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Thermochimica Acta 405 (2003) 195–205

thermochimica acta

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# Thermo-oxidative reactions of Nigerian oil sand bitumen

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Received 6 September 2002; received in revised form 24 February 2003; accepted 25 February 2003

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## Abstract

The thermal behavior of the Nigerian oil sand bitumen in an oxidizing environment was studied using non-isothermal thermogravimetric analysis (TGA) and differential thermal analysis (DTA). This condition can occur during in situ thermal recovery. The kinetics of the reactions was also determined by Arrhenius plot method.

Three regions of weight loss corresponding to low-temperature oxidation, fuel deposition and high temperature oxidation were identified. Increasing the heating rate caused a shift in the reaction regions and peak temperatures to higher temperatures. No effect of gas flow rate was observed on the reactions. The oil sands have lower peak temperatures and activation energies compared with their corresponding bitumen extracts, suggesting a catalytic effect of sand on the reactions. The DTA revealed the exothermic nature of the reactions. The exothermicity increased with increasing heating rate.

The results of this study showed that the heating rate and the presence of sand have significant effect on the thermo-oxidative reactions of the bitumen.

*Keywords:* Oil sand; Bitumen; Thermal analysis; In situ combustion; Kinetics

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## 1. Introduction

In situ combustion is a thermal recovery method suitable for heavy oil deposit such as oil sand. Energy is generated within the reservoir by partial burning of the bitumen with the introduction of air, oxygen or mixture of both to facilitate burning. The heat of combustion generated cracks the heavy oil hydrocarbons, vaporizes the lighter hydrocarbons and deposit heavier hydrocarbons as coke. In this process, exothermic oxidation reactions involving oxygen and hydrocarbons lead to a wide variety of reactions intermediate and reaction products.

The great overburden reported in most oil sand deposits and environmental problems usually associated with the disposal of spent sand in open-cast mining method has made the in situ recovery an important aspect of oil sand development. Obviously, the thermo-oxidative behavior of oil sand bitumen needs to be well characterized for better design and optimization of this thermal process. Themoanalytical methods such as thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) have proved to play an important role in the combustion studies of fossil fuels [1,2]. Yoshiki and Philip [3] have studied the thermo-oxidative and thermal cracking reactions of Athabasca bitumen using differential thermal analysis (DTA). They concluded that heating rate can be used effectively to control the extent of low-temperature oxidation and hence

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doi:10.1016/S0040-6031(03)00192-8

fuel availability during in situ combustion. DSC and TGA have been used to characterize the pyrolysis and combustion properties of two heavy crude oils [4]. In combustion with air, three distinct reaction regions were identified known as low-temperature oxidation (LTO), fuel deposition (FD) and high-temperature oxidation (HTO). Heat values and kinetic parameters of the reactions were also determined. Studies on the pressure thermo-oxidative behavior of oil/sand and coked sand samples have been reported by Indrijarso et al. [5]. Three major reactions regions were identified as distillation/LTO, cracking/first combustion and HTO/second combustion. Philips et al. [6] have investigated the thermal degradation of Athabasca oil sand, bitumen and its fractions using thermogravimetry (TG) and high pressure differential scanning calorimetry (PDSC). Two regions of weight loss are detected both in the air and nitrogen atmosphere. Increasing the pressure of nitrogen and air was reported to cause an increase in the endothermicity and exothermicity of the respective reactions.

In Nigeria, oil sand deposits are found in the Southwest with the total oil-in-place estimated to be over 30 billion barrels [7]. Active research on the exploration of the oil sand has just begun. It has been suggested that the in situ recovery will be inevitable in the Southern part of the belt where the overburden is in excess of 50 m [8]. Presently, only few reports are available on the thermal behavior of the oil sand. The effect of temperature on the viscosity, product yield and chemical composition of the oil sand bitumen has been reported [9–11]. Apparently, much has not been done on the thermal characterization of the oil sand. Presently, there is no information about the temperature intervals

