

Kinetic parameters of different asphalt binders by thermal analysis

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Abstract Each year, 100 millions tons of asphalt are manufactured worldwide and 88% of them are designated to act as binder in mineral aggregate producing asphalt mixtures in the paving industry. The present study investigates the kinetics parameters of thermal degradation through thermal analysis behavior of three different asphalt binders' samples: an asphalt cement C and two asphalt binders modified by polymers: copolymer styrene–butadiene–styrene S and polyphosphoric acid L. By Thermokinetics software a model-free kinetic analysis could be made using two models: Friedman and Ozawa–Flynn–Wall. Kinetic parameters following both models, through Thermogravimetric curves, showed that for the first step, the binder L presented the highest activation energy followed by binder S. Between all simulations, the FnF1 model was the one which best correspond to the experimental data for all samples.

Keywords Asphalt binder · Thermal analysis · Kinetic · Thermokinetics software

Introduction

Asphalt can be defined as a non-volatile binder material, obtained product from the bottom of the crude oil vacuum distillation tower, waterproof, or present in reserves in the form of natural asphalt, completely soluble in toluene, and very viscous or nearly solid at room temperature [1]. The term bitumen is often found in place of asphalt. Brazilian specification (EB-78) from Brazilian Institute of Oil and Gas (IBP) and Brazilian Association for Technical Standards (ABNT), refers to cement asphalt petroleum, CAP, as a product obtained to fulfill the quality and consistency to be applied on a pavement and also it should exhibit flexibility, strength, and resistance. To consider an asphalt binder having a satisfactory performance in the pavement, it should present improved behavior properties when compared to other asphaltic materials. A binder should have greater cohesion and adhesion to aggregates, high resistance to aging, thermal susceptibility appropriate to the temperature range use at the pavement, high resistance to fatigue and to thermal deformation.

Certainly improvements in paving roads and highways will have a direct impact on reducing the number of accidents. It is worth mentioning that only 12% of Brazilian roads are paved, as compared to the American highways, they reached 60%. In Brazil, there is a shortage of investment and financial resources for the infrastructure of roads. The use of modifying agents in binders such as polymers, has been researched for almost 40 years by countries possessing high technology, while in Brazil, preliminary tests have been done only on the last decade [2]. The study of physical and chemical properties has increasingly intrigued researchers in the area [3], especially when these binders are modified by polymers such as styrene–butadiene–styrene (SBS), copolymer of ethylene and vinyl acetate (EVA),

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polyethylene (PE), poly (phosphoric acid) (PPA), among others. According to Yildirim [4], a surface-modified polymer exhibits more resistance to thermal subsidence and deformation, reduces fatigue damage and scratching, and also decreases the thermal susceptibility.

While several studies in literature have given focus to the rheological behavior of asphalt binders and their mechanical properties, very few studies involve kinetics of asphalt [5]. Kinetic data are extremely important for performance and understanding the mechanism of a material, through mathematical models and numerical predictions, especially due to the combination of factors such as heat transfer, mass transfer phenomena, chemical reactions, and thermal stability [3, 6, 7]. Knowledge of kinetic parameters as activation energy and pre-exponential factor would help elucidate the reactions' mechanism in solid state, which could be useful to determine the lifetime of a given material, its thermal stability and others [8, 9]. According to Mothé and Azevedo [10], thermal stability is defined as the ability of substance to keep their properties during thermal processing.

Kinetic study of thermal degradation

Isoconversional methods

The basis of the "Model-Free" is the transformation of a signal (heat flow, mass loss) on conversion degree (α) for each stage of decomposition. Thus, it is possible to calculate the activation energies, pre-exponential factor, and other kinetic parameters for different degrees of conversion [11]. The model-free kinetic study consist on the determination of the decomposed fraction (α) as a function of reaction time (t) in cases in which the temperature was kept constant, or in cases that the temperature varied linearly with time. On thermogravimetry, the decomposed fraction (α) is defined according to Eq. 1:

$$\alpha = \frac{m_o - m_t}{m_o - m_f} \quad (1)$$

where m_o represents the initial mass, m the mass at time t , and m_f the final mass [5]. Thus, the method is based on the following equation:

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{RT}\right) dT \quad (2)$$

where α represents the conversion degree, A the pre-exponential factor, β the heating rate, T the absolute temperature, E the activation energy, R the gas universal constant. $G(\alpha)$, in Eq. 2, represents the reaction mechanism. Some approximations were proposed using different

kinetic models to determine the parameters on Eq. 2. Using Thermokinetics software through model-free analysis, a kinetic study could be achieved based on the approximation models Ozawa–Flynn–Wall and Friedman.

