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Effects of thermally pretreated temperature on bio-hydrogen production from sewage sludge

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Abstract: Hydrogen can be obtained by anaerobic fermentation of sewage sludge. Therefore, in this paper the effects of thermally pretreated temperatures on hydrogen production from sewage sludge were investigated under different pre-treatment conditions. In the thermal pretreatment, some microbial matters of sludge were converted into soluble matters from insoluble ones. As a result, the suspended solid(SS) and volatile suspended solid(VSS) of sludge decreased and the concentration of soluble COD(SCOD) increased, including soluble carbohydrates and proteins. The experimental results showed that all of those pretreated sludge could produce hydrogen by anaerobic fermentation and the hydrogen yields under the temperatures of 121℃ and 50℃ were 12.23 ml/g VS(most) and 1.17 ml/g VS (least), respectively. It illuminated that the hydrogen yield of sludge was affected by the thermally pretreated temperatures. Additionally, the endurance of high hydrogen yield depended on the translation of microbial matters and inhibition of methanogens in the sludge. The temperatures of 100℃ and 121℃ (treated time, 30 min) could kill or inhibit completely the methanogens while the others could not. To produce hydrogen and save energy, 100℃ was chosen as the optimal temperature for thermal pretreatment. The composition changes in liquid phase in the fermentation process were also discussed. The SCOD of sludge increased, which was affected by the pretreatment temperature. The production of volatile fatty acids in the anaerobic fermentation increased with the pretreatment temperature.

Keywords: anaerobic fermentation; hydrogen production; sewage sludge; thermally pretreated temperature

Introduction

Making up about three-quarter of matter, hydrogen is the most plentiful elements in the universe. The heat value of hydrogen is 142.35 kJ/g H_2 (considering water as final product). Hydrogen is regarded as a clean fuel and an environmental ideal fuel since water is the only product in combustion(Das and Veziroğ, 2001). It is believed that hydrogen will replace fossil fuel as the energy source of next generation. Hydrogen can be produced chemical-physically and biologically. In contrast, the biological methods are environmentally favorable and less energy is consumed (Cai *et al.*, 2004). It is technically feasible to produce hydrogen from organic matter by anaerobic fermentation.

Conventional activated sludge processes transform organic pollutants into gas, water and biomass (sludge). The treatment and disposal of the excess sludge produced in the processes has become one of the most important and complex problems in wastewater treatment plants today. The sludge contains high bioenergy because it is composed large of organic matters (59%—88%, w/v)(Weemaes and Verstraete, 1998). A better economic benefit can realize if the bioenergy of sludge can be recovered in the treatment and disposal of excess sludge. Anaerobic digestion is a traditional technique, which has been employed to reduce the volume and weight of sludge and recovered part energy from sludge through producing methane (Parkin and Owen, 1986). However, the conventional digestion techniques require long hydraulic retention time (20—30 d) (Weemaes and Verstraete, 1998). Thermal pretreatment has been used to improve anaerobic digestion of sludge. For example, Haug *et al.*(1977, 1978, 1983) proposed a thermal pretreatment process prior to anaerobic digestion of sludge. It was found that the methane yield increased by 14% with 100℃ pretreatment and by 60%—70% with 175℃ pretreatment. Thermal pretreatment could increase the biodegradability of sludge.

Hydrogen is an intermediary metabolite of the anaerobic sludge digestion, which is rapidly taken up and conversed to other products by hydrogen consuming microorganisms at the methanogenesis stage of anaerobic digestion (Parkin and Owen, 1986; Harper and Pohland, 1986; Reith *et al.*, 2003). However, it is more favorable to harvest hydrogen than methane. In order to harvest hydrogen, the anaerobic digestion of sludge should be blocked before the methanogenesis stage. At laboratory scale, several methods of limiting methanogenesis are used, for example, operation at a short HRT to wash out

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methanogens, operation at low pH to inhibit them and inactivating or killing them by various pretreatments, like thermal pretreatment (Hawkes *et al*., 2002). For example, Sung *et al*. (2002) studied hydrogen production from sucrose by anaerobic microbial communities exposed to repeated heat treatments and Lay *et al*. (2003) succeeded producing hydrogen by heat-shock digested sludge.

