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Oxidative Thermal Treatment of Oil Sludge at Low Heating Rates

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Oil sludge is one of the major industrial wastes that needs to be treated for the refinery or petrochemical industry. Efforts have been made to convert the oil sludge into available resources such as lower molecular weight organic compounds and carbonaceous residues. In this study, the oil sludge from the oil storage tank of a typical petroleum refinery plant located in northern Taiwan is used as the raw material of thermal treatment using oxygen-containing gas. The treatment of oil sludge is conducted by the use of carrier gas with different concentrations of oxygen (4.83, 8.62, 12.35, and 20.95 vol % O_2) in the temperature range of 380−1123 K and at various constant heating rates of 5.2, 12.8, and 21.8 K/min. The significant reactions occur in the range 415−931 K. Below a temperature of 613 K, pyrolysis reactions are predominant. Including the pyrolysis reactions, the overall oxidative thermal decomposition of oil sludge can be adequately described by a five-parallel-reaction model. The activation energies (E), reaction orders (n for residual solid and m for oxygen) and frequency factors (A) of corresponding five-parallel-reaction model for oil sludge are 69.93, 93.79, 123.22, 208.67, and 120.87 kJ/mol of E, 2.94, 2.42, 1.24, 2.91, and 1.36 of n, 0, 0, 0, 2, and 0.32 of m, and 7.69×10^5, 9.09×10^6, 2.95×10^8, 1.66×10^{17}, and 9.45×10^7 1/min of A, respectively. The proposed reaction kinetic equations can provide useful information for the proper design of an oxidative thermal processing system for the treatment of oil sludge.

Introduction

In the petroleum refineries, a considerable quantity of oil sludge accumulates from refining processes. The major sources of oil sludge include oil storage tank sludge, biological sludge, dissolved air flotation (DAF) scum, American Petroleum Institute (API) separator sludge, and chemical sludge. In Taiwan, most oil sludges are from oil storage tank sludge and the biological sludge of refinery wastewater treatment plants.[1] Some oil sludges are included in the Hazardous Waste listings under the wastes originating from specific sources of Resource Conservation and Recovery Act (RCRA) regulations.[2] The Hazardous Waste listings are (1) dissolved air flotation sludge (DAF) (K048), (2) slop oil emulsion solids (SOES) (K049), (3) heat exchanger bundle sludge (K050), (4) API separator sludge (API) (K051), and (5)

tank bottoms lead (K052).[2] The other oil sludges not included in the Hazardous Waste listings are dependent on the results of toxicity characteristic leaching procedure (TCLP).

The previous study[3,4] of target oil sludge has reported the proximate, elemental, and heating value analyses of oil sludge as listed in Table 1. The elemental analysis of metal of oil sludge was also performed by Shie et al. as presented in Table 2.[3] The total amount of metal relative to wet basis of oil sludge is 0.93 wt %. However, the ash relative to wet basis of oil sludge is 1.88 wt % and with a red color which is different from the black color of pyrolysis residues. The increase of mass of ash maybe due to the metal oxide, but for the precise reasons, further research would be needed. Also, the major products from the oxidative thermal treatment of oil sludge with different oxygen concentrations were studied by Shie et al.[5,6] From experimental results,[5,6]

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Table 1. Some Properties of Oil Sludge Used in This Study[3]

item	property
Proximate analysis (wt %)	
moisture	39.15 (1.16)[a]
combustible	58.97 (0.82)
ash	1.88 (0.4)
Heating value analysis (kJ/kg)	
heating value of dry basis	44 647
high heating value of wet basis	27 170
low heating value of wet basis	24 537
Ultimate analysis (dry basis of oil sludge, wt %)	
C	83.94 (0.9)
H	12.01 (0.58)
N	0.81 (0.53)
O	0.96
S	2.06
Cl	0.22

[a] Numbers in parentheses are standard deviations.

the improvement effects of oxygen on the qualities of the oil portion of liquid products are obvious.

The current major method of disposal of oil sludge is by incineration. The incinerators used are aggregate types such as fluidized bed combustors, circulating fluidized bed combustors (CFBC), and kiln, rotary, rack, and step-type furnaces with combustion temperatures of 1073−1173 K.[7−12] However, during incineration, the following major problems are encountered: (1) excessive bed temperature, (2) frequent clinker formation, (3) high flue gas temperature, and (4) excessive pressure drop.[11] The resolution of these problems is a current major concern.[11] Incineration has been deemed an effective method for destroying the majority of organic constituents by conversion to innocuous carbon dioxide and water. Other methods considered for the disposal of oil sludge are landfarming with microbial treatment to convert the hydrocarbons to combustible gases (such as CH_4), use in a delayed coker, utilization for industrial bitumen, and separation of water and sediment at elevated temperature by the use of diluents and emulsifiers with subsequent burning.[10,13−17] Landfill has pollution risks if stabilization of oil sludge is not complete.

It may pollute groundwater and cause health problems.[14] Landfarming requires a large surface area and usually takes a long time to complete. It also causes air pollution problems.[17] The organic compounds of oil sludge include some aromatics and polyaromatic hydrocarbons (PAHs) that are carcinogenic, while some inorganic compounds may contain toxic heavy metals.[16]

For the thermal treatment and pretreatment of oil sludge, some works had proceeded. Separation and Recovery Systems Inc. (SRS) introduced a new generation of dryer technology, the MX-2500, for the treatment of refinery wastes and secondary materials including API sludges, DAF float, and slop oil emulsion solids.[18] The MX-2500 is an electrically heated dryer system for the objectives of waste minimization and oil recovery, while producing a solid residue meeting EPA Land Disposal Restriction (LDR) treatment levels.[18] Ayen and Swanstrom tested a low temperature thermal treatment process for petroleum refinery waste sludges coded as waste codes K048, K049, K050, K051, and K052 under the RCRA.[7] The reaction temperatures of the low temperature thermal treatment process were between 588 and 698 K (laboratory unit) or 463 and 633 (pilot plant) under nitrogen atmosphere, providing effective waste minimization up to a 40% decrease in the mass of sludge to be disposed of. The heating value of sludge was increased simultaneously by one-third. The process was demonstrated with its effectiveness of removal of organics of concern from the sludges meeting the RCRA best demonstrated available technology (BDAT) treatment standards.[7] In a previous study,[3,4] for the sake of simplicity and engineering use, a simple global reaction kinetic model was proposed to predict the pyrolysis experimental results. The simulation results were satisfactory. However, for precise use, the two- and three-reaction models were further proposed to describe the pyrolysis.[3,4] Among the three models proposed, the three-reaction model gives the best fit. This is reasonable regarding the complex compositions of oil sludge. A significant variation in the instantaneous reaction rate of pyrolysis of oil sludge occurs at about 640−765 K.[3] Comparing the references above, one can roughly find out the difference of temperature ranges between the pyrolysis process (at lower temperatures of 640−765 K) and incineration process (at higher temperatures of 1073−1173 K). The oxidative thermal treatment of oil sludge is a technology between the pyrolysis and incineration. Extensive study has been conducted on the analyses of major products obtained from the pyrolysis of oil sludge and effects of additives on the pyrolysis of oil sludge in separate papers.[19−22] The major gaseous

