Journal of Thermal Analysis and Calorimetry, Vol. 79 (2005) 653–662

THERMOGRAVIMETRIC COMBUSTION KINETICS OF PETROLEUM EFFLUENT TREATMENT PLANT SLUDGE

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This communication reports the thermal characteristics of an oil field effluent treatment plant (ETP) sludge and organic materials separated from it (SOM) as investigated by thermogravimetric (TG) and infrared (IR) spectroscopic methods. The calorific value of the sludge is approximately 4000 Kcal kg^{-1} and the fuel value of the sludge may be utilized in production of various materials. Analysis and evaluation of kinetic parameters in the 100–600°C region of non-isothermal TG curves obtained in air atmosphere and also analysis of IR spectra of the decomposed products reveal considerable effect of inorganic materials present in the sludge on the thermal decomposition of organic materials. A simple kinetic model has been proposed to describe the thermal behaviours of the sludge and its organic materials.

Keywords: *IR analysis, petroleum ETP sludge, thermal analysis, thermokinetics*

Introduction

A variety of wastes, containing high amounts of hydrocarbons are generated during production and refining of petroleum. These wastes are hazardous in nature and their disposal/gainful utilization is an important global issue. Combustion, pyrolysis, gasification etc. offer considerable benefits over conventional landfills for disposal of such wastes as these processes considerably reduce the volume of waste and in many cases the energy can be utilized [1–5].

Lakwa oil field, situated in the northeastern region of India is one of the largest oil producing area and the ETP of this oil field produces about 12 m^3 of sludge per day. The organic material content in the sludge is not so high like some other petroleum derived sludge for their economical recovery. However, the fuel value of the sludge, like in many other carbonaceous wastes [6, 7] can be used in the preparation of masonry bricks, lightweight aggregates, calcined clay pozzolana etc. ceramic materials [8–11]. Utilization of the organic materials of the sludge as a fuel for various purposes requires knowledge of its thermoanalytical characteristics. The thermal characteristics of the sludge can be conveniently carried out isothermally and non-isothermally using a thermogravimetric analyzer with a small amount of sample. The isothermal experiments may lead to some error due to difficulty in accounting for the reaction occurring during the heating up period [12] and thus non-isothermal methods, based on heating the sample at a constant heating rate and recording the mass change is more practical for simulating large-scale processes. The combustion behaviour of Lakwa ETP sludge, as investigated by non-isothermal thermogravimetric and IR methods has been presented in this communication. The kinetic parameters were also determined by applying standard methods and a simple thermokinetic model has been proposed to explain the reaction steps.

Experimental

The detailed methods of sample preparation, chemical analysis, trace metal analysis, separation and characterization of organic matter, determination of calorific value were reported in our previous communications [8–11].

The thermoanalytical curves were obtained in a computerized TA instruments (model STD 2960 simultaneous DTA TG), under dynamic airflow at the rate of 100 cm^3 min^{-1}. The samples (~10 mg) were heated in a platinum crucible at the heating rates of 5 and 10°C min^{-1} using α-Al_2O_3 as the reference material. The airflow and amount of samples were previously standardized to obtain better thermal curves.

In another set of experiments, approximately 5–10 g of the separated organic materials (SOM) and the sludge were taken in platinum crucibles and heated in an electric furnace in air atmosphere to 250,

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1388–6150/$20.00

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350 and 450°C for 0 and 60 min at the heating rate of 10°C min^{-1}. The zero time was taken as the time when the desired temperature had attained. The samples were withdrawn from the furnace, allowed to cool rapidly in a desiccator and their IR and FTIR spectra were recorded in a PerkinElmer IR spectrometer, model 640B. The spectra of the oily products were recorded from thin film of the neat sample on NaCl disk and for the rest, from KBr disks. A small amount of the sludge, taken in a platinum crucible was also heated in an electric chamber furnace at different temperatures up to 550°C with 30 min soaking time. The colour of the sample was recorded after cooling.

Kinetic analysis

The rate expression for a decomposition reaction can be written as:

$$dX/dt = k\,(1-X)^n \qquad (1)$$

where X – fractional conversion, t – time, k – rate constant and n – reaction order.

Under non-isothermal conditions for a constant heating rate $\beta=dT/dt$ in K min^{-1} and with the rate constant expressed in Arrhenius form i.e. $k=A\exp(-E/RT)$, Eq. (1) can be written as:

$$dX/dt = \beta dX/dT = A(1-X)^n \exp(-E/RT) \qquad (2)$$

$$\int_0^X dX/(1-X)^n = (A/\beta)\int_0^T \exp(-E/RT)dT \qquad (3)$$

where, A – frequency factor, E – activation energy, R – gas constant and T – absolute temperature in K.

Coats and Redfern [13] integrated Eq. (3) by expanding it into series with the limit conditions of $X=0$ for $T=T_0$ and $X=X$ for $T=T$. Thus by ignoring the higher order terms they obtained the Eq. (4)

$$\ln[\{g(X)\}/T^2]=\ln[\{AR/\beta E\}\{1-2RT/E\}]+(-E/R)1/T \qquad (4)$$

where $g(X)= -\ln(1-X)$ for $n=1$ and $g(X)=[\{1-(1-X)^{1-n}\}/(1-n)]$ for $n\neq 1$.

The first term of the right hand side of Eq. (4) is approximately constant for large value of E/RT (>20). Therefore, when $g(X)$ is calculated using correct n value, then the plot of $\ln[g(X)/T^2]$ *vs.* $1/T$ gives a straight line with a slope $-E/R$, which is used to calculate the apparent activation energy, E. The frequency factor, A is determined from the intercept of the straight line.

