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Research Article

Study on Supercritical Water Oxidation of Oily Wastewater with Ethanol

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Abstract: The conventional treatments are unable to effectively remove the Chemical Oxygen Demand (COD) of oily wastewater, which has seriously threatened the environment and the normal production of oil field. In this paper, an advanced method was proposed for oily wastewater treatment, Supercritical Water Oxidation (SCWO). The co-oxidative effect of ethanol on oily wastewater is characterized for the initial COD of oily wastewater (4000 mg/L) and ethanol concentration (20 mg/L) for a range of temperatures (390°C-450°C), a pressure of 23 Mpa for the complete combustion of both ethanol and oily wastewater. High concentrations of ethanol caused an increase in the conversion of oily wastewater at T = 450°C, p = 23 MPa and t = 9 min, the oily wastewater removal increases 8%.

Keywords: Co-oxidation, ethanol, oily wastewater, removal, supercritical water oxidation

INTRODUCTION

With the development of economy and water transport, consumption of petroleum and related fabricated products keeps increasing. This will bring out great deal of oily wastewater, resulting in serious environmental pollution. At present, the conventional oily wastewater treatment processes include air floatation, membrane separation, chemical coagulation, chemical oxidation, physical adsorption, biodegradation and so on Hongliang and Guoyi (2011). However, these traditional technologies have often encountered some problems, such as complex procedures, poor performances, high management requirement (Gu *et al.*, 2002). Supercritical Water Oxidation (SCWO) can oxidize organic waste in an aqueous mediumat temperatures (>374.3°C) and pressures (>22.1 Mpa). Oxygen or peroxide is used as oxidants. SCWO is applied to destroy a lot of organic wastes. When residence time is shorter than 1 min, removal efficiency of organic wastes is able to get to 99% (Tester and Cline, 1999; Kritzer and Dinjus, 2001). SCWO is clean, pollution-free and environmentally friendly for treating the organic waste. It has a unique effect on treating toxic and biodegradable organic waste. The organic wastes will be treated for CO_2, H_2O and N_2 when SCWO is applied. Therefore, secondary pollution will disappear. Technology for treating polluted water by SCWO is a deep oxidation technology proposed by Medoll (1982) in 1982, structure of organic waste is completely destroyed and the reaction is completed very shortly. Currently, treatment of rocket fuels; industrial waste and physiology garbage (Takahashi *et al.*, 1991) by SCWO is accomplished in the USA. Polymers (Masaru *et al.*, 2001) and dioxins (Linghui *et al.*, 2000) treatment by SCWO is implemented in many European countries. A lot of scientific and technological workers (Botao *et al.*, 2002; Yanhua *et al.*, 2010; Veriansyah and Kim, 2007) have achieved satisfactory results about SCWO in recent years.

Currently, SCWO of oily waste water with ethanol is not reported. The function of ethanol is not yet well known. This study investigated the oxidation effect of methanol on oily wastewater under supercritical conditions, which contained reaction products and pathways in the presence of methanol. Accordingly, this study focused on COD removal of oily wastewater in the presence of ethanol.

It is well known that the oxygenated additivecan improve the oxidation efficiency of organic compounds in combustion (Jason *et al.*, 2006) and people found that the oxygenated additivecangain similar effects in SCWO. The results are expressed in some studies (Phillip *et al.*, 2000) Researchers firmly believe that the oxidation mechanism of SCWO is similar with combustion.

In the past years, methanol benzene and phenol (Ivette *et al.*, 2004) were investigated as oxygenate additive. The oily wastewater contained substances other than oil, including natural petroleum, petroleum products, tar and its fractions, as well as consumption of animal and vegetable oils and fats. From water pollution, oil and tar, the concentration of oil substances contained in the wastewater discharged from various industrial sectors very different. The wastewater produced in the refining process, oil is about 150 to 1000 mg/L and the coking plant wastewater tar content of approximately 500 to 800 mg/l, up to 2000 to 3000

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mg tar content in the gas generating station discharged wastewater/liter. Therefore, ethanol is used in this experiment as oxygenate additive.

The aim of this study was at investigating the performance of ethanol in SCWO of oily waste water and testing the applicability of SCWO process as a treatment for remediation of oily contaminants. The influence of reaction temperature, reaction time, initial COD of the oily waste water and hydrogen peroxide excess (HE) on COD removal of the oily waste water was investigated.

EXPERIMENTAL

Feature of the oily wastewater: The oily wastewater sample is taken from oil fields. The oily wastewater sample contains water 59.1wt%, crude oil 40.9 wt%.

Experimental procedure: Figure 1 is the installation drawing of SCWO reactor.

