Coal pyrolysis and gasification – advanced ways of utilisation

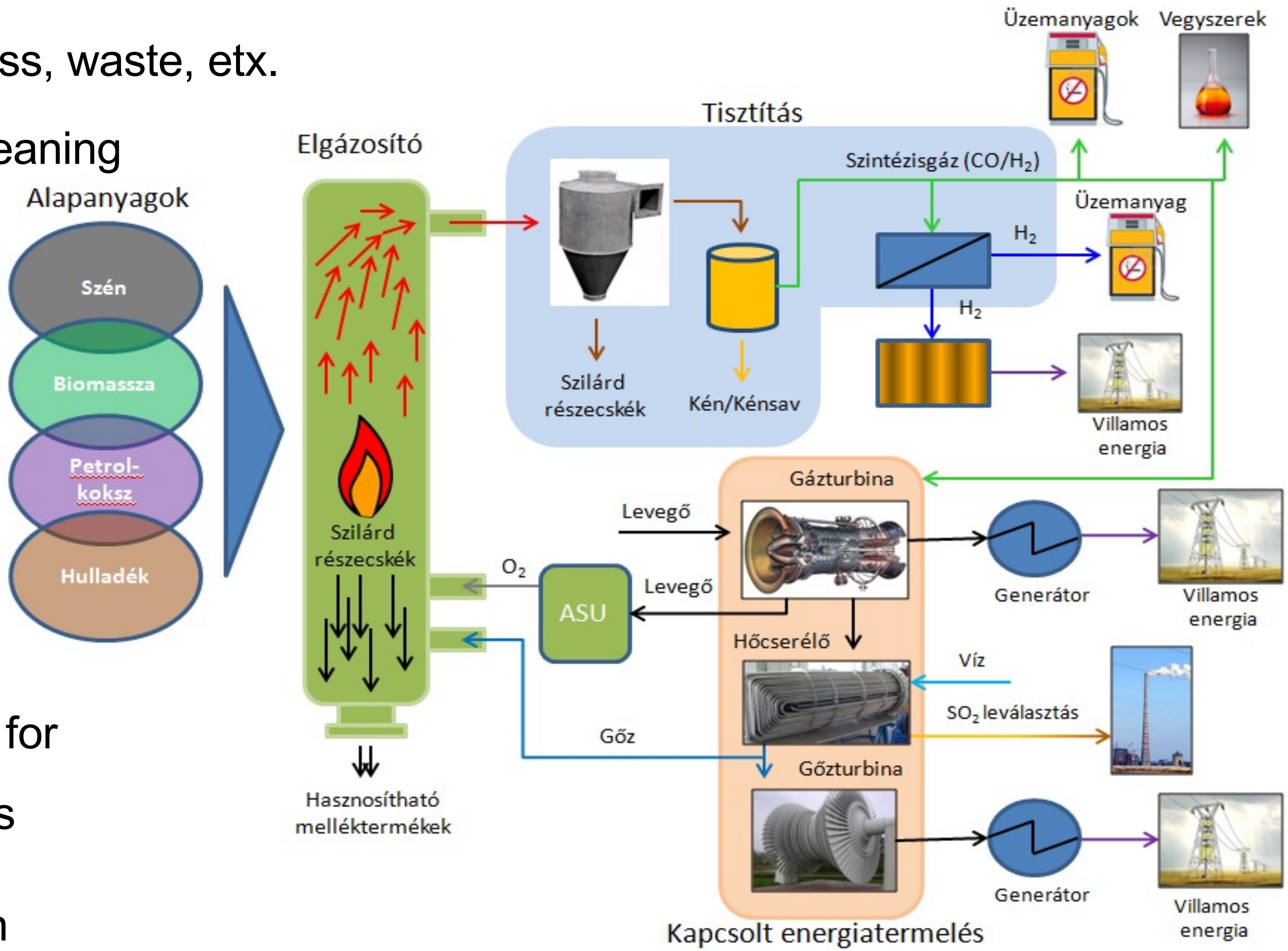
Kállay András Arnold, Szemmelveisz Hodvogner Katalin,
Woperáné Serédi Ágnes, Nagy Gábor

PROSPECTS FOR THE EXPLOITATION OF COAL

- Energy production
  - Coal plant (PAKS 2 in progress)
  - Gasification → energy production from synthesis gas
- Secundary raw material
  - Gasification → secondary raw material production
  - Direct procedures for secondary raw materials production

THE POTENTIAL OF GASIFICATION

- Coal + … biomass, waste, etx.
- Synthesis Gas Cleaning



- Primary materials for chemical and fuels
- Energy prodcution
-

THREE MAIN PHASE OF THE GASIFICATION

Drying

The moisture content of the raw material is generally 5-40%. Evaporates above 100 °C,. During this procedure the raw material does not undergo any chemical breakdown.

Pyrolysis

Pyrolysis is a thermal decomposition of fuels in the absence of oxygen. Pyrolysis produces three different phase products – solid, liquid and gas phases.

Oxidation and reduction processes

Reaction of steam and oxygen at high temperatures with carbon from the raw material (coal)

MAIN REACTIONS DURING GASIFICATION

Reaction equation	ΔH$_0$ (kJ/mol)	Equilibrium constant (800 °C)
$C + O_2 \rightleftharpoons CO_2$	$-406{,}4$	$1{,}5 \cdot 10^{13}$
$2C + O_2 \rightleftharpoons 2CO$	$-246{,}3$	$4{,}5 \cdot 10^{16}$
$2C + CO_2 \rightleftharpoons 2CO$	$+160{,}9$	7.7
$C + H_2O \rightleftharpoons CO + H_2$	$+118{,}4$	8,0
$C + 2H_2O \rightleftharpoons CO_2 + 2H_2$	$+16{,}3$	8,3
$C + 2H_2O \rightleftharpoons CH_4$	$-87{,}4$	$1{,}8 \cdot 10^{-3}$
$2CO + O_2 \rightleftharpoons 2CO_2$	$-567{,}3$	$2{,}4 \cdot 10^{14}$
$2H_2 + O_2 \rightleftharpoons 2H_2O$	$-482{,}2$	$2{,}2 \cdot 10^{10}$
$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O$	$-801{,}1$	$9{,}0 \cdot 10^{31}$
$CO + 2H_2O \rightleftharpoons CO_2 + H_2$	$-42{,}3$	$3{,}3 \cdot 10^{-1}$
$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$	$-205{,}8$	$5{,}9 \cdot 10^{-3}$
$2CO + 2H_2 \rightleftharpoons CH_4 + CO_2$	$-248{,}4$	$6{,}2 \cdot 10^{-3}$

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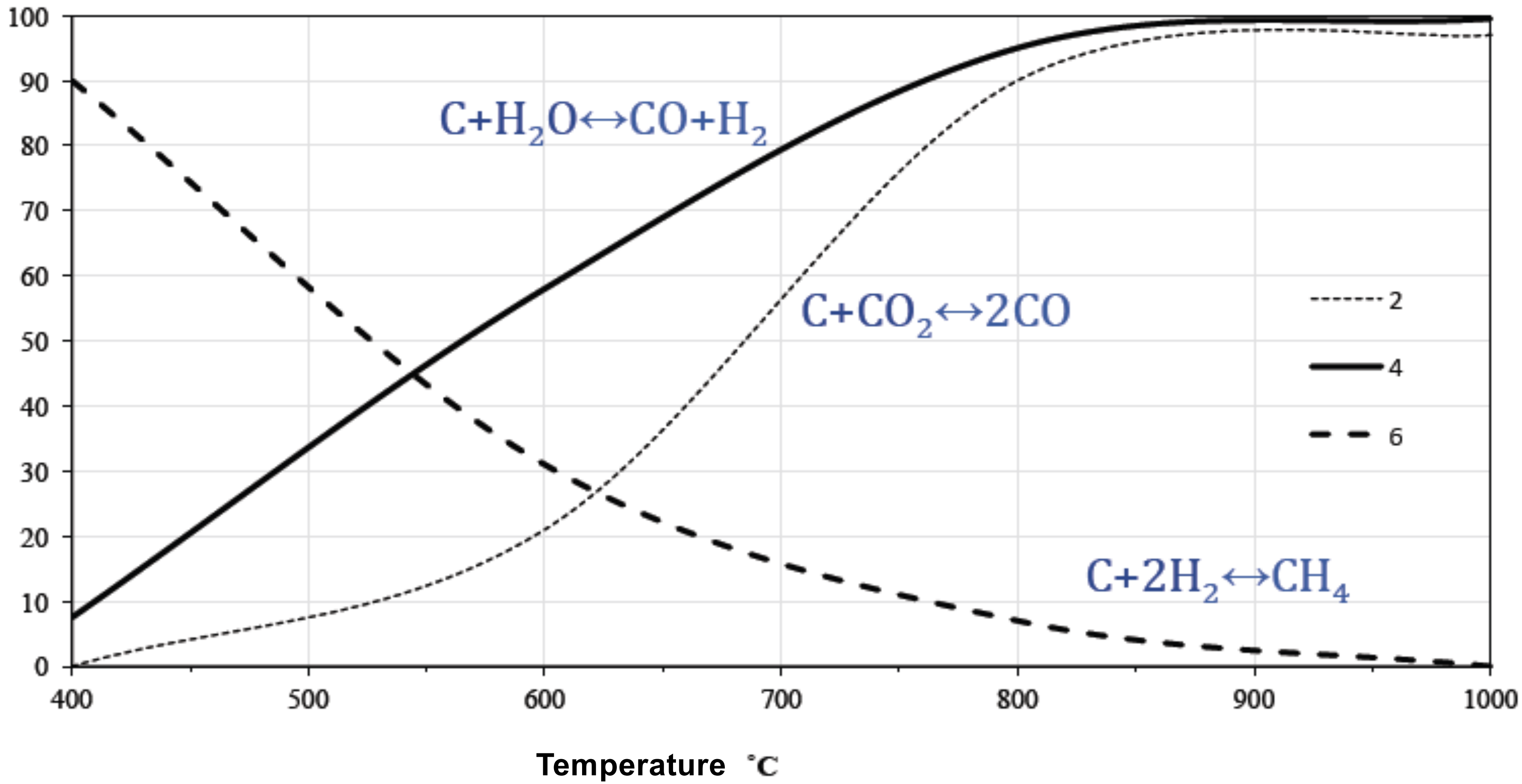
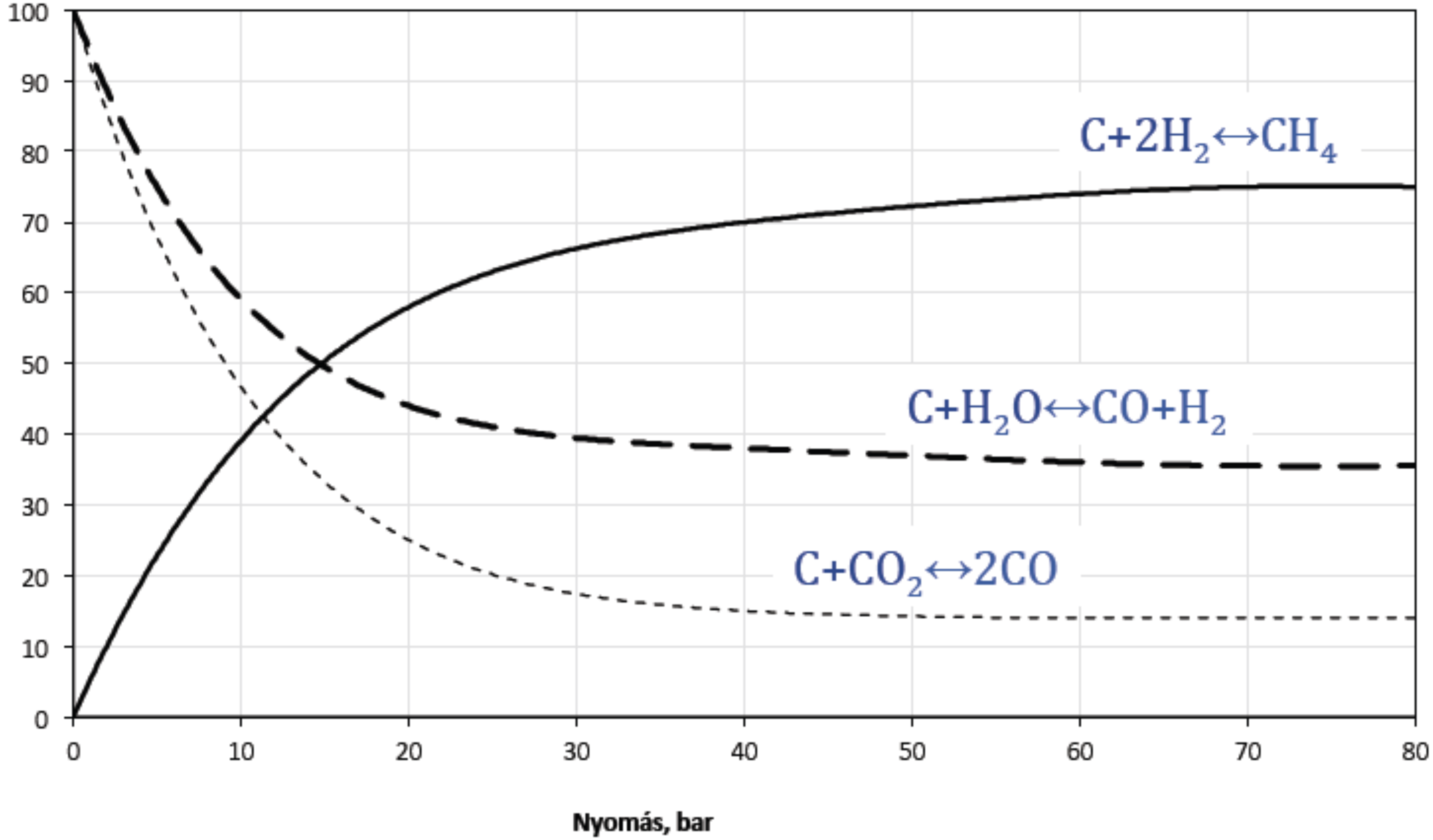
EFFECT OF TEMPERATURE ON THE MAIN REACTIONS DURING GASIFICATION



