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Note

On the thermal behavior of petroleum asphaltenes

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Abstract

The glass transition temperature of petroleum asphaltenes has been determined using DSC. From this temperature, a hypothetical melting temperature of the asphaltenes can be calculated as falling within the range of the pyrolysis temperature of asphaltenes.

Asphaltenes are one of the two colloidal components present in crude oils and their distillation residues. However they are not a uniform class of substances. They are only defined by the chemical composition of the precipitation medium used for their separation [1]. Therefore, asphaltenes which are precipitated with the same solvent react relatively uniformly regardless of the origin of the crude oils. The investigated asphaltenes are from vacuum residues of crudes from Venezuela, Arabia, Iran, Russia, and from a British offshore field. Despite the different sources, the arithmetical mean of their C:H ratios $\bar{x}$ is 1.146, with a coefficient of variation V of $\pm 2.85\%$.

The technical literature does not supply any melting point or melting range temperatures because asphaltenes pyrolyze below the estimated melting temperature. Pyrolysis experiments in an inert atmosphere by means of DSC using a heating rate of $10\ \mathrm{K\ min^{-1}}$ have yielded an onset temperature of 403°C ($\pm 1.9\%$) and a peak maximum temperature of 466°C ($\pm 0.55\%$), which are the arithmetical means of sixteen samples [2].

Several papers mention second-order transition ranges or glass transition temperatures in bitumens. Quedeville [3] describes glass transitions in bitumens and in the saturated and aromatic components of their molten phase. However he does not mention the existence of glass transitions in the asphaltenes. A critical inspection of the recorded curves of the bitumen colloids investigated in ref. 2 confirms the absence of glass transitions in the petroleum resins, but give evidence of such reactions in the asphaltenes. The curves recorded with three different heating rates (used for the investigation of pyrolysis kinetics according to ASTM 698-79) reveal inconstancies in the slope of the energy versus temperature plot (Fig. 1). This is similar to the slopes demonstrating glass transitions in amorphous or partially crystalline

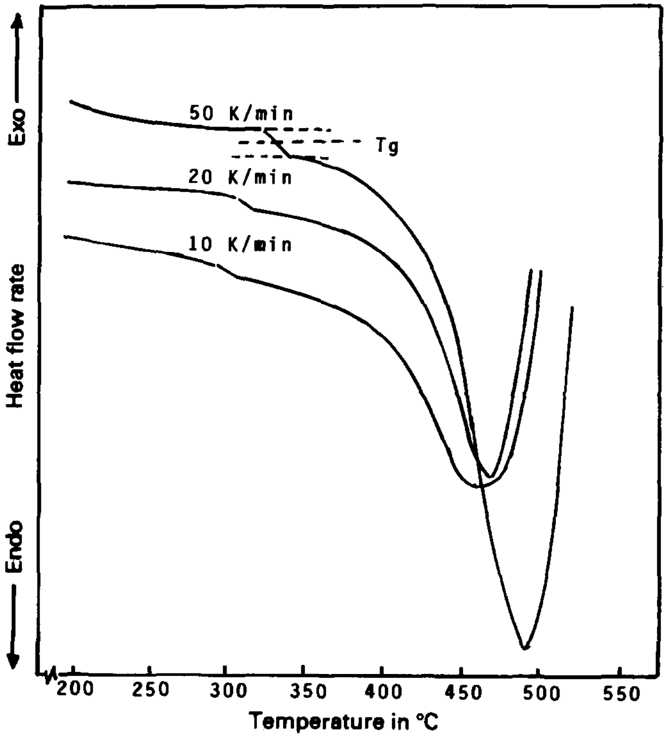

Fig. 1. DSC diagram of the pyrolysis of the asphaltenes from a vacuum residue of Kirkuk crude oil. Parameter: heating rate.

polymers [4]. The temperatures measured for each heating rate differ so little from each other for the different asphaltenes that the statistical evaluation results in means with very small coefficients of variation (Table 1).

Applying ASTM E 698-79, the following kinetic parameters of the Arrhenius equation can be calculated: activation energy, $E = 115\ \mathrm{kJ\ mol^{-1}}$ ($\pm 11.4\%$); pre-exponential factor, $A = 7.466 \times 10^9\ \mathrm{min^{-1}}$ ($\pm 1.39\%$).

