

Supercritical water oxidation of acetic acid by potassium permanganate

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Abstract

Supercritical water oxidation (SCWO) of acetic acid by potassium permanganate (KMnO_4) was studied. The experiments were performed in a batch reactor at temperatures and pressures, respectively, ranging from 400 °C to 460 °C and from 275 bar to 350 bar. For comparison purposes, other oxidants, such as oxygen, hydrogen peroxide, $\text{Cu-H}_2\text{O}_2$, $\text{Fe-H}_2\text{O}_2$ and $\text{MnSO}_4\text{-H}_2\text{O}_2$, were studied. Subcritical tests with potassium permanganate were also conducted at temperatures of 250 °C, 300 °C and 350 °C. The order of acetic acid destruction effectiveness was found to be $\text{KMnO}_4 > \text{Cu-H}_2\text{O}_2 > \text{Fe-H}_2\text{O}_2 > \text{MnSO}_4\text{-H}_2\text{O}_2 > \text{H}_2\text{O}_2 > \text{O}_2$ at a temperature of 400 °C, density of 0.3 g/ml and reaction time of less than 10 min. The acetic acid destruction efficiency by potassium permanganate was 77% at a temperature of 400 °C, density of 0.3 g/ml and a reaction time of 2.5 min. Under similar conditions, only 40% of acetic acid was destroyed at 250 °C. Potassium permanganate was demonstrated to be an effective oxidant for SCWO of acetic acid.

1. Introduction

Supercritical water oxidation (SCWO) is potentially a means for hazardous waste destruction and sludge volume reduction [1–3]. When aqueous phase oxidation is carried out above the critical point of water (374.15 °C and 221.2 bar), more than 99.99% conversion of complex organic molecules to carbon dioxide and other stable entities, such as acetic acid, can be achieved within minutes [4, 5]. The rate of transformation becomes more rapid as the temperature increases. Unfortunately, at higher temperatures the materials of construction become more costly and reactor designs become more challenging. Therefore, to achieve complete organic conversion and minimize the materials problem, attention must be directed to temperature adjustment, an alternative oxidant and use of catalysts.

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First, lower reaction temperatures ranging from 200 °C to 350 °C have been explored in wet air oxidation (WAO). WAO reportedly achieved about 85% organic conversion with a reaction time of one hour [6–8]. The incomplete oxidation products in the effluent were primarily volatile acids. In particular, acetic acid was found in the effluent from WAO of municipal and biological sludges [9–12] and WAO of phenol [13]. The transformation of acetic acid was studied in SCWO of sludges [14] and other volatile acids [4].

Second, regarding the oxidant source, oxygen and enriched air have been studied in conjunction with SCWO [1, 15, 16]. However, not until recently has hydrogen peroxide been used as the oxidant for SCWO [4, 5, 17, 18]. Although oxygen is highly favorable for use in full-scale SCWO processes, other oxidants may become attractive for specific applications. Further investigations, such as this work, are needed.

Third, catalysts have been used in WAO to

- (a) enhance the conversion of complex organic compounds,
- (b) shorten reaction time, and
- (c) lower required reaction temperature.

Aqueous phase catalytic oxidation of organic wastewaters has been studied extensively [19–21]. More recently, the fundamental, technical, catalytic and economical aspects of WAO processes have been critically reviewed [22].

In the presence of hydrogen peroxide, copper salts were reported to be the most active catalyst [23]. The conversion of acetic acid and ammonia, respectively, increased two and eight-fold when copper(II) nitrate was added [24]. The chemical oxygen demand (COD) reduction of raw municipal wastewaters was more than doubled in a WAO reaction catalyzed by CuSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ in conjunction with H_2O_2 [20]. The presence of catalysts can enhance the overall reaction rate as well as the distribution of by-products. For example, addition of ferric sulfate [$\text{Fe}_2(\text{SO}_4)_3$] resulted in a higher percentage of volatile acids (formic acid and acetic acid) relative to the total acid formed in the WAO of softwood and hardwood [25].

