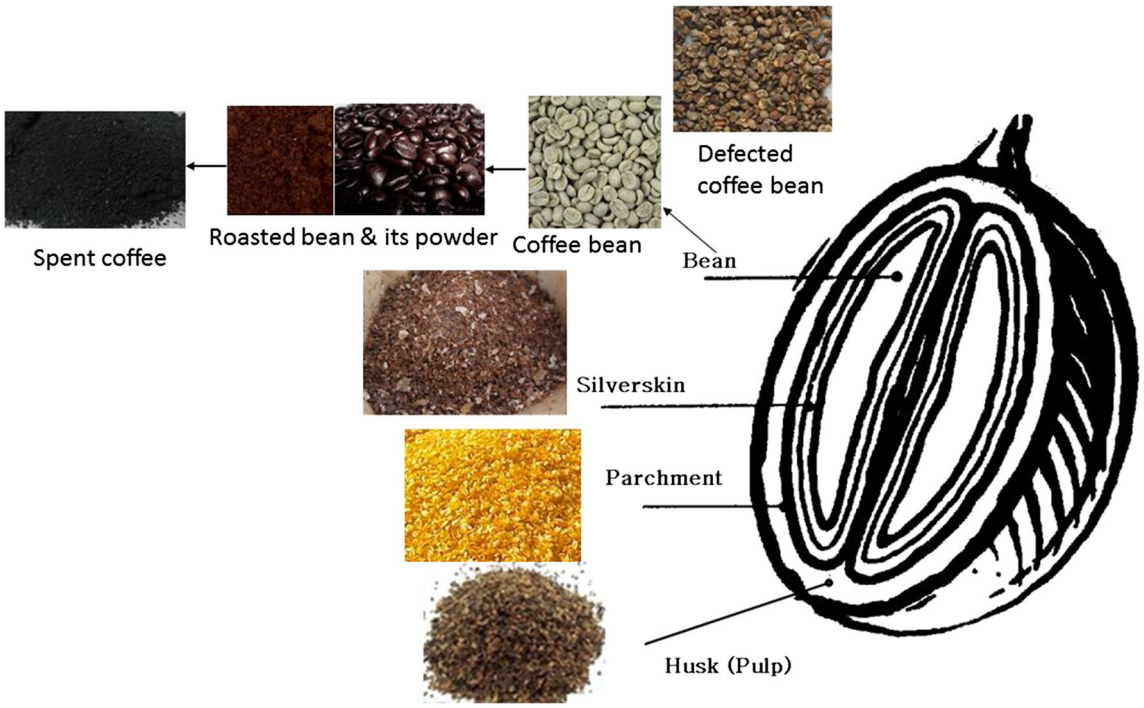


Fig. 1 Cross-section of coffee cherry and origin of the different coffee waste fractions

International Company, USA). All the coffee waste samples were air dried, ground and collected in well-dried polyethylene plastic containers and stored in dry place until analysis.

Determination of physicochemical properties

The ground and sieved coffee waste samples were characterized by the following methods: The pH was determined using a Docu pH meter (Sartorius, Germany). For determination of electrical conductivity (EC), 5 g of air-dried ground coffee waste sample was transferred into a bottle and 25 ml of deionized water was added to obtain a suspension at 1:5 ratio. The bottles were capped and homogenized at 200 rpm for 15 min (D72379 Hechingen, Edmund Buhler GmbH®, Germany). The electrical conductivity (EC) was measured using pre-calibrated Hach HQ40d dual-input multi-parameter. For the determination of the moisture content, oven drying and a gravimetric method was used. Samples of fresh coffee waste were weighed and placed in a forced air oven at 105 °C for 24 h. After drying, the samples were weighed to determine the moisture content. The volatile suspended solids fraction (VSS) and ash content of the samples were determined by ashing the samples in a furnace (LH 60/13, Naberthem, Germany) at 550 °C for 1 h. For the determination of biological oxygen demand (BOD) and chemical oxygen demand (COD), 1 g of ground coffee sample was mixed with 10 ml of distilled water and they were determined using BOD HACH dilution method 8043 and dichromate reactor digestion method 8000, respectively.

