AIDIC EFCE
ISCRE25 FLORENCE 2018
BRIDGING SCIENCE & TECHNOLOGY
The 25th International Symposium on Chemical Reaction Engineering
20-23 May 2018
Florence, Italy
www.aidic.it/iscre25

Detailed Physicochemical & Thermochemical Analyses of Indian oil shale

Bhargav Baruah[1], Rupam Kataki[2], Parash Thakur[3], Pankaj Tiwari[1]*
1 Department of Chemical Engineering, Indian Institute of Technology Guwahati, Assam, India 781039
2 Department of Energy, Tezpur University, Assam, India 784028
3 Oil India Limited, Duliajan, Assam, India 786602
**Corresponding author: pankaj.tiwari@iitg.ernet.in*

Highlights

- Thermal decomposition of Indian oil shale using thermogravimetric analysis (TGA-DTG).
- Study of the kinetic parameters using isoconversional methods.
- Inline TGA-FTIR analysis of the products evolved during pyrolysis.
- Characterization of the products obtained from lab scale pyrolysis of oil shale.

1. Introduction

With depletion of petroleum reservoirs, the unconventional petroleum reserves are gaining importance. One such unconventional petroleum reserve is oil shale. Oil shale is a finely grained, porous, sedimentary rock which contains organic matter known as kerogen. When subjected to high temperature, the kerogen converts into bitumen which further breaks down into oil, gas and char. The most common and suitable method for production of oil and gas from oil shale is pyrolysis retorting). The decomposition of organic matter in oil shales is a complex process and the kinetic parameters of the pyrolysis process needs to be studied. The present work aims to produce a detailed physicochemical and thermochemical analysis of Indian oil shale. The pyrolysis kinetics was studied using various models. A lab scale pyrolysis setup was used to quantify the products distribution and the products were characterized using various analytical techniques.

2. Methods

Oil shale samples were collected from the East mine of the Tikak Colliary, Makum Coal fields, Upper Assam, India. The samples were grounded to size of 100 mesh (150 micron). Thermogravimetric analysis (TGA) was performed to identify the decomposition characteristics and the weight loss data were mathematically interpreted considering single stage decomposition of the organic matter. Isoconversional methods were considered for the kinetic study [1]. The distribution of activation energy was determined using Friedman, Kissinger Akahira & Sunnose (KAS) and Flynn Wall & Ozawa (FWO) methods. The reaction model and pre-exponential factors were determined using the Criado master plot [2, 3]. The gaseous products evolved during pyrolysis were identified using Fourier transform infrared spectrometry (FTIR) coupled with TGA. The lab scale pyrolysis experiments were performed at three heating rates to reach final pyrolysis temperature (450, 500, 550, 600 and 650 °C).

3. Results and discussion

TGA-DTG analysis provided the decomposition profiles (zones) which occur during the pyrolysis of oil shale. The onset and offset temperatures of the organic decomposition zone were found in the range of 350 °C and 650 °C respectively (Figure 1). The weight loss data of the organic decomposition zone were used to estimate the distribution of activation energy using Friedman, FWO and KAS methods and the mean values of activation energy were found to be 249.75 kJ/mol, 241.20 kJ/mol and 239.68 kJ/mol respectively (Figure 2). The reaction model was determined using the Criado differential-integral master plot. It was observed that the organic decomposition followed two different models. From α = 0.1 to 0.8 the pyrolysis process followed 3-D Diffusion model and from α = 0.9 to 1 the model shifted to Avrami Eroffev. The occurrence of 3-D diffusion model signifies the initial heat and mass transfer in the oil shale pores and the occurrence of Avrami Eroffev towards the end signifies the nucleation of the products and coking of the pyrolytic shale oil. Lab-scale pyrolysis experiments of the oil shale samples were performed under the conditions determined by TGA-DTG analysis. The distribution of the products formed during the pyrolysis at different conditions (temperatures and heating rates) is summarizes in Table 1. It was observed that with

increase in the heating rate the percentage of oil formation decreased and gas formation increased. The optimum oil production was observed at 10 °C/min and 600 °C. The collected products were analyzed using various characterization methods.

