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Petroleum Refinery Effluents Treatment by Advanced Oxidation Process with Methanol

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ABSTRACT. Petroleum refinery effluents are waste originating from industries primarily engaged in refining crude oil. It is a very complex compound of various oily wastes, water, heavy metals and so on. Conventional processes are unable to effectively remove the chemical oxygen demand (COD) of petroleum refinery effluents. Supercritical water oxidation (SCWO) was proposed to treat petroleum refinery effluents. In this paper, methanol was used to investigate co-oxidative effect of methanol on petroleum refinery effluents treatment. The results indicated that supercritical water oxidation is an effective process for petroleum refinery effluents treatment. Adding methanol caused an increase in COD removal. When reaction temperature is 440 °C, residence time is 20 min, OE is 0.5 and initial COD is 40000 mg/L, and COD removal increases 8.5%.

Key words: Petroleum refinery effluents, Advanced Oxidation Process, SCWO, COD removal

INTRODUCTION

Petroleum refinery effluents (PRE) are wastes originating from industries primarily engaged in refining crude oil and manufacturing fuels, lubricants and petrochemical intermediates.[1] These effluents are a major source of aquatic environmental pollution.[2] The effluents are composed of oil and grease along with many other toxic organic compounds. Although concerted efforts have been made to replace fossil fuels, crude oil remains an important rawmaterial. The need to satisfy the ever-increasing global energy demand, which is expected to soar by 44% over the next two decades,[3] makes the processing of crude oil and the generation of PRE globally important issues.

The process of refining crude oil consumes large amounts of water. Consequently, significant volumes of wastewater are generated,[4] 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.[5] However, these traditional technologies have often encountered some problems, such as complex procedures, poor performances, and high management requirement.[6]

SCWO is a deep oxidation technology proposed by Modell[7] in 1982, it can completely and thoroughly destroy the structure of organic effluent, and the reaction completes in a very short time. Most hydrocarbons and oxygenated hydrocarbons are converted to CO_2 and H_2O. Nitrogen in the feed is converted to N_2 or N_2O. Heteroatoms in the feed such as chlorine, sulfur, or phosphorus are converted to their corresponding mineral acids (HCl, H_2SO_4, or H_3PO_4) or salts if pre-neutralized with base. Typical operating conditions are usually well above the critical point in the range of 500–650 °C and 250–300 bar, with reactor residence times under one minute for complete destruction. Under these conditions, dioxins, furans, NOx and other noxious by-products that plague incineration-based processes do not form in SCWO.[8]

After 1982, the researchers began to study nuclear waste, and later SCWO is widely used petrochemicals, paper mills, hospitals, electronics, industrial and domestic wastewater.[9–10] Currently, treatment of rocket fuels, industrial waste and physiology garbage[11] by SCWO is accomplished in the USA. Polymers[12] and dioxins[13] treatments by SCWO are implemented in many European countries. Many scientific and technological workers[14–20] have achieved satisfactory results about SCWO in recent years.

It is well known that the oxygenated additive can improve the oxidation efficiency of organic compounds in combustion,[21,22] and the oxygenated additive can gain similar effects in SCWO. The results are expressed in some studies.[23–25] Researchers firmly believe that the oxidation mechanism of SCWO is similar with combustion.

In the past years, methanol benzene, and phenol[26] were investigated as oxygenate additive. Currently, SCWO of petroleum refinery effluents with methanol is not reported. The function of methanol has not yet well known. This paper investigated the oxidation effect of methanol on petroleum refinery effluents under supercritical conditions, which contained reaction products and pathways in the presence of methanol. Accordingly, this paper focused on COD removal of petroleum refinery effluents in the presence of methanol.