The material of the installation is 1Cr18Ni9Ti and volume of the reactor is 0.8 L. The intermittent installation for SCWO of oily wastewater contains a heater, reactor, separator for gas and liquid, bottle of Nitrogen storage, container of hydrogen peroxide, controller and high pressure pump. We choose hydrogen peroxide as oxidant of experiment. Thermocouple and pressure transducer are used to measure reaction pressure and reaction temperature. Before the experiment is started, the installation is needed to flow by a certain amount of nitrogen to make sure that the air does not exist in the installation. And then oily wastewater is added to reactor by the graduate. Hydrogen peroxide is injected into the reactor by high pressure pump. Finally, screw is tightened and the valve is closed. When the reaction pressure and reaction temperature of experimental setting value is reached, the experiment is stopped. After that, the valve is opened to take out the liquid for analysis.

Experimental conditions choice:
Temperature: Reactor design temperature is 500°C; this operational parameter is selected in the range [390°C, 450°C] of the reaction temperature. Experimental results show that the COD removal of oily wastewater has appeared obvious changes with the reaction temperature of 20°C interval.
The experiments are implemented at 390, 410, 430, 450°C, respectively and at 23 MPa. The reaction apparatus has good stability, so the range of temperature and pressure is1-2°C and 0.5-1MPa, respectively.

Pressure: The working pressure of the reactor is 40MPa, mostly, pressure under SCWO is from 22MPa to 30MPa and the removal has increased with increasing pressure. But operability is reduced and risk is increased when pressure is increased further. So the operating pressure is identified as in the range [22 MPa, 30 MPa]. The COD removal of oily wastewater has increased when pressure is increasing, when the pressure is more than 23 MPa; the COD removal of oily wastewater was gentle upward trend. So 23 MPa is selected as reaction pressure.

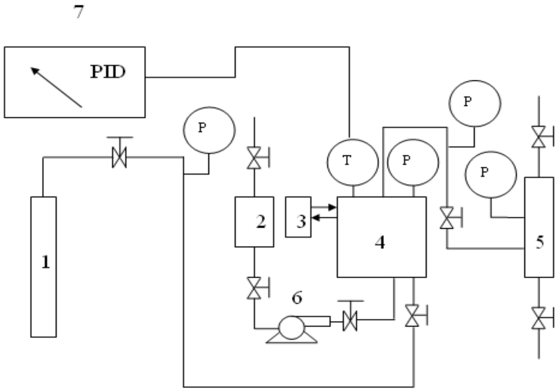

Fig. 1: The installation drawing of SCWO reactor 1; bottle of nitrogen storage, 2; container of hydrogen peroxide, 3; heater, 4; reactor, 5; separator for gas and liquid, 6; high pressure pump and 7; controller

Reaction time: Reaction time is one of the import factors of the impact of the COD removal of oily wastewater, it is crucial that a suitable reaction time is decided in the experiment. The reaction time is identified as in the range [1 min, 9 min] and the COD removal of oily wastewater has increased with increasing reaction time.

Oxygen excess: The influence of Oxygen Excess (OE) on the removal efficiency of wastes is applied to the lot of experiments that is widely reported in many studies.
The OE is defined by the relationship (Cocero *et al*., 2002):

$$OE = O_{2,Excess} = \frac{(O_2)_{in} - (O_2)_{stoichiometric}}{(O_2)_{in}} \times 100 \tag{1}$$

In experiment, the oxidant chosen is hydrogen peroxide and formula (1) is instead of formula (2):

$$HE = H_2O_{2,Excess} = \frac{(H_2O_2)_{in} - (H_2O_2)_{stoichiometric}}{(H_2O_2)_{in}} \times 100 \tag{2}$$

This parameter is identified as in the range [0, 100%] of the stoichiometric amount and we can notice that total crude oil removal increases when concentration of hydrogen peroxide increases. Total crude oil removal increases slowly and is negligible when HE is more than 70%. So HE is selected for 70% in the experiment.

RESULTS AND DISCUSSION

COD removal affected by reaction temperature and reaction time: The results are given in Fig. 2. As expected, rising temperature increased the COD removal. At 450°C the COD removal reached about 82 and 90% after 1and 9 min, respectively. Therefore, temperature had a significant impact on the oxidation of oily wastewater.

That is because when the temperature increases, the rate of all reaction accelerates. Eventually, it will accelerate the degradation rates of organic matter in oily wastewater. Therefore, when the temperature is higher, COD removal increases faster.

Figure 2 showed that COD removal of oily wastewater increases rapidly at first of 1 min and it becomes slow. When the reaction time is 1min, the COD removal reached about 70%. But the COD removal reached about 71% after 3 min. It is need to be considered from the perspective of the reaction rate. The concentration of the reactant is bigger; response rate of overall reaction is soon. As the reaction proceeds, the concentration of the reactants is reduced; the reaction rate starts to slow down. Therefore, COD removal of oily wastewater increases rapidly at first of 1 min and it becomes slow.

