

CHEMICAL PROCESSES MATHEMATICALLY MODELLED WHICH TAKES PLACE IN COAL EXTRACTION WITH SOLVENTS

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abstract: The liquefaction of coals followed by the extraction of the black products with the help of some solvents is a very complex process. For this reason, the knowledge of this process's mechanism was extremely difficult to decipher. Hiel's studies led to the proposal of several possible reaction mechanisms. Paying particular attention to the study of the Jiu Valley coal's liquefaction, there could be underlined a mathematical pattern of the reactions that took place during the process. This model complies with the ones proposed by the speciality literature in this filed.

Introduction

The coal is an organogenic rock that comes, mainly, from the accumulation of residual vegetal and from their slow carbon enrichment. Generally speaking, in the geological profile, the organic material alternates with other rocks laid in a certain order. This order is connected to the cyclical sedimentation process. The material assembly of organic – inorganic matter could be affected, in some cases, by the earth's crust's movements. Judging by the nature of the organic rests, the method of accumulation and the conditions under which their transformation occurred, the various types of coal can be classified in: humic coal, sapropel coal and liptobiolithic coal. The deposits of humic coal are the most frequent ones, so that it is customary to label the various types of humic caustobiolits with the general term of “coal”: turf, brown coal, pit coal, hard coal (anthracites).

Theoretical basis

The coal is made of three components: organic matter (substances with a complex structure made of carbon, oxygen, brimstone and nitrogen); inorganic matter (mineral substance that, by roasting, transform into ash) and water. The three components represent the limit-aspects of the same unit called coal. All three aspects are tightly connected physically and

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chemically. This aspect conditions the behaviour of the material during the burning process, the mechanical and chemical preparation process or during the pyrogenetic process.

The organic matter represents the assembly of organic substances made of carbon, hydrogen, oxygen, brimstone and nitrogen. It has a complex structure that by burning generates carbon dioxide, water vapours, brimstone vapours and nitrogen and, at the same time, releases a significant quantity of heat. The chemical composition and the properties of the organic matter depend on the genetic material, the conditions under which it was formed, on the chemical and geological age of the coal. This composition is illustrated in table 1.

Table 1. Elementary Chemical Composition of the Organic matter for Various Types of Humic Coal

Coal Type	C (%)	H (%)	O (%)	N (%)	Caloric Power Kcal/Kg	Raw Materials
0	1	2	3	4	5	6
Turf	55-60	5-6	33-37	2	5000-5700	60
Lignite	60-70	5-6	21-29	1	5400-6200	60
Mat Brown coal	60-70	5-6	21-29	0.8	5400-6200	50-60
Shiny Brown Coal	70-78	3-5	14-17	0.8	6200-7200	50-60
Axial Compressed Flexing Pit Coal	75-80	4.5-5.5	14	0.7	7200-7600	40-50
Gas Pit Coal	80-85	5.0-5.8	10-12	0.7	7800-8000	35
Semi-fat pit coal	84-89	5.0-5.5	9-11	0.5	8000-8300	26
Cocking Pit Coal	86-88	5	7-9	0.5	8300-8500	18
Poor Anthracite Pit Coal	90-92	4-5	4-5	0.3	8700-8800	12
Anthracite	94-98	1-3	1-3	rests	8200-8500	4

From the table we can observe the fact that along with the increase of the carbon content there takes place a decrease of the oxygen, nitrogen, volatile materials content and there is an increase of the coal's caloric power.

According to some authors, coal is a macromolecular composite with a very complex structure. It is formed of polycondensed aromatic nuclei with monomer units that do not repeat an index that shows the trend to dissolve in various solvents according to the treatment conditions.

The dissolution of the coal's organic matter with the help of a hydrogen donor solvent has a long history that begins with the experiments of dissolution in air – pressure tanks in 1862.

Kiebler and Dryden published these attempts of dissolution. The Pittsburgh Energetic Technology Centre conducted works concerning the coal hydrogenation kinetics in the presence of a catalyst. Here were elaborated mathematical patterns for the dissolution of coal and for the extraction of the organic matter's components, mainly of the asphaltenes according to a certain amount of time at four different temperatures. The velocity constants were evaluated as well.

In the literature there are presented several types of mathematical patterns regarding coal dissolution, patterns as the following one presented in Fig. 1.

Cronaner completes the scheme with the formation reactions of gases and pre-asphaltene, according to Fig. 2, and at the same time, assumes all processes to be of 1st order.

