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NON-ISOTHERMAL THERMOGRAVIMETRIC PYROLYSIS KINETICS OF WASTE PETROLEUM REFINERY SLUDGE BY ISOCONVERSIONAL APPROACH

D. Choudhury, R. C. Borah[*]*, R. L. Goswamee, H. P. Sharmah and P. G. Rao*

Chemical Engineering Division, Regional Research Laboratory (CSIR) Jorhat, Jorhat 785006, Assam, India

Pyrolysis of petroleum refinery sludge has received global acclamation as a clean conversion technique for providing solution of sludge disposal as well as efficient resource utilization. This communication reports the kinetics study of pyrolysis of petroleum refinery sludge. Experiments were carried out by means of thermogravimetric analysis at different heating rates of 5, 10 and 20°C min^{-1}. The pyrolytic reaction is significant in the temperature range of 200–350°C and analysis and evaluation of kinetic parameters is done in the 100–500°C region of non-isothermal TG curves obtained in nitrogen atmosphere.

The activation energy is calculated by iso-conversional method, then other kinetic parameters are determined by considering single reaction and two reaction global kinetic model. Two-reaction model is found to fit satisfactorily the experimental results.

Keywords: *isoconversional, kinetics, non-isothermal, pyrolysis, refinery sludge, TG*

Introduction

Petroleum residue sludge is the main waste of a petroleum refinery after recovery of oil by steam heating and contains considerable amount of combustibles with high heating values. This waste is hazardous in nature and their disposal or effective resource recovery is an important global issue [1–3]. Land filling and incineration [4] are some major current methods for disposal of refinery sludge but these techniques fails to provide the useful resource efficiently. On the other hand, the conversion of refinery sludge into lower molecular mass hydrocarbon by pyrolysis not only solves the disposal problem, but also has the appeal of resource utilization [5–7]. An approach has been made to study the thermal behavior of petroleum distillation residues but not in terms of kinetics [8].

The aim of the present work is to study the pyrolysis kinetics of the petroleum refinery sludge by means of thermogravimetric analysis (TG) in the temperature range of 100–500°C. TG can provide kinetic data of pyrolysis at raised temperature. However, data interpretation is generally encountered with major difficulties in distinguishing the mass *vs.* temperature data to yield a complex reaction scheme. For engineering application, a global kinetic model is frequently adopted to correlate pyrolysis data [9]. In this study, non-isothermal experiments were carried out at three different heating rates 5, 10, 20°C min^{-1} in nitrogen gas atmosphere. Isoconversional methods are used for the determination of activation energy as a function of conversion [10–12]. The advantage is that, this dependence of activation energy on conversion can be made without making any assumption about the reaction model. Based on the average activation energy, other kinetic parameters are calculated by using one-reaction and two-reaction global kinetic model for the sake of simplicity and engineering application convenience [13].

Experimental

Materials

The refinery solid waste sludge in this study was collected from common storage pit from IOCL, Guwahati refinery of northeast region of India. The major sources of refinery sludge includes the oil storage tank sludge, the biological sludge, the dissolve air flotation (DAF) scum, the American Petroleum Institute (API) separator sludge and the chemical sludge. The sludge was expected to be highly heterogeneous and greasy in nature. The physico-chemical characteristics that have been determined are total solid residue, moisture content, volatile solid or organic content, fixed residue and oil contents by methods as reported in standard texts [14], which is represented in Table 1. The components extractable by chloroform are herein referred to as 'oil' contents in the sludge.