EFFECT OF PRESSURE ON THE MAIN REACTIONS DURING GASIFICATION



SYNTHESIS GAS REQUIREMENTS ACCORDING TO THE INTENDED USE

Product	Synthetic fuel	Methanol	Hydrogen	Heating gas	
	FT benzin			Boiler	Gas turbine
H_2/CO	0,6	~2,0	Magas	Negligible	Negligible
CO_2	Low	Low	Non-significant	Non-critical	Non-critical
Hydrocarbons	Low	Low	Low	High	High
N_2	Low	Low	Low	Decreases heating value	Decreases heating value
H_2O	Low	Low	Low	Low	Reduces NOx formation
Pollutants	<1 ppm suplhur	<1 ppm sulphur	<1 ppm sulphur	Low-amount is alowed	Small amount particulate pollutants
	Small amount particulate pollutants	Small amount particulate pollutants	Small amount particulate pollutants		Small quantities of metals
Pressure, bar	~20-30	~50 (Liquid phase)	~28	Low	~400
		~140 (Steam phase)			
Temperature, °C	200-300[j]	100-200	100-200	250	500-600
	300-400				

SYNTHESIS GAS REQUIREMENTS ACCORDING TO THE INTENDED USE

Product	Synthetic fuel	Methanol	Hydrogen	Fűtőgáz	
	FT benzin			Boiler	Gas turbine
H_2/CO	0,6	~2,0	Magas	Negligible	Negligible
CO_2	Low	Low	Non-significant	Non-critical	Non-critical
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	300-400				

TYPES OF GASIFICATION TECHNOLOGIES, TEMPERATURE AND HEATING

- The basic types of thermal breakdown are based on the temperature conditions of the procedure:
  - low and medium-temperature procedures (450-600 °c),
  - high-temperature processes (800-1200 °c),
  - high-temperature melting processes (> 1200 °c).
- The volume and composition of gases resulting from the thermal breakdown depends on:
  - raw materials and the physical properties of the gasification,
  - reaction conditions of the chemical transformation,
  - reactor's operating conditions and the structural construction

TYPES OF GASIFICATION TECHNOLOGIES, MATERIAL FLOW AND HEATING METHOD

Different technologies based on the flow rate of the sythesys gas relative to the raw material

- same current,
- counter-current,
- ross-current.

Reactors are separated in two groups, according to heating method:

- indirect (through the reactor wall or using a heating medium),
- direct.

BASIC TYPES OF GASIFICATION SYSTEMS

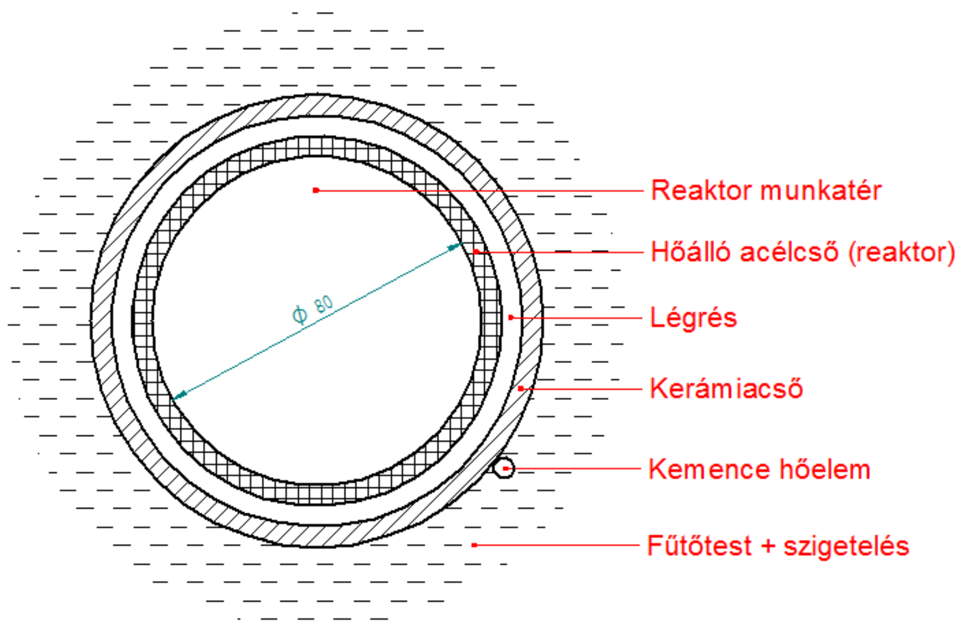
- Fixed or moving beds
    - Direct-flow systems
    - Counterflow Systems
    - Cross-current systems
    - Twin-fired systems
- Fluidised Bed
    - Bubbler Gasification
    - Circulation gasification

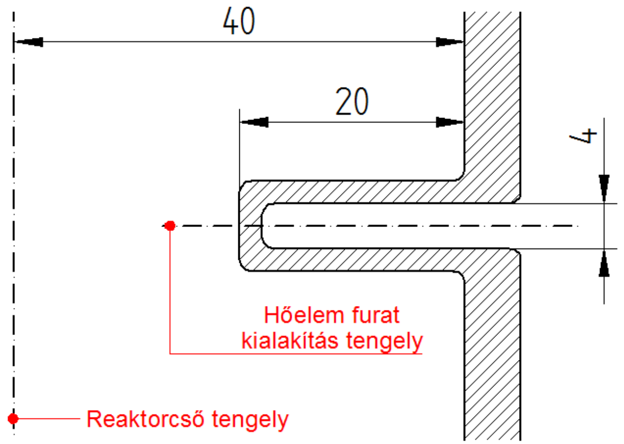
STRUCTURE OF THE EXPERIMENTAL SYSTEM

- **Main components of the experimental equipment:**
  - **Gasification reactor**
  - **Furnace**
  - **Steam generator**
  - **Venturi Scrubber**
- **Data collection and logging**
  - **Total volume/flow rate measurement**
  - **Temperature monitoring**
  - **Gas composition Analysis**
  - **Composition analysis of input and output materials**

Made of heat-resistant steel

- Length: 1200 mm
- Diameter: x100 mm
- Thickness: 10 mm
- Bottom (gas draining) and top (steam feed) lid with truncation





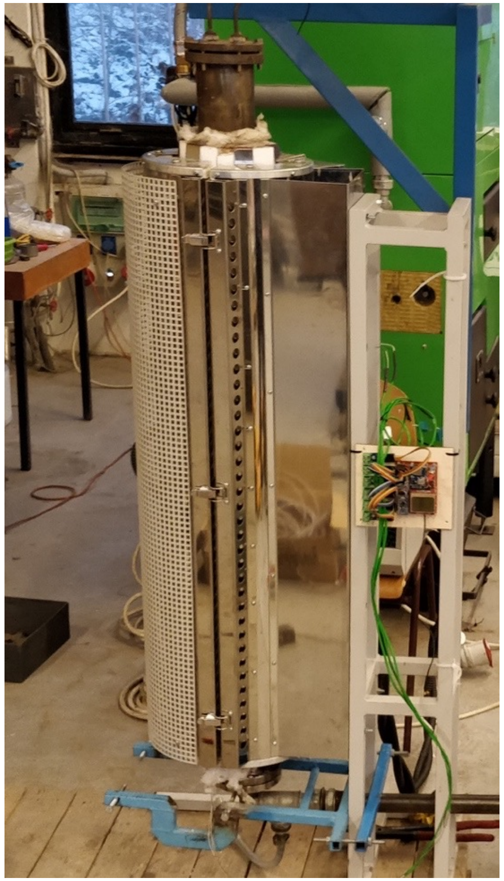
Thermocouple placement of the electrically heated tube furnacein a blind hole

Mérőhely kialakítása hőmérséklet méréshez

ELECTRICAL TUBE FURNACE

Carbolite VST-12/900 type of tube furnace

- Internal diameter: 110 mm
- Max. temperature: 1200 °C
- max. heating rate: ~20 °C/min
- INSULFRAX Ceramic insulation between the ends of rector tubes and furnace



Carbolite VST-12/900 type of tube furnace (left) and reactor in the tubefurnace (right)

STEAM GENERATION AND REACTOR PRESSURE MEASUREMENT

Bieffe, Maxi vapor type steam generator

- Built-in tank: 3,5 l
- Power: 1300 W
- Vapour pressures: 2,8 bar (In the tank)
- Manually adjustable flowrate

Maxi Vapor type steam generator

The pressure measurement was done by an MRU-DM9100 type pressure gauge isntrument