The values of apparent activation energies and frequency factors, which do not follow the condition, $E/RT>20$, the kinetic parameters are calculated by using differential method. The Eq. (1) can be rearranged and expressed in Arrhenius form as:

$$(dX/dt)/(1-X)^n = A\exp(-E/RT)$$

or

$$\ln[(dX/dt)/(1-X)^n]=\ln[A]+(-E/R)\,1/T \qquad (5)$$

Table 1 Some properties and composition of oil sludge used in this study

Physical characteristics	Colour: brown	Odour: mineral oil	State: slurry
Drying/calcining characteristics:	100±10°C	500±10°C	950±10°C
mass loss/%	68.57	80.45	87.73
Calorific value:	As received material:	3980	
kcal kg^{-1}	After drying at (100±5°C)	4353	
Separated organic materials:	Resin	26.50%	
	Wax	8.50%	
	Asphaltene	0.35%	
	Other heavy oil components	64.00%	
Oxide	Amount/%	Elements	Amount/mg kg^{-1}
SiO_2	18.98	Cr	414.1
Al_2O_3	48.12	Pb	nd
CaO	25.04	As	24.0
Fe_2O_3	1.30	Cd	1.7
MgO	0.56	Hg	0.6
Na_2O	1.01	Ni	144.6
K_2O	0.39	Mn	228.6
SO_4^{2-}	3.21		

A straight line with slope ($-E/R$) and intercept $\ln A$, which respectively give apparent activation energy, E and frequency factor, A, can be obtained by plotting $\ln[(\mathrm{d}X/\mathrm{d}t)/(1-X)^{\mathrm{n}}]$ *vs.* $1/T$ if correct n value is used.

Kinetic curves were analysed by using MS Excel package (version 9.0.2719) in a computer. The statistical parameters (R^2 value and standard error, S_e) were also evaluated for determination of probable reaction mechanisms.

Results and discussion

The composition of the sludge, SOM and sludge ash are shown in Table 1. The sludge contains 4.8% organic and 7% inorganic materials, which corresponds respectively to 40.68 and 59.32% of the dried sludge. The organic materials contain heavy oil, resin, wax and very small amount of asphaltene. The calorific value of the as received sludge is ~4000 kcal kg^{-1} and it increases slightly on drying the sludge at 100±5°C (4353 kcal kg^{-1}), may be due to the lowering of moisture content. Al_2O_3, CaO, SiO_2, Fe_2O_3, SO_4^{2-} and Na_2O are the major inorganic constituents of the sludge along with various toxic elements.

The thermoanalytical curves of the SOM and sludge are shown in Fig. 1. The mass loss in the temperature ranges of 100–250, 250–400 and 400–600°C for SOM are 40.69, 46.07 and 13.24% respectively. The same for sludge are respectively 18.01 (35.24), 19.75 (38.55) and 13.31 (26.21)%. It is assumed that the mass loss for sludge at the temperature region of 100–600°C correspond to the loss from the organic materials of the sludge. The data indicated in the parenthesis are obtained after this assumption and correspond to the percentage loss of organic materials in the temperature ranges with respect to the total loss of organic materials from sludge at the temperature region of 100–600°C.

