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Thermogravimetric analysis of petroleum asphaltenes along with estimation of average chemical structure by nuclear magnetic resonance spectroscopy

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Abstract

Combining with the ^{1}H and ^{13}C nuclear magnetic resonance (NMR) determinations, elemental analysis and molecular weight measurement, average molecular formula of the chemical unit for the asphaltenes from Chinese Daqing crude oil were calculated. Thermal pyrolysis kinetics of the asphaltenes had been studied using thermogravimetric analysis (TGA). The distributed activation energy model (DAEM) was used to analyze these complex systems. The results show that the peak activation energy for pyrolysis of the asphaltenes is 245 kJ mol^{-1} and the pre-exponential factor is 5.88×10^{14} s^{-1}. The DAEM method presented reasonably good results of the prediction of the weight loss curves. A linear relationship can be found from the plots of logarithm of the pre-exponential factor against the activation energy at selected conversion values. This phenomenon known as the compensation effect was explained and it was in agreement with the estimated chemical structure determined by NMR.

Keywords: Asphaltene; Pyrolysis; Thermogravimetric analysis (TGA); Nuclear magnetic resonance (NMR); Distributed activation energy model (DAEM)

1. Introduction

Asphaltenes are the essential components with the largest average molecular weight in crude oils or petroleum vacuum residues [1]. Some experimental evidence [2–6] suggested that these oils be at continuous colloidal aggregated states, in which asphaltene aggregates with resins adsorbed on their surface. The stability for this special structure strongly depends on the solubility and the interfacial properties of asphaltenes. The precipitation of asphaltenes in crude oil well production tubing is a practical as well as theoretical problem, owing to its negative impact on the petroleum industry. The thermal decomposition of asphaltenes is of interest because of the tendency of them to form high yields of coke and to cause catalyst deactivation during processing. Many studies [7–12] have been reported on the chemical structure, interfacial property and pyrolysis kinetics of asphaltenes. Pyrolysis of asphaltenes is viewed chemically as depolymerization in parallel with thermal decomposition of functional groups, which can supply clues to the structure of the parent hydrocarbon. When asphaltenes are heated prior to gasification, their large volatile content is released, leaving a char. Pyrolysis is the rapid first step in combustion and gasification processes in which the resulting char subsequently reacts with oxygen, steam, hydrogen or carbon dioxide. Hence, knowledge of thermal conversion kinetics of asphaltenes is of considerable importance. Recently, Geng and Liao [13] gave a reasonable review of asphaltene pyrolysis and reported the kinetic studies and the geochemical applications. Dieckmann et al [14] used asphaltene pyrolysis kinetics to infer information about oil expulsion temperatures.

In this work, asphaltenes for Daqing crude oil, one typical Chinese crude oil, were separated and the thermal pyrolysis

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kinetics was studied using thermogravimetric analysis. Combining with the NMR determination, elemental analysis and molecular weight measurement, the average molecular formula of the asphaltene unit was calculated. The aim is to give internal relations between the NMR and the TGA results.

2. Experimental

2.1. Separation of asphaltenes

Asphaltenes used in the experiments were extracted from Daqing crude oil coming from Daqing Oil Field Co. Ltd. in China. The separation of asphaltene fractions from the crude oil was carried out by *n*-pentane precipitation. Thirty volumes of *n*-pentane was added to the crude oil. The mixture was in a state of reflux for 1 h, and then was cooled and left to stand for 24 h. The precipitated asphaltene fraction was filtered and Soxhlet-extracted with *n*-pentane and dried in a vacuum drying oven. The asphaltene sample is a laminate brittle solid with metal luster.

2.2. Characteristic parameters

Elementary composition of the asphaltenes was determined by an elemental analyser of Carlo Erba EA1110. The molecular weight was measured by the VPO method using a Knauer type molecular weight meter with benzene as solvent. The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance DMX500 NMR spectrometer with $CDCl_3$ as solvent. The chemical shift is referred to the TMS standard.

2.3. Thermogravimetric analysis

The experiments used a NETZSCH STA 409 PG/PC TGA. The heating rates employed were 10, 15 and 20 °C min^{-1} up to the final temperatures of 800 °C. Ultra-high-purity nitrogen at room temperature was used at a flow rate controlled to 50 ml min^{-1} for 20 min before starting each run. The initial temperature of the furnace was controlled at 30 °C and lasted for 5 min. The samples were then heated to the final temperature at each heating rate and were held at that final temperature for 10 min. The sample weight was over the range from 9 to 11 mg. During the TGA experiments, the sample temperature increased linearly with time and the weight loss of volatiles was recorded directly.

