J. Mater. Environ. Sci. 7 (1) (2016) 293-298 *Barbooti et al.*
ISSN : 2028-2508
CODEN: JMESCN

Thermogravimetric studies on Iraqi paving asphalts

Mahmood M. Barbooti*, Hussein H. AI-Soufi and Hisham AI-Saleem

Department of Applied Chemistry, School of Applied Sciences, University of Technology, Baghdad, Iraq).

Received 17 Jan2015, Revised 14 Dec 2015, Accepted 26 Dec 2015
**Corresponding Authors. E-mail: brbt2m@gmail.com Tel: +964 750 241 5259*

Abstract
The thermal behavior of two asphalts, Quayarah and Daura, employed for paving in Iraq, was studied during mixing and laying conditions using dynamic thermogravimetry, TG, under air and nitrogen atmospheres. Quayarah asphalt is produced by direct topping of process Quayarah heavy crude oils (API= 15-20). Meanwhile, the Daura asphalt is produced from Kirkuk crude oil by blending soft and hard stocks obtained by vacuum distillation of the reduced crude. Quayarah is characterized by lower saturates, lower polar aromatics and higher naphthene-aromatics and higher viscosity than Daura asphalt. The asphalts were prepared in such a way to have the same penetration value. The main features of the TG curve were explained and correlated with the chemical composition, method of preparation and performance of the asphalts. Thermogravimetry can be used to aid the standard methods of asphalt testing.

Keywords: thermal behavior, asphalt, thermogravimetry, heavy crude oil asphalt, Quayarah and Daura asphalt

Introduction
Asphalts are subjected to various heating regimes during their processing. Paving grade asphalts are usually reheated at approximately 160°C for defined intervals of time to facilitate their mixing with aggregates. These intervals are extended until the termination of the final laying of the paving materials. The paving asphalt, applied at the surface in the Middle East, was subjected to severe long-term heating conditions where temperatures as high as 70°C were experienced [1]. Thin film oven tests, TFOT, were exclusively used to account for the effect of heating and mixing processes on the characteristics of asphalts during their applications and use [2]. However, there was no agreement on a certain procedure which evaluates the effects of service condition on the paving asphalts.
The applications of thermoanalytical techniques in the study and characterization of petroleum and petroleum products are gaining growing field of interest for analysts, petroleum chemists and engineers [3-7]. The results were often correlated with those obtained by the standard methods [4, 5]. Several authors reported on the thermogravimetry, TG and differential scanning calorimetry of the heavy residues of crude oils and asphalts [8, 9]. Lucena, et al., [10] combined IR, empirical tests with thermal analysis techniques for the characterization of styrene-butadiene-styrene modified asphalt cement. After aging in the rolling thin-film oven, the polymer-modified asphalt presented structural changes relating to oxidation of the material. The infrared spectra showed an increase in hydroxyl groups and the formation of carbonyl compounds and sulfoxides. The percentage of

crystallized fraction calculated from differential scanning calorimetry, DSC, was 0.41%. Kuszewski, et al. [11], studied the role of volatilization in the aging of asphalt on the roof tops with TGA and Iatroscan analyses. They concluded that the aging is associated with the loss of saturates. Al-Sammerrai, et al., [12] utilized TG and proton and 13C- NMR techniques for the identification of the source of asphalt used in the building of the old city of Babylon. Moth et al., [13] used thermoanalytical techniques: TG, DTG, and DTA in combination with Fourier transform infrared spectroscopy, FTIR, for the characterization of asphalt mixtures. Thermal characterizations showed that the main decomposition stage refers to asphaltenes and samples with additives exhibited a slight increase in thermal stability. The FTIR analysis suggested that these asphalt samples were originated from light oil. Jing-Song et al., [14] have studied the pyrolysis of asphalt with the aid of TGA at atmospheric pressure and with nitrogen as the ambient gas using relative fast heating rate. They found that the process can be fitted with a two-stage first-order model with different values of the activation energy, $\boldsymbol{E}$, for each stage that are independent of the type of asphalt and its heating rate. Ahmedzade and Geckil [15] utilized the TG analysis to study the role of carbon black as filler on the thermal stability of asphalt in comparison with limestone. Wei, et al., [16] utilized DSC for the determination of glass transition temperature of asphalt binders to be in the range from 60-90o C.

In the present work, dynamic TG technique was employed to account for the thermal behavior of Daura and Quayarah asphalts which represent most of the commercially produced and used asphalt cements in Iraq at present. The two asphalts were produced by two different methods using crude oils of different origins and characteristics as the performance of asphalt throughout the working conditions were affected by its origin, composition and processing method [2].