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Table 2. Elemental Analysis of Metal of Oil Sludge (wet basis) Used in This Study[3]

Major metal	Fe	Ca	Na	Al	Mg	Zn	Mn	Hg	Sr	K
ppmw[a]	7340.7 (477.7)[b]	1055.6 (107.9)	348.6 (2.57)	118.3 (3.67)	95.3 (8.99)	91.5 (2.11)	64.4 (9.26)	35.3 (0.01)	28.3 (5.6)	27.5 (3.62)

Minor metal	Pb	Cu	Ba	Ni	Cr	Mo	As	Co	Cd	Se
ppmw	19.6 (1.87)	14.1 (0.45)	13.7 (0.25)	11.7 (0.12)	6.5 (0.14)	1.3 (0.01)	0.96 (0.02)	0.88 (0.27)	0.14 (0.01)	0.12 (0.001)

[a] ppmw: ppm in wt/wt. [b] Numbers in parentheses are standard deviation (σ_{n-1}).

products (noncondensable gases at 298 K) excluding N_2 are CO_2 (50.88 wt %), HCs (hydrocarbons, 25.23 wt %), H_2O (17.78 wt %), and CO (6.11 wt %). The HCs consist mainly of low molecular weight paraffins and olefins (C_1-C_2, 51.61 wt % of HCs). The distillation characteristics of liquid product (condensate of gas at 298 K) from the pyrolysis of oil sludge is close to diesel oil. However, it contains a significant amount of vacuum residue of about 9.57 wt %. The heating value of liquid product is about 45 311 kJ/kg.

An investigation on the incineration of oil sludge has been carried out by the use of a fluidized-bed technique.[11] Under the temperatures of an ignition-burner at 1073 K and after-burner at 1473 K, more than 98.5% combustion efficiency ($CO_2/(CO_2 + CO)$) and 99% incineration efficiency ((input − output)/input) were achieved for all three types of oil sludge. Regarding the ash and scrubber sludge that resulted from the incineration of oil sludge, the low contents of heavy metals in both samples confirm that they are not toxic in terms of level of heavy metal and hence can be sent for landfill disposal. However, no reports have been found in the literature considering detailed kinetic studies of oxidative pyrolysis of oil sludge. Effects of oxygen concentration on the decomposition kinetics are rarely investigated but are important in the actual combustion systems. Conesa et al.[23] proposed a kinetic model for the combustion of tire wastes and indicated that the mass loss takes place in four steps. The first three steps probably correspond to the decompositions of (1) an oil fraction (activation energy, $E_1 = 70$ kJ/mol), (2) natural rubber ($E_2 = 212.6$ kJ/mol), and (3) styrene−butadiene rubber ($E_3 = 249.3$ kJ/mol). The fourth step corresponds to the combustion of a carbonaceous fraction (carbon black and other material) ($E_4 = 252.0$ kJ/mol). The four-step kinetic model involves three pyrolysis reactions and one oxidative reaction. The activation energy of the fourth step (combustion of the carbonaceous fraction) is higher than those of the other three steps of pyrolysis reactions. This implies that oxygen takes part in the thermal degradation reaction mainly at the last reaction stage and higher reaction temperatures. The effects of oxygen content on the mass conversion at a constant heating rate are not obvious. However, the final residues of oxidative reaction are lower than that of the pyrolysis

reaction. All of this information is useful for assisting the study on the pyrolysis and oxidation reactions of sludge, for which multi-reactions may be involved. Kashiwagi and Nambu[24] used the Kissinger approach for determining the kinetic constants. They pointed out that competition between the pyrolysis reaction and oxidative degradation coexisted (parallel reactions) for the thermal oxidative treatment of cellulose paper, and the dependence on the oxygen concentrations. After the pyrolysis and oxidative degradation of cellulose paper, char was produced and then subjected to oxidative degradation. This also indicates that the thermal decomposition of solid wastes with the presence of oxygen is not simply an oxidation process. The solid wastes are in both pyrolysis and oxidative conditions for incineration. In general, the solid waste incineration involves oxidizing the waste in excess air and high temperature. In the combustion of solid waste, an initial step of pyrolysis usually occurs producing organic volatiles and residues containing char and tar. In the next stage, the residue of char or tar is then oxidatively reacted. The organic volatiles are oxidatively decomposed in the post-combustion chamber. The oxidative decomposition process is exothermic. The combustion heat released, in turn, can supply the heat needed for the endothermic pyrolysis reactions.

Wey et al.[25] performed oxidative pyrolysis of mixed solid waste in a fluidized sand bed with freeboard reaction under an oxygen-deficient atmosphere and lower temperature (813−903 K). The primary gas and residue tended to produce alkyl and alkene compounds rather than being oxidized to produce CO, CO_2, and H_2O because the oxygen was in short supply. Lee et al.[26] found that the effects of oxygen concentration (0−6.5 vol %) on the yield and production rate of product gas are small. With increasing pyrolysis temperature, the gas yield and energy recovery increase, but oil yield decreases, whereas the char yield remains constant.[26]

The objective of the present work was to study the kinetics of oxidative decomposition of oil sludge. The experiments were performed by the use of a dynamic thermogravimetric (TG) reaction system at various constant heating rates (5.2, 12.8, and 21.8 K/min) and different concentrations of oxygen atmosphere (4.83, 8.62, 12.35, and 20.95 vol % O_2). Oxidative thermal

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treatment of oil sludge can involve pyrolysis and oxidative reactions. The kinetics of oxidative decomposition of oil sludge provides basic information for the design and operation of thermal treatment system.

Experimental Section

Materials. The oil sludge used in this study was sampled from the crude oil storage tank of a typical petroleum refinery plant located in the northern Taiwan. The oil storage tank sludge accumulates at the bottom of the tank, where crude oil, product oil, vapor, slop, asphalt, etc., are stored. It is taken out during periodic tank cleaning and dumped separately from other sludges in ponds with or without covers.[3] The oil sludge sample was dried in a recycle ventilation drier for 24 h at 378 K before use. Nitrogen gas for the purge gas, with 99.99% purity, was purchased from the Ching-Feng-Harng Co. Ltd. in Taipei, Taiwan.

