MODELING OF PRETREATMENT AND ACIDOGENIC FERMENTATION OF THE ORGANIC FRACTION OF MUNICIPAL SOLID WASTES

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ABSTRACT

The organic fraction of municipal solid waste represents a potential feedstock to be treated through biorefining. However, the process feasibility strongly depends on the effectiveness of a chemical pretreatment. Consequently, experimentation aimed at choosing the optimal type of reagent (alkali or acids) and optimal operating conditions was carried out. The best results were obtained using NaOH at room temperature. Solubilization data are in good agreement with a kinetics based on two competing reactions. Simulation of the overall process (pretreatment and acidogenic fermentation) taking place in two CFSTR reactors shows that an optimum ratio exists between the hydraulic residence times of the two stages of the process.

KEYWORDS

Municipal solid wastes; acidogenic fermentation; alkaline pretreatment.

INTRODUCTION AND AIMS

Shortage of fossil fuels has stimulated interest in the production of liquid fuels and valuable chemicals from ubiquitous and renewable feedstocks by biotechnological processes.

In this context, biorefining (Levy *et al.*, 1981a) appears to be one of the most attractive options; this process is based on the acidogenic fermentation of feedstock, followed by extraction of the volatile fatty acids (VFAs) from the fermented broth and their esterification (or electrolytic oxidation) to obtain valuable chemicals (e.g. octane-improving additives for gasoline).

The organic fraction of municipal solid wastes (MSWOF) represents a potential feedstock to be treated through biorefining; however, process feasibility depends on the possibility that cellulose and hemicellulose, which are present in the feedstock in high percentages (sometimes higher than 50% on dry basis), can be effectively a substrate suitable for microorganisms during acidogenic fermentation. In this regard, hydrolytic enzymes have difficulty penetrating the substrates owing to various factors (e.g. the crystallinity and poor surface extension of cellulose, the presence of a lignocellulosic shield around fibrous cellulose).

Hence, the ability of MSWOF to be suitable feed for fermentation seems strongly dependent on the effectiveness of a pretreatment of the substrate.

A comparative survey of the pretreatment alternatives (Langton, 1981; Tsao, 1984) shows that chemical

pretreatment seems preferable to techniques based on mechanical, physical or biological means.

In a previous work (Beccari *et al.*, 1989) batch tests of acidogenic fermentation of MSWOF were carried out both with and without mild alkaline pretreatment. Experimentation has shown that pretreatment can double the yield of bioconversion to VFAs compared with the rather low value (<20%) obtained without pretreatment. However, pretreatment operating conditions were not optimized through specific research, but chosen according to experiments performed on substrates to some extent resembling the MSWOF (Datta, 1981a; Rajan *et al.*, 1989).

Consequently, a laboratory scale experiment was carried out as a first step in order to choose the type of reagents (alkali or acids) and the optimal operating conditions for chemical pretreatment; pretreatment efficiency was evaluated both through its solubilization action and its fermentation yield.

Experimentation on pretreatment was completed by runs aimed at setting up the process kinetics. The kinetic behaviour of the acidogenic fermentation was known from a previous work. By combining the kinetic descriptions of the two stages (pretreatment and acidogenic fermentation), the overall process taking place in two CFSTR reactors (with and without biomass recycle in the bioreactor, with and without an intermediate liquid/solid separation) was simulated.

METHODS

The waste (MSWOF) came from the municipal collection plant of a small town (about 50,000 inhabitants). In this plant glass and metals are separated by sieving and the residual waste is aerobically stabilized for 24 h in a swirling drum. The waste was dried at 105 °C in the laboratory and accurately chopped and sieved (Beckers *et al.*, 1986) after hand elimination of some residual glass and metals. All experimentation was performed on aliquots of the same well mixed stock of MSWOF.