Materials and Methods

Quayarah and Daura asphalts were produced as follows: In Qaiyarah refinery, direct topping of process Quayarah heavy crude oils was used to produce the required paving grade asphalt cement. While at Daura refinery, where Kirkuk crude oil is the main feedstock, asphalt cement was produced by blending soft and hard stocks obtained by vacuum distillation of the reduced crude. Samples from each refinery were selected and preliminary penetration tests were made for each sample. By blending two different penetration grades of Daura asphalt, it was possible to prepare an asphalt of penetration equal to that of the asphalt from Quayarah refinery (55 mm). The main characteristics of the asphalts are shown in Table 1.

Table 1: Physico-Chemical Properties of Daura and Quayarah Asphalts.

Property '	Daura		Quayarah		Method of Test
	Before TFOT	After TFOT	Before TFOT	After TFOT	
Penetration, 25°C	55	35	55	25	ASTMD5
Softening pt, (^{o}C)	50	54	55	64	IP 58
Ductility, 25°C (cm)	100+	100+	75	57	ASTM D113
Sp. Gravity15/15°C	1.0456 1	1.0453	1.0576	1.0623	ASTM D70
viscosity, 135°C (cSt)	370	470	760	1418	ASTM D2170
Viscosity, 60°C	3212	-	7499	-	ASTM D2493
PI (pen/R&B)	-0.98	-1.07	+0.2	+0.24	
Loss on Heating, (wt%), 163^{o} C., 5 hr	-	0.01	-	+0.43	ASTM D4124
Asphaltene , (wt%)	12.52	12 .53	25.67	28.21	ASTM D41 24
Saturates, (wt%)	32.96	19.59	14.22	12.6	= =
Naphthene-Aromatics	45.79	57.86	52.20	53.13	= =
Polar Aromatics	8.7	9.17	6.9	5.27	= =

The simultaneous TG curve and its derivative, DTG, of the asphalt samples were recorded on a Stanton-Redcroft TG-760 Thermobalance. The samples weighing 3-5 mg were heated in platinum crucibles at a rate of 20°C min^{-1} under flowing nitrogen gas or air (25 $ml.min^{-1}$). Standard ASTM test No. 754 (TFOT) was used to account the effect of heat on the properties of both asphalts.

Results and Discussion

The TG and DTG curves of Qayarah asphalt under purging N_2 and air atmosphere are shown in Fig. 1. Fig. 2 shows the TG and DTG curves corresponding to Daura asphalt under different purging atmospheres (air and N_2). Under inert atmosphere, Quayarah asphalt underwent degradative volatilization above 170°C at a slightly increasing rate (DTG signal) up to 400^o C, where 30% of the material was lost. Beyond 400°C, the rate of loss increased rapidly and attained a maximum at 450°C, where almost 60% of the material was lost. The process was terminated at 540°C with a total loss of 75%.

Daurah asphalt started volatilization very slowly and the rate became appreciable beyond 192°C after the loss of 2% of the sample. The rate gradually increased with temperature and attained a maximum at 480°C with the loss of 57% of the asphalt. The overall weight loss up to the final temperature of 550°C was 85± 0.2%. Michelle, et al., 2008, have shown that the main decomposition stage refer to asphaltene [17]. The final yield of volatiles depends on the type of asphalt [14].

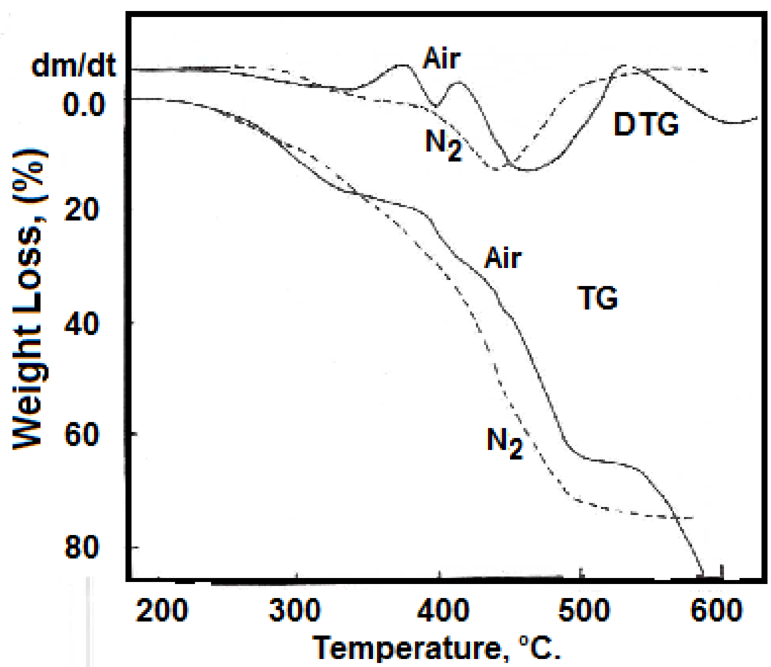

Figure 1: TG and DTG curves of Quayarah asphalt under air and nitrogen.

