

Manuscript Number:

Title: Pyrolysis of petroleum pitches. 1. Non-isothermal kinetics

Article Type: Research Paper

Keywords: Pyrolysis; petroleum pitches; non-isothermal kinetics

Corresponding Author: Professor Yuda Yurum, Ph.D.

Corresponding Author's Institution: Sabanci University

First Author: Firuze Okyay, M.Sc

Order of Authors: Firuze Okyay, M.Sc; Yuda Yurum, Ph.D.

Abstract: The chemical composition and reactivity of petroleum pitches under non-isothermal thermogravimetric conditions were studied. Thermogravimetry (TG) was used to study pyrolysis of petroleum pitches. Non-isothermal thermogravimetric data were used to evaluate the kinetics of the pyrolysis of this carbonaceous material. The paper reports application of Ozawa-Flynn-Wall model to deal with non-isothermal TG data for the evaluation of the activation energy corresponding to the pyrolysis of two different petroleum pitches. Non-isothermal kinetic studies of pyrolysis of the pitches based on the TGA measurements at different heating rates resulted that the average activation energy of the pyrolysis of pitch B (213.2 kJ/mol) was higher than that of the average activation energy of pitch A (185.7 kJ/mol). The reaction orders of pitch A and pitch B were calculated to be 1.6 and 0.9, respectively. These calculated reaction orders were considered to be as second-order and first-order kinetics.

Suggested Reviewers: M Granda Ph.D.

Instituto Nacional del Carbon, CSIC, C/Francisco Pintado Fe, 26, Apartado 73, 3

mgranda@incar.csic.es

Expert in pyrolysis of pitches

Q Xu Ph.D.

School of Mechanical Engineering, Nanjing University of Science and Technology, China

j0805481@public1.ptt.js.cn

Expert of pyrolysis of biomass

N Tancredi Ph.D.

Facultad de Química, DETEMA, Cátedra de Fisicoquímica y Laboratorio de Físico, Universidad de la República, General Flores 2124, PO Box 11800, CC 1157 Montevideo, Uruguay

nestor@fq.edu.uy

Expert in thermal analysis

November 1, 2012

Professor D. Fabbri
Editor,
Journal of Analytical and Applied Pyrolysis
Lab. of Chemistry - C.I.R.S.A.
Università di Bologna, Via S. Alberto 163,
48100 Ravenna, Italy

Dear Professor Fabbri,

In the attachment please find the manuscript entitled “Pyrolysis of petroleum pitches. 1. Non-isothermal kinetics” by Firuze Okyay and Yuda Yurum, submitted for publication in the Journal of Analytical and Applied Pyrolysis.

We confirm that the manuscript has not been published elsewhere and it has not been submitted simultaneously for publication elsewhere.

I hope you will accept it for publication in Journal of Analytical and Applied Pyrolysis.

Sincerely,



Yuda Yürüm

Pyrolysis of petroleum pitches. 1. Non-isothermal kinetics

Firuze Okyay and Yuda Yürüm*

Faculty of Engineering and Natural Sciences, Sabanci University

Orhanli, Tuzla, Istanbul 34956, Turkey

*Corresponding Author:

Yuda Yürüm

Faculty of Engineering and Natural Sciences, Sabanci University

Orhanli, Tuzla, Istanbul 34956, Turkey

yyurum@sabanciuniv.edu

Pyrolysis of petroleum pitches. 1. Non-isothermal kinetics

Firuze Okyay and Yuda Yürüm*

Faculty of Engineering and Natural Sciences, Sabanci University, Istanbul 34956, Turkey

Abstract

The chemical composition and reactivity of petroleum pitches under non-isothermal thermogravimetric conditions were studied. Thermogravimetry (TG) was used to study pyrolysis of petroleum pitches. Non-isothermal thermogravimetric data were used to evaluate the kinetics of the pyrolysis of this carbonaceous material. The paper reports application of Ozawa–Flynn–Wall model to deal with non-isothermal TG data for the evaluation of the activation energy corresponding to the pyrolysis of two different petroleum pitches. Non-isothermal kinetic studies of pyrolysis of the pitches based on the TGA measurements at different heating rates resulted that the average activation energy of the pyrolysis of pitch B (213.2 kJ/mol) was higher than that of the average activation energy of pitch A (185.7 kJ/mol). The reaction orders of pitch A and pitch B were calculated to be 1.6 and 0.9, respectively. These calculated reaction orders were considered to be as second-order and first-order kinetics.

Keywords: Pyrolysis; petroleum pitches; non-isothermal kinetics

1. Introduction

Due to the less toxic and carcinogenic behavior of petroleum pitch during pyrolysis processes, it is becoming a popular alternative for market exclusively dominated by coal-tar pitches [1-3]. In addition to its less toxic and carcinogenic properties, petroleum pitches have less metal, ash and heteroatom, especially sulfur, content [3-5], they are capable to produce highly oriented graphitic carbon materials and high-density carbon precursors [1, 6], and its raw material production's accessibility and standardization is warrant in medium to long term [3]. Petroleum and coal-tar pitches turned from worthless wastes into important raw materials of aromatic and carbonaceous materials production. Manufacturing of graphite electrodes (for aluminum and steel industry), PAHs (for lithium ion batteries and hydrogen storage), carbon fibers, carbon-carbon composites, nuclear graphites, activated carbons, mesophase carbon fibers, and mesocarbon microbeds can be approached by pyrolysis and carbonization processes of pitches [2,7]. Formation of graphitic carbons and cokes can be achieved in high yields during pitch pyrolysis reactions [8]. It is very difficult to explain mechanism of pitch pyrolysis and carbonization, because of the complex chemical structure of it. There are thousands of different types of molecules with various molecular sizes and functions in pitch structure. For this reason, there is a potential for each different molecule to react distinctively.