Measuring range: 0 – 100 mbar

MRU-DM9100 Type pressure gauge

GAS PURIFICATION

Venturi Scrubber

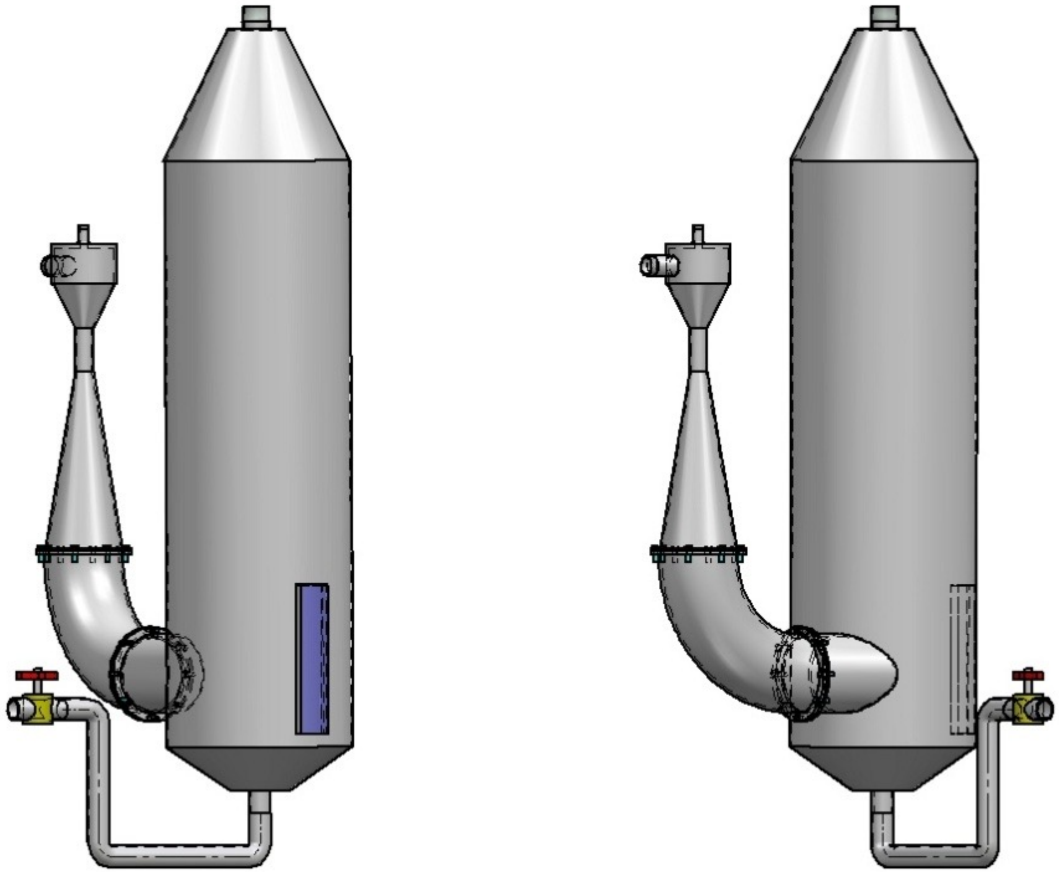
For the separation of solid particulate matter

Suitable for cleaning low-volume gas

Adjustable injection flow rate

Washing Liquid: running water (2.5 bar, 15 °c)

It also serves as a synthesis gas cooler



3d design of Venturi washer (Solid Edge).

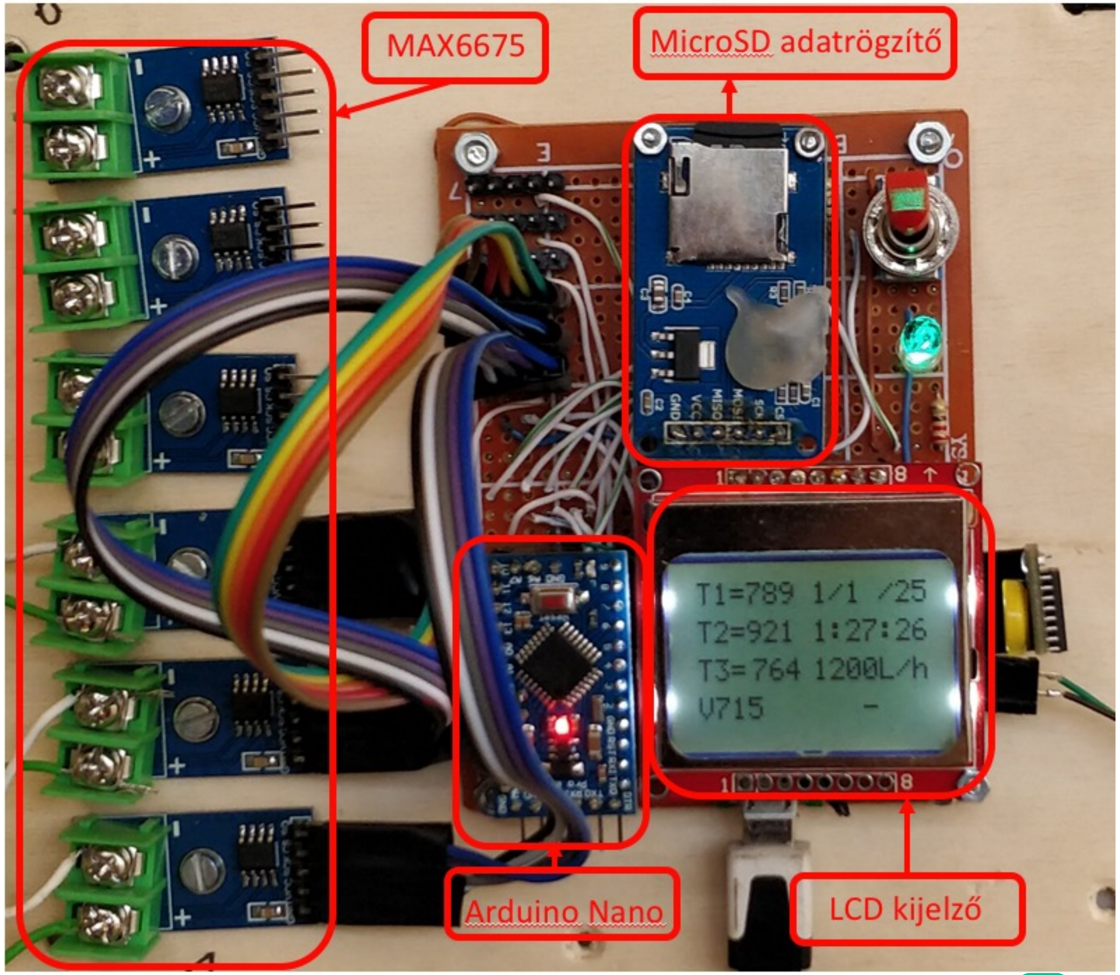
In house developed measuring and data collection device

ATMEGA328 Microcontroller based temperature, volumetric flow meter and data collector

K-type thermocouples (MAX6675 Ics)

RTC and MicroSD

- Logging data every minute with timestamps
- Total gas volume and volumetric flow indication and recording using a chromschröder BK4 type gas meter equipped with a signal transmitter



Developed data collector and logger

Agilent MicroGC490:

- With COX Column
- The main components of synthesis gas are:
- H2, CO, CO2, CH4 and O2
- Automatic data logging and evaluation
- Sampling every 3 minutes
- **DANI 500:**

- With flame ionization and thermal conductivity detector
- Also suitable for detection of low concentrations of gas present

- C_2H_4, C_2H_6 and H_2S

Agilent 490 MicroGC Gas chromatograph

HOGYAN ÁLLT ÖSSZE A BERENDEZÉS….

DETAILS AND WORKFLOW OF THE EXPERIMENTS

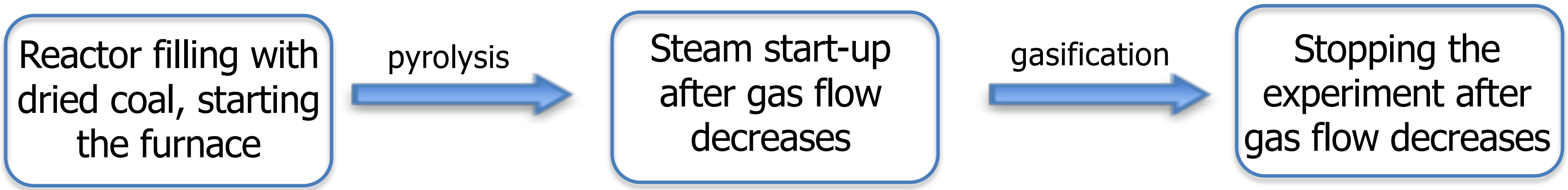
Coal samples

- Brown coal from Felsőnyárád
- Brown coal from Bükkábrány
- Black coal from Pécs

Experimental parameters:

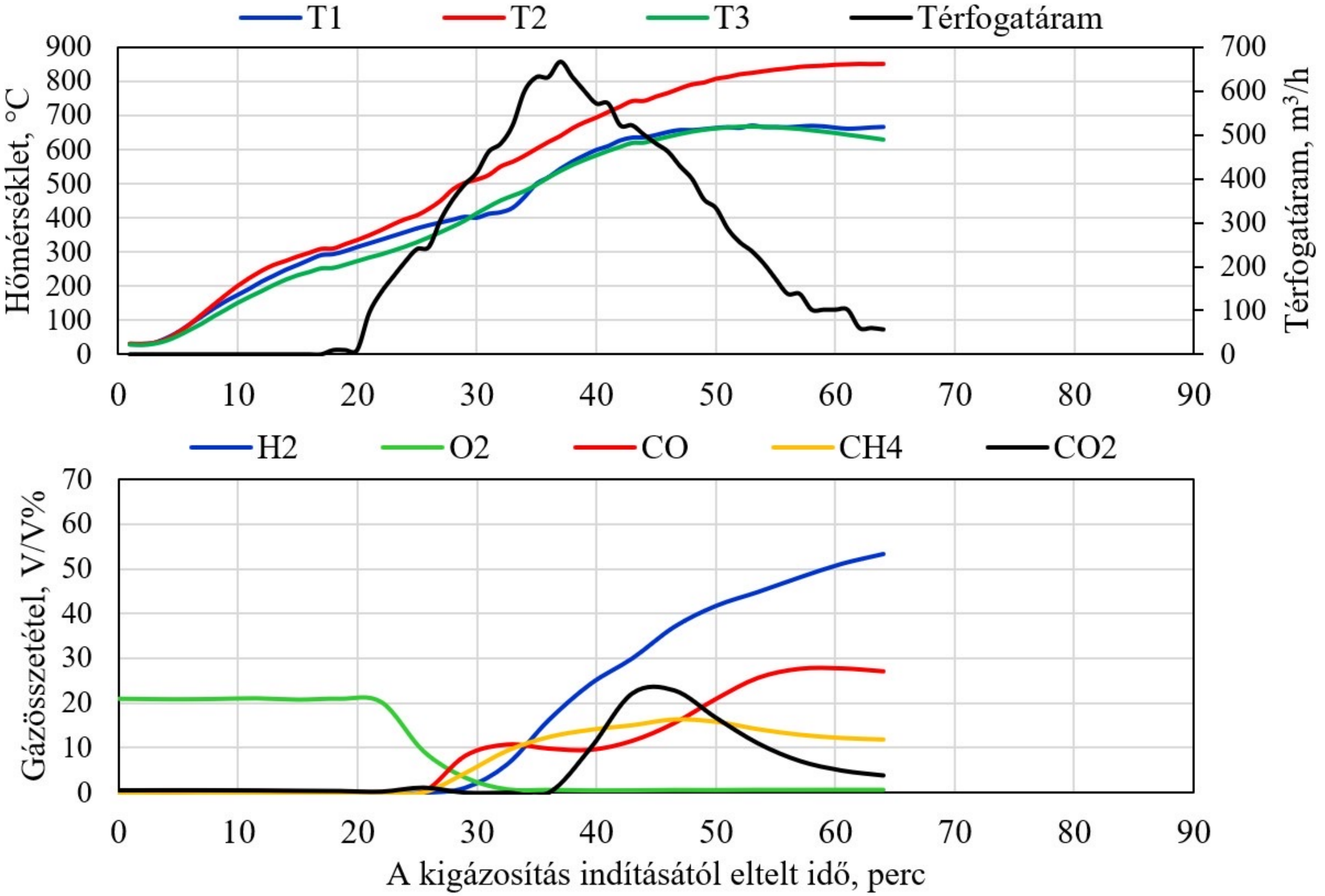
- Temperature: 800 °C és 900 °C
- Heating rate : ~20 °C/min
- Steam Feed: 10g/min
- Venturi Washer flow rate 6 L/h
- Experiment with 3 kg of dried coal (exception of blcak coal from Pécs 5 kg)