It was apparent that the complex thermal and chemical processes encountered in the processing of Daurah asphalt shifted the initial temperatures of degradative volatilization to higher values in comparison with straight run Quayarah asphalt. The processing of Daura asphalt resulted in the loss of the relatively volatile species. The overall thermal stability of Quayarah asphalt, therefore, was less than that of Daura asphalt. This accounts for the effects of pronounced effects of the thermal treatment on the characteristics of the Quayarah which was reported elsewhere [18].

The significant differences in the composition of the two asphalts (Table 1) might lead to differences in the features of the TG curves. The composition of Daura asphalt made the loss of the material to occur in a gradually increasing rate. The thermal behavior of Quayarah asphalt involves the loss of the volatilizable fraction remaining in the asphalt due to the termination of the distillation below 300° C and the degradation of asphalt at the high temperature range (>400° C.) [19]. Thus, the features of the TG curves beyond 400°C could refer to the completion of the distillation. The difference in the total weight loss between the two samples (~10%) is entirely attributed to the high asphaltene content of Quayarah sample which resulted in comparatively high C/H ratio and consequently larger percentages of the remaining material, at the end of the heating program (700°C). However, there are chromatographic evidences that the loss of saturates is a major contributing factor [11].

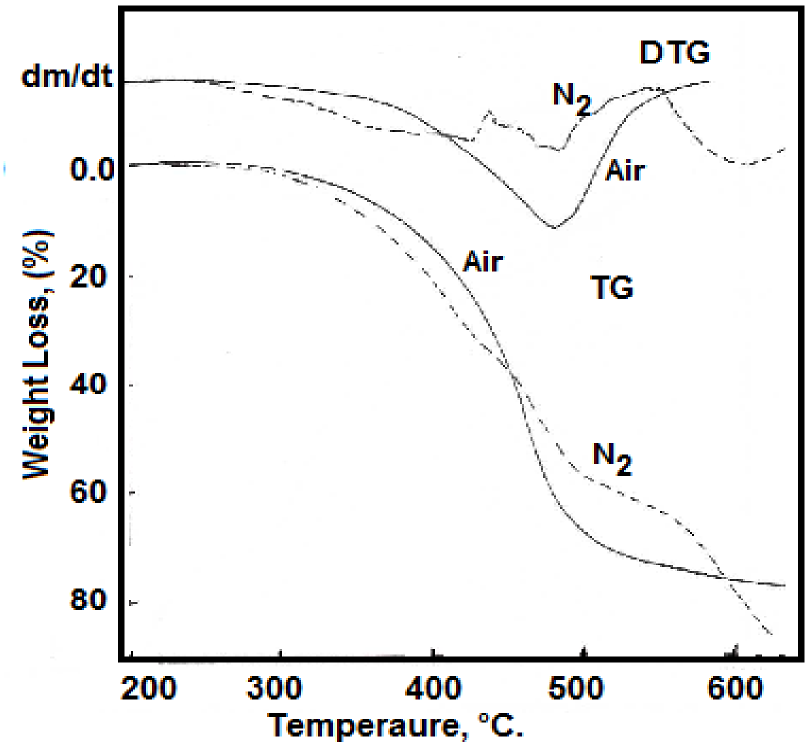

Figure 2: TG and DTG curves of Daura asphalt under air and nitrogen.

The flowing air significantly altered the shape of the TG curves of Quayarah asphalt. Three principle steps of weight loss could be seen at 192-365, 385-521, and 540-700° C, while those of Daura asphalt occurred at 190-438, 440-530, and 537-700° C. The first and second steps occurred over a temperature range that was identical to the main decomposition steps under nitrogen and yet involved 65.8% weight loss for Quayarah and 62.8% for the Daura sample. Daura asphalt, therefore, is more susceptible to oxidation than Quayarah asphalt. The superimposition of DTG signals under air and N_2 atmospheres (Fig. 2) indicated that the rate of weight loss at the first stage significantly exceeded that obtained under N_2. This was attributed to the air blowing effect which results in the dehydrogenation of asphalt and the formation of a hard product [20], i.e., in addition to normal decomposition, processes like partial oxidation, dehydrogenation and emulsified water loss [9], are responsible for the weight loss. On the contrary, the rate was much smaller under air during the second stage, relative to nitrogen atmosphere. The hard and highly viscous material formed at the end of the first stage accounted for the inhibited evolution of the degradation products from the core of the materia1 in addition to the formation of oxygen compounds of higher molecular weight relative to their parent hydrocarbons.

