

# Pyrolysis of Coal

KUI – 15/2006.

Received December 20, 2005

Accepted March 2, 2006

A. Rađenović

University of Zagreb, Faculty of Metallurgy  
Aleja narodnih heroja 3, 44000 Sisak, Croatia

The paper presents a review of relevant literature on coal pyrolysis.

Pyrolysis, as a process technology, has received considerable attention from many researchers because it is an important intermediate stage in coal conversion.

Reactions parameters as the temperature, pressure, coal particle size, heating rate, soak time, type of reactor, etc. determine the total carbon conversion and the transport of volatiles and thereby the product distribution. Part of the possible environmental pollutants could be removed by optimising the pyrolysis conditions. Therefore, this process will be subsequently interesting for coal utilization in the future.

Keywords: *Coal, pyrolysis, mechanism, structure change, reaction parameters, environment*

## Introduction

Coal is a feedstock that can be converted to energy, to chemicals or to carbon materials. As carbon-rich solids, coals are potential starting materials for higher value materials via conversion processes. It is well known that various useful carbon-based materials can be made from coals; coal tars, petroleum pitch and coal liquids derived from coal pyrolysis and liquefaction.<sup>1</sup>

Pyrolysis is a common stage of many coal utilization processes such as carbonization, gasification, combustion, liquefaction, which are operated usually in close systems under inert, reductive or oxidative atmospheres at different pressures and residence time. The products of the pyrolysis of coals are coke (or char), liquids and gases.

The basic understanding of the chemistry of coal pyrolysis are a base for process design and optimization. Moreover, the yields and the properties of the pyrolysis products and their rate of formation during thermal treatment under different conditions provide more insight into the fundamental chemical and physical structure of coal and its reaction behaviour.<sup>2-12</sup> A basic coal pyrolysis process are shown in Fig. 1.

## A reactive model of coal structure

Coal is structured heterogeneously by organic and inorganic constituents. It has a resistant chemical structure, grown and preserved over millions of years.

A model of coal structure should represent data on the properties and behaviour of coal.

The basic assumptions and main characteristics of the coal models have been described earlier.<sup>13-18</sup> Fig. 2. shows model of the molecular structure of bituminous coal (84 % C).<sup>9</sup> Aromatic and hydroaromatic structural units, with some three to five rings only, are bound to each other by short aliphatic and ether bridges to form a macromolecular network (Fig. 2 showing only a small section of this). Nitrogen and sulphur are found in heterocyclic bonds in most cases, oxygen is bound in the form of phenolic structures or as ether. With increasing rank of coal the share of aromatic carbon increases. The average size of the aromatic units does not vary much with rank but is found to be markedly higher for anthracite coals only, an astonishing finding.

Today, these models do not give the full picture of the known facts of coal's chemical structure. From experiments on coal swelling in organic solvents, it is known that the image of a "flat" two-dimensional ugljena<sup>4</sup> net had to give way

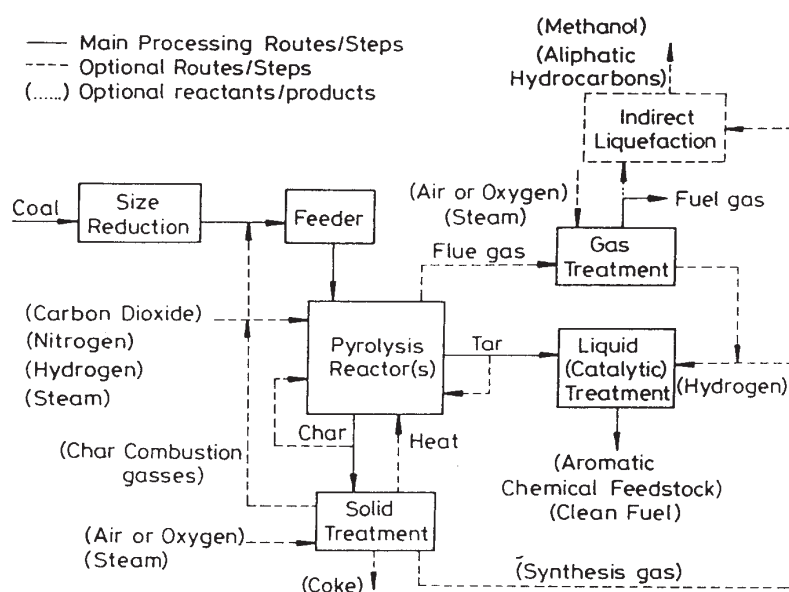


Fig. 1 – The basic coal pyrolysis process<sup>4</sup>

Slika 1 – Temeljni proces pirolize ugljena<sup>4</sup>

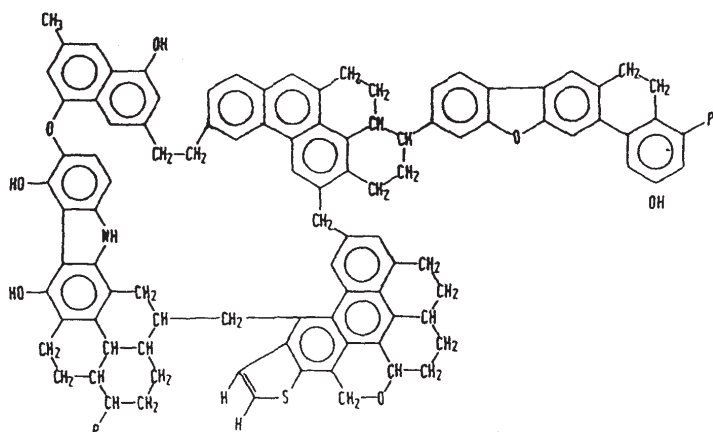
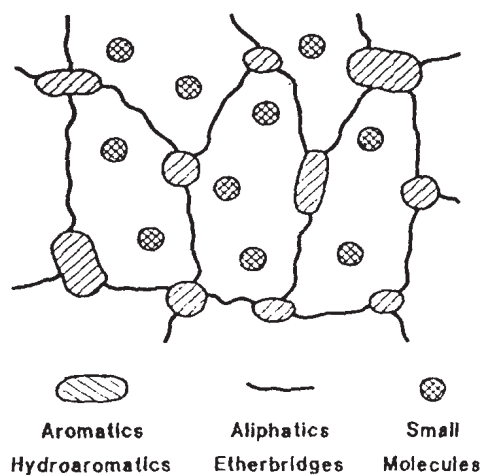


