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The pyrolysis of coffee paper cup waste samples using non-isothermal thermo-analytical techniques. The use of combined kinetic and statistical analysis in the interpretation of mechanistic features of the process

Bojan Janković *

Faculty of Physical Chemistry, Department for Dynamics and Matter Structure, University of Belgrade, Studentski trg 12-16, P.O. Box 137, 11001 Belgrade, Serbia

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ABSTRACT

Pyrolysis process of coffee paper cup samples was investigated in a flow stream of nitrogen at different heating rates (10, 20, 30 and 40 °C min^{-1}), using thermo-analytical techniques. It was found that second pyrolysis stage can be described by Šesták–Berggren (SB) autocatalytic model, with mechanism function $f(\alpha) = \alpha^{0.011}(1-\alpha)^{1.459}$. Based on analysis of SB kinetic exponents (designated by M and N), it was found that second pyrolysis stage is mainly controlled by chemical process, involving reactions with reaction-order (n) higher than unity. Applying specific statistical analysis, in order to obtain precise distribution of reactivity, the discrete (binomial) distribution has shown that there are two important areas of current distribution for corresponding energy outcomes, within the apparent activation energy as random variable. The first "concentration" area of energy outcomes corresponds to start of chain end depolymerization reaction forming levoglucosan at high enough temperature region, while second "concentration" area of energy outcomes includes occurrence of macro-radicals in liquid phase propagate with radical addition on unsaturated C–C bonds, with cross-linking and formation of small chemical species. It was found that further elevating of temperature (above 340 °C), will leads to fact that rate of tar-forming reactions increases and formation of char decreases.

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1. Introduction

Urbanization is an important determinant of both the quantity and the type of fuel used in developing countries. In general, urbanization leads to higher levels of energy consumption, also accompanied with increases in income levels. Therefore, there is a shift from traditional to commercial fuels. Several other factors that contribute to this trend include decline in access to biomass fuels, inconvenience of transportation and storage of biomass fuels, and improvement unavailability of commercial fuels in urban areas [1,2]. The disposal of solid biomass and waste is becoming an enormous problem because they are very difficult and costly to manage. Pyrolysis has proved itself to be a new type of solid biomass and waste utilization technique that transforms biomass and waste material of low-energy density into bio-oil of high-energy density and recover higher value chemicals [3].

The paper cups used as coffee or cold drinks cups are accumulating as wastes on the earth surface at a rapid rate. Considering only US, 14.4 million disposable paper cups are used for drinking coffee each year. For example, over 6.5 million trees were cut down to make 16 billion paper cups used by US consumers in 2006, using 4 billion gallons of water and resulting in 253 million pounds of waste [4]. Very little recycled paper is used to make paper cups because of contamination concerns and regulations. Because most paper cups are coated with plastic, both composting and recycling of paper cups is uncommon. Although paper cups are made from renewable resources (wood chips 95% by weight), paper products in a landfill may not decompose, or may release methane if decomposed anaerobically. The manufacture of paper usually requires inorganic chemicals and creates water effluents. Paper cups may consume more non-renewable resources than cups made of polystyrene foam (whose only significant effluent is pentane) [5,6]. In addition, one paper cup represents 4.1 g equivalent petrol with a production cost 2.5 times higher than plastic cups. More petroleum is needed to make a paper cup than a polystyrene one. This is because the wood for the paper cups has to be transported by road