Experiment Process



PYROLYSIS OF THE COAL SAMPLE FROM BÜKKÁBRÁNY 800 °C

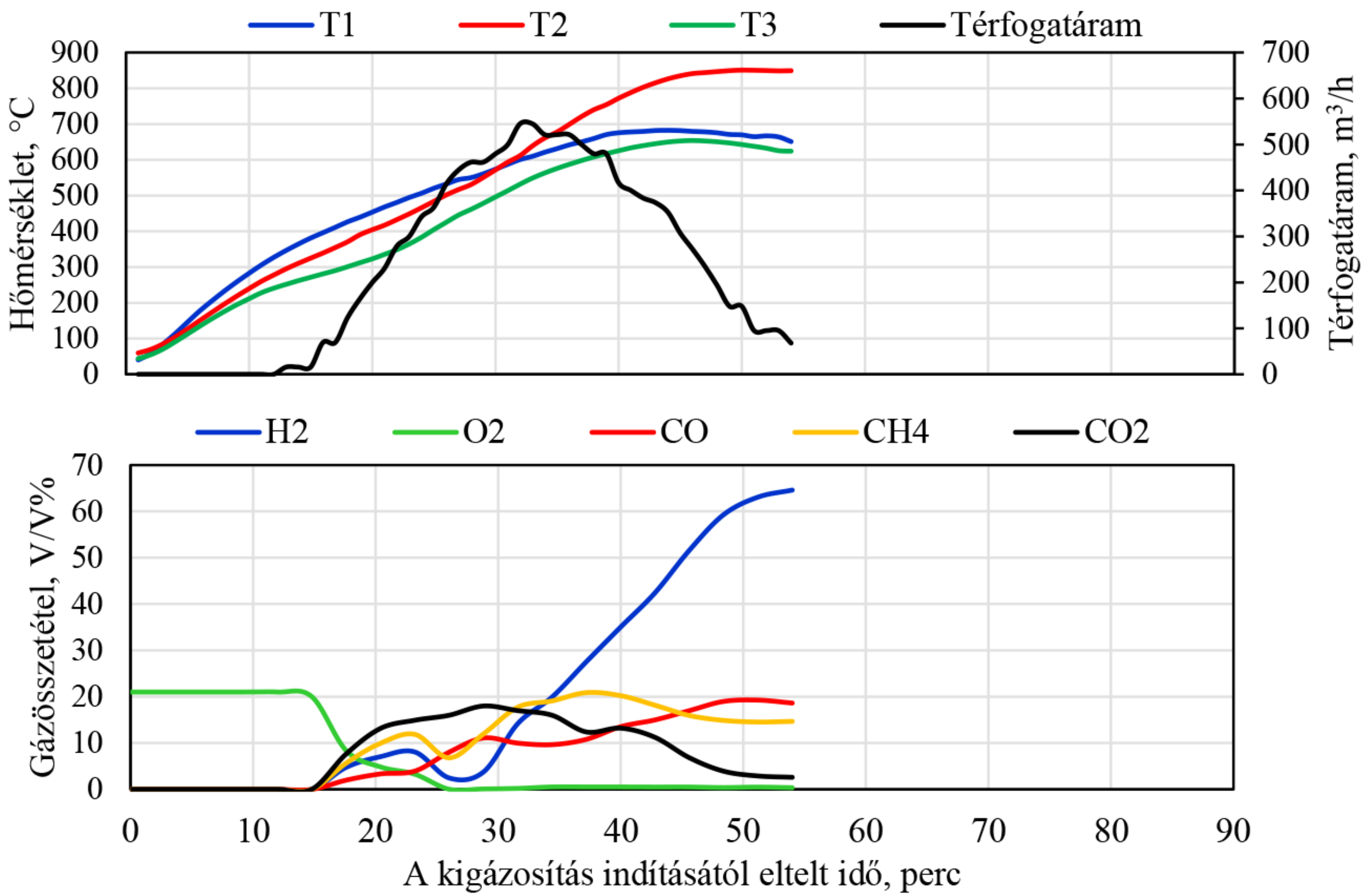
- Experimental parameters:
- Temperature: 800 °C
- Heating rate: ~ 20 °C/min
- Venturi scrubber flow rate 6 L/h
- Quantities recalculated for 1 tone of starting material



- Upper and lower zones have the same temperature
- H_2, CO, CH_4 ratio steadily increases
- CO_2 ratio increases and then decreases

PYROLYSIS OF THE COAL SAMPLE FROM FELSŐNYÁRÁD 800 °C

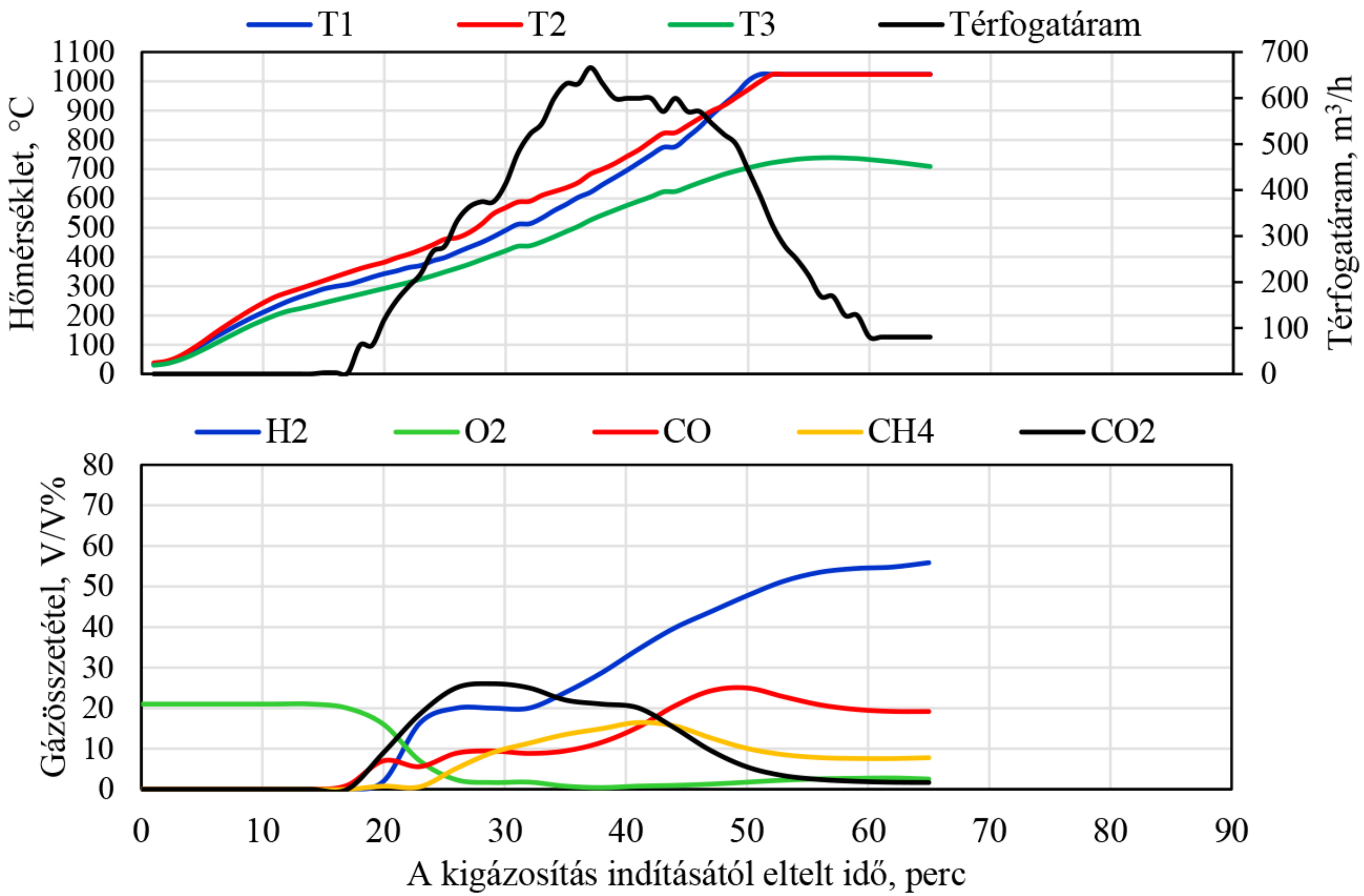
- Experimental parameters:
- Temperature: 800 °C
- Heating rate: ~ 20 °C/min
- Venturi scrubber flow rate 6 L/h
- Quantities recalculated for 1 tone of starting material



- Ratio of the H_2 is higher than in the coal from Bükkábárny
- CO ratio is smaller than in the coal from Bükkábárny
- CH_4 rate has a slightly higher peak rate

PYROLYSIS OF THE COAL SAMPLE FROM BÜKKÁBRÁNY 900 °C

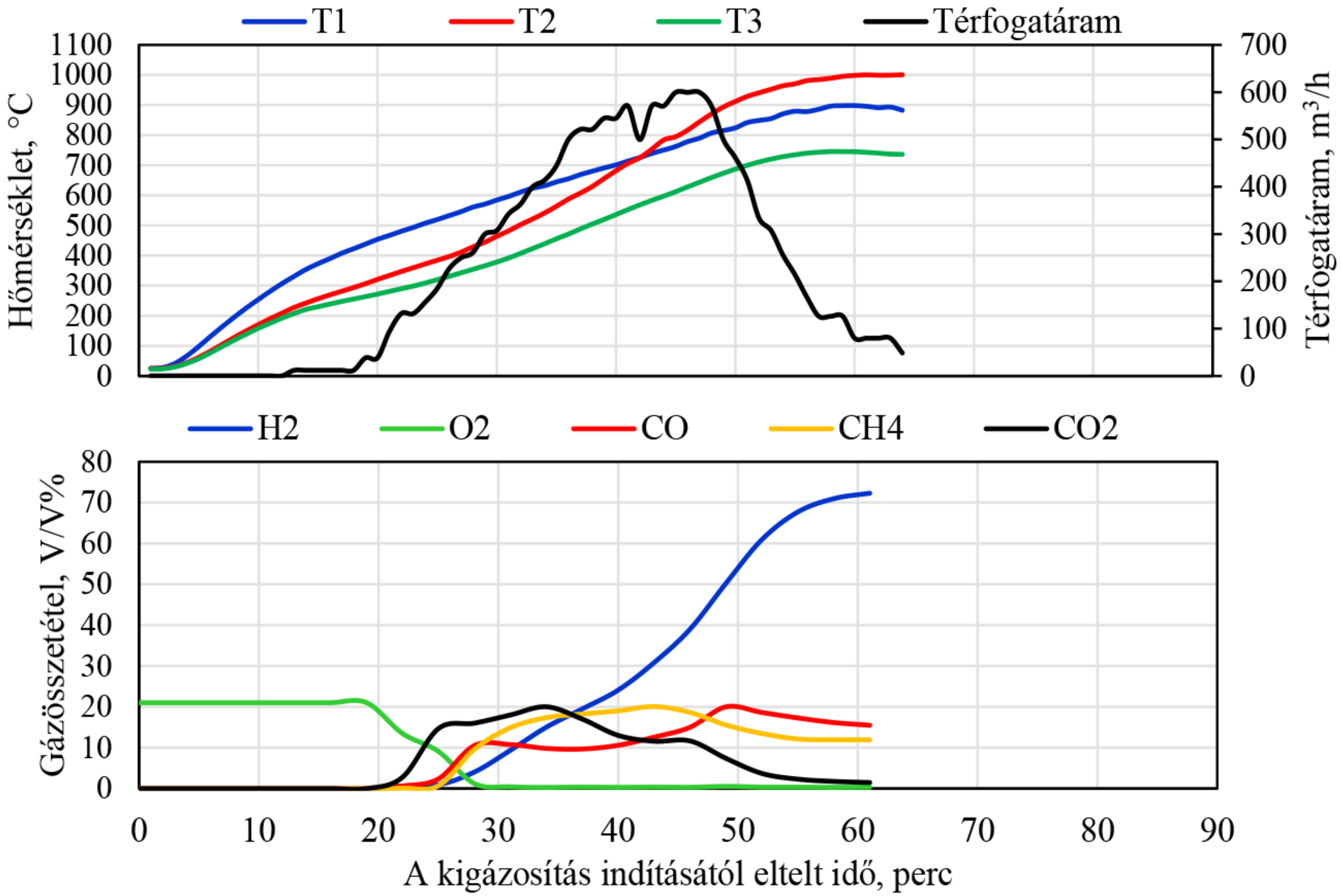
- Experimental parameters:
- Temperature: 900 °C
- Heating rate: ~ 20 °C/min
- Venturi scrubber flow rate 6 L/h
- Quantities recalculated for 1 tone of starting material