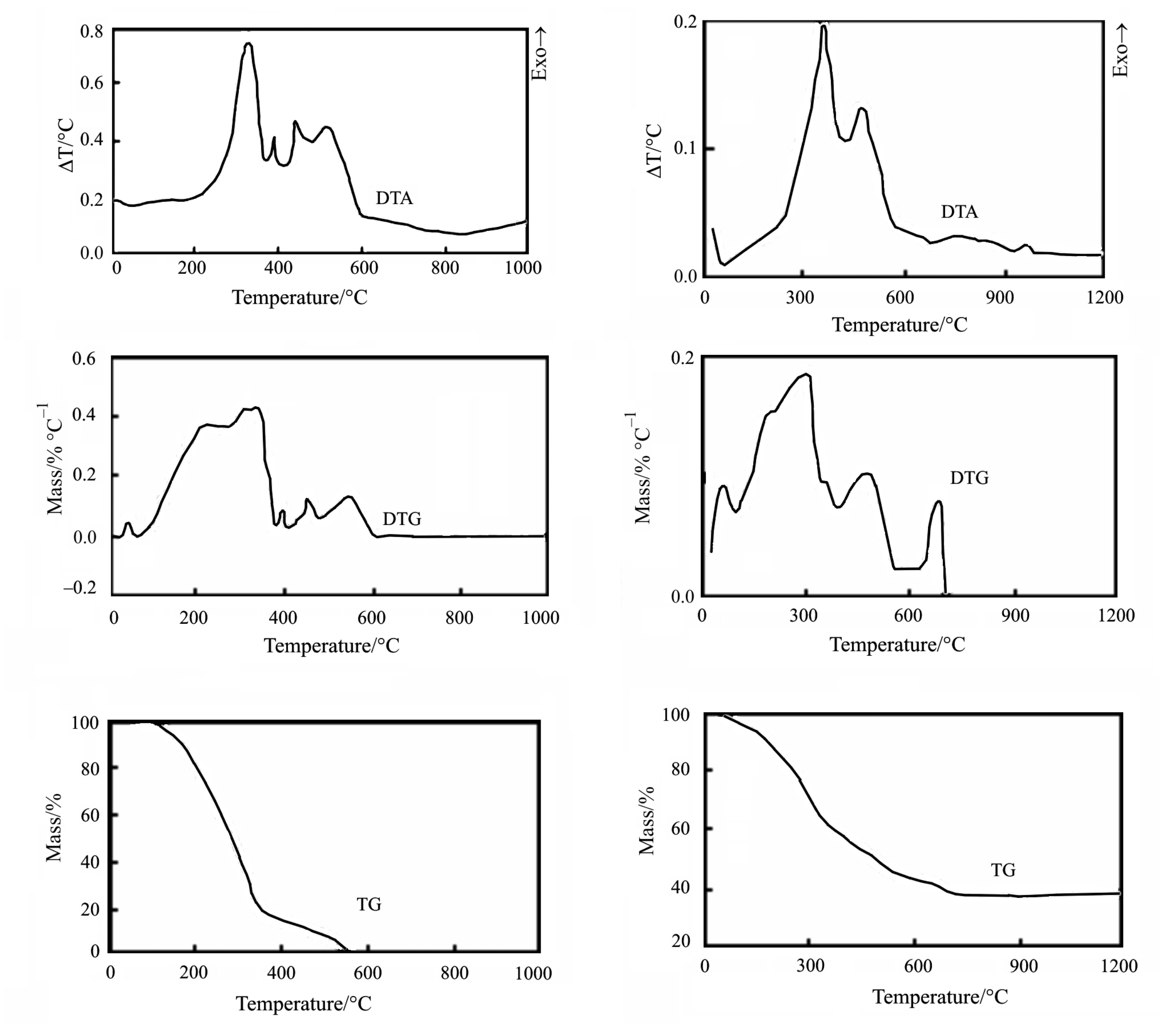

Fig. 1 Thermal curves of SOM and sludge

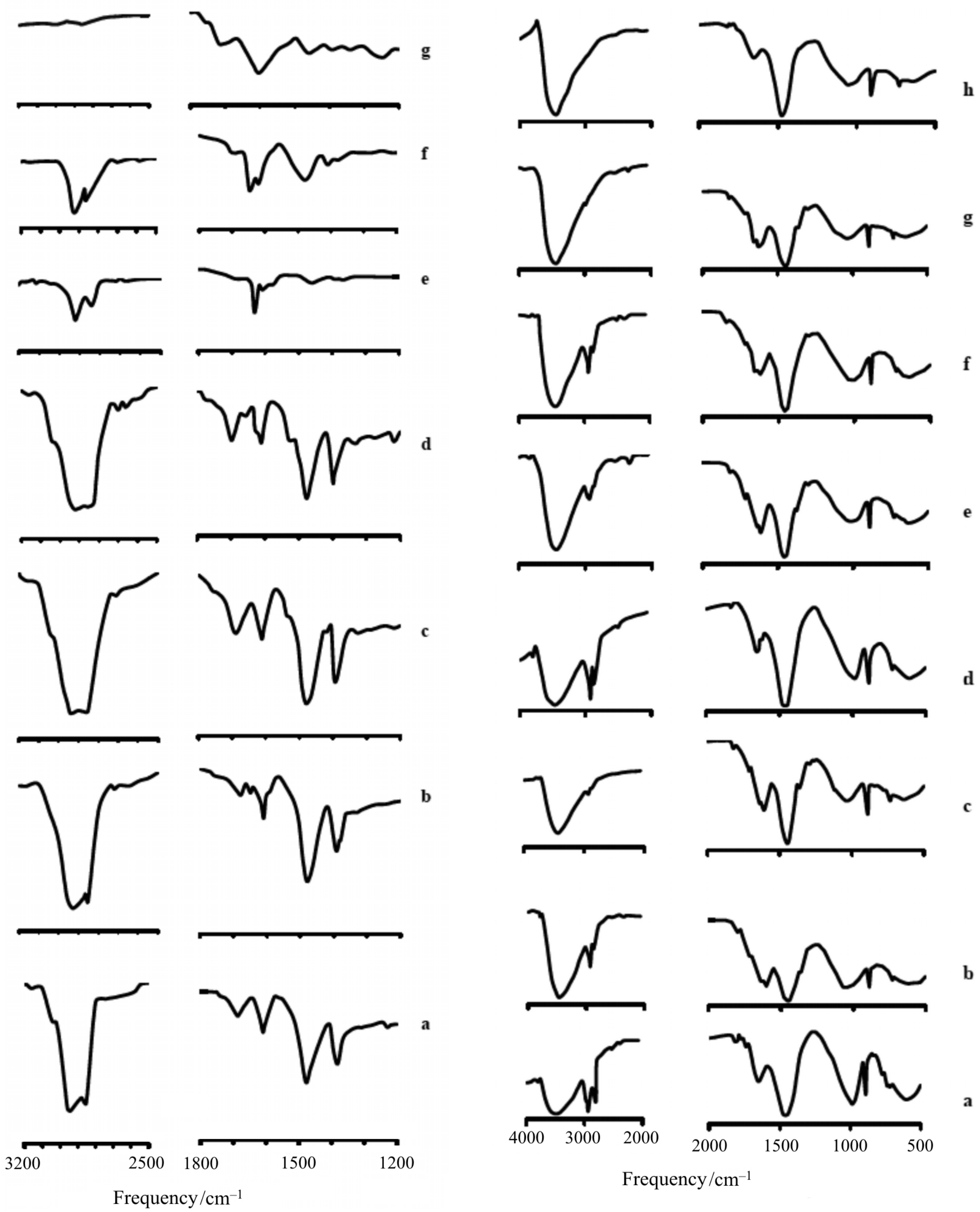

Fig. 2 IR spectra of SOM and FTIR spectra of sludge, heat treated at different temperatures and times: a – original; b – 250°C for 0 min; c – 250°C for 60 min; d – 350°C for 0 min; e – 350°C for 60 min; f – 450°C for 0 min; g – 450°C for 60 min; h – 550°C for 0 min (sludge only)