Table 1
Results of elemental analysis of asphaltenes

C (%)	84.17
H (%)	9.06
N (%)	1.94
S (%)	2.67
O[a] (%)	2.2

[a] Calculated by difference.

3. Results and discussion

3.1. Structrual parameters and model molecule

Elemental analysis results for the asphaltenes are listed in Table 1. The ^{1}H and ^{13}C NMR measurement results are given in Table 2.

It appears that carbon and hydrogen are two major elements with total mass fractions of 93% in Daqing asphaltenes. Heteroatoms, nitrogen, sulphur and oxygen, with the range from about 2 to 3% are observed, which may give rise to strong intermolecular forces for asphaltene aggregations. Recently, nuclear magnetic resonance spectroscopy has become a powerful tool for the analysis of petroleum products [15–18]. The average structural group parameters as the usual definition [19,20] obtained from NMR measurements for the investigated asphaltenes are presented in Table 3.

It is known that the asphaltenes have been proposed to be repeating units of similar composition and that the unit sheets are conceived as being held together in the particle by intermolecular forces and by aliphatic chains [1,4,8,9]. The apparent molecular weight of the asphaltenes is dependent on the nature of solvent and also on the temperature because of the different association degree in different environment or under different condition. Published data for the molecular weights of petroleum asphaltenes generally range from 1000 to 5000 [7]. In this work, the molecular weights determined in benzene at 45 °C by the VPO method for the asphaltenes are 3950. The average molecular weight of a unit sheet in the asphaltene model molecule can be calculated from a combination of NMR measurements and elemental

Table 2
Relative contents of hydrogen and carbon atoms on different positions in asphaltenes from ^{1}H and ^{13}C NMR determinations

H/C type	Chemical shift (δ)	Definition	Relative content
H_{aro}	10.0 ∼ 6.0	Hydrogens attached to aromatic ring carbons	0.1152
H_{ali}	4.0 ∼ 0.4	Aliphatic hydrogen atoms	0.8848
H_{α}	4.0 ∼ 2.0	Hydrogens attached to carbons in alkyl substitution α to aromatic ring carbons	0.1332
H_{β}	2.0 ∼ 1.0	Hydrogens in alkyl substitution β or further from aromatic ring	0.5432
H_{γ}	1.0 ∼ 0.4	Hydrogens in terminal or isolated CH_3 groups of saturates or hydrogens in alkyl groups substituted in position γ- and further from aromatic ring	0.2084
C_a	160 ∼ 100	Aromatic carbon atoms	0.4427
C_{ali}	60 ∼ 5.0	Aliphatic carbon atoms	0.5573

Table 3
Average structural parameters calculated for asphaltenes

Parameter	Definition	Average structural parameters
n	Carbons per alkyl side chain	6.6
f_c	Carbon-hydrogen weight ratio of total alkyl groups	5.9
x	Hydrogen-carbon atomic ratio of alkyl groups	2.1
$\%C_A$	Percent aromatic carbon	37.3
$\%C_1{}^S$	Percent substituted aromatic carbon	7.1
$\%C_1{}^U$	Percent unsubstituted aromatic carbon	12.5
$\%C_1$	Percent non-bridge aromatic carbon	19.6
$\%A_S$	Percent substitution of aromatic rings	36.1
C_A	Aromatic carbons per average molecule	24.9
C_1	Aromatic non-bridge carbons per average molecule	13.1
R_A	Aromatic rings per average molecule	6.9
R_S	Alkyl substituents per average molecule	4.7
R_N	Naphthenic rings per average molecule	1.6
C_{ali}	Aliphatic carbon per average molecule	31.3
H_{ali}	Aliphatic hydrogen per average molecule	64.2

