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EVOLUTION AND CONJUGATING MODEL OF CARBONIC MATERIAL THERMOCHEMICAL CONVERSION USING A NONISOTHERMAL KINETIC APPROACH

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Abstract

The evolution of carbonic material thermochemical conversion and the associative conjugating model are presented by the example of pitch carbonization to see the development of the complex system on the whole. Methodological approach is suggested to simplify the kinetics of complicated processes during heating and to calculate apparent activation energies of the product formation processes at various temperatures. The diagnostics of pitch thermochemical conversion is carried out from the point of view of evolutional conjugated pathway of the complex system development.

1. Introduction

Processes of thermochemical conversion underlie the big-volume raw material processing, resulting with production of coke, oils, electrodes for aluminum or steel industry, carbon fibres, carbon-carbon composites, activated carbons and etc. [1, 2]. At the same time it is one of the basic sources of pollution of the natural environment by toxic carcinogenic substances [3, 4]. Moreover, growing necessity of the carbonic products production leads to exhaustion of natural resources (petroleum, coal, wood and etc.) and abruptly makes worse the ecological balance. So, issue of the day is to bring to light a nature of interaction of the man-caused processes and ecosystem degradation that, in turn, requires grouping of general and specific knowledge as well as a creation of a new methodologies and models for study of the evolution of complex system as a whole. In addition, it can give a chance to establish a connection between structure conversion of living and lifeless carbonic matter.

It is not surprising that there has been continuous research on many aspects of carbonic material thermoconversion such as the dependence of product yields on carbonic material type and reaction conditions, kinetics of processes and etc.. However, the heterogeneous nature of carbonic raw materials and complexity of the carbonization process which includes a multitude of single reactions proceeding

simultaneously have made its very difficult to perform unambiguous experiments to determine the rates and mechanisms in carbonic material conversion [1, 5-9]. The resulting lack of agreement on the rates and mechanisms in carbonic material thermoconversion has hindered the development of predictive methods. Recent years have provided a number of new experimental and theoretical approaches considering the recent progress on kinetics, the formation of volatile products, network models, crosslinking, rank effects, 'two-component' model of coal structure and others

[7-11] which, unfortunately, don't give universal simple methodology of thermodynamic consideration of complex carbonic system as evolutionary process in general.

The aim of this paper is to present methodological approach and model considering thermoconversion of carbonic materials as evolutionary process of complex system on the whole by the example of pitch thermochemical conversion.

2. Nonisothermal kinetic approach of thermochemical conversion of carbonic substance

Nonisothermal process at constant heating rates supplies mechanistic and kinetic data on the decomposition of carbonic substances, but a large number of various rates complicates a calculation and analysis of complex process kinetics. To simplify the kinetics of complex processes during heating, to calculate apparent activation energies of the product formation processes and to consider the temperature-time evolution of a system on one scale, there is suggested to use the heating rate of $1^{\circ}C \cdot min^{-1}$. The constant heating rate of $1^{\circ}C \cdot min^{-1}$

 $(dT \cdot dt^{-1} = 1)$ allows writing the kinetic equation of the process vs time and temperature by one dependence, using simple transformations:

 $\mathbf{V} = -\mathbf{d}\mathbf{C}\cdot\mathbf{d}\mathbf{t}^{-1} = \mathbf{k}\cdot\mathbf{c}^{n}$

 $dC \cdot dt^{-1} = dC \cdot dt^{-1} \cdot dT \cdot dT^{-1} = dC \cdot dT^{-1} \cdot dT \cdot dt^{-1} = dC \cdot dT^{-1} \cdot \alpha,$

where $\alpha = dT \cdot dt^{-1} = const = 1$

By substituting a rate constant from Arrhenius equation, we receive

 $V = -dC \cdot dT^{-1} \cdot \alpha = A \cdot e^{-E/(RT)} \cdot C^{n},$

where n – the order of reaction; A – the pre-exponential factor; E - activation energy; R - universal gas constant; T - temperature; C - concentration of a reagent; t - time.

This equation can be used to calculate the apparent activation energy of product formation process under following assumptions:

• The pre-exponential factor practically doesn't depend on temperature (A = const).

• The first order reaction (n = 1). It is quite correct, because the first order reaction is usually considered for description of kinetic of coal, pitch, biomass and other hydrocarbon raw pyrolysis.

• Concentration of reagent is assumed to be a constant (C=const) if the system is in stationary or quasi-stationary state.