Acid hydrolysis of coffee waste and fermentation using a baker's yeast

All five coffee waste samples (husk, silver skin, defective coffee bean, spent coffee, parchment) and their mixture were acid hydrolyzed with 3% (v/v) H_2SO_4 (99%, Sigma Aldrich) or distilled water and autoclaved (1 bar pressure, 121 °C for 20 min) in a SystecV-150 autoclave (Systec, Germany). After the hydrolysis, samples were centrifuged and the supernatant was filtered using 0.2 µm filter. To verify the impact of the duration of autoclaving on the reducing sugar concentration, all samples hydrolyzed with 3% H_2SO_4 were autoclaved once and twice. The samples were then filtered and analyzed.

For determination of reducing sugar, the 3, 5-Dinitrosalicylic acid (DNS) method (Miller 1959) was used with boiling water bath incubation (GP200, Grant, United Kingdom). The absorbance (546 nm) was measured using a Genesys 10S UV–VIS spectrophotometer (Thermo Scientific, United States).

The acid-pretreated materials from spent coffee and husk were neutralized with pure pellets of KOH (VWR International, United States) to pH 5 for fermentation. The baker's yeast (*Saccharomyces cerevisiae)* is commercial yeast distributed by Algist Bruggeman (Belgium) for bread making and other food applications. The final fermentation

was conducted in an Erlenmeyer flask of 5 L with 2L of working volume. The filtered hydrolysate of the coffee waste was not supplemented with nutrients. The baker's yeast was precultured overnight, and the cells were harvested by centrifugation for 10 min at 4000 rpm (Eppendorf 5810 R, Eppendorf AG, Germany). The dry weight of the harvested yeast was measured by drying a known amount of harvested wet yeast in an oven overnight (at about 105 °C) and the difference in mass was calculated. The dry weight of the baker's yeast used in this experiment was 2 g/l. For fermentation of the samples using baker's yeast, the samples were incubated at 30 °C and shaken at 250 rpm for 108 h (Incubator KB8182, Termaks, Norway).

For sugar and ethanol determination, samples were centrifuged at 14,000 rpm for 10 min and the supernatant was filtered using a 0.22 μm filter. The samples were stored at −20 °C prior to analysis. Ethanol and sugar concentrations were measured with an Agilent 1200 series HPLC with a refractive index detector, the column BioRad Aminex HPX-87H (7.8 × 300 mm) was kept at 40 °C. The eluent was 5 mM H_2SO_4 at the flow rate of 0.6 mL/min.

Enzymatic hydrolysis and fermentation using lignocellulosic yeast

The husk and spent coffee were first acid hydrolyzed using 3% (v/v) H_2SO_4 (99%, Sigma Aldrich) and autoclaved one time (1 bar pressure, 121 °C for 20 min) in a SystecV-150 autoclave (Systec, Germany). The slurry was neutralized and the pH adjusted to 6 using pure pellets of KOH (VWR International, United States). The neutralized material was saccharified using 5% w/w (total solid) of cellulases from *Trichoderma reesei* ATCC26921 (NS50013, Novozymes, Denmark) and 0.5% w/w (total solid) of β-glucosidases from *Aspergillus niger* (C6105, Novozymes, Denmark). The saccharification was conducted at 50 °C and 160 rpm for 48 h.

The pH of the hydrolysate was adjusted to 5 using sulfuric acid (99%, Sigma Aldrich) and fermentations with the lignocellulosic yeast *Saccharomyces cerevisiae* GSE16-T18 (Demeke et al. 2013a, b) was carried out in Erlenmeyer flasks with different volumes (300 ml to 5 L) depending on the amount of hydrolysate to be fermented. Incubation was done in an incubator shaker (Innova 4300, Brunswick Scientific, United States) at 30 °C with and 100 rpm. Fermentation was performed for 96 h. Ethanol and sugar concentrations were measured with HPLC like previously mentioned.