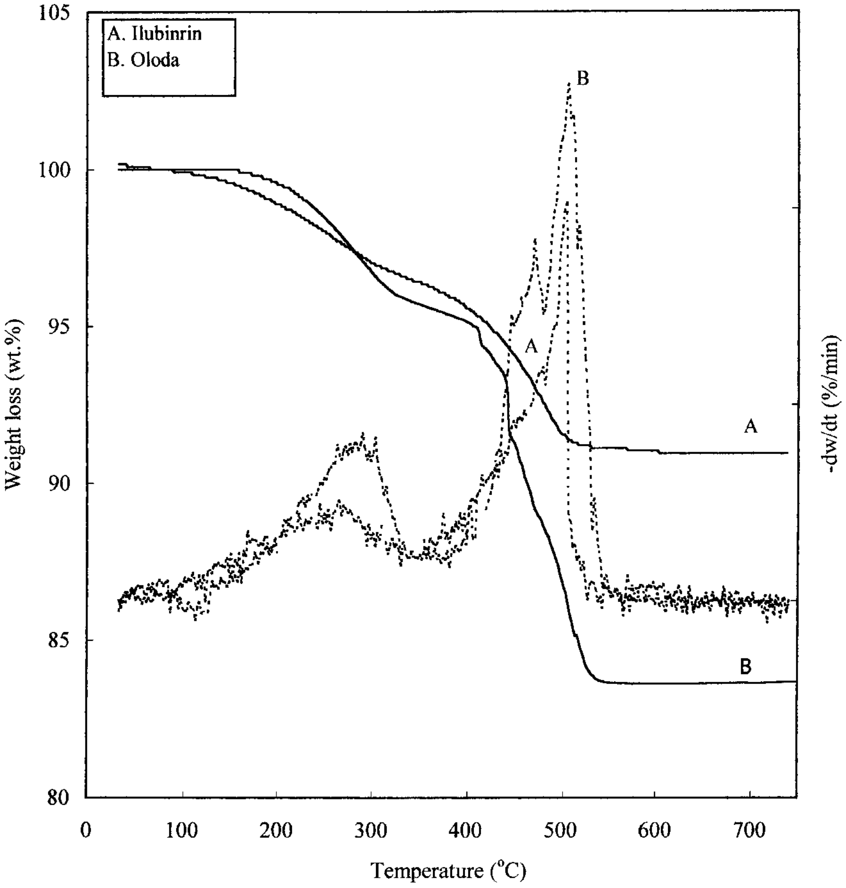

Fig. 1. TGA (—) and DTG (- - -) curves of Nigerian oil sands.

and the kinetic data of various oxidation reactions that can take place during the thermal decomposition of the oil sand in air. This information is necessary for simulation calculations of in situ thermal recovery method. In this paper, results on the thermo-oxidative reactions of Nigerian oil sand bitumen are presented.

## 2. Experimental

### 2.1. Sample

Two oil sands collected from Ilubinrin and Oloda are used in this study. The sample sites are located in Ondo state in the Southwest of Nigeria. Bitumen was soxhlet extracted from the oil sand using toluene.

### 2.2. Equipment and procedure

TG and DTA measurements were conducted simultaneously in a TG/DTA 320 Seiko thermogravimetric and differential thermal analyzer.

The experiments involved placing 10–15 mg of oil sand or 3–8 mg of bitumen in a platinum sample holder and heating from 25 to 750 °C in a flowing atmosphere of air. Experiments were performed at different heating rates (5, 10, 30 and 50 °C/min) and air flow rates (50, 75 and 100 ml/min). For reproducibility, all the experiments were performed at least twice. The equipment was calibrated for temperature readings using indium as a reference material. The data presented in this paper are those averaged from duplicate measurements.

## 3. Results and discussion

### 3.1. Themogravimetry analysis

TG/DTG curves of the oil sands containing bitumen and pure bitumen extracts are shown in Figs. 1 and 2, respectively. The weight loss observed in the oil sands was assumed to represent the thermal decomposition of the indigenous bitumen. The DTG curves revealed that reactions occurred at three different stages

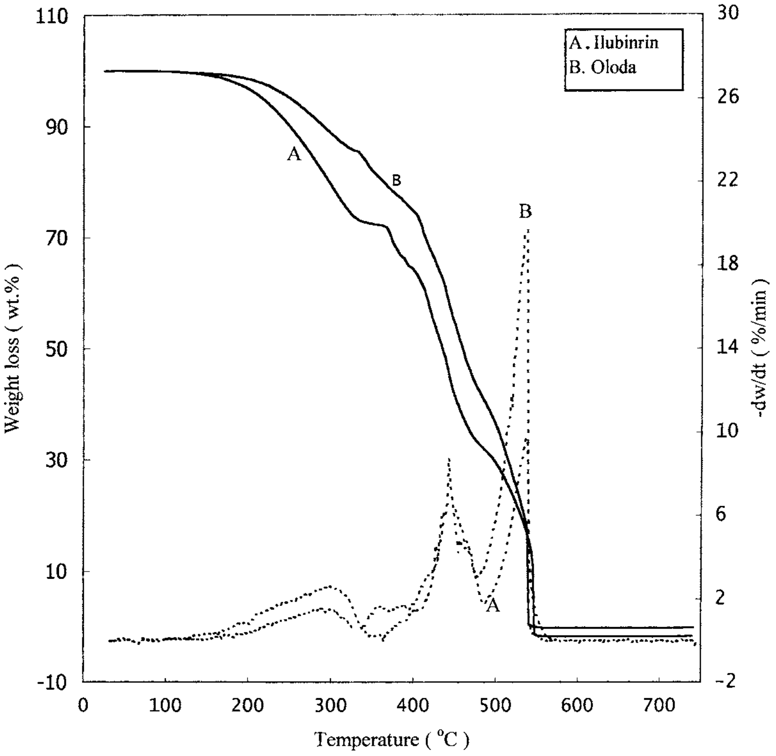

Fig. 2. TGA (—) and DTG (- - -) curves of Nigerian bitumen.