A recent study of homogeneous catalysts in SCWO showed that manganese(II) chloride, manganese(II) acetate and copper(II) tetrafluoroborate exhibited little effect on the rate of oxidation of *p*-chlorophenol in supercritical water [26]. The disadvantages of homogeneous (water-soluble) catalysts were found to be the toxicity of metal ions and subsequent post-treatment requirements. In this respect, heterogeneous (water-insoluble) catalysts could be superior because it was easier to separate them from the effluent. Heterogeneous catalysts were either metals or metal oxides, usually coated onto porous carriers. In addition, heterogeneous catalysts are generally more active as compared to homogeneous catalysts.

Mn/Ce composite oxide has been shown to exhibit higher activity than homogeneous copper(II) nitrate in the WAO of acetic acid, poly(ethylene glycol), pyridine and ammonia [24]. The rate of oxidation of *p*-chlorophenol in

supercritical water was enhanced more by increasing the surface-to-volume ratio of the reactor (Inconel 600) than by adding copper(II) tetrafluoroborate [26].

Of the precious metals, such as ruthenium, rhodium, palladium, iridium and platinum when supported by cerium(IV) oxide, ruthenium was the most active catalyst in WAO of *n*-propyl alcohol, *n*-butyl alcohol, phenol, acetamide, poly(propylene glycol) and acetic acid [27]. The catalytic activity of copper oxide and manganese oxide immobilized on a γ -Al₂O₃ carrier was studied in the WAO of phenol [19]. Of the most refractory compounds, acetic acid was catalytically oxidized by various metal salts including Co–Bi complex oxides [23] and ferric oxide [28]. Similarly, WAO of ammonia catalyzed by cerium-based composite oxides [29], and WAO of many oxygen and nitrogen-containing organic compounds catalyzed by cobalt(III) oxide [30] have been reported. These studies showed that most heterogeneous catalysts increased the rate of organic conversion.

Heterogeneous catalysts have limited applications. Heterogeneous catalysts can treat only homogeneous waste streams. The catalyst activity might be decreased as a result of contaminated catalyst surface. Therefore, the criteria for selecting a catalyst should include

- (1) catalyst recovery and regeneration,
- (2) catalyst poisoning,
- (3) catalyst toxicity, and
- (4) catalyst costs.

Potassium permanganate is a suitable candidate acting both as an effective oxidant and a possible catalyst. Potassium permanganate is a strong, water-soluble oxidant, easy to handle and readily available. Although the toxicity of potassium ion that remains in the effluent may pose a practical concern, calcium permanganate could be used since the reaction product, calcium hydroxide, is non-toxic and has limited solubility in water.

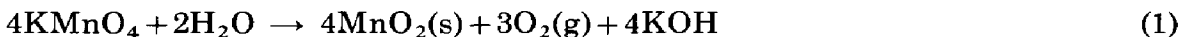
The effect of potassium permanganate on organic compounds has been well documented [31, 32]. Potassium permanganate has been used occasionally in water treatment to remove refractory organic compounds present in a concentration of a few parts per million [33–5]. Yet it should be noted that at room temperatures and atmospheric pressures potassium permanganate does not react with most organic acids [31, 32]. Potassium permanganate decomposes, upon heating, into oxygen and manganese dioxide (MnO₂). The latter has been shown to be catalytically active in WAO [19, 23, 24, 36, 37]. Manganese compounds have been used extensively as oxidizing agents for organic compounds [38]. Since manganese dioxide is water insoluble [39], it can be separated from the effluent by filtration or sedimentation.

Recently, an experimental study on catalytic SCWO was conducted [40]. The purpose of this study was to evaluate potassium permanganate as an SCWO oxidant for achieving high organic conversion at temperatures of about 400 °C. Because of the refractory nature of acetic acid, it was used to test the

effectiveness of potassium permanganate. This paper discusses the results from the experimental study.

2. Experimental procedures

Experiments were conducted in batch reactors made of 0.635 cm outside diameter and 0.0889 cm wall thickness coiled Stainless Steel 316 tubing. The internal volume of the reactor was 20 cm³. A stoichiometric amount of potassium permanganate (8/3 [permanganate]: 1 [acetic acid] mole ratio) was used, according to eqs. (1) and (2).



