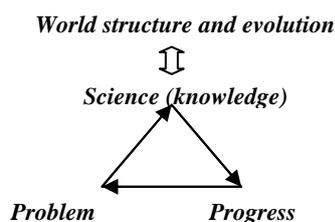


Thermochemical conversion research of a substance as evolutionary study of a complex system

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1. Introduction

Modern research and tasks of chemistry first of all direct to the creation of a new materials and technologies; it's a result of a growth of a technical and an economical progress. At the same time consequences of the progress are frequently underestimated and cause serious ecological problems. At present a struggle against the consequences of the progress takes on a global scale. As a result, many research activities are carried out "over one cycle" of "problem" and "progress", and "science" doesn't have time to study a main source of their origin and to understand the wholeness of a prototype system.



In early papers the research of thermochemical conversion of carbonic materials were described [Anshits 2001, Kurteeva 2002, Tsyganova 2002]. The ultimate goal of the research was to solve some ecological problems. Finding a correlation between the chemical composition, structure, yield of the products including toxic substances, and the thermoconversion processes in the system is very important for practical task solution. Unfortunately, a large number of theoretical and experimental researches don't often give a correct interpretation of facts and their comparison; so it's rather difficult to present complete picture of the thermochemical conversion as a system development in whole. The main reason of it is a complex composition and structure of the hydrocarbon materials in combination with the multitude reactions, which take place under heating.

In this paper we attempted to generalize well-known theoretical and experimental information concerning the thermoconversion of pitch and other hydrocarbon materials and to describe a heating process as physic-chemical evolution of complex system, using a kinetic approach and conjugating principle.

2. Main principles of the thermoconversion research as an evolutionary study of a process

Physical-chemical approach underlies process evolution of any system that in turn obeys the universal laws of nature. Conversion of a substance in open system

both on a single stage and on the whole process obeys three main laws of the motion trend [Slesarev 2000]:

1. Tendency of a system to minimize free energy.
2. Tendency of a system to maximize entropy.
3. Tendency to maximize information for the system in a steady state is a law of the system ordering.

The following restrictive measures are entered to show up evolutionary trajectory of investigated object at heating in the open system; they decrease alternate versions and limits of various changes at overall evolutionary pathway:

1. Investigation should be carried out at the inert medium for visualization of an “internal life” of a substance without “intervention” reducing and oxidizing media.
2. External steady heat source should be introduced because a deviation from the linear steady heat action will characterize the change of system itself.
3. The kinetic approach should be used for universal description of concerned processes:

A key condition for study of physical-chemical thermoconversion of any substance is selection of heating rate. Non-isothermal study at heating rate of $1^{\circ}\text{C}\cdot\text{min}^{-1}$ is suggested to simplify the kinetics of complicated 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.

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

$$V = -dC\cdot dt^{-1} = k\cdot c^n$$

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

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

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 is used to calculate the apparent activation energy of gas formation process under following assumptions:

- The pre-exponential factor practically doesn't depend on temperature ($A = \text{const}$).
- 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 ($C = \text{const}$). It is correct for the initial segment of gas evolution curve, where changing of concentration of initial reagents can be neglected.

Differential rates of gas formation during carbonization of pitch at heating rate of $1^{\circ}\text{C}\cdot\text{min}^{-1}$ are shown in Figure 1 [Tsyganova 2002]. On the basis of these data apparent activation energies of CH_4 , H_2 , C_2H_6 , CO formation processes are calculated.