Ozawa–Flynn–Wall method

Ozawa–Flynn–Wall method is an isoconversional method used to estimate the activation energy. One of the relevant information of this method is the approach expression to Arrhenius integration equation. Thermogravimetry technique is very useful to do kinetic analysis about thermal decomposition at a defined temperature range. On this way to perform a kinetic study based on a non-isothermal data, isoconversional methods are the most appropriate to provide reliable kinetic parameters, such as activation energy and pre-exponential factor [12, 13].

Since the isoconversional method needs at least three different heating rates, many values for activation energy (E) could be obtained from the $\{\log \beta$ vs. $1000/T\}$ graphic, for each conversional degree α . Considering $\alpha = \phi(\theta)$, the Eq. 3 could be written as

$$\theta = \int_0^t e^{\frac{-E}{RT}} dt \quad (3)$$

Solving Eq. 3 and using the (p) function proposed by Doyle (1962), the OFW method to determinate the activation energy could be attained by the following equations:

$$\frac{\partial \log \beta}{\partial \left(\frac{1}{T}\right)} \cong -\left(\frac{0.457}{R}\right) E \quad (4)$$

$$E \cong -18.2 \left(\frac{\partial \log \beta}{\partial \left(\frac{1}{T}\right)}\right) \quad (5)$$

Friedman method

The isoconversional method of Friedman is based on the model-free kinetic analysis, which could be applied to different heating rates and it can give information about reaction mechanisms that can occur in more than one step. The method is based on the following equation [8]:

$$\ln\left(\frac{d\alpha}{dT}\right) = \ln\left(\beta \frac{d\alpha}{dT}\right) = \ln A + \ln[f(\alpha)] - \frac{E}{RT} \quad (6)$$

Objective

The objective of the present study is to investigate the kinetic parameters of thermal degradation through thermal analysis behavior of three different asphalt binders samples:

one asphalt cement (C) and two asphalt binders modified by polymers, first by copolymer styrene–butadiene–styrene (S) and the second by polyphosphoric acid (L), with a