Analysis of lignocellulosic contents was performed by a fractionation method (Datta, 1981b): the sample was treated in successive steps with boiling water, boiling 0.5 N H_2SO_4 and boiling 96% H_2SO_4 and weight loss after each step gave the fraction of water soluble compounds, hemicellulose, cellulose and residual solids (comprehensive of lignin). In spite of mixing, MSWOF composition changed to some extent from one aliquot to another: the four fractions ranged from 15.0 to 30.0 % w/w, from 2.4 to 17.1 % w/w, from 31.6 to 40.0 % w/w, and from 38.0 to 45.6 % w/w, respectively. VSS ranged from 60.6 to 79.1 % w/w.

Solubilization tests at 20 °C were performed in 250 mL magnetically stirred bottles. A ten-minute continuous flushing of nitrogen gas preceded the start up of solubilization tests in order to avoid the dissolved oxygen oxidizing soluble organic matter.

After preliminary tests for all reagents, 5 days were sufficient for exerting most solubilization action. From previous research (Beccari *et al.*, 1989) MSWOF was 5g per 80 mL of solution; all reagents were made 1% w/v. At this time, samples were collected and centrifuged for a period of 10 minutes at 3784 x g. The supernatant was filtered on 0.45 μm filters and filtrate COD determined by the dichromate titrimetric method (IRSA, 1985). pH was also measured by the combined glass electrode method. In kinetic tests, samples were collected at selected time intervals from 1 to 120 hours. COD of the soluble fraction at the initial time was difficult to measure because of the dryness of the MSWOF. The value of soluble COD after one hour's treatment in distilled water was then considered.

The procedure for solubilization tests at boiling point (in the range 101-103 °C) was almost the same. In this case samples were taken under continuous nitrogen flushing and cold water reflux and 1 hour resulted to be sufficient for most of the solubilization action to be exerted.

The biotreatability tests were performed in 200 mL assay bottles immersed in thermostatic water baths and periodically stirred; incubation temperature was 25 °C. Assay bottles were filled with seed inoculum consisting of anaerobically digested sewage sludge (non acclimatized), and with the substrate diluted in distilled water in order to obtain the desired final COD concentration. Tests were conducted at a substrate concentration of 10 gCOD/L (the COD added with the inoculum being 10 % of the COD added with the substrate). A glucose solution was always used as reference substrate in testing inoculum activity. Anaerobic conditions during the filling operation were maintained by continuously flushing with nitrogen gas. No nutrient solution was added. The initial pH ranged from 6 to 7, and tests were performed in the presence of the sodium salt of bromoethansulfonic acid (5.0×10^{-4} mol/L) which inhibits methanogenesis (Levy *et al.*, 1981b). At regular time intervals, samples were collected taking care to maintain anaerobic conditions in the test bottles. The samples were centrifuged for a period of 30 minutes

TABLE 1 Influence of the Pretreatment Conditions on Solubilization and VFAs Conversion Yield (% on COD Basis); Data Represent the Average of Three Runs.

Pretreatment conditions			Pretreatment solubilization yield (%) (mean values)	Fermentation yield to VFAs (%) (mean values)
Reagent	Temperature (°C)	Time (h)		
NaOH 1%	20	120	24.00	34.65
NaOH 1%	100	1	30.43	23.38
$Ca(OH)_2$ 1%	20	120	14.95	29.97
$Ca(OH)_2$ 1%	100	1	19.37	20.09
HCl 1%	20	120	14.12	22.67
HCl 1%	100	1	17.44	20.20
H_2SO_4 1%	20	120	12.69	17.99
H_2SO_4 1%	100	1	17.72	14.75
H_2O	20	120	13.37	22.70
H_2O	100	1	17.55	13.96

and the supernatant filtered on 0.45 μm filters. Both pH and VFAs content were determined on the filtrate. VFA analysis was performed by gas chromatography with a flame ionization detector on a Supelco SP1200 separation column according to Ottenstein and Bartley (1971).

