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Oxidation of oily sludge in supercritical water

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ABSTRACT

The oxidation of oily sludge in supercritical water is performed in a batch reactor at reaction temperatures between 663 and 723 K, the reaction times between 1 and 10 min and pressure between 23 and 27 MPa. Effect of reaction parameters such as reaction time, temperature, pressure, O_2 excess and initial COD on oxidation of oily sludge is investigated. The results indicate that chemical oxygen demand (COD) removal rate of 92% can be reached in 10 min. COD removal rate increases as the reaction time, temperature and initial COD increase. Pressure and O_2 excess have no remarkable affect on reaction. By taking into account the dependence of reaction rate on COD concentration, a global power-law rate expression was regressed from experimental data. The resulting pre-exponential factor was $8.99 \times 10^{14}\,(\mathrm{mol\,L^{-1}})^{-0.405}\,\mathrm{s^{-1}}$; the activation energy was 213.13 ± 1.33 kJ/mol; and the reaction order for oily sludge (based on COD) is 1.405. It was concluded that supercritical water oxidation (SCWO) is a rapidly emerging oily sludge processing technology.

1. Introduction

Oily sludge is one of the largest categories of wastes generated by oil industry petroleum production and petroleum refinery plant. The main source of oily sludge is tank bottoms. Other sources include API separator bottom, operating slop, oil spills, operating residues and other miscellaneous sources [1,2]. The composition of the oily sludge is complex and depends on the type of petroleum and its source. Generally, it contains waste oil 5–60 wt%, water 30–90 wt% and mineral particles 5–40 wt% [3]. This waste oil is a mixture of compounds, mainly hydrocarbons. Advance analyses on waste oil showed that it is composed of 40–52 wt% alkane, 28–31 wt% aromatics, 7–22.4 wt% resins, and 8–10 wt% asphaltenes [4,5]. Many of these components are toxic, mutagenic and carcinogenic [6–8]. Therefore, their release to the environment is strictly controlled and they are classified as priority environmental pollutants by the US Environmental Protection Agency, due to posing a serious threat to the environment [9].

The treatment and disposal of oily sludge represents major challenges for petroleum industries. The oily sludge consumes a high portion of budget of oil production plant and refiner. Several conventional technologies, such as landfill, biological treatment, incineration and so on, for the treatment and disposal of oily sludge have been implemented. Various treatment options are compared in terms of their effectiveness, ease of operation, and cost. Of the technologies mentioned above, landfill is a cheap and straightforward treatment method for oily sludge. However, without volume reduction and appropriate treatment before disposal, oily sludge will reduce the service-life of landfill sites and may result in an odor problem and create the risk of contamination, particularly of ground water, thus causing adverse health effects. Biological treatment of organic pollutants is a promising, reliable, simple and cheap technology over chemical and physical processes [10–12]. However, it is reported as being very difficult or non-practical because it takes a relatively long time to treat and the removal rate is low [13–15]. Incineration is a valuable means of waste disposal with the advantage of being highly effective in reducing the volume of waste. Unfortunately, incinerators generate large volumes of off-gases containing polycyclic aromatic hydrocarbons. Furthermore, the auxiliary fuel must be added to the incinerator to keep the incineration temperature constant [16]. As mentioned above, no technology currently has reached a satisfactory solution from the environmental and highly effective point of view. Consequently, there is a need for environmentally benign technologies capable to effectively neutralize the oily sludge and reduce its adverse impacts on the environment.

Supercritical water oxidation (SCWO) has been drawing much attention due to its capability to effectively destroy a large variety of high-risk wastes resulting from complex industrial chemical and regarded as one of the promising technologies for alternative

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Table 1
Studies on SCWO of petroleum hydrocarbons and oily wastes or sewage found in literature.