- The results are similar to those carried out at 800 °C
- The pyrolysis process ended in a shorter time period compared to the experiment carried out at 800 °C

PYROLYSIS OF THE COAL SAMPLE FROM FELSŐNYÁRÁD 900 °C

- Experimental parameters:
- Temperature: 900 °C
- Heating rate: ~ 20 °C/min
- Venturi scrubber flow rate 6 L/h
- Quantities recalculated for 1 tone of starting material

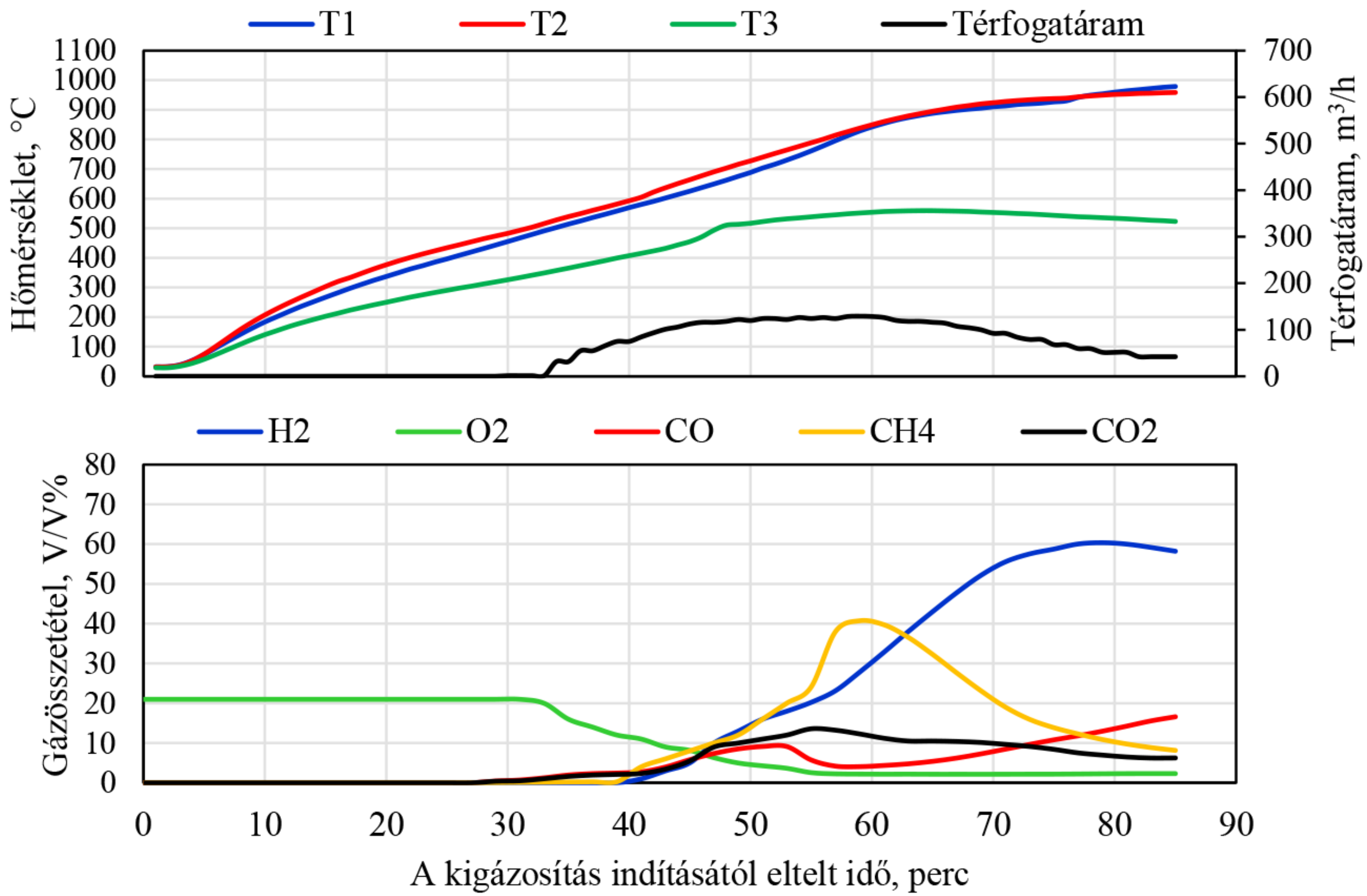


- The results are similar to those carried out at 800 °C
- The pyrolysis process has produced a sligthly higher total amount of sythesis gas compared to the experiment carried out at 800 °C

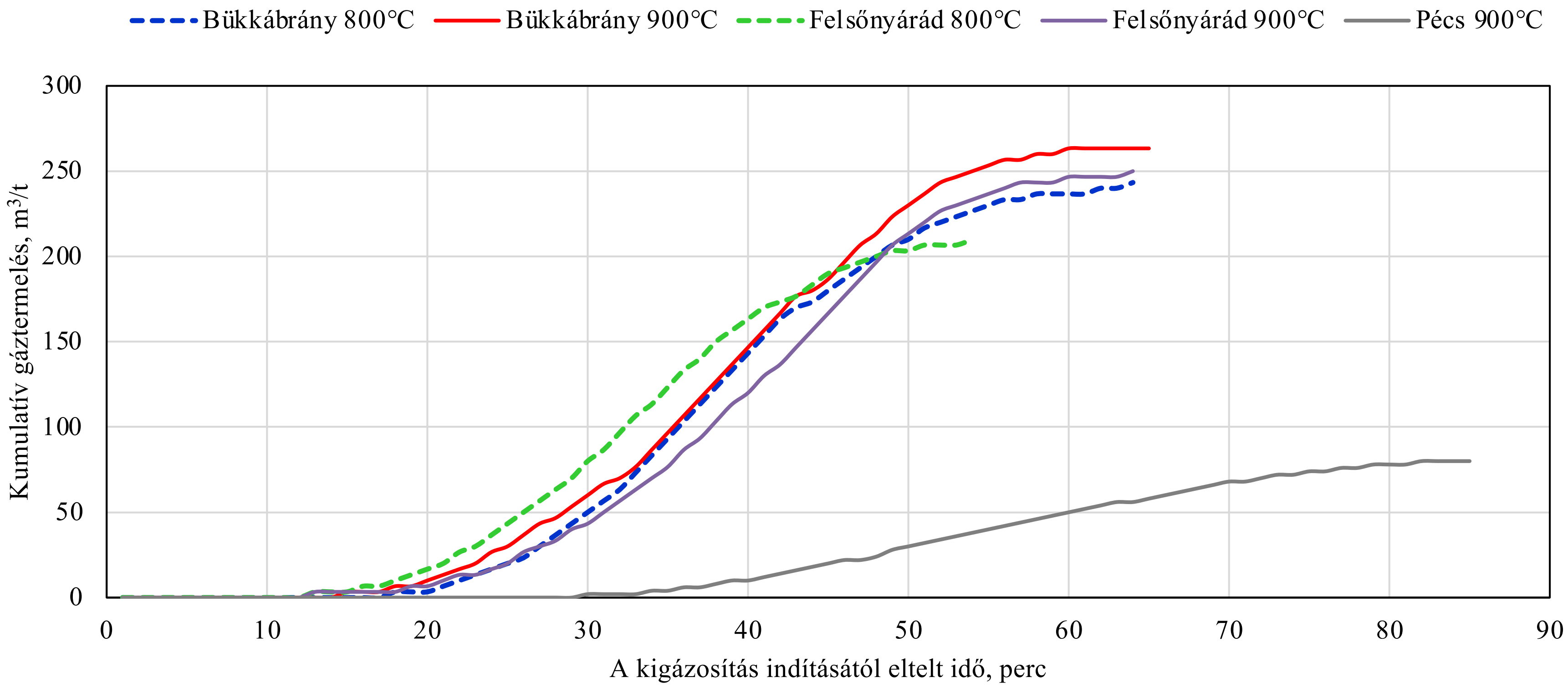
PYROLYSIS OF THE COAL SAMPLE FROM PÉCS 900 °C

- Experimental parameters:
- Temperature: 900 °C
- Heating rate: ~ 20 °C/min
- Venturi scrubber flow rate 6 L/h
- Quantities recalculated for 1 tone of starting material

- The system reached the set temperature much more slowly
- The flow rate and the total gas produced are also smaller
- CH_4 concentration was slightly higher



CUMULATIVE GAS PRODUCTION

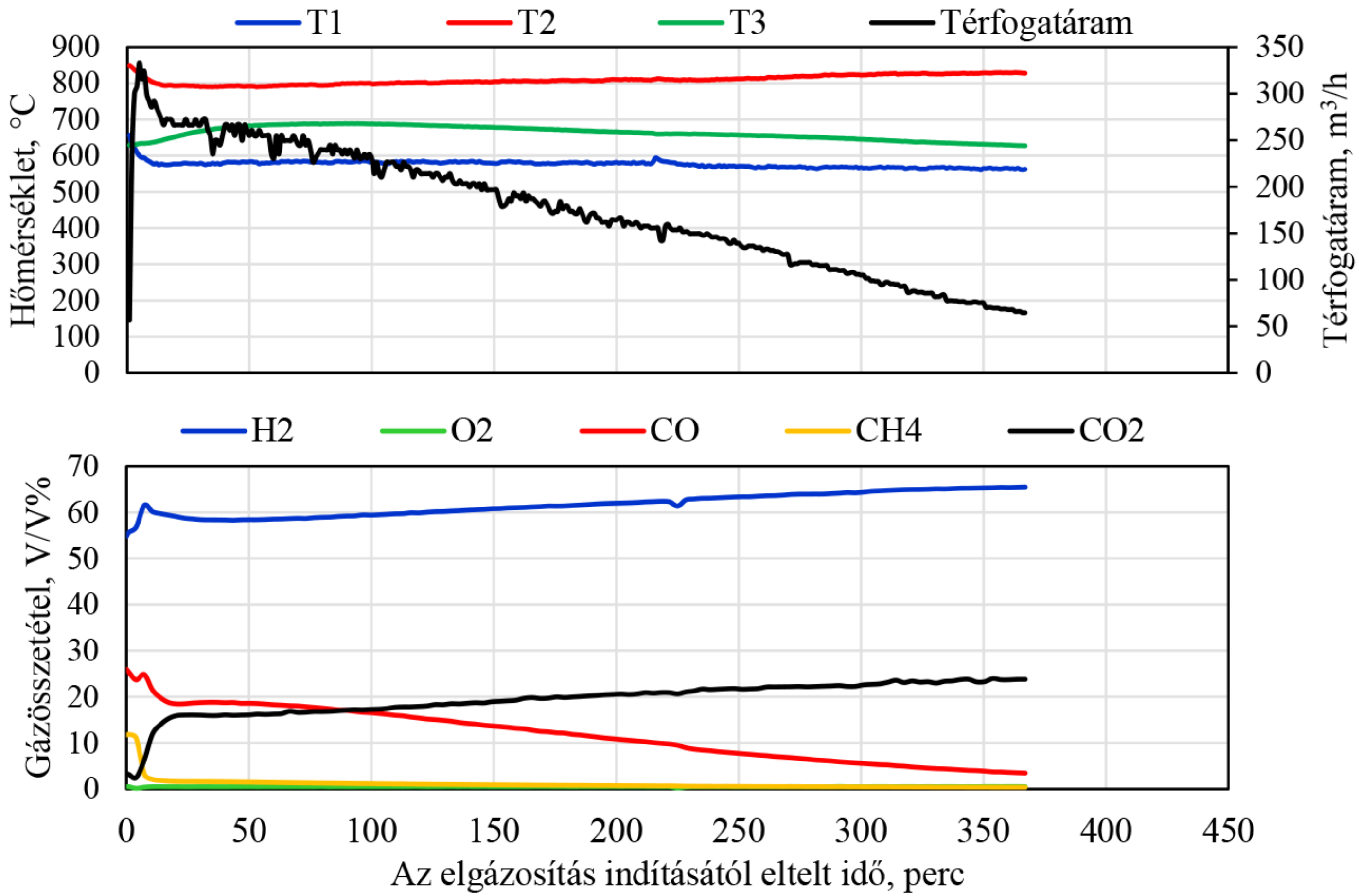


- For both brown coal, it can be seen that a higher temperature will result in slightly larger amounts of gas production
- In the case of the coal sample from Pécs, the total quantity of gas produced is far below compared to the other two carbon samples (~30%)
- The coal sample from Bükkábrány has produced slightly larger amount of sythesis gas at every temperature.