The glass transition in polymers is a kinetically controlled reaction, which can be described with the help of an activation energy. The latter has been derived by DTA experiments (Barton [5]) on poly-(5-ethylresorcinol iso-

TABLE 1

Glass transition temperature T_g (°C) of asphaltenes

	Heating rate $\beta/(\mathrm{K\ min^{-1}})$		
	10	20	50
Mean $\bar{x}$	313.8	331.4	353.3
Standard deviation s	5.93	8.99	11.07
Coefficient of variation V	1.89%	2.71%	3.13%

TABLE 2

Arrhenius reaction constant k and half life time $t_{1/2}$ of the glass transition of asphaltenes

Temperature/°C	k/min^{-1}	$t_{1/2}$/min
100	5.169×10^{-7}	1.341×10^{6}
150	4.196×10^{-5}	1.652×10^{4}
200	1.345×10^{-3}	5.153×10^{2}
250	2.222×10^{-2}	3.119×10^{1}
300	2.251×10^{-1}	3.080×10^{0}
350	1.572×10^{0}	4.409×10^{-1}

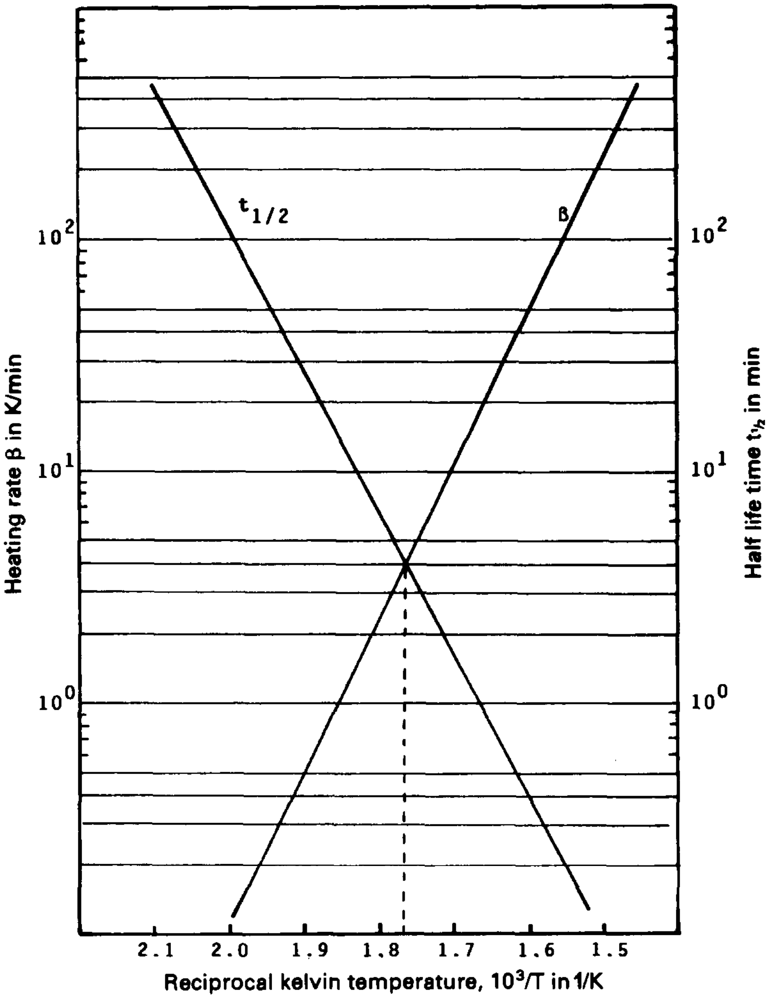

Fig. 2. Heating rate β and half life time $t_{1/2}$ of the glass transition of asphaltenes versus reciprocal Kelvin temperature.

TABLE 3

Values at the point of intersection

Heating rate β	3.95 K min^{-1}
Half life time $t_{1/2}$	3.95 min
$1000/T$	1.7625
T	567.4 K
T_g	294.2°C

phthalate), resulting in an activation energy $E = 310.7$ kJ mol^{-1}. Similar results are described by Roberts and White [6], obtained from relaxation experiments on polystyrene ($T_g = 104$°C, $E = 335$ kJ mol^{-1}) and on polymethylmethacrylate (isotactic: $T_g = 53$°C, $E = 230$ kJ mol^{-1}; syndiotactic: $T_g = 115$–120°C, $E = 335$ kJ mol^{-1}).

The results of the calculation of the Arrhenius reaction constant k and the half life time $t_{1/2}$ for the glass transition of the asphaltenes are given in Table 2. The glass transition is a relaxation process. Therefore, the half life time can be regarded as a sort of relaxation time. Plotting the heating rates and the half life times, both as a function of the reciprocal Kelvin temperature (Fig. 2), results in an intersection of the two lines which represents the temperature at which the heating rate corresponds to the half life time (Table 3).

According to approximations there is a relation between the glass transition temperature T_g and the melting temperature T_m [7]

$$T_g = 0.65 T_m$$

A T_g value equal to 294°C will result in a hypothetical T_m of 452°C, which falls in the pyrolysis range. However, DSC tests performed in air do not reveal any glass transitions. This is because the statistical means of the temperatures of the ‘low temperature oxidation’ ($T_{\text{onset}} = 190$°C and $T_{\text{peak maximum}} = 313$°C) are far below the glass transition temperature.

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