Reactant	*T* (K)	*p* (MPa)	Reaction time (s)	Oxidant	Reactor type	Results	References
Benzene	750–860	13.9–27.8	3–7	O_2	–	Benzene conversion is above 95%	[23]
Pyrene	473–653	9.5–22.5	0–7200	H_2O_2	Batch	Rapid dissolution and oxidation of pyrene started from 573 K	[17]
Biphenyl, fluorene, hexadecane, eicosane	573–653	10.5–22.5	0–3600	H_2O_2	Batch	Conversion of the feeds is 99%	[24]
PAHs[a]	658–698	26.5–32	18–169	H_2O_2	Continuous	Conversion of PAHs is 97–99.9%	[25]
Cutting oil waste	573–773	–	5.9–40.2	H_2O_2, O_2	Continuous	TOC[b] removal is above 90%	[18]
PAHs in real soil	658–698	26–30	35–246	H_2O_2	Continuous	TOC removal is 91%	[26]
Oil-bearing sewage	663–703	24–28	30–90	H_2O_2	Batch	COD[c] removal is approach to 90%	[27,28]
Waste drilling fluid	773–873	25–30	30–600	O_2	Continuous	COD removal is above 93%	[29]

[a] Polynuclear aromatic hydrocarbons.
[b] Total organic carbon.
[c] Chemical oxygen demand.

to incineration [17–20]. SCWO uses water above its critical point (647 K, 22.1 MPa) as a reaction medium where both gases, oil and aromatics form a homogeneous single phase, thus avoiding interfacial mass transfer limitations. At supercritical operation conditions, oxidation proceeds quickly and completely by converting most H–C–N compounds to water, carbon dioxide, and molecular nitrogen as the main products [21]. The output liquid effluent and gas effluent can be released in natural media without post-treatment [22].

Studies on SCWO of petroleum hydrocarbons and oily wastes or sewage are summarized in Table 1. These results in Table 1 suggest that SCWO may be suitable for decomposing petroleum hydrocarbons and treating real oily wastes or sewage.

However, there are no references in the literature about SCWO of oily sludge. In this study, we are first to, discuss the effect of reaction time, temperature, pressure, O_2 excess and initial COD on SCWO of oily sludge in a batch reactor; and second, to investigate kinetics of oily sludge for oxidation in supercritical water. The information obtained so far is useful in the development of the method and equipment for the needs of larger scale operation.

2. Experimental

2.1. Apparatus and procedure

The experiments were conducted in a laboratory-scale, batch reactor with a volume capacity of 650 mL designed to a maximum temperature and pressure of 723 K and 40 MPa. The flow diagram of the experimental setup is shown in Fig. 1. All wetted parts, from the pumps to the condenser, were made of stainless steel (1Cr18Ni9Ti). The stirrer was used to keep from the formation of char resulting from thermal cracking of oily sludge at the walls of the reactor. The electric furnace was used as heater. The heating wires of electric furnace were placed below and around the reactor. The reaction temperature was monitored directly using thermocouple (inserted inside the reactor) and controlled within 1 K by a temperature controller (Shanghai Yatai Instrumentation Co., N-8000 Digital Controller). Before the experiment, the reactor was loaded with oily sludge and deionized water to bring the total volume of liquid to 95–130 mL, and concentration of oily sludge is approximately corresponding to initial COD of 1500–2250 mg/L. Then, nitrogen gas was used to purge the reactor for 10 min. After purging, the reactor was heated for about 65 min. Upon reaching the reaction condition of reaction temperatures from 663 to 723 K and pressures from 23 to 27 MPa, reaction temperature remained stable within 1 K, then the specified amount of H_2O_2 was pressured and fed into the reactor using a syringe pump within 2 s at room temperature. The reaction was conducted for a given reaction time from 1 to 10 min. After the reaction, the sample valve of reactor was opened and the effluent was cooled rapidly in a shell and tube heat exchanger and then depressurized to ambient condition. The product stream was then separated into liquid and vapor phases. The liquid products were collected in a graduated cylinder. Gaseous samples were collected with sample tubes.

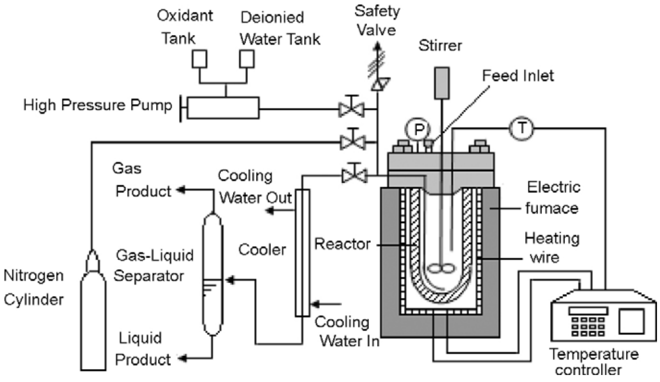

Fig. 1. Schematic diagram of the experimental setup.

