

Hydrogen-containing gaseous combustion products encountered during fires breaking out at North-Bohemian brown coal mines.

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- The paper is intended to assist elucidating the mechanism whereby combustible components are formed in the gaseous products generated during fires and conflagrations breaking out in the longwall faces of brown coal mines in the North Bohemian mining district. It is focused on the effect of hydrogen upon the explosion risks faced in cases where the combustion products become blended with brown coal dust.
- It presents the results of technical analyses of the products formed during fires, with particular attention to hydrogen.
- It presents the results of experimental pyrolytic tests carried out for the purpose of clarifying the preponderant hydrogen formation mechanism.
- Based on the results presented it renders more accurate the notions passed on among the rescue services concerning the degree of danger faced in cases of hydrogen occurring as a consequence of fires being fought by means of pressure water.

Mining technology and the fire hazard.

- Mechanized longwall extraction of thick, multi-bench brown coal seams represents the chief mining technology used at the Centrum Mine in Horní Jiřetín, Czech Rep. High tendency to spontaneous fires coupled with a high rate of progress of the self-ignition process are characteristic features of the seams; this brings about a high risk of endogeneous fires of which a number have actually occurred.
- At the initial stage, the fires breaking out in the longwall faces and in the caved fields produced by fall of face often tend to include several smaller, dispersed fire sources which are difficult to access.
- At the beginning the direct liquidation of such fires involves direct firefighting where pressure water is either injected into the caved ground and in-between the sections of supports using the forepoling technique or is applied via 'lost' piping.
- The goal is to effectively dampen the focal points of the fires and to leave them in the caved ground while the longwall extraction continues, thus employing to advantage the self-inertizing properties of the atmosphere present in the caved-in field to subdue the fire. Fire suppression tends to be a process extending over considerable periods of time. In certain cases, even the heavy and medium-weight mechanical nitrogen foams were applied.
- In cases where the fire cannot effectively be constrained and extinguished by the aforementioned methods, explosion-resistant underground dams are constructed immediately to seal off the entire affected area.

