Chapter 26
Comparison of Acid and Alkaline Pretreatment Methods for the Bioethanol Production from Kitchen Waste



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26.1 Introduction

Pretreatment methods can be categorized as mechanical, thermal, chemical, biological, or a combination of these methods. Among the widely reported pretreatment methods tested at the lab scale, only a few mechanical, thermal, and thermochemical methods have been successfully applied at full scale [4].

Biomass is a renewable resource, which causes problems when it is not used. The challenge, therefore, is to convert biomass into a resource for energy and other productive uses. There are advantages in the use of biomass. Biomass is a renewable resource and has a steady and abundant supply, especially those biomass resources that are by-products of agricultural activity. Biomass use is carbon neutral, can displace fossil fuels, and helps reduce greenhouse gas (GHG) emissions, while closing the carbon cycle loop. As the debate on food versus fuel intensifies, biomass can provide added income for farmers without compromising the production of main food and even nonfood crops [9].

Kitchen waste, which is a renewable biomass, is one of the major components of municipal solid waste, which mainly includes leftover food and vegetable residue waste generated from the kitchens at various places of food preparation such as restaurants, cafes, hospitals, hotels, canteens, jails, and picnic spots, as well as from different food-processing industries. It is highly biodegradable, which has been found to pose pollution problems during its disposal and treatment. Its biodegradation is the main source of decay/odor and leachate during collection and transportation. It is not suitable for landfilling and incineration, because of its rapid

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putrescibility, moisture content, and low heat value. Moreover, these processes do not accomplish the dual goals of waste reduction and energy production. Furthermore, the valuable energy contained in organic waste is lost to the energy cycle [9].

Many technologies have been developed recently—including physical, chemical, and biological pretreatments—in order to treat biomass stock. Every treatment has different effects on the subsequent processing and the yield of the products. Pretreatment with acid such as sulfuric acid (H_2SO_4) has been commercially used to treat biomass such as switchgrass, corn stover, and spruce (softwood). Other acids such as hydrochloric acid (HCl), phosphoric acid (H_3PO_4), and nitric acid (HNO_3) can also be applied in a pretreatment process to remove hemicelluloses [7].

This study reviews pretreatment techniques that are thermal, chemical, or a combination of the two, to enhance the production of fermentable sugars. The effects of acid and alkaline pretreatment methods are discussed independently and in thermal combinations. Pretreatment methods are compared in terms of their efficiency in production of reducing sugars. On the basis of the comparison, thermal pretreatment at low temperatures (<110 °C) and HCl and sodium hydroxide (NaOH) methods result in a more cost-effective process performance than other pretreatment methods.

26.2 Materials and Methods

26.2.1 Kitchen Waste Sample Preparation

The kitchen waste (KW) sample was collected from the students' cafeteria at the Köseköy Vocational School, Kocaeli University. Plastics, glasses, tissues, and other inorganic materials were separated out. The remaining organic fractions (consisting of rice, meats, and vegetables) were ground with water at a 1:1 volume ratio, using a commercial blender (Waring, Torrington, CT, USA) to ensure liquidity of the sample. The samples were stored at −20 °C for a maximum of a month prior to hydrolysis to prevent the degradation of organic matter and formation of organic acids. The ground sample was dried at 55 °C until it was a fixed mass. Then, the waste sample was screened to obtain a particle size of <2 mm to be used for the prehydrolysis treatment. The flow diagram for saccharification of kitchen waste is shown in Fig. 26.1.

Various methods of prehydrolysis pretreatment were investigated, including different chemical pretreatments combined with steam and enzyme treatment, and various combinations of chemicals coupled with microwave treatment. Additionally, the effects of H_2SO_4, HCl, and NaOH combined with enzyme/steam treatment (in an autoclave) were investigated in this research project [13]. However, only the results of pretreatment with HCl and NaOH at different concentrations, at different temperatures, and for different durations are described in this chapter.