Apparatus and Procedures. *Thermogravimetry (TG).* The lab-scale experimental apparatus and detailed description of operating procedures for the pyrolysis of oil sludge are the same as in the previous study.[3,27−28] The Cahn 1000 Electrobalance (C-1000) was used for thermogravimetric analysis (TGA). Some specifications of the balance are capacity of 100 g, sensitivity of 1 μg, and ultimate repeatability of 1.5 μg. A sample of known mass (8 ± 0.5 mg) was placed on a small quartz disk, 2 cm in diameter and 1 mm in thickness. The disk was hung on the extension wire, made of Nichrome wire 0.1 mm in diameter and 0.68 mg/cm in weight, of the electrobalance. The disk and wire were enclosed in a quartz shell and tube reactor. The outer shell was 92 cm long and 3.5 cm inside diameter. The inner tube was 20 cm long and 1.2 cm in inside diameter. The reactor was placed in the heating furnace (HAS 100/250G and 7000 W). A K-type thermocouple was inserted into the reactor for measuring the temperature, and placed 5 mm below the center of the disk. Nitrogen gas at a given flow rate was introduced into the electrobalance and reactor for at least 8 h for purging. Then the flow rate was adjusted to the desired value, for example, 50 cm³/min under 101.3 kPa (1 atm) and 293 K, and was controlled by a Cole-Parmer N062-01 rotameter. After about 1 h, the control unit (Eurotherm 815 S, Eurotherm International Ltd.) of the furnace was set at a specific heating rate (5.2, 12.8, and 21.8 K/min). Meanwhile, the data acquisition unit (IBM PC-486 DX33 with 4 1/2 digit DVM card and RS232 interface), with a sampling interval of 15 s, logged the results. The system was operated at atmospheric pressure. The effluent gas was cold-trapped at 298 K and then vented to a fume hood. When the run was finished, the nitrogen gas was kept flowing till the temperature of the system was below 373 K.

The oil sludge sample was dried in a recycle ventilation drier for 24 h at 378 K before use. The dried sample was placed on a quartz disk that was enclosed in a quartz shell and tube reactor with purging nitrogen gas overnight (at least 16 h) at 378 K for further drying to a constant mass prior to starting the temperature rise under a specific heating rate. The gas, which was a combined mixture of nitrogen and air to the concentrations of 4.83, 8.62, 12.35, and 20.95 vol %, was then adjusted to the desired value, for example, 50 cm³/min under 101.3 kPa (1 atm) and 293 K and was controlled by the Cole-Parmer N062-01 rotameter. A sample mass of 8 ± 0.5 mg was found to be suitable for yielding kinetic data. From the test results, the longitudinal temperature gradients were about 0.0098, 0.0097, and 0.01 K/mm for heating rates of 5.2, 12.8, and 21.8 K/min, respectively. Noting that all of the longitu-

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dinal temperature gradients were less than 0.01 K/mm, one may reasonably obtain the temperature near the disk by extrapolation. The radial temperature gradients were about 0.24, 0.55, and 0.43 K/mm for heating rates of 5.2, 12.8, and 21.8 K/min, respectively. In this study, the sample was well spread and homogenized around the center of disk. The temperature of the center of the disk was calculated by extrapolation from the temperature difference (about 0.01 K/min × 5 mm = 0.05 K).

It is noted that a buoyancy effect occurs when working at elevated temperatures and with the different reaction gases because the increasing temperature will affect the density of the gas. The experimental curves presented below are the results with deduction of a blank run corresponding to each specific condition.

Oxygen Analysis. For the analysis of the concentration of oxygen (O_2), a China Chromatography 8900 GC equipped with a thermal conductivity detector (TCD) and a Supelco packing column (60/80 carbonxen-1000, 15 ft, 2.1 mm i.d.) was used. An integrator from Hewlett-Packard (HP 3396) was connected to the GC for graphing and integrating purposes. The operation conditions were set as follows: injector temperature of 393 K, detector temperature of 373 K, column temperature (following the sampling injection) held at 333 K for 20 min, helium carrier gas flow rate of 35 mL/min for A and B columns, and sample volume of 250 μL.