The TG and DTG patterns of the SOM and sludge show that the mass loss from these materials takes place in three different temperature regions. The DTA patterns of both the samples exhibit endothermic tendency in the temperature regions of 100–250°C accompanied with mass loss due to distillation/volatilization of the organic materials. This is followed by an exotherm (250–400°C) with exothermic maxima at 350.3°C for sludge and 338.1°C for SOM, due to thermal oxidative cracking. The DTA pattern of the sludge shows a weak inflexion at 330°C accompanied by a break in the TG curve and is attributed to onset of polymerization of some cracked products. Thus exothermic maximum observed at 350.3°C in the DTA curve of the sludge corresponds to both the oxidative cracking and polymerization processes. The DTA curve of SOM shows the exothermic maximum at 338.1°C accompanied by a break in the TG curve in the same temperature indicating initiation of polymerization reaction. The DTA curve of the SOM exhibits two other exotherms in the temperature regions of 400–500 and 500–600°C, attributed to polymerization of cracked products and their combustion. The sludge sample however exhibits a broad exotherm due to combustion of polymerized products (char) in the 400–600°C region with maximum at 476°C. This maximum is at a lower temperature than that of the SOM (530°C) indicating influence of inorganic materials present in the sludge on the combustion of the organic materials. The mass loss from the sludge in the temperature regions of 100–250 and 250–400°C are less and 400–600°C are more than those from the SOM. The inorganic materials, therefore, reduce the conversion in the thermal cracking and thermal oxidative cracking stages but increases the amount of polymerized products.

The IR spectra of the SOM as such and after heating under isothermal conditions at 250, 350 and 450°C for various durations are shown in Fig. 2. The SOM exhibits sharp and strong bands at 2800–3000 and 1377–1475 cm^{-1} regions characteristics of aliphatic compounds and prominent bands of aromatic hydrocarbons and compounds containing >CO group respectively at 1600 and 1713 cm^{-1}. The intensity of the band at 1713 cm^{-1} decreases on heating the samples to 250°C for 0 min. The DTA curve of the SOM (Fig. 1) also shows an exothermic tendency up to 250°C suggesting thermal degradation of the low volatile components containing >CO groups. The intensities of the bands due to compounds containing >CO group and aromatic hydrocarbons increase due to oxidative thermal degradation and aromatization of hydrocarbon and those of aliphatic group remains almost unaltered on prolonging the heating time to 60 min, which is also suggested by the thermal curves. The same effect of prolonging the heating time at 250°C on the intensities of the bands at 1713 and 1600 cm^{-1} can be achieved by increasing the temperature to 350°C for 0 min. The heated product exhibits a peak at 1224 cm^{-1} indicating the formation of –COOH group. This peak completely disappear as well as the bands at 1713, 2800–3000 and 1377–1475 cm^{-1} decrease sharply and that at 1600 cm^{-1} increases due to oxidative thermal degradation of aliphatic hydrocarbons and aromatization of organic compounds on increasing the heating time at 350°C to 60 min. The same changes are observed on heating the sample at 450°C for 0 min. The intensities of the bands in the region of 2800–3000 cm^{-1} decrease and a new band appear at 1600 cm^{-1} indicating enhanced combustion of aliphatic compounds and formation of aromatic products on prolonging the heating time at 450°C.

FTIR spectra of the sludge and its heat-treated products are also shown in Fig. 2. The bands at ~2922 and ~2851 cm^{-1} are due to aliphatic hydrocarbons and the sharp band around 1630 cm^{-1} may be due to C=C vibration or O–H stretching vibration of adsorbed water. The aliphatic band region (1377–1475 cm^{-1}) is less informative due to presence of large amount of calcite in the sludge. The intensities of the peaks at 2922 and 2851 cm^{-1} slightly decrease on heating the sludge up to 250°C for 0 min indicating degradation of aliphatic materials. The decreasing intensities of these peaks and increasing intensities of peaks due to aromatic (1600 cm^{-1}), >CO, –COOH and –OH groups indicating oxidation of degraded products and formation of aromatics on prolonging the heating at 250°C to 60 min. The intensities of the peaks at 2800–3000 cm^{-1} increase and those at 1700, 1366, 1300 and 1600 cm^{-1} decrease on heating the sludge at 350°C for 0 min indicating degradation of aromatic structures and formation of aliphatic compounds. Increasing the heating time up to 60 min, again decreases the intensities of the peaks due to aliphatic groups and increases the intensities of the bands due to aromatic as well as compounds containing >CO, –COOH and –OH groups indicating the increase oxidation and aromatization of the organic material. The intensities of the peaks due to aliphatic groups increase and those due to aromatics (1600 and 3010 cm^{-1}), >CO, –COOH and –OH groups decrease on heating the sludge up to 450°C for 0 min. The intensities of the peaks due to aromatic, >CO, –COOH and –OH groups increase and those due to aliphatic compounds decrease on increasing the heating time to 60 min. Thus polymerization and combustion are the major reactions taking place at 450°C. The sample heated to 550°C for 0 min does not exhibit peaks due to aromatic groups indicating completion of the combustion reaction. The disappearance of the bands due to aliphatic compounds accompanied with appearance of the bands due to aromatic, >CO, –COOH and –OH groups indicates the thermal oxidation of the organic compounds with aromatization. The formed –COOH and –OH groups possibly combine with the alkaline metal ions present in the sludge forming M^{2+}–O type surface groups which accelerate the combustion of the polymerized products like chars [14].

Visual observation showed that the sludge ash produced at 350°C is black in colour indicating that it is rich in char. The colour fades on heating at 450°C, due to combustion of the char. The 550°C heated ash is almost white indicating complete combustion of the carbonaceous materials.

Thus the decompositions of the organic materials in the sludge and SOM proceed through the following different steps:

For sludge: I. 100–250°C: distillation and volatilization; II. 250–400°C: oxidative thermal cracking and formation of aromatic polymerized products; III.