Fig. 2 – Model of the molecular structure of bituminous coal<sup>9</sup> ("P" is polymer sign)

Slika 2 – Model molekularne strukture bituminoznog ugljena<sup>9</sup> ("P" označuje polimer)

to a three-dimensional structure. This was indicated by *Given* and *Wender*<sup>14</sup> in their respective model figures, e. g. *Wender's* indication is a "P" for polymer in Fig 2. *Spiro* has given notice to this fact in the form of vivid space models in a very clear way.<sup>17,18</sup> An additional important feature is the discovery of 'guest molecules', hosted by the network, forming the so-called "mobile phase", first described by *Given* and co-workers (Fig. 3).<sup>19,20</sup>



### Characteristics :

#### 2-component system

- macromolecular  
3-dimensional network  
- immobile phase -
- various small molecules ,  
included in the network ,  
of very different structure  
- mobile phase -  
share : 10 - 50%

Fig. 3 – Chemical coal model after *Collin*, *Haenel* and *Zander*<sup>15,16</sup>

Slika 3 – Kemijski model ugljena *Collina*, *Haenela* i *Zandera*<sup>15,16</sup>

The models as explained above have been utilised with great success to investigate the mechanisms of pyrolysis, hydrogenation and hydrocracking reactions including the formation of the products and their control by experimental conditions.

The organic coal mass has a complex structure and consists of macromolecular and low-molecular phases.<sup>21-23</sup> The low-molecular phase predetermines coal properties in the plastic state. The macromolecular phase is a three-dimensionally ordered lattice structure (coal matrix). Cross links in coals can be of a physical and chemical nature. The thermoplastic properties are substantially affected by the density of these links (methylene, ethylene and ether bridges) which are observed just at the thermoplastic stage.<sup>24,25</sup>

It is also known that when coals are heated the atom groups, having different chemical bonds, disaggregate thermally. By their bond strength these groups can be put in the following row: carbonyl < anhydride < lactonic < ether methylene < heterocyclic < naphthene < aromatic (linear and angular). The transition of coals into the plastic state is preceded by the thermal destruction accompanied by disproportionation of hydrogen as well as by evolution of volatile matter (mainly coal tar and gaseous products). As a result of re-arrangement of atomic groups supermolecular coal structures become looser. That is why the higher swelling of carbonized coals in solvents can be connected not only with lower density of cross links but also with the re-arrangement of the molecular and supermolecular structure as a whole.<sup>12,26-28</sup>

### Mechanism of coal pyrolysis

Coals of different rank have very different thermal stabilities. The intensity of thermal decomposition (measured by the "Volatiles") – is the well-known parameter for the characterisation of rank. Coals with a high content of volatiles are the more interesting subject of research and are therefore mainly addressed when coal pyrolysis is being discussed.

On the basis of the chemical structure model of coal, *Jüntgen* has generated a reaction scheme for the description of the mechanism of coal pyrolysis.<sup>29</sup> Two different phases can be readily seen: the primary cleavage of weaker bonds between the aromatic units and the secondary reactions of further cracking, hydrogenation or agglomeration of the primary products resulting in gas, condensable liquids, and coke or char.

The mechanism of the primary and secondary coal pyrolysis reactions is shown in Fig. 4.

The mechanism of coal pyrolysis is summarized with the following main reaction steps (without diffusion of trapped molecules):

1. Cracking of the bridges between ring systems, with formation of radical groups.
2. Partial saturation of the radicals by hydrogen with formation of methane, other aliphatics, and water which diffuses out of the coal particles.
3. Simultaneous saturation of the radicals of the larger molecules to yield tar products (of medium molecular weight); diffusion from the coal particles.

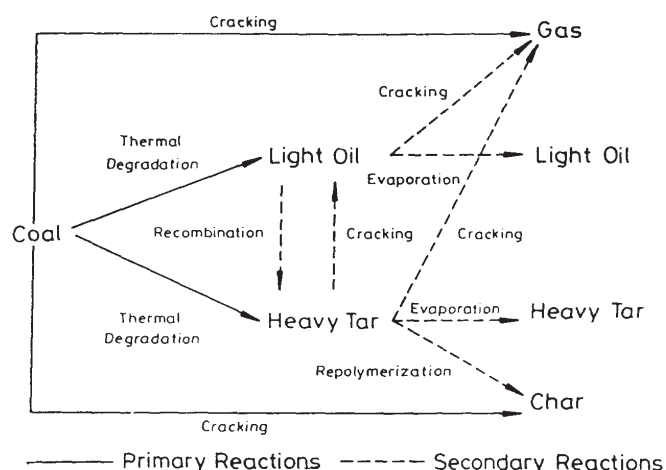


Fig. 4 – Model of the primary and secondary coal pyrolysis reactions<sup>4</sup>

Slika 4 – Model primarnih i sekundarnih reakcija pirolize ugljena<sup>4</sup>

4. Condensation of the substances of higher molecular weight to yield coke, with elimination of hydrogen which is also released as gas from the coal particle.

The above mechanism are supported by the carbon-, hydrogen-, and oxygen-balances both for the pyrolysis products as well as for the functional groups of the coal molecule. Paths of the pyrolysis reactions on the basis of coal's model as proposed by Jüntgen are shown in Fig. 5.

### Structural changes of the coal organic mass during pyrolysis

To better understand the pyrolysis behaviour of coal, it is desirable to reduce its complexity. One of the methods is to separate macerals from coal. Macerals are the microscopically identified organic components of coal and have distinct physical and chemical properties, which reflects differences in original plant during deposition and the degree of coalification or rank, and affects the overall behavior of the coal. Characterizing the chemistry of the individual maceral was the first step to further understanding of the whole coal. However, there is relatively little information on structure characteristics and chemical reactivity for macerals. This is partly due to the fact that it is very difficult to separate pure macerals from a parent coal. In the past, some works had been conducted on structural characteristics and chemical reactivity for macerals. Vassallo<sup>30</sup> studied the infrared spectroscopy of coal maceral concentrates during pyrolysis. Resinite, vitrinite and inertinite from three Chinese and one Australian coal were pyrolyzed under N<sub>2</sub> from room temperature up to 625 °C. They found that the main changes of resinite in chemical structure were the loss of protonated aliphatic carbon and a change in the distribution of carbon function groups. Pyrolysis of vitrinite produced increased absorption of protonated aromatic carbon, particularly in the 700–900 cm<sup>-1</sup>, but a steady decrease in intensity of 1600 cm<sup>-1</sup>. Inertinite showed no appreciable change in its infrared spectroscopy until 300 °C; above 300 °C the increased absorption in carbonyl region showed that some oxidation had occurred. Machnikowska<sup>31</sup> applied diffuse reflectance Fourier transform infrared (DRIFT) spectroscopy