The COD removal rate, product yield and O_2 excess are defined as follows:

$$\text{COD removal rate}\,(\%) = \frac{[\text{COD}]_0 - [\text{COD}]_t}{[\text{COD}]_0} \times 100 \tag{1}$$

where $[\text{COD}]_0$ and $[\text{COD}]_t$ are chemical oxygen demand of oily sludge at reaction time of 0 and *t* min, respectively (mg/L).

$$\text{Product yield}\,(\%) = \frac{[\text{C}]}{[\text{C}]_0} \times 100 \tag{2}$$

where $[\text{C}]_0$ and [C] are carbon concentration in oily sludge and products such as carbon dioxide, carbon monoxide and acetic acid, respectively (mg/L).

$$O_2\ \text{excess}\,(\%) = \frac{[O_2]_{\text{actual}}}{[O_2]_{\text{stoich.}}} \times 100 \tag{3}$$

where $[O_2]_{\text{actual}}$ is the concentration of O_2 from complete decomposition of hydrogen peroxide fed into the reactor at the beginning of the reaction (mg/L). $[O_2]_{\text{stoich.}}$ is the stoichiometric requirement concentration of O_2 to obtain a complete oxidation of the feed (based on COD) and equal to $[\text{COD}]_0$ of oily sludge (mg/L).

2.2. Materials and analytical methods

Hydrogen peroxide (analysis purity, 35 wt% aqueous solution) was used as a source of oxygen. The oily sludge sample consisted of the bottom sludge taken from a crude oil storage tank

Table 2
Summary of operating conditions and results from oxidation experiments[a].

T (K)	p (MPa)	O_2 excess (%)	Reaction time (min)	Heat-up time (min)	Initial COD (mg/L)	Final COD (mg/L)
663	25	427	1	65.1	2015	584.4
663	25	427	3	65.2	2011	530.9
663	25	427	5	65.4	2021	499.2
663	25	427	10	64.8	2012	430.6
683	25	427	1	64.9	2006	501.5
683	25	427	3	65.0	2020	438.3
683	25	427	5	65.1	2011	406.2
683	25	427	10	65.5	2015	316.4
703	25	427	1	65.2	2016	443.5
703	25	427	3	65.1	2019	383.6
703	25	427	5	64.7	2022	323.5
703	25	427	10	65.2	2012	221.3
723	25	427	1	65.1	2008	401.6
723	25	427	3	65.3	2012	321.9
723	25	427	5	65.1	2018	262.3
723	25	427	10	64.9	2011	160.9
703	23	427	1	65.1	2017	463.9
703	23	427	3	64.8	2006	401.2
703	23	427	5	65.0	2010	341.7
703	27	427	1	64.8	2024	425.0
703	27	427	3	64.9	2011	382.1
703	27	427	5	65.0	2012	321.9
703	25	217	1	65.4	2019	464.4
703	25	217	3	65.0	2008	381.5
703	25	217	5	65.2	2021	323.4
703	25	605	1	64.9	2014	443.1
703	25	605	3	65.3	2016	362.9
703	25	605	5	64.9	2010	301.5
703	25	427	1	65.0	1507	391.8
703	25	427	3	65.1	1509	369.7
703	25	427	5	65.2	1510	347.3
703	25	427	1	64.8	1756	407.4
703	25	427	3	65.1	1753	357.6
703	25	427	5	65.0	1750	311.5
703	25	427	1	64.9	2252	475.2
703	25	427	3	65.5	2250	409.5
703	25	427	5	65.0	2254	344.9

[a] Initial COD of the feed in the reactor was calculated from amounts of oily sludge and water.

in the 4th oil production plant of Daqing oil fields. The oily sludge sample contains water 23.2 wt%. COD of the oily sludge is 856,000 mg/L.