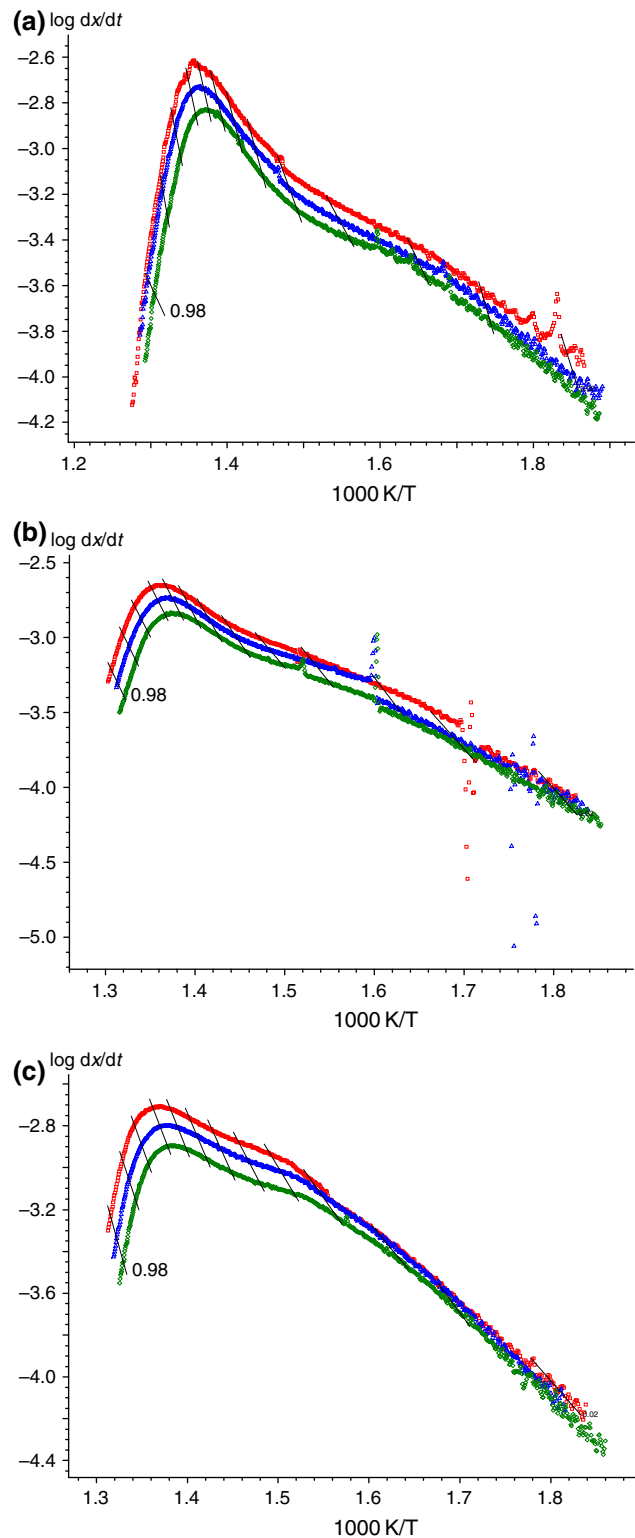


Fig. 1 Friedman analysis for asphalt cement C (a), asphalt binder S (b), and asphalt binder L (c)

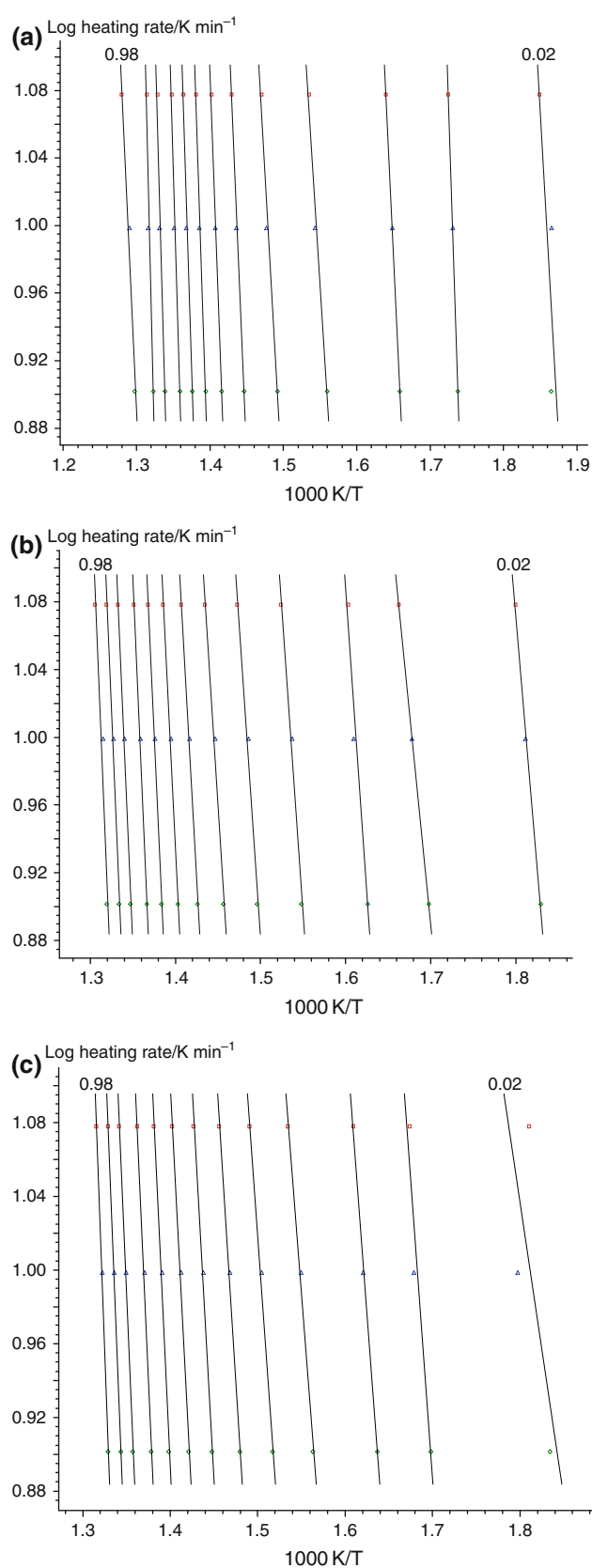


Fig. 2 Isoconversional graphic of Ozawa–Flynn–Wall for sample C (a), sample S (b), and sample L (c)