Pervaporation

The acid-treated and autoclaved samples were incubated and fermented in 5 l flasks. After fermentation of the samples using the two yeasts (baker's yeast and lignocellulosic yeast) independently, the filtrates were pervaporated using GFT GmbH pervaporating equipment. Permeate was collected every 30 min in a cold trap consisting of a U-glass immersed in liquid nitrogen inside a Dewar flask. At least three permeate samples under steady-state conditions were taken per experiment. The membranes were immersed in the feed solution at least 24 h prior to the experiment and then placed into the membrane test cell. For pervaporation of the filtered samples, an alcohol selective pervaporation membrane (Type POL_AL_M1, PolyAn GmbH, Germany), with a diameter of 58.78 mm, was used. The thickness of the membrane was measured by fowler ip54 caliper and was found to be 0.171 mm. The membrane used is dense. Pervaporation of the fermented samples using baker's yeast (for spent coffee) and lignocellulosic yeast (for both spent coffee and husk) was conducted at 23, 30, 40 and 50 °C.

Results and discussion

Characterization of the coffee waste samples

The analysis of the different coffee waste samples is presented in Table 1. As shown in Table 1, all coffee waste samples were observed to have moisture content lower than 10% and a slightly acidic pH. Similar characteristics of coffee waste are also reported by the studies of Woldesenbet et al. 2014 which reported the coffee pulp juice and mucilage having pH values of 4.75 and 3.67, respectively. Mucilage is a thick, gluey substance which is removed from coffee bean during wet coffee depulping and fermentation processes.

The COD:BOD ratio is frequently used as an indicator of biological degradability and the ratios below 5:1 indicate high digestibility (Woldesenbet et al. 2014). The COD:BOD ratios of most of the coffee waste samples were below 5:1, which indicates good biodegradability. The % volatile solid content of the waste fractions was in the range of 85 to 93, whereas the % ash content ranged from 7 to 15. These results are in agreement with similar study (Woldesenbet et al. 2014), which reported a % volatile solid of 90.2 and a % fixed solid of 9.8 for mucilage. The samples with the highest BOD and highest % volatile solid content were selected and investigated for bio-ethanol production.

Acid hydrolysis of the coffee waste samples

All samples, SS, SC, husk, parchment and DCB were mixed in solid to liquid ratio of 1:10. Before autoclaving, the following observations were made. First, after the

Table 1 Physicochemical characterization of coffee waste samples

Waste fraction	No. of sample	MC (%)	pH	EC (μS/cm)	BOD (g/kg)	COD: BOD	VS (%)	Ash content (%)
SS	3	1.05 ± 0.265	5.4 ± 0.12	917 ± 135	8.61 ± 0.19	4.3 ± 1.03	89 ± 1.1	11.5 ± 1.1
Husk	4	4.70 ± 0.229	4.6 ± 0.10	1164 ± 117	8.55 ± 0.16	5.0 ± 0.90	87 ± 0.9	13.0 ± 1.0
Parchment	8	6.33 ± 0.162	5.6 ± 0.07	365 ± 82	8.42 ± 0.12	2.5 ± 0.63	92 ± 0.7	7.7 ± 0.7
DCB	3	3.23 ± 0.265	5.7 ± 0.12	875 ± 135	9.34 ± 0.19	10.7 ± 1.03	87 ± 1.1	13.2 ± 1.1
SC	3	6.00 ± 0.265	5.7 ± 0.12	748 ± 135	8.86 ± 0.19	1.5 ± 1.03	90 ± 1.1	10.0 ± 1.1
Mixture	3	5.33 ± 0.265	5.1 ± 0.12	923 ± 135	9.08 ± 0.19	2.0 ± 1.03	89 ± 1.1	11.0 ± 1.1
F-test		69.8	19.4	7.7	4.6	11.6	6.5	6.5
P value		0.0000	0.0000	0.0005	0.0073	0.0000	0.0013	0.0013

MC moisture content, *EC* electrical conductivity, *VS* volatile solid, *SS* silver skin, *SC* spent coffee, *DCB* defected coffee bean, *MIXTURE* mix of all of them in equal proportion

addition of distilled water, none of the samples dissolved and they floated on the water surface. However, after addition of 3% (v/v) H_2SO_4, DCB and husk formed a partial precipitation and the other samples (parchment, SS and SC) did not precipitate at all and they remained on top of the water without getting settled in 3% (v/v) H_2SO_4. After autoclaving, all samples hydrolyzed with distilled water or 3% (v/v) H_2SO_4 gave a clear filtrate and clear precipitate. Thus, there is dissolution after autoclaving in both cases. Any sugar that acts as a reducing agent because of the presence of free aldehyde or ketone groups can be defined as a reducing sugar (Loow et al. 2016b). The reducing sugar yield determined by dinitrosalicylic acid (DNS) method of samples hydrolyzed with distilled water or diluted acid is presented in Fig. 2.