Table 2 Activation energies (kJ mol^{-1}), reaction rates and frequency factors (s^{-1}) according to Coats and Redfern (CR) and differential (DM) methods

Temperature/°C	CR method			DM method			*F* value
	Reaction order	Activation energy	Frequency factor	Reaction order	Activation energy	Frequency factor	
A. Separated organic materials at the heating rate of 10°C min^{-1}							
100–250	1.5	59.91	$1.29\cdot10^{6}$	1.25	58.23	$8.43\cdot10^{5}$	0.40
250–400	1.5	102.35	$5.70\cdot10^{8}$				0.45
400–500	2.0	243.92	$1.55\cdot10^{18}$				0.07
500–600	2.0	457.83	$1.71\cdot10^{29}$				0.08
B. Sludge I at the heating rate of 10°C min^{-1}							
100–250	1.0	38.66	$3.48\cdot10^{3}$	1.0	33.69	$1.10\cdot10^{3}$	0.35
250–400	2.0	110.71	$3.82\cdot10^{9}$				0.39
400–600	2.0	149.00	$8.33\cdot10^{9}$				0.26
C. Sludge I at the heating rate of 5°C min^{-1}							
100–250				1.0	34.22	$6.81\cdot10^{2}$	
250–400	2.0	83.90	$5.34\cdot10^{6}$	2.0	96.10	$7.67\cdot10^{7}$	
400–600	2.0	109.36	$6.58\cdot10^{6}$	2.0	107.00	$6.58\cdot10^{6}$	
D. Sludge II at the heating rate of 10°C min^{-1}							
100–285	1.5	41.60	$6.08\cdot10^{3}$	1.0	27.07	$1.27\cdot10^{2}$	
250–420	1.5	86.84	$4.66\cdot10^{6}$	1.5	72.13	$3.70\cdot10^{5}$	
400–500	2.0	300.11	$2.63\cdot10^{21}$				

400–600°C: combustion of aromatic polymerized products.

For SOM: I. 100–250°C: distillation and volatilization; II. 250–400°C: oxidative thermal cracking and formation of aromatic polymerized products; III. 400–500°C: formation and combustion of aromatic polymerized products; IV. 500–600°C: combustion of aromatic polymerized products.

Figure 3 shows the plots of $\ln[(g(X)/T^2)]$ *vs.* $1/T\cdot10^3$ for the SOM and sludge respectively in different temperature regions. The kinetic parameters calculated for different steps of the thermal conversion reactions of the organic materials associated with the sludge and SOM are shown in Table 2.

The reaction orders of the SOM in the temperature regions of 100–250 and 250–400°C are 1.25 and 1.50 respectively and at 400–500 and 500–600°C, it is 2.0. The reaction orders of the organic materials associated with the sludge at 100–250°C is 1.0 and at 250–400°C and 400–600°C, it is 2.0. The reaction order for vaporization of pure organic substances like benzene has been reported as 0 and that for crude oil distillation as 2.2 [15, 16]. The relatively high reaction orders for distillation and volatilization of the organic materials associated with the sludge (1.0) and SOM (1.25) is probably due to complex nature of the organic materials.

The apparent activation energy for distillation and volatilization of organic materials associated in the sludge (~33 kJ mol^{-1}) is lowers than that (~58 kJ mol^{-1}) for the SOM and is in good agreement with the generally observed activation energy of adsorption. The low activation energy and reaction order for the organic materials associated in the sludge than those for the SOM are possibly for adsorption of the organic materials on the inorganic surfaces of the sludge. The apparent activation energies for the organic materials present in the sludge (110.71 kJ mol^{-1}) and SOM (102.35 kJ mol^{-1}) at 250–400°C region are approximately same, possibly due to the presence of $CaCO_3$ and clay bearing materials in the sludge [17], which have opposite character [18]. The former enhances and the later inhibits oxidation of the carbonaceous materials [18]. The inorganic materials present in the sludge profoundly influence the combustion (400–600°C) of organic materials. It takes place in a single step against two steps conversions found for the SOM. In determination of the kinetic parameters, the TG data of the SOM at this temperature region could not be fitted for one stage conversion (R^2<0.90). The apparent activation energy for the combustion of the organic materials in the sludge (149 kJ mol^{-1}) is considerably lower than those for the SOM (~244 and 458 kJ mol^{-1}) and is attributed to the catalytic activity [19] of some of the inorganic materials like $CaCO_3$ present in the sludge [18]. The DTA pattern of the sludge and also the energy