model-free kinetic analysis using two models, Friedman and Ozawa–Flynn–Wall by a Thermokinetics software.

Experimental

Materials

Three asphalt binders' samples were used: asphalt cement (C), asphalt binder modified by 3% (m/m) copolymer styrene–butadiene–styrene (S), and a binder modified by 1% (m/m) polyphosphoric acid (L).

Methods

Thermal characterization of asphalt binders by thermogravimetry was performed on a TA Instruments model SDT 2960, with heating rate of 8, 10 and 12 °C/min at a nitrogen atmosphere. The determination of all asphalt binders kinetic parameters was performed by the package “Model-Free” with Netzsch Thermokinetics software for kinetic modeling.

Results and discussion

Figure 1 shows Friedman analysis for the three asphalt binders samples studied. In Fig. 1a, it can be observed only one peak, which occurs around 431–473 °C. The presence of a peak by Friedman's analysis shows that the decomposition for sample (C) occurs in only one step. Figure 1b presents the analysis of Friedman for the asphalt binder with 3% elastomer. It reveals only one peak, confirming the decomposition in one step, which occurs around 431–473 °C. The analysis of Friedman for the binder with 1% polyphosphoric acid, is shown in Fig. 1c. The graph shows a peak between 431 and 462 °C, covering the prime decomposition and a shoulder at 385 °C suggesting the decomposition of the additive polyphosphoric acid.

Figure 2 exhibits Ozawa–Flynn–Wall analysis for the three asphalt binder's samples. It was observed that values for each heating rate were located together with isoconversional zone for each asphalt binders (C, S, and L), indicating that the model fits properly the experiment. The values obtained for the OFW analysis initially showed, from left to right, a greater distance between the lines regarding the isoconversional (Fig. 1c).

To overview the results obtained for activation energy and log (*A*) values for the three samples, Table 1 was build up, summarizing all values. The higher values for activation energy was for sample (C), which confirms that this last one is the most stable asphalt for either OFW or Friedman models.

Table 1 Activation energy/*E* and log *A* with different (α) for asphalt binders C, S, L, on Friedman and Ozawa–Flynn–Wall (OFW) analysis

α	C				S				L			
	Friedman		OFW		Friedman		OFW		Friedman		OFW	
	E/kJ/mol	Log A/s ⁻¹	E/kJ/mol	Log A/s ⁻¹	E/kJ/mol	Log A/s ⁻¹	E/kJ/mol	Log A/s ⁻¹	E/kJ/mol	Log A/s ⁻¹	E/kJ/mol	Log A/s ⁻¹
0.1	136	8	165	11	151	9	128	7	99	5	112	6
0.2	117	6	121	6	145	8	128	7	117	6	106	5
0.3	176	10	137	8	134	7	130	7	136	7	117	6
0.4	237	15	184	11	169	10	142	8	160	9	132	7
0.5	251	15	219	13	198	12	161	9	181	11	149	8
0.6	269	17	238	15	218	13	180	11	196	12	165	10
0.7	287	18	252	16	225	13	195	12	208	12	180	11
0.8	300	19	275	17	229	14	206	12	213	13	192	11
0.9	323	20	290	18	221	13	213	13	231	14	204	12