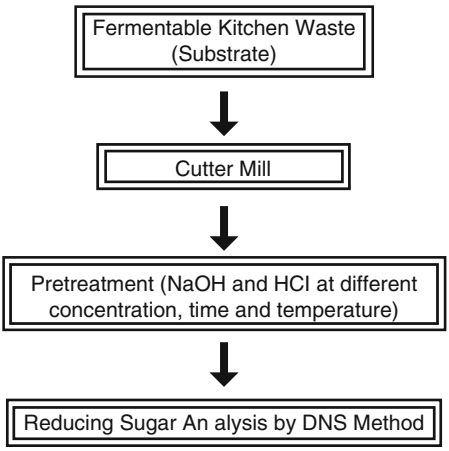


Fig. 26.1 Pretreatment of fermentable kitchen waste

26.2.2 Acid and Alkaline Pretreatments

26.2.2.1 Acid Hydrolysis

The kitchen waste sample was soaked in HCl at different concentrations of 0–5% at a solid-to-liquid ratio of 10 g in 100 mL. After pretreatment for increasing durations and at increasing temperatures, both raw and treated kitchen waste were analyzed. The reducing sugar concentration was assayed by the dinitrosalicylic acid (DNS) method [8]. The maximized parameter in this study was set to be the amount of soluble sugars. Three replicates were done for each experiment.

26.2.2.2 Alkaline Hydrolysis

The kitchen waste sample was soaked in NaOH at different concentrations of 0–5% at a solid-to-liquid ratio of 10 g in 100 mL. After pretreatment for increasing durations and at increasing temperatures, both raw and treated kitchen waste were analyzed. The reducing sugar concentration was assayed by the DNS method [8]. The maximized parameter in this study was set to be the amount of soluble sugars. Three replicates were done for each experiment.

26.2.3 Analytic Methods

The physicochemical analysis of kitchen waste included determination of pH, total solids (TS) and total volatile solids (TVS), moisture, ash, and total carbohydrates. The analyses were based on the standard method [3]. Moisture and ash were

determined on the basis of the standard method [1, 2]. The remaining percentage was assumed to be the total carbohydrate content [10]. The total carbohydrate amount was determined according to the method described by Dubois et al. [5].

26.2.4 Effect of Solid Loading on Hydrolysis Performance

In order to test the effect of solid loading on hydrolysis performance, the best conditions of the pretreatment hydrolysis method in this work were tested with different KW loadings: 0.5%, 1%, and 2%. The reducing sugar concentration was assayed by the DNS method after each experiment [8]. Three replicates were done for each experiment.

26.3 Results and Discussion

Prior to pretreatment of kitchen waste, a detailed physicochemical characterization was performed. The main characteristics of the kitchen waste are listed in Table 26.1.

The main characteristic of the sample was its high content of carbohydrates (>50% of the total composition of the sample) because the kitchen waste was taken from cafeterias. Thus, this waste was suitable for production of ethanol and other biofuels. Comparable compositional analyses have previously been reported by Vavouraki et al. [12] and Thembehurkar and Mhaisalkar [9]. In particular, their analyses of volatile solids (VS) were in agreement with our measurements, whereas our total solid value was quite a lot higher than their values. A similar total KW solid value was also reported by Uncu and Çekmecelioğlu [10]. The chemical pretreatment of the substrate was aimed at increasing the content of soluble sugars in the sample in order to facilitate its subsequent biochemical conversion into

Table 26.1 Characteristics of fermentable food waste used in this study

Parameter	Value[a] (%) [w/w]
Total solids	35.02
Total volatile solids[b]	97.00
Moisture	58.18
pH	6.50
Ash	5.20
Total sugars[c]	67.20
Soluble sugars[c]	32.35

[a]Results for three replicates
[b]Composition of food waste per gram of dry mass. The percentages of total and soluble sugars correspond to the equivalent grams of glucose per 100 g of kitchen waste dry mass
[c]The percentages of total and soluble sugars correspond to the equivalent grams of glucose per 100 g of kitchen waste dry mass

Table 26.2 Total soluble sugar yields after pretreatment of kitchen wastes with increasing NaOH concentrations, temperatures, and durations

	Soluble sugar yield (mg glucose/g dry sample)					
	30 °C			60 °C		
NaOH concentration	30 min	60 min	90 min	30 min	60 min	90 min
0%	153.16	–	145.04	36.01	–	153.05
1%	205.20	218.02	244.12	115.30	48.62	154.85
2%	180.16	162.14	360.32	72.06	68.43	165.65
3%	216.19	261.23	414.35	61.26	61.26	174.66
4%	126.11	234.21	288.25	57.62	42.31	151.25
5%	144.13	162.14	284.65	46.82	39.61	169.25

ethanol. Different concentrations of chemical solutions (HCl and NaOH) were tested at different temperatures and for different durations of contact.