analysis. This is done in the following steps: (1) Total saturated carbon atoms (C_s), total aromatic carbon atoms (C_a), peripheral carbon atoms in a condensed aromatic sheet (C_p) and the C_p/C_a ratio are determined by NMR results, using the equations given by Speight [21]. On the basis of a 100 g sample, C_a (100) and C_p (100) are obtained. (2) Plot the C_p/C_a and average C_a values calculated for aromatic compounds. The corresponding average C_a of the asphaltenes is determined. (3) The average molecular weight of a unit sheet is calculated from C_a (100) and C_a (average): MW (unit) = (C_a (average)/C_a (100)) × 100. The detailed description can be found in the original references [7,21,22]. The C_a (100), C_p/C_a and C_a (average) values are 3.321, 0.496 and 26.6 for the investigated asphaltenes. Similarly, the values of 3.637, 0.422 and 38.8, 4.056, 0.367 and 38.9, 3.935, 0.490 and 25.5 can be obtained for three asphaltenes ASP-M, ASP-H and ASP-D [9], respectively. So, the calculated NMR molecular weight of unit sheet should be 801. It is very clear that there have large difference between the VPO molecular weight and the calculated value. This indicates obviously that the asphaltenes are aggregated in the solvent of benzene. It was also verified in previous work [2–4]. Depending on the different molecular weights, the average number of the unit sheet or layer (association number) is calculated as 4.9 in the asphaltenes, which is similar to those reported in the literature [7–9]. From the calculated molecular weight and elemental analysis results in Table 1, the average formula of unit sheet for the asphaltenes can be given by $C_{56.1}H_{72.5}N_{1.1}S_{0.7}O_{1.1}$.

With the average structural parameters from ^{1}H and ^{13}C NMR determinations in Table 3 and the average formula of unit sheet, the C–C and C–H skeleton such as the aromatic rings, aromatic carbons, aromatic non-bridge carbons, alkyl substituents, naphthenic rings, aliphatic carbon and aliphatic hydrogen, with tentative incorporation of S, N and O heteroatoms, for the asphaltene may be clear. Oxygen, nitrogen and sulfur may play major roles in binding unit sheets, probably through hydrogen bonding or ether-type bonding. The high aromatic character also provides strong π–π interaction between aromatic rings of the molecule. This chemical structure may throw some light on the compensation effect on the thermal pyrolysis of the asphaltenes, which will be discussed below.

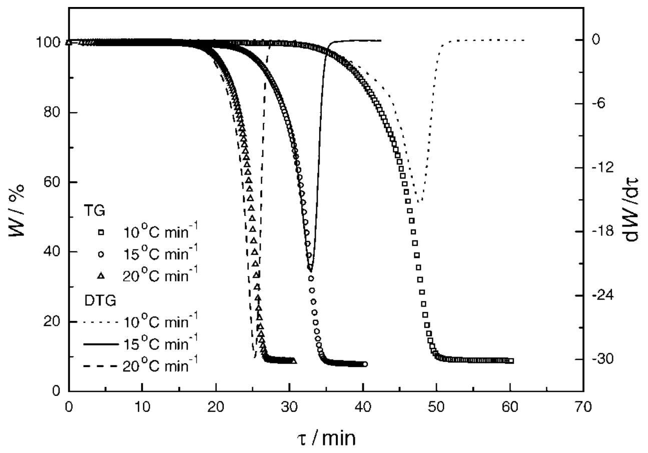

Fig. 1. Plots of weight loss and weight loss rate vs. time at different heating rates.

3.2. Thermogravimetric analysis

Fig. 1 presents the weight change with time (TG) and compares the corresponding rate of weight loss versus time (DTG) for the asphaltenes at different heating rates.

As shown in Fig. 1, the final volatile yield (V^*) for pyrolysis of the asphaltenes is 91.6%. The pyrolysis process of the asphaltenes mainly occurs at a narrow temperature range from 390 to 500 °C ($V/V^* = 0.1 \sim 0.9$). The temperatures corresponding to the maximum weight loss rates at three different heating rates change in a narrow temperature range with the values of 481 ± 5 °C. The pyrolysis of the asphaltenes can be roughly divided into three stages referring to Fig. 1. From the initial experimental temperature to 350 °C is the first stage. In this stage, the weight has no noticeable change and the value of $dW/d\tau$ is near to zero, which indicates that there are little chemical changes taking place. From 350 to 450 °C is the second stage. This is the first stage for producing volatiles with relatively slow weight loss rate. The third stage is above 450 °C, which is the second stage for producing volatiles with $dW/d\tau$ sharply decreasing to a minimum and then changing to zero. With the NMR measurements and average molecule assumptions above, it is known that the asphaltenes contain complex large molecules composed of polycyclic aromatics linked with naphthalene rings and side aliphatic chains along with heteroatoms. During the second stage, the intermolecular associations and weaker chemical bonds are destroyed. The side aliphatic chains may be broken and some small gaseous molecules are produced because of the lower temperature. During the third stage with higher temperature, the stronger chemical bonds are broken and the parent molecular skeletons are destroyed. As a result, the larger molecules decompose into smaller molecules in the gas phase. Finally, only coke remains.