GASIFICATION OF THE COAL SAMPLE FROM BÜKKÁBRÁNY 800 °C

- Experimental parameters:
- Temperature: 800 °C
- Steam flow rate: 10g/min
- Venturi scrubber flow rate 6 L/h
- Quantities recalculated for 1 tone of starting material

- Flowrate shows linear decreasing trend
- H_2 rati is above 60%
- CO and CO_2 ratio becomes reversed after the 90th minute



GASIFICATION OF THE COAL SAMPLE FROM FELSŐNYÁRÁD 800 °C

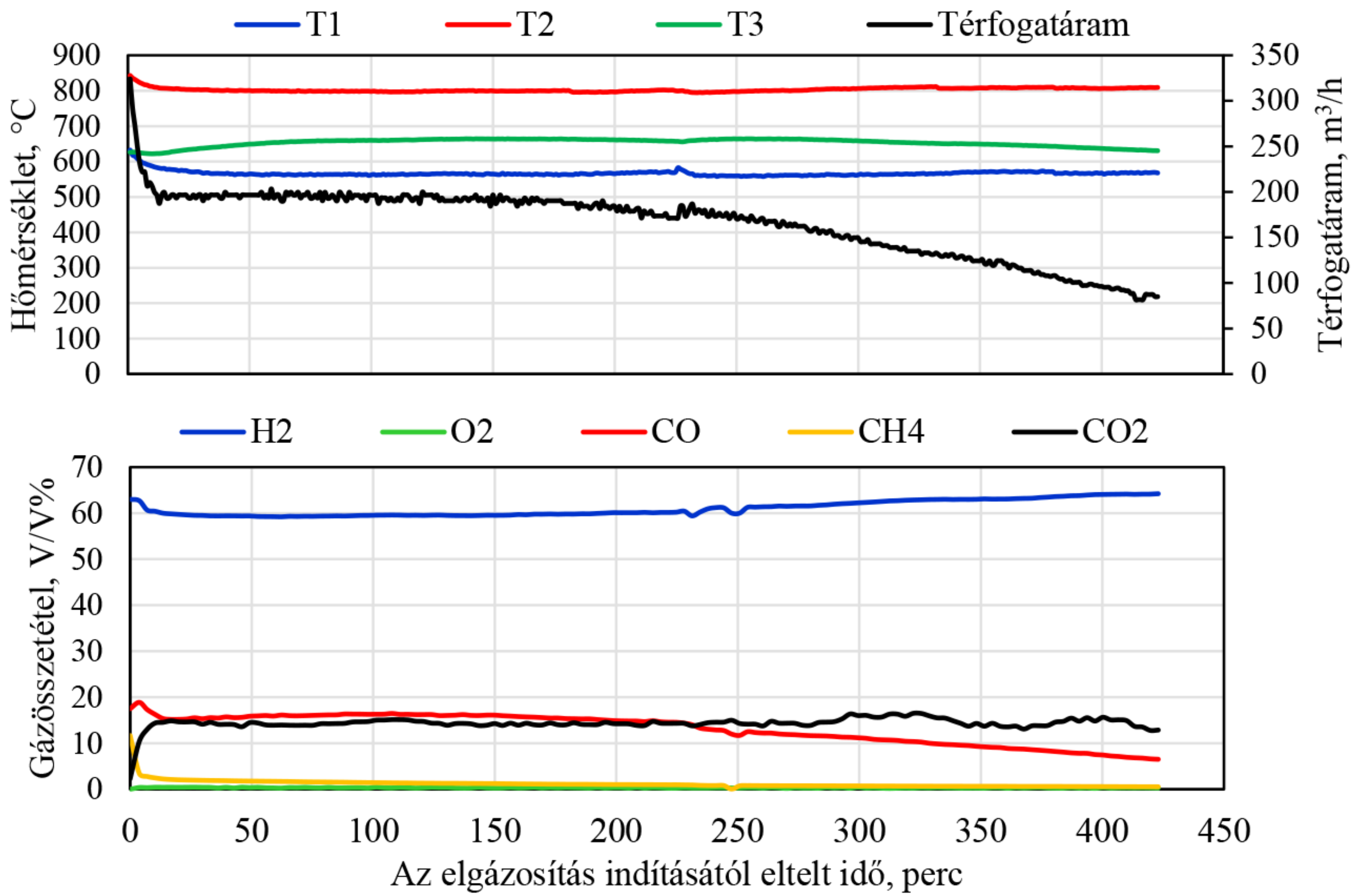
- Experimental parameters:
- Temperature: 800 °C
- Steam flow rate: 10g/min
- Venturi scrubber flow rate 6 L/h
- Quantities recalculated for 1 tone of starting material

○ Gas production in a more onctinuous manner than in the case of the coal sample from Bükkábrány

○ H_2 ratio above 60%

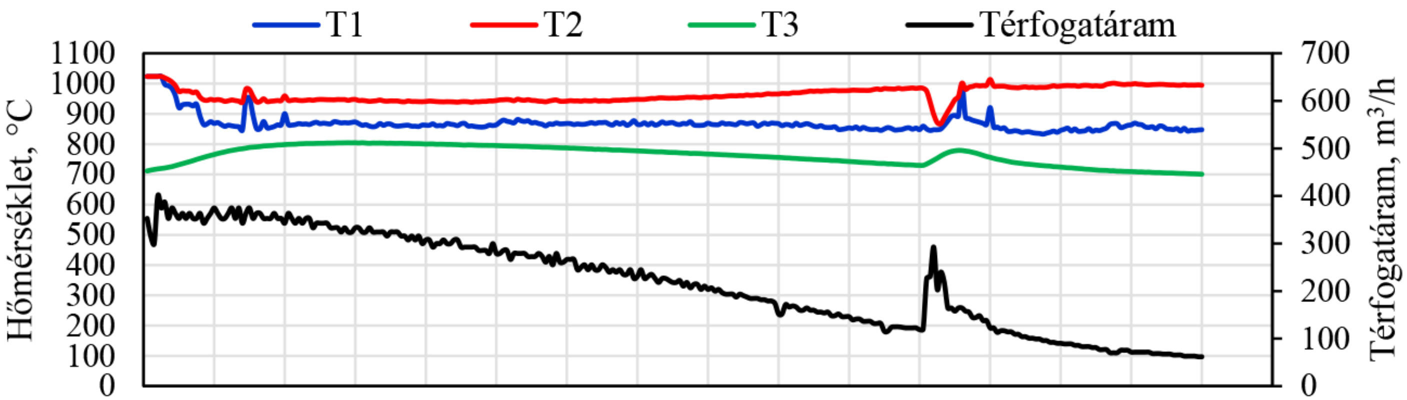
○ CO and CO_2 ratio only reverses after the 4th hour of the experiment

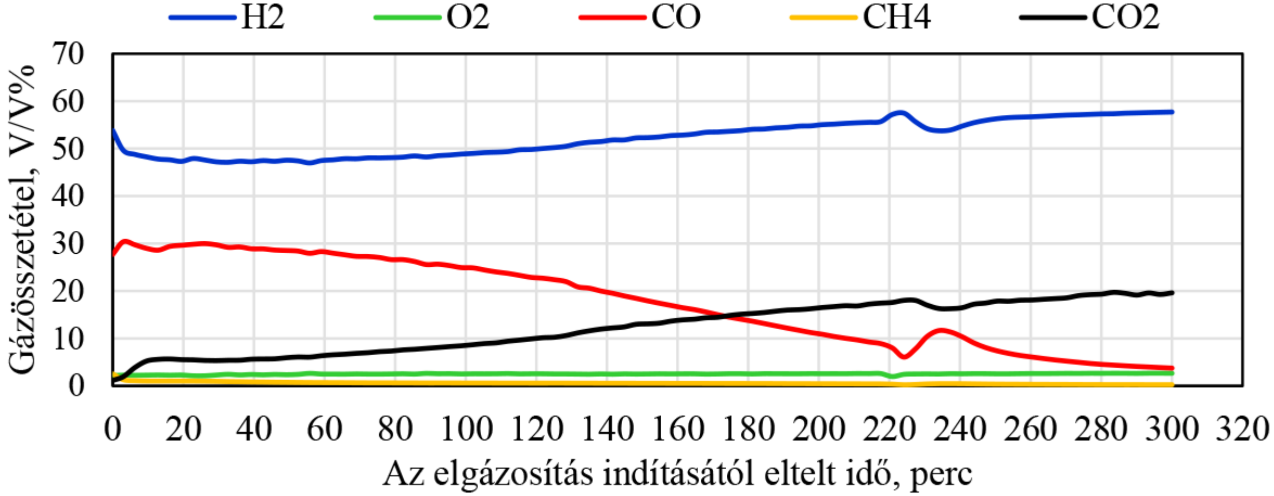
○ CH_4 productions falls below 1% after a few minutes



GASIFICATION OF THE COAL SAMPLE FROM BÜKKÁBRÁNY 900 °C

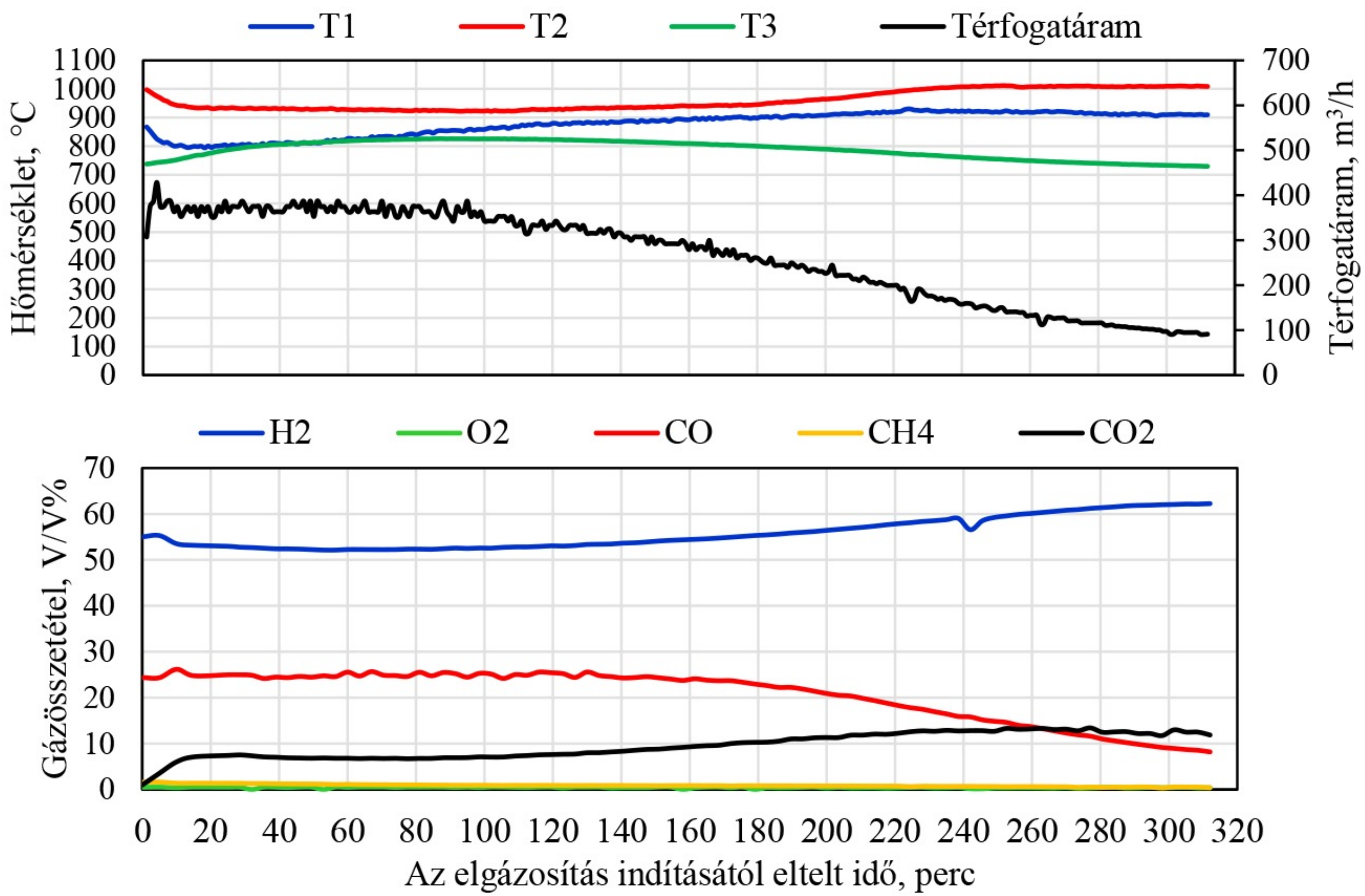
- Experimental parameters:
- Temperature: 900 °C
- Steam flow rate: 10g/min
- Venturi scrubber flow rate 6 L/h
- Quantities recalculated for 1 tone of starting material
  - The results are similar to those carried out at 800 °C
  - H_2 ratio is between 50-60%
  - CO and CO_2 starting ratio is very different compared to the experiment at 800 °C and their ratio only changes after 3 hours