EXPERIMENTAL

Materials and Methods

SCWO experiments

SCWO of the petroleum refinery effluents was carried out in a 0.6L batch autoclave (*Fig*. 1). Firstly, water and petroleum refinery effluents were put into the reactor, and then the system was flowed by nitrogen to remove the air within the system; the valves around the reactor were closed when the air was removed entirely. Secondly, a specific amount of required methanol was put into the reactor. Finally, pure O_2 was put into the reactor until the predefined pressure was reached, and the reaction started. Liquid samples (ca.15 mL) were periodically withdrawn from the reactor and analyzed.

Analytical methods

The COD of collected liquid are measured by potassium dichromate method of Chinese Standard 11914-89. OE is defined as equation 1.

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

RESULTS AND DISCUSSION

SCWO of Petroleum Refinery Effluents

Effect of reaction temperature

The experimental results are given in *Fig*. 2. As it is expected, rising temperature made the COD removal greatly increased. At 440 °C, COD removal reached more than 80% after 5 and 20 min, respectively. Therefore, temperature had a significant impact on the oxidation of petroleum refinery effluents.

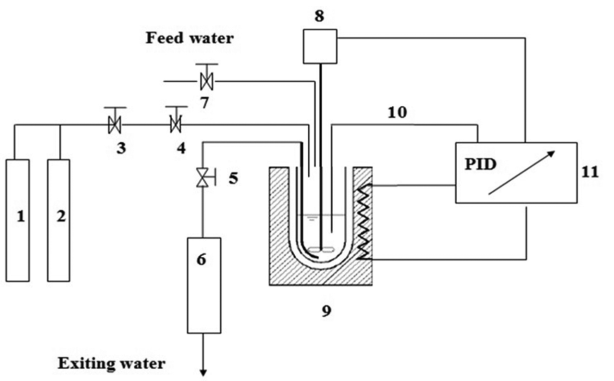

***Figure* 1.** Schematic diagram of the experimental setup.

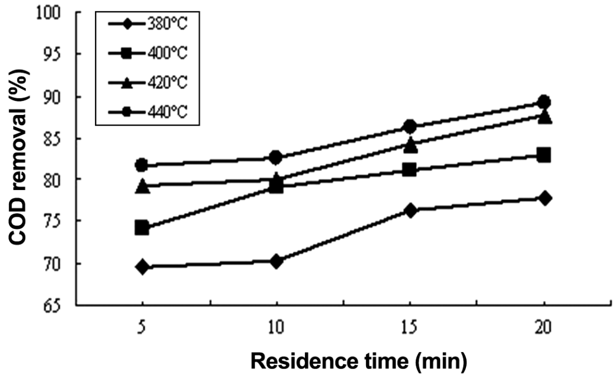

***Figure* 2.** Effect of temperature on SCWO of petroleum refinery effluents.

According to the thermodynamic and kinetic principles, it is known that rate of all reaction will accelerate as temperature increasing. Eventually, it can accelerate the degradation of oily matter. Therefore, the temperature is higher, COD removal increases faster. When reaction temperature comes to 440 °C, COD removal reaches 90.33%.

Effect of residence time

In *Fig*. 2, it is seen that at first of 5 min, the COD removal reached about 70%. The COD removal reached about 80% after 15 minutes. It is need to be considered from the perspective of the reaction rate. The concentration of the reactant is high at first, so the response rate is slow. As the reaction proceeds, the concentration of the reactants reduced. So the reaction rate starts to react quickly. Therefore, COD removal increased slowly at first of 5 min, and it became quickly afterwards.

Effect of initial COD

It is seen that COD removal increases as initial COD increasing from *Fig*. 3. When initial COD is 10000 mg/L, the COD removal reaches 69.51%.When initial COD is 40000 mg/L, the COD removal reaches 90.33%. When initial COD is between 30000 mg/L and 40000 mg/L, the upward trend of the COD removal is gentle.