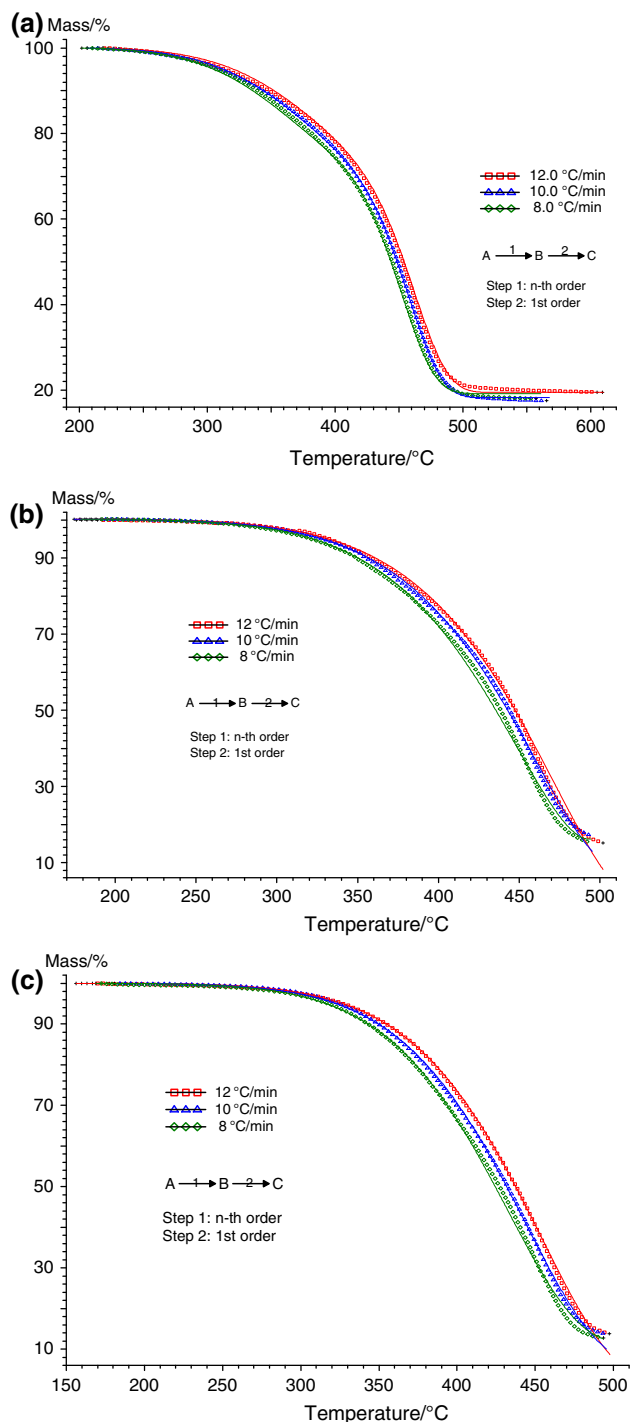


Fig. 3 Simulation of kinetic model for asphalt cement (C) with two steps using model Fn (1st step) and F1 (2nd step), $R = 0.9998$ (a), asphalt binder (S) with two steps using model Fn (1st step) and F1 (2nd step), $R = 0.9993$ (b) and asphalt binder (L) with two steps using model Fn (1st step) and F1 (2nd step), $R = 0.9996$ (c)

As Friedman's analysis showed only one peak, initially it was proposed a model of only one step $A \rightarrow B$, but after some simulations made, it was found that for all samples

Table 2 Kinetic parameters using model FnF1 for binders

Binder	E/kJ/mol		Log A/s^{-1}	
	1st	2nd	1st	2nd
C	66.9259	170.1003	3.0116	9.9615
S	74.735	83.3312	2.8698	-85.068
L	77.415	86.2361	3.1862	-86.2997

studied the most appropriate model should be two steps, $A \rightarrow B \rightarrow C$. Through simulation it was verified that the first step refers to the reaction order- n , and the second step refers to a reaction order-1 as shown in Fig. 3 for all asphalt samples. The values found for the activation energy, E , and pre-exponential factor, $\log A$, for the three samples are shown in Table 2.

Conclusions

In the literature it was not found any kinetic study about modified asphalt binders using Friedman and Ozawa–Flynn–Wall models by Thermokinetics software. Since the kinetic parameters are extremely important for understanding the mechanism and material performance predictions using mathematical and numerical models thus this study has a unique character. According to the evaluation of the statistical F -test of the software, the simulation that best described the experimental data was the model FnF1. The values found for the reaction order of the first step for asphalt binders were 0.79 for binder C, 0.60 for S, and 0.75 for L.

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