COD analysis was performed according to standard method (GB11914-89). A gas chromatograph (SP3420, Beijing Beifenruili Analytic Instrument Co., Ltd.) equipped with a flame ionization detector (FID) was used to analyze the acetic acid content. The column used was 3 m long with 3 mm diameter packed with 80–100 mesh GDX-103 + 2% H_3PO_4. Samples of 1 μL were injected into a hydrogen carrier flow (30 mL/min). The acetic acid was added as external standard for calculation of concentrations. Gas samples were analyzed using a gas chromatograph (GC-14C, Shimadzu) with a thermal conductivity detector (TCD). The carbon molecular sieve column (TDX-01) was used to separate the carbon monoxide and carbon dioxide from gaseous samples. Argon was used as the carrier gas. The system was calibrated with a standard gas mixture containing H_2, O_2, N_2, CO, CO_2 and CH_4.

Individual hydrocarbons were analyzed by gas chromatographic methods. The oily sludge and liquid products samples were extracted with dichloromethane. The extracts were dissolved in *n*-pentane and separated into soluble and insoluble fractions (asphaltene). The soluble fraction was loaded on a silica gel column and eluted with hexane to obtain the alkane fractions. The alkane fractions were analyzed by a gas chromatograph (Agilent 6890N) equipped with a FID and a HP-5 30-m long capillary column (0.32 mm × 0.25 μm film thickness). The injector and the detector were kept at a temperature of 573 K. The oven temperature was programmed to rise from 353 to 553 K with a gradient of 7 K/min. Helium was used as carrier gas. Individual hydrocarbon concentrations in the oily sludge were calculated by comparing the peak areas of samples with internal standard (1-Hexadecen, Chevron Phillips Chemical Company LP, 99% purity). Identification of compounds was aided by a gas chromatography/mass spectrometry (GC/MS, Finnigan Trace DSQ/GC ultra).

3. Results and discussion

Experimental conditions and results obtained from oxidation experiments are presented in Table 2. Initial COD of the feed in the reactor was calculated from the amounts of oily sludge and water.

3.1. Effect of reaction time

The oily sludge conversion experiments were conducted at 663–723 K for 10 min. Figs. 2–5 show COD removal rate, carbon dioxide yields, carbon monoxide yields and acetic acid yields for SCWO of oily sludge at different temperatures, respectively. Those results appear that the reaction time has a significant effect on oily sludge conversion. Within each set of isothermal experiments, the COD removal rate increased rapidly during the first 1 min of reaction and slowed down afterwards. The initiating faster conversions of organic compounds in supercritical water oxidation conditions have been reported [30,31]. The experiment shows also that effect of reaction time on carbon dioxide yields is similar. The color of the liquid effluent changed from brownish to colorless as the reaction

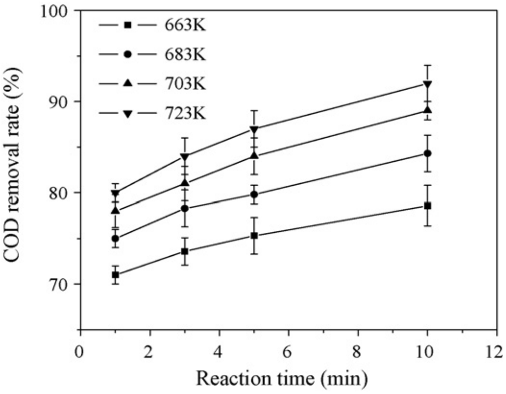

Fig. 2. COD removal rate for SCWO of oily sludge at different temperatures; $p = 25$ MPa, O_2 excess = 427%.

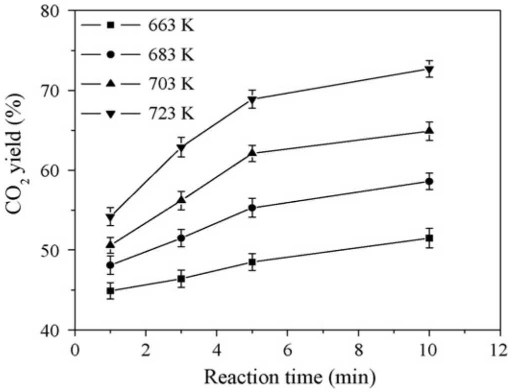

Fig. 3. Carbon dioxide yields for SCWO of oily sludge at different temperatures; $p = 25$ MPa, O_2 excess = 427%.

proceeded from 0 to 10 min at each set of isothermal experiments. Analysis of the liquid and gas effluents obtained from those runs showed that carbon monoxide and acetic acid yields at short times (<1 min) increased with the increase of reaction time, and both yields eventually reached a maximum and then decreased. The trace amounts of H_2 and CH_4 were detected in these oxidation experiments in agreement with the reported [18]. Hence it is clear that oxidation of oily sludge can produce final product of carbon dioxide and intermediate products of carbon monoxide and acetic acid in supercritical water.