Table 1
Thermogravimetric characteristics of the Nigerian oil sands and bitumen (heating rate: 10 °C/min; air flow rate: 50 ml/min)

| Sample | First region (LTO) | | Second region (FD) | | Third region (HTO) | | PT (°C)[a] |
|---|---|---|---|---|---|---|---|
| | Temperature range (°C) | Weight loss (wt.%)[b] | Temperature range (°C) | Weight loss (wt.%)[b] | Temperature range (°C) | Weight loss (wt.%)[b] | |
| Oil sands | | | | | | | |
| Ilubinrin | 25–330 | 3.4 ± 0.2 | 330–480 | 4.0 ± 0.3 | 480–530 | 1.5 ± 0.08 | 505 ± 10 |
| Oloda | 25–340 | 4.2 ± 0.2 | 340–485 | 7.5 ± 0.5 | 485–540 | 4.7 ± 0.1 | 510 ± 12 |
| Bitumen | | | | | | | |
| Ilubinrin | 25–345 | 27.5 ± 1.2 | 345–480 | 39.6 ± 1.4 | 480–550 | 32.9 ± 1.2 | 535 ± 10 |
| Oloda | 25–330 | 14.5 ± 0.9 | 330–480 | 43.1 ± 1.3 | 480–545 | 42.4 ± 0.7 | 535 ± 5 |

[a] Peak temperature.

[b] Mean (±S.D.) of duplicate measurements.

in all the samples. The temperature intervals, fractional weight loss and peak temperatures for each reaction regions are given in Table 1. The differences noticed in the thermogravimetric characteristics values of the two samples, especially in terms of weight loss are due to the difference in the origin of the bitumen. The first reaction occurred between 25 and 335 °C, called the low-temperature oxidation (LTO). Light hydrocarbons evolved during the thermal decomposition were oxidized in this region [12,13]. The second transition

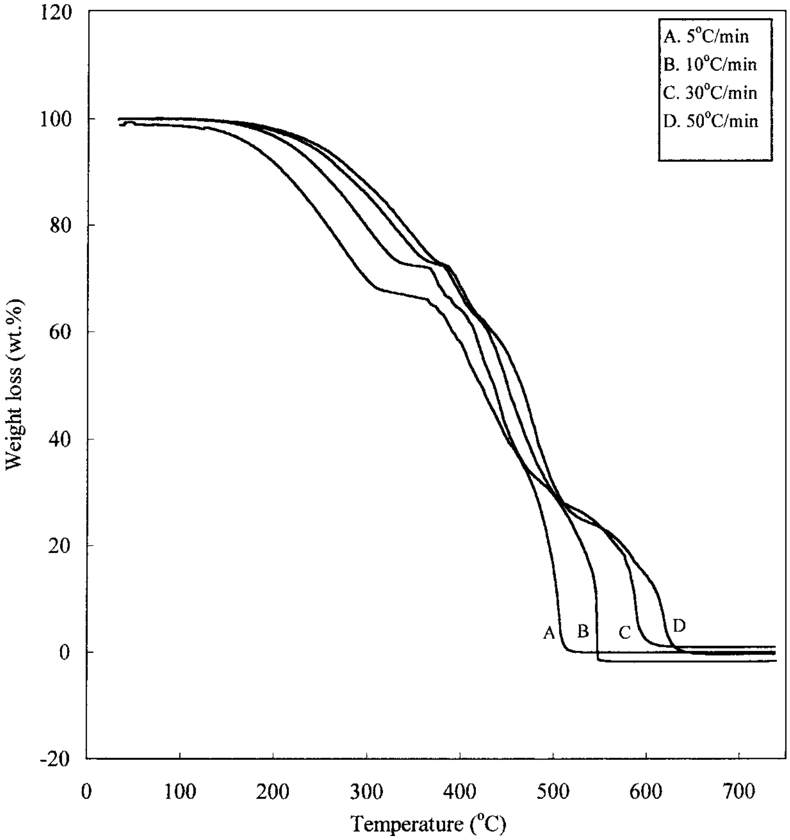

Fig. 3. TGA curves of Ilubinrin bitumen at various heating rates (air flow rate: 50 ml/min).