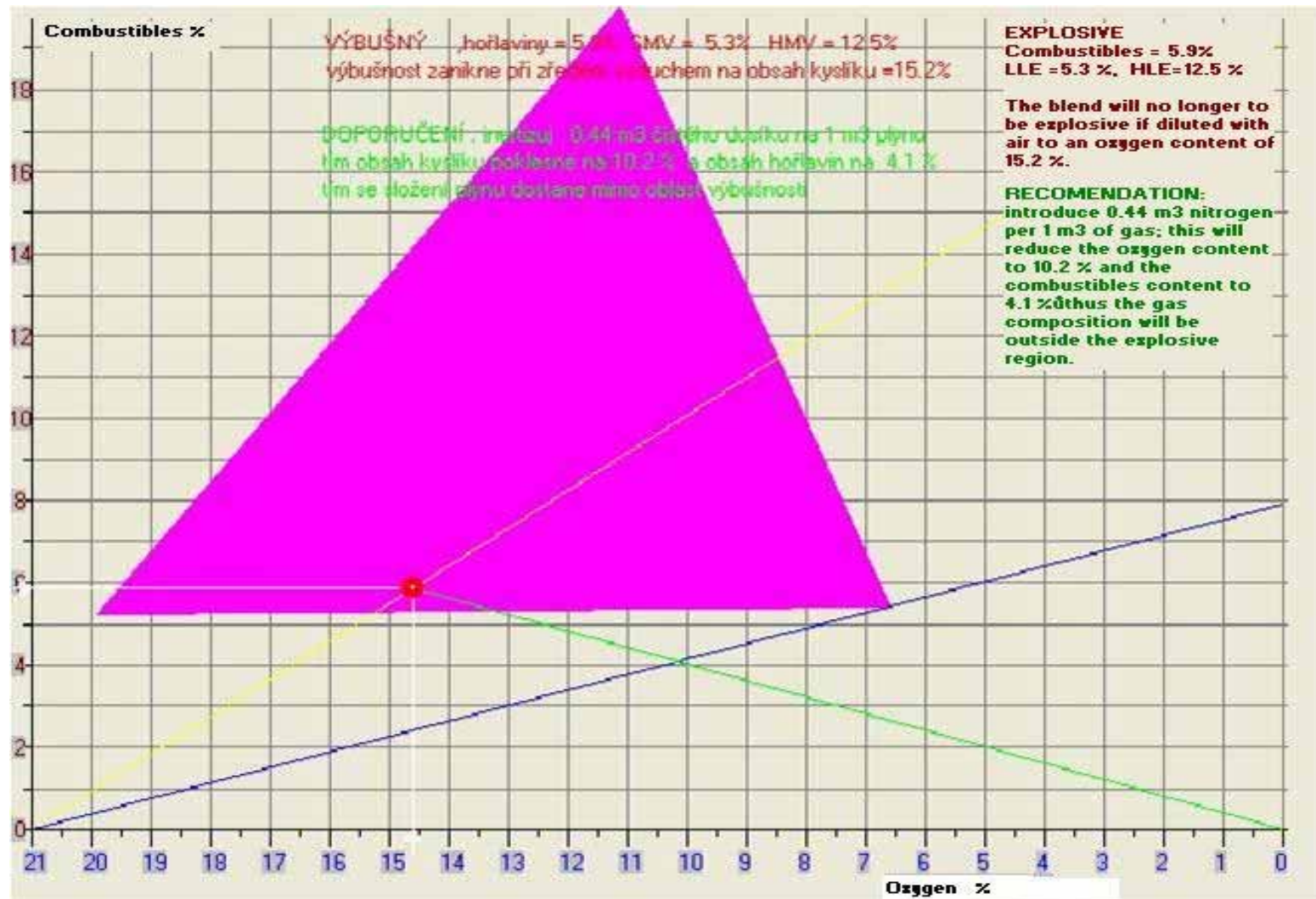
Composition of the combustion products verified by technical analyses.

- While combating the fire the spreading of fire and the hazards of explosion of the combustion products are monitored by explosion meters and also, without exception, by technical analyses of the atmosphere. For this purpose, averaged samples are taken across the entire profile of the exhaust roadway, usually at intervals of 8 hours or less, depending on the requirements of the Fire Chief in command of the emergency operation.
- The analyses are performed by the laboratory of the Main Mine Rescue Station at Most. Simultaneously, automated computations of the degree of explosiveness of the gas mixture are performed.
- In addition to the combustible products methane and carbon monoxide, it frequently happens that surprisingly high quantities of hydrogen are also detected, amounting to as much as one half of the volume of all the gaseous combustibles combined. Considerable percentages of hydrogen also tend to be found in the gases sampled immediately on completion of the area sealing operation; later they drop off rapidly.
- The rescue services often interpret the high hydrogen contents encountered with these types of fires as being related to the use of water in firefighting, due to its decomposition on glowing coals pursuant to the water gas equations.

Examples of composition of the products in the exhaust airways exiting the sites of fire.

	Date - Time	CO ₂	O ₂	CO	CH ₄	H ₂	N ₂	Explosive ness
1.	Kohinoor Mine –combustion products sampled during the course of fighting a fire which broke out in a longwall, exhaust gallery 72042 (maximum values)							
	18.2.96 - 5:00	5.6	9.2	0.460	0.78	0.5	83.46	no
2.	Kohinoor Mine –combustion products sampled on completion of the area sealing off operation, behind the dam erected at 72041 after the longwall area has been sealed off (maximum values obtained)							
	6.3.96 - 6:40	12.2	1.6	5.6	2.4	8.7	69.50	potential
	Date- time	CO ₂	O ₂	CO	CH ₄	H ₂	N ₂	Explosive ness
1.	Centrum Mine – maximum values of combustion products sampled at the exhaust roadway during the course of firefighting where water was used as the extinguishing medium, prior to starting the operation to seal off the area							
1a	29.10.01 - 1:10	4.2	14.9	1.80	0.86	3.2	75.34	yes
1b	29.10.01 - 9:30	2.2	17.8	0.30	0.26	0.4	79.04	no
2.	Centrum Mine – combustion products sampled immediately after the area has been sealed off (maximum values)							
	29.10.01 - 23:55	8.7	0.1	1.20	0.44	0.4	89.16	no