RESULTS AND DISCUSSION

Choice of Pretreatment (Kind of Reagent and Temperature)

Table 1 reports the mean results obtained. Acids are markedly less effective than NaOH both in terms of solubilization and fermentation yields; $Ca(OH)_2$ shows low solubilization yield, but its conversion to VFAs almost reaches NaOH performance. For every reagent, the higher the temperature, the higher the solubilization and the lower the fermentation yield.

All pretreatments, with the exclusion of $Ca(OH)_2$ pretreatment at 100 °C, show a conversion yield that is higher than the solubilization yield; consequently, further hydrolysis of the particulate fraction during fermentation contributes to acid production. Quantitative evaluation of this effect was carried out by performing separate fermentations of total and soluble MSWOF. Table 2 shows that the conversion yields of the soluble fraction range from about 60 to 85% (reference glucose fermentation shows the same level of conversion) and account for about 45 and 60% of total acid production at pretreatment temperatures of 20 and 100 °C respectively. Moreover, VFAs analysis shows that, independently of the type of pretreatment, acetic and butyric acids are produced mainly when the soluble fraction is the only substrate, whereas fermentation of substrate obtained by biohydrolysis of residual particulate fraction produces chiefly propionic acid.

In summary, best results were obtained by using NaOH at room temperature; pretreatment markedly increases the yield of bioconversion to volatile fatty acids compared with the rather low values obtained without pretreatment. Both solubilization and swelling are effective.

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TABLE 2 VFAs Conversion Yields (% on COD Basis) from Total and Soluble MSWOF after Alkaline Pretreatment (Single Run).

Reagent	Pretreatment Temperature (°C)	Solubilization Yield (%)	Fermentation Yield to VFAs (%) on total MSWOF	on soluble MSWOF	VFAs from soluble fraction as a percentage of VFAs from total MSWOF
NaOH	20	23.73	30.69	58.08	44.91
NaOH	100	26.27	26.25	61.56	61.61
$Ca(OH)_2$	20	14.21	27.73	83.33	42.70
$Ca(OH)_2$	100	18.19	20.34	66.43	59.41

Kinetics of the Pretreatment

The results of the kinetic runs are reported in table 3.

From the state of the art on the degradation mechanisms of a cellulose-type material undergoing a mild alkaline pretreatment it results that a solubilization reaction characterized by a first order kinetics competes with a stopping reaction producing an unreactive end group (Machell *et al.*, 1957; Krochta *et al.*, 1984).

TABLE 3 Pretreatment Kinetic Runs (at 20 °C): Solubilization Yield (gCOD/gCOD) versus Time; Data Represent the Average of Three Runs.

Time (h)	Concentration of NaOH (% w/v)						
	0.50[a]	0.75[a]	1.00[a]	1.00[b]	1.00[c]	1.50[a]	2.00[a]
0	0.098	0.098	0.098	0.098	0.098	0.098	0.098
1	0.097	0.100	0.101	0.125	0.143	0.122	0.128
2	0.120	0.123	0.130	0.161	0.152	0.140	0.162
4	0.142	0.142	0.158	0.168	0.181	0.159	0.180
7	0.145	0.152	0.175	0.202	0.204	0.177	0.203
22			0.205	0.232	0.238		
24	0.191						
26			0.226	0.238	0.248		
30			0.227	0.259	0.260		
46			0.239	0.267	0.285		
48	0.234	0.210				0.278	0.315
70			0.257	0.294	0.323		
94			0.285	0.327	0.340		
96	0.234						0.351
120						0.288	

Substrate/Solvent Ratio (g/mL): (a) 1/16, (b) 1/24, (c) 1/32.

The mathematical treatment of kinetic run data by applying the non linear regression analysis according to Marquardt's algorithm (Marquardt, 1963) shows a good agreement with the above-reported mechanism; in particular, the stopping reaction is accurately described by a second order kinetics.

The mathematical treatment of data also shows that kinetic constants of the two competing reactions depend on NaOH dosage.