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[*] Author for correspondence: borahrc1@rediff.com

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Table 1 Compositions and constituents of the refinery sludge

	mass/mass%	Hydrocarbon distribution in the oil/mass%	
Total solid residue	44.55	Heptadecane	2.10
Moisture	55.11	Dodecane	1.90
Organic content	39.26	Eicosane	1.70
Inorganic matter	5.68	Tridecane	0.93
Oil content	28.07	Pentadecane	0.89
(Chloroform extractable)		Undecane	0.83
		Nonadecane	0.81
Elements	(ppm)	Decane	0.75
Fe	107.670	Dodecane-2,6,11-trimethyl	0.56
Mg	5.570	Decane-2,5,9-trimethyl	0.26
Ni	0.230	Nonadecane-3-methyl	0.24
Co	0.065	Benzene-1-ethyl-3-methyl	0.21
Pb	0.010	Others	0.59
Na	0.472		
K	6.350		

The concentrations of all the components are expressed in terms of mass% of wet sludge. Inorganic contents in terms of elements, such as Fe, Mg, Ni, Co, Pb, Na, and K present in the fixed residue are determined by Atomic Absorption Spectrometer (AAS, Model: Perkin Elmer 2380, USA). The chloroform extractable oil was analyzed by GC-MS (Model: HP5181-7487) to ascertain the probable composition of hydrocarbon presents in the sludge.

Apparatus and procedure

The sludge was dried in an air oven at a temperature of 100±5°C for 24 h and the dried sludge sample was used for TG/DTG. The TG/DTG of the sludge sample were carried out in an inert atmosphere of nitrogen gas (purity 99.99% and moisture free) and a flow rate of 100 mL min^{-1} in SDT-2960, DTA-TG equipment (M/S TA Corporation, USA), with approximately 20 mg of sample mass in a Platinum crucible, α-aluminum oxide was taken as a reference material. The experiment was performed in three different heating rates of 5, 10 and 20°C min^{-1} and heated to a temperature of 500°C.

Results and discussion

Effect of heating rate on pyrolysis

The fractional conversion (X) in pyrolysis is expressed on a normalized basis, where $X=(W_0-W)/(W_0-W_f)$; W, W_0 and W_f=present, initial and final masses of the sample, respectively. The variation of X with temperature (T) is illustrated in Fig. 1. The results indicate that a higher heating rate gives a lower value of X for the same temperature. The pyrolysis reaction is significant in the temperature range of 200–350°C.

TG and DTG curves of pyrolysis of oil sludge

The TG and DTG curves of the pyrolysis of refinery solid waste sludge in an inert atmosphere of nitrogen were obtained at different heating rates (5, 10, 20°C min^{-1}). All the thermogravimetric curves are asymmetric (Fig. 1) and moves to higher temperature with increase in heating rates.

The peak conversion rates and the maximum peak temperature and the corresponding conversion can be identified from Fig. 2. A higher heating rate result in higher peak value of reaction rate and a higher temperature for its occurrence. Values of T_p, X_{max}, $(dX/dt)_{max}$ at various heating rates are presented in Table 2.

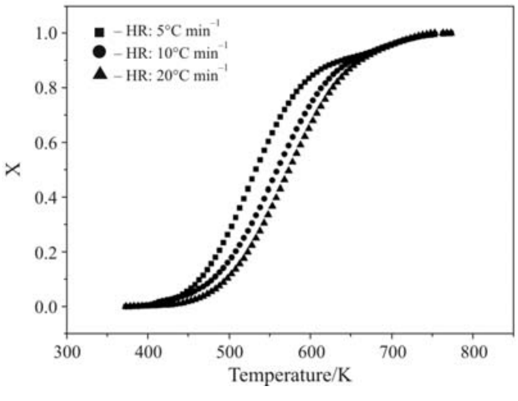

Fig. 1 Normalized conversion (X) curves for different heating rates for pyrolysis of oil sludge in nitrogen atmosphere

Table 2 Values of T_p, X_{max}, $(dw/dt)_{max}$ for pyrolysis of oil sludge at various heating rates

β/ C° min^{-1}	T_p/ K	X_{max}	$(dw/dt)_{max}$/ g min^{-1}	$(dX/dt)_{max}$/ min^{-1}
5	524.28	0.42	0.3489	0.0474
10	554.65	0.50	0.7309	0.0876
20	563.71	0.51	1.3090	0.1770