Computational exercise of apparent activation energies of gas formation process for carbonization of coal-tar pitch is presented below.

The integral dependences of formation rates of gaseous products (CH₄, H₂, C₂H₆, CO) during carbonization of pitch at heating rate of 1° C·min⁻¹ vs temperature were taken from [12] and transformed to the differential dependences which are shown in Figure 1 [13]. On the basis of these data the

apparent activation energies of CH₄, H₂, C₂H₆, CO formation processes are calculated. In Figure 2 lgV - T^{-1} dependences of CH₄, H₂, C₂H₆ and CO evolution in the temperature interval of 300-800°C are presented. Linear segments are found in two temperature ranges (390-460°C and 580-680°C), for which apparent activation energies of CH₄, H₂, C₂H₆ and CO formation process are calculated and listed in Table.



Figure 1. Evolution rates H_2 , CH_4 , C_2H_6 and CO as a function of temperature for coal tar pitch $(V_{heating}=1^{\circ}C\cdot min^{-1})$.

Table.

Apparent activation energies of gas formation process $(kJ \cdot mol^{-1})$ during the heating of coal tar pitch.

gas	E_1	E_2
H ₂	226±13	30±14
CH_4	199±10	67±31
C ₂ H ₆	207±20	_
СО	197±27	137±41

 E_1 – activation energy determined in the temperature range of 390-460°C

E₂ – activation energy determined in the temperature range of 580-680°C



Figure 2. Logarithmic dependence of evolution rates of H_2 , CH_4 , C_2H_6 and CO on reciprocal temperature for coal tar pitch.

Thus, using the only heating rate $(1^{\circ}C \cdot min^{-1})$, the apparent activation energies of product formation process can be calculated in different temperatures (or times) and its changes can be revealed both at the individual stage and at the all system.

3. Principle of carbonic substance evolution modeling and associative conjugating model of pitch thermochemical conversion

It is known that many carbonic materials, including pitch, have paramagnetic properties due to existence of stable radical centers and formation of polyconjugated system during heating [1, 5, 10, 13-15]. So, we can consider the system in stationary or quasi- stationary state during passing of radical processes; it makes the kinetic calculations easier.

We suppose that the principle of energetic conjugation underlies the modeling of complex carbonic system evolution; the term "conjugation" means driving mechanism of physic-chemical conversion caused by availability of high-energy electron-migratory intermediates. It is also suggested the principle of 'all conjugation' including conjugation of bonds, reactions, processes, phases and structures in this system.

With regard to the foregoing and also to the data concerning pitch carbonization, we suggest the associative conjugating model of pitch thermoconversion presented in Figure 3 in the form of elementary aryl intermediate – phenyl; here carbon atoms are associatively substituted by specific

products (pitch – mesophase – semicoke – semiconductor – coke – tar) formed at the different stages of pitch conversion.



Figure 3. Associative or conjugation model of thermoconversion of pitch (L - liquid phase, S - solid phase, G - gas phase).

Thermoconversion of pitch is considered as continuous multiplex heterogeneous conjugated process in liquid, solid and gas phases, where initiators of all processes are aromatic π -radicals. Moreover, phase transfers are accompanied by appreciable physic-chemical changes of the system. The description of pitch thermoconversion gives below subject to the conjugating model and the kinetic approach.

4. Diagnostic of pitch thermochemical conversion

Under heating up to 200-400°C pitch undergoes the liquid-phase process of thermopolymerization that is initiated by the stable radical centers existing in pitch. Propagation of this process leads to accumulation of high-molecular aromatic molecules in pitch and their ordering with formation of anisotropic structure (**mesophase**).

Apparent activation energies of gas formation process (200-230 kJ·mol⁻¹) in low-temperature area (Table) are in close agreement with activation energy of mesophase formation (170-260 kJ·mol⁻¹) [1, 6, 16, 17]. Hence, two-phase states (condensed state - mesophase and gaseous state - gas) in this system are simultaneously formed from the same initial reagents. It characterizes the passing of liquid-phase conjugated processes of polymerization, cracking and polycondensation by the radical mechanism.

The most probable reactions of cracking initiation can be shown in the following way:



Methylenephenyl (or methilenearyl) radicals (reaction I) interaction with the main components of pitch easily proceeds with formation of high-molecular-weight and gaseous products:

 $Ph-CH_2 \bullet + Ar (2H) \to Ph-Ar \bullet + CH_4$ (III)

 $Ph-CH_2 \bullet + Ar (2H) \rightarrow Ph-CH_2 - Ar \bullet + H_2$ (IV)

Hydrogen elimination from biradical (reaction II) can leads to diene bond formation and to formation and growth of an aromatic molecule.