According to the kinetic principles, it is known that COD concentration of petroleum refinery effluents increases, activated molecular generated quickly and the numbers of them are more. Therefore, effective collision presented more active and reaction probability of particles becomes larger. Thereby the oxidation rate speeds up and oxidation

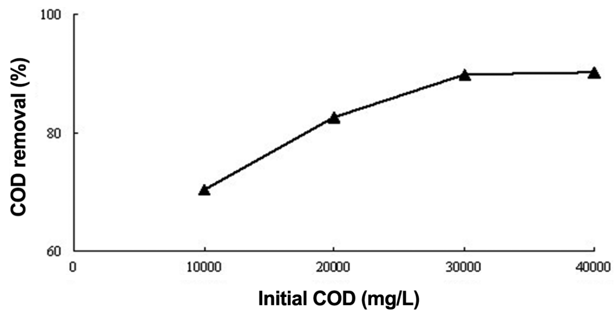

***Figure* 3.** Effect of initial COD on SCWO of petroleum of refinery effluents.

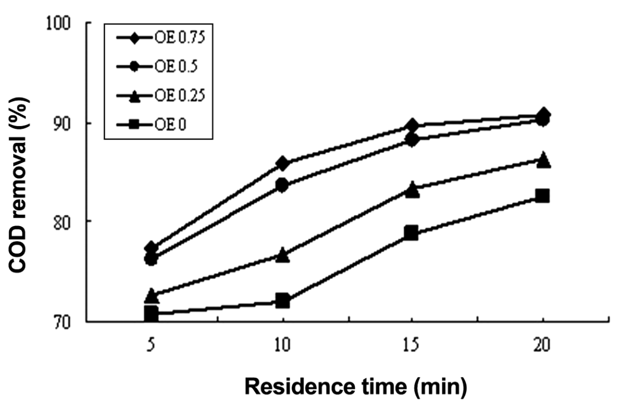

***Figure* 4.** Effect of OE on SCWO of petroleum refinery effluents.

effect of petroleum refinery effluents promoted.

Effect of OE

Fig. 4 indicates that COD removal increases when OE increases. When HE is above 0.5, the upward trend of COD removal becomes gentle. When OE is 0.5 and residence time is 20 min, COD removal is 76.11%. When OE is 0.7 and residence time is 20 min, COD removal is 76.76%. COD removal only increases by 0.65%. Therefore, OE is selected for 0.5.

Co-oxidation of Petroleum Refinery Effluents

Effect of methanol

Table 1 showed the COD removal without methanol and adding methanol. It is showed that adding a small amount of methanol can raise the COD removal. The high concentrations of methanol causes an increase in the the COD removal of at 440 °C, residence time is 20 min, OE is 0.5 and initial COD is 40000 mg/L. COD removal increases 8.5% with adding 200 mg/L of methanol.

CONCLUSION

SCWO of petroleum refinery effluents co-oxidative effect of methanol on petroleum refinery effluents were investigated. The results showed that greater than 80% COD removal from petroleum refinery effluents was achieved via SCWO. The results indicated that supercritical water oxidation is an effective process for petroleum refinery effluents treatment. Adding methanol caused an increase in COD removal. When reaction temperature is 440 °C, residence time is 20 min, OE is 0.5 and initial COD is 40000 mg/L, and COD removal increases 8.5%.

***Table* 1.** The COD removal is effected by methanol

Reaction temperature (T/°C)	Initial COD (mg/L)	OE	Residence time (t/min)	COD removal without methanol (%)	COD removal with 200 mg/L of methanol (%)
380	40000	0.5	5	70.77	70.95
			15	71.54	73.42
			20	75.33	79.51
			25	78.88	81.64
400	40000	0.5	5	75.46	76.44
			15	80.41	84.66
			20	82.18	85.77
			25	82.79	86.43
420	40000	0.5	5	80.41	83.87
			15	81.36	88.88
			20	84.55	91.62
			25	89.47	96.55
440	40000	0.5	5	81.75	88.63
			15	83.99	90.87
			20	87.41	93.62
			25	90.33	98.83

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