COD removal of oily wastewater affected by HE: Figure 3 indicates that COD removal increases when HE increases. When HE is above 70%, the upward trend of COD removal becomes gentle. When HE is 70% and reaction time is 1 min, COD removal is 76.30%. When HE is 90% and reaction time is 1 min, COD removal is 77.31%. COD removal only increases by 1.01%. Therefore, HE is selected for 70%.

The reason is that the dissolved oxygen will increase in the reaction system when HE increases, which is conducive to form strong oxidizing group ($O_2 \bullet^-$, $HO_2 \bullet$, $OH \bullet$, etc.). Therefore, we need high HE to form more strong oxidizing group for improving the oxidation efficiency of the oily wastewater.

COD removal of oily wastewater affected by initial COD of oily wastewater: Foe Fig. 4, it is seen that COD removal increases when initial COD increases. When initial COD of oily wastewater reaches 1000 mg/L, the COD removal reaches 69.40%.When initial COD of oily wastewater reaches 4000 mg/L, the COD removal reaches 90.26%. Content of the oil system in 3000 mg/L-4000 mg/L, the upward trend of the COD removal is gentle.

The reason is that when concentration of oily wastewater increases, activated molecular in unit volume will increase quickly, which makes effective collision more active and increases reaction probability of particles. There by the oxidation rate speeds up and oxidation effect of oily wastewater is promoted. Therefore, SCWO is suitable for high concentration of oily waste water treatment.

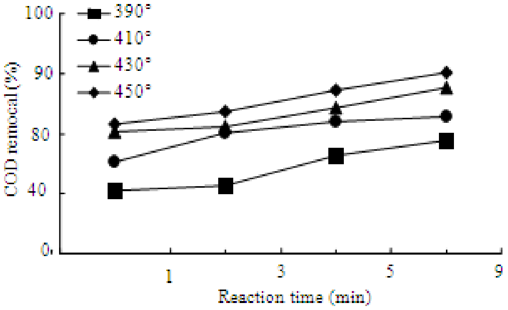

Fig. 2: Effect of temperature on SCWO of oily wastewater

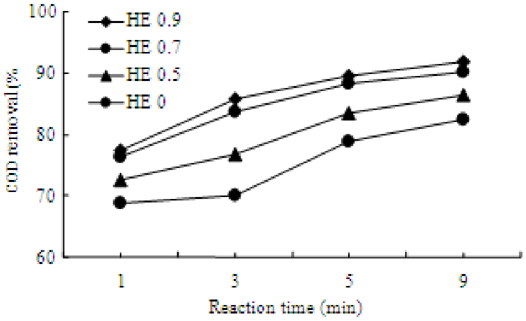

Fig. 3: Effect of HM on SCWO of oily wastewater

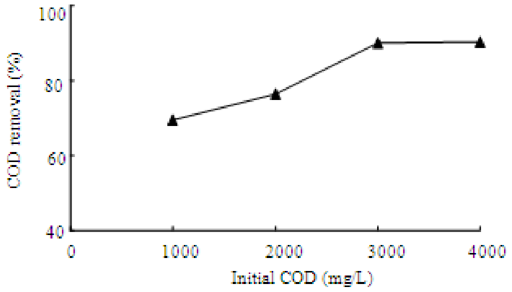

Fig. 4: Effect of initial COD on SCWO of oily wastewater

COD removal of oily wastewater affected by ethanol: Table 1 shows the COD removal of oily wastewater in SCWO of oily wastewater in relation to the effect of temperature from 390°C to 450°C without ethanol, or with ethanol. Experimental results show that the COD removal increases when reaction temperature increases. Table 1 also shows the COD removal in supercritical water oxidation of oily wastewater in relation to the effect of reaction time from 1 min to 9 min without ethanol, or with ethanol. There is 20 mg/L of ethanol in supercritical water oxidation of oily wastewater with ethanol.

The main gases produced are carbon dioxide and carbon monoxide. As the crude oil becomes increasingly oxidsed with the increasing temperature and increasing pressure of system, increasing amount of carbon dioxide and decreasing amount of carbon monoxide are produced. Correspondingly, there is a

Table 1: The COD removal is effected by ethanol

Reaction temperature (T/°C)	Reaction pressure (P/MPa)	Initial COD (mg/L)	Hydrogen peroxide excess (%)	Reaction time (t/min)	COD removal without ethanol (%)	COD removal with 20 mg/L of ethanol (%)
390	23	4000	70	1	70.61	70.92
				3	71.43	73.36
				5	75.41	79.41
				9	78.93	81.53
410	23	4000	70	1	75.34	76.31
				3	80.36	84.55
				5	82.16	85.66
				9	82.99	86.32
430	23	4000	70	1	80.37	83.78
				3	81.25	88.76
				5	84.44	91.53
				9	89.33	96.44
450	23	4000	70	1	81.67	88.55
				3	83.88	90.93
				5	87.36	93.77
				9	90.26	98.26

decrease in the concentration of crude oil in oily wastewater. The formation products from the decomposition of crude oil in the liquid phase are mainly acetic acid.