Results and Discussion

Effects of Oxygen Concentrations and Heating Rates. The residual mass fractions of reactant (M and M') in thermal decomposition are expressed on a normalized basis, where $M = (W - W_f)/(W_0 - W_f)$, $M' = W/W_0$, and W, W_0, W_f represent present, initial, and final masses of sample, respectively. The variations of M and M' with reaction temperature (T) for various oxygen concentrations are illustrated in Figures 1a and 1b under a heating rate of 5.2 K/min. For comparison, the pyrolysis case (100% N_2) studied by Shie et al.[3] is also included. The results indicate that the effects of oxygen at the concentrations studied are not significant at temperatures below 613 K. The presence of oxygen in the carrier gas gives a higher value of M and thus a lower conversion of X ($X = 1 - M$) when the temperature is higher than 613 K. This may be attributed to the high activation energy (E) of oxidative reaction of carbonaceous residue resulting from pyrolytic carbonization, as noted in the following section. Pyrolysis is significant for all cases with various oxygen concentrations at temperatures below 613 K. Above 613 K, pyrolysis becomes insignificant while oxidative thermal decomposition tends to dominate. From these results, one can assume that both pyrolysis and oxidation reactions of oil sludge occurred with the presence of oxygen via parallel reactions.
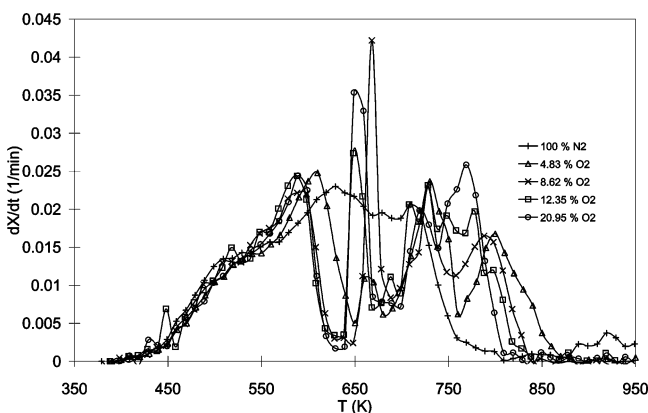
The variation of instantaneous reaction rate ($r = dX/dt$) with T for various oxygen concentrations under the heating rate of 5.2 K/min is presented in Figure 2 including the pyrolysis case (100% N_2) studied by Shie et al.[3] The oxidative thermal decomposition reactions are significant in the range 415−931 K and the reaction scheme is complex. Figure 2 shows that there are about four major peak rates for the cases with 4.83 and 8.62 vol % O_2 and three major peak rates for those with 12.35 and 20.95 vol % O_2, respectively. The initial (T_i) and final (T_f) reaction temperatures with significant reaction rates for various oxygen concentrations can be estimated
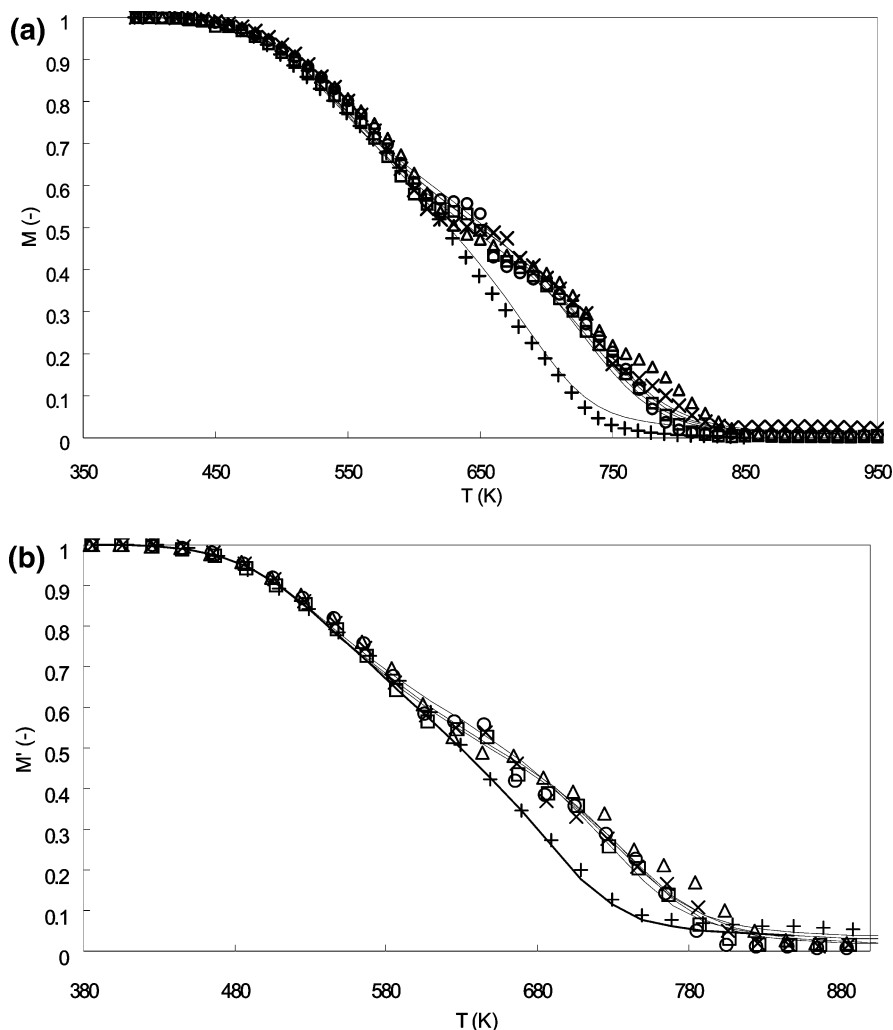
Figure 1. (a) Residual mass ratio (M or M') vs reaction temperature (T). M vs T and comparison of M predicted by proposed model with experimental data at 5.2 K/min heating rate (HR, β) for thermal decomposition of oil sludges in various oxygen concentrations. (1, +), (2, $\triangle$), (3, ×), (4, $\square$), (5, $\bigcirc$): 100% N_2,[3] 4.83, 8.62, 12.35, 20.95 vol % O_2. Line: computed; symbol: experimental; R_1^2, R_2^2, R_3^2, R_4^2, R_5^2 = 0.9981, 0.9922, 0.9927, 0.9975, 0.9926. T = temperature. (b) Residual mass ratio (M or M') vs reaction temperature (T). M' vs T for experimental data at 5.2 K/min heating rate (HR, β) for thermal decomposition of oil sludges in various oxygen concentrations. +, $\triangle$, ×, $\square$, $\bigcirc$: 100% N_2,[3] 4.83, 8.62, 12.35, 20.95 vol % O_2. Line: computed; symbol: experimental.

Figure 2. Variation of instantaneous reaction rate ($r = dX/dt$) with T at 5.2 K/min heating rate for thermal decomposition of oil sludge in nitrogen gas and various oxygen concentrations. +, $\triangle$, ×, $\square$, $\bigcirc$: 100% N_2,[3] 4.83, 8.62, 12.35, 20.95 vol % O_2.

**Table 3. Reaction Characteristics of Oxidative Thermal Decomposition of Oil Sludge[a]**

Carrier gas	β (K/min)	T_i (K)	T_f (K)	$\Delta T = T_f - T_i$
100% N_2[3]	5.2	425	810	385
	12.8	421	820	399
	21.8	417	825	408
4.83% O_2	5.2	447	859	412
	12.8	435	914	479
	21.8	425	926	501
8.62% O_2	5.2	433	831	398
	12.8	428	858	430
	21.8	420	912	492
12.35% O_2	5.2	423	820	397
	12.8	429	850	421
	21.8	415	903	488
20.95% O_2	5.2	437	806	396
	12.8	427	849	422
	21.8	432	875	443

[a] β: heating rate; T_i, T_f: initial and final temperatures with significant reaction rates.

from the rate curves. These are listed in Table 3 including the pyrolysis case (100% N_2) studied by Shie et al.[3] It is seen in Table 3 that T_i ($dX/dt > 0.002$ min^{-1}) decreases as heating rate (HR, β) increases for fixed concentrations of O_2, except the cases with the heating

rates of 12.8 K/min for 12.35 vol % O_2 and 21.8 K/min for 20.95 vol % O_2. The value of T_f ($dX/dt > 0.002$ min^{-1}) increases as heating rate increases. In view of the presence of oxygen, the effect of oxygen concentration
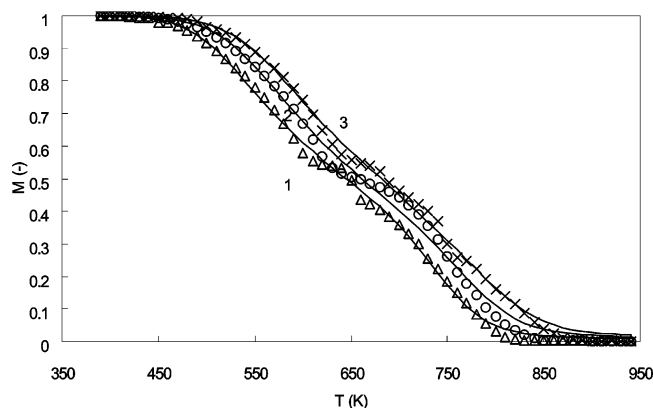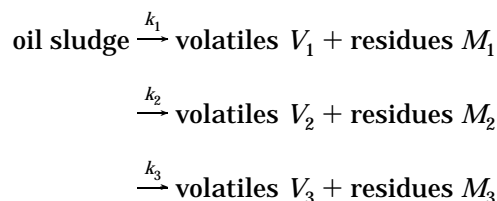
Figure 3. Comparison of M predicted by proposed five-parallel-reaction model with experimental data at different HR for oxidative thermal decomposition of oil sludges in 12.35 vol % O_2. 1 ($\triangle$), 2 ($\bigcirc$), 3 ($\times$): HR = 5.2, 12.8, 21.8 K/min. Line: computed; symbol: experimental; R_1^2, R_2^2, R_3^2 = 0.9975, 0.9918, 0.9966.