Carbonaceous materials such as graphite, graphene, hydrographene, coke, pitch, and coal have characteristic structures which vary from high amorphous to perfect graphitic structure. Thermal treatment of the carbonaceous materials and types of the precursors are the main factors that orderliness of their structure depends on [9]. Coal, biomass, and pitches are the main feedstock of pyrolysis process in order to generate useful materials such as chemicals and substitutes of petroleum [10]. As a result, it is very essential to study the pyrolysis mechanism of at least one of these materials. Among these materials, petroleum pitches were chosen due to their less toxic and carcinogenic properties with respect to coal-tar pitches, and due their less complex structure. Two different types of petroleum pitches were pyrolyzed under different temperatures and times, in order to investigate the effect of temperature, time, and precursor on the formation of carbonaceous structures. Thermal analysis methods have been extensively used in recent years, because they offer a quick quantitative technique for the assessment of pyrolysis or combustion processes under non-isothermal conditions and allow guessing the effective kinetic parameters for the various decomposition reactions [11-21].

The reaction kinetics parameters of pitch pyrolysis under inert N₂ atmosphere at different heat rates can be calculated according to the method given in Sanchez et al. [22], Dumanli, Tas and Yürüm [23] and Tas and Yürüm [24]. The rate of heterogeneous solid-state reactions can generally be explained as,

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where $f(\alpha)$ is a function that describes the reaction model, t is time, and $k(T)$ is the temperature-dependent constant. The function $f(\alpha)$, states the dependence of the reaction rate, β , on the extent of reaction. Arrhenius equation describes the relation between rate constant and the temperature. As a result, the rate of a solid-state reaction can generally be explained as,

$$\frac{d\alpha}{dt} = Ae^{-\frac{E}{RT}}f(\alpha) \quad (2)$$

In this equation, A is the pre-exponential Arrhenius factor, E is the activation energy and R is the gas constant. To convert Eq. (2) to the non-isothermal rate expressions, constant heating rate as expressed below can be inserted into Eq. (2).

$$\beta = \frac{dT}{dt} = \text{constant} \quad (3)$$

This placement will result in equation below with non-isothermal rate expressions, which describes reaction rates as a function of temperature at a constant β .

$$\frac{d\alpha}{dT} = \frac{1}{\beta} A e^{-\frac{E}{RT}} f(\alpha) \quad (4)$$

By integrating Eq. (4) up to conversion, α , it becomes,

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{A}{\beta} \int_{T_0}^T e^{-\frac{E}{RT}} dT \quad (5)$$

Vyazovkin [25], Khawam and Flanagan [26], and Dumanli, Tas and Yürüm [23] revealed that isoconversional methods need a series of experiments at different heating rates, β . According to the isoconversional methods applied by Ozawa [27,28], Flynn and Wall [29] using the Doyle's approximation of $p(x)$, which involves measuring the temperatures corresponding to fixed values of α from experiments at different heating rates [30], the activation energies from dynamic data can be estimated. In order to make this estimation of activation energy, the following equation is required,

$$\ln(\beta) = \ln \left[\frac{AE}{Rg(\alpha)} \right] - 5.331 - 1.052 \frac{E}{RT} \quad (6)$$

From this equation, the activation energy E may be estimated by plotting $\ln(\beta)$ versus $1/T$.

The reaction orders of pitch pyrolysis reactions can be figured out by applying Avrami's theory for non-isothermal case description [31-33]. In the theory of Avrami, degree of conversion (α) changes with respect to heating rate (β) and temperature. This theory can be illustrated by the following equation,

$$\alpha(T) = 1 - \exp\left[-\frac{k(T)}{\beta^n}\right] \quad (7)$$

Taking the double natural logarithm of both sides of Eq. (7), with $k(T) = Ae^{-E/RT}$, gives

$$\ln[-\ln(1 - \alpha(T))] = \ln A - \frac{E}{RT} - n \ln \beta \quad (8)$$

From this equation, reaction orders, n , of the pyrolysis reactions can be estimated by plotting $\ln[-\ln(1 - \alpha(T))]$ versus $\ln \beta$, which were obtained at the same temperature from a number of isotherms taken at different heating rates. The plot of $\ln[-\ln(1 - \alpha(T))]$ versus $\ln \beta$ should give in straight lines whose slope will have the value of the reaction order or the Flynn–Wall–Ozawa exponent n [27,34]. Extra aspects of the technique applied to examine the process are explained by Ozawa [28].

In the present work, the chemical composition and reactivity of two petroleum pitches in pyrolysis reactions under non-isothermal thermogravimetric conditions were studied. Thermogravimetric (TG) analysis was used to study pyrolysis of petroleum pitches. Non-isothermal thermogravimetric data were used to evaluate the kinetics of the combustion of this carbonaceous material. The paper reports application of Ozawa–Flynn–Wall model to deal with non-isothermal TG data for the evaluation of the activation energy corresponding to the pyrolysis of two different petroleum pitches.

2. Experimental

2.1. Materials and Characterization

The main raw materials of this study were two petroleum pitches. One of them was obtained from Turkish Petroleum Refineries Co. (TÜPRAŞ), Batman Refinery and it was named as pitch A. The other petroleum pitch was obtained from TUBITAK Marmara Research Center, Gebze and it was named as pitch B. Both petroleum pitches were used as they received. Elemental analyses (C, H, N, and S) of pitch A and pitch B were conducted at the Instrumental Analysis Laboratory of the TUBITAK Marmara Research Center, Gebze by

using a standard C-H-N-S analyzer. Data of the elemental analyses of the pitch samples are presented in Table 1.