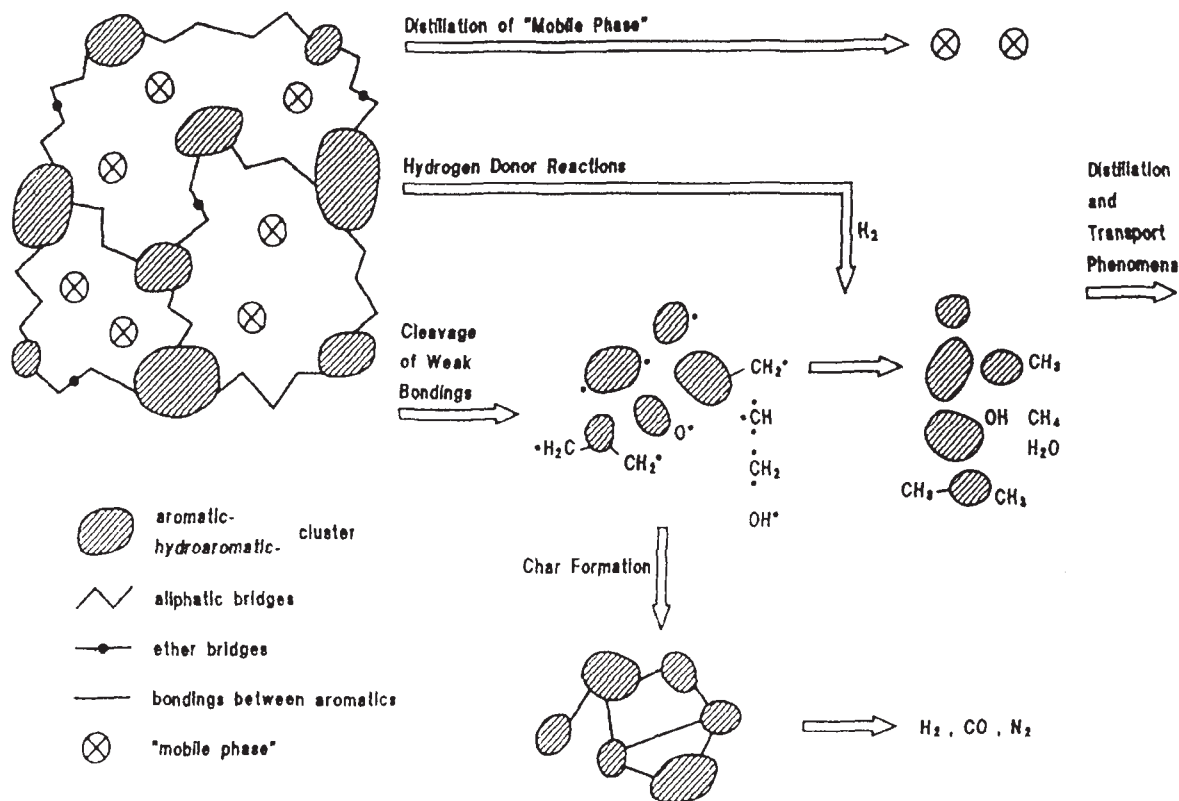


Fig. 5 – Paths of pyrolysis reactions on the basis of coal's structural model as proposed by Jüntgen<sup>29</sup>

Slika 5 – Smjer reakcija pirolize na bazi Jüntgenovog modela strukture ugljena<sup>29</sup>

to study the structure of vitrinite, liptinite and fusinite isolated from different rank coal (77.0–91.5 % C) using a centrifugation float-sink procedure. They found that  $CH_{ar}/CH_{al}$  ratio did not vary with carbon content in liptinite, but increased in vitrinite and fusinite in the case of liptinite and vitrinite, a linear relationship between  $CH_{ar}/CH_{al}$  and reflectance was observed. For all macerals, the  $CH_3/C=C$  increased with reflectance, but at different rate. Zilm et al.<sup>32</sup> studied the coal maceral concentrate isolated from several different subbituminous to high-volatile bituminous coals using CP/MAS spectroscopy. They found that aromaticities decreased in the order fusinite > vitrinite > sporinite > alginite. Based on the obtained data they concluded that macerals are chemically more homogenous than the parent coal.

The ultimate analysis, FTIR and NMR were used to investigate the Chinese bituminous coal and the structural characteristics of the vitrinite and inertinite before and after pyrolysis.<sup>33</sup> The results indicated that vitrinite had lower carbon content, more aliphatic C–H and hydrogen bonding, higher evolution of light hydrocarbons ( $C_2$ – $C_4$ ) and lower aromaticity than inertinite. Vitrinite char always had higher H and lower C content than inertinite char at the same pyrolysis temperature. With increasing temperature the weaker aliphatic chains are gradually broken and finally left is the aromatic carbon skeleton, which led to the increase of the aromaticity. Hence, higher aromaticity and lower aliphatic carbon content of inertinite should be able to explain the fact, that inertinite had higher thermal stability and lower volatile matter yield than vitrinite during pyrolysis.

Studying the thermochemical transformations during carbonization, especially coal pyrolysis products and coal macerals, it was found that the amount of aliphatic CH bonds decreases with the temperature rising at the plasticity stage, so the content of aromatic CH-links increases. During heating, the aliphatic chains break gradually, and leave the carbon frame during devolatilization with lead to an increase in aromaticity. The density of cross-links increases during re-solidification of the coal plastic mass.<sup>24,34-36</sup>

According to the X-ray data the organic mass of coals is represented by the two phases: an ordered and nonordered (amorphous) ones.<sup>37,38</sup> In the stage of carbonisation *in vacuo* under 500 °C the 'evaporation of edge- and interstitial groups' occurs in the amorphous material that brings the remaining aromatic nuclei into a high reactive state. These nuclei at the temperature over 500 °C and appropriate orientation can coalesce to form larger layers. The processes, however, occurring during heating coals at the atmospheric pressure with the absence of air are characterized, as a rule, by greater complication. Two concurrent reactions proceed within the organic mass when heated with the absence of air: depolymerization on the one hand and condensation and secondary polymerisation on the other hand.<sup>39</sup> Cyclic polymerisation processes can lead to an increase in the ordered phase. However, it remains unclear whether the relationship between the devolatilization and cyclic polymerisation of coals of different caking capacity during conventional heating exists and what is the influence of the latter on the plastic properties of coal. Till now it has not been found how the amount of the ordered phase changes at different stages of carbonization (preplastic, plastic, and resolidification).