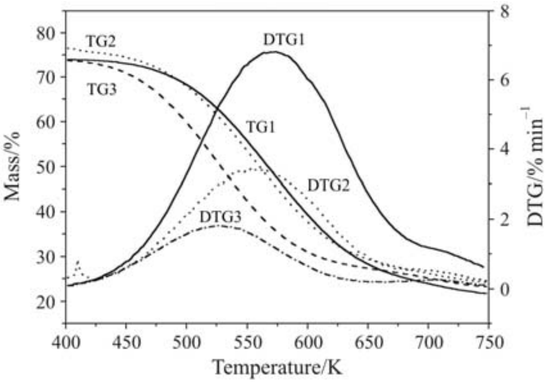

Fig. 2 TG and DTG curves for different heating rates for pyrolysis of oil sludge in nitrogen atmosphere, TG1 and DTG1 – rate of heating 5°C min^{-1}, TG2 and DTG2 – rate of heating 10°C min^{-1}, TG3 and DTG3 – rate of heating 20°C min^{-1}

Non-isothermal isoconversional analysis

Compared with isothermal experiments, non-isothermal runs are more convenient to carry out without a sudden temperature jump of the sample at the beginning [15]. The commonly used method based on single heating rate that involves fitting experimental data to assumed forms of the reaction model fails to produce trustworthy kinetic information for nonisothermal experiments [16]. The reason arises from the fact that 'model fitting methods' do not achieve a clean separation between the temperature dependent $K(T)$ and the reaction model, $f(X)$. It also arises partly because many reactions follow complex mechanisms involving multiple series and parallel steps with different activation energies. Therefore, model-fitting methods, which are aimed at extracting a single value of the activation energy for an overall process, are unable to reveal this type of complexity. However, the 'model-free iso-conversional methods' can be used to eliminate the aforementioned drawbacks of model fitting [17, 18]. These methods allow the activation energy to be determined as a function of conversion and temperature without making any assumptions about the reaction model. In this paper, we have determined the activation energy as a function of conversion by three different iso-conversional methods of Flynn–Wall–Ozawa, KAS and Friedman [19–27] and presented in Table 3.

Flynn–Wall–Ozawa method [19, 20]: The rate of solid-state degradation reaction can be generally described by

$$\frac{dX}{dt}=K(T)f(X) \tag{1}$$

where t is the time, T the temperature and X, the extent of conversion makes the implicit assumption that the temperature dependence of the rate constant, $K(T)$ can be separated from the reaction model, $f(X)$. The reaction model may take various forms. The explicit temperature dependence of the rate constant is introduced by replacing $K(T)$ with Arrhenius equation, which gives:

$$\frac{dX}{dt}=A\exp\left(\frac{-E}{RT}\right)f(X) \tag{2}$$

where A (the frequency factor) and E (the activation energy) are Arrhenius parameters and R the gas constant. Under non-isothermal conditions in which samples are heated at a constant rate, the explicit temperature dependence of Eq. (2) can be eliminated through the trivial transformation

$$\frac{dX}{dT}=\frac{A}{\beta}\exp\left(\frac{-E}{RT}\right)f(X) \tag{3}$$

where $\beta=dT/dt$ is the heating rate.

The iso-conversional integral method suggested independently by Flynn and Wall [19, 20] and Ozawa [21] uses Doyle's approximation of $p(x)$ [22–24]. This method is based on the equation

$$\ln\beta=\ln\left(\frac{AE}{g(X)R}\right)-5.3305-1.052\frac{E}{RT} \tag{4}$$

where

$$g(X)=\int_0^X\frac{dX}{f(X)},\ P(x)=\exp(-x/x)\ \text{and}\ x=\frac{-E}{RT}.$$

Now, for different heating rates (β), we have different sets of T at different X levels and plotting lnβ *vs.* $1/T$ we get a straight line with slope of $(-E/R)$. Therefore variation of activation energy as a function of conversion can be obtained.