In a typical test, an aqueous mixture of acetic acid and potassium permanganate was loaded in the batch reactor. The reactor was then submerged in a fluidized sand bath (Techne Model SBL2) which had been set at a temperature slightly above the test temperature (15 °C for 250 °C tests and 30 °C for 400 °C tests). The test temperature was monitored by a digital display (Gordon Model 5072-X-1-P-X-J-C with a readability of 1 °C). A J-type thermocouple (Omega) was in contact with the reaction fluid. The fluid pressure was monitored using a Viatran transducer (Model 3405BH3DHA20), interfaced with a Viatran digital meter (Model 2002AE). After a preset reaction time, the reactor was quenched in a water bath. A heat-up time of about 0.5 min was observed in all tests.

The test conditions included the following: five densities (0.2, 0.25, 0.3, 0.35 and 0.4 g/ml); five temperatures (250, 300, 350, 400 and 460 °C); and six reaction times (2.5, 4.5, 6.5, 10, 15 and 30 min) including the heat-up period of 0.5 min.

The acetic acid destruction efficiency was based on total organic carbon (TOC) analyses. A correlation study on acetic acid detection using TOC and gas chromatography (GC) was reported [4]. Acetic acid destruction efficiency based on TOC analyses was 5% to 10% lower than that based on GC analyses for the effluent from subcritical tests, and less than 1% for the effluent from supercritical tests. The organic by-product resulting from acetic acid destruction was likely to be formic acid, and formic acid was reportedly less stable than acetic acid even in WAO [12].

A Beckman model 915A TOC analyzer was used. The effluents were filtered using a 0.45 m membrane filter (Fisher Scientific). Following the filtration, the sample was acidified according to a ratio of 0.1 ml phosphoric acid (Fisher Scientific, 85%) to 6 ml sample. The acidified samples were then purged with nitrogen (Zero-grade) for about 10 s to strip away dissolved carbon dioxide. This procedure was verified in a blank test with a known concentration of

acetic acid. Two or three TOC injections were made for each sample, and the variations in results were less than 1%.

3. Results and discussion

The variables that were investigated in this study included density, temperature, reaction time, catalyst, oxidant and pH. Acetic acid concentration in the feed solution was 1000 mg/l for all tests. All tests were conducted with an oxidant loading of 100% stoichiometric demand, unless stated otherwise. The acetic acid destruction was related to TOC reduction. Three to six tests were made at each specified condition. The average deviations in TOC reduction were less than $\pm 6\%$.

3.1 Temperature and density effects

An increase in temperature from 250 °C (subcritical) to 400 °C (supercritical) nearly doubled the destruction efficiency as shown in Table 1. However, the destruction efficiency levelled off at about 80% between 400 °C and 500 °C. To make sure this limited destruction efficiency was not due to oxidant deficiency, two parallel experiments were conducted using 50% less than and 100% more than stoichiometric requirements of potassium permanganate. A 75% destruction of acetic acid was observed when excess potassium permanganate was present. Conversely, 65% destruction resulted when insufficient potassium permanganate was used. These results suggested that temperature was the controlling factor for the destruction of acetic acid below 400 °C.

As shown in Table 2, the density change from 0.2 g/ml (subcritical) to 0.4 g/ml (supercritical) only moderately affected the destruction efficiencies at both temperatures. Table 2 also contains the results of SCWO of acetic acid by hydrogen peroxide and manganese sulfate ($\text{H}_2\text{O}_2\text{-MnSO}_4$). The destruction efficiencies of acetic acid by $\text{H}_2\text{O}_2\text{-MnSO}_4$ at 400 °C and all five densities were lower as compared to KMnO_4 at either 250 °C or 400 °C. The destruction efficiency obtained from $\text{H}_2\text{O}_2\text{-MnSO}_4$ (35%) was even lower than that from H_2O_2 alone (46% given in Table 3). Manganese sulfate might have played a role of scavenging hydroxyl radicals, and hence inhibiting the destruction of acetic acid under the given SCWO conditions.

TABLE 1

Effect of temperature on destruction of acetic acid by potassium permanganate

Temperature (°C)	250	300	350	400	460
Destruction (%)	40	51	66	79	75

Notes: Density = 0.3 g/ml and reaction time = 6.5 min.

Critical temperature of water = 374.15 °C and critical density of water = 0.322 g/ml [41].