3.3. Kinetics of thermal pyrolysis

For the systems with complex reactions such as pyrolysis of polymers, coal, oil shale, bitumen and biomass, thermal regeneration reaction of activated carbon, the distributed activation energy model (DAEM) should be used [23–28]. A variety of global kinetic analyses for complex materials were reviewed by Burnham and Braun [28].

The DAEM method assumes that many irreversible first-order parallel reactions that have different rate parameters occur simultaneously. Change in the total volatiles, *V*, against time, τ, is given by

$$1-\frac{V}{V*}=\int_0^\infty \exp\left(-k_0\int_0^\tau \mathrm{e}^{-E/RT}\,\mathrm{d}\tau\right) f(E)\,\mathrm{d}E \qquad (1)$$

where V^* is the effective volatile content, $f(E)$ the normalized distribution curve of the activation energy representing the differences in the activation energies of many reactions, k_0 the frequency factor corresponding to E value, T the pyrolysis temperature and R the universal gas constant. Researchers have developed and described some different methods for estimating $f(E)$ and k_0. Miura and Maki [27] presented a new and simple method to estimate $f(E)$ and $k_0(E)$ from three sets of experimental data obtained at different heating rates without assuming functional forms for $f(E)$ and $k_0(E)$ and described the procedure in detail. The following kinetic equation is derived and used:

$$\ln\left(\frac{\beta}{T^2}\right)=\ln\left(\frac{k_0R}{E}\right)+0.6075-\frac{E}{R}\frac{1}{T} \qquad (2)$$

where β is a constant heating rate. With Eq. (2), both E and k_0 at selected V/V^* values can be determined from the slope and the intercept in the Arrhenius plots of $\ln(\beta/T^2)$ versus $1/T$. $f(E)$ is obtained by differentiating the V/V^* versus E relationship and $k_0(E)$ is obtained by the least square correlation between k_0 and E values. With the Miura's method, we here discussed the kinetics of the pyrolysis of the investigated asphaltenes.

Fig. 2 shows the Arrhenius plots of $\ln(\beta/T^2)$ versus $1/T$ at selected V/V^* values for the asphaltenes. On the basis of these plots, the conversion-dependent activation energy values were obtained. It follows that many parallel reactions with different rate parameters really occur simultaneously during the thermal pyrolysis of the asphaltenes. The distribution curves $f(E)$ of the activation energy are shown in Fig. 3.

Fig. 4 represents the plots of logarithm of the pre-exponential factor k_0 against the activation energy E. The k_0 values are correlated to be a function of E, represented by $k_0 = 5.88 \times 10^{14}\,\mathrm{e}^{0.1395(E-245)}$. The straight-line relationship is known as the compensation effect [24]. From the Arrhe-

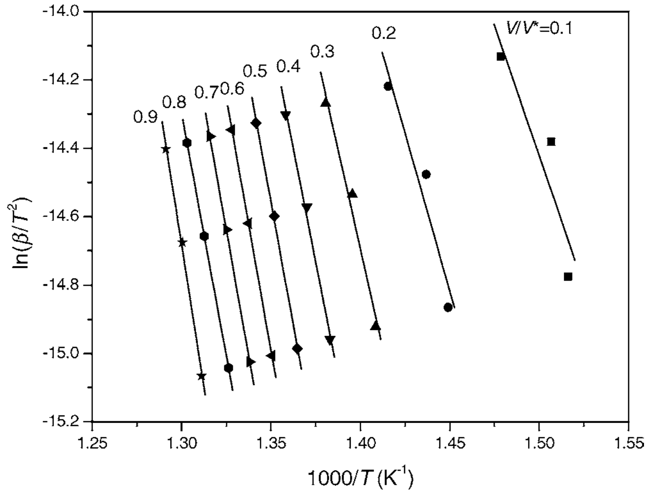

Fig. 2. Arrhenius plots of $\ln(\beta/T^2)$ vs. $1/T$ at selected V/V^* values.