## Modelling of pyrolytic reactions

Pyrolysis has been modelled by the simultaneous occurrence of two reactions that compete for the hydrogen content in coal. The first reaction, of low activation energy, releases volatiles of high H/C ratio (mainly heavy tars) while the second reaction, of high activation energy and hence predominant at high temperatures, generates volatiles of low H/C ratio. Thus, the pyrolysis yield increases as the coal hydrogen is preferably released through the high temperature reactions. On the other hand, the favourable effect of high heating rate on the volatiles yield is related to a lesser occurrence of secondary re-polymerization and cracking reactions of the reactive fragments initially formed, thus producing a fast vaporization and release of volatiles from the carbonaceous structure.

Different approaches for the pyrolysis modelling are found in the literature.<sup>10,11,40-46</sup> They include those that consider a global kinetics and a simple reaction as well as more complex ones, such as multiple reactions and network models, based on the physicochemical description of the coal structure.

Simple reaction models consider the occurrence of a first order reaction with respect to the remnant volatile fraction, neglecting the intrinsically complex nature of pyrolysis.<sup>4,29</sup>

The decomposition of a substance e. g.:



can be described as:  $-\frac{dc_s}{dt} = k c_s = r$

with

- $r$  – reaction rate  
– brzina reakcije
- $c_s$  – concentration of the substance  
– koncentracija supstancije
- $k$  – reaction rate coefficient  
– koeficijent brzine reakcije

Assuming the pyrolytic reaction is of first order in terms of the functional groups decomposed and taking into account both the relation between temperature and time (which is determined by the heating rate) and the temperature dependency of a reaction rate (reflected by the Arrhenius' law) an expression of the reaction rate is obtained:

$$\frac{dV}{dT} = \frac{k_0}{v} V_0 \exp\left\{-\frac{E}{RT} - \frac{k_0}{v} \frac{RT^2}{E} \exp\left(-\frac{E}{RT}\right)\right\}$$

where:

- $dV/dT$  – rate of evolution of a given gaseous product,  $cm^3 K^{-1}$   
– brzina isplinjavanja,  $cm^3 K^{-1}$
- $k_0$  – frequency factor,  $s^{-1}$   
– frekventni čimbenik,  $s^{-1}$
- $v$  – rate of temperature rising,  $dT/dt$ ,  $Ks^{-1}$   
– brzina podizanja temperature,  $dT/dt$ ,  $Ks^{-1}$
- $E$  – activation energy,  $J mol^{-1}$   
– energija aktivacije,  $J mol^{-1}$
- $T$  – temperature, K  
– temperatura, K
- $R$  – gas constant,  $J mol^{-1} K^{-1}$   
– opća plinska konstanta,  $J mol^{-1} K^{-1}$
- $V_0$  – total volume of resulting gas during pyrolysis,  $cm^3$   
– ukupan obujam plina razvijen pirolizom,  $cm^3$



This consists of the product of two exponential functions, the first describing the temperature dependency, and the second, the dependency on concentration. The reaction rate, therefore, initially increases and with increasing temperature passes through a maximum, and then falls off. Fig. 6 represents the kinetic curves of gaseous product (methane and hydrogen) formation during coal pyrolysis in non-isothermal conditions.<sup>40</sup> The reaction order can be derived from the shape of the curve; there is a slow rise and a steep decline for  $n = 1$ , and  $n = 2$  gives an almost symmetrical curve. Activation energy and frequency factors can be determined by the temperature level of the maximum and by the half-value width of the curve.

A more complicated model, referred to as the distributed rate model, assumes pyrolysis to occur through an infinite series of parallel, independent reactions. In this model, a distribution of activation energies and a common value for the frequency factor are used, and the continuous distribution is described by a Gaussian function.

The network model considers phenomenological aspects of the pyrolysis, allowing a better representation of the process. But, they require a significant computer effort and additional calculations for the kinetic parameter estimation. Attractive is an intermediate approach as work of *Ulloa* at all.<sup>46</sup> They have described the modelling of the pyrolysis of coal blends under conditions similar to those found in a pulverized coal boiler with a multiple reaction model and distribution of activation energy model.

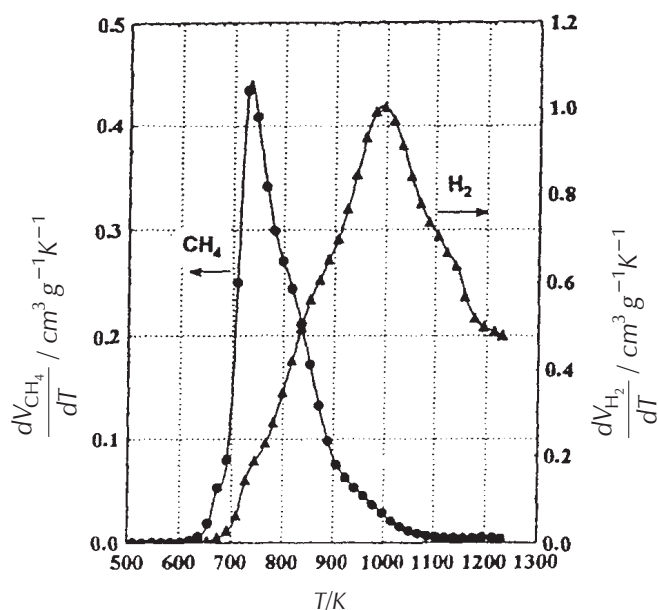


Fig. 6 – Rates of methane and hydrogen formation during coal pyrolysis: (•) methane, (▲) hydrogen<sup>40</sup>.

Slika 6 – Brzina nastajanja metana i vodika tijekom pirolize ugljena: (•) metan, (▲) vodik<sup>40</sup>.

**Effect of reaction parameters on pyrolysis**

**Temperature** is the most important parameter affecting pyrolysis. Other important variables that influence the nature of the products from coal pyrolysis are pressure, coal partic-

le size, atmosphere, heating rate and coal type as well as the type of reactor used.<sup>2-12, 47-50</sup>

Pyrolysis processes involve the destructive distillation of organic substances by thermal energy in the absence of air. The products are highly carbonaceous residue (coke or char), together with liquids and gases. Coke or char is nearly always the main product.<sup>6,51</sup>

The liquid products after secondary processing yield a variety of chemicals that historically formed the start of the organic chemical industry before the dominance of petrochemicals. The gases produced during carbonization are mainly used as fuel.