However, few studies discussed the possibility of hydrogen production from sewage sludge by anaerobic fermentation with thermal pretreatment. This paper presented four thermal pretreatments on sewage sludge and studied the effects of thermally pretreated temperatures on hydrogen production from sewage sludge by anaerobic digestion.

1 Materials and methods

1.1 Sewage sludge

The sewage sludge was obtained from a municipal wastewater treatment plant in Beijing (China), which used activated sludge process. The characteristics of the sludge are listed in Table 1. The sludge as gravitationally thickened to certain concentration before used.

Table 1 Characteristics of sewage sludge used in the tests

DS, g/L	VS, g/L	Density, g/L	pH	SCOD, mg/L	Proteins*, mg/L	Carbohydrates*, mg/L
4.52—6.15	3.16—4.61	999.85 1002.34	6.85—7.15	118.17	45.50	0.67

Notes: * Soluble matters; DS. dry solid; VS. volatile solid; SCOD. concentration of soluble COD

1.2 Thermal pretreatment of sewage sludge

The thermal pretreatments of sewage sludge were carried out under different temperatures and pretreated time. The thermal pretreatments of sludge under low temperatures (<100℃) were accomplished with water bath and under high temperatures (≥100℃) in an autoclave(VARIOKLAV steam sterilizer, 300/400/500 EP). After thermal pretreatments, the sludge samples were cooled about 2 h and the final temperatures were near ambient temperature(20—24℃), Then the sludge were used to produce hydrogen by anaerobic fermentations.

1.3 Hydrogen production of thermally pretreated sludge

The thermally pretreated sludge samples(150 ml) were added into plexiglass fermentors (300 ml), respectively. No other materials were added into the fermentors. The fermentors were equipped with two ports for sampling gas and sludge. The headspaces of the fermentors were purged with nitrogen and the liquid phase was bubbled also with nitrogen to provide an anaerobic environment. The fermentors were quickly sealed and put in an air bath shaker(HKZ-C, China) to incubate at 37±1℃ with 140—150 r/min. Tests of all sludge samples were carried out in triplicate.

1.4 Analyses

Biogas production was measured periodically by displacement of saturated aqueous NaCl in a graduated cylinder. The biogas in the headspace of fermentors was sampled with a 1 ml gastight syringe. Hydrogen production was calculated from the measurements of gas composition and the total volumes of biogas produced. The contents of hydrogen in the biogas were analyzed by a gas chromatograph (GC122, China) equipped with a thermal conductivity detector (TCD) and a 2 m stainless column packed with activated carbon(60—80 mesh). Injection, column and detector temperatures were kept at 70℃, 140℃ and 140℃, respectively. Nitrogen was used as the carrier gas with a flow rate of 30 ml/min. The contents of methane in biogas were also determined with the same GC-TCD and a 2 m stainless column filled with PorapakT(80—100 mesh). The operational temperatures of the injection port, the column, and the detector were set at 110℃, 60℃, and 200℃, respectively. Hydrogen was used as the carrier gas with a flow rate of 40 ml/min.

The sludge was sampled with a 5 ml gastight syringe. The concentrations of volatile fatty acids (VFA) in the liquid phase were analyzed using another gas chromatograph (Shimadzu GC-9A, Japan) equipped with a flame ionization detector (FID) and a 2 m glass column packed with Chromosorb 101 (60—80 mesh). The temperatures of the injection port, the column and the detector were 250℃, 200℃ and 250℃, respectively. The carrier gas also used nitrogen at 50 ml/min.

The pH was measured with a pH meter(PHS-3C, China). The concentration of soluble COD (SCOD) and total COD (TCOD) were analyzed by a CTL-12 COD meter (Huatong Company, China). The samples were filtered through a 0.45 μm membrane before determining the concentrations of SCOD. The biomass was measured by total solid (TS, namely dry solid: DS), volatile solid (VS), suspended solid (SS) and volatile suspended solid (VSS) according to standard methods (APHA, 1992). Soluble proteins in the liquid phase were measured by the Lowry's method using bovine serum albumin as a standard solution (Lowry *et al.*, 1951) and soluble carbohydrates by the phenol-sulfuric acid method using glucose as a standard solution (Dubois *et al.*, 1956). All results were mean to triplicate analyses.