A higher amount of reducing sugar was released from the different coffee waste fractions with 3% (v/v) H_2SO_4 compared to distilled water (Fig. 2). Dilute acid hydrolysis effectively solubilizes hemicellulose and alters the biomass structure by interacting with the bonds between the biomass components (Limayem and Ricke 2012). Dilute acid can also catalyze disruption of glucosidic bonds between sugar monomers within lignocellulosic biomass in the hydrolysis step (Aguilar et al. 2002). The mechanism of dilute acid hydrolysis in breaking down polysaccharides into monomers is based on the cleavage of the glycosidic linkages, defined as the ether bond which holds monomeric sugar units together in a polymer chain (Harmsen et al. 2010). Thus, dilute acid application can be extended in duration and strength to encompass both the pretreatment and hydrolysis step, resulting in total hydrolysis of lignocellulosic biomass into fermentable sugar monomers (Rehman et al. 2014). Hence, it is more advantageous to use dilute acid for the hydrolysis so that more reducing sugar can be obtained, which in turn increases the yield of bioethanol (Chovau et al. 2013). The reducing sugar yield was calculated using the method described by Miller (1959). The increase in total reducing sugar content that resulted from the acid hydrolysis is similar to the report of Navia et al. 2011. A higher total reducing sugar yield (85.0%) with 3% (v/v) H_2SO_4 hydrolysis than 56.7% yield with distilled water hydrolysis is also reported (Woldesenbet et al. 2014).

In addition, the results for the reducing sugar yield from the different coffee waste fractions (except for DCB and husk) are also in agreement with other similar experimental results of Urbaneja et al. (1996). They found a reducing sugar yield in the range of 0.65–21.81 g/l after acid hydrolysis of coffee pulp. However, our result is not in agreement with the other study findings of Ayele (2011), who reported that the amount of sugar obtained decreases as the acid concentration increases and reaches a maximum in acid-free (distilled water) hydrolysis. With 3% (v/v) H_2SO_4 hydrolysis, DCB and husk samples produced a higher yield in reducing sugar than spent coffee, parchment and silver skin (Fig. 2). Since coffee husk and spent coffee are available in larger amounts than DCB, this study further continued with the former waste fractions.

Impact of autoclaving frequency on the yield of reducing sugars

The coffee waste samples were autoclaved once or twice to study the impact of the autoclaving frequency on fermentable sugar liberation and the amount of acetic acid produced. The results obtained from the HPLC analysis are presented in Table 2.

Urbaneja et al. (1996) also reported about the concentrations of xylose (0.08–3.23 g/l), glucose (1.30–6.31 g/l) and arabinose (0.23–11.26 g/l) released by acid hydrolysis of coffee pulp. However, the amount of xylose found in this study is greater than the concentration indicated by Urbaneja et al. (1996). This may be due to differences in the type of coffee waste samples investigated. The amount