Table 1 – Temperature regions in coal pyrolysis<sup>6</sup>

Tablica 1 – Temperaturna područja pirolize ugljena<sup>6</sup>

Region Područje	Temperature, °C Temperatura, °C	Reactions Reakcije	Products Proizvodi	Use Uporaba
	< 350	mainly evaporation uglavnom isparavanje	water and volatile organics voda i isparljive organske tvari	fundamental osnovna
low niska	400 – 750	primary degradation primarna razgradnja	gas, tar and liquor plin, katran i tekućina	smokeless fuels and chemicals bezdimna goriva i kemikalije
medium srednja	750 – 900	secondary reactions sekundarne reakcije	gas, tar plus additional hydrogen plin, tekući katran plus dodatni vodik	smokeless fuels and chemicals metallurgical coke
high visoka	900 – 1100			bezdimna goriva i kemikalije metalurški koks
plasma plazma	> 1650		acetylene carbon black acetilen čađa	uneconomic neekonomična

Table 1 shows temperature regions in coal pyrolysis. When coals are heated below 350 °C they begin to lose weight. Initially, this is due to loss of water, (even below 100 °C); hydrocarbons, including aromatic hydrocarbons such as benzene and toluene and even HCl, are released from coal. The volatiles, obtained at these relatively low temperatures, have evaporated from the coal matrix rather than being formed by thermal breakdown of the coal molecule. At the temperature increase (400–750 °C) the yield of gas increases, while that of the char decreases. The yields of the bulk products obtained by low-temperature carbonization are

compared with those achieved in high-temperature carbonisation in Table 2. The major differences are the much increased yield of gas and corresponding reductions in the yields of liquor, light oils, and tar. There is also a small increase in the yield of coke, which results from the production of some carbonaceous products during the thermal cracking that occurs during high-temperature carbonization.

Table 2 – Product yields from low (400–750 °C) and high (900–1100 °C) temperature of carbonization<sup>6</sup>

Tablica 2 – Produkti karbonizacije ugljena pri niskim (400–750 °C) i visokim (900–1100 °C) temperaturama<sup>6</sup>

Products Produkti	Carbonization Karbonizacija	
	low-temperature niskotemperaturna w/%	high-temperature visokotemperaturna w/%
gas plin	7.6	17.2
liquor kapljevina	13.0	2.5
light oils laka ulja	1.4	0.8
tar katran	8.0	4.5
coke koks	70.0	75.0

Region between 900 °C and 1100 °C is the most important temperature region concentrating on the production of coke for the iron and steel industry. The product yield from high-temperature carbonization has already been given in Table 2. Gas (17.2 %) and coke (75 %) account well for over 90 % of the products.

Coke is a highly carbonaceous product of coal pyrolysis which have passed through a liquid of liquid – crystalline state (mesophase stages) during the carbonization process. Generally, carbonaceous mesophase, first reported by Brooks and Taylor,<sup>52</sup> is a discotic liquid crystal that appears during the condensed-phase carbonization of many but not all organic materials, that pass through a fluid state during thermal decomposition. The stages of mesophase formation within, e. g. pyrolyzing coals (and pitches) are as follows:<sup>53,54</sup>

1. The increase in average molecular weight of the constituent molecules of the system, i. e. the so-called mesogen molecule.
2. The self-assembly of mesogens to form nematic liquid crystals known as the mesophase spheres.
3. Growth in size of these mesophase spheres.
4. Coalescence of mesophase spheres, on contact, to form bulk mesophase.
5. Solidification of mesophase to form coke.

Chars from coal pyrolyzed at temperatures below 1000 °C have a medium reactivity, whereas metallurgical coke (or

pitch coke), produced at higher temperatures, shows distinctly lower values.<sup>55</sup>

At temperatures above 1650 °C the formation of acetylene and other unsaturated hydrocarbons is thermodynamically favoured and the quenched gas derived from coal heated to these temperatures is rich in acetylene. The gas obtained at these very high temperatures contains relatively little saturated hydrocarbons and negligible tar is produced as nearly all the volatiles are cracked to gaseous components. Carbon black is an important by-product from the plasma pyrolysis of coal, probably derived as much from decomposition of some of the acetylene produced as from the coal itself. Unfortunately, the separating of this finely divided carbon from the residual char is very costly and quench medium used to prevent further decomposition of the acetylene.<sup>12</sup>

The effect of **pressure** depends on the nature of the pressurising gas. If the pressurising gas is inert, a decrease in the tar and total volatile yields is observed with increasing pressure. The observed decrease in the volatile yield is due to increases in the mass transfer resistances during the transport of the volatiles both from the site of formation to the surface of the coal particle and from the surface of the particle into the bulk gas phase.<sup>56</sup>

The effect of heating coal in **reactive atmospheres** is quite different from that observed when using an inert medium, especially at elevated pressure. The most extensively investigated reactive gas is hydrogen. Hydrolysis is the reaction between coal and hydrogen at elevated temperatures and pressures. The term hydrogasification being used when methane is the desired product.<sup>29</sup>

Whereas, increase in the pressure of an inert gas reduces volatile evolution, hydrogen interacts with the coal substance to bring about an increase, which becomes appreciable at high pressures.

It was stated that at high **rate of temperature rising**, tar devolatilisation shifts to higher temperatures and the maximum devolatilisation rate of pyrolysis increases. However, the effect of the heating rate could not be isolated from the effect of reactor geometry. Experiments with a wire-mesh reactor that can cover a wide range, (0.5 °C s<sup>-1</sup> to 1000 °C s<sup>-1</sup>), show the effect of the heating rate on total volatile and tar yields independent of the other parameters. The increase in the heating rate increases both the total volatile and the tar yields.<sup>4,50</sup> These experiments were carried out with 30 s hold time at the maximum temperature (900 °C). The effect of secondary reactions can be seen when the yields from the hot-rod reactor and wire mesh reactor are compared. The effect of rapid heating as in the achieved with stirred reactors, fluidised beds, wire mesh heaters, and entrained flow reactors is to increase the yield of volatiles, specially tar, over that obtained in fixed bed equipment such as used in standard assay tests, like Fischer or Gray-King. The increase is brought about by the nature of the equipment necessary to achieve rapid heating rather than the rapid heating itself.<sup>57</sup> For rapid heating, fine coal in a dispersed phase is used which has the effect of reducing secondary reactions. If coal is heated at different rates in the same reactor using a wire mesh heater, then there is no difference in total weight loss.