Shalabi introduces into the process's mechanism the formation reactions for gas and oil from pre-asphaltene, according to the Fig. 3.

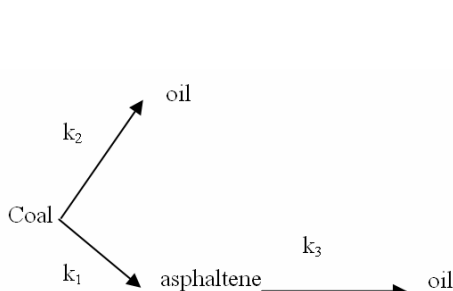


Fig. 1 Coal dissolution pattern according literature

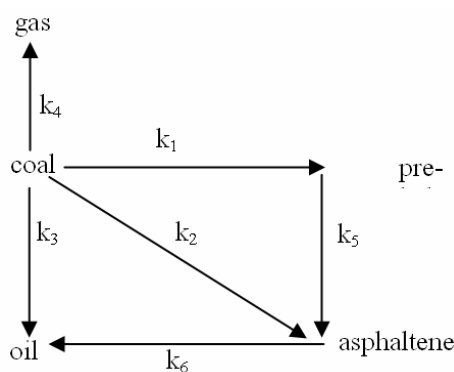


Fig. 2 Coal dissolution pattern according Cronaner

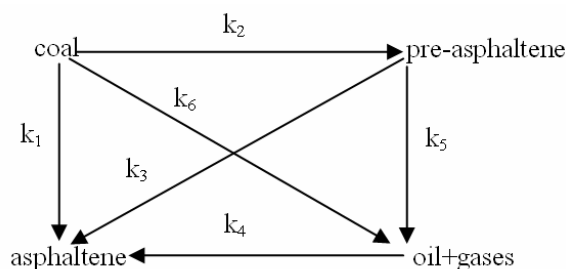


Fig. 3 Coal dissolution pattern according to Shalabi

From the point of view of the chemical reactions that take place during coal dissolution, the process is extremely complex and can only be regarded globally, taking into account the formation of product groups of the oil and asphaltene type, in consecutive or parallel reactions, as well as more complex schemes that involve liquid products, gases and reactive fractions. The equations deduced based on these reaction models failed to satisfactorily correlate the experimental data and it was necessary to complicate the reaction mechanism by taking into account both some parallel reactions and some consecutive reactions.

Experimental research

In order to find a mathematical model in the extraction process of the organic matter's components with the help of various solvents, it is necessary to transform solid coal into liquid coal. This can be achieved with the help of a hydrogen donor substance, circulating agent, and an adequate catalyst under the influence of factors such as: temperature, pressure, maceration time, etc. This way liquid coal was obtained at different temperatures:

350 °C, 375 °C and 400 °C. The liquid fractions were analysed according to the scheme in Fig. 4.