The difficult evolution of the volatile products was clearly shown by the sharply changing DTG signal which could only be explained by the accumulation of the volatiles and escape as bubbles. The last stage was the ashing of the residual material which occurs only under oxidative atmospheres. Fig. 3 shows the TG and DTG curves of

TFOT treated Quayarah asphalt under inert and oxidative atmospheres. The sample started decomposition at 184°C slowly and the rate increased gradually until 400°C where the ' increase in rate became significant. The DTG peak maximum occurred at 466°C and the process ended at 540^{o} C. The quantitative evaluation of the TG curves indicated some variation from that of the untreated asphalt (Fig.1). At 400^{o} C the weight loss was 25.8%, which was indicative of the volatilization of almost 5% of the material during the TFOT. The thermal stability of asphalt, therefore, was improved by the processing of its paving mixtures since it involved heating treatment similar to that of the TFOT, provided that the physical properties remain within the customer requirements.

The rest of the TG signals indicated similar weight loss extent as with the untreated sample, i.e. only a minor effect of the TFOT on the asphaltene fraction occurred.

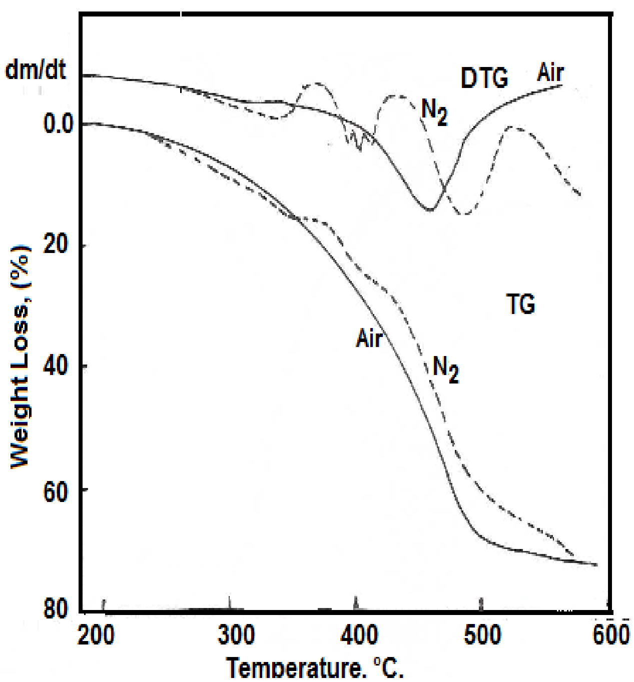

Figure 3: TG and DTG curves of Quayarah asphalt after TFOT treatment under air and nitrogen.

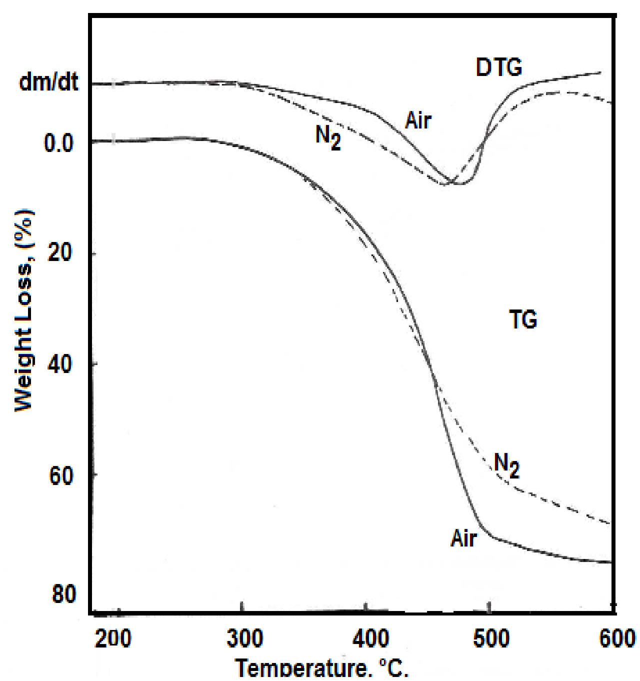

Fig. 4: TG and DTG curves of Daura asphalt after TFOT treatment under air (solid line) and nitrogen (dashed line).