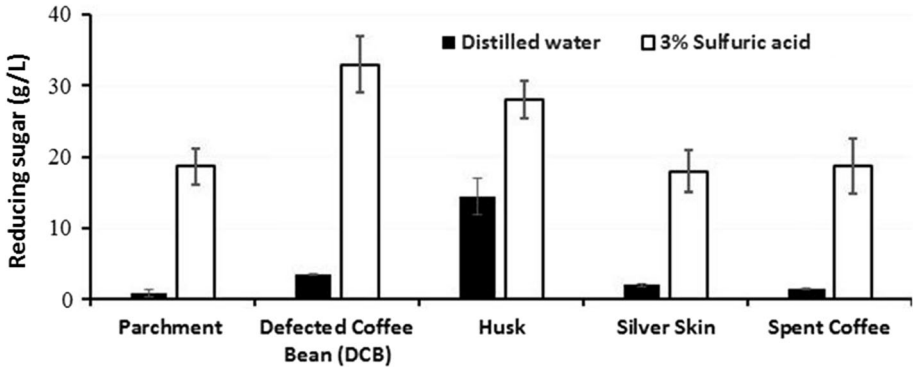


Fig. 2 Reducing sugar of coffee waste fractions pretreated with distilled water or 3% (v/v) H_2SO_4 at 121 °C for 20 min

Table 2 Amount of sugars and acetic acid generated after single or double autoclaving of coffee samples

Coffee sample	Autoclaving frequency	Glucose (g/l)	Xylose (g/l)	Arabinose (g/l)	Acetic acid (g/l)
Silver skin	Once	0.39	7.05	2.51	ND
	Twice	0.96	5.91	2.25	0.10
DCB	Once	1.53	5.20	1.71	ND
	Twice	1.57	4.99	1.77	ND
Parchment	Once	ND	9.41	ND	2.38
	Twice	0.25	12.65	ND	3.15
Spent coffee	Once	6.06	20.24	2.12	ND
	Twice	5.98	23.32	2.67	ND
Husk	Once	6.00	10.86	4.29	1.32
	Twice	5.47	8.74	4.19	1.19
Mixture	Once	1.67	12.41	2.61	ND
	Twice	1.66	12.35	2.60	ND

ND not detected

of reducing sugars decreases when the samples were autoclaved twice, while the amount of acetic acid increases (Table 2).

The acetic acid production is probably due to the deacetylation of the hemicellulose by the intensification of the pretreatment. Thus, it is advisable not to increase the autoclaving frequency because it stimulates the formation of unwanted byproducts (Palmqvist and Hahn-Hägerdal 2000), like acetic acid, which can affect the fermentation process. These compounds also limit efficient utilization of the hydrolysates for bioethanol production by microbial fermentation. In general, the acetic acid concentrations measured in our work (Table 2) are lower than those reported by the study of O'brien et al. (2004), who measured an acetic acid level of 6.2 g/l in corn fiber hydrolysate neutralized by lime.

Fermentation of spent coffee and husk produced by acid hydrolysis with baker's yeast

For this study, first, different conditions using baker's yeast to ferment husk and spent coffee samples were evaluated to select the optimum conditions. Both fractions were fermented for 108 h and samples were taken every 12 h. The optimal ethanol yield was obtained after 24 h of fermentation. The ethanol titers obtained were 4.30 g/l for husk and 7.08 g/l for spent coffee. Similar findings were also reported by (Ayele 2011) with a maximum ethanol concentration of 7.4 g/l obtained in coffee pulp fermentation after 24 h. There was no production of acetic acid during the fermentation of spent coffee but there was production of acetic acid at all stages of fermentation of husk resulting in a final value of 1.15 ± 0.54 g/l. Thus, spent coffee was selected as the best candidate for the further fermentation and pervaporation studies.

Impact of enzymatic hydrolysis on the yield of sugar

Cellulolytic enzymes were used to complement the acid hydrolysis (Table 2), aiming at a higher sugar level by digestion of both cellulose and hemicellulose. To determine the sugar concentration after enzymatic hydrolysis, both spent coffee and husk samples were pretreated with sulfuric acid once and subsequently hydrolyzed with the enzymes. Glucose and xylose concentration was analyzed as a reference. The results are

Table 3 Glucose and xylose concentration after enzymatic hydrolysis of spent coffee and husk concentrations at time zero are for glucose and xylose concentration before enzymatic hydrolysis