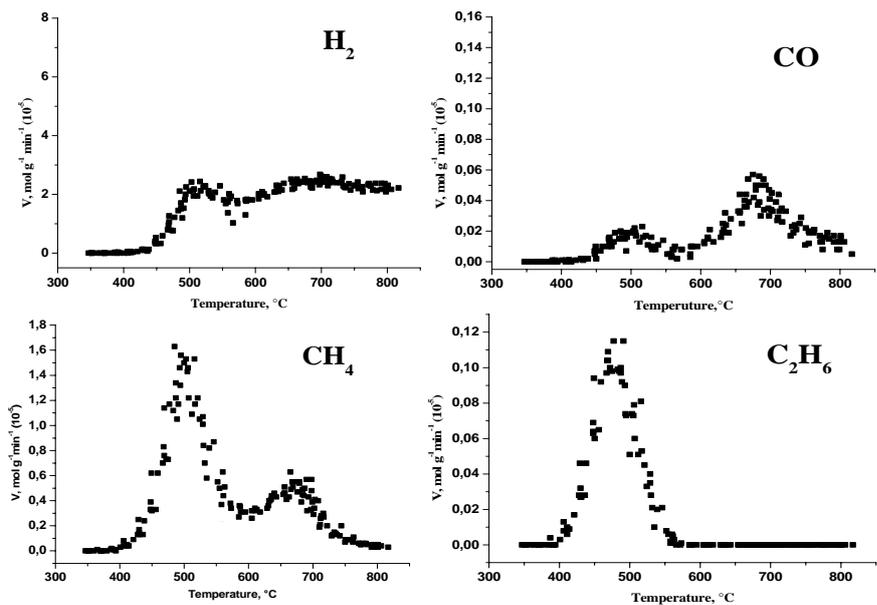


Figure. 1. Evolution rates of H_2 , CH_4 , C_2H_6 and CO as a function of temperature for coal-tar pitch ($V_{\text{Heating}} = 1^\circ\text{C}\cdot\text{min}^{-1}$).

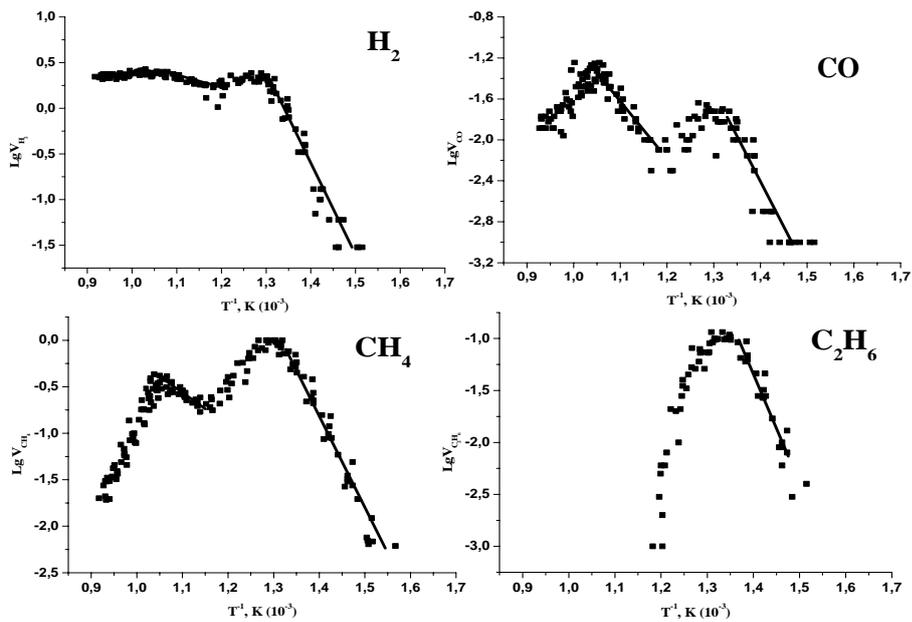


Figure. 2. Logarithmic dependence of evolution rates of H_2 , CH_4 , C_2H_6 and CO on reciprocal temperature for coal-tar pitch.

In Figure 2 $\lg V - T^{-1}$ dependences of CH_4 , H_2 , C_2H_6 and CO evolution in the temperature interval of 300-800°C are presented for pitch carbonization. Linear segments are found in two temperature ranges (390-460°C and 580-680°C), for which apparent activation energies of CH_4 , H_2 , C_2H_6 and CO formation process are calculated and listed in Table.