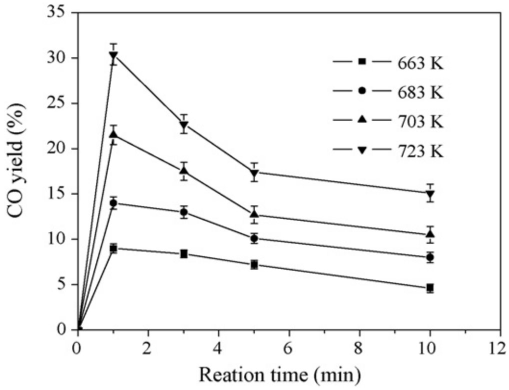

Fig. 4. Carbon monoxide yields for SCWO of oily sludge at different temperatures; $p = 25$ MPa, O_2 excess = 427%.

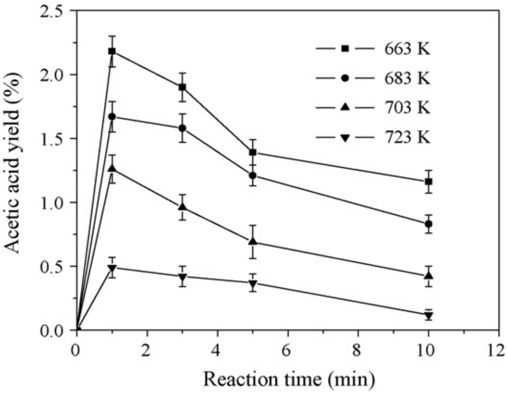

Fig. 5. Acetic acid yields for SCWO of oily sludge at different temperatures; $p = 25$ MPa, O_2 excess = 427%.

3.2. Effect of reaction temperature

Figs. 2–5 clearly show that the COD removal rate and end production carbon dioxide yields increased with the increase of temperature. It is interesting to note that the intermediate carbon monoxide yields increased with the increase of temperature, on the contrary, intermediate acetic acid yields decreased with the increase of temperature. Table 3 shows the distribution of carbon in products such as carbon dioxide, carbon monoxide and acetic acid. The percentage did not total to 100%. Some of the organic compounds formed may have presented in liquid products. We made no attempt to analyze what compounds they are, but acetic acid in liquid products was analyzed particularly since acetic acid has been identified by researches [32,33] as one of the refractory intermediates in oxidation of many complex organics in supercritical water. The concentration of acetic acid remained very low in all experiments. Acetic acid was not the only liquid product because COD of the liquid products (see Table 2) was markedly higher than theory oxygen demand of acetic acid in the liquid products. Carbon monoxide yields are higher than acetic acid yields in one order of magnitude. The contributions of carbon monoxide and carbon dioxide to mass balances were significantly higher. Carbon monoxide and carbon dioxide should be the only gaseous products detected if the trace amounts of hydrogen and methane detected were neglected. The acetic acid was converted to carbon dioxide and carbon monoxide under condition of SCWO [32]. Therefore, the

Table 3
Carbon distribution in products at different temperatures; $p = 25$ MPa, O_2 excess = 427%.

T (K)	Reaction time (min)	Product yield (%)			
		CO_2	CO	Acetic acid	Total
663	1	44.9	9.0	2.18	56.08
663	3	46.4	8.4	1.90	56.70
663	5	48.5	7.2	1.39	57.09
663	10	51.5	4.6	1.16	57.26
683	1	48.1	14.0	1.67	63.77
683	3	51.5	13.0	1.58	66.08
683	5	55.3	10.1	1.21	66.61
683	10	58.6	8.0	0.83	67.43
703	1	50.6	21.5	1.26	73.36
703	3	56.2	17.5	0.96	74.66
703	5	62.1	12.7	0.69	75.49
703	10	64.9	10.5	0.42	75.82
723	1	54.2	30.4	0.49	85.09
723	3	62.9	22.7	0.42	86.02
723	5	68.9	17.4	0.37	86.67
723	10	72.7	15.1	0.12	87.92