Time (h)	Husk		Spent coffee	
	Glucose (g/l)	Xylose (g/l)	Glucose (g/l)	Xylose (g/l)
0	6.0 ± 0.2	3.58 ± 0.03	6.0 ± 0.6	7.48 ± 0.06
12	6.0 ± 0.8	3.75 ± 0.03	7.0 ± 1.5	7.74 ± 0.15
24	10.0 ± 1.1	6.65 ± 0.30	15.5 ± 0.7	14.09 ± 0.73
36	11.3 ± 0.7	6.88 ± 0.06	15.8 ± 0.9	15.05 ± 0.39
48	11.5 ± 0.9	7.37 ± 0.05	16.0 ± 1.0	15.55 ± 0.09

Table 4 Permeate levels obtained after pervaporation of spent coffee fermentations (SCF) with baker's yeast

IC (feed solution) (g/l ethanol)	PT (°C)	PP (mbar)	EPAP (g/l)	TF (kg/h m^2)
7 ± 0.08	23	4 ± 0.5	34.8 ± 1.3	1.05 ± 0.2
	30	3.6 ± 0.1	33.9 ± 0.4	0.88 ± 0.1
	40	4.6 ± 0.6	34.7 ± 2.1	1.28 ± 0.2
	50	5.6 ± 0.9	33.25 ± 0.1	1.56 ± 0.2

IC initial concentration, *PT* pervaporation temperature, *PP* pervaporation pressure, *EPAP* ethanol produced after pervaporation, *TF*,total flux

shown in Table 3. Application of the enzymes resulted in higher sugar levels.

Subsequently, both hydrolysates that were hydrolyzed for 48 h were fermented for 96 h and samples were taken every 12 h. The optimal ethanol yield was obtained after 12 h of fermentation. It was 47.9 g/l for spent coffee and 36.6 g/l for husk. Hence, by using the lignocellulosic yeast GSE16-T18, the bioethanol yield increased. In addition, acetic acid generation was not detected during the fermentation of spent coffee but there was production of acetic acid at all stages of husk fermentation reaching a final value of 1.14 ± 0.28 g/l. The acetic acid is generated by release of acetyl groups from the hemicellulose during the pretreatment of the biomass.

After the optimum ethanol concentration was obtained, the ethanol concentration was found to slightly decrease with time. This might be because the yeasts are shifting to use the ethanol as a source of carbon. During husk fermentation, when the ethanol concentration reached an optimum, 3.56 ± 0.00 g/l xylose was remaining and no glucose was left; while for spent coffee, both glucose and xylose were fully consumed. To secure the fermentation medium from any source of possible contamination, only autoclaved and sterilized samples and equipment were used. Both the husk and spent coffee samples were selected for the pervaporation experiments.

Ethanol pervaporation of the fermented waste fraction

The total ethanol flux through the membrane increased with increasing temperature (Table 4). In this regard, it is reported that increasing the temperature typically produces an increase of the total and individual solute fluxes through the membrane due to the increase in vapor pressure and consequent increase in the driving force (Luis et al. 2013). Chovau et al. (2013) also reported that the total permeate flux significantly increases as the temperature increases.

The feed ethanol solution concentration was 7.00 ± 0.08 g/l (Table 4). In addition, the maximum level of ethanol obtained from the pervaporation of spent coffee using baker's yeast was 34.7 ± 2.1 g/l. Thus, the bioethanol level obtained is upgraded by a factor of 5 due to the pervaporation. The spent coffee samples were also hydrolyzed with the cellulolytic enzymes and fermented with the lignocellulosic yeast GSE16-T18. In this case, the ethanol level was 47.9 ± 0.06 g/l. Finally, the fermented broth was filtered and pervaporated at different temperatures (23, 30, 40 and 50 °C) and the results revealed that the total flux increases with temperature (Table 5).

The feed ethanol solution concentration was 47.9 ± 0.06 g/l. The maximum amount of ethanol obtained by pervaporation was 51.7 ± 7.4 g/l and this was obtained with pervaporation of the sample at room temperature. This shows that a much better ethanol yield from spent coffee samples was obtained when using cellulolytic enzymes (cellulase and β-glucosidase) and lignocellulosic yeast compared to using only baker's yeast.