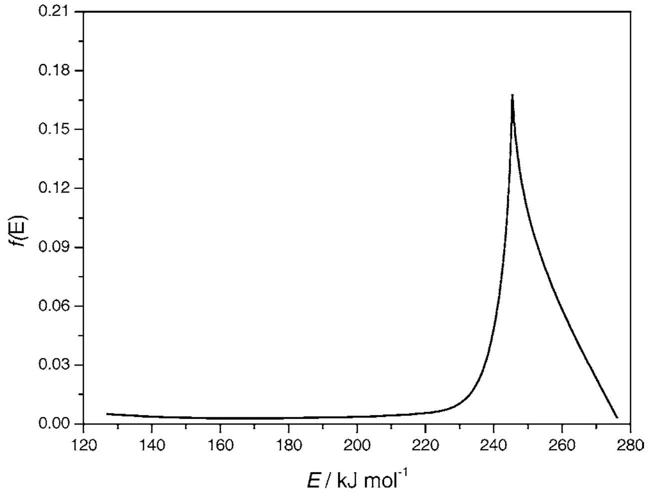

Fig. 3. The distribution curves $f(E)$.

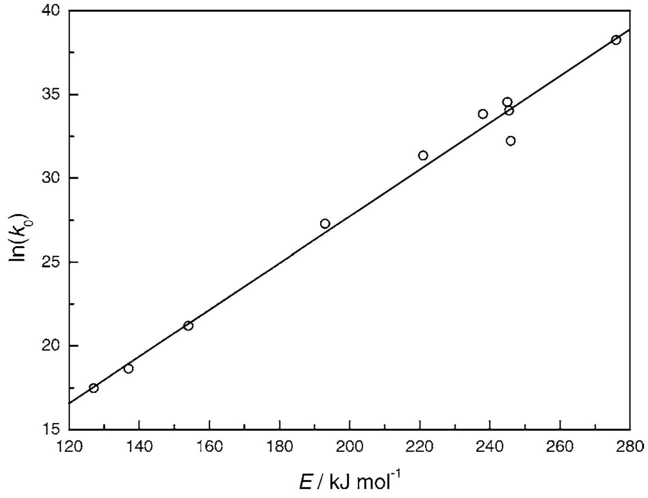

Fig. 4. Plots of $\ln(k_0)$ vs. E.

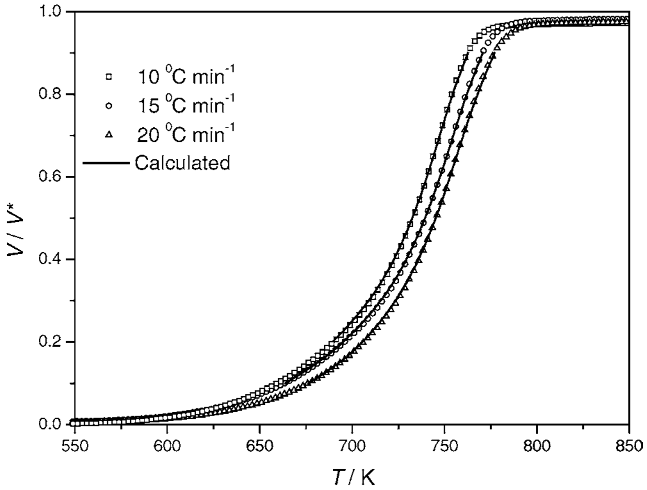

Fig. 5. Comparison of experimental V/V^* data vs. T and those calculated using the DAEM method.

nius equation and the transition state theory, there have the following equations

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \quad (3)$$

$$k_0 = \frac{k_\mathrm{B}T}{h} \exp\left(\frac{\Delta S^*}{R}\right) \quad (4)$$

where k is the rate constant, k_B the Boltzmann constant, h the Planck constant and ΔS^* the entropy change from the initial state to the transition state (or, the entropy of activation). From the average model molecule deduced from NMR, we can consider as follows. In the initial stage, the pyrolysis was carried out along a reaction path with low activation energy and with relatively large negative value of ΔS^* because of the interactions between molecules from the heteroatoms and the functional groups. Therefore, there is a small value of k_0 when E is low. With the destroy of the intermolecular forces and the weak chemical bonds, the number of the functional groups decreases and the molecules of he asphaltenes change from a flaccid structure into a tight structure. As a result, the activation energy for the pyrolysis becomes larger. The lost of functional groups may lead to weaker interaction between molecules and to quasi-unimolecular reaction for the pyrolysis with relatively small negative value of ΔS^*. It follows that the value of k_0 is large when E is high. The increase of k_0 in the exponential form of ΔS^* with a positive contribution to the rate constant can make compensation for the increase of the activation energy with negative effect on the rate constant.

