Optimization of thermo-chemical hydrolysis of kitchen wastes

Aikaterini Ioannis Vavouraki, Evangelos Michael Angelis, Michael Kornaros *

Chemical Engineering Department, University of Patras, 1 Karatheodori Str., University Campus, 26500 Patras, Greece

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ABSTRACT

Municipal Solid Wastes (MSWs) in Greece consist mainly of fermentable organic material such as food scraps (~50%) and paper residuals (~20%). The aim of this work was to study the thermo-chemical pretreatment of the kitchen waste (KW) fraction of MSW focusing on biotechnological exploitation of pretreated wastes for biofuel production. A representative sample of municipal food residues was derived by combining weighted amounts of each individual type of residue recognized in daily samples obtained from the University of Patras' students restaurant located at the Students Residence Hall (Greece). Chemical pretreatment experiments of the representative KW sample were performed using several types of chemical solutions (i.e. H_2SO_4, HCl, NaOH, H_2SO_3) of different solute concentration (0.7%, 1.5%, 3%) at three temperatures (50, 75, 120 °C) and a range of residence times (30–120 min). Optimized results proved that chemical pretreatment of KW, using either 1.12% HCl for 94 min or 1.17% HCl for 86 min (at 100 °C), increased soluble sugars concentration by 120% compared to untreated KW. The increase of soluble sugars was mainly attributed to the mono-sugars glucose and fructose.

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1. Introduction

The progressive use of biofuels for transportation strongly affects climate change, depletion of fossil fuel reserves and diminishing dependence on imported fuels (EC Directive, 2003). This leads to international, national and regional level to focus on alternative energy sources. The European Commission has proposed indicative targets for 10% biofuels in transportation fuels by 2020 (European Commission, 2008). Biofuels and most specifically bioethanol may be produced biotechnologically from energy crops, such as sugar beet and rapeseed (first-generation biofuels) as well as by utilizing ligno-cellulosic sources (second-generation biofuels), such as crop residues, grass, sawdust, wood chips and Municipal Solid Wastes (MSWs) via new technologies of biomass bioconvertion (Wyman, 1994; Sánchez and Cardona, 2008; Wang et al., 2008). Moreover, the European legislative framework (e.g. EC Landfill Directive, 1999) is strongly promoting the minimum use of landfills in European countries. The EU Directive requires Member States to reduce the amount of biodegradable municipal wastes going to landfills to 75% of 1995 levels by 16 July 2006, to 50% by 16 July 2009 and to 35% by 16 July 2016. Indeed, the implementation of European legislation reduced the share of landfilling in the EU-27 from 68% in 1995 to 38% in 2008, with the landfill rate in Greece being 81% in 2008 (Eurostat, 2011). Municipal solid wastes in Greece consist mainly of fermentable organic material (~50%) and paper residuals (~20%) (Bosdogianni, 2007).

In the aim to divert as much wastes from landfills as possible, the kitchen waste (KW) fraction of MSW has been recognized as an alternative source for the production of bio-ethanol (Anselmo Filho and Badr, 2004; Mtui and Nakamura, 2005). KW may alternatively be directly incinerated with other combustible wastes and residual ash will then be disposed of in landfills. However, incineration is commonly an expensive MSW management technique. The fact, also, that KW contains high levels of moisture may lead to the production of dioxins when burned together with other wastes of low humidity and high calorific value. Anaerobic digestion process (Khalid et al., 2011) and, even more, composting (Chang and Hsu, 2008) are proposed as attractive methods of KW management. Two-phase anaerobic digestion may convert waste into biofuels, primarily to hydrogen and then into methane. However, imbalances in feedstock supplying and the high-cost demand for constructing anaerobic digesters have prevented the widespread adoption of such alternative approaches.