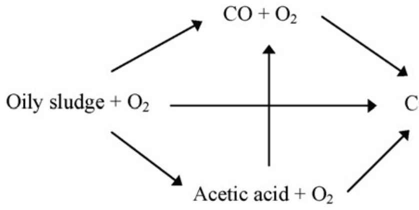

Fig. 6. Pathways for oxidation of oily sludge.

main refractory intermediate is not acetic acid but carbon monoxide in supercritical water oxidation of oily sludge. This agrees with those obtained by Portela et al. [33]. The possible pathways for oxidation of oily sludge may be illustrated in Fig. 6.

3.3. *Effect of reaction pressure*

Fig. 7 shows effect of reaction pressure on SCWO of oily sludge. According to Fig. 7, it can be found that the pressure does not have a significant affect on oily sludge conversion. Note the increase of pressure was obtained by means of increasing amount of water when the temperature should remain practically constant. As a result, this leads to an increase of density of supercritical water due to a constant volume in a batch reactor. On the one hand, oxidation reaction rate constant and density of supercritical water increased with the increase of pressure [34]. This is in favor of removing COD. On the other hand, the dielectric constant of supercritical water increased with the increase of density [35], resulting in a reduction of solubility of oily sludge in supercritical water. This is not propitious to oxidation of oily sludge in supercritical water. Therefore, we believe that the combined effect of pressure and density is responsible for a little increase of COD removal rate with the increase of pressure.

3.4. *Effect of O_2 excess*

It is well known that *n*-alkanes should be the most instable among petroleum hydrocarbons from the pyrolysis perspective. Pyrolysis of hydrocarbons is closely related to the cleavages of the C–C and C–H bonds, and produces alkenes, H_2 and CH_4, etc. In order to examine the stability of oily sludge in the absence of oxygen source, two separate experiments without oxidant were performed at 25 MPa and the same final temperature of 723 K but heat-up rates of 6 and 6.5 K/min, respectively. Gas chromatography studies showed that the trace amounts of alkenes were detected in the liquid products. H_2, CH_4, CO and CO_2 were not detected in gaseous effluent stream. These findings indicated that pyrolytic reactions of the oily sludge occurred slightly. One can speculate that the reaction temperature of 723 K did not exceed the temperature threshold of pyrolysis of the oily sludge. In addition, high pressure of 25 MPa is not propitious to pyrolysis of hydrocarbons from the point of view of thermodynamics. On the other hand, no obvious changes in concentrations of the various *n*-alkanes detected in the reaction liquid products at two heat-up rates were observed. Compared with the original oily sludge, the changes in concentrations of the various *n*-alkanes detected were certainly within the error made by analytical method (±3%). Therefore, the influence of heat-up rate on constitutes of the reactants was not considered hereafter. The influence of pyrolytic reactions on the measured oxidation rate is small and can be neglected.

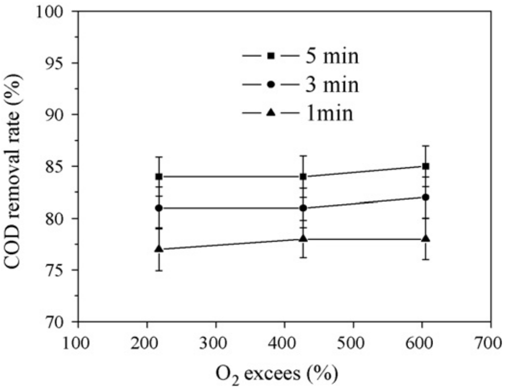

Fig. 8. Effect of O_2 excess on SCWO of oily sludge; T = 703 K, p = 25 MPa.

A series of experiments were conducted to determine the effect of O_2 excess on SCWO of oily sludge at given COD concentration. The experimental results are presented in Fig. 8. As can be seen in Fig. 8, the COD removal rate keeps almost constant. The data indicate that the rate of oxidation is independent of oxygen feed concentration above an O_2 excess of 217%. This implies that the global reaction order for oxidant is zero. The observation is consistent with the findings of many investigations [28,29,34,36,37]. In order to assure that oily sludge react sufficiently with O_2, and in consideration of operating cost, the O_2 excess of 427% is selected in the research.