Experimental results show that the supercritical water oxidation of oily wastewater system by adding a small amount of ethanol can be a certain extent, raise the COD removal of oily wastewater. The high concentrations of ethanol causes an increase in the COD removal of oily wastewater at T = 450°C, p = 23 MPa and t = 9 min from 90.26% without ethanol present to 98.26% with 20 mg/L of ethanol, the COD removal increases 8%.

MECHANISM OF SCWO OF OILY WASTEWATER WITH ETHANOL

SCWO of oily wastewater and SCWO of ethanol-oily wastewater are different. While ethanol can produce more free radicals involved in oily waste water treatment during SCWO of ethanol-oily wastewater.

Radical reaction mechanism is proposed by Li, the oxygen free radicals attack the weak organic molecules of the C-H bond. Responses indicate the entire process is as follows:

$$RH + O_2 \rightarrow R\bullet + HO_2\bullet \quad (3)$$

Hydrogen peroxide is further decomposed into hydroxyl radical (HO•):

$$2H_2O_2 + M \rightarrow 2HO\bullet \quad (4)$$

M can be homogeneous or heterogeneous interface. Under the reaction conditions, hydrogen peroxide can also be pyrolysis to hydroxyl radical. Hydroxyl radical has a strong pro-electrical, electronic affinity for 586KJ, standard electrode potential of 2.8V and it is a strong oxidizing species oxides. Almost all of the hydrogen compounds are oxidized by hydrogen radical, their gradual dehydrogenation, decarbonization, until thoroughly oxidized:

$$RH + HO\bullet \rightarrow R\bullet + OH_2 \quad (5)$$

The radical (R•) that it is generated in Formula (3) and (5), can react with O_2 to generate peroxide radicals and the peroxide radicals can capture hydrogen atomic to form peroxide radicals and peroxide compounds:

$$R\bullet + O_2 \rightarrow ROO\bullet \quad (6)$$

$$ROO\bullet + RH \rightarrow ROOH + R\bullet \quad (7)$$

Peroxide radicals and compounds are usually divided into smaller molecular compounds, which continue to fast fracture, until formic acid or acetic acid production and formic acid or acetic acid is oxidation of the end of CO_2 and water. The radical (HO•) and ($HO_2\bullet$) in the chain reaction is essentially through H removal mechanism achieved.

When hydrogen peroxide is injected into the reactor, the hydrogen peroxide is decomposed into O_2 and O_2 reacts with the organic reaction as the formula (3) showing. Accordingly, possible free radical reactions of oily waste water in the presence of ethanol are following:

$$CH_3CH_2OH + O_2 \rightarrow CH_3CHO + H_2O \quad (8)$$

$$R\bullet + CH_3CHO \rightarrow CH_3\text{-}R + CHO\bullet \quad (9)$$

$$R\bullet + CHO\bullet = R\text{-}CHO \quad (10)$$

$$HCHO + 2OH\bullet = CO_2 + H_2O + 2H\bullet \quad (11)$$

$$O_2 + H\bullet = OH\bullet + O\bullet \quad (12)$$

Ethanol has increased oily waste water removal, because ethanol may be small molecules, they more readily react with hydrogen peroxide and oxygen and produce more free radicals. They has not only promoted the reaction rate of the oily wastewater, but also increased the COD removal. The COD removal is 98.26% in co-oxidation of oily wastewater and ethanol at 23 MPa and the COD of emission water is below the

20 mg/L and the water can be discharged and will not pollute the environment.

CONCLUSION

An advanced method for oily wastewater treatment, Supercritical Water Oxidation (SCWO), was proposed. The co-oxidative effect of ethanol on oily wastewater is characterized for the initial COD of oily wastewater (4000 mg/L) and ethanol concentration (20 mg/L) for a range of temperatures (390°C-450°C), a pressure of 23 Mpa for the complete combustion of both ethanol and oily wastewater. SCWO is considered as a treatment method to convert bioresistant organics to more readily biodegradable intermediates, knowledge of the impact of the operating conditions such as temperature, the initial COD, reaction time and HE, is required. Experimental results indicated that in the SCWO process, 90.26% Chemical Oxygen Demand (COD) removal was obtained after 9 min reaction at temperature of 450°C, HE of 70% and the initial COD of 4000 mg/L.

Ethanol accelerates the destruction of oily wastewater. Significantly higher COD removal with ethanol is found compared without ethanol: 8% increase.

The study investigatedthe reaction pathways about SCWO of oily wastewater. Because of the reaction of the ethanol, less toxic intermediates are produced and the it is a radical reaction.

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