1.5 Kinetic analysis

The modified Gompertz equation (Eq.(1)) was used to fit the experimental data of accumulative hydrogen production(Lay, 1998, 2001).

$$H(t) = P\times\exp\left\{-\exp\left[\frac{R_m e}{P}(\lambda - t)+1\right]\right\} \qquad (1)$$

where H (t) is the accumulative hydrogen production (ml) during the fermentative time t (h), P is the hydrogen production potential (ml), R_m is the maximum production rate (ml/h), λ is the lag time (h), and e is 2.718281828. The values of P, R_m and λ are determined by best fitting the hydrogen producing data for Eq.(1) using the Matlab 6.5 (Math Works Inc. Cory right 2001—2002)(Fang and Liu, 2002; Zhang *et al.*, 2003). The maximum specific hydrogen production rate(ml/(gVS·h)) was calculated by dividing R_m by the initial sludge VS. The hydrogen yield(ml/gVS) was calculated by dividing P by the quantity of sludge (VS) added in the fermentors.

2 Results and discussions

2.1 Effects of thermal pretreatments on sewage sludge

The microbial cells are disrupted by heat treatment and the intracellular matters are released into water and became soluble matters. Moreover, extracelluar polymers of sludge, such as polysaccharides and proteins, were also released into water (Bhatti *et al.*, 1995). The destroyed part of cells is different in the thermal treatment of sludge under different temperatures, for example, cell membrane is broken under 45—65℃ and cell wall is destroyed under 65—90℃(Hamer *et al.*, 1994).

Four temperatures were selected in the test and the thermal pretreatments of sludge were carried out as Table 2 and the pretreated sludge samples were names as TS1, TS2, TS3 and TS4, respectively. Table 3 summarizes some parameters of sludge before and after thermal pretreatments. Owing to the insoluble organic matters converting into soluble ones, the SS and VSS of sludge decreased with the increase of pretreated temperatures as listed in Table 3. For example, the SS and VSS were 9.93 g/L and 7.12 g/L for TS1 and 8.72 g/L and 6.03 g/L for TS4, respectively. The pH value of sludge dropped after thermal pretreatments, it resulted from VFA production in the process of thermal pretreatment (Hiraoka *et al.*, 1984). The changes of pH value for the four pretreated sludge were similar. The SCOD of sludge increased after thermal treatments due to the release of intracellular matters. With the increase of temperature, the SCOD of pretreated sludge samples also increased, when the temperature increased from 50℃ to 80℃ and 100℃ to 121℃, the SCOD increased from 1378.21 mg/L to 2172.61 mg/L and 2008.21 to 2714.41 mg/L, respectively. Higher temperature and longer treatment time were favorable to the release of intracellular organic matters. Proteins and carbohydrates were main organic matters released from the microbial cell of sludge. Both of soluble proteins and carbohydrates increased with the thermally treated temperatures.

Table 2 Thermal pretreatments of sewage sludge

Sample	Temperature of thermal pretreatment, ℃	t, min
TS1	50	60
TS2	80	60
TS3	100	30
TS4	121	30

Table 3 Various parameters of sludge before and after thermal pretreatments

Item	Rs	TS1	TS2	TS3	TS4
SS, g/L	11.16	9.93	9.31	9.16	8.72
VSS, g/L	8.08	7.12	6.58	6.38	6.03
pH	7.11	6.65	6.61	6.58	6.63
SCOD, mg/L	118.17	1378.21	2172.61	2008.21	2714.41
Proteins*, mg/L	45.50	620.92	1164.23	1268.61	1493.43
Carbohydrates*, mg/L	0.67	70.00	292.78	319.70	512.86