TABLE 2

Subcritical and supercritical water oxidation of acetic acid by KMnO_4 and $\text{H}_2\text{O}_2\text{-MnSO}_4$ at different densities

Oxidant/ catalyst	Destruction efficiency (%) at density (g/ml) of				
	0.2	0.25	0.3	0.35	0.4
KMnO_4 (at 250 °C)	24	45	40	44	39
KMnO_4 (at 400 °C)	71	73	79	81	78
$\text{H}_2\text{O}_2\text{-MnSO}_4$ (at 400 °C)	22	23	35	28	30

Notes: Run time = 6.5 min; pressures = 275–300 bar for supercritical (400 °C) tests and 45–50 bar for subcritical (250 °C) tests. All effluents from KMnO_4 tests contained some dark brown particulates. The density values for subcritical (250 °C) tests only reflect different feed loadings (i.e. 4, 5, 6, 7 and 8 g of feed solution per 20 ml reactor volume), since water is in a two-phase region at this temperature.

The color of the influent and effluent was a distinguishable feature. For example, the color of the water soluble permanganate ion (MnO_4^-), was violet; the insoluble manganese dioxide (MnO_2) was a brownish-black precipitate; and the water soluble manganese acetate [$(\text{CH}_3\text{CO}_2)_2\text{Mn}$] was pale red [42]. The latter was suspected to be present in the reaction mixture. A distinguishable yellow color was observed in the effluents from most tests at densities less than or equal to 0.30 g/ml (resulting from loadings of 4, 5 and 6 g of the feed solution into 20 ml reactors), while the color of the effluents from most tests at densities greater than 0.30 g/ml (resulting from loadings of 7 and 8 g of feed solution into 20 ml reactors) was clear. These unaccounted colors may have resulted from a mixture of different manganese ions or from reactor corrosion products.

3.2 Reaction time and catalytic effects

The reaction rate experiments were performed at a density of 0.3 g/ml and a temperature of 400 °C. The destruction efficiencies given in Table 3 showed no substantial change over the observed reaction times ranging from 2.5 min to 30 min. The initial oxidation reaction was fast, but then stabilized at about 70% to 80% destruction of acetic acid.

SCWO of acetic acid by hydrogen peroxide [4] and oxygen [43] in continuous-flow reactors was evaluated. As a comparison, it was reported that 44% and 58% acetic acid conversion, respectively, with residence times of 1.8 min and 3.7 min were obtained [4]. These tests were conducted at 400 °C, 276 bar, 10% excess (stoichiometric) hydrogen peroxide, premixed in 2500 mg/l acetic acid feed solution. Wightman [43] observed a 32% acetic acid destruction using oxygen at 403 °C, 421 bar, 525 mg/l acetic acid feed concentration, oxygen pressure of 12 bar (at the feed tank), and a 34 s residence time.

TABLE 3

Destruction of acetic acid by different oxidants/catalysts

Oxidant/ catalyst	Destruction efficiency (%) at time (min) of					
	2.5	4.5	6.5	10	15	30
KMnO ₄	77	70	79	76	83	—
H ₂ O ₂	—	—	46	—	62	81
H ₂ O ₂ -Cu (0.1 g)	—	—	69	84	90	—
H ₂ O ₂ -Fe (0.1 g)	—	—	58	68	71	—

Notes: Temperature=400 °C; and densities=0.3 g/ml (H₂O₂ and KMnO₄) and 0.35 g/ml (H₂O₂-Cu and H₂O₂-Fe).

Table 3 also presents test results on the destruction of acetic acid by hydrogen peroxide, hydrogen peroxide plus copper (powder), and hydrogen peroxide plus iron (powder). At a reaction time of 6.5 min, the conversion rate of acetic acid was significantly influenced by the oxidant and catalyst. The destruction of acetic acid by potassium permanganate was nearly twice as high as that exhibited by hydrogen peroxide, 10% higher than that by hydrogen peroxide plus copper, and 20% higher than that by hydrogen peroxide plus iron. As the reaction time increased to 15 min, the level of acetic acid destruction by hydrogen peroxide plus copper increased 21%. Conversely, the conversion for potassium permanganate was only 4%, for hydrogen peroxide 16%, and for hydrogen peroxide plus iron 13%. The results indicated that potassium permanganate was the most effective for the shorter reaction times (less than 10 min). The fact that potassium permanganate was more effective than hydrogen peroxide in the destruction of acetic acid also suggested that oxidation could possibly be catalyzed by manganese dioxide and/or other manganese species.