2.2. Non-isothermal kinetics of pitch pyrolysis

Non-isothermal kinetics of pitch pyrolysis experiments were performed in a Netzsch STA 449 C Jupiter differential thermogravimetric analyzer (precision of temperature measurement $\pm 2^{\circ}\text{C}$, microbalance sensitivity $< 5\ \mu\text{g}$), with which the sample weight loss and rate of weight loss as functions of time or temperature were recorded continuously, under dynamic conditions, in the range $25\text{--}1000^{\circ}\text{C}$. The experiments were carried out at atmospheric pressure, under inert (N_2) atmosphere, with a flow rate of $60\ \text{ml/min}$, at a linear heating rate of 10°C/min . Pyrolysis of the pitches was performed in the furnace of the thermobalance under controlled temperature to obtain the corresponding thermogravimetric (TG) curves with heating rates (β) of 5°C/min , 10°C/min , 20°C/min and 30°C/min . It was found appropriate to use sample amounts around $20\ \text{mg}$ of each pitch to reduce the heat and mass transfer limitations. The experiments were replicated at least twice to determine their reproducibility, which was found to be very acceptable.

3. Results and Discussion

3.1. Elemental Analysis

Due to complex structure of pitches, each pitch may show different properties. Both pitch types were complex mixtures of organic molecules consisting of polycyclic aromatic hydrocarbons (PAH) including numerous alkyl-substituted PAHs [8]. Petroleum pitches differ among themselves due to their production method and feedstock. The elemental analyses of the pitches demonstrated that the carbon percentages of the pitch A and pitch B were 82.85 and 85.40, respectively. Hydrogen content of the pitch B was slightly higher than that of pitch A, 10.26 and 9.72, respectively. The H/C atomic ratios of the pitch A and pitch B were 1.40 and 1.44, respectively. This indicated that the pitches were petroleum derivatives. The significant difference between the two pitches was in their sulfur contents. While pitch A contained 6.44% sulfur, the sulfur content of pitch B was 4.03%. This difference in sulfur content points out to the variation of the origin of the pitches.

3.2. TG Experiments

DTG curves of the pyrolysis of the pitch A and pitch B between 25°C and 1000°C at a heating rate of 30°C/min are presented in Fig. 1. Both pitches exhibited similar trends of mass loss in the pyrolysis reactions. While pitch A continued to produce volatiles approximately up to 625°C, in pitch B the production of volatiles stopped at about 550°C. It seemed that pyrolysis reactions continued even at higher temperatures in the case of pitch A.

Non-isothermal kinetic studies of pyrolysis of the pitches were based on the thermogravimetric measurements. The TG curves measured from the temperature programmed pyrolysis of the pitch A and pitch B at the heating rates (β) of 5 °C/min, 10 °C/min, 20 °C/min and 30 °C/min are illustrated in Fig. 2 and Fig. 3, respectively. As it might be examined, on raising the temperature, both pyrolysis of pitch A and pitch B occurred with a related mass loss. Once the volatile content of the pitches were consumed, the mass corresponding to the formed carbon structures remained almost constant. Given the small sample amounts and relatively slow heating rates, the weight loss versus temperature curves showed one main zone, as in the examples for pyrolysis of two biomass fuels (wood chips and pine seed shells) [35] and pitch pyrolysis [10] under inert atmosphere. This main zone of weight loss, temperatures below 500°C and conversion up to 75%, was the pyrolysis (or devolatilization) stage. The sequel zone after the main pyrolysis zone showed very low conversion value indicating that the exclusion of volatile matters occurred in the first zone.

Fig. 2 and Fig. 3 respectively showed the TG mass loss curves of the pyrolysis of the pitches A and B at various heating rates (β) (5, 10, 20 and 30 °C/min) in order to study the effect of heating rate on non-isothermal kinetics. Fig. 2 and Fig. 3 indicated the temperature ranges in which the main mass losses occurred at different heating rates during the pyrolysis of pitches A and B, respectively. For pitch A, 72.3-73.4% of the amount of pitch was lost in the temperature range of 479-515°C. For pitch B, in the temperature range of 489-533°C, 74.6-77.2% of the amount of the pitch was lost. Residual masses obtained after pyrolysis of pitch A at 1098°C and 1099°C changed between 18.3% and 20.0%, respectively. While residual masses after pyrolysis of pitch B at 1097°C and 1099°C were found to be 15.8% and 21.7%, respectively. At the end of the pyrolysis experiments, the total material loss of pitch A and pitch B were in the range of 80.0-81.8% and 78.3-84.2%, respectively. Higher heating rates caused less material loss compared to the loss of material at lower heating rates in both pyrolysis of pitches. Since small masses of pitches (20-25 mg) were utilized in each

experiment, mass and heat transfer limitations were eliminated. The data obtained using different heating rates during pyrolysis experiments therefore did not contain any restrictive resistances. As the heating rate was increased, the maximum mass loss shifted to higher temperatures. This was attributed to the changes in the rate of heat transfer with the increase in the heating rate and the short exposure time to a particular temperature at high heating rates, as well as the effect of the kinetics of pyrolysis.

Seven different percentages of conversion (α) were pointed out in each curve of pitch A pyrolysis mechanisms; 10, 20, 30, 40, 50, 70, and 80%, whereas, six different percentages of conversion (α) are pointed out in each curve of pitch B pyrolysis mechanisms; 10, 20, 30, 40, 50, and 70%. By plotting $\ln(\beta)$ versus $1/T$, activation energy, E , was estimated. Fig. 4 illustrated the kinetic model proposed by Ozawa–Flynn–Wall to various conversion percentages corresponding to the pyrolysis of pitch A and pitch B at different heating rates for the calculation of activation energies.

After the plotting of these graphs, it was clear that there were linear relations for the conversion percentages. So the activation energies of both pitches were calculated from the corresponding slopes according to the Ozawa–Flynn–Wall kinetic method. The results for the estimations of activation energies of pyrolysis of pitch A and pitch B are illustrated in Table 2 and 3, respectively.