on T_i (about 415−447 K) is moderate while that on T_f (about 806−926 K) is vigorous. The temperature difference between final and initial reactions ($\Delta T = T_f − T_i$) increases as heating rate increases at a fixed oxygen concentration. However, except for the case of 100% N_2, the value of ΔT decreases as the oxygen concentration increases at a fixed heating rate. The final fraction residues W_f/W_o are about 6.63−7.99 wt % in the inert atmosphere and about 0.97−6.28 wt % in the oxidative atmosphere. Therefore, in the oxidative environment, there is about 0.35−7.02 wt % reduction of residue. Except for the case with the heating rate of 21.8 K/min for 20.95 vol % O_2, the fraction residue W_f/W_o increases as the heating rate increases. The final residues of oxidative thermal decomposition of oil sludge may be contributed by the oxidation of metals with oxygen. Because there are many metals in oil sludge (Table 2), it is difficult to identify all kinds of oxidative reactions of metals in oil sludge. For simplicity, due to the low fraction of residues (0.97−6.28), we neglect the effects of the final fraction residues and propose the kinetic model according to Figure 1a with $M = (W − W_f)/(W_o − W_f)$ and Figure 1b with $M = W/W_o$.

For 12.35 vol % O_2 under the three heating rates (5.2, 12.8, and 21.8 K/min), the variations of M and dX/dt with T are presented in Figures 3 and 4, respectively. Clearly, the results indicate that a higher heating rate gives a larger value of M (lower value of X). At a lower heating rate, the retention time that is required for the sample to reach a given temperature was longer. This would generally result in a higher conversion (a lower value of M).[29] The peaks of dX/dt shift to the high-temperature region and increase as heating rate increases. Kashiwagi and Nambu[18] used quite low heating rates to ensure that any transport effects on derived kinetic constants were negligible. A recent experimental study[30] was performed on the effect of heating rate on the kinetics of pyrolytic mass loss of cellulose. Cellulose is rapidly heated to above 600 K, giving apparently low

activation energies, mainly between about 140 and 155 kJ/mol. However, cellulose heated more slowly to temperatures below 600 K appears to lose mass with an apparent activation energy of about 218 kJ/mol.[30] It is hypothesized that evaporative escape of tars, the main product of cellulose pyrolysis, might be the process that is transport-limited.[31] Transport limitations impede outflow of volatiles from the sample pans, and are more significant at higher heating rates. As more volatiles are quickly formed at the higher temperatures, more mass per unit time must pass through sample. Therefore, transport limitation is more severe at 60 K/min than at 1 K/min.[32] Generally speaking, the composition of degradation products might be affected by heating rates, but global kinetic constants might not be influenced by heating rates at the conditions without transport limitations (low heating rates).[24] This study is applicable for low heating rates. For high heating rates, further research would be needed.

Kinetic Model. *Kinetic Model of Pyrolysis of Oil Sludge.* It is known that oxidative thermal decomposition is more complicated than pyrolysis alone. During the course of oxidative thermal decomposition, pyrolysis may occur first. For the sole pyrolysis of oil sludge, Shie et al.[3] employed the Friedman method[33] to evaluate the apparent kinetic parameters from the TG data. Their pyrolysis model assumes three independent and parallel reactions with the following scheme:

$$\text{oil sludge} \xrightarrow{k_1} \text{volatiles } V_1 + \text{residues } M_1$$

$$\xrightarrow{k_2} \text{volatiles } V_2 + \text{residues } M_2$$

$$\xrightarrow{k_3} \text{volatiles } V_3 + \text{residues } M_3$$

The instantaneous reaction rates are

$$\frac{dX_1}{dt} = 7.69 \times 10^5 \exp\left(-\frac{69.9}{RT}\right)(1 − X)^{2.94} \quad (1)$$

$$\frac{dX_2}{dt} = 9.09 \times 10^6 \exp\left(-\frac{93.8}{RT}\right)(1 − X)^{2.42} \quad (2)$$

$$\frac{dX_3}{dt} = 2.95 \times 10^8 \exp\left(-\frac{123.2}{RT}\right)(1 − X)^{1.24} \quad (3)$$

For the above reaction scheme, the kinetic equation for the total mass loss rate is

$$\frac{dX}{dt} = \sum F_i \frac{dX_i}{dt}, \quad i = 1, 2, 3 \quad (4)$$

where F_i = weighting factors of reactions.

Reaction Rate Equations of Oxidation Reactions. Conesa et al.[23] indicated that the pyrolysis step of tire

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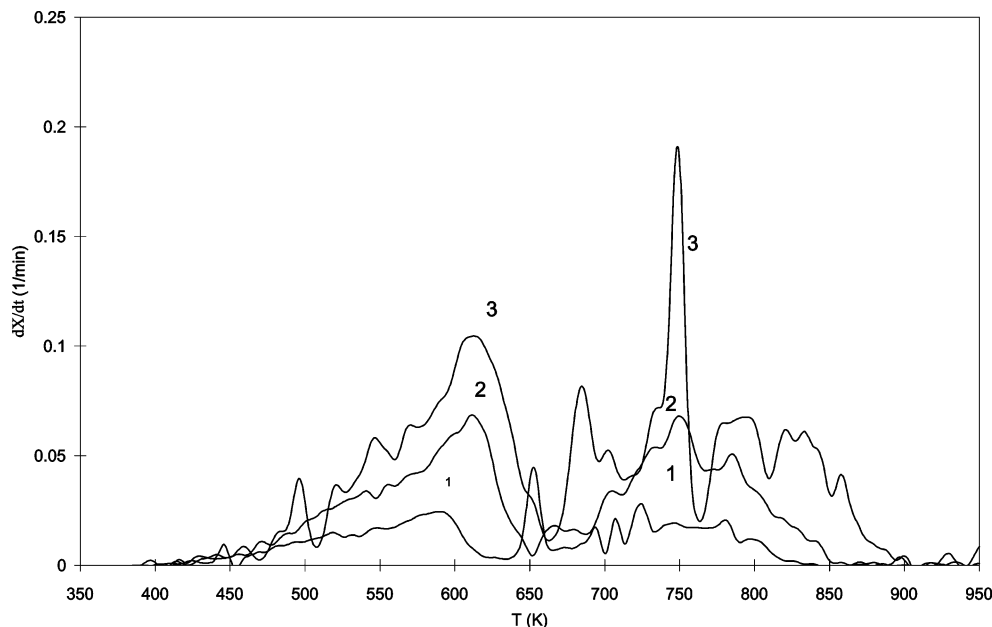
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Figure 4. Variation of dX/dt with T at various HR for oxidative thermal decomposition of oil sludges in 12.35 vol % O_2. Other notations are the same as in Figure 3.