Table 2
Thermogravimetric characteristic of Nigerian bitumen at various heating rates (air flow rate: 50 ml/min)

| Sample | Heating rate (°C/min) | First region (LTO) | | Second region (FD) | | Third region (HTO) | | PT (°C)[a] |
|---|---|---|---|---|---|---|---|---|
| | | Temperature range (°C) | Weight loss (wt.%)[b] | Temperature range (°C) | Weight loss (wt.%)[b] | Temperature range (°C) | Weight loss (wt.%)[b] | |
| Ilubinrin | 5 | 25–325 | 32.6 ± 1.2 | 325–460 | 29.6 ± 1.5 | 460–525 | 37.8 ± 0.7 | 505 ± 11 |
| | 10 | 25–345 | 27.5 ± 1.2 | 345–480 | 39.6 ± 1.4 | 480–550 | 32.9 ± 1.2 | 535 ± 10 |
| | 30 | 25–375 | 27.4 ± 0.9 | 375–515 | 45.1 ± 1.2 | 515–625 | 26.5 ± 0.8 | 575 ± 5 |
| | 50 | 25–380 | 27.4 ± 1.1 | 380–528 | 47.5 ± 1.4 | 528–640 | 25.0 ± 1.2 | 580 ± 5 |
| Oloda | 5 | 25–320 | 15.3 ± 1.0 | 320–460 | 38.5 ± 0.7 | 460–515 | 45.3 ± 0.8 | 510 ± 8 |
| | 10 | 25–330 | 14.5 ± 0.9 | 330–480 | 43.1 ± 1.3 | 480–545 | 42.4 ± 0.7 | 535 ± 5 |
| | 30 | 25–350 | 14.3 ± 0.8 | 350–515 | 54.4 ± 1.2 | 515–595 | 31.0 ± 1.1 | 555 ± 10 |
| | 50 | 25–370 | 15.5 ± 0.8 | 370–530 | 51.0 ± 1.4 | 530–625 | 31.5 ± 1.2 | 570 ± 5 |

[a] Peak temperature.

[b] Mean (±S.D.) of duplicate measurements.

took place between 335 and 480 °C called the fuel deposition (FD) according to the classification of Kok [4]. The observed weight loss in this region was due to a combination of hydrocarbon combustion which compete with thermal cracking reactions [2]. Carbon rich residue (coke) was formed at this stage and deposited as fuel. The final reaction which involved the combustion of the remaining hydrocarbons and carbon residue occurred between 480 and 540 °C and is called the high-temperature oxidation (HTO).The oil sands have lower peak temperatures compare with the bitumen extracts. The peak temperature represents the maximum rate of weight loss.

Fig. 3 shows the effect of heating rate on the thermal decomposition of Ilubinrin bitumen. The thermogravimetric characteristics of the bitumen at various heating and gas flow rates are listed in Tables 2 and 3, respectively. A general shift in the reaction region and peak temperatures to higher temperature with increasing heating rates was observed. This behavior suggests a slow rate of oxidation at high heating rates which caused the combustion to reach completion at higher temperature. The weight loss in the fuel deposition zone increased with increasing heating rate with a subsequent decrease in the high temperature oxidation zone. Statistical analysis indicated that there was no effect of gas flow rates on the reactions at $P < 0.05$ (Table 3; Fig. 4).

### 3.2. Differential thermal analysis

The DTA curves of the oil sands and bitumen extracts are all similar (Table 4). The DTA traces were characterized by a mild exothermic peak up to about 470 °C followed by a pronounced exothermic peak that extended to the end of the combustion reaction.

Table 3
Thermogravimetric characteristics of Nigerian bitumen at various air flow rates (heating rate: 10 °C/min)

| Sample | Air flow rate (ml/min) | First region (LTO) | | Second region (FD) | | Third region (HTO) | | PT (°C)[a] |
|---|---|---|---|---|---|---|---|---|
| | | Temperature range (°C) | Weight loss (wt.%)[b] | Temperature range (°C) | Weight loss (wt.%)[b] | Temperature range (°C) | Weight loss (wt.%)[b] | |
| Ilubinrin | 50 | 25–345 | 27.5 ± 1.2 | 345–480 | 39.6 ± 1.4 | 480–550 | 32.9 ± 1.2 | 535 ± 10 |
| | 75 | 25–340 | 29.5 ± 1.2 | 340–480 | 38.2 ± 1.0 | 480–550 | 32.3 ± 1.5 | 530 ± 12 |
| | 100 | 25–340 | 29.8 ± 1.1 | 340–480 | 38.8 ± 0.9 | 480–560 | 31.4 ± 1.4 | 540 ± 5 |
| Oloda | 50 | 25–330 | 14.5 ± 0.9 | 330–480 | 43.1 ± 1.3 | 480–545 | 42.4 ± 0.7 | 535 ± 5 |
| | 75 | 25–330 | 16.5 ± 0.5 | 330–480 | 43.6 ± 1.4 | 480–550 | 39.9 ± 2.1 | 540 ± 11 |
| | 100 | 25–350 | 16.3 ± 0.8 | 330–480 | 43.3 ± 0.9 | 480–550 | 40.2 ± 1.8 | 535 ± 13 |

[a] Peak temperature.

[b] Mean (±S.D.) of duplicate measurements.