Comparison of experimental V/V^* versus T relationships and those calculated using the $f(E)$ curves and k_0 (E) relationships estimated by the DAEM method for the asphaltenes are shown in Fig. 5. The reasonable agreements indicate that the DAEM method is useful for the analysis of the pyrolysis kinetics for the system with complex reactions.

4. Conclusions

Average model molecule of the asphaltenes from Chinese Daqing crude oil is proposed from combining with the ^{1}H and ^{13}C NMR determinations, elemental analysis and molecular weight measurement. With the thermogravimetric analysis carried out at three different heating rates, the distributed activation energy model (DAEM) was used to analyze the pyrolysis kinetics with successful prediction of the weight loss curves. The changes of the kinetic parameters are in reasonable agreement with the estimated chemical structures determined by NMR.

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References

[1] T.F. Yen, W.H. Wu, G.V. Chilingar, Energy Sources 7 (1984) 275.
[2] S. Acevedo, B. Mendez, A. Rojas, Fuel 64 (1986) 1741.
[3] K.W. Brian, Energy Fuels 12 (1998) 1008.
[4] D. Liu, Z. Wang, G. Que, J. Fuel Chem. Tech. (Chinese) 30 (2002) 281.
[5] R.A. Mohammed, A.I. Bailey, P.E. Luckham, S.E. Taylor, Colloids Surf. 91 (1994) 129.
[6] M. Li, M. Xu, Y. Ma, Z. Wu, A.A. Christy, Colloids Surf. 197 (2002) 193.
[7] L.H. Ali, K.A. Al-Ghannam, Fuel 60 (1981) 1043.
[8] L.H. Ali, K.A. Al-Ghannam, J.M. Al-Rawi, Fuel 69 (1990) 519.
[9] J. Christopher, A.S. Sarpal, G.S. Kapur, A. Krishna, B.R. Tyagi, M.C. Jain, S.K. Jian, A.K. Bhatnagar, Fuel 75 (8) (1996) 999.
[10] L. Michon, D. Martin, J.P. Planche, B. Hanquet, Fuel 76 (1) (1997) 9.
[11] J.G. Reynolds, A.K. Burnham, T.O. Mitchell, Org. Geochem. 23 (1995) 109.
[12] J.M. Jimenez-Mateos, L.C. Quintero, C. Rial, Fuel 75 (1996) 1691.
[13] A. Geng, Z. Liao, Appl. Geochem. 17 (2002) 1529.
[14] V. Dieckmann, P.G. Caccialanza, R. Galimberti, Org. Geochem. 33 (2002) 1501.
[15] G.S. Kapur, A. Exker, R. Meusinger, Energy Fuels 15 (2001) 943.
[16] G.S. Kapur, S. Berger, Fuel 81 (2002) 883.
[17] Y. Yang, B. Liu, H. Xi, X. Sun, T. Zhang, Fuel 82 (2003) 721.
[18] J. Burri, R. Crockett, R. Hany, D. Rentsch, Fuel 83 (2004) 187.
[19] E.M. Dickinson, Fuel 59 (1980) 290.
[20] P.L. Gupta, P.V. Dogra, R.K. Kuchhal, P. Kumar, Fuel 65 (1986) 515.
[21] J.G. Speight, Fuel 49 (1970) 76.
[22] L.H. Ali, Fuel 50 (1971) 298.
[23] R.L. Braun, A.K. Burnham, J.G. Reynolds, J.E. Clarkson, Energy Fuels 5 (1991) 192.
[24] C.C. Lakshmanan, M.L. Bennett, N. White, Energy Fuels 5 (1991) 110.
[25] K. Miura, Energy Fuels 9 (1995) 302.
[26] T. Maki, A. Takatsuno, K. Miura, Energy Fuels 11 (1997) 972.
[27] K. Miura, T. Maki, Energy Fuels 12 (1998) 864.
[28] A.K. Burnham, R.L. Braun, Energy Fuels 13 (1999) 1.