Automated computation of explosiveness for sample (1a) – The lower limit of explosiveness of the blend of combustibles corresponds to 5.3 % of combustible matter. The actual content of combustible matter is 5.9 %, of which more than one half is accounted for by hydrogen. The explosiveness triangle of the sample provides a good illustration of why a higher relative content of hydrogen in the blend of combustibles produced by the fire gives rise to a higher level of hazard; **it is mainly hydrogen which reduces the level of minimum oxygen content required for explosiveness to pose a threat**. Also, the lower limit of explosiveness is lower than that of those blends of combustibles which mainly contain methane and carbon monoxide.



Recapitulation of the properties of gaseous combustibles and of brown coal dust blended with air

Constituent	Explosiveness limits [vol.%]		Limiting safe content of O2 [vol.%]	Ignition temperature [°C]	Initiation energy of the blends [mJ]
	lower	upper			
Gases					
Hydrogen H ₂	4.0	74.0	5.0	510-590	0.02
Carbon monoxide CO	12.5	74.0	5.5	600-660	-
Methane CH ₄	5.0	15.0	12.0	560-750	0.3
Lignite dust, Kohinoor Mine - Pluto II district					
	> 36 [g/m ³]	-	-	300-350	300

Impact of coal dust on explosiveness and the synergies of gaseous combustibles pushing down the lower limit of explosiveness of the dust.

The primary firefighting action by the mine rescue team takes place while mining is still in progress at the longwall; consequently, high local dust emissions cannot be prevented during certain stages of the operations, mainly when the so-called coal backlog is being taken away, particularly if the longwall in question is one that is being extracted at its higher benches where cave-in coal from the roof tends to have a crushed consistency, with a high percentage of dust. **Coal dust fire hazard arises here, in an environment enriched in the combustion products, due to synergies which are conducive to lowering even further the lower limits of explosiveness of the dust when gaseous combustibles are present.**

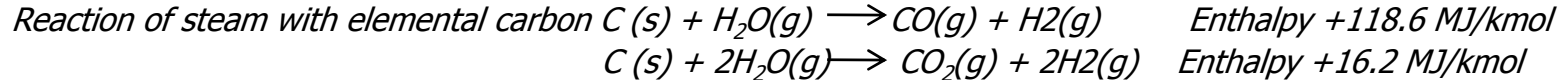
For lignite, numeric data on the synergies are play are available merely for the methane / lignite dust combinations encountered in the Pluto II mining district (at Kohinoor Mine). For instance, 1.5% methane would depress the lower limit of explosiveness from 36 g/m³ to 21.5 g/m³.

In spite of the absence in literature of numeric data that would characterize the impact of hydrogen on the lower limit of explosiveness of the North-Bohemian types of lignite dust, there is no reason to believe that the synergies there are much different; to the contrary, in view of the fact that the characteristics of hydrogen are much more unfavorable, even greater synergies and, thus, even greater hazards posed by hydrogen can be expected.

Another risk factor at play here is the presence of potential initiation sources. In case of persistent fires affecting longwall working faces, the problem is compounded by secondary local focal points of fire always springing up, as a rule in the immediately adjoining sections of the headings serving as transport roadways and exhaust airways. In rescuers' speak, these local points on fire or aglow are termed 'tomcats'.