As a result of this kinetic study, the basic equations are:

$$dS/dt = k_a F_a \qquad (1)$$

$$dF_b/dt = k_b F_a{}^2 \qquad (2)$$

where F_a is the concentration of solubilizable particulate substrate, S is the concentration of soluble substrate. The kinetic constants k_a and k_b are given by the following expressions (characterized by a correlation factor of 0.962):

$$k_a(h^{-1}) = (9.1 \pm 1.1)\ 10^{-2}\ (NaOH) \qquad (3)$$

$$k_b(h^{-1}) = (6.3 \pm 1.1)\ 10^{-1}\ (NaOH)^{0.6 \pm 0.1} \qquad (4)$$

where (NaOH) is the alkali dosage expressed as NaOH g/MSWOF g.

Obviously, the values of these constants and their dependence on NaOH dosage can vary markedly according to source and aging of substrate.

Kinetics of Acidogenic Fermentation

The kinetic behaviour of acidogenic fermentation is described by the following equations:

$$(-r_f) = k_h\ F \qquad (5)$$

$$(r_x) = \overline{\mu}[S/(K+S)]\ X \qquad (6)$$

$$(-r_s) = (\overline{\mu}/Y)[S/(K+S)]\ X \qquad (7)$$

$$(r_p) = \alpha[(1-Y)-1]\overline{\mu}[S/(K+S)]\ X \qquad (8)$$

where $(-r_f)$, (r_x), $(-r_s)$ and (r_p) are the rates of particulate substrate biohydrolysis, of biomass growth, of soluble substrate consumption and of product formation, respectively; F, S, X are the concentrations of particulate substrate, soluble substrate, and biomass, respectively; concentrations for all the components of the system are expressed in terms of COD so that both reactants and products can be compared directly (Eastman and Ferguson, 1981). The biokinetic constants (k_h, biohydrolysis rate constant; $\overline{\mu}$, maximum specific biomass growth rate; K, Michaelis-Menten half velocity coefficient; Y, net biomass yield coefficient; α, VFA yield coefficient) were evaluated in a previous work (Beccari et al., 1989) through an acidogenic fermentation test carried out at 25 °C and at pH 6 on a MSWOF subjected to a 72-hour pretreatment with NaOH solution (NaOH concentration : 0.5% w/v, substrate/solvent ratio : 1/16 g/mL, corresponding to 0.08 NaOH g/substrate g). A value of $k_h = 5.2\ 10^{-4}\ h^{-1}$ was obtained with a linear correlation coefficient of 0.971; the very small value of k_h shows that the hydrolysis of particulate substrate controls the performance of the overall biological process; no biomass influence on hydrolysis was observed.

Differential method of analysis of the experimental data gave $\overline{\mu} = 2.7\ 10^{-2}\ h^{-1}$ and $K = 2.83\ gCOD\ L^{-1}$ with a correlation coefficient of 0.974.

The integral method of analysis of the experimental data gave Y=0.46 (with a correlation coefficient of 0.974) and α=0.89 (with a correlation coefficient of 0.969).

In order to verify whether the inevitable uncertainty implicit in the differential method of analysis had possibly

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altered to a high degree the values of $\bar{\mu}$ and K, a biokinetic new run was carried out in which the experimental apparatus was fed with only the soluble fraction of pretreated MSWOF.

In such a case it is possible to calculate $\bar{\mu}$ and K by applying the integral method of analysis (Ong, 1983); this procedure gives values ($\bar{\mu}$=2.1 10^{-2} h^{-1} and K=1.76 gCOD L^{-1}) very close to those obtained through the experimentation on the total substrate (particulate plus soluble).

Simulation of the Overall Process

By introducing the kinetic descriptions of pretreatment and acidogenic fermentation in the balance equations for substrate (particulate and soluble), biomass and VFAs, the overall process taking place in the two CFSTR reactors (with and without an intermediate liquid/solid separation) was simulated.