Note: * Soluble matters

2.2 Hydrogen production from thermally pretreated sludge

The pretreated sludge samples were used to produce hydrogen by anaerobic fermentations. Fig.1 shows the change of hydrogen yield from the four pretreated sludge samples and Table 4 summarizes the kinetic parameters of hydrogen production. Hydrogen was produced in the anaerobic fermentations of the four pretreated sludge samples. It suggested that all the four pretreatments could select hydrogen-producing microorganisms from the mixed microflora of sludge. In practice, many hydrogen-producing microorganisms (for example, *Clostridium* sp.) can form endospores, which are very resistant to heat or harmful chemical (including acid and alkaline) and cannot be killed easily (Brock *et al.*, 1994). Once favorable conditions return, the spores germinate and become vegetative cells(Chen *et al.*, 2002; Sung *et al.*, 2002). So certain thermal pretreatment can be used to select hydrogen-producing microorganisms from mixed microorganisms. Many researchers have used thermal treatment to select hydrogen-producing microorganisms from mixed communities. For example, Lay *et al.*(2000) and Okamoto *et al.*(2000) used wet heat treatment (boiling for 15 min) of anaerobic digester sludge, whereas Van Ginkel *et al.* (2001) used dry heat treatment (baking at 104℃ for 2 h) of compost and soils. In addition, thermal pretreatment had another action, namely, it could transform some insoluble matters into soluble ones and make them easier to be hydrolyzed by microorganisms.

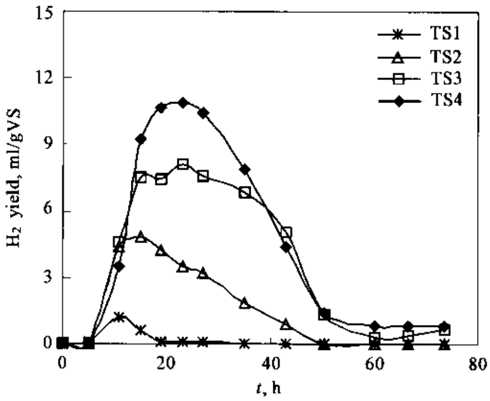

Fig.1 Change of hydrogen yield in the anaerobic fermentations of various pretreated sludge

Table 4 Kinetic parameters of hydrogen production from the thermally pretreated sludge

Pretreated sludge samples	P, ml	R_m, ml/h	λ, h	Maximum specific hydrogen production rate, ml/(gVS·h)	Hydrogen yield, ml/gVS
TS1	1.49	0.47	6.26	0.37	1.17
TS2	6.19	1.85	6.88	1.45	4.85
TS3	10.34	1.39	6.40	1.09	8.09
TS4	15.62	2.01	8.59	1.57	12.23

On the other hand, the hydrogen yield of sludge was affected by the thermally pretreated temperature. When the temperature was 121℃(treatment time of 30 min), the hydrogen yield of sludge was maximal(12.23 ml/gVS) and when the temperature was 50℃ (treatment time of 60 min), the hydrogen yield was minimal (only 1.17 ml/gVS). Moreover, the lag time (λ) to sludge sample TS4 was maximal (8.59 h) and that of others were similar(6.2—6.9 h). The difference of the lag time might be owing to the temperature of thermal pretreatments: the higher temperature of pretreatment is, the stronger inhibition of microorganisms is.

Table 5 shows the change of methane content in the gas phase of fermentors during the anaerobic fermentations. Methane could not be detected in the anaerobic fermentations of TS3 and TS4, while methane could in the different stage of anaerobic fermentations of TS1 and TS2. It suggested that the methanogens could kill or inhibit completely in 100℃ and 121℃ pretreatments. The thermal pretreatment of 80℃ could only inhibit temporarily the methanogens and the activities would resume once the condition was favorable. The thermal pretreatment of 50℃ could not inhibit the activity of methanogens. However, because of the growth rate of hydrogen consuming microorganisms was lower than that of hydrogen producing ones, the hydrogen produced by the later would accumulate in the gas phase of fermentor and could be detected. Although there was no methane production in the anaerobic fermentations of TS3 and TS4, hydrogen consumption occurred in the certain stage (Fig.1). It illustrated that other hydrogen consuming actions such as homoacetogenesis, propionic acid production and sulfate reduction might exist (Hussy *et al.*, 2003; Oh *et al.*, 2003). Some studies showed that there were in deed homoacetogenesis and propionic acid production when carbon dioxide and hydrogen coexist inanaerobic circumstance. For example, Goldberg and Cooney(1981) found a mixed culture of bacteria could utilize carbon dioxide and hydrogen to form short-chain fatty acids, such as acetic acid.