Raising the temperature, pyrolysis of the pitch A occurred with mass losses and related decrease in activation energies at the second zone. Activation energy calculated at 10% conversion was 87.9 kJ/mol and steadily increased until 70% conversion to a value of 262.7 kJ/mol then as the material loss increased beyond this point, the activation energy again decreased to 83.9 kJ/mol at conversion of 80%. It seemed that the first phase of reactions constituted the rate determining set of reactions with average activation energy of 185.7 kJ/mol. The overall average activation energy of the pyrolysis of the pitch A was calculated to be 173 kJ/mol. This value calculated for pitch A was higher than the activation energy of pyrolysis of pitch (produced from bitumen) by Yue and Watkinson [10].

For pyrolysis of pitch B there was only one reaction zone that was available to be calculated for estimation of activation energy. Due to the raising the temperature, pyrolysis of the pitch A occurred with mass losses in the reaction zone with a continuous increase in activation energies, and then a slight decrease in the last conversion step. Activation energy calculated at 10% conversion was 189.4 kJ/mol and steadily increased until 60% conversion to a value of 222.5 kJ/mol. Then due to the material loss, at conversion of 70% activation energy slightly decreased to 206.4 kJ/mol. The overall average activation energy of the

pyrolysis of the pitch B was calculated to be 213.2 kJ/mol. According to these values, overall average activation energy of pitch B was higher than both the overall and the average rate determining activation energy of pitch A. In order to make a more accurate comparison, only the activation energies of both pyrolysis up to a conversion 70% was compared. The activation energy of pitch B, 213.2 kJ/mol, was higher than activation energy of A, 185.7 kJ/mol. These results indicated that pitch B contained probably structures that were harder to pyrolyze relative to those present in pitch A. So that pitch B was harder to pyrolyze whereas pitch A had probably more degradable compounds in its structure. Activation energies of both pitches A and B were higher than the activation energy measured by Yue and Watkinson [10] in pyrolysis of a pitch produced from a bitumen.

The next step was figuring out the reaction orders of pitch pyrolysis reactions. For this purpose, Avrami's theory for non-isothermal case description was applied [30-32]. The plots of $\ln [-\ln (1 - \alpha (T))]$ versus $\ln \beta$ is represented in Fig. 5 and Fig. 6 for the computation of the reaction orders of pitch A and B, respectively.

The n values as a function of temperature for pyrolysis of pitch A and B are represented in Table 4. The reaction orders of pitch A and pitch B were calculated to be 1.6 and 0.9, respectively. These calculated reaction orders were considered to be as second-order and first-order kinetics. Variation of the reaction orders was probably due to the dissimilarities in the complex structure of pitches which acted differently during the pyrolysis reactions.

4. Conclusion

Non-isothermal kinetic studies of pyrolysis of the pitches were based on the thermogravimetric measurements at different heating rates (β) of 5 °C/min, 10 °C/min, 20 °C/min and 30 °C/min. The main zones of the weight loss versus temperature curves of both pitch A and pitch B indicated the devolatilization reactions taking place during pyrolysis process. Pyrolysis of pitch A showed, depending on the heating rate at about 479-515°C, 72-73% of the volatiles were lost. On the other hand, pyrolysis of pitch B showed, depending on the heating rate at about 489-533°C, 75-77% of the volatiles were lost. So, mass loss of the pitch B was higher than the mass loss of pitch A. The calculated activation energies of pyrolysis of pitch A and pitch B were compared up to conversion of 70% due to the absence of fast reactions in pyrolysis of pitch B. The average activation energy of pitch B, 213.2 kJ/mol, was higher than the average activation energy of A, 185.7 kJ/mol. These results

indicated that pitch B was harder to pyrolyze whereas pitch A had probably more degradable compounds in its structure. The reaction orders of pitch A and pitch B were calculated to be 1.6 and 0.9, respectively. These calculated reaction orders were considered to be as second-order and first-order kinetics. Variation of the reaction orders was probably due to the dissimilarities in the complex structure of pitches which acted differently during the pyrolysis reactions.

References

- [1] M. Pérez, M. Granda, R. García, R. Santamaría, E. Romero, R. Menéndez, Pyrolysis behaviour of petroleum pitches prepared at different conditions, *Journal of Analytical and Applied Pyrolysis* 63 (2002) 223-239.
- [2] V. Slovák, P. Susák, Pitch pyrolysis kinetics from single TG curve, *Journal of Analytical and Applied Pyrolysis* 72 (2004) 249-252.
- [3] V. G. Rocha, Pyrolysis behaviour of pitches modified with different additives, *Journal of Analytical and Applied Pyrolysis* 73 (2005) 276-283.
- [4] M. Pérez, M. Granda, R. García, R. Santamaría, T. Morgan, R. Menéndez, A thermoanalytical study of the co-pyrolysis of coal-tar pitch and petroleum pitch, *Fuel* 83 (2004) 1257-1265.
- [5] B. Sakintuna, Y. Yürüm, S. Çetinkaya, Evolution of carbon microstructures during the pyrolysis of Turkish Elbistan lignite in the temperature range 700-1000°C, *Energy and Fuels* 18 (2004) 883-888.
- [6] M. Martinez-Escandell, P. Carreira, M. A. Rodriguez-Valero M A, F. Rodriguez-Reinoso, Self-sintering of carbon mesophase powders: effect of extraction/washing with solvents, *Carbon* 37 (1999) 1662.
- [7] H. Marsh, M. Martinez-Escandell, F. Rodriguez-Reinoso, Semicokes from pitch pyrolysis: mechanisms and kinetics, *Carbon* 37 (1999) 363-390.
- [8] H. Marsh, E. Heintz, F. Rodriguez-Reinoso, *Introduction to carbon technologies*. Universidad de Alicante, Alicante, Spain, 1997.
- [9] D. Erçin, Y. Yürüm, Carbonization of Fir (*Abies bornmulleriana*) wood in an open pyrolysis system at 50-300°C, *Journal of Analytical and Applied Pyrolysis*, 67 (2003) 11-22.
- [10] C. Yue, A. P. Watkinson, Pyrolysis of pitch, *Fuel* 77 (1998) 695-711.
- [11] G. Várhegyi, P. Szabó, E. Jakab, F. Till, Mathematical modeling of char reactivity in Ar-O₂ and CO₂-O₂ mixtures, *Energy Fuels* 10 (1996) 1208-1214.
- [12] K. Ceylan, H. Karaca, Y. Önal, Thermogravimetric analysis of pretreated Turkish lignites, *Fuel* 78 (1999) 1109-1116.
- [13] J. Adánez, L.F. De Diego, F. García-Labiano, A. Abad, J. C. Abanades, Determination of biomass char combustion reactivities for fbc applications by a combined method, *Ind. Eng. Chem. Res.* 40 (2001) 4317-4323.
- [14] M. Otero, C. Díez, L. F. Calvo, A. I. García, A. Mordu, Analysis of the co-combustion of sewage sludge and coal by TG-MS, *Biomass Bioenergy* 22 (2002) 319-329.