The modelling shows that the higher the feed of soluble fraction to the bioreactor the higher the VFA concentration whereas biomass recycle exerts only a small effect (fig.1). Consequently, an optimum ratio between the hydraulic residence times of the two stages of the process (pretreatment and acidogenic fermentation) should exist.
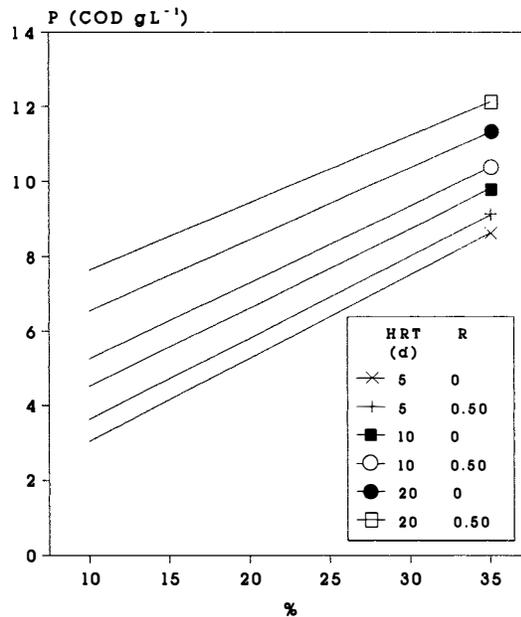

Fig. 1. VFAs concentration (P) as function of the percentage of influent soluble substrate on total influent substrate (soluble and particulate at various fermenter hydraulic residence times (HRTs) and recycle ratio (R). Total influent MSWOF: 50 gCOD/L.

This is confirmed by the simulation study (fig.2), the validity of which depends on the assumption that the time of pretreatment does not markedly affect the biokinetic constants.

CONCLUSION AND FINAL REMARKS

Alkaline pretreatment markedly increased the efficiency of bioconversion of MSWOF to VFAs. The best results were obtained by using NaOH at room temperature; experimental data are in good agreement with a kinetics based on two competing reactions: a first order solubilization reaction and a second order stopping reaction.

Further research will conceivably deal with pretreatment carried out with $NaOH/Ca(OH)_2$ mixtures.

Acidogenic fermentation kinetics was evaluated in a previous work; the values of the biokinetic constants concerning the conversion of the soluble substrate were confirmed in an ad hoc experiment.

Simulation of the overall process (pretreatment and acidogenic fermentation) has shown that an optimum ratio exists between the hydraulic residence times of the two stages of the process. More complete simulation for obtaining the final assessment of the process will be performed after a further research aimed at pointing out the influence of pretreatment conditions (time, reagent dosage) on the values of the biokinetic constants.
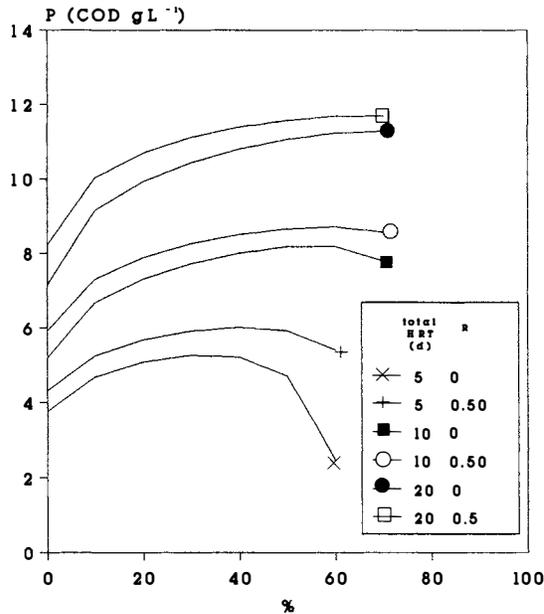

Fig. 2. VFAs concentration (P) as a function of the percentage of pretreatment HRT on total HRT(pretreatment and fermenter). Total influent MSWOF: 50 gCOD/L.

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