Kissinger–Akahira–Sunose method [25, 26]: KAS method may be originally obtained through the derivation of the Eq. (3)

$$\frac{dX^2}{dT^2}=\frac{A}{\beta}\left[\exp\left(\frac{-E}{RT}\right)\frac{df(X)}{dT}+\frac{Ef(X)}{RT^2}\exp\left(\frac{-E}{RT}\right)\right] \tag{5}$$

At peak temperature T_p, putting $dX^2/dT^2=0$ and rearranging the equation, we can get:

$$\ln\frac{\beta}{T_{\mathrm{p}}^{2}}=\left(\frac{-E}{RT}\right)+\ln\left(\frac{AR}{E}\frac{\mathrm{d}f(X)}{\mathrm{d}T}\right)\tag{6}$$

Again by plotting $\ln(\beta/T_{\mathrm{p}}^{2})$ *vs.* $1/T$, at different conversion levels for different heating rates, we get a straight line with slope of $(-E/R)$.

Friedman method: The differential isoconversional method suggested by Friedman [9, 27] is based on Eq. (3) in logarithmic form and leads to:

$$\ln\frac{\mathrm{d}X}{\mathrm{d}t}=\ln Af(X)+\left(\frac{-E}{R}\right)\left(\frac{1}{T}\right)\tag{7}$$

By plotting $\ln(\mathrm{d}X/\mathrm{d}t)$ *vs.* $1/T$ for different conversion levels we get a straight line with slope of $(-E/R)$.

The arithmetic means of the activation energy calculated by KAS, Flynn–Wall and Friedman method are 112, 117, 113 kJ mol^{-1}, respectively, which are almost same. Advantages that can be attributed to KAS method are that it can locate the peak maximum temperature besides the unnecessary knowledge of the reaction mechanism to calculate E. Nevertheless its dependence in the accuracy of the peak position may be the main disadvantage of the method. Considering the difficulty in locating the values of maximum peak temperature and other parameters associated with the peak temperature by using KAS method, Flynn and Wall method could give a better result. But since it is based on mathematical approximation, therefore Friedman method can be considered to be the best among the three methods.

Kinetic parameters

Reaction order and Arrhenius constant

Rearranging Eq. (2), one obtains

$$\ln\left[\frac{(\mathrm{dX/dt})}{\exp\,(-\mathrm{E/RT})}\right]=\ln A+n\ln(1-X)\tag{8}$$

Taking, arithmetic mean of activation energy (E), at same temperature (T), X and $\mathrm{d}X/\mathrm{d}t$ can be specified from Figs 1 and 2, respectively. A straight line with slope n (reaction order) is then obtained by plotting $\ln[(\mathrm{d}X/\mathrm{d}T)/\exp(-E/RT)]$ and $\ln(1-X)$. Further to obtain a refined value of E, one can rearrange Eq. (8) to give:

$$\ln\left[\frac{\mathrm{dX/dt}}{(1-X)^{\mathrm{n}}}\right]=\ln K=\ln A+\left(\frac{-E}{R}\right)\left(\frac{1}{T}\right)\tag{9}$$

Thus, a slope of $(-E/RT)$ can be obtained by plotting $\ln K$ and $(1/T)$ giving the refined value of E and A (Table 4).

One-reaction kinetic model

Using one-reaction kinetic model to represent the pyrolysis of oil sludge, one has:

$$\text{Oil sludge}\xrightarrow{\mathrm{k}}\text{volatiles V }(M_{\mathrm{v}})+\text{residues }(M)$$

Therefore the mass balance of pyrolysis gives:

$$X=1-M=M_{\mathrm{v}}\tag{10}$$

The production rate of V (volatiles) could be expressed as

$$\frac{\mathrm{d}M_{\mathrm{v}}}{\mathrm{d}t}=A\exp\left(\frac{-E}{RT}\right)(1-M_{\mathrm{v}})^{\mathrm{n}}\tag{11}$$

The initial conditions are M=1, M_{v}=0, at t=0.