- [15] L. Quanrum, H. Haoquan, Z. Qiang, Z. Shengwei, C. Gouohua, Effect of inorganic matter on reactivity and kinetics of coal pyrolysis, *Fuel* 83 (2004) 713-718.
- [16] A. Mianowski, R. Bigda, V. Zymła, Study on kinetics of combustion of brick-shaped carbonaceous materials, *Journal of Thermal Analysis and Calorimetry* 84 (2006) 563–574.
- [17] E. Franceschi, I. Cascone, D. Nole, Thermal, XRD and spectrophotometric study on artificially degraded woods, *Journal of Thermal Analysis and Calorimetry* 91 (2008) 119–125.
- [18] Q. Xu, G. J. Griffin, Y. Jiang, C. Preston, A. D. Bicknell, G. P. Bradbury, N. White, Study of burning behavior of small scale wood crib with cone calorimeter, *Journal of Thermal Analysis and Calorimetry* 91 (2008) 787–790.
- [19] L. J. Yu, S. Wang, X. M. Jiang, N. Wang, C. Q. Zhang, Thermal analysis studies on combustion characteristics of seaweed, *Journal of Thermal Analysis and Calorimetry* 93 (2008) 611–617.
- [20] M. Otero, X. Gómez, A. I. García, A. Morán, Non-isothermal thermogravimetric analysis of the combustion of two different carbonaceous materials coal and sewage sludge, *Journal of Thermal Analysis and Calorimetry* 93 (2008) 619–626.
- [21] A. C. Suarez, N. Tancredi, P. Cesar, C. Pinheiro, M. I. Yoshida, Thermal analysis of the combustion of charcoals from *Eucalyptus dunnii* obtained at different pyrolysis temperatures, *Journal of Thermal Analysis and Calorimetry* 100 (2010) 1051–1054.
- [22] M. E. Sanchez, M. Otero, X. Gomez, A. Moran, Thermogravimetric kinetic analysis of the combustion of biowastes, *Renewable Energy* 34 (2009) 1622-1627.
- [23] A. G. Dumanli, S. Tas, Y. Yürüm, Co-firing of biomass with coals Part 1. Thermogravimetric kinetic analysis of combustion of fir (*abies bornmulleriana*) wood, *Journal of Thermal Analysis and Calorimetry* 103 (2011) 925-933.
- [24] S. Tas, Y. Yürüm, Co-firing of biomass with coals. Part 2. Thermogravimetric kinetic analysis of co-combustion of fir (*abies bornmulleriana*) wood with Beypazari lignite, *Journal of Thermal Analysis and Calorimetry* 107 (2012) 293-298.
- [25] S. Vyazovkin, Evaluation of activation energy of thermally stimulated solid-state reactions under arbitrary variation of temperature, *Journal of Computational Chemistry* 18 (1997) 393–402.
- [26] A. Khawam, D. R. Flanagan, Role of iso-conversional methods in varying activation energies of solid-state kinetics: II. Nonisothermal kinetic studies, *Thermochimica Acta* 436 (2005) 101–112.
- [27] T. Ozawa, A new method of analyzing thermogravimetric data, *Bull. Chem. Soc. Japan* 38 (1965) 1881–1886.

- [28] T. Ozawa, Kinetic analysis of derivative curves in thermal analysis, *Journal of Thermal Analysis* 2 (1970) 301–324.
- [29] J. H. Flynn, L. A. Wall, Structures and thermal analysis of 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol, *Polymer Letters* 4 (1966) 323–328.
- [30] C. D. Doyle, Estimating isothermal life from thermogravimetric data, *Journal of Applied Polymer Science* 6 (1962) 639–642.
- [31] M. J. Avrami, Kinetics of phase change. I. General theory, *Chemical Physics* 7 (1939) 1103-1112.
- [32] M. J. Avrami, Kinetics of phase change. II. Transformation-time relations for random distribution of nuclei, *Chemical. Physics* 8 (1940) 212-224.
- [33] M. J. Avrami, Kinetics of phase change. III. Granulation, phase change, and microstructure, *Chemical Physics* 9 (1941) 177-184.
- [34] J. H. Flynn, L. A. Wall, A general treatment of the thermogravimetry of polymers, *Journal of Research of the National Bureau of Standards* 70A (1966) 487–523.
- [35] O. Senneca, Combustion and gasification of three biomass fuels, *Fuel Processing Technology* 88 (2007) 87-97.