The **particle diameter** of the coal affect the transport of volatiles from the site at which they are formed to the surface of the coal particle.<sup>48,58</sup> Increasing the particle size of the coal increases the residence time of the volatiles in the particle. This increase of residence time enhances the likelihood of secondary reactions in the particle, the temperature gradient within the particle is also high. The combined effect of heat and mass transfer on the pyrolysis rate becomes significant.

**Coal type** (rank) is often regarded as the major factor governing the utilization characteristics of a given feedstock. Coal rank, usually measured by its carbon content and its maceral composition, affects on the carbonization behaviour of the coal.<sup>59-62</sup> For bituminous coals, the main volatile product of pyrolysis is tar. The proportion of hydrocarbon gases, water, and carbon oxides in the volatile products increases at the expense of tar, as the rank of the coal is changed from bituminous to subbituminous coals and lignites.

## Coal pyrolysis and environment

The major problem for coal utilization is the emission of pollutants to the environment. During pyrolysis of coal some parts of inorganic elements contained in the coal are released. In particular the air cleanness is at risk as result of emission of dusts and gases including sulphur oxides, carbon monoxide and nitric oxide and numerous organic aromatic polynuclear hydrocarbons. Potentially hazardous air polluting elements such as As, Be, Cd, Co, Cr, Hg, Mn, Ni, Pb, Sb, Se, V, Zr are present in coal as trace elements (concentrations  $w < 100 \mu\text{g g}^{-1}$ ). The emission behaviour of the trace elements during coal processes varies with elements, chemical forms of the elements, coal type and processing conditions. Many researchers have examined the relationship between inorganic components and the reactivity of organic matter conversion in coal during pyrolysis, but little has been reported on the relationship between inorganic matter and the kinetics of coal pyrolysis.<sup>63-77</sup>

According to the thermodynamic equilibrium calculation, vaporization tendency of minor elements in coal is (K, Na, P, Mg) > (Ca, Mn) > (Fe, Ti) > (Si, Al).<sup>78</sup> Coal type, ash component and oxidation / reduction condition affect on the partitioning of these elements.<sup>79</sup> For example, Sugawara et al.<sup>73</sup> reported release behaviour of Na, K and Se in coal during pyrolysis. Effects of temperature (300–1000 °C), atmosphere (N<sub>2</sub> and H<sub>2</sub>), and holding time (0,3–10 min) on release behaviour of As, Pb, Cd, Cr and Mn in pyrolysis of Datong coal (China) are studied in a closed, simulated drop-tube reactor.<sup>63</sup> The coal and the trace elements, except As, are stable at 300 °C. At temperatures greater than 300 °C, the release of the trace elements increase with increasing pyrolysis temperature. H<sub>2</sub> atmosphere and release of volatiles from the coal promote the release of all the investigated elements. As, Pb and Cd show similar behaviour and their volatilities are higher than that of Cr and Mn. The elements which undergo the transformation are resulting in reduced content in the char.

Keener et al.<sup>80</sup> proposed a mild pyrolysis method to remove mercury from coal, based on the high volatility of these element. Obtained results are shown that more than 50 % of mercury in a coal released at temperatures as low as 300 °C

in 10 min. Authors<sup>9</sup> refer to the dynamics of the release of some selected trace elements (As, Be, Cd, Mn, Ni, Pb, Hg and Se) at carbonization temperatures 400°, 600°, 850° and 1000 °C. During coal carbonization some parts of investigated elements are released. The release rate is the highest for Cd, Hg and Pb, mean for Se, and the lowest for Ni, Mn, As and Be.

Turning of the great part of the trace elements into gaseous products during carbonization proves that the limited airtight sealing of the coal coking process, as well as coke-oven gas combustion, contribute to the pollution of the environment with trace elements. During Yima coal pyrolysis, the volatilities of Pb and Cd vary greatly with temperature, while volatility of Cr only has slight changes over the temperature range (500–900 °C). The modes of occurrence of Pb, Cd, Cr in coal and char samples were determined.<sup>72</sup>

From the viewpoint of environmental protection, it is an important subject to reduce sulfur content of coal prior to use. For this purpose, the transformation of coal sulfur during pyrolysis has been extensively investigated. It is known that sulfur in coal exists in both inorganic and organic forms.<sup>81</sup> The inorganic sulfur exists mostly as pyrite and for marcasite with a small amount of sulfates. The organic sulfur exists either in aromatic rings or in aliphatic functional groups, usually categorized as mercaptans, aliphatic and aryl sulfides, disulfides, and thiophenes. The functionality distribution of organic sulfur varies from coal to coal even for the same rank.<sup>82</sup> In pyrolysis, pyrite transforms into sulfide and sulfur at temperature above 350 °C. The nascent sulfur is very active, and it captures hydrogen from coal to form H<sub>2</sub>S that converts to gas, or is captured by organic matrix to form organic sulfur that remains in char or tar. Part of them is fixed by mineral matters in coal, mainly calcium, sodium and iron compounds, to form sulfide that remains in char. The behaviour of organic sulfur during pyrolysis depends on the functionality; the larger the proportion of organic sulfurs in non-thiophenic structures in coal, the greater the extent of organic sulfur removal is.<sup>65,68,83,84</sup>

Among the reaction conditions (heating rate, time, pressure, type of reactor, velocity of carrying gas etc.) temperature is most important factor affecting the transformation of sulfur during coal pyrolysis. The external hydrogen and a high heating rate is preferred.<sup>69,76,84-86</sup> According to literature data<sup>76</sup> sulfur removal during coal pyrolysis at different conditions varies from 15 % to 40 % depending on coal sample, pyrolysis temperature, and time. Under oxidative conditions the emitted sulphur is mainly SO<sub>2</sub>, while under reductive conditions is mainly H<sub>2</sub>S. During pyrolysis under inert, lean oxygen or lean hydrogen atmospheres other sulfur species may also form, such as COS, CH<sub>3</sub>SH, CS<sub>2</sub>, and thiophene. The gaseous hydrocarbon compounds are also released, which include usually CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>8</sub>, and C<sub>4</sub>H<sub>10</sub>.