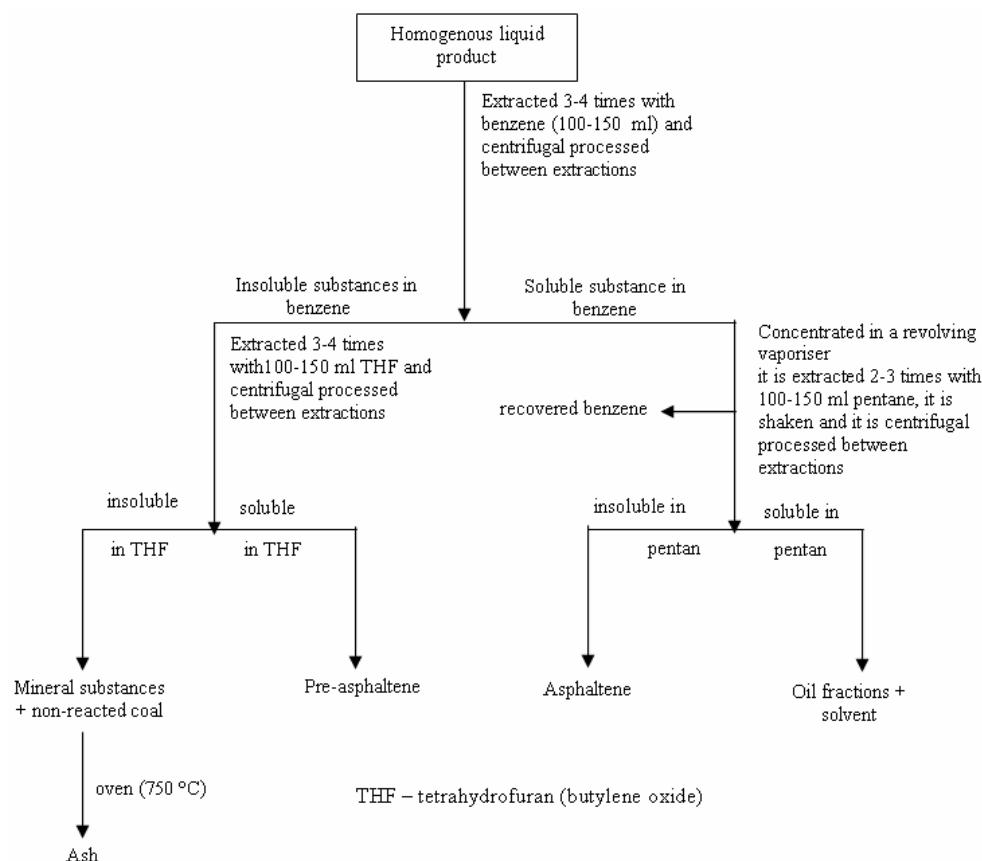


Fig. 4 The characterisation scheme of the liquid products from coal.

The pattern was analysed at three different temperatures.

By writing the differential equations of the disappearance of the reactive substances and of the formation of the reaction products, there can be determined the values corresponding to A, B, C and D. The values are given in Table 2.

Taking into account the liquefaction products obtained through the extraction with the help of solvents, as shown in figure 1, from the special Jiu Valley coal, there was reached the conclusion that the reactions that take place during the coal liquefaction process follow the mathematical pattern. Its reaction mechanism is presented in Fig. 5.

The graphic representation of oil fractions according to time is illustrated in Figs. 6÷8.

Table 2

Temperature °C	Time (minutes)	A' Non-reacted coal (%)	C Pre-asphaltene (%)	B Asphaltene (%)	D Oil + gas (%)
350	30	59	20	17	4
	60	46	29	20	5
	120	34	31	22	13
	180	26	32	24	18
375	10	45	27	16.5	11.5
	30	30	34	21.5	15
	60	19	32.5	28.4	20
	120	15	25	30	30
400	10	32	30	23	15
	30	15.8	37	27	20.2
	60	13.5	31	31	21.5
	180	12.5	25	30	33.5

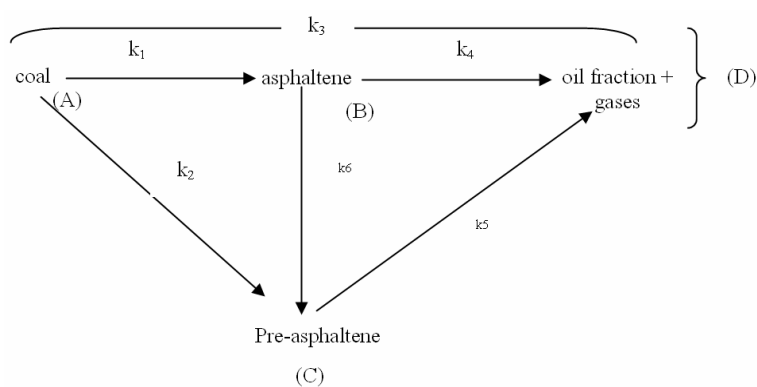


Fig. 5 The mechanism of reactions that take place during the coal liquefaction process