Table 1

Elemental analysis data for pitch A and pitch B (wt. %)

	%N	%C	%H	%S	H/C
Pitch A	0.7	82.9	9.7	6.5	1.40
Pitch B	0.6	85.2	10.2	4.0	1.44

Table 2Slopes and correlation coefficients (R^2) corresponding to linear fittings to kinetic model proposed by Ozawa–Flynn–Wall to various conversion percentages corresponding to the

pyrolysis of pitch A at different heating rates together with the resultant activation energy (E) values.

Conversion, %	R²	Slope	Activation Energy, kJ/mol	Average Activation Energy, kJ/mol
10	0.841	-11.12	87.9	
20	0.854	-17.85	141.1	
30	0.915	-21.36	168.9	
40	0.955	-25.09	198.3	Rate determining reactions 185.7
50	0.973	-27.38	216.4	
60	0.982	-28.46	224.9	
70	0.998	-33,24	262.7	
80	0.773	-10,61	83.9	Fast reactions 83.9
Overall Average Activation Energy, 173 kJ/mol				

Table 3

Slopes and correlation coefficients (R^2) corresponding to linear fittings to kinetic model proposed by Ozawa–Flynn–Wall to various conversion percentages corresponding to the pyrolysis of pitch B at different heating rates together with the resultant activation energy (E) values.

Conversion, %	R²	Slope	Activation Energy, kJ/mol
10	0.994	-23.96	189.4
20	0.992	-26.61	210.3
30	0.991	-27.64	218.4
40	0.991	-28.07	221.8
50	0.991	-28.30	223.7
60	0.991	-28.15	222.5
70	0.991	-26.12	206.4
Overall Average Activation Energy, 213.2 kJ/mol			

Table 4
Reaction orders (n) of the pitch pyrolysis reactions

	T, K	R²	Calculated Reaction Order, n	Apparent Reaction Order, n
Pitch A	723	0.949	1.6	2
Pitch B	723	0.998	0.9	1

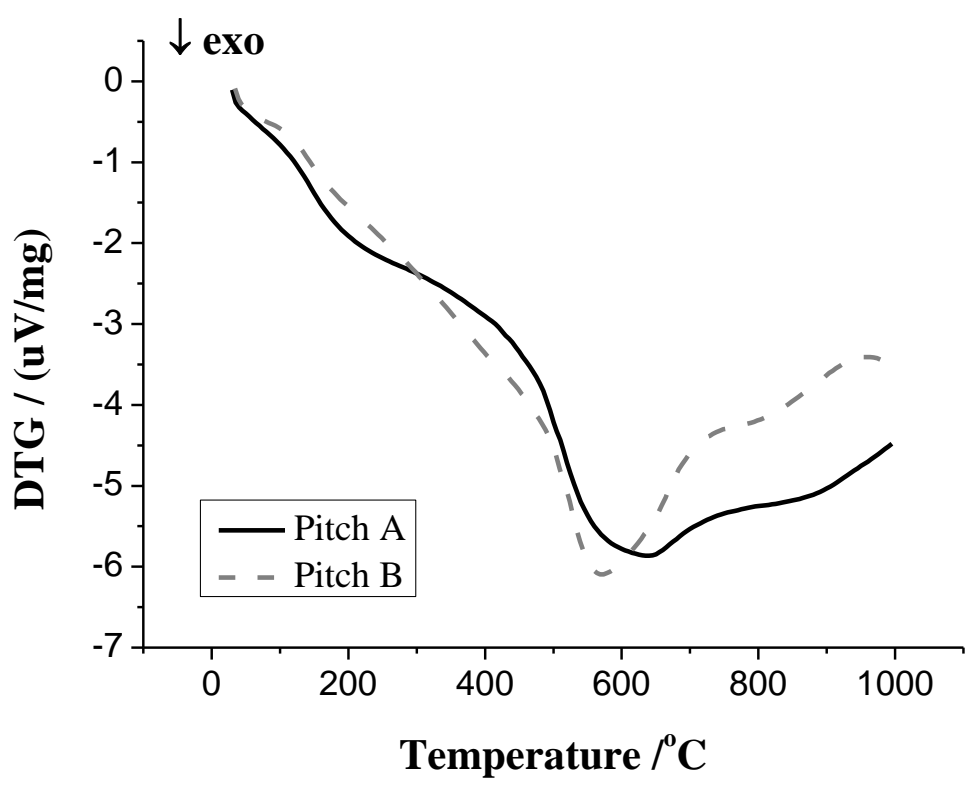


Fig. 1. DTG tracings obtained during the pyrolysis of pitch A and pitch B at heating rates of 30°C/min.