The reactor inner surface was also evaluated for its catalytic effect on SCWO of acetic acid. During the course of these experiments, it was noted that the reactor surface exhibited a considerable effect on acetic acid destruction. For example, SCWO experiments were first conducted with five new reactors (Type I). Later, fifteen modified reactors (Type II) were made to reduce the dead volume at the reactor head. To test the performance of the modified reactors, experiments were re-run at 250 °C, and a comparison was made with the previous data. Surprisingly, the destruction efficiencies at all densities (except 0.2 g/ml) were drastically reduced (about 50%). However, when Type II reactors were re-used at the same conditions, the destruction efficiencies became comparable with the previous data derived from Type I reactors. It was assumed that the oxidizing nature of potassium permanganate might have caused structural and compositional changes at the inner surface of the reactor (SS 316). These changes created new surfaces and reactive sites which played

a catalytic role in the oxidation of acetic acid, permitting an increase in destruction efficiency. Such conditions did not exist in a new reactor, the oxidation was not catalyzed and, therefore, the destruction efficiency was relatively low.

Lastly, it was reported that the free permanganic acid (likely to be present at pH 3.2) was highly corrosive [34]. However, metallurgical tests performed by Technical Inspection Services, Inc. (Houston, TX), found little evidence of excessive corrosion or cracking in the SS 316 reactor after an accumulative use of 1 hour with potassium permanganate (the initial concentration = 7022 mg/l) at 400 °C.

3.3 Oxidants

In addition to the potassium permanganate experiments, hydrogen peroxide, oxygen and potassium permanganate plus oxygen were evaluated. In the potassium permanganate tests and hydrogen peroxide tests the oxidant was added in stoichiometric amounts. In the case of oxygen, excess oxidant was applied. The effect of different oxidants in conjunction with and without KMnO_4 on acetic acid destruction was studied at selected temperature (400 °C), density (0.30 g/ml) and reaction time (6.5 min). The results given in Table 4 showed that potassium permanganate was more effective than oxygen and hydrogen peroxide. Oxygen resulted in lower destruction levels of acetic acid as compared to hydrogen peroxide, but this difference was probably due to less effective mixing of the oxygen during the heat-up period which was about 30 s. The results implied that potassium permanganate not only provided an oxygen source but also promoted the oxidation. The combination of potassium permanganate and oxygen rendered the highest acetic acid destruction level. Without the presence of an oxidant, acetic acid remained unchanged under all test conditions.

Literature data relating to the oxidation of acetic acid indicated that potassium permanganate was effective with a short residence time (6.5 min) even at subcritical temperatures. For example, at 247 °C, 5000 mg/l acetic acid feed concentration, 10 bar oxygen pressure, and a 6.5 min reaction time, TOC reductions by both $\text{Cu}(\text{NO}_3)_2$ and Co/Bi (5/1) were less than 5%, and TOC reduction

TABLE 4

Comparison of acetic acid destruction efficiencies for potassium permanganate, hydrogen peroxide, oxygen and potassium permanganate + oxygen

Oxidant	None	Air	O_2	H_2O_2	KMnO_4	$\text{KMnO}_4 + \text{O}_2$
Destruction (%)	0	23	34	46	79	89

Notes: Temperature = 400 °C; density = 0.30 g/ml; run time = 6.5 min; initial oxygen pressure = 4 bar; initial air pressure = 1 bar; and both H_2O_2 and KMnO_4 loading = 100% stoichiometric demand.

by Mn/Ce (7/3) was about 40% [24]. Under similar conditions (except for acetic acid feed concentration = 1000 mg/l), potassium permanganate alone destroyed 40% of acetic acid. These results further suggest that oxidation of acetic acid by potassium permanganate involves relatively large rate constants. According to the power law reaction kinetics, large rate constants ensure high oxidation rates even at relatively low reactant concentrations. Based on the results provided in Table 1, the order of destruction effectiveness was found to be $\text{KMnO}_4 > \text{Cu-H}_2\text{O}_2 > \text{Fe-H}_2\text{O}_2 > \text{MnSO}_4\text{-H}_2\text{O}_2 > \text{H}_2\text{O}_2 > \text{O}_2$ at a temperature of 400 °C, a density of 0.3 g/ml and a reaction time of less than 10 min.