decomposition can contribute to the initial stage of the combustion process and the kinetic constants of pyrolysis alone could be somewhat different from those of combined oxidation and pyrolysis reactions. The residues of pyrolysis of oil sludge exhibit very high viscous form before 623 K (pyrolysis temperature), while low viscous or solid form after 713 K. This indicates that the pyrolysis processes before 623 K would include physical volatilization with the transformation reaction (the first reaction of the three-reaction model of pyrolysis of oil sludge[3]). In the temperature range of 623–713 K, the residues of oil sludge form aggregated solid residues (solid form).[19] From Figure 1, the curves are different for the oxidative thermal decomposition and sole pyrolysis processes for temperatures greater than 613 K ($X = 0.5$), while about the same below 613 K. Above 613 K, the residues of oil sludge for the oxidative thermal decomposition form aggregated solid residues and then react mostly with the oxygen. This step acts like the combustion of the carbonaceous fraction (carbon black and other material). Thus, one can assume that the three-reaction model of pyrolysis is applicable to the oxidative thermal decomposition of oil sludge below a certain temperature, say 613 K ($X = 0.5$). The other reactions contributing to the oxidative thermal decomposition can be deduced by the extension of the Friedman method,[33] as described briefly below.

The foundation for the study of oxidative kinetic data from the mass-loss curve is based on the kinetic reaction rate equation

$$dX/dt = k\, f(\text{X})\, (\text{O}_2)^m \qquad (5)$$

where dX/dt = reaction rate (1/min), k = Arrhenius rate constant, $k = A \exp(-E/RT)$, f(X) = function of conversion $X(-)$, f(X) = $(1 - X)^n$, (O_2) = oxygen concentration (volume %) in carrier gas, and A, E, n, m = frequency factor (1/min), activation energy (kJ/mol), reaction order of unreacted material ($-$), and reaction order of oxygen ($-$), respectively.

Activation Energy of Oxidation Reactions. The differential, iso-conversion method for determining the activation energy was employed in this study. Taking natural logarithms of eq 5, one obtains

$$\ln(dX/dt) = \ln[A(1 - X)^n(\text{O}_2)^m] + (-E/R)(1/T) \qquad (6)$$

At the same residual mass fraction and a fixed oxygen concentration, the reaction temperatures corresponding to the various heating rates with specific residual mass fraction are obtain from Figure 3 (for 12.35 vol % O_2). Meanwhile, the instantaneous reaction rates corresponding to the reaction temperatures would be deduced from Figure 4 (for 12.35 vol % O_2). A straight line with slope $-E/RT$ is obtained by plotting $\ln(dX/dt)$ vs $1/T$ for every residual mass fraction at a fixed oxygen concentration. The activation energy corresponding to the selected residual mass fraction could then be obtained. Examining the activation energies under various conversions and oxygen concentrations and comparing those with the pyrolysis case (100% of N_2) studied by Shie et al.,[3] one notes that the activation energies for the cases of oxidative thermal decomposition and sole pyrolysis are only slightly different for the conversions (X) in the ranges of 0–0.4 and 0.85–1, but are very different for X of 0.45–0.85. For simplicity, one can assume that the reactions for X of 0–0.5 are mainly contributed by pyrolysis. Further for $X > 0.5$, one can divide the activation energies into two conversion ranges that are mainly contributed by the oxidation reactions for various oxygen concentrations, namely, $X = 0.51–0.75$ and 0.76–1. The corresponding average activation energies are 229.8 and 123.3 kJ/mol, respectively.

Reaction Order and Frequency Factor of Oxidation Reactions. Rearranging eq 6, one obtains
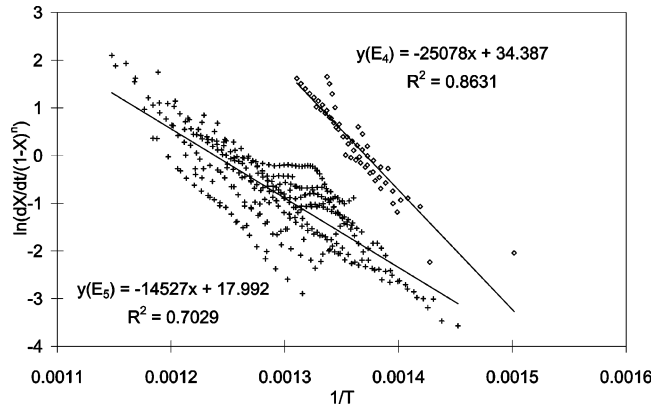
$$\ln[(dX/dt)/\exp(-E/(RT))] = [\ln A + m \ln(\text{O}_2)] + n \ln(1 - X) \qquad (7)$$

Again, at the same degree of conversion, dX/dt and T
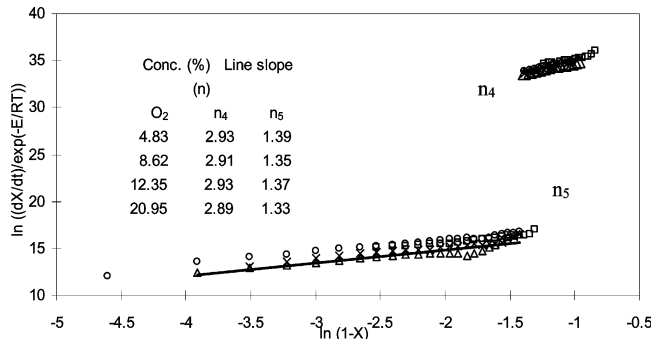
Figure 5. Variation of $\ln[(\mathrm{d}X/\mathrm{d}t)/\exp(-E/(RT))]$ with $\ln(1 - X)$ for determination of reaction order n_4 and n_5 for oxidative thermal decomposition of oil sludge. Other notations are the same as in Figure 3.