Experiment proposed as a means for arriving at a decision as to which mechanism of hydrogen generation in the products of fire is of decisive importance:

- There are two major processes whereby hydrogen is generated, which may assume different proportions:
 - **Decomposition of steam on glowing coals** pursuant to the equations describing water gas generation.

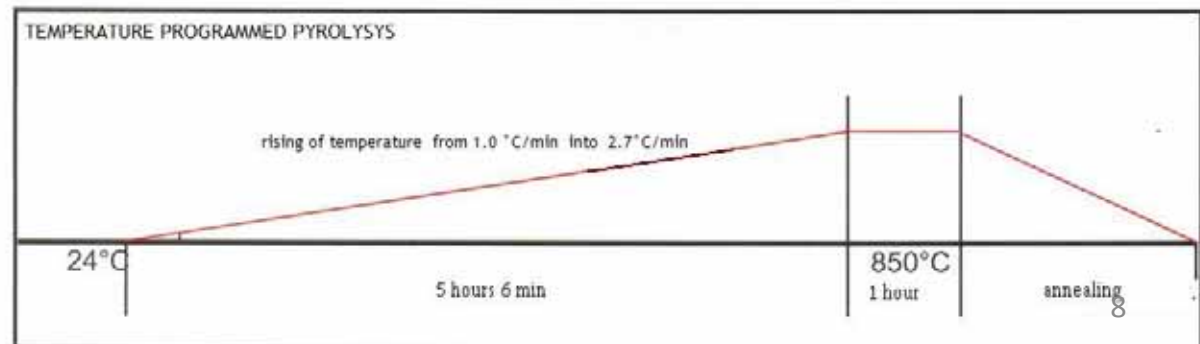
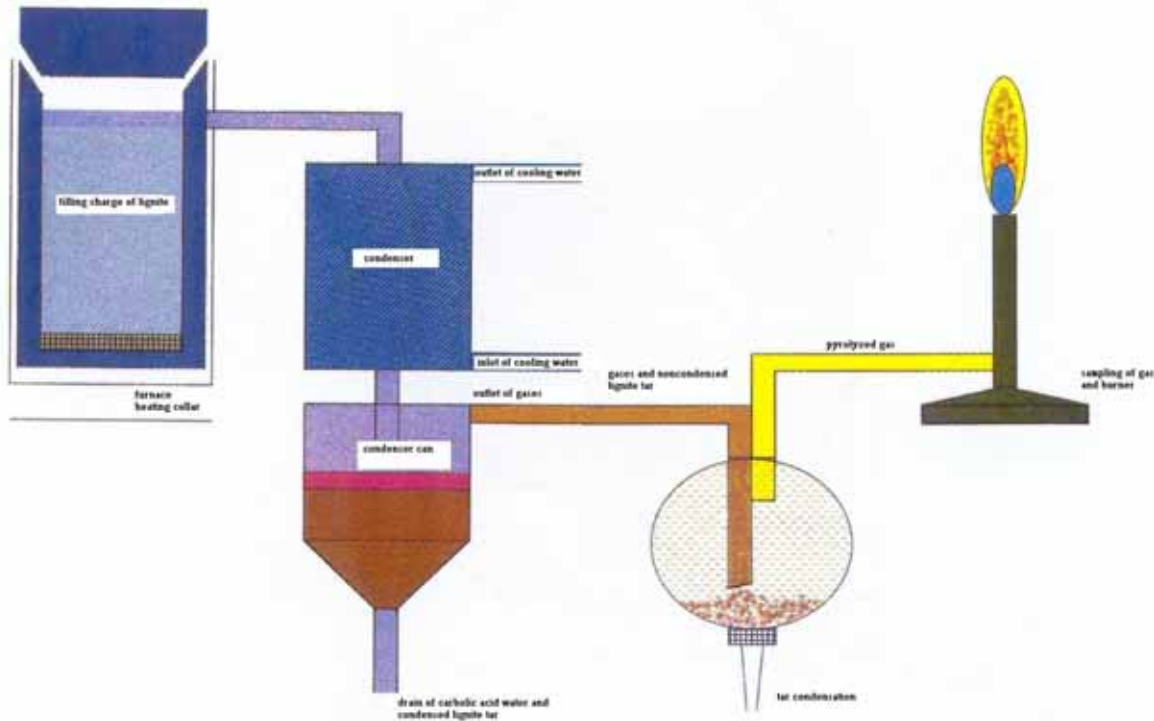