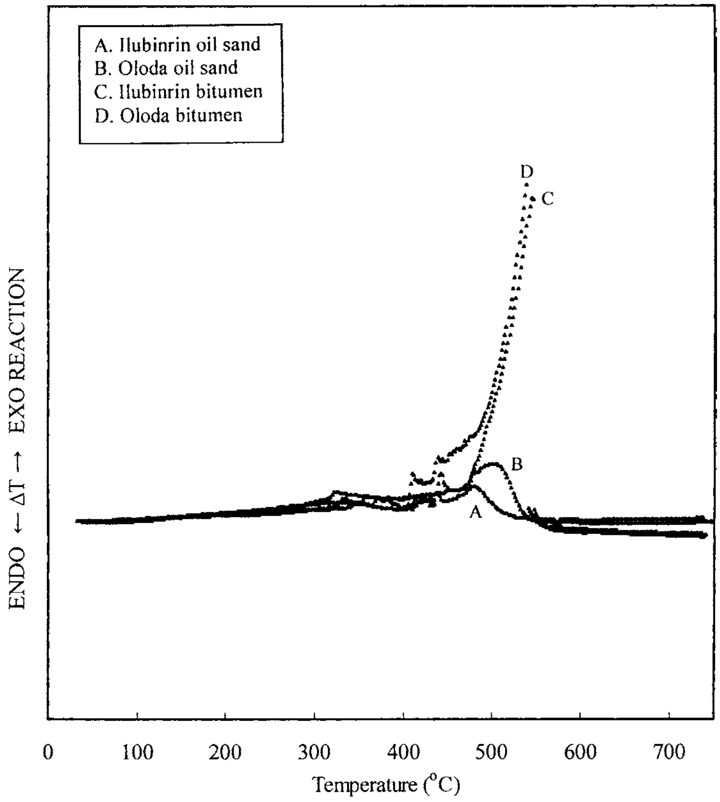

Fig. 4. DTA curves of Nigerian oil sands and bitumen.

The pronounced exothermic peak occurred within the HTO region. Similar observation has been reported by Indrijarso et al. [14] using high-pressure differential scanning calorimetry (DSC) with samples of heavy oil/sand. The DSC curves showed that the HTO reaction produced much more exothermic curve compared with the LTO reaction. The DTA curves of Oloda bitumen at various heating and air flow rates are shown in Figs. 5 and 6, respectively. It was observed that the exothermicity of the HTO reaction increases with increasing heating rates at air flow rate of 50 ml/min. No effect was noticed at different gas flow rates at 10 °C/min. Similar effects were noticed in Ilubinrin bitumen.

Table 4

Kinetic parameter of Nigerian oil sand and bitumen (heating rate: 10 °C/min; air flow rate: 50 ml/min)

| Sample | First region (LTO) | | | Third region (HTO) | | |
|---|---|---|---|---|---|---|
| | $E$ (kJ/mol)[a] | $A$ (min$^{-1}$) | cc | $E$ (kJ/mol)[a] | $A$ (min$^{-1}$) | cc |
| Oil sand | | | | | | |
| Ilubinrin | 36.9 ± 2.0 | $6.6 \times 10^{-1}$ | 0.994 | 324.8 ± 3.2 | $5.1 \times 10^{18}$ | 0.978 |
| Oloda | 46.7 ± 1.5 | $5.5 \times 10^{-1}$ | 0.995 | 287.7 ± 5.2 | $6.2 \times 10^{19}$ | 0.991 |
| Bitumen | | | | | | |
| Ilubinrin | 53.9 ± 2.5 | $2.7 \times 10^{1}$ | 0.997 | 344.0 ± 4.3 | $9.7 \times 10^{18}$ | 0.969 |
| Oloda | 57.9 ± 3.3 | $6.7 \times 10^{1}$ | 0.998 | 382.8 ± 2.2 | $6.5 \times 10^{21}$ | 0.970 |

[a] Mean (±S.D.) of duplicate measurements; cc: correlation coefficient.

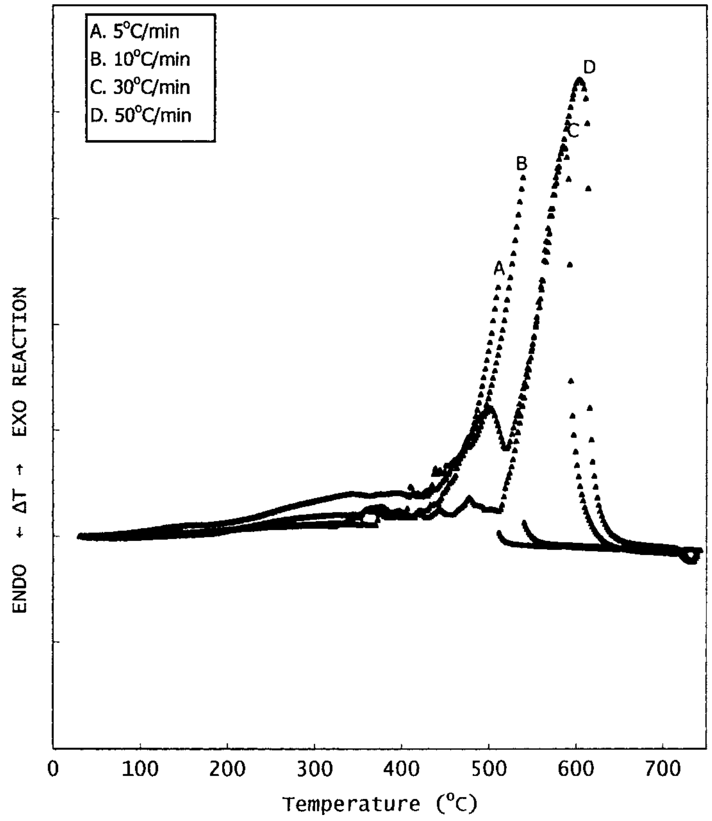

Fig. 5. DTA curves of Oloda bitumen at various heating rates (air flow rate: 50 ml/min).