Figure 6. Arrhenius plot of $\ln(\mathrm{d}X/\mathrm{d}t/(1 - X)^n)$ vs $1/T$ for determination of refined activation energies E_4 ($\diamond$) and E_5 (+) for oxidative thermal decomposition of oil sludge.

could be specified from Figures 3 and 4 (for 12.35 vol % O_2), respectively. A straight line with slope of n is then obtained by plotting $\ln[(\mathrm{d}X/\mathrm{d}t)/\exp(-E/(RT))]$ vs $\ln(1 - X)$ for the reaction and showed in Figure 5. Therefore, the average orders of reactions of 2.91 and 1.36 could be acquired for the two conversion ranges that are contributed mainly by oxidation reactions with various oxygen concentrations. Should a refined value of E be needed, one could rearrange eq 7 and obtain

$$\ln[(\mathrm{d}X/\mathrm{d}t)/(1 - X)^n] = [\ln A + m \ln(O_2)] + (-E/RT)(1/T) \quad (8)$$
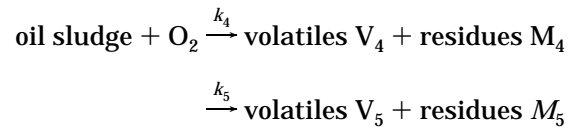
Thus, a straight line with slope of $-E/RT$ can be obtained by plotting $\ln[(\mathrm{d}X/\mathrm{d}t)/(1 - X)^n]$ vs $1/T$ for the reaction as shown in Figure 6. From the curve fittings with R^2 of 0.8631 for E_4 and 0.7209 for E_5, the average refined activation energies for the two conversion ranges of oxidation reactions with various oxygen concentrations are 208.7 and 120.9 kJ/mol. The intercept ($\ln A + m \ln(O_2)$) of eq 8 is plotted against $\ln(O_2)$ to yield a straight line by the least-squares method, for which the slope is m and the intercept is $\ln A$ as shown in Figure 7. The orders of oxidation reactions (m) are 2 and 0.32, and the frequency factors are 1.66×10^{17} and 9.45×10^7 min^{-1} for the two conversion ranges that are contributed mainly by oxidation reactions with various oxygen concentrations.

Oxidation Scheme of Oxidation Reactions. With the kinetic parameters obtained above, the two oxidation reactions deduced are then available for the kinetic
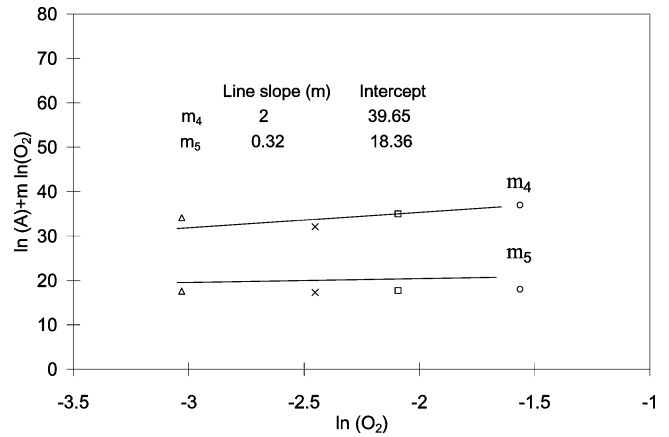
Figure 7. Variation of $[\ln(A) + m \ln(O_2)]$ with $\ln(O_2)$ for determination of reaction orders (m_4 and m_5) and frequency factors (A_4 and A_5) for oxidative thermal decomposition of oil sludge. Other notations are the same as in Figure 3.

model describing the oxidative thermal decomposition. The oxidation reaction scheme is proposed as below:

$$\text{oil sludge} + O_2 \xrightarrow{k_4} \text{volatiles } V_4 + \text{residues } M_4$$

$$\xrightarrow{k_5} \text{volatiles } V_5 + \text{residues } M_5$$

The instantaneous reaction rates are listed below:

$$\frac{\mathrm{d}X_4}{\mathrm{d}t} = 1.66 \times 10^{17} \exp\left(-\frac{208.7}{RT}\right)(1 - X)^{2.91}(O_2)^2 \quad (9)$$

$$\frac{\mathrm{d}X_5}{\mathrm{d}t} = 9.45 \times 10^7 \exp\left(-\frac{120.9}{RT}\right)(1 - X)^{1.36}(O_2)^{0.32} \quad (10)$$

Rate Equations of Oxidative Thermal Decomposition of Oil Sludge. For a reaction scheme of oxidative thermal decomposition of oil sludge considering the roles of both pyrolysis and oxidation, the overall kinetic equations for the total mass loss can be obtained by combining eqs (1)−(3) and (9)−(10) with weighting factors (F_i). This gives

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \sum F_i \frac{\mathrm{d}X_i}{\mathrm{d}t}, \quad i = 1, 2, 3, 4, 5 \quad (11)$$

and

$$-\frac{\mathrm{d}M}{\mathrm{d}t} = -C\frac{\mathrm{d}M}{\mathrm{d}t} = C\frac{\mathrm{d}X}{\mathrm{d}t} = C\sum F_i \frac{\mathrm{d}X_i}{\mathrm{d}t} \quad (12)$$

where C = contribution factor to reaction, $(W_0 - W_f)/W_0$.

The weighting factors of the five-parallel-reaction model for the various oxygen concentrations are listed in Table 4. The weighting factors are obtained by curve fitting with adjustment of the values of F_i so as to have maximal values of R^2. The F_i values thus obtained are about 0.5−0.54, 0.06−0.12, 0−0.02, 0−0.1, and 0.28−0.38 for the five reactions, respectively. Table 4 indicates that when the oxygen concentrations are zeroes, $\mathrm{d}X_4/\mathrm{d}t$ and $\mathrm{d}X_5/\mathrm{d}t = 0$. The overall kinetic equations for the oxidative thermal decomposition of oil sludge can be reduced to those of sole pyrolysis of oil sludge (eq 4).

Table 4. Weighting Factors of Five-Parallel-Reaction Model and Coefficients of Determination (R^2) at Three Heating Rates for Cases with Pure Nitrogen and Oxygen Concentrations of 4.83, 8.62, 12.35, and 20.95 vol % O_2

Gas concentration vol %	F_1	F_2	F_3	F_4	F_5	R^2 5.2 K/min	R^2 12.8 K/min	R^2 21.8 K/min
100 N_2[3]	0.5	0.22	0.28	0	0	0.9981	0.9945	0.9981
4.83 O_2	0.5	0.12	0.02	0.1	0.28	0.9922	0.9934	0.9929
8.62 O_2	0.5	0.12	0.01	0	0.37	0.9927	0.9967	0.9923
12.35 O_2	0.54	0.09	0	0.05	0.32	0.9975	0.9918	0.9966
20.95 O_2	0.5	0.06	0	0.06	0.38	0.9926	0.9924	0.9913
4.83−20.95 O_2	0.51[a]	0.1[a]	0.01[a]	0.05[a]	0.34[a]			

[a] Average value of results of weighting factor for oxygen concentrations of 4.83−20.95% O_2.