* Tel./fax: +381 11 2187 133.
E-mail address: bojanjan@ffh.bg.ac.rs

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Nomenclature

$d\alpha/dt$	the rate of the process [min^{-1}]
t	the time [min]
dT/dt	the linear heating rate [°C min^{-1}]
A	pre-exponential factor [min^{-1}]
E_a	apparent (*effective*) activation energy [J mol^{-1}]
R	gas constant [J mol^{-1} K^{-1}]
T	absolute temperature [K]
$f(\alpha)$	differential analytical form of the reaction mechanism function
$g(\alpha)$	integral analytical form of the reaction mechanism function
T_o	the starting experimental temperature [°C]
x	reduced apparent activation energy
$p(x)$	analytical approximation of Arrhenius (temperature) integral
$\overline{T}$	the average experimental temperature [°C]
b	the intercept
$E_{a,\alpha}$	apparent activation energy for each given conversion fraction [J mol^{-1}]
t_α	the time at a given conversion fraction
$\Delta\alpha$	the small conversion fraction interval
J	the temperature integral
T_{max}	peak (maximum) temperature [°C]
α_{max} or α_p	conversion value at peak temperature
n	the reaction order
$y(\alpha)$	the first special function for the identification of the reaction mechanism
$z(\alpha)$	the second special function for the identification of the reaction mechanism
α_m	the kinetic parameter related to $y(\alpha)$ special function
α_p^∞	the kinetic parameter related to $z(\alpha)$ special function
$\Delta H^{\neq o}$	the change of the standard enthalpy [kJ mol^{-1}]
$\Delta S^{\neq o}$	the change of the standard entropy [J K^{-1} mol^{-1}]
$\Delta G^{\neq o}$	the change of the Gibbs free energy [kJ mol^{-1}]
e	Neper number
k_B	Boltzmann constant [J K^{-1}]
h	Plank constant [J s]
$E^{\neq o}$	apparent activation energy obtained from advanced non-linear isoconversional method [J mol^{-1}]
ε_a	the individual outcomes for the considered random variable designated by E_a [J mol^{-1}]
$p(\varepsilon_a)$	the discrete probability [mol $(kJ)^{-1}$]
N^*	total number of real values of a random variable
$B(\lambda,p)$	Binomial distribution
$f(\delta,\lambda,p)$	discrete density probability/distribution function (*ddf*)
$F(\delta,\lambda,p)$	discrete cumulative probability/distribution function (*cdf*)
$[\delta]$	greatest integer
ΔT	the temperature range [°C]
$T_{shoulder}$	the "shoulder" temperature on the derivative thermogravimetric curves [°C]
T_i	initial (onset) temperature [°C]
T_f	final temperature [°C]
$<E_a>$	the average value of the apparent activation energy [J mol^{-1}]
3D	three-dimensional space
a	CE – artificial compensation effect
a^*	the first apparent compensation effect coefficient [min^{-1}]
b^*	the second apparent compensation effect coefficient [mol $(kJ)^{-1}$]
k_{iso}	the isokinetic rate constant [min^{-1}]
T_{iso}	the isokinetic temperature [°C]
M	the first Šesták–Berggren autocatalytic parameter
N	the second Šesták–Berggren autocatalytic parameter
$M + N$	the total reaction order
$A_{FR\text{-}Miura}$	pre-exponential factor obtained by the Friedman–Miura's approach [min^{-1}]
$\varepsilon_a{}^b$	boundary value of the individual outcomes for the random variable, E_a [J mol^{-1}]

List of acronyms

LDPE	low-density polyethylene
TA	thermo-analytical
TG	thermogravimetry
TGA	thermogravimetric analysis
DTG	derivative thermogravimetry
DTA	differential thermal analysis
ICTAC	International Confederation for Thermal Analysis and Calorimetry
DAEM	distributed apparent activation energy model
TG/DTG	thermogravimetry/derivative thermogravimetry
CR	Coats-Redfern method
RSS	the residual sum of squares
AC	Achar method
KAS	Kissinger–Akahira–Sunose method
FR	Friedman method
VY	Vyazovkin method
(S)	"Successfully" deployed values
SB	Šesták–Berggren model
S	the ratio of the Šesták and Berggren kinetic exponents
(F)	Fisher test

Greek letters

φ	the gas flowing rate [mL min^{-1}]
β	the heating rate [°C min^{-1}]
α	the conversion fraction
χ	the transition factor
ε	the individual outcomes
μ	the mean value [J mol^{-1}]
λ	parameter of the binomial distribution
δ	number of successfully deployed values of ε_a
ξ	the random variable of regularized incomplete beta function
σ	the standard deviation [J mol^{-1}]
φ_o	additional correction (energy) parameter of the modified Gauss (normal) distribution [J mol^{-1}]
Ψ	the cumulative distribution function of the standard normal distribution

Subscripts

i	the ordinal number of a non-isothermal experiments
max	the values related to the maximum of the derivative thermogravimetric curve at a given heating rate
a	the apparent
a, α	the apparent value at a given conversion fraction

Superscripts

l	the total number of the heating rates
Models	attached to the tested reaction mechanisms

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