Hydrogen and carbon monoxide are produced by these processes. The rates of these processes as well as the equilibria established depend on the partial pressure of water vapor. Among the rescue services teams, notions persist that there are causal relationships between hydrogen generated by these processes and the use of water in firefighting.

- **Decomposition of the coal mass during low- and medium-temperature carbonization** (pursuant to the complex equations governing the generation of town gas) yields hydrogen, methane, carbon monoxide, and higher hydrocarbons. The process is not significantly affected by the partial pressure of water vapor.

- Both these mechanisms have been investigated almost to perfection by now, from the aspects of thermodynamics, chemical kinetics, and the reaction equilibria involved. In spite of all this, theory alone is not enough for arriving at a decision on which of these mechanisms will be the dominant one. The main reason is that every scene of fire in a mine is unique, representing a system far removed from any equilibrium; the system always is an open one, nonsteady-state, and involving rapid changes of external conditions.
- Rather, any answers to these question must be expected to come from a critical assessment of the results of technical analyses of the combustion products from a greater number of fires of similar type, and also from model experiments imitating as far as possible the actual conditions prevalent on the scene of fire.
- **This is why in 2003, on the initiative of the Main Mine Rescue Station at Most, the Brown Coal Research Institute of Most has undertaken 3 series of model experiments** making use of a suitable experimental facility, aiming to verify the dominant mechanism whereby hydrogen and the other combustibles are generated as well as the effect of water.

Layout of the installation and the temperature control program used in the experimental series



Conditions of the pyrolysis tests

- **A total of 3 raw coal samples from Centrum Mine were used in the tests. The parameters characterizing the fuel technology properties of the samples were rather different.**
- **The contents of analytical water (W_A) in the samples were within the range of 6.8-11.1 %.**
- **Each sample was subjected to 3 carbonization experiments (the tests A, B, C) run under the same temperature control conditions.**

Test A	carbonization of brown coal, with no water added
Test B	carbonization under conditions involving an addition of 3% of water
Test C	carbonization under conditions involving an addition of 9% of water

- **In the analytic part of each experiment, the mass balances of the carbonization products – semi-coke, phenol water, tar, and gas – were examined by gravimetry.**
- **Only the gas fraction was subjected to a detailed compositional analysis. Gas chromatography determinations involving various configurations were performed.**
 - o **to ascertain the contents of hydrogen, nitrogen, oxygen, and carbon monoxide – a 1.5 m packed column with type 5A molecular sieve;**
 - o **to ascertain the contents of carbon monoxide – a 2 m packed column with Porapak Q, TCD detection;**
 - o **to ascertain the contents of methane and of higher hydrocarbons – a capillary column wetted with Squalan, FID detection.**

Results of the pyrolysis tests

Normalized average composition of gaseous combustibles of carbonization in the presence of various quantities of water

Average composition [vol.%]	TEST A no water added			Test B With water addition, To the amount of 3 wt.%			Test C With water addition, To the amount of 3 wt.%		
	300°C	500°C	700°C	300°C	500°C	700°C	300°C	500°C	700°C
H ₂	9.12	8.7	31.3	11.8	13.6	39.1	13.3	12.2	29.5
CO	11.8	11.8	9.5	10.3	15.2	10.4	10.9	15.0	10.6
CH ₄	12.5	26.1	25.1	10.5	20.0	19.8	11.2	18.6	13.2
ethane+ ethene	4.6	7.6	3.1	2,5	6.9	2.0	2.4	4.4	1.1
	Non-combustible constituents								
CO ₂	29.6	17.6	8.3	31.5	19.4	13.1	24.7	20.1	12.7
N ₂	17.0	4.8	2.5	30.2	12.5	3.52	24.6	4.1	0.3