Organic wastes rich in carbohydrates, such as KW residuals, can relatively easily be converted into valuable products (i.e. lactic acid, bioethanol). Several studies have been reported on the production of lactic acid from food wastes, with periodic or continuous monitoring of pH (Sakai and Ezaki, 2006; Sakai and Yamanami, 2006; Ohkouchi and Inoue, 2007), but limited studies have reported on bioethanol production from food waste (Ozmihci and Kargi, 2007; Wang et al., 2008; Yan et al., 2011). Anaerobic digestion of KW resulted into the production of biohydrogen and accumulation of lactic acid (Wang et al., 2001; Han and Shin, 2004). Open fermentation has several advantages compared with the conventional sterile and closed one, such as to prevent Mail-

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* Corresponding author. Tel.: +30 2610 997418; fax: +30 2610 993070.
E-mail address: kornaros@chemeng.upatras.gr (M. Kornaros).

lard reactions which reduce fermentable substrates, like sugars and amino acids, and increase the production of furfural compounds, which inhibit bacterial growth (Sakai and Yamanami, 2006; Akao and Tsuno, 2007). Research on the production of ethanol from starch-full material by fermentation has been successfully introduced (Krishnan et al., 2000). A sequential process of hydrolysis and fermentation (SHF) for bioethanol production includes a series of steps such as liquefaction, saccharification and fermentation. Implementation of a one stage by simultaneous saccharification and fermentation (SSF) has been proposed in order to reduce total fermentation time and investment construction cost. A large number of studies have been focused on the SSF process aiming at utilization of cellulosic biomass and industrial wastes of paper-type wastes and wasted crops (Philippidis et al., 1993; Kadar et al., 2004; Kim and Dale, 2004). However, little attention has been devoted to the thermo-chemical pretreatment of the organic fraction of KW prior to fermentation for the production of bioethanol or other biofuels (Wang et al., 2008).

KW residues are composed mainly of carbohydrate polymers (starch, cellulose, hemicellulose), lignin, other organics (proteins, lipids, acids, etc.) and a remaining, smaller inorganic part (ash). Hydrolysis of a cellulosic material, such as KW, may improve the rate of subsequent enzymatic hydrolysis and increase the yields of fermentable sugars from cellulose and/or hemicelluloses. Lignocellulosic biomass and in particular difficult-to-degrade hemicellulosic sugars can be also bioconverted into value-added compounds other than bioethanol (Mosier et al., 2005; Carvalheiro et al., 2008). Hydrolysis of starch components, as those contained in KW, may result into the breakage of glycoside bonds of polysaccharides emerging oligosaccharides $(3 < n < 10)$ and/or maltodextrins $(2 < n < 20)$ and monosaccharides, which are amenable to fermentation into valuable products, e.g. gaseous and liquid biofuels. Chemical hydrolysis of starch in combination with ultrasonic and steam pretreatment may result into degradation of glycosidic bonds in starch (Losev et al., 2003; Palmarola-Adrados et al., 2004). Starch-full feedstocks of fresh and processed vegetables contain considerable amount of soluble sugars released in the hydrolysates for bioethanol production (del Campo et al., 2006). In a recent review, Sun and Cheng (2002) provided an extensive research on conversion of lignocellulosic materials to ethanol and indicated that optimization of saccharification and fermentation process is possible by optimum rate of cellulose hydrolysis and cellulase enzyme loading for an applicable economic ethanol production system.

Different technologies for producing fuel ethanol from sucrose-containing feedstocks (mainly sugarcane i.e. in Brazil), starchy materials and lignocellulosic biomass are described along with the major research trends for improving them. However, most of these processes are too slow limiting their application at industrial level (recent review by Sánchez and Cardona (2008)). The techno-economic performance of various hydrolysis-fermentation technologies to produce ethanol from lignocellulosic biomass has been analyzed and seemed promising (Hamelinck et al., 2005). The processing of starch-containing food wastes by adding malt to the pulverized feedstock has been patented (Chung and Nam, 2002). Despite achieving high-sugar yields by degrading cellulosic and starchy biomass with low acid loadings, equipment configurations and the high ratio of water to solids employed in flow-through systems require significant energy for pretreatment and product recovery. Large scale application systems of lignocellulosic feedstock hydrolysis have not been yet demonstrated widely (Mosier et al., 2005). However, first attempts are under way, such as Blue-Fire's Technology (2012) in which the cellulosic fraction of post-sorted MSW is hydrolyzed using concentrated acid, and then the remaining acid–sugar solution is separated into its acid and sugar

components by means of chromatographic separation and sugars are fermented to ethanol.