Because the constant heating rate is employed, it can be shown that ($n\neq1$):

$$X=1-\left[1-(1-n)\frac{A}{\beta}\frac{RT^{2}}{E}\exp\left(\frac{-E}{RT}\right)\sum(E,\,T)\right]^{\frac{1}{1-\mathrm{n}}}\quad[28](12)$$

where

$$\sum(E,\,T)=1-2\left(\frac{R}{E}\right)+6\left(\frac{RT}{E}\right)^{2}-24\left(\frac{RT}{E}\right)^{3}+\ldots\tag{13}$$

Table 3 Values of E at different conversion levels calculated by three different isoconversional methods

X	E/kJ mol^{-1}			X	E/kJ mol^{-1}		
	KAS	Flynn–Wall	Friedman		KAS	Flynn–Wall	Friedman
0.05	74.80	83.14	39.00	0.55	78.15	88.50	85.135
0.10	72.39	81.35	67.46	0.60	78.50	89.20	89.00
0.15	73.99	53.14	70.59	0.65	76.68	86.96	86.00
0.20	74.80	83.00	73.00	0.70	74.56	84.52	88.80
0.25	70.69	79.60	71.00	0.75	80.14	91.00	104
0.30	72.66	82.12	73.00	0.80	92.28	103.9	126.87
0.35	74.57	84.30	75.00	0.85	99.21	111.98	141.338
0.40	74.47	84.23	77.00	0.90	144	162.12	241
0.45	74.00	83.00	77.15	0.95	657	610	473
0.50	76.30	86.29	88.80				

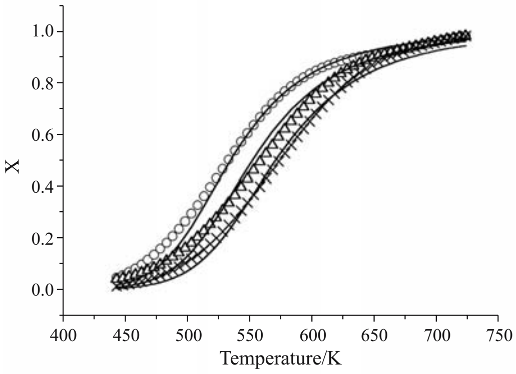

Fig. 3 Comparison of fractional conversion (*X*) predicted by proposed one-reaction model with experimental data at three different heating rates, HR: ○ – 5°C min^{-1}, Δ – 10°C min^{-1}, x – 20°C min^{-1} and — – simulated

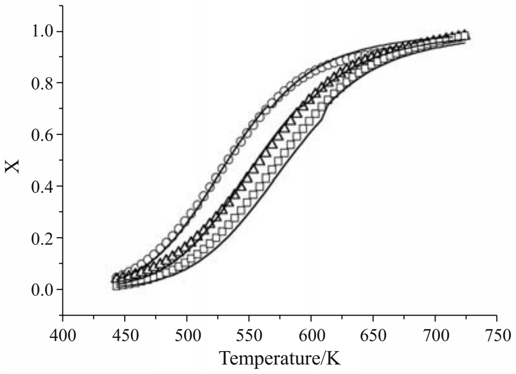

Fig. 4 Comparison of fractional conversion (*X*) predicted by proposed two-reaction model with experimental data at three different heating rates, HR: ○ – 5°C min^{-1}, Δ – 10°C min^{-1}, x – 20°C min^{-1} and — – simulated

Table 4 Activation energy (*E*), frequency factor (*A*), reaction orders (*n*) and weighting factor (*F*) for one- and two-reaction models of oil sludge pyrolysis

Model		E/kJ mol^{-1}	A/min^{-1}	n	F
One-reaction		88.286	$12.2\cdot10^7$	2.88	1.0
Two-reaction	1st reaction	64	$2.97\cdot10^5$	2.08	0.7
	2nd reaction	112	$1.498\cdot10^{10}$	2.98	0.3

A comparison of fractional conversion predicted by the proposed one-reaction model with those obtained by experiments is shown in Fig. 3. To verify the applicability of the kinetic parameters and the validity of the proposed model, the coefficient of determination (R^2) [29] and mean relative error (ε_r) [30] is examined for $0.05<X<0.95$ which is represented in Table 4.

$$\varepsilon_r=\sqrt{\frac{\sum_{i=1}^{N}\left(\frac{X_{i,\exp}-X_{i,\text{cal}}}{X_{i,\exp}}\right)^2}{N}} \tag{14}$$

where $X_{i,\exp}$, $X_{i,\text{cal}}$ are experimental and calculated conversion and N is the number of data.