3.5. *Effect of initial COD*

The study of the effect of initial COD on SCWO of the oily sludge was undertaken at reaction temperature of 703 K, pressure of 25 MPa and O_2 excess of 427%. The results are shown in Fig. 9.

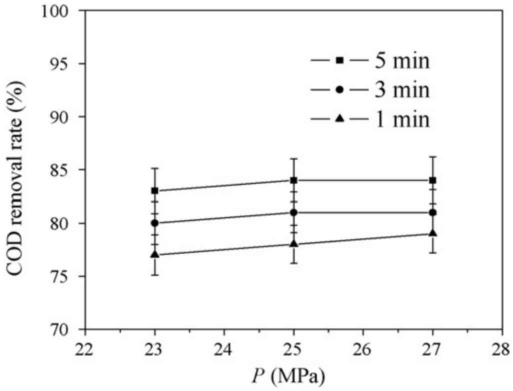

Fig. 7. Effect of pressure on SCWO of oily sludge; T = 703 K, O_2 excess = 427%.

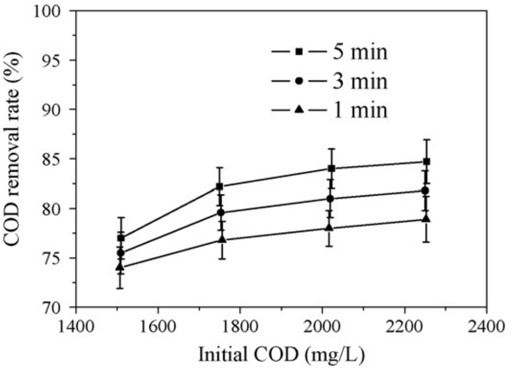

Fig. 9. Effect of initial COD on SCWO of oily sludge; T = 703 K, p = 25 MPa, O_2 excess = 427%.

It can be observed from Fig. 9 that the initial COD had influence on the COD removal to some extent. An increasing initial COD from 1500 to 1750 mg/L resulted in the rapid increase in the COD removal rate. However, beyond initial COD of 2000 mg/L, COD removal rate increases slowly with increasing initial COD. For example, COD removal rate increases from 84.0 to 84.7% as initial COD increases from 2022 to 2254 mg/L under the condition of reaction time of 5 min.

3.6. *Kinetics for supercritical water oxidation of oily sludge*

In order to develop reliable reaction rate expression, 16 data were taken under various conditions. The global power-law reaction rate can be described as follows:

$$\text{rate} = -\frac{\mathrm{d[COD]}}{\mathrm{d}t} = k[\mathrm{COD}]^a[\mathrm{H_2O_2}]^b[\mathrm{H_2O}]^c \tag{4}$$

where [COD] is chemical oxygen demand of reactant (mg/L), $[H_2O_2]$ the concentration of oxidant (mg/L), $[H_2O]$ the concentration of water, t the reaction time (s), a, b and c are the reaction orders of COD, H_2O_2 and H_2O, respectively. k is the rate constant, which can be expressed in Arrhenius form in equation as follows:

$$k = A\exp\left(\frac{-E_a}{RT}\right) \tag{5}$$

where A is the pre-exponential factor($(\mathrm{mol\,l^{-1}})^{1-a-b-c}\,\mathrm{s^{-1}}$), E_a the activation energy (J/mol), R the universal gas constant ($8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$) and T is the temperature (K). In this study, we assumed the global oxidation of oily sludge depends only on the temperature, the reactant concentration. Besides, in a reaction medium containing more than 99 wt% of water, the reaction order of water could be considered equal to zero. It is mentioned above in the paper that the global reaction order for oxidant is zero. So the global power-law reaction rate can be expressed as follows:

$$\text{rate} = -\frac{\mathrm{d[COD]}}{\mathrm{d}t} = k[\mathrm{COD}]^a \tag{6}$$

For each temperature, the kinetic parameters k and a were obtained by a multi variable non-linear least squares, using lsqnonlin function provided in optimization toolbox of MATLAB, on experimental [COD] values and reaction time according to Eq. (6). Table 4 shows the different k values obtained at the different temperatures for the supercritical water oxidation experiments on oily sludge. The average of values is used as reaction order, namely, $a = 1.405$.