Table 5 Content of methane in the gas phase of fermentors during the anaerobic fermentation

Time, h	TS1, %	TS2, %	TS3, %	TS4, %
0	-*	-	-	-
19	0.060	-	-	-
45	0.066	0.013	-	-
73.5	0.099	0.028	-	-

Note: * No methane could be detected

The endurance of high hydrogen yield depended on the translation of microbial matters and inhibition of methanogens in the sludge. The transformation of microbial matters increased with the pretreated temperature, while the methanogens in the sludge could be inhibited at temperature above 100℃.

Thermal pretreatments of sludge required energy. The thermal pretreatment of sludge could be divided into two processes: the heating process and the heat preservation one. Under good heat preservation, the required energy of the heat preservation process was few and the main energy consumption of thermal pretreatment came from the heating process. So the energy consumption of thermal pretreatment could be substituted by the required energy of heating process. The required energies of heating process of four pretreatments could be calculated with Equation (2).

$$Q = C_p \cdot (T - T_0) \quad (2)$$

where Q is the required energy in heating process of unit sludge (J/gVS), C_p is the specific heat of sludge and about 1.50 J/(gVS·K)(Naylor, 1996), T_0 and T are the initial and final temperature of sludge, respectively.

So, the energy consumptions of four pretreatments of unit sludge (TS1, TS2, TS3, TS4) were 45.0, 90.0, 120.0, and 151.5 J/gVS, respectively. In other words, the higher pretreated temperature was, the more energy was consumed. So, for hydrogen production and saving energy, the optimal temperature of pretreatment was 100℃.

2.3 Changes in the liquid phase in the anaerobic fermentation process

In the anaerobic fermentations of the four thermally pretreated sludge, the organic matters were decomposed. Microorganisms convert those matters (such as amino acids and glucose) into CO_2, VFA or new microbial biomass and produce hydrogen in the process (Parkin and Owen, 1986). Fig.2 and 3 show change of soluble proteins and soluble carbohydrates in the anaerobic fermentations of various pretreated sludge. All soluble proteins of the four pretreated sludge decreased: the more initial proteins there were, the more the proteins decreased. The soluble carbohydrates of TS2, TS3 and TS4 also decreased in the whole process, while that of TS1 was different. It was the result of insoluble organic matters converting into soluble ones in the anaerobic fermentation. In addition, the decreases of the two matters were quicker in the early stage(about 0—23 h) than those in the later stage (after 23 h). The early stage fit the hydrogen production stage like a glove. It suggested that the decomposing rate of those organic matters in the hydrogen producing stage was quicker than that in the hydrogen consuming stage. It is reasonable since hydrogen-consuming microorganisms could utilize CO_2 or VFA as carbon source and the kind of nitrogen source increased in the hydrogen consuming stage.

Fig.4 shows the change of SCOD in the anaerobic fermentations of the four pretreated sludge.

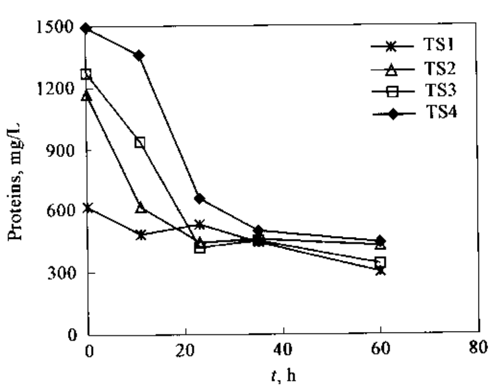

Fig.2 Change of soluble proteins in the anaerobic fermentations of various pretreated sludge

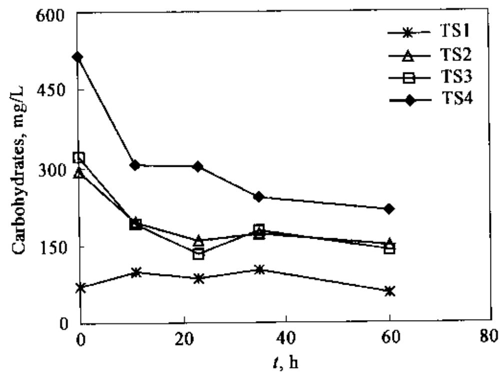

Fig.3 Change of soluble carbohydrates in the anaerobic fermentations of various pretreated sludge

Insoluble organic matters of sludge were converted into soluble ones in the anaerobic fermentation and that resulted in the increase of SCOD. The lower the start SCOD was, the more SCOD increased. For example, the SCOD of TS1 increased 1438.50 mg/L, while that of TS4 only 671.70 mg/L. it was owing to the insoluble organic matters of high temperature pretreated sludge which could convert into soluble ones in the anaerobic process were lower than those of low temperature pretreated sludge.