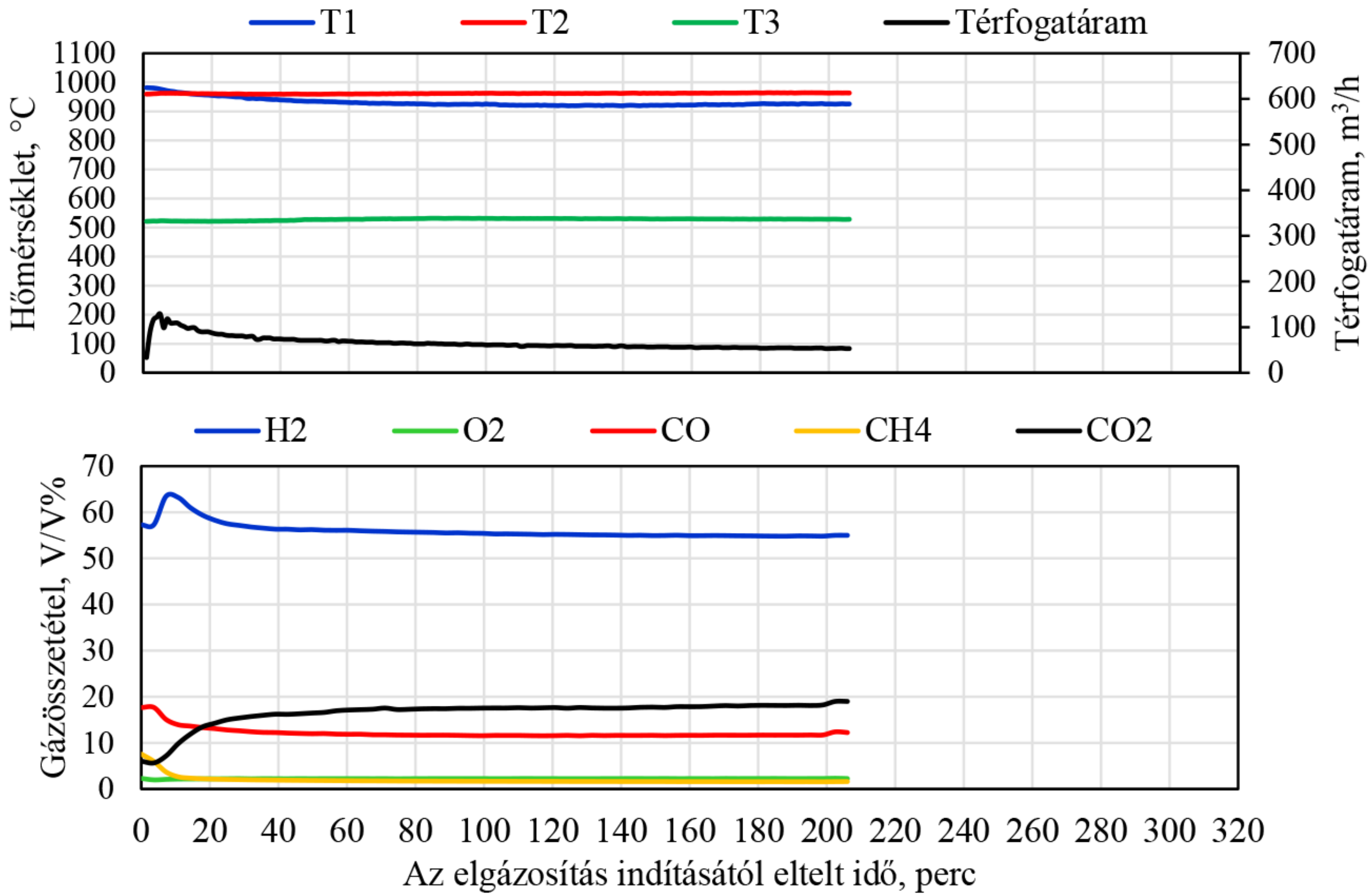
GASIFICATION OF THE COAL SAMPLE FROM FELSŐNYÁRÁD 900 °C

- Experimental parameters:
- Temperature: 900 °C
- Steam flow rate: 10g/min
- Venturi scrubber flow rate 6 L/h
- Quantities recalculated for 1 tone of starting material
  - The results are similar to those carried out at 800 °C
  - H_2 ratio is between 50-60%
  - CO and CO_2 starting ratio is very different compared to the experiment at 800 °C and their ratio only changes at the end of the experiment

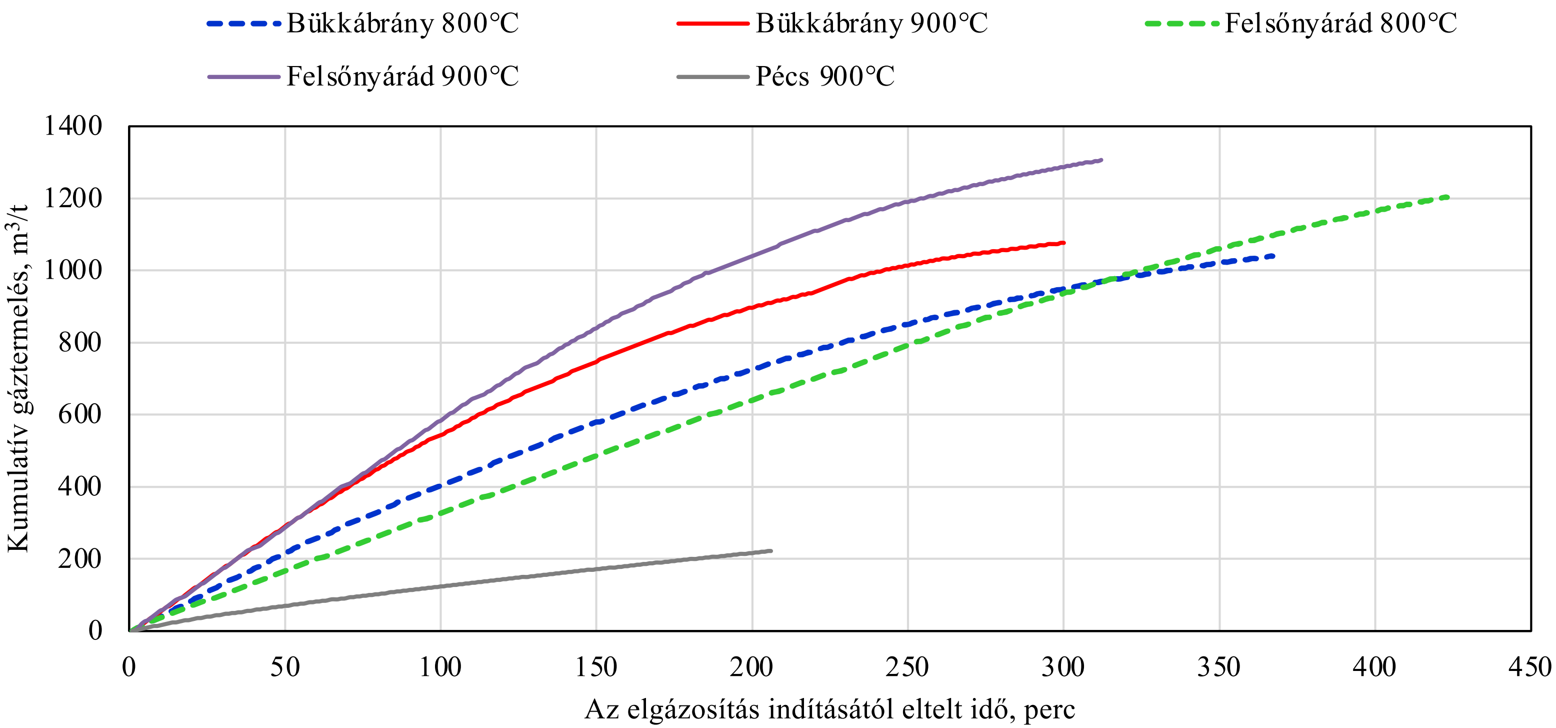


GASIFICATION OF THE COAL SAMPLE FROM PÉCS 900 °C

- Experimental parameters:
- Temperature: 900 °C
- Steam flow rate: 10g/min
- Venturi scrubber flow rate 6 L/h
- Quantities recalculated for 1 tone of starting material
  - Gas production is significantly lower than of the two brown coasl
  - H_2 ratio is between 50-60%
  - CO and CO_2 ratio developemtn within the sythesis gas shows more similarities to the results from the brown coal gasification experiment at 800 °C
  - As a cosequence of the low flow rate the experimetn was stopped after 200 min



TOTAL SYNGAS PRODUCED

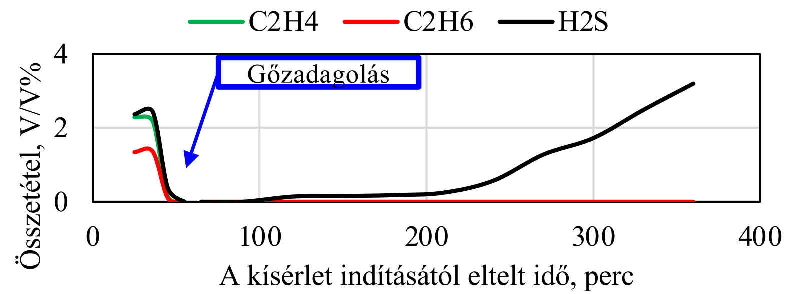


- For both brown coal, it can be seen that higher temperatures have resulted in faster gasification process
- In the case of the coal sample from Pécs, the total amount of gas produced fallen below 25% of the other two samples.
- Larger quantities of synthesis gas was produced in the case of the coal sample from Felsőnyárád.