## Conclusion

Coal pyrolysis has been widely investigated, and many useful results have been obtained. Pyrolysis is the initial step in all thermal conversion processes of coal. For the understanding of the basic chemical reactions during thermal decomposition of coal, it is necessary to start from the knowledge



about the molecular structure of the coal. In pyrolysis, coal is converted thermally into gas, liquid and solid products through primary devolatilisation reactions. Thermally unstable primary volatile products can undergo secondary reactions. Such reactions lead either to cracking into smaller molecular mass tar or repolymerisation towards coke or char production. Coke (or char) is nearly always the main product. The significant factor among pyrolysis conditions are temperature, coal type, heating rate, but other factors such as time, pressure, velocity of carrying gas, type of reactor, etc., also play important roles during coal pyrolysis.

Most of the pollutants could be removed by optimising the pyrolysis conditions. Transformation of any inorganic elements in coal (especially trace elements), sulphur and nitrogen compounds, by heat treatment is essential for effective and economic removal, and consequently for environmental protection.

## Literatura References

1. C. Song, H. H. Schobert, *Fuel Process. Technol.* **34** (1993) 157.
2. K. Miura, *Fuel Process. Technol.* **62** (2000) 119.
3. H. H. Schobert, C. Song, *Fuel* **81** (2002) 15.
4. O. Kural, *Coal*, Istanbul Technical University, Istanbul, 1994, pp. 337-351.
5. G. Gryglewicz, *Fuel Process. Technol.* **46** (1996) 217.
6. W. R. Ladner, *Fuel Process. Technol.* **20** (1988) 207.
7. Q. Liu, H. Hu, Q. Zhou, Sh. Zhu, G. Chen, *Fuel* **83** (2004) 713.
8. W. C. Xu, M. Kumagai, *Fuel* **82** (2003) 245.
9. K. H. van Heek, *Fuel* **79** (2000) 1.
10. W. Wanzl, *Fuel Process. Technol.* **20** (1988) 317.
11. L. P. Wiktorson, W. Wanzl, *Fuel* **79** (2000) 701.
12. R. Loison, P. Foch, A. Boyer, *Coke, Quality and Production*, Butterworths, London, 1989, pp. 25-59.
13. J. H. Shin, *Fuel* **63** (1984) 1187.
14. I. Wender, *Chemical reactions and the constitution of coal. Chemistry of coal utilization*, New York, Wiley, 1981, pp. 520.
15. M. W. Haenel, G. Collin, M. Zander, *Erdöl Erdgas Kohle* **105** (1989) 71.
16. M. W. Haenel, *Fuel* **71** (1992) 1211.
17. C. L. Spiro, *Fuel* **60** (1981) 1121.
18. C. L. Spiro, *Fuel* **61** (1982) 1080.
19. P. H. Given, A. Marzec, W. A. Barton, L. I. Linch, B. C. Gerstein, *Fuel* **65** (1986) 155.
20. P. H. Given, A. Marzec, *Fuel* **67** (1988) 242.
21. A. Marzec, *Fuel Process. Technol.* **14** (1986) 39.
22. J. N. Rouzand, D. Vogt, A. Oberlin, *Fuel Process. Technol.* **20** (1988) 143.
23. F. Fortin, J. N. Rouzand, *Fuel* **72** (1993) 245.
24. F. E. Ndaji, I. M. Butterfield, K. M. Thomas, *Fuel* **76** (1997) 169.
25. V. V. Zubkova, *Fuel* **84** (2005) 741.
26. A. I. Olfert, J. A. Fessenko, J. B. Amerik, *Koks i Khimiya* (1986) 3,7.
27. M. G. Sklyar, J. S. Vasilev, N. A. Valters, E. M. Soldatenko, V. V. Zubkova, *Koks i Khimiya* (1986) 6,13.
28. K. H. van Heek, W. Hodek, *Fuel* **73** (1994) 886.
29. H. Jüntgen, *Fuel* **63** (1984) 731.
30. A. M. Vassallo, Y. L. Liu, LSK. Pang, M. A. Wilson, *Fuel* **70** (1991) 635.
31. H. Machnikowska, A. Krztoń, J. Machnikowski, *Fuel* **81** (2002) 245.
32. K. W. Zilm, RJ Pugmire, SR Larter, L. Allan, DM. Grant, *Fuel* **60** (1981) 717.
33. Q. Sun, W. Li, H. Chen, B. Li, *Fuel* **82** (2003) 669.
34. S. Namura, K. M. Thomas, *Fuel* **77** (1998) 829.
35. P. R. Solomon, M. A. Serio, G. V. Despande, E. Kroo, *Energy Fuels* **4** (1990) 42.
36. P. R. Solomon, D. G. Hamblen, M. A. Serio, *Fuel* **69** (1990) 754.
37. L. Lu, V. Sahajawalla, C. Kong, D. Hawis, *Carbon*, **39** (2001) 1821.
38. D. L. Wertz, *Fuel* **77** (1998) 43.
39. A. M. Mastral, M. T. Izquierdo, B. Rubio, C. Mayoral, *Carbon* **30** (1992) 375.
40. S. Porada, *Fuel* **83** (2004) 1191.
41. S. Niksa, *Combust. Flame* **100** (1995) 384.
42. S. Niksa, *Energy Fuels* **5** (1991) 673.
43. Y. Tian, K. Xie, S. Zhu, T. H. Fletcher, *Energy Fuels* **15** (2001) 1354.
44. L. Xu, J. Yang, Y. Li, Zh. Liu, *J. Anal. Appl. Pyrolysis* **71** (2004) 591.
45. E. Donskoi, D. L. McElwain, *Fuel* **78** (1999) 825.
46. C. Ulloa, A. L. Gordon, X. Garcia, *J. Anal. Appl. Pyrolysis* **71** (2004) 465.
47. V. Seebauer, J. Petek, G. Staudinger, *Fuel* **76** (1997) 1277.
48. S. Hanson, J. W. Patrick, A. Walker, *Fuel* **81** (2002) 531.
49. A. G. Borrego, G. Marban, M. J. Alonso, D. Alvarez, R. Menendez, *Energy Fuels* **14** (2000) 117.
50. J. R. Gibbins, Z. S. Gönenc, R. Kandiyoti, *Fuel* **70** (1991) 621.
51. A. Arenillas, F. Rubiera, C. Pevida, J. J. Pis, *J. Anal. Appl. Pyrolysis* **58/59** (2001) 685.
52. J. D. Brooks, G. H. Taylor, *Nature* **206** (1965) 697.
53. Y. Hu, R. H. Hurt, *Carbon* **39** (2001) 887.
54. R. Menendez, M. Granda, J. Bermejo, In: H. Marsk, E. A. Heintz, F. Rodriguez-Reinoso, (Eds), *Introduction to carbon technologies*, University of Alicante, 1997, pp. 461-490.
55. F. Fortin, J. N. Rouzand, *Fuel* **73** (1994) 795.
56. J. R. Gibbins, Z. S. Gönenc, R. Kandiyoti, *Fuel* **70** (1991) 621.
57. G. R. Johnson, P. Murdoch, A. Williams, *Fuel* **67** (1989) 834.
58. J. N. Rouzand, E. Totino, J. M. Guet, J. Kister, *Fuel Process. Technol.* **20** (1988) 133.
59. H. Takagi, K. Maruyama, N. Yoshizawa, Y. Yamada, Y. Sato, *Fuel* **83** (2004) 2427.
60. R. Sakurovs, *Fuel* **82** (2003) 439.
61. J. H. Slaghuys, L. C. Ferreira, M. R. Judd, *Fuel* **70** (1991) 471.
62. K. Ch. Xie, Y. F. Zhang, Ch. Zhn. Li, D. Q. Ling, *Fuel* **70** (1991) 474.
63. R. Guo, J. Yang, Z. Liu, *Fuel* **83** (2004) 639.
64. N. A. Oztas, Y. Yurum, *Fuel* **79** (2000) 1221.
65. P. Samaras, E. Diamadopoulou, G. P. Sakekarpoulos, *Fuel* **75** (1996) 1108.
66. D. P. Ye, J. B. Agnew, D. K. Zhang, *Fuel* **77** (1998) 1209.
67. R. L. Meormick, M. C. Jha, *Energy Fuels* **96** (1995) 1043.
68. T. Kyotani, K. Kubot, J. Cao, H. Yamashita, A. Tomita, *Fuel Process. Technol.* **36** (1993) 209.
69. T. P. Yakovleva, Y. B. Dolzhanskaya, *Koks i Khimiya* (1995) 5, 31.
70. Q. Liu, H. Hu, Q. Zhou, Sh. Zhu, G. Chen, *Fuel* **83** (2004) 713.