Comparison of Experimental Data and Proposed Model. The mass balance of the overall oxidative thermal reaction gives

$$M = 1 - \Sigma M_{vi}, \quad \text{where } X_i = M_{vi}/F_i, \text{ and } i = 1, 2, 3, 4, 5 \quad (13)$$

The production rate of V_i (volatile gas of i reaction) could be expressed as

$$d(M_{vi}/F_i)/dt = A_i \exp(-E_i/RT)(1 - (M_{vi}/F_i))^{ni}, \quad i = 1, 2, 3 \quad (14)$$

and

$$d(M_{vi}/F_i)/dt = A_i \exp(-E_i/RT)(1 - (M_{vi}/F_i))^{ni}(O_2)^{mi}, \quad i = 4, 5 \quad (15)$$

where M_{vi} = mass fraction of volatile V_i of ith reaction (−), A_i = frequency factor of ith reaction (1/min), E_i = activation energy of the ith reaction (kJ/mol), n_i = reaction order of unreacted material of ith reaction (−), and m_i = reaction order of oxygen of the ith reaction (−).

The initial conditions are

$$M = 1, M_{vi} = 0, \text{ at } t = 0 \quad (16)$$

Because the constant heating rate is employed, eqs (13) and (14) can be solved with the initial conditions of eq (15). It can be shown that

$$M_{vi} = F_i\left[1 - \left[1 - (1 - n_i)\frac{A_i RT^2}{\beta E_i} \times \exp\left(-\frac{E_i}{RT}\right)\sum(E_i, T)\right]^{1/1 - n_i}\right], \quad i = 1, 2, 3, \quad (17)$$

and

$$M_{vi} = F_i\left[1 - \left[1 - (1 - n_i)\frac{A_i RT^2}{\beta E_i}(O_2)^{m_i} \times \exp\left(-\frac{E_i}{RT}\right)\sum(E_i, T)\right]^{1/1 - ni}\right], \quad i = 4, 5 \quad (18)$$

where

$$\sum(E_i, T) = \sum_{j=0}^{\infty}\left[\left(-\frac{RT}{E_i}\right)^j\prod_{k=0}^{j}(k+1)\right] = 1 - 2\frac{RT}{E_i} + 6\left(\frac{RT}{E_i}\right)^2 - 24\left(\frac{RT}{E_i}\right)^3 + 120\left(\frac{RT}{E_i}\right)^4 - \ldots \quad (19)$$

A comparison of residual mass fractions predicted by the proposed model with those obtained by experiments is also shown in Figure 1 for various oxygen concentrations of heating rate 5.2 K/min and in Figure 3 for the 12.35 vol % O_2 of three heating rates, indicating satisfactory agreement. To verify the applicability of kinetic parameters and the validity of the proposed model, the coefficient of determination (R^2) is examined for $0.05 < M$ (predicted) < 0.95. The values of R^2 for various oxygen concentrations are 0.9922−0.9975, 0.9918−0.9967, and 0.9913−0.9966 for the heating rates of 5.2, 12.8, and 21.8 K/min, respectively, as listed in Table 4 along with those for the pyrolysis case (100% N_2) studied by Shie et al.[3] This supports the validity and practical applicability of the proposed reaction kinetic model for describing the oxidative thermal decomposition of oil sludge without specifying the detailed chemical reactions involved. The oxidative thermal decomposition model can be used for both cases of sole pyrolysis ((O_2) = 0) and oxidative thermal decomposition ((O_2) < 20.95 vol %) of oil sludge. However, the model is an empirical one. It doses not enter into reaction mechanisms or the chemical and physical nature of the materials involved. On the basis of the multi-reaction kinetic model (five-reaction), the reaction pathways would involve a multi-reaction mechanism. Multi-gross categories of combustible reactants, which in turn yield their distinct products correspondingly, might exist in the oil sludge.

A reaction scheme with eqs (1), (9), and (10) has also been tested. The values of R^2 for various oxygen concentrations are 0.9634−0.99, 0.9731−0.9921, and 0.9589−0.9913 for the heating rates of 5.2, 12.8, and 21.8 K/min with the weighting factors of 0.5−0.54, 0.11−0.22, and 0.28−0.38 for the three reactions, respectively. Adding eqs (2) and (3) into eqs (1), (9), and (10) would give the proposed model for the overall oxidative thermal decomposition of oil sludge. With a five-reaction model, the values of R^2 of simulation results for various oxygen concentrations would be improved, giving 0.9922−0.9975, 0.9918−0.9967, and 0.9913−0.9966 for the heating rates of 5.2, 12.8, and 21.8 K/min, respectively. Thus, it is adequate for proposing a five-parallel-reaction model in this study.

Conclusions

The oxidative thermal decomposition of oil sludge was carried out by a TGA reaction system at four oxygen concentrations (4.83, 8.62, 12.35 and 20.95 vol % O_2). A five-parallel-reaction kinetic model was proposed to predict the experimental results. The activation energies, frequency factors, and reaction orders were deter-

mined for the corresponding reactions under experimental conditions. The proposed model can adequately describe the oxidative thermal decomposition of oil sludge. This study greatly assists the utilization of oil sludge as an energy resource.

Glossary

A	frequency factor (1/min)
C	contribution factor to reaction, $(W_o - W_f)/W_o$
E	activation energy (kJ/mol)
$f(X)$	the function of conversion X $(-)$, $f(X) = (1 - X)^n$
F_i	weighting factor of reaction i contributing the oxidative thermal treatment
i	ith reaction contributing the oxidative thermal treatment
k	the Arrhenius rate constant of one-reaction model, $k = A \exp(-E/RT)$
k_1, k_2, k_3, k_4, k_5	the Arrhenius rate constants of five-parallel-reaction model
M	residual mass fraction of active reactant, $M = (W - W_f)/(W_o - W_f)$
M'	residual mass fraction of reactant, $M' = W/W_o$
M_{vi}	mass fraction of volatile V_i $(-)$
m	reaction order of oxygen $(-)$
n	reaction order of residual solid $(-)$
(O_2)	oxygen concentration by volume in carrier gas
r	dX/dt
R	universal gas constant, 8.314×10^{-3} kJ/mol K
T	reaction temperature (K)
ΔT	reaction range ($\Delta T = T_i - T_f$)
T_i	initial reaction temperature
T_f	final reaction temperature
W	present mass of sample
W_o	initial mass of sample
W_f	final mass of sample
X	conversion, $1 - M$
$dX/dt, r$	the reaction rate (1/min), $r = dX/dt$
β	heating rate (K/min)

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