Table. Apparent activation energies of gas formation process ($\text{kJ}\cdot\text{mol}^{-1}$) 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_2H_6	207±20	-
CO	197±27	137±41

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

E_2 – activation energy determined in the temperature range of 580-680°C

In the general case, using the only heating rate ($1^\circ\text{C}\cdot\text{min}^{-1}$) the apparent activation energies of product formation process can be calculated in different discrete intervals of temperature (or time) under the some assumptions; thus, information can be obtained both about passing processes at the individual stages and about the evolution of all system as a whole.

3. Associative model of physic-chemical pitch evolution

It is known that pitch has paramagnetic properties as many other hydrocarbon materials due to existence of stable radical centers and formation of polyconjugated system during heating [Fitzer 1971]. Aromatic π -radicals are assumed to use as initiators of thermoconversion for considering the pitch evolution.

“Conjugation” is driving mechanism of physic-chemical conversion caused by availability of conjugated π -bonds in the system. It suggests ‘all conjugation’ including conjugation of bonds, reactions, processes, phases in this system. Associative model of pitch thermoconversion is shown in Figure 3 in the form of elementary aryl intermediate – phenyl, in which carbon atoms are associatively substituted by specific products (pitch – mezophase - semicoke - semiconductor – coke - tar) formed at the different stages of pitch conversion.

Thus, 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, changes of phase are accompanied by appreciable physic-chemical changes of the system.

Description of pitch thermoconversion gives below using conjugation model, kinetic approach and main principles of open system evolution.

4. Evolution of pitch thermoconversion

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**).

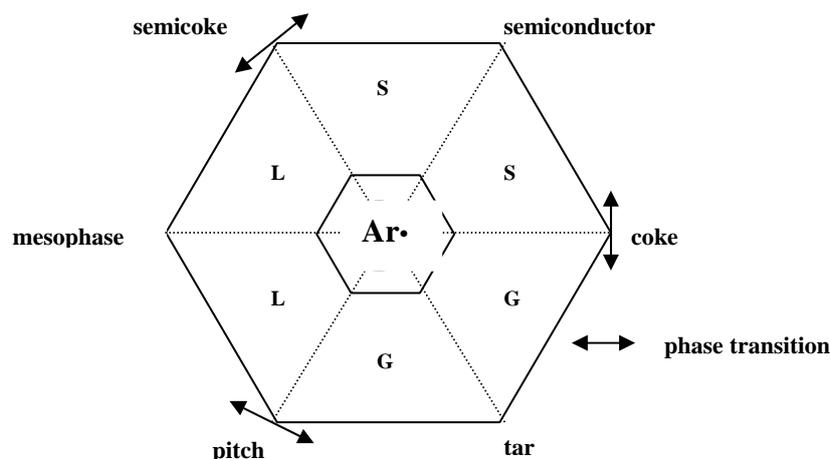


Figure 3. Associative, or conjugation model of thermoconversion of pitch (L - liquid phase, S - solid phase, G - gas phase).

Apparent activation energies of gas formation process ($200\text{-}230\text{ kJ}\cdot\text{mol}^{-1}$) in low-temperature area (Table) are in close agreement with activation energy of mesophase formation ($170\text{-}260\text{ kJ}\cdot\text{mol}^{-1}$) [Marsh H 1999, Fitzer 1971]. 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.

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) [Fitzer 1971, Tsyganova 2002, Shklyev 1997]. 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 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 [Shklyev 1997] and migration of hydrogen becomes a motive force of structure formation to minimize free energy. At this stage, evolution of tar (complex mixture of polyaromatic compounds) is occurred also [Kurteeva 2002]. 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 high-temperature 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 [Tsyganova 2002].

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 [Fitzer 1971]. 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 [Tsyganova 2002].

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 starting 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.

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