71. E. Z. Zubek, J. Konieczynski, *Fuel* **82** (2003) 1281.
72. H. Lu, H. Chen, W. Li, B. Li, *Fuel* **83** (2004) 39.
73. K. Sugawara, Y. Enda, H. Inoue, T. Sugawara, M. Shirai, *Fuel* **81** (2002) 1439.
74. R. Guo, J. Yang, Z. Liu, *Fuel Process. Technol.* **77/78** (2002) 137.
75. Y. Soneda, M. Makino, H. Yasuda, O. Yamada, M. Kobayashi, M. Kaiho, *Fuel* **77** (1998) 907.
76. H. Hu, Q. Zhou, S. Zhu, B. Meyer, S. Krzack, G. Chew, *Fuel Process. Technol.* **85** (2004) 849.
77. W. C. Xu, M. Kumagai, *Fuel* **82** (2003) 245.
78. R. Yan, F. Gauthier, J. M. Badie, *Fuel* **78** (1999) 1817.
79. D. Thompson, B. Argent, *Fuel* **78** (1999) 1679.
80. T. C. Keener, A. C. Gieske, S. J. Khang, *Proc. of 8<sup>th</sup> Int. Conf. on coal science*, Vol. II, Elsevier, Oviedo, 1995, pp. 1605.
81. A. Rađenović, *Kem. Ind.* **53** (2004) 557.
82. I. I. Maes, G. Gryglewicz, H. Machnikowska, J. Yperman, D. V. Franco, J. Muelens, L. C. Poucke, *Fuel* **76** (1997) 391.
83. H. K. Chen, B. Q. Li, B. J. Zhang, *Fuel* **79** (2000) 1627.
84. K. Sugawara, Y. Tozuka, T. Sugawara, Y. Nishiyama, *Fuel Process. Technol.* **37** (1994) 73.
85. H. K. Chen, B. Q. Li, J. L. Yang, B. J. Zhang, *Fuel* **77** (1998) 487.
86. L. Xu, J. Yang, Y. Li, Zh. Liu, *J. Anal. Appl. Pyrolysis* **71** (2004) 591.

## SAŽETAK

### Piroлиза ugljena

A. Rađenović

Neovisno o tome da li se ugljen rabi za proizvodnju energije, ugljičnih materijala ili kemikalija, piroliza je početni korak procesa njegove konverzije. S obzirom na važnost i značenje još uvijek je predmetom brojnih istraživanja.

Piroлиза je proces zagrijavanja ugljena bez pristupa zraka kojim se dobivaju razni čvrsti, tekući i plinoviti produkti. Iako prema ovoj osnovnoj definiciji piroliza predstavlja jednostavan proces, u praksi on je složen od brojnih kemijskih reakcija i fizikalnih promjena koje opisuju razni mehanizmi. Za bolje razumijevanje mogućih reakcija i mehanizama u radu je ukazano na povezanost strukture ugljena i pirolize. Izdvojen je mehanizam pirolize najbliži stvarnim promjenama u strukturi (maceralima) ugljena pod utjecajem topline. Na dobivanje produkata primarnim i sekundarnim reakcijama utječu brojni faktori (temperatura, tlak, atmosfera, brzina i vrijeme zagrijavanja, vrsta ugljena, i sl.). Temperatura se izdvaja kao najvažniji faktor, a koks kao najčešće glavni produkt pirolize. Ukazano je na povezanost produkata karbonizacije pri niskim (400–750 °C) i visokim (750–1100 °C) temperaturama s reakcijama odgovornim za njihovo dobivanje i uporabu.

Kao složena smjesa organskih i anorganskih tvari, ugljen može biti izvor brojnih onečišćivača okoliša. Optimiranjem procesnih parametara moguće je utjecati na emisiju štetnih tvari (naročito anorganskih elemenata u tragovima i spojeva sumpora i dušika) odnosno na smanjenje njihovog sadržaja u produktima pirolize.

Sveučilište u Zagrebu, Metalurški fakultet,  
Aleja narodnih heroja 3, 44000 Sisak, Hrvatska

Prispjelo 20. prosinca 2005.  
Prihvaćeno 2. ožujka 2006.