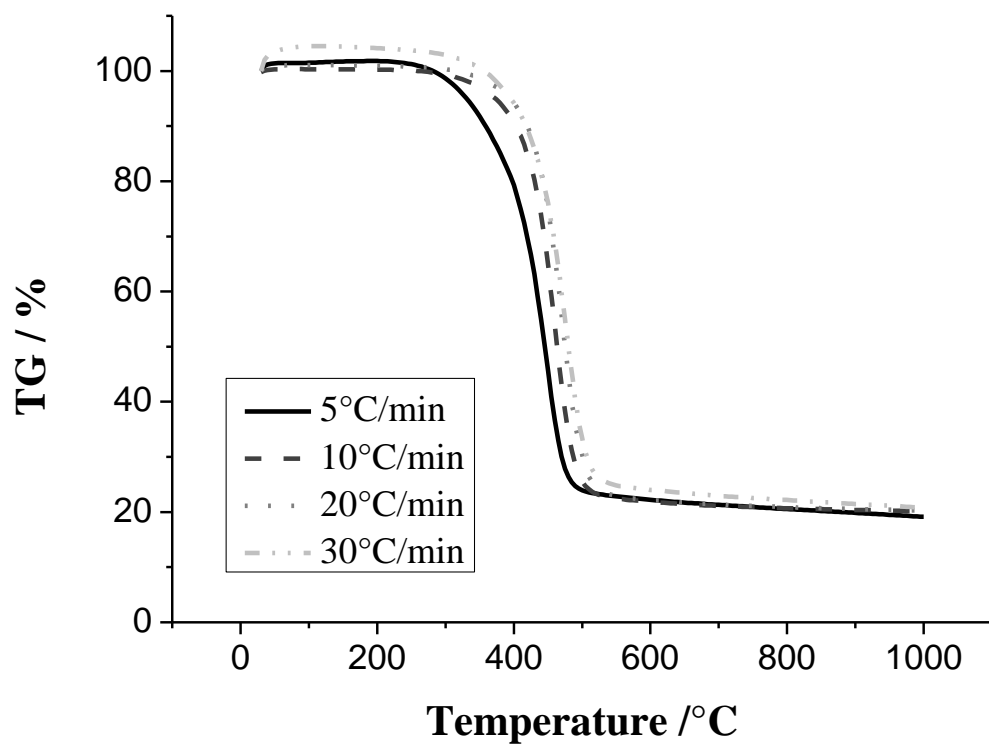


Fig. 2. TGA tracings obtained during the pyrolysis of pitch A with different heating rates in the temperature range of 25-1000°C.

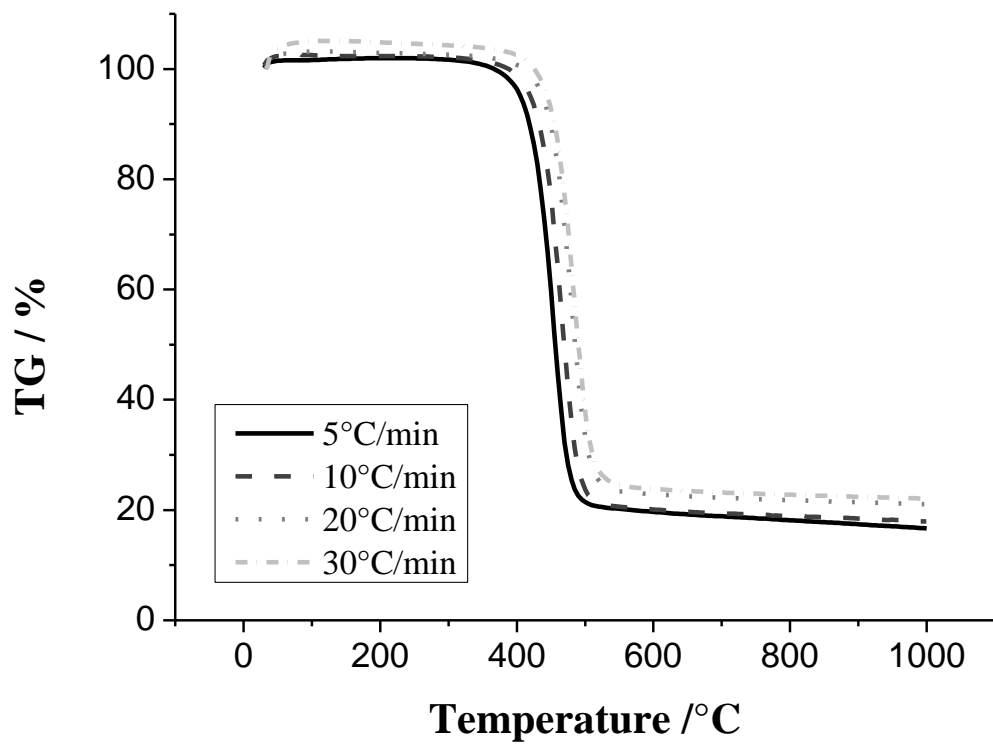


Fig. 3. TGA tracings obtained during the pyrolysis of pitch B with different heating rates in the temperature range of 25-1000°C.