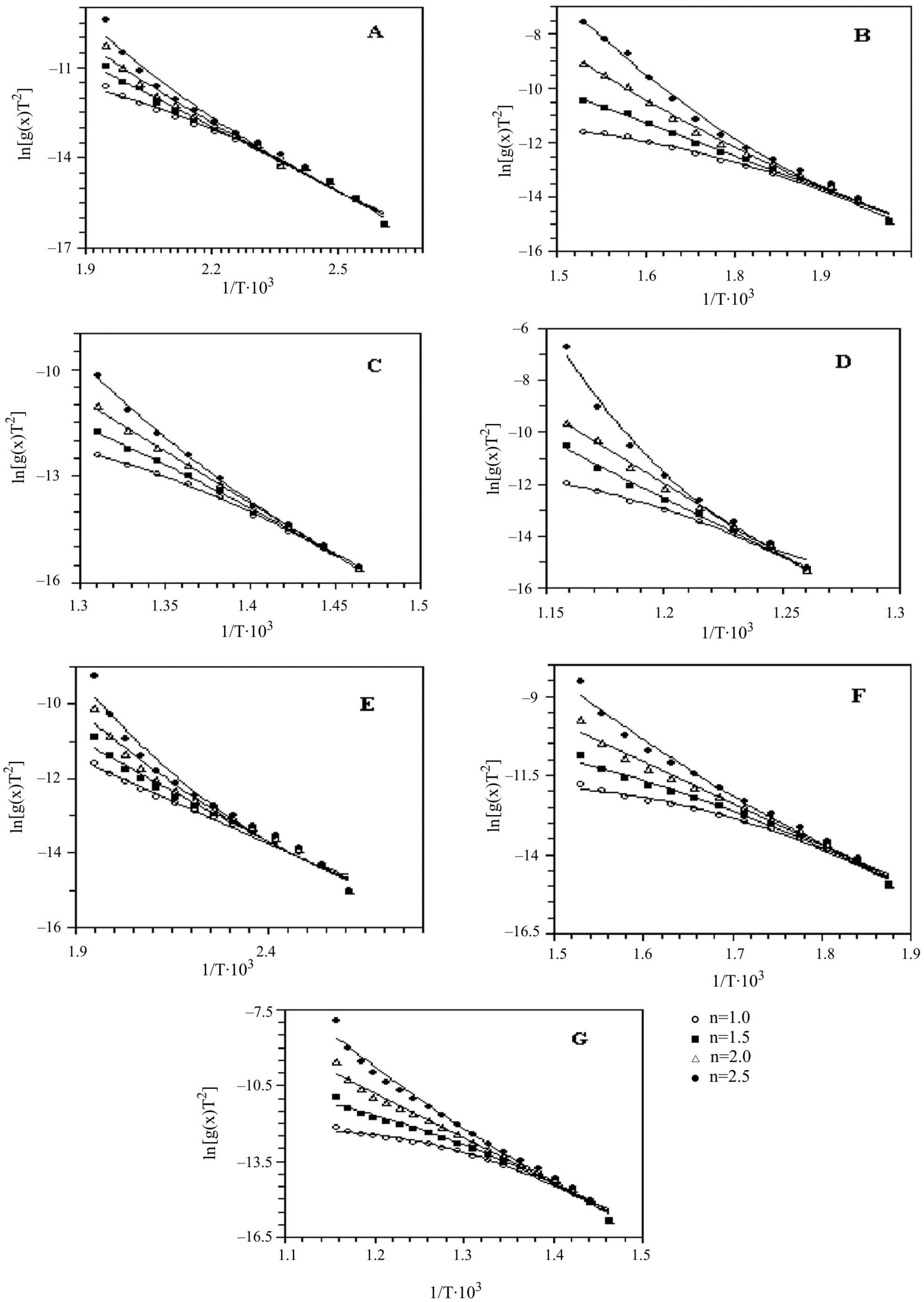

Fig. 3 1/T·10^3 (K^{-1}) *vs*. ln[$g(x)/T^2$] plots for SOM (A, B, C, D) and sludge (E, F, G) at different temperature regions: (A, E) 100–250°C, (B, F) 250–400°C, (C) 400–500°C, (D) 500–600°C, (G) 400–600°C

parameters evaluated for the temperature ranges of 250–400 and 400–600°C of sludge are similar to oxidation of oil shale reported by other workers [20]. The apparent activation energies for carbon burning process increases with the increase in the orderliness of carbon structure and for activated carbon, char etc. it is in the range of 119–459 kJ mol^{-1} [21]. The apparent activation energies for decomposition of the char produced in the sludge and SOM are although in the above range, but it is higher for the char produced from the later. The char produced from SOM undergo combustion at relatively higher temperature than that in the sludge too. The char produced in decomposition of the SOM is therefore more ordered. The inorganic materials in the sludge, therefore affect the mechanism of char formation.

The thermal change of organic materials present in the sludge is very complex because various complex concurrent/consecutive reactions are taken place due to decomposition of wax, resin, different heavy oil fractions etc. constituents. The mechanism and corresponding kinetic parameters for thermal conversions of the various organic materials present in the sludge are different from the SOM due to presence of various inorganic constituents and therefore extremely difficult to determine the exact kinetic parameters from the TG curve. However changes occurring in a certain temperature range can be represented by simple conversion reactions and kinetic parameters for these reactions can be determined by using thermogravimetric curve.

The following reaction models are assumed for thermal decomposition of organic materials present in the sludge and SOM based on the TG and IR analyses:

Sludge $\xrightarrow{K_1^s,\,100\text{–}250℃}$ decomp. product (d_1^s) +residues (r_1^s) $\xrightarrow{K_2^s,\,250\text{–}400℃}$ decomp. product (d_2^s) +residues (r_2^s) $\xrightarrow{K_3^s,\,400\text{–}600℃}$ decomp. product (d_3^s) +residues (r_3^s)

SOM $\xrightarrow{K_1^0,\,100\text{–}250℃}$ decomp. product (d_1^0)+residues (r_1^0) $\xrightarrow{K_2^0,\,250\text{–}400℃}$ decomp. product (d_2^0)+residues (r_2^0) $\xrightarrow{K_3^0,\,400\text{–}500℃}$ decomp. product (d_3^0)+residues (r_3^0) $\xrightarrow{K_4^0,\,500\text{–}600℃}$ decomp. product (d_4^0)

Based on the proposed models and Arrhenius law, the fraction converted of j^{th} sample in the temperature range of 0–f (f for final temperature), X_t^j for sludge and SOM may be obtained by the following equations:

$$X_\mathrm{t}^\mathrm{j}=\frac{(W_0^\mathrm{j}-W_\mathrm{t}^\mathrm{j})}{(W_0^\mathrm{j}-W_\mathrm{f}^\mathrm{j})}=\sum_{\mathrm{i}=1}^{3}md_\mathrm{i}^\mathrm{s}\text{ and }\sum_{\mathrm{i}=1}^{4}md_\mathrm{i}^0 \qquad (6)$$

where $\sum_{i=1}^{3}md_\mathrm{i}^\mathrm{s}$ and $\sum_{\mathrm{i}=1}^{4}md_\mathrm{i}^0$ correspond amounts of decomposed products of sludge in the three consecutive reactions and SOM in the four consecutive reactions respectively, W_0^j, W_t^j and W_f^j are masses in mg of the sample '*j*' at the beginning, at any time *t* and at the end of the reaction, respectively.