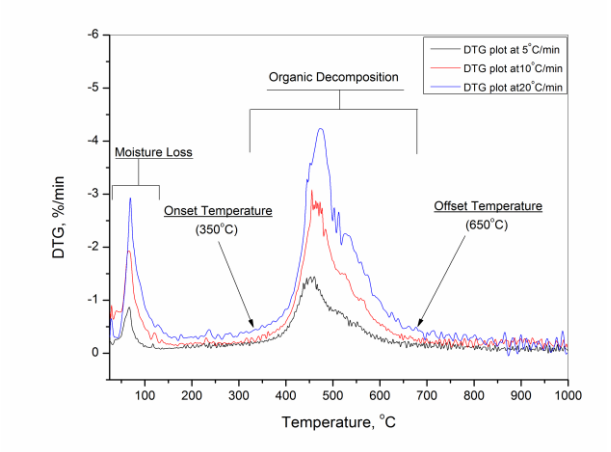

Figure 1. Various decomposition zones identified using TGA-DTG

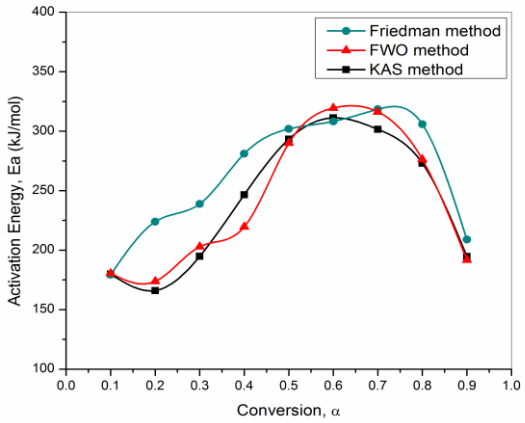

Figure 2. Distribution of activation energy with respect to conversion

Table 1. Percentage of products formed during pyrolysis

Temp °C	Heating Rate °C/min	Mass Loss, wt%	Products, wt%			
			Oil	Gas	Oil in Water	Spent Shale
650	5	25.72	13.25	8.79	2.87	74.84
600	5	25.16	13.25	8.79	2.87	74.84
550	5	23.75	11.01	10.06	2.68	76.25
500	5	20.66	9.79	8.13	2.74	79.34
450	5	15.02	5.63	6.51	2.88	84.98
650	10	28.00	14.45	11.65	1.35	72.00
600	10	27.50	15.45	9.85	2.15	72.50
550	10	24.23	11.23	10.11	2.71	75.67
500	10	21.15	10.00	8.75	3.00	78.85
450	10	16.40	5.45	7.88	3.07	83.60
650	20	26.25	14.65	10.23	1.37	73.75
600	20	25.27	12.54	9.76	2.97	74.73
550	20	22.37	10.89	8.36	3.12	77.63
500	20	19.34	7.54	8.58	3.22	80.66
450	20	15.23	4.45	6.73	3.05	84.77

4. Conclusions

Detailed characterization of Indian oil shale was performed. TGA based kinetic study for thermal decomposition of oil shale was established. The reaction kinetic, following two models viz. 3D diffusion model and Avrami Eroffev justifies the occurrence of multiple parallel reactions during oil shale pyrolysis. Analysis of produced oil showed higher percentage of aliphatic and presence of sulfur compounds.

References

[1] P. Tiwari, M. Deo, AIChE J. 58 (2012) 505-16.
[2] P.E. Sánchez-Jiménez, L.A. Pérez-Maqueda, A. Perejón, J.M. Criado, Thermochim. Acta. 552 (2013) 54-9.
[3] P.E. Sánchez-Jiménez, L.A. Pérez-Maqueda, A. Perejón, J.M. Criado, Polym. Degrad. Stab. 95 (2010) 733-9.

Keywords
Indian oil shale, model free isoconversional, Criado master plot, pyrolysis.