Two-reaction kinetic model

Complex reaction may be involved in the pyrolysis of oil sludge as indicated by the variation of *E* (Table 3), one can further try the two-reaction model to test the validates for describing the pyrolysis reactions. From Figs 1 and 2, one may divide the conversion *X* into different regions as 0–0.7 and 0.7–1 for the two-reaction model. Using two-reaction kinetic model to represent the pyrolysis of oil sludge, one has:

$$\text{Oil sludge}\xrightarrow{k_1}\text{volatiles }(V_1)+\text{residues }(M_1)$$
$$\xrightarrow{k_2}\text{volatiles }(V_2)+\text{residues }(M_2)$$

Referring to the methods for deducing two-reaction models proposed by Lin *et al.* [31], one can obtain the values of *E*, *A*, *n* and *F* (weighing factors of the reaction contributing to the pyrolysis) for two reaction models as presented in Table 3. All the kinetics parameters are refined values to improve the simulation results. The comparison of fractional conversion predicted by the proposed two-reaction models with those obtained by experiments is shown in Fig. 4. Among the two proposed models two-reaction model gives best fit (Table 5). This is reasonable as the pyrolysis of the refinery sludge is supposed to be com-

Table 5 Mean relative error (ε_r) and coefficient of determination (R^2) for the experimental and simulated results obtained for the three heating rates of oil sludge pyrolysis in nitrogen atmosphere

Model	Heating rates, β/°C min^{-1}	R^2	ε_r
One-reaction	5	0.9990	0.0218
	10	0.9936	0.0265
	20	0.9969	0.0267
Two-reaction	5	0.9990	0.0067
	10	0.9987	0.0147
	20	0.9984	0.0160

plex in nature. Therefore, the two-reaction model is precise model for describing the pyrolysis of petroleum refinery sludge of northeast region of India.

Conclusions

The pyrolysis of petroleum refinery sludge was carried out in a TG/DTA system under a nitrogen gas atmosphere. The activation energy is calculated as a function of conversion by using isoconversional methods of Friedman, KAS and Flynn–Wall and found to be similar. For the sake of engineering application convenience, a simple one-reaction and two-reaction global kinetic model was proposed to predict the kinetic parameter n, A and E under experimental conditions. Two-reaction kinetic model is found to fit satisfactorily the experimental data with (R^2) 0.999, 0.9987 and 0.9984 for heating rates of 5, 10 and 20°C min^{-1}, respectively in the conversion range of $0.05<X<0.95$. The proposed model can adequately describe the pyrolysis of oil sludge. Since, there is no data available on TG studies on pyrolysis of refinery sludge from northeast region of India, this approach and results could be very useful for the proper design of the pyrolysis system of the oil sludge under investigation.

Nomenclature

A	frequency factor, Arrhenius constant, min^{-1}
E	activation energy, kJ mol^{-1}
$f(X)$	function of conversion X, dimensionless, $f(X)=(1-X)^n$
M	residual mass fraction of active reactant
N	order of reaction, dimensionless
r	instantaneous rate, dX/dt
R^2	coefficient of determination
X	fractional conversion, $1-M$
β	heating rate, °C min^{-1}
K	Arrhenius rate constant
T_p	peak maximum temperature
k_1, k_2	Arrhenius rate constants of two-reaction model
ε_r	mean relative error
X_{max}	conversion at T_p
$(dX/dt)_{max}$	instantaneous rate at T_p

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