Thus we get the differential equation:

$$\mathrm{d}(md_\mathrm{i}^\mathrm{j}/F_\mathrm{i}^\mathrm{j})/\mathrm{d}t=K_\mathrm{i}^\mathrm{j}[1-md_\mathrm{i}^\mathrm{j}/F_\mathrm{i}^\mathrm{j}]^{n_\mathrm{i}^\mathrm{j}} \qquad (7)$$

where $K_\mathrm{i}^\mathrm{j}=A_\mathrm{i}^\mathrm{j}\exp(-E_\mathrm{i}^\mathrm{j}/RT)$ and n_i^j are the Arrhenius rate constant and reaction order of i^{th} reaction of sample 'j', A_i^j and E_i^j are respectively the frequency factor and apparent activation energy for the i^{th} reaction of the sample '*j*', *T* is the absolute temperature in K, *R* is gas constant in kJ K^{-1} mol^{-1}, $md_\mathrm{i}^\mathrm{j}=(W_\mathrm{i}^\mathrm{j},_{\mathrm{T=0}}-W_\mathrm{i}^\mathrm{j},_{\mathrm{T=T}})/W_\mathrm{i}^\mathrm{j},_{\mathrm{T=0}}-W_\mathrm{i}^\mathrm{j},_{\mathrm{T=f}})$ is the mass fraction of the decomposed product in i^{th} reaction of sample '*j*', where for a particular decomposition step, *T* varies from 0 to *f*. The weighting factor for the i^{th} reaction of the sample '*j*' i.e. F_i^j, which accounts for the evolution of decomposed products at various stages of the reaction, is given by: $F_\mathrm{i}^\mathrm{j}=X_{\mathrm{i\,f}}^\mathrm{j}-X_{\mathrm{i\,0}}^\mathrm{j}$, where *i*=1, 2, 3, 4 for SOM and *i*=1, 2, 3 for sludge and 0, *f* denotes the initial and final temperature of a particular decomposition step or reaction, *i*. The weighting factors for various reactions for the SOM and sludge are shown in Table 2.

The equation follows the following equilibrium condition:

$$\text{when}\quad t=0,\ md_\mathrm{i}^\mathrm{j}(0)=0\text{ and }X_\mathrm{i}^\mathrm{j}(0)=0 \qquad (8)$$

Theoretically, it is not possible to obtain the condition as described by Eq. (8) because at the initial stage of the reaction, a small amount of the products may be formed. Introduction of some other parameters is therefore necessary to exact determination of the kinetic parameters. We have not introduced such terms, as the same bring complicacy to the described process.

Solution of the Eq. (7) and neglecting the term (1–*RT*/*E*) for large value of *E*/*RT*, lead to the following equation:

$$md_\mathrm{i}^\mathrm{j}/F_\mathrm{i}^\mathrm{j}=1-[1-(1-n_\mathrm{i}^\mathrm{j})(A_\mathrm{i}^\mathrm{j}RT^2/\beta E_\mathrm{i}^\mathrm{j})\{\exp(-E_\mathrm{i}^\mathrm{j}/RT)\}]^{1/(1-\mathrm{n}_\mathrm{i}^\mathrm{j})}\quad\text{for } n_\mathrm{i}^\mathrm{j}\neq 1 \qquad (9)$$

and

$$md_\mathrm{i}^\mathrm{j}/F_\mathrm{i}^\mathrm{j}=1-\exp[(-A_\mathrm{i}^\mathrm{j}RT^2/\beta E_\mathrm{i}^\mathrm{j})\{\exp(-E_\mathrm{i}^\mathrm{j}/RT)\}]\quad\text{for } n_\mathrm{i}^\mathrm{j}=1 \qquad (10)$$

In case of differential method,

$$\mathrm{m}d_\mathrm{i}^\mathrm{j}/F_\mathrm{i}^\mathrm{j}=1-[1-(1-n_\mathrm{i}^\mathrm{j})(A_\mathrm{i}^\mathrm{j}RT^2/\beta E_\mathrm{i}^\mathrm{j})\{1-2RT/E_\mathrm{i}^\mathrm{j}\}\{\exp(-E_\mathrm{i}^\mathrm{j}/RT)\}]^{1/(1-n_\mathrm{i}^\mathrm{j})}\quad\text{for } n_\mathrm{i}^\mathrm{j}\neq 1 \qquad (11)$$

and

$$md_\mathrm{i}^\mathrm{j}/F_\mathrm{i}^\mathrm{j}=1-\exp[(-A_\mathrm{i}^\mathrm{j}RT^2/\beta E_\mathrm{i}^\mathrm{j})\{1-2RT/E_\mathrm{i}^\mathrm{j}\}\{\exp(-E_\mathrm{i}^\mathrm{j}/RT)\}]\text{ for } n_\mathrm{i}^\mathrm{j}=1 \qquad (12)$$

The activation energies and frequency factors calculated for the various decomposition reactions of the SOM and sludge as given in Table 2 are applied to determine $m_{d_\mathrm{i}}^\mathrm{j}$. The same for SOM and sludge are shown in Fig. 4. The theoretical X values as calculated from Eq. (6) are also included in the same figures along with the experimental values. The good agreement between