The total flux also increased with temperature; however, the increment of temperature did not increase the bioethanol yield (Table 6). The feed ethanol solution concentration and the maximum ethanol produced were found to be 36.6 ± 0. 2 g/l and 132.2 ± 40 g/l, respectively, after pervaporation of the sample at room temperature. Hence, we observed that bioethanol production is upgraded by a

Table 5 Permeate levels obtained after pervaporation of spent coffee samples hydrolyzed with cellulolytic enzymes (cellulase and β-glucosidase) and fermented with lignocellulosic yeast GSE16-T18

IC (feed solution) (g/l ethanol)	PT (°C)	PP (mbar)	Acetic acid (g/l)	EPAP (g/l)	TF (kg/h.m^2)
47.9 ± 0.06	23	12.6 ± 0.8	6.7 ± 0.4	51.7 ± 7.4	0.25 ± 0.03
	30	13.3 ± 0.4	7.2 ± 0.6	53.0 ± 4.6	0.37 ± 0.02
	40	14.3 ± 0.8	7.2 ± 0.1	47.5 ± 5.4	0.54 ± 0.02
	50	15.1 ± 0.7	6.7 ± 0.2	43.7 ± 1.6	1.24 ± 0.94

IC initial concentration, *PT* pervaporation temperature, *PP* pervaporation pressure, *EPAP* ethanol produced after pervaporation, *TF* total flux

Table 6 Permeate levels obtained after pervaporation of husk samples hydrolyzed with cellulolytic enzymes (cellulase and β-glucosidase) and fermented with lignocellulosic yeast GSE16-T18

IC (feed solution) (g/l ethanol)	PT (°C)	PP (mbar)	Acetic acid (g/l)	EPAP (g/l)	TF (kg/h.m^2)
36.6 ± 0.02	23	12.8 ± 0.27	14.3 ± 2	132.2 ± 40	0.66 ± 0.30
	30	16.7 ± 2.92	10.5 ± 2	50.5 ± 24	0.56 ± 0.05
	40	18.9 ± 0.85	8.5 ± 0.2	36.4 ± 0.8	0.85 ± 0.07
	50	18.5 ± 0.84	9.1 ± 0.5	37.7 ± 0.1	1.32 ± 0.03

IC initial concentration, *PT* pervaporation temperature, *PP* pervaporation pressure, *EPAP* ethanol produced after pervaporation, *TF* total flux

factor of 3.5 when using pervaporation. Similarly, O'Brien et al. 2004 reported the production of 150–170 g/l ethanol from corn fiber hydrolysate fermentations followed by pervaporation.

As indicated in Table 7, production of ethanol by fermentation and pervaporation of both spent coffee and husk was quite satisfactory in comparison with literature data for other substrates. The ethanol yield obtained after husk hydrolysis with cellulolytic enzymes (cellulase and β-glucosidase), fermentation with lignocellulosic yeast GSE16-T18 and pervaporation resulted in a yield of 132.2 ± 40 g/l, which is similar to the ethanol obtained from corn fiber (150–170 g/l) with the same processes (O'Brien et al. 2004). Ethanol produced after pervaporation was found to be significantly lower when the pervaporation temperature was increased. This is due to the difference in pressure at the permeate side. Since the pressure at the permeate side is very variable between experiments, the driving force for pervaporation of the ethanol also varies quite strongly, which can explain the different concentrations of ethanol in the permeate.

Fermentation media are often complex and may result in membrane fouling. Fouling is defined as a reduction in the rate of permeation with time of membrane operation (Qureshi and Blaschek 1999a). Pervaporation membranes are often sensitive to the fermentation broth components, which are very complicated and consist of microorganisms and fermentation nutrients, by-products and inhibitors (Vane 2005; Yi et al. 2015). These complicated components can affect the separation performance of bioethanol from broths (Yi and Wan 2017). Numerous researchers reported either a positive or negative impact of fermentation by-products and inhibitors on the pervaporation performance using different membrane materials (Aguilar-Valencia et al. 2012; Chen et al. 2014; Fan et al. 2014; Gaykawad et al. 2013; Yi et al. 2015).