Results of the pyrolysis tests – continued

Balances by mass and by volume of the chief constituents of pyrolytic gas

Gaseous consti- tuent	TEST A no water added			Test B with water addition to the amount of 3 wt.%			Test C with water addition to the amount of 3 wt.%		
	Mol. wt.	Quantity of gas generated from 1 kg of lignite		Mol.wt.	Quantity of gas generated from 1 kg of lignite		Mol.wt.	Quantity of gas generated from 1 kg of lignite	
		[g]	[m ³]		[g]	[m ³]		[g]	[m ³]
H ₂	2	3.6	0.040	2	3.6	0.040	2	2.76	0.031
CO	28	34.1	0.027	28	28.2	0.023	28	25.6	0.021
CH ₄	16	37.4	0.052	16	22.2	0.031	16	17.2	0.024
Non-combustible components									
CO ₂	44	89.6	0.046	44	78.8	0.040	44	95.0	0.048
N ₂	28	25.0	0.020	28	36.3	0.029	28	20.3	0.016
*total quantity of gas 189.7 g				*total quantity of gas 169.1 g			*total quantity of gas 160.9 g		

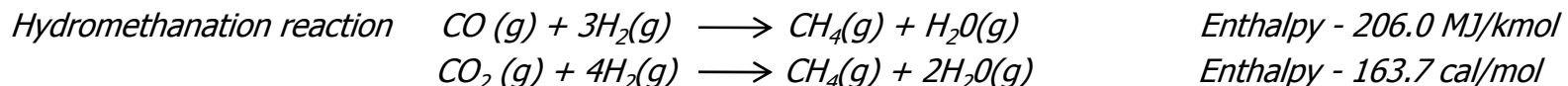
*The total quantity of gas has been computed from the mass balance. It also includes constituents not listed in the table.

Assessment of the experiments from the point of view of the generation of hydrogen, carbon monoxide, methane, and higher hydrocarbons

- The following conclusions can be drawn based on the two tables shown above:
- **Additions of water to the carbonization process have provoked merely an insignificant growth of the volumetric percentage of hydrogen** in the pyrolytic gas; this effect was observed mainly at the lower temperatures. Indeed, even a small decrease was observed at the temperature of 700°C.
- Additions of water to the carbonization process have failed to provoke any more significant changes of the percentage of carbon monoxide.
- **Additions of water to the carbonization process have demonstrated that an unambiguous correlation exists between the reduction of the methane content and the increase of the amount of water added**, throughout the entire range of temperatures employed in the experiments.
- The higher hydrocarbons (ethane + ethylene) exhibit a maximum at medium temperatures. With growing water content their contents definitely go down.
- **The total amount of gas produced from 1kg of coal is insignificantly lower in the presence of water. In all cases, the greatest share of the combustibles by volume is taken up by hydrogen.**
- In terms of mass however, it is methane and carbon monoxide which constitute the dominant shares of the gaseous combustibles.

Assessment of the experiments from the standpoint of the mechanism by which hydrogen and the other gaseous combustibles are formed

- In view of the fact that the relative contents by volume of hydrogen and carbon monoxide do not show any particularly pronounced growth with growing water additions to the process, it appears that **under the conditions of these experiments, the mechanism of formation of water gas is of only a marginal importance.**
- **Thus, most of the hydrogen and of the other gaseous combustibles are produced by pyrolytic decomposition** taking place during the course of the lignite carbonization process.
- Hence, it is mainly the hydrogen bonded in the combustible coal substance which represents the source of gaseous hydrogen. The combustible matter of the North-Bohemian types of lignite contains ca. 6% of bonded hydrogen.
- The incineration reactions and the carbonization reaction represent the chief source of carbon monoxide. The mechanism described by the water gas equations is insignificant.
- **The observed reduction of the methane content due to the effect of water vapor suggests the presence of a considerable influence of the hydromethanation reactions** whereby the water vapor shifts the equilibrium in favor of methane decomposition.