In this study the best results were obtained with HCl pretreatment methods. Acid pretreatment at 90 °C resulted in high concentrations of soluble sugars. In particular, chemical pretreatment with 1% HCl for 90 min at 60 °C resulted in a yield of 638.24 mg of carbohydrates per gram of dry sample, which was very close to the total sample content of carbohydrates (672 mg of carbohydrates per gram of dry KW). When pretreatment is conducted with a higher percentage of acids at an elevated temperature (>100 °C), it may lead to negative effects on the sugar content of samples. This is due to the formation of sugar degradation compounds such as furfural and 5-hydroxymethyl furfural (5-HMF) [7, 11]. Undesirable formation of sugar degradation compounds such as furfural, 5-HMF, and other compounds was avoided by applying mild acid hydrolysis conditions (<100 °C); therefore, measurement of those by-products was omitted in this study [6, 11]. When the glucose recovery from the dry kitchen wastes was evaluated, the best pretreatment method to obtain maximum glucose generation was the HCl pretreatment method, but those findings are not detailed in this chapter; they have been submitted for publication elsewhere as an original research article.

Besides the HCl pretreatment, which yielded 672 mg of carbohydrates per gram of dry KW, the second best results were obtained with 3% NaOH pretreatment, yielding 414.35 mg of carbohydrates per gram of dry sample) (Table 26.2, Figs. 26.2 and 26.3). The effect of the NaOH concentration on the glucose yield in terms of milligrams of glucose per gram of dry kitchen waste sample is shown in Table 26.2. The highest glucose yield of 414.35 mg of carbohydrates per gram of dry sample was achieved after treatment with 3% NaOH at 30 °C for 90 min (Fig. 26.2). This is much more glucose than that released by 3% NaOH treatment at 60 °C for 90 min (174.66 mg of carbohydrates per gram of dry sample (Fig. 26.3).

Additionally, detailed information on the soluble sugars obtained, in terms of glucose recovery percentages, from NaOH pretreatments for 30-, 60-, and 90-min durations are presented in Table 26.3 and Fig. 26.4.

On the other hand, kitchen waste subjected to pretreatment with 2% H_2SO_4 was found to have the lowest glucose recovery, with a value of 14.89% (data not shown).