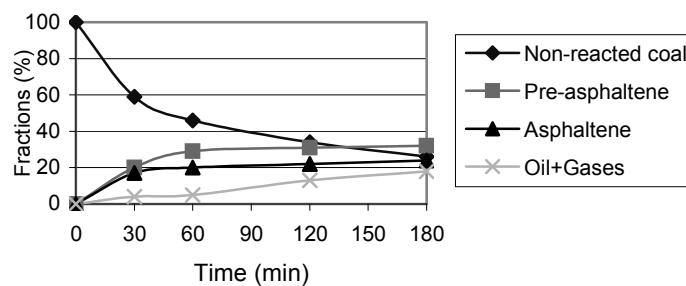


Fig. 6 Mathematical pattern at 350 °

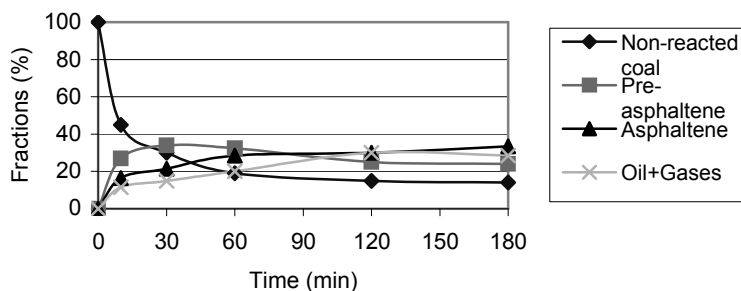


Fig. 7 Mathematical pattern at 375 °C

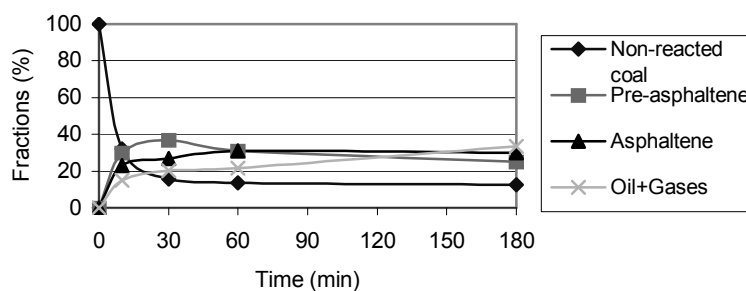


Fig. 8 Mathematical pattern at 400 °C

Discussion of the results

The reaction products resulted at the beginning are called pre-asphaltenes and asphaltenes. Lighter liquid products (oil fractions) follow them.

The concentration of the pre-asphaltenes greatly increases around some values over 30% of the liquid products, for three hours at a temperature of 350 °C, while the same quantity of pre-asphaltene is present in the liquid product after only 10 minutes at 400 °C. This fraction of pre-asphaltenes degrades later on rather slowly. The hydrogenation reactions are predominant. They lead to the appearance of asphaltenes and oil fractions by consuming the pre-asphaltene fraction.

For a temperature of 400 °C there were obtained values similar to the ones of the velocity constants specific for a temperature of 375°C.

By non-linear regressions there were determined the velocity constants specific for the proposed pattern. These constants are given in Table 3.

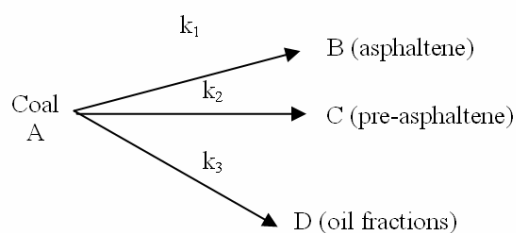
Table 3. Velocity constants specific for the proposed pattern

Temperature (°C)	Velocity constant [h ⁻¹]	Time (minutes)				Average
		30	60	120	180	
350	K1	0.008632	0.005800	0.003951	0.00347	0.005488
	K2	0.010511	0.009259	0.006567	0.005989	0.008082
	K3	0.001444	0.000398	0.000758	0.000433	0.000757
	K4	0.00081	0.0007	0.0007	0.0007	0.000728
	K5	0.00269	0.003	0.003	0.003	0.002923
	K6	0.0001	0.00001	0.00001	0.00001	3.25·10 ⁻⁵
375	K1	0.016489	0.016074	0.011351	0.00856	0.013119
	K2	0.022358	0.024314	0.013941	0.009786	0.0176
	K3	0.009299	0.00829	0.004485	0.004345	0.006605
	K4	0.00081	0.0007	0.0007	0.0007	0.000728
	K5	0.00269	0.003	0.003	0.003	0.002923
	K6	0.0001	0.00001	0.00001	0.00001	3.25·10 ⁻⁵

The asphaltene concentration increases with the reaction time for temperatures of 350 °C, 375 °C. The trend for asphaltene formation at 400 °C is less clear. It registers a maximum of 31% at a reaction time of 1 hour. There after can be observed a decrease of the concentration for higher reaction times due, probably, to the acceleration of the hydrogenation reactions and to the formation of oil products.

Conclusions

1. The non-reacted coal decreases from the quantity point of view along with the temperature increase and the reaction time.
2. According to the velocity constants, one may say that the first three constants k_1 , k_2 , k_3 observe Arrhenius's law and all the others are less accurate and don't observe this law.
3. For these reasons, the intended model may be simplified $k_4=k_5=k_6=0$, under the form of a simpler model presented in Fig. 9.

**Fig. 9** Simplified coal dissolution pattern

4. As a conclusion, the pattern proposed verifies from the experimental point of view at a certain degree. But the search continues for more adequate patterns for this coal transformation process into liquid coal.

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