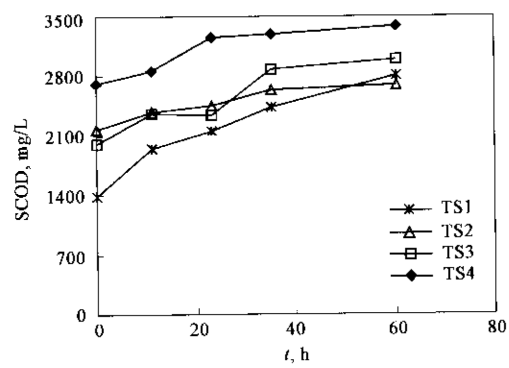

Fig.4 Change of SCOD in the anaerobic fermentations of various pretreated sludge

VFA were produced with the hydrogen production in the anaerobic fermentation. Fig.5 shows the concentrations of VFA at 76.5 h. The concentration of

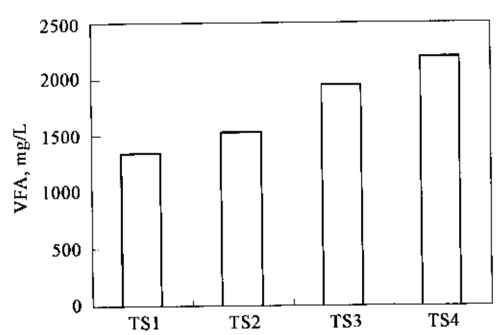

Fig.5 VFA production in the anaerobic fermentations of various pretreated sludge; sampling time: 76.5 h

VFA increased with the pretreated temperature. For example, the concentrations of VFA for TS4 were 2196.35 mg/L, while only 1350.98 mg/L for TS1. The difference was caused by organic matters released and microorganisms screened by different pretreatments. Although the VFA was produced in the process, the change of sludge's pH values was little (Fig.6). It was the results producing NH_4^+-N in the decomposition of proteins (data are not shown), which could neutralize the VFA and stabilize the pH value of sludge.

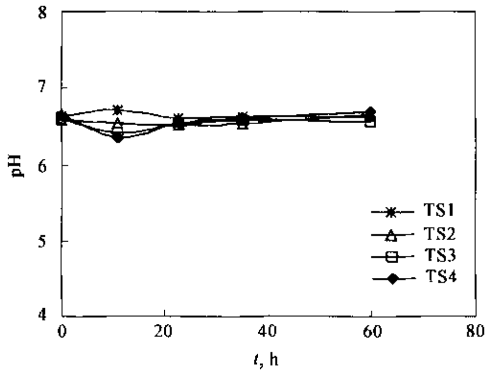

Fig.6 Change of pH value in the anaerobic fermentations of various pretreated sludge

3 Conclusions

Thermal pretreatment could solubilize some microbial matters and decrease the SS and VSS of sludge and increase the SCOD included carbohydrates, proteins, and so on. The effects of thermal pretreatment were increased with the pretreated temperature.

Hydrogen could be produced from sludge pretreated under the conditions of 50℃ for 60 min, 80℃ for 60 min, 100℃ for 30 min and 121℃ for 30 min by anaerobic fermentations. It suggested that the four pretreatments could select hydrogen-producing microorganisms from the microflora of sludge. The hydrogen yield of sludge was increased with the pretreated temperature. The temperatures of 100℃ and 121℃ could kill or inhibit completely the methanogens while the others could not. For producing hydrogen and saving energy, 100℃ was the optimal temperature for thermal pretreatment.

In the anaerobic fermentation of thermally pretreated sludge, the organic matters were decomposed. The soluble proteins and carbohydrates decreased in the anaerobic fermentation. While the SCOD of sludge increased because the insoluble organic matters were converted into soluble ones in the fermentation. The production of VFA in the anaerobic fermentation was also increased with the pretreated temperature.

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