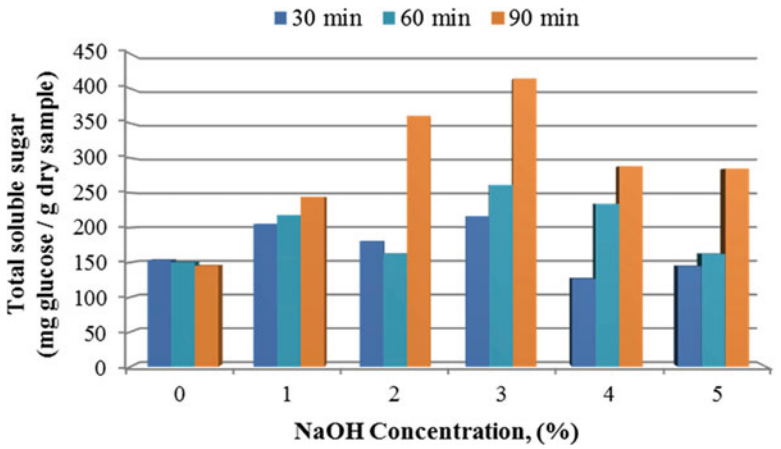


Fig. 26.2 Glucose yield from kitchen waste after NaOH pretreatment at 30 °C

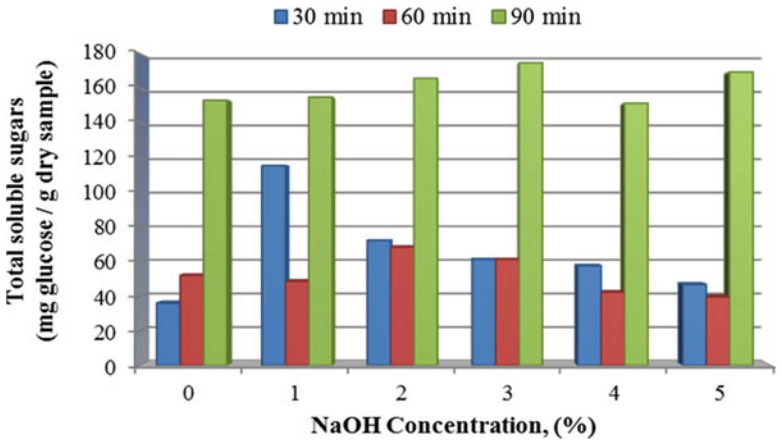


Fig. 26.3 Glucose yield from kitchen waste after NaOH pretreatment at 60 °C

Table 26.3 Glucose recovery from kitchen waste after pretreatment with increasing NaOH concentrations and durations

	Glucose recovery (%)		
NaOH concentration	30 min	60 min	90 min
0%	22.79	22.75	21.58
1%	30.53	32.43	36.33
2%	26.80	24.12	53.62
3%	32.16	38.86	61.66
4%	18.76	34.84	42.89
5%	21.42	24.12	42.35

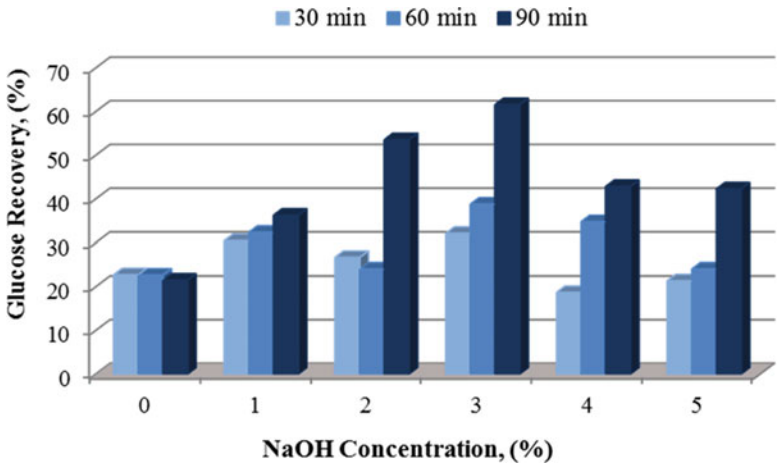


Fig. 26.4 Glucose recovery (%) from kitchen waste after pretreatment at 30 °C with increasing NaOH concentrations and durations

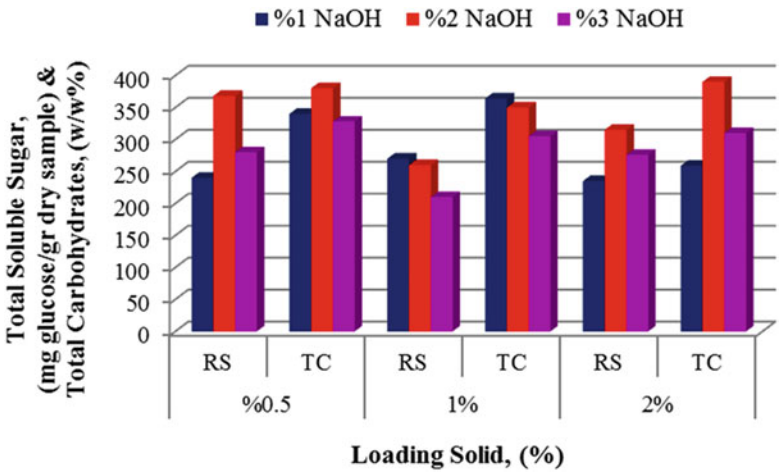


Fig. 26.5 Effects of solid material loading (0.5%, 1%, and 2%) on hydrolysis performance of kitchen waste at 100 °C with 120-min incubation and pretreatment with increasing NaOH concentrations. RS reducing sugars, TC total carbohydrates

In order to test the effect of solid loading on hydrolysis performance, the conditions of the pretreatment hydrolysis methods in this work were tested with different KW loadings: 0.5%, 1%, and 2%. The best result was achieved with a 2% solid loading at 100 °C after 120-min incubation in the presence of 2% NaOH. The effect of solid loading on hydrolysis performance of kitchen waste in the presence of NaOH at 100 °C after 120-min incubation is shown in Fig. 26.5 and that in the presence of HCl at 100 °C after 120-min incubation is shown in Fig. 26.6.