Significant thermochemical conversions of pitch and phase change in the system are occurred at heating up to 500°C. Intensive gas evolution (Fig. 1), formation of condensed products, endothermic effects, growth of paramagnetic centers, exchange spin-spin interaction between π -radicals with oriented ordering in short and long ranges are observed for **semicoke** formation (about 500°C) [1, 13, 15]. One can say that conjugated transition of radical processes from liquid-phase to solid-phase medium takes place.

At temperatures above 500°C hydrogen evolution with the constant rate is discovered (Fig. 1), which creates the constant hydrogen pressure in system during further heating due to dehydrocondensation process of aromatic fragments of pitch:



Consequently, reducing medium is produced by system itself at temperatures above 500°C.

The next stage of thermoconversion of pitch (about 600°C) is characterized by appearance of **paramagnetic properties** of the solid product (Fig. 3). Transformation from microdomain structure, where single domains are isolated, to monolithic one takes place; maximization of paramagnetic center concentration is observed [15] and migration of hydrogen becomes a motive force of structure formation to minimize free energy. At this stage, evolution of tar is occurred also [13, 18]. In other words, "defect structures" that are disconnected with basic carbon matrix are accumulated in solid residue and evolved in gas phase. Thus, it is proposed that at this stage, solid-phase conjugated radical processes of microstructural ordering and macrostructural changes start to proceed.

It is our opinion that calculated apparent activation energies of gas formation process in hightemperature area (Table) characterize the pyrolysis and linking processes passing in the condensed phase. One can suppose that low apparent activation energies of the hydrogen formation process in this temperature range are connected with diffusion-controllable process (recombination) – a relay-race migration of hydrogen in condensed phase. Higher values of apparent activation energy of CO formation process than for other gases (Table) can be caused by relay-race effect of long range ordering of oxygen.

At the stage of **coke** formation (about 700° C), as well as **semicoke** formation, the phase transition is observed accompanied by appreciable physical and chemical changes in the system, such as conversion of the carbon residue to single condensed phase, intensive evolution of the gas products, desorption of tar and exothermic effects [13, 18].

According to the presented associative model (Fig. 3), gas-phase processes occur at this stage. Really, at temperatures of 600-1000°C a vapor-phase pyrolysis of aromatic hydrocarbons proceeds forming phenyl(aryl)radicals, which undergo straight nuclear condensation [1]. Therefore, **tar**, including polycyclic aromatic compounds, is subjected to vapor-phase pyrolysis at these temperatures. At the same time, at temperatures above 800°C significant conversion of solid residue doesn't occur - ordering structure of carbon residue is only observed with hydrogen evolution.

Thus, a reducing medium is created in the system that facilitated passing of solid-phase radical processes and it is a "bridge" for realization of process transfer from liquid to solid and then to gas phase. Evolution of this system is an uninterrupted conjugated transfer from processes of synthesis to processes of degradation in each phase. Simultaneously, these processes promote a conjugated transfer of one phase in another as well as conjugated micro-, macrostructure changes.

To return to stating point of our model – **pitch** (Fig. 3) the system must give up the thermal energy to the surrounding environment, approximately such amount that have expended on external influence (heating), except the energy required for proceeding polymerization. Consequently, thermoconversion of pitch as evolution system can pass with insignificant total energy consumption.

Finally, presentation of evolution of this system has shown up elements of self-organization and self-reproduction, which living matter has; so, common features for living and lifeless carbonic matter are found.

5. Conclusion

Nonisothermic process at constant heating rate of 1° C·min⁻¹ have been allowed to calculate the apparent activation energies of gas formation process during pitch carbonization. It has been established that the apparent activation energies of gas formation process during of pitch carbonization in low-temperature range are in good agreement with activation energies of mesophase formation.

Suggested associative conjugating model has been well considered the pitch thermochemical conversion as complex system on a whole and revealed a renewal of this system requiring insignificant total energy consumption.

Analysis of experimental and theoretical data concerning thermochemical processes of pitch has been visualized consecutive conjugated transfer from processes of synthesis to processes of degradation in liquid, solid, gas media.

It have been revealed that reducing medium is produced by system itself at temperatures above 500°C which facilitate passing high-temperature processes. We suggest that hydrogen is a "bridge" supporting uninterrupted conjugated transfer from one to other state of system.

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