Conclusions drawn and recommendations made to mitigate the explosion hazards of the combustibles produced during a fire while active fire suppression measures are in progress simultaneously with longwall face mining operations

- Based on an assessment of the composition of combustibles produced during actual mine fires, combined with the results of pyrolysis experiments described hereinabove, it can be stated that **the presence of hydrogen in the products generated during the fire basically derives from two sources, each of which contributing differently depending on the conditions prevailing on the scene of fire in progress while firefighting measures are being applied.**
- It appears that **pyrolysis of the coal mass is a more important source of hydrogen** than the decomposition of water vapor on glowing coals. In principle, it is only the pyrolytic processes which are a source of methane and hydrocarbons; in contract, the presence of water vapor acts to slightly mitigate their formation.
- **The intensity of formation of the combustible gases during pyrolysis depends on the amount of coal mass heated to a sufficient temperature, while the intensity of formation of the combustible gases by reactions involving water gas depends on the active *i.e.*, sufficiently glowing free surface of the coals and on the water vapor tension, since this is a heterogeneous reaction between a gaseous and a solid phase.**
- **Hence, for the type of fires under consideration here, this does not confirm the traditional theory that the generation of hydrogen is due to water vapor decomposition on glowing coals relating to the water being gushed upon the scene of fire.**

- Nevertheless, the possibility of local hydrogen explosions cannot be excluded if the water stream directly hits the focal point of the fire. The tactical rule of cooling the scene of fire by applying the water jets from the outside around its circumference has been confirmed many times over by practical experience and is indisputably true. That is the correct procedure to adopt, which prevents not only hydrogen generation but mainly, any dangerous or even explosive generation of steam.
- **Therefore, the most important factor which mitigates the contents of combustible matter in the products generated from the fire is adopting measures to cool down the coal mass, as speedily as possible,** to temperatures at which the pyrolytic reaction no longer takes place. In essence, this cooling can only be achieved by water applied in targeted fashion and in sufficient quantities upon the caved-in field, or by forepoling in-between the supports in cases where the focal points of the fire are difficult to access.
- **Hence, the preferred tactics of the primary firefighting action to be adopted at a longwall working face where mining is in progress is a massive, targeted application of sufficient amounts of firefighting water,** both directly in those locations where the focal points of the fire can be accessed, and by forepoling if the focal points are situated in a caved-in area or behind mechanized supports.

- Other firefighting measures can also be adopted, such where effects other than cooling are preponderant; these include inertizing the cave-in, mechanical nitrogen foams etc. where the chief objective is to constrain the access of oxygen to the caved-in field. These measures cannot immediately influence the formation of the combustible matter constituents in the exhaust air, because of their lower cooling effect.
- Owing to the fact that during some, time-constrained stages of combating fires that broke out in a longwall face the formation of explosive blends of combustible products and dust cannot be precluded, such locations potentially acting as initiation sites have to be targeted by the firefighting measures immediately. It is an important task of the rescue crews operating in exhaust airways to seek out and to liquidate any local fires initiated in the adjoining sections of the headings serving as transport roadways and exhaust airways. These local spots which are aglow (termed 'tomcats' in the rescuers' jargon) are generated by local overheating of the coal in locations under the roof where the streaming hot fire products are concentrated.

Dear friends: this has exhausted the topic of my presentation. May I thank you for your attention. Any comments and questions from you are welcome, and I will do my best to answer them.