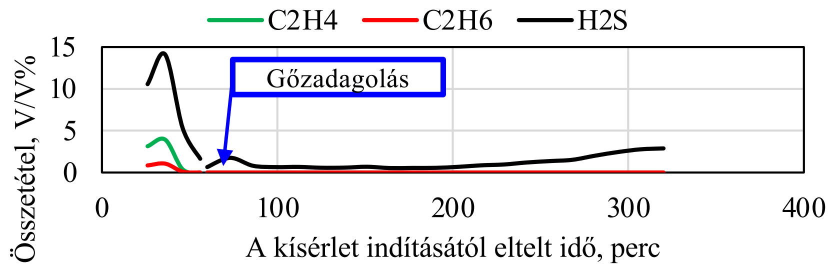
OTHER COMPONENTS IN THE SYNTHESIS GAS

- **Pyrolysis**:
  - C_2H_4, C_2H_6 ratio is higher in synthesis gas at the stage of the pyrolysis than the gasification
  - H_2S ratio is 3 V/V% at its peak in the coal sample from Bükkábrány
  - H_2S reaches values as high as 14 V/V% in the coal sample from Felsőnyárád
  - H_2S ratios are significantly lower in the coal samples from Pécs
- **Gasification:**
  - The hydrocarbons in all three coal samples are below 1 V/V%

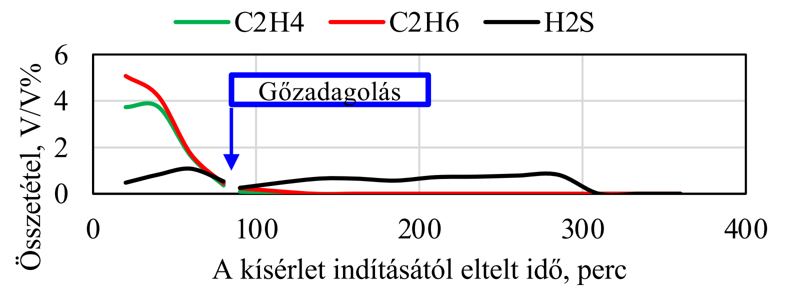
bükkábrányi



felsőnyárádi



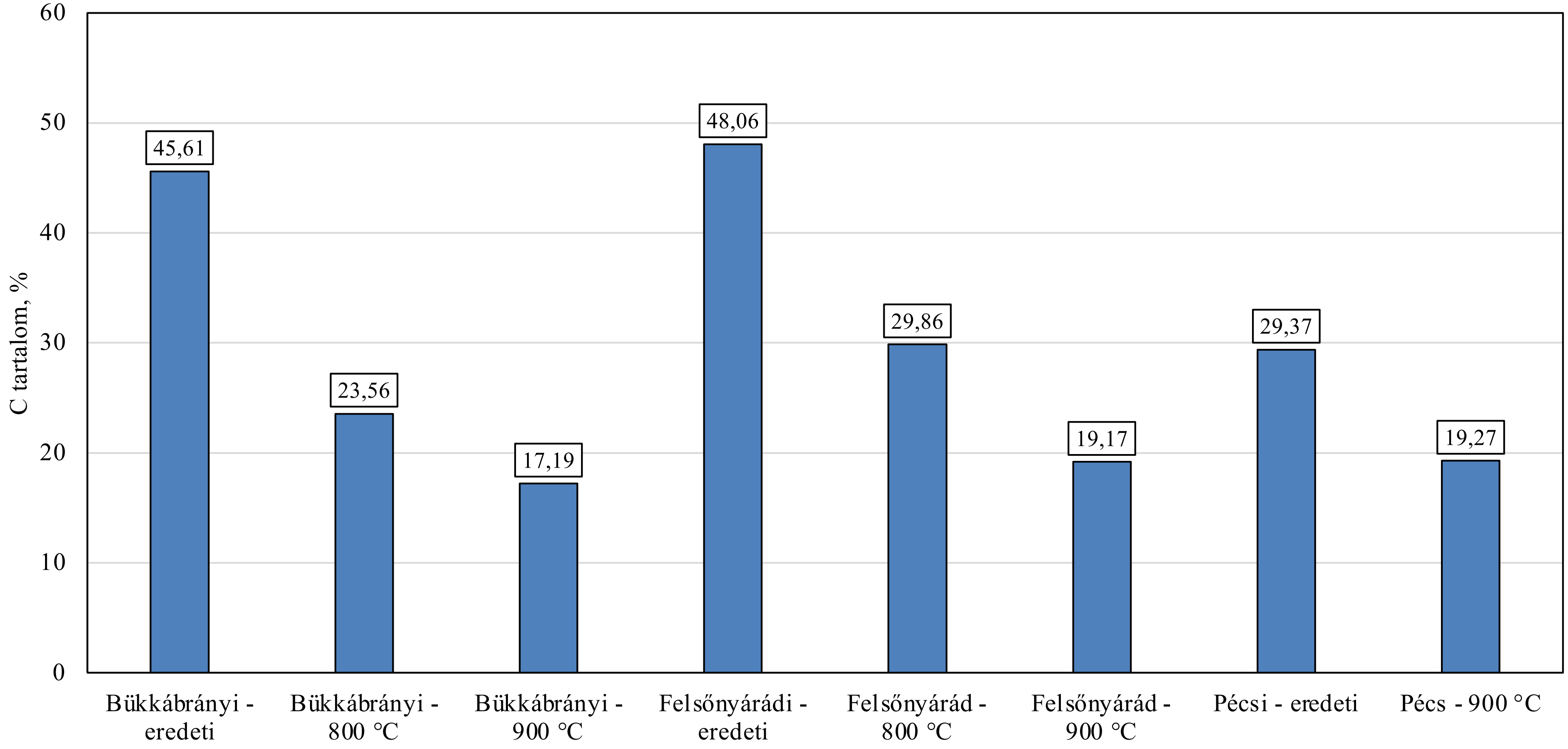
pécsi



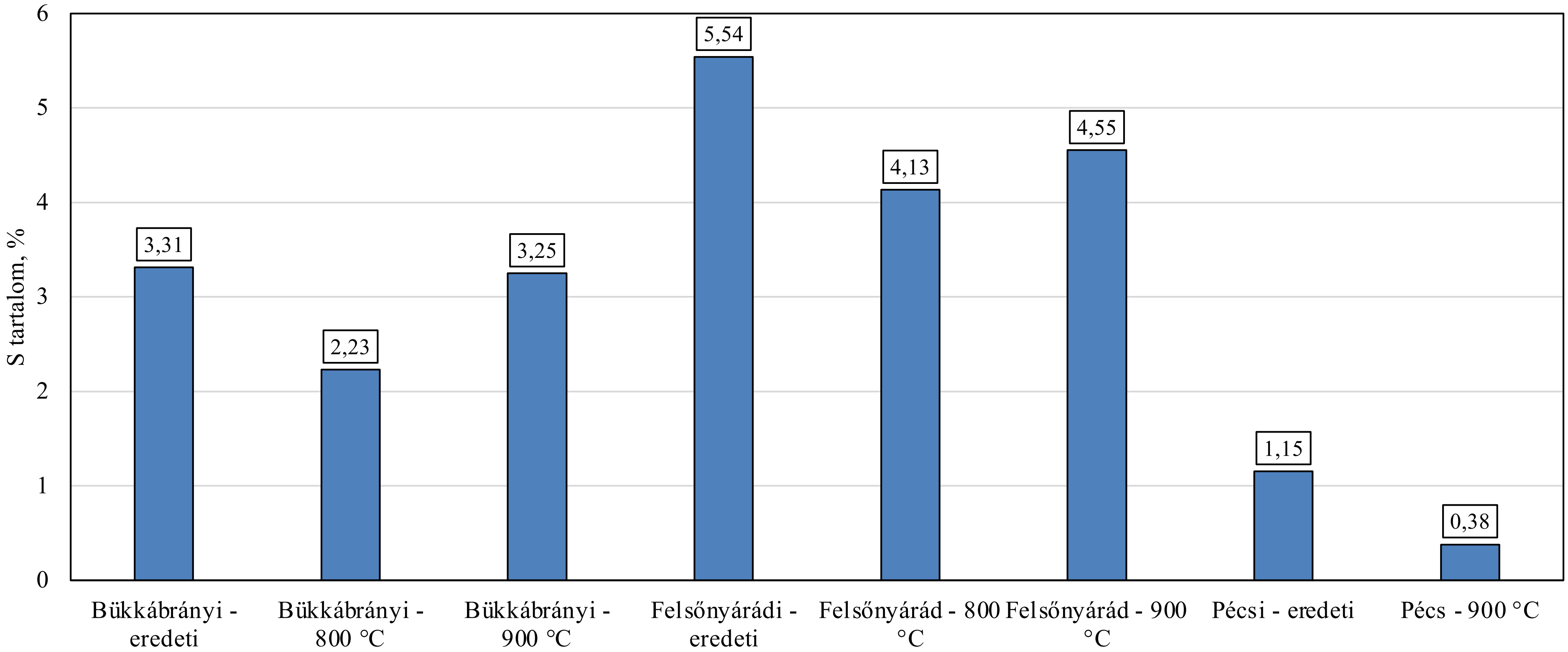
CHNS RESULTS FROM THE COAL SAMPLES

Coals	Dry state, m/m%						Moisture content, m/m%
	N	C	H	S	O	ASH	
Bükkábrányi	0,42	45,61	3,46	3,31	22,20	25,00	8,85
Felsőnyárádi	0,37	48,06	3,64	5,54	16,80	25,60	3,55
Pécsi	0,23	29,37	2,13	1,15	5,71	61,40	1,39

CARBON CONTENT OF THE COALAND COKE SAMPLES



SULPHUR CONTENT OF COAL AND COKE SAMPLES



EVALUATION OF DERIVATIVES FROM THE THERMAL ANALYSIS

Structural composition of carbon samples based on thermal analysis

Coal	Moisture content, m/m%	Volatile content, m/m%	Fixed carbon content, m/m%	Ash content, m/m%
Bükkábrányi	9,5	28,6	36,9	25,0
Felsőnyárádi	2,2	31,0	41,4	25,4
Pécsi	0,2	11,5	26,9	61,4

Coal	Drying, °C	Volatile separation, °C	Intense combustion, °C
Bükkábrányi	25-220	220-460	240-914
Felsőnyárádi	25-170	260-460	260-950
Pécsi	25-150	280-520	288-768

ASH SAMPLES SOFTENING, MELTING PROPERTIES

- **The difference in temperature between the softening properties of brown coal samples:**
- Deformation temperature 85 °C
  - Sphere temperature 25 °C
  - Hemispherical temperature ~25 °C
- **Coal sample from Pécs**
  - Non-identifiable characteristic temperatures, soft at 1250 °c.

Coal sample from Pécs after gasification

Parameter		Deform. temp.	Sphere temp.	Hemisphe-rical temp.	Flow temp.
Temperature		°C	°C	°C	°C
Marking		DT	ST	HT	FT
Bükkábrány Ash	1.	1165	1255	1275	-
	2.	1165	1255	1280	-
	átl.	1165	1255	1277,5	>1 290

Parameter		Deform. Temp.	Ball temp.	Hemisphe-rical temp.	Flow temp.
TEmperature		°C	°C	°C	°C
Marking		DT	ST	HT	FT
Felsőnyárád Ash	1.	1250	1280	1305	-
	2.	1250	1280	1305	-
	átl.	1250	1280	1305	>1 330

SUMMARY

- Based on the gasification experiments, both brown coals are suitable for the production of good quality synthesis gas.
- Based on the large ash content of the coal sample from Pécs, its low ash melting point and the resulted volume of the sythesis gas during the experiments cannot be recommended for such use.
- With the increase in temperature, we have achieved faster processes, which can be problematic at significantly higher temperatures than 900 °C.
- High percentage of methane and other hydrocarbons in the stage of the pyrolysis can be reduced with a multistage gasification setup.
- For both brown coal, we managed to produce significant quantities of gas with a high hydrogen content, which may be suitable for the prodcution of secondary raw materials, as methanol
- The produced 2-3 %V/V of H_2S can be removed from the sythesis gas and recovered and retailed in the form of Sulphur or Sulphuric acid to further increase cost effectiveness
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Thank you
for your attention!