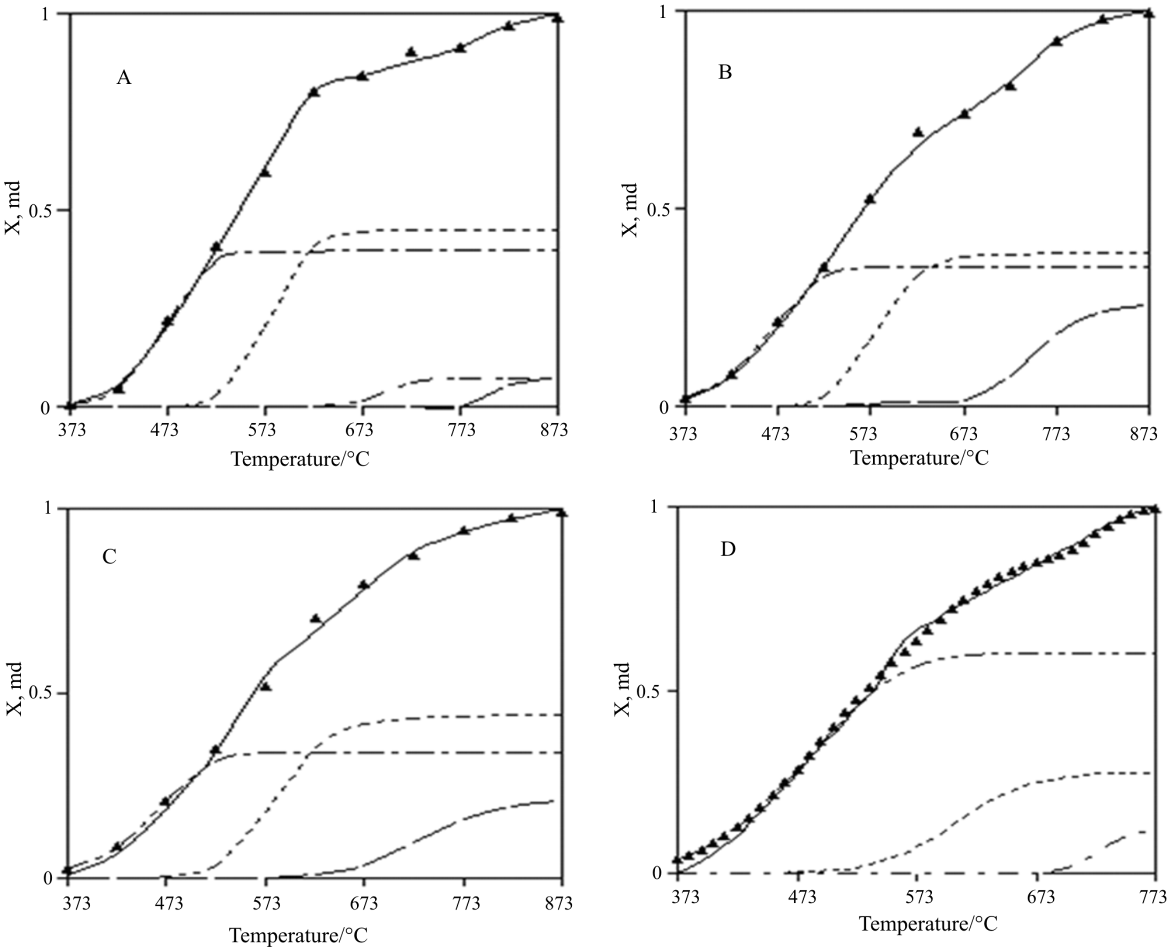

Fig. 4 Experimental data (—) and computed values (▲) of fractional conversion (X) and computed values of mass fractions of decomposed products (m_d) predicted from proposed model for combustion of (A) separated organic material at heating rate of 10°C min^{-1}, (B) Sludge at heating rate of 10°C min^{-1}, (C) Sludge at heating rate of 5°C min^{-1} and (D) another ETP sludge at heating rate of 10°C min^{-1}

the computed data with the experimental data indicate that the proposed model adequately describe the combustion of the ETP sludge and SOM with no detailed chemical composition of combustion products. The kinetic parameters for the thermal conversion reactions of the same sludge at the heating rate of 5°C min^{-1} and another ETP sludge (sludge II in Table 2) with different compositions with the heating rate of 10°C min^{-1} are also evaluated to ascertain the suitability of the model. The good agreement of the theoretical and experimental values of X and $m^{s}_{d_i}$ values as shown in Fig. 4 support the validity of the model. It is also observed that the evolution of the decomposed product of the SOM at the initial heating time is ~0, which is a consequence of Eq. (8). But for sludge, the value is slightly higher than 0, may be due to the fact that apart from the loss of organic materials as assumed other materials present in the sludge may also be lost in the 100–600°C temperature range. The complex surface chemical reactions that may take place in the inorganic-organic composition of the sludge may also be responsible for the same. In spite of the limitation, the kinetic model as presented in this communication is adequate to describe simple thermal conversion reactions of organic materials of sludge.

Conclusions

The oxidative thermal treatment of ETP sludge could be summarized as:

The SOM undergo conversion in four different stages. The presence of inorganic materials in the sludge changes the thermal decomposition process to a three-stage process. The inorganic constituents do not effect the temperature of distillation and volatilization processes of the organic materials but considerably effect the conversion processes of the organic materials above 400°C. It decreases the oxidative thermal decomposition products and lowers the temperature of the polymerization reactions and combustion of aromatic polymerized products, may be due to formation of alkali-oxygen surface complex. The derivation of kinetic parameters also supports the observations regarding the effect of inorganic constituents. The kinetic model proposed to explain the experimental results adequately describe the combustion of ETP sludge at different rates and compositions.

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Received: August 9, 2004
In revised form: August 16, 2004