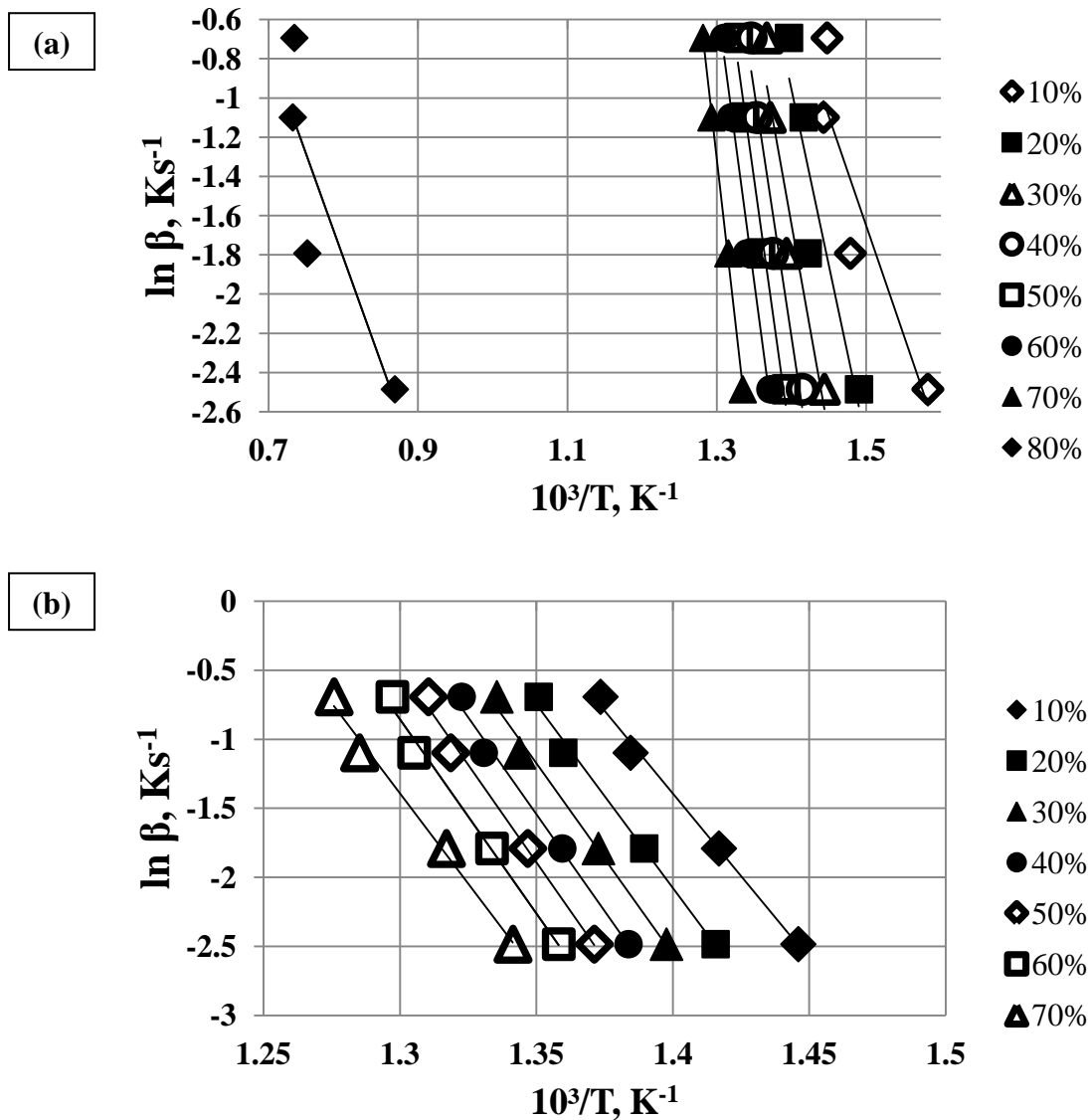


Fig. 4. Curves of fitting to kinetic model proposed by Ozawa–Flynn–Wall to various conversion percentages corresponding to the pyrolysis of (a) pitch A and (b) pitch B at different heating rates for the calculation of activation energies.

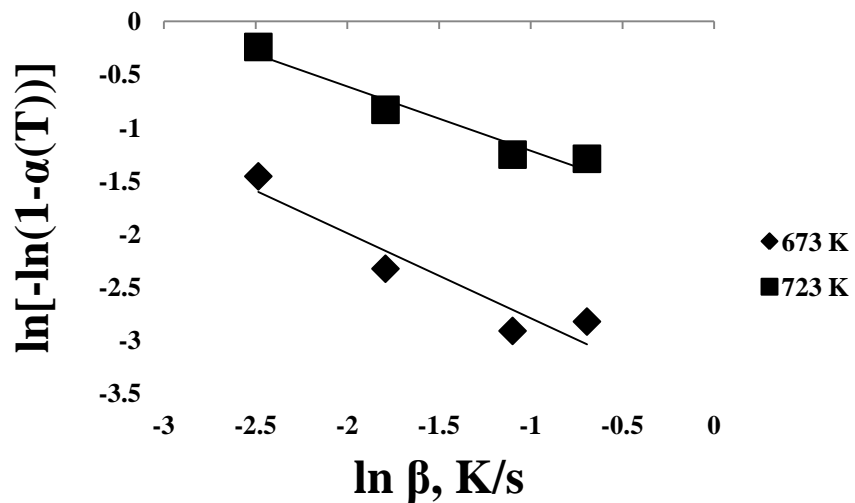


Fig. 5. Straight lines fitting to Ozawa–Flynn–Wall kinetic model for various conversion percentages corresponding to the pyrolysis of pitch A at different heating rates for the determination of reaction order n .

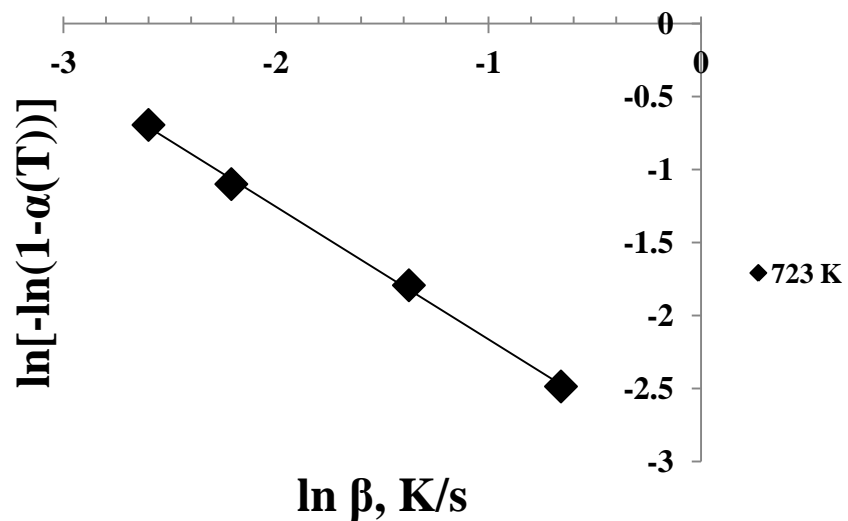


Fig. 6. Straight lines fitting to Ozawa–Flynn–Wall kinetic model for various conversion percentages corresponding to the pyrolysis of pitch B at different heating rates for the determination of reaction order n .

Highlights

In the present work, the chemical composition and reactivity of two petroleum pitches in pyrolysis reactions under non-isothermal thermogravimetric conditions were studied. Thermogravimetric (TG) analysis was used to study pyrolysis of petroleum pitches. Non-isothermal thermogravimetric data were used to evaluate the kinetics of the combustion of this carbonaceous material. The paper reports application of Ozawa–Flynn–Wall model to deal with non-isothermal TG data for the evaluation of the activation energy corresponding to the pyrolysis of two different petroleum pitches.