The aim of this study was to perform chemical hydrolysis experiments using a representative sample of KW obtained from the Students Residence Hall of University of Patras (Greece). To the best of our knowledge there is a lack of optimization studies on the acidic pretreatment of such material. Therefore, after a preliminary screening for assessing the most promising type of chemical to be used for KW pretreatment, our goal was to use a genetic algorithm (GA) for multi-objective experimental optimization in order to estimate the optimum values of the most critical parameters (acid concentration, temperature and residence time) in our hydrolytic experiments in an attempt to boost degradation of such a starch-full material, like KW, to fermentable soluble sugars.

2. Materials and methods

The representative sample of kitchen waste (KW) used in the present study was collected from the Students' restaurant at the Students Centre of the National Youth Foundation, which is located at the University of Patras (Greece). KW collection lasted for a period of 1 week and included two daily samples (morning and noon). KW consisted of 50% raw (46.8% vegetables, 3.2% minced meat) and 15.6% cooked food (4.2% meat, 0.9% fish, 2.1% legumes, 3.7% potatoes, 1.9% rice and 2.8% others), 14.5% fruits, 9.7% salads, 8% bread and 2.2% dessert (on a wet-weight basis). For the characterization and testing of chemical pretreatment of KW, the wet sample (4 kg in total) was mixed and homogenized using laboratory cutting equipment (Sorvall) and then stored and kept frozen at $-20\ ^{\circ}C$, during the whole experimentation period, in order to maintain constant characteristics. For both the characterization of sample and the pretreatment experiments 30–50 g of homogenized wet sample were dried at 55 °C for 24 h or more, until constant weight, and then pulverized manually (final particle size less than 1 mm) in order to obtain homogenized and representative dry material for testing.

The physicochemical analysis of KW included determination of key parameters such as moisture, residual ash, total and volatile solids, total and soluble sugars, oil and grease, total nitrogen and phosphorus (APHA, 1995). Additionally, starch analysis was performed according to the total starch assay procedure (amyloglucosidase/a-amylase method, Megazyme AOAC Method 996.11, AACC Method 76.13). For the determination of sugars, before and after chemical pretreatment, a colored sugar derivative was produced through the addition of L-tryptophan, sulfuric and boric acid, which was subsequently measured colorimetrically at 520 nm (Joseffson, 1983). Determination of structural carbohydrates in KW included cellulose and hemicellulose content analysis. Cellulose was hydrolyzed with acetic-nitric acid reagent, whereas isolation of hemicellulose was achieved after a multi-step process (Sloneker, 1971; Myhre and Smith, 1960). Lignin of dried extracted material was determined using sulfuric acid (12 M for 1 h at 30 °C; 1 M for 3 h at 100 °C) after a two-step hydrolysis (Panagiotopoulos et al., 2010). Values of characterization and sugar yields derived from KW pretreatment were means and standard deviations were estimated by conducing three replicates per analysis.

Monosugars derived from KW acid hydrolysis pretreatment were analyzed by HPLC (Agilent Technologies 1200 series) using an Evaporative Light Scattering Detector (ELSD). A separation column (Phenomenex, Rezex ROA-Organic Acid 300×7.8 mm, I.D., 8 µm) and a guard pre-column (SecurityGuard™ Carbo-H+, 50×7.8 mm I.D., 8 µm cartridges) were used at adjusted constant column temperature (60 °C). An aqueous mobile phase of H_2O (18 MΩ cm) was used at a flow rate of 0.6 mL/min. The temperature of the heated drift tube was 60 °C at nitrogen pressure