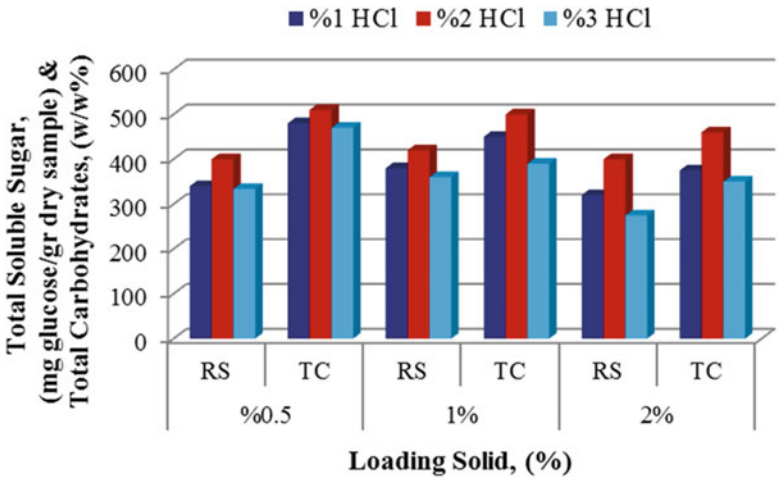


Fig. 26.6 Effects of solid material loading (0.5%, 1%, and 2%) on hydrolysis performance of kitchen waste at 100 °C with 120-min incubation and pretreatment with increasing HCl concentrations. RS reducing sugars, TC total carbohydrates

Table 26.4 Effects of solid loading on reducing sugar (RS) and total carbohydrate (TC) content

	RS and TC content (%)					
	0.5% solid loading		1.0% solid loading		2.0% solid loading	
NaOH concentration	RS	TC	RS	TC	RS	TC
1%	240	340	270	364	235	259
2%	368	380	260	350	315	390
3%	280	328	210	305	276	310

The effect of solid loading on total carbohydrate solubilization into fermentable sugars was observed using the acid and alkaline conditions described in this chapter. When half of the solid loading was tested (i.e., 0.5%), no significant increase was observed, whereas the total carbohydrate and soluble sugar yields remained unaffected (Table 26.4).

26.4 Conclusions

Different pretreatment methods for kitchen waste have been described and widely studied to improve ethanol production processes. Among the different methods, chemical, thermochemical, and enzymatic methods, and combinations of them, are currently the most effective methods and the most promising technologies for industrial applications. Combinations of different pretreatments have been also considered and might be interesting to obtain optimal fractionation of the different components and achieve very high yields.

This study investigated the influence of single and combined pretreatments by acid and alkaline hydrolysis of kitchen waste on fermentable sugar production. The optimum experimental conditions for single pretreatment were 1% HCl incubation for 90 min at 60 °C, which produced 638.24 mg of carbohydrates per gram of dry sample fermentable sugars, and 3% NaOH pretreatment for 90 min at 30 °C, which produced 414.35 mg of carbohydrates per gram of dry sample fermentable sugars and 61.66% glucose recovery. The worst pretreatment method was H_2SO_4 pretreatment, which had the lowest glucose recovery (14.89%). These results indicated that the NaOH pretreatment method can be used for glucose generation in a saccharification process.

All pretreatment and hydrolysis techniques used for KW are of great importance for bioconversion of KW to bioproducts. Thus, optimization of hydrolysis techniques may result in both environmental and economic benefits. Hence, this study investigated the impact of acid and alkaline chemical pretreatment methods on the hydrolysis of KW to glucose and other fermentable sugars used in bioethanol production.

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Nomenclature

5-HMF	5-Hydroxymethyl furfural
AACC	American Association of Clinical Chemistry
DNS	Dinitrosalicylic acid
GHG	Greenhouse gas
H_3PO_4	Phosphoric acid
HCl	Hydrochloric acid
HNO_3	Nitric acid
H_2SO_4	Sulfuric acid
KW	Kitchen waste
NaOH	Sodium hydroxide
RS	Reducing sugars
TC	Total carbohydrates
TS	Total solids
TVS	Total volatile solids
VS	Volatile solids

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