### 3.3. Kinetics analysis

The kinetic parameters were determined from the TGA data. Kinetics of weight loss during bitumen combustion is extremely complex because of the numerous components and species which are simultaneously oxidized. The oxidation reaction cannot be described by an exact kinetic scheme. Kinetics

Table 5
Kinetic parameters of Nigerian bitumen at various heating rates (air flow rate: 50 ml/min)

| Sample | Heating rate (°C/min) | First region (LTO) | | | Third region (HTO) | | |
|---|---|---|---|---|---|---|---|
| | | $E$ (kJ/mol)[a] | $A$ (min$^{-1}$) | cc | $E$ (kJ/mol)[a] | $A$ (min$^{-1}$) | cc |
| Ilubinrin | 5 | 54.9 ± 1.9 | $3.0 \times 10^1$ | 0.994 | 397.1 ± 7.8 | $2.5 \times 10^{23}$ | 0.996 |
| | 10 | 53.9 ± 2.5 | $2.7 \times 10^1$ | 0.997 | 344.0 ± 4.3 | $9.7 \times 10^{18}$ | 0.969 |
| | 30 | 51.0 ± 2.3 | $2.3 \times 10^1$ | 0.992 | 322.6 ± 6.8 | $6.9 \times 10^{16}$ | 0.993 |
| | 50 | 48.1 ± 3.2 | $1.6 \times 10^1$ | 0.995 | 299.8 ± 4.6 | $1.4 \times 10^{15}$ | 0.992 |
| Oloda | 5 | 60.6 ± 2.1 | $9.6 \times 10^1$ | 0.998 | 412.5 ± 6.3 | $2.5 \times 10^{24}$ | 0.964 |
| | 10 | 57.9 ± 3.3 | $6.7 \times 10^1$ | 0.998 | 382.8 ± 2.2 | $6.5 \times 10^{21}$ | 0.970 |
| | 30 | 60.8 ± 3.5 | $2.2 \times 10^2$ | 0.997 | 287.1 ± 4.6 | $4.4 \times 10^{14}$ | 0.990 |
| | 50 | 63.3 ± 2.3 | $4.1 \times 10^2$ | 0.996 | 324.2 ± 8.2 | $6.8 \times 10^{16}$ | 0.982 |

[a] Mean (±S.D.) of duplicate measurements; cc: correlation coefficient.

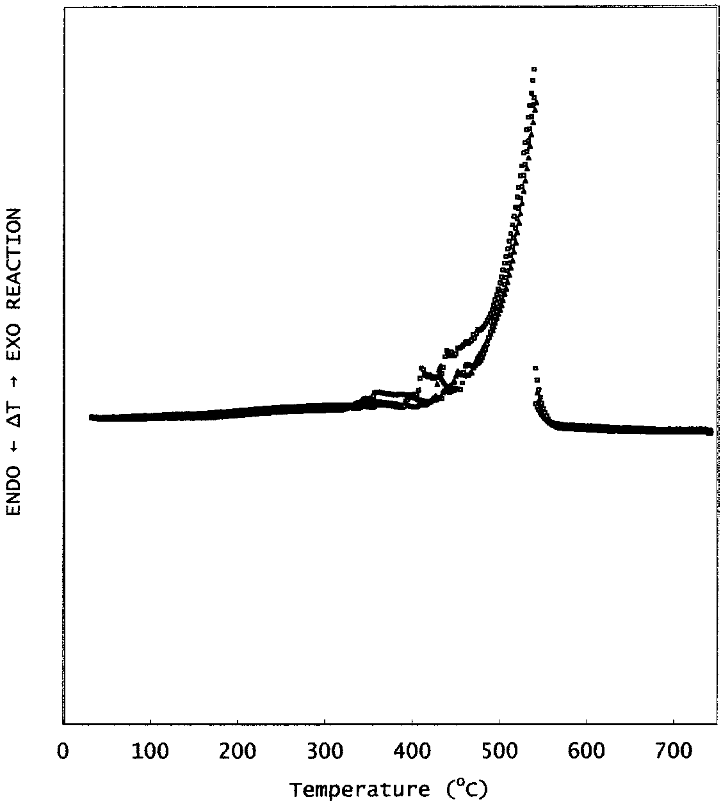

Fig. 6. DTA curves of Oloda bitumen at various air flow rates (heating rate: 10 °C/min).