Fig. 10 shows the Arrhenius plot of the reaction rate constants for the supercritical water oxidation of oily sludge. Arrhenius parameters (pre-exponential factor and activation energy) have been estimated by linear regression of ln(k) versus 1/T. The apparent activation energies and pre-exponential factor of oxidative reaction for the supercritical water oxidation experiments on oily sludge were obtained from the slopes and intercept of Arrhenius plots. The calculated apparent activation energy and pre-exponential factor of supercritical water oxidation of oily sludge are 213.13 ± 1.33 kJ/mol and $8.99 \times 10^{14}\,(\mathrm{mol\,L^{-1}})^{-0.405}\,\mathrm{s^{-1}}$, respectively. Therefore, the global power-law reaction rate can be expressed as:

$$\text{rate} = -\frac{\mathrm{d[COD]}}{\mathrm{d}t} = 8.99\times10^{14}\exp\left(\frac{-213.13(\pm1.33)\times10^3}{RT}\right)[\mathrm{COD}]^{1.405} \tag{7}$$

Table 4
Kinetic parameters at different temperatures.

T (K)	k $((\mathrm{mol\,L^{-1}})^{1-a}\,\mathrm{s^{-1}})$	a
663	0.0130	1.45
683	0.0532	1.41
703	0.155	1.39
723	0.347	1.37

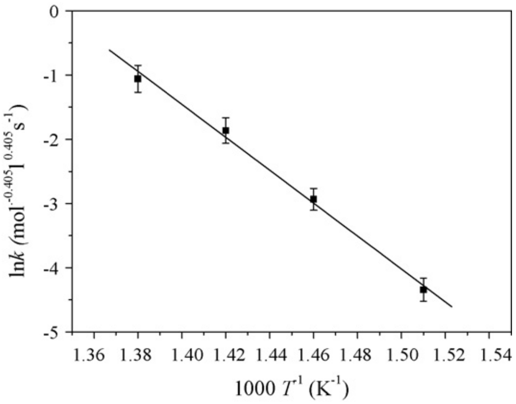

Fig. 10. Arrhenius plot for SCWO of oily sludge on COD (95% confidence levels are presented).

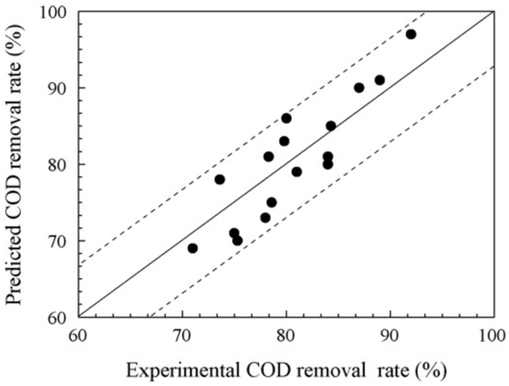

Fig. 11. Comparison between experimental COD removal rate and those predicted by kinetic model.

Fig. 11 shows the comparison between experimental COD removal rate and those predicted by the global power-law reaction rate (Eq. (7)). The dashed lines, indicating a deviation of ±7% COD removal rate from the 45° line (perfect match), contain all of the data point. The predictions made are quite satisfactory.

4. Conclusions

Based on the results obtained from laboratory study, SCWO could be considered as a key technique in the clean-up strategy developed in the future for treatment of oily sludge. The COD removal rate of 92% can be reached in 10 min on SCWO of oily sludge. Carbon monoxide is a main refractory intermediate and acetic acid is a minor intermediate. Moreover, carbon monoxide yields increased with the increase of temperature, whereas acetic acid yields decreased with the increase of temperature. COD removal rate increases as the reaction time, temperature increase and initial COD. Pressure and O_2 excess have no remarkable affect on SCWO of oily sludge. A kinetics analysis of the experimental data for COD, which employed global power-law rate expressions assuming a zero-order dependence on water concentration and oxidant concentration, was performed with a non-linear regression analysis. Reaction parameter values were determined to be activation energy of 213.13 ± 1.33 kJ/mol, pre-exponential factor of $8.99 \times 10^{14}\,(\text{mol}\,\text{L}^{-1})^{-0.405}\,\text{s}^{-1}$ and the reaction order of 1.405 (based on COD).

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