3.4 Effect of pH

The pH of the solution was an important factor in the oxidation of acetic acid. The oxidizing ability or catalytic effect of potassium permanganate was largely controlled by pH at the subcritical water conditions. The pH was reported to affect the decomposition of potassium permanganate [34], which in turn established the oxidation rate. The pH of feed solutions containing 1000 mg/l acetic acid was about 3.2. As given in Table 1, acetic acid destruction of 79% was achieved at 400 °C. When pH of feed solutions was adjusted with sodium phosphate to 7 and 11.5, respectively, the destruction efficiencies were 73% and 86%.

These results were in agreement with the fact that most permanganate oxidations of organic compounds are found to be catalyzed by hydroxyl ions. Furthermore, slightly acidic conditions generally stop permanganate action, while in a strong acidic medium permanganate becomes very oxidative [34].

3.5 Economic analysis

The cost-effectiveness of potassium permanganate, hydrogen peroxide and oxygen has been compared for an overall evaluation of the use of these oxidants in SCWO processes. Current market prices of the three oxidants are listed in Table 5. The effective costs have been calculated based on the cost of

TABLE 5

Cost comparison of potassium permanganate, hydrogen peroxide and oxygen

Oxidant	Cost ^a (\$/kg)	Cost (\$/kg O ₂)	Oxidation efficiency (%)	Effective cost ^b (\$/kg O ₂)
KMnO ₄	2.66	17.51	29.6	59.16
H ₂ O ₂ (35% solution)	0.54	3.28	17.3	18.95
O ₂ (Industrial grade)	1.12	1.12	1.1	101.82

^aPrices for KMnO₄ and H₂O₂ were based on truck and tank load quantity (*Chemical Marketing Report*, April 20, 1992), and price for oxygen was based on cylinder quantity (Big-Three Industries, Inc.).

^bEffective cost is defined as Cost/kg O₂ divided by the oxidation efficiency.

the actual amount of oxygen generated over the oxidation efficiency defined as,

$$\text{Oxidation efficiency (\%)} = \Delta\text{TOC}(\text{mg/l}) / \text{available O}_2 (\text{mg/l}) \times 100 \quad (3)$$

where the values for ΔTOC have been calculated from the destruction efficiency data given in Table 4 and the values for available O_2 have been calculated from the oxidant loading in each test.

Equations 1 and 2 were used for evaluating the oxygen equivalency of potassium permanganate. Similarly, a simplified equation for hydrogen peroxide decomposition ($\text{H}_2\text{O}_2 \rightarrow \frac{1}{2}\text{O}_2 + \text{H}_2\text{O}$) was assumed in the calculation of the cost per unit mass of oxygen generated. Oxygen appeared to have the lowest bulk cost among these oxidants, but the effective cost for oxygen was the highest. In addition, the use of oxygen required higher capital cost because of the pressure boosting system. If the destruction efficiency of these oxidants is considered, potassium permanganate may become a practical oxidant for SCWO of organic compounds. Because of the effectiveness of potassium permanganate, this potential may become more attractive when the organic concentration is relatively low.

4. Conclusions

At SCWO conditions (400 °C and 0.3 g/ml), the destruction of acetic acid by potassium permanganate was about 80% for a residence time of 2.5 min, while at a subcritical temperature (250 °C) the acetic acid destruction efficiency was only about 40%. In all SCWO tests, the destruction efficiencies with potassium permanganate were higher than those obtained from either oxygen or hydrogen peroxide. This fact also suggests that the oxidation be promoted by manganese dioxide and other manganese species. The order of destruction effectiveness was found to be $\text{KMnO}_4 > \text{Cu-H}_2\text{O}_2 > \text{Fe-H}_2\text{O}_2 > \text{MnSO}_4\text{-H}_2\text{O}_2 > \text{H}_2\text{O}_2 > \text{O}_2$ at a temperature of 400 °C, a density of 0.3 g/ml and a reaction time of less than 10 min. Potassium permanganate is an effective SCWO oxidant and under certain conditions it may be feasible. This oxidant is particularly applicable when the organic concentration is low.

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