parameters calculated here are regarded as apparent data representing complex and consecutive reactions. The overall thermal process responsible for the weight loss can be described by the following rate expressions:

$$d\alpha/dt = k(1-\alpha)^n \tag{1}$$

$$k = A\exp(-E/RT) \tag{2}$$

$$\alpha = W_o - W_t/W_o - W_f \tag{3}$$

where $k$ is the rate constant, $\alpha$ the extent of conversion, $n$ the order of reaction, $W_o$ the initial weight of the sample, $W_t$ the weight of the sample at time $t$, $W_f$ the

Table 6
Kinetic parameters of the bitumen at various air flow rates (heating rate: 10 °C/min)

| Sample | Air flow rate (ml/min) | First region (LTO) | | | Third region (HTO) | | |
|---|---|---|---|---|---|---|---|
| | | E (kJ/mol)[a] | A (min$^{-1}$) | cc | E (kJ/mol)[a] | A (min$^{-1}$) | cc |
| Ilubinrin | 50 | 53.9 ± 2.5 | $2.7 \times 10^1$ | 0.997 | 344.0 ± 4.3 | $9.7 \times 10^{18}$ | 0.969 |
| | 75 | 51.2 ± 1.8 | $1.6 \times 10^1$ | 0.991 | 392.7 ± 4.6 | $2.1 \times 10^{22}$ | 0.976 |
| | 100 | 50.9 ± 2.3 | $1.4 \times 10^1$ | 0.991 | 382.1 ± 1.8 | $3.9 \times 10^{21}$ | 0.974 |
| Oloda | 50 | 57.9 ± 3.3 | $6.7 \times 10^1$ | 0.998 | 382.8 ± 2.2 | $6.5 \times 10^{21}$ | 0.970 |
| | 75 | 52.5 ± 2.2 | $1.7 \times 10^1$ | 0.995 | 347.5 ± 2.1 | $3.1 \times 10^{20}$ | 0.988 |
| | 100 | 55.8 ± 2.9 | $3.0 \times 10^1$ | 0.995 | 391.1 ± 1.2 | $1.9 \times 10^{22}$ | 0.973 |

[a] Mean (±S.D.) of duplicate measurements; cc: correlation coefficient.

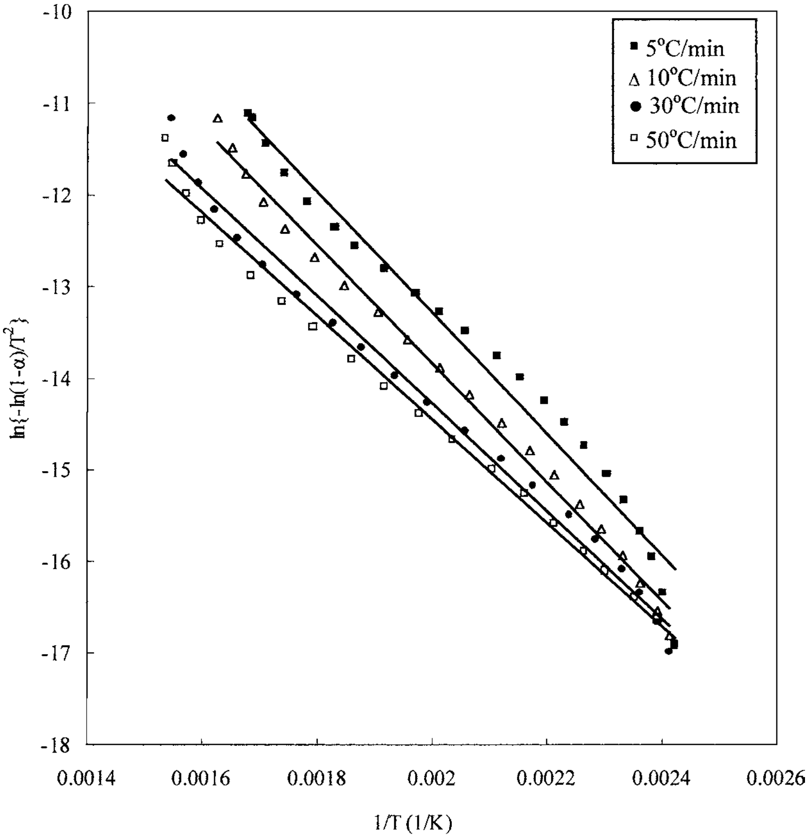

Fig. 7. Arrhenius plot of Ilubinrin bitumen at various heating rates (air flow rate: 50 ml/min), LTO region.

final weight of the sample at the end of the reaction, $A$ the Arrhenius constant, $E$ activation energy, $R$ gas constant and $T$ absolute temperature.