The shift in the DTG peak maximum to 466^{o} C (14^{o} from that of the untreated asphalt) can be a result of the formation of higher molecular weight species due to the secondary reactions such as inter and intramolecular condensation [21], and requiring more energy to break up. Furthermore, the asphaltene content of Quayarah asphalt increased after TFOT [22].

Under the flowing air conditions, the TG and DTG signals of Quayarah asphalt are further complicated than those of the untreated sample. However, similar explanation might be forwarded to the processes taking place during this oxidative treatment as that given for the untreated sample. On the other hand, only minor differences could be observed on the shape and quantitative evaluation of the TG and DTG curves of the TFOT treated Daura asphalt in comparison with the untreated sample under inert atmosphere (Fig.4). Meanwhile, the heating under air indicated regular weight loss process and rather undisturbed DTG signal. These findings indicated that the TFOT treatment had a stabilizing effect on Daura asphalt towards oxidation. However, Quayarah asphalt undergoes serious changes in physical characteristics throughout TFOT treatment [18].

Conclusion

Thermogravimetry can be used successfully as a supporting method for the evaluation of the behavior of asphalt samples. The main features of the TG curve were explained and correlated with the chemical composition, method of preparation and performance of the asphalts. The use of air flow during the TG experiments can be efficiently indicative of the heat treatment of asphalt. The thermal stability of asphalt can be best evaluated by TG analysis. The TG method can, thus, be used for the characterization of asphalt samples.

Acknowledgements-The authors are grateful to Miss E.B. Hassan and S. Naom for their help in the experimental work.

References

1. Bissada A.F., *Proc. Assoc. Asphalt Pav. Technol*., 49, (1980) 578-605.
2. Puinauskas V. P., *Proc. Assoc. Asphalt Pav. Technol*., 48, (1979) 647-710.
3. Wesolowski M., *Thermochim. Acta*, 46 (1981)21.
4. AI-Madfai S. H., Al-Sammerrai D. A., Barbooti M.M., *J. Thermal Anal. Calorim.*, 29 (1984) 1123.
5. AI-Sammerrai D. A., Barbooti M.M., *Ind. Eng. Chem. prod. Res. Dev*., 24, (1985) 171.
6. Al- Sammerrai D.A., Barbooti M. M., *Arab Gulf J. Sci. Res*., 3 (1985) 97.
7. Barbooti M. M., Al- Sammerrai D. A., *J. Thermal Anal. Calorim.*, 30(1985) 587.
8. Cardillo P., Giavarini C., Vecchi C., *Fue1*, 63, (1984) 1518.
9. Al-Samerrai F.M., Al-Sammerrai D.A., *Thermochim. Acta*, 94 (1985) 295.
10. Lucena M.C.C., Soares S.A., Soares J.B., *Mater. Res*., 7(2004) 4.
11. Kuszewski J.R., Gorman W.B., Kane E. G., 1999, *Proc. 4th Internat. Symp. Roofing Technol*., 285-291.
12. Al-Sammerrai F., Al-Sammerrai D., Al-Rawi J., *Thermochim. Acta,* 115(1987) 181–188
13. Moth M. G., Leite L. F. M., Moth C. G., *J. Thermal Anal. Calorim.,* 93(1) (2008) 105.
14. Jing-Song G., Wei-Biao F., Bei-Jing Z., *Fuel*, 82(1) (2003)49–52.
15. Ahmedzade P., Geckil T., *Indian J. Eng. Mater. Sci*., 14(2007)358-364.
16. Wei J., Shull J.C., Barak J., Martin C., Hawley M.C., *Int. GPC Symp.*, 1994 https://www.waters.com/webassets/cms/library/docs/950365.pdf
17. Michel J., P. Keane, Benggio B., *Proc. Inter. Oil Spill Conf., Amer. Petrol. Inst*., Washington, D.C., 2008, pp. 345-348.
18. Soufi, H. H., Al- Saleem, H. E. Luzan, N., Naoom, S., *J. Petroleum Res*., 4 (1985)47.
19. Khulbe K. C., Sachdeve A.K., Mann R.S., Davis S., *Fuel Proc. Technol*., 8, (1984) 259.
20. Hobson G.D., *Applied Science*, London, 1975, PP 808-9.
21. Hus M., *Oil Gas J*., 79 (1981) 109.
22. Al- Jarrah M.M.F., Al- Soufi H.H., Al- Saleem H.E., Naoom S. S., *Fuel Sci. Technol*, 4 (1986) 249.