Several studies have also reported pervaporation membrane fouling in a fermentation-pervaporation coupled processes (Huang and Meagher 2001; Qureshi and Blaschek 1999a, b; Qureshi et al. 2001). Accordingly, the studies of Liu et al. (2011) reported that membrane fouling was related to adsorption of active cells on the membrane surface, and it could be accelerated by microbial growth and metabolism in the live fermentation broth. However, membrane fouling could be easily removed by a simple water rinse, which properly restored membrane pervaporation performance. Besides, the studies of O'Brien and Craig (1996) also confirmed that periodic cleaning of the membranes improved the consistency of performance of the pervaporation operation and minimized problems due to fouling.

The results from this investigation also demonstrate that coffee husk and spent coffee can be used as an alternative substrate for ethanol production, in comparison to different biomass resources (Barley straw, 10 g/l; Wheat stillage, 11 g/l; sweet sorghum bagasse, 16.2 g/l; corn stover, 16.8 g/l; wheat straw, 18.1; Korean food waste leachate, 24.17 g/L, kitchen waste, 30 g/L and coffee pulp, 7.4 g/L) (Table 7).

Table 7 Comparison of ethanol yields obtained after enzymatic hydrolysis, fermentation and pervaporation of various substrates, as reported in the literature with the results obtained in the present study

Residue	Ethanol concentration (g/l)	References
Corn stalks	5	(Belkacemi et al. 2002)
Anaerobic digested sludge	10	(Bashiri et al. 2016)
Barley straw	10	(Belkacemi et al. 2002)
Wheat stillage	11	(Davis et al. 2005)
Sweet sorghum bagasse	16.2	(Ballesteros et al. 2004)
Corn Stover	16.8	(Öhgren et al. 2007)
Wheat straw	18.1	(Ballesteros et al. 2004)
Korean food waste leachate	24.17	(Le Man et al. 2010)
Kitchen waste	30	(Tang et al. 2008)
Coffee pulp	7.4	(Ayele 2011)
Corn fiber hydrolysate fermentations by pervaporation	150–170	(O'brien et al. 2004)
Spent coffee fermentation with bakery yeast	7 ± 0.08	This study
Spent coffee fermentation with bakery yeast and pervaporation	34.7 ± 2.1	This study
Spent coffee hydrolysis with cellulolytic enzymes and fermentation with lignocellulosic yeast GSE16-T18	47.9 ± 0.06	This study
Spent coffee hydrolysis with cellulolytic enzymes and fermentation with lignocellulosic yeast GSE16-T18 and then pervaporation	51.7 ± 7.4	This study
Husk fermentation with bakery yeast	4.3 ± 0.03 g/l	This study
Husk hydrolysis with cellulolytic enzymes and fermentation with lignocellulosic yeast GSE16-T18	36.6 ± 0. 02	This study
Husk hydrolysis with cellulolytic enzymes and fermentation with lignocellulosic yeast GSE16-T18 and then pervaporation	132.2 ± 40	This study

Conclusion

The present study describes the bioethanol yield from different coffee waste fractions obtained by fermentation with *Saccharomyces cerevisiae* baker's and lignocellulosic yeasts, followed by product purification by an alcohol selective pervaporation membrane. No earlier work has reported bioethanol production from coffee waste fractions by pervaporation for purification of the fermented broth. The results of the study revealed that pervaporation resulted in a bioethanol yield of 132.2 ± 40 g/l from coffee husk at the optimum conditions. This is promising for future studies in bioethanol production and pervaporation technology. The utilization of coffee waste fractions for bioethanol production is a sustainable and ecofriendly approach for renewable biofuel production. The results from this investigation also demonstrate that coffee husk and spent coffee can be used as an alternative substrate for ethanol production, in comparison to different biomass resources. This result is very promising and could be improved further by using distillation and hydrophilic membranes for pervaporation. Further research is also needed to examine the economic viability of the process.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Abbreviation

HPLC	High-performance liquid chromatography
MC	Moisture content
EC	Electrical conductivity
VS	Volatile solid
SS	Silver skin
SC	Spent coffee
DCB	Defected coffee bean
IC	Initial concentration
PT	Pervaporation temperature
PP	Pervaporation pressure
EPAP	Ethanol produced after pervaporation

TF Total flux
BOD Biological oxygen demand
COD Chemical oxygen demand

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