By combining Eqs. (1) and (2), we obtain

$$d\alpha/dt = A\exp(-E/RT)(1-\alpha)^n \quad (4)$$

For a non-isothermal kinetics expression with linear heating rates, $\beta$, Eq. (4) becomes

$$d\alpha/dt = A/\beta\exp(-E/RT)(1-\alpha)^n \quad (5)$$

By integrating Eq. (5), taking the natural logarithms and assuming that $n = 1$, we obtain

$$\ln\{-\ln(1-\alpha)/T^2\} - \ln AR/\beta E - E/RT \quad (6)$$

By using the $\alpha$ and temperature values from the TGA data. A plot of $\ln\{-\ln(1-a)/T^2\}$ versus $1/T$ should result in a straight line. Arrhenius constant, $A$, and activation energy, $E$, can be obtained from the intercept and slope of the line. Typical plots to obtain activation energies for the low- and high-temperature oxidation reactions of the bitumen are shown in Figs. 7 and 8. A regression analysis with the least square method was used in drawing the best straight line. The linear least square correlation varied between 0.970 and 0.998. The oil sands have lower activation energy and Arrhenius constant values compare with the bitumen extracts (Table 4). The apparent activation energy values for the low- and high-temperature oxidation reactions varied from 36.9 to 46.7 and 287.7 to 324.8 kJ/mol for the oil sands and from 53.9 to 57.9 and 344.0 to 382.8 kJ/mol for the bitumen, respectively. This result suggests a catalytic effect of sand on the oxidative reactions taking place during the thermal decomposition of the bitumen contained in the oil sand. The activation energies of the low- and high-temperature oxidation reactions of the bitumen samples at different

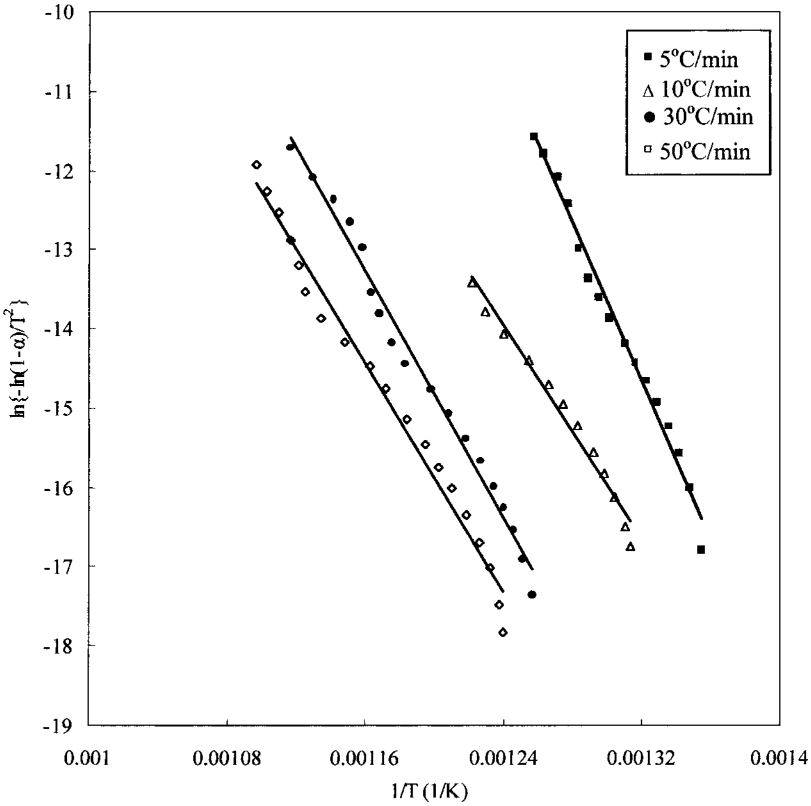

Fig. 8. Arrhenius plot of Ilubinrin bitumen at various heating rates (air flow rate: 50 ml/min), HTO region.

heating and air flow rates are given in Tables 5 and 6, respectively. Both the heating and gas flow rates have no significant effect on the activation energies in the LTO region at $P < 0.05$ but the values decreased with increasing heating rate in the HTO region.

## 4. Conclusions

Thermogravimetry analysis showed that the thermal decomposition of Nigerian bitumen in air atmosphere occurred at three different reaction regions, known as low-temperature oxidation, fuel deposition and high-temperature oxidation. Increasing the heating rate caused a shift in the reaction regions and peak temperatures to higher temperature. Gas flow rate had no effect on the reactions. The activation energies of the LTO and HTO reactions of the oil sands were lower than that of the corresponding bitumen extracts. This observation suggests a catalytic effect of sand on the various thermo-oxidative reactions taking place during the thermal decomposition. Differential thermal analysis (DTA) revealed the exothermic nature of the reactions especially at the HTO region.

## Acknowledgements

The authors thank the Japanese Ministry of Education (MONBUSHO) and UNESCO for the 1 year Research Fellowship granted to one of the authors, O.O. Sonibare of Tokyo Institute of Technology. Prof. H. Sekiguichi and Mr. Kodama are gratefully acknowledged for their assistance in the thermal analysis.

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