

**SMALL-SCALE ENGINEERED HIGH
FLEXIBILITY GASIFIER**

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Abstract

This project advances a small-scale gasification unit as the first step in syngas-based hydrogen, chemicals, and synthetic fuels production. This unit is associated with an enhanced flexibility to different carbonaceous feedstocks including different types of coals, biomass, and plastics.

The purpose of the project was to demonstrate feasibility and efficiency of

- coal pyrolysis in an auger reactor (pyrolyzer);
- supplemental methane and pyrolysis gas conversion into syngas in a proprietary non-catalytic converter;
- combined performance of pyrolyzer and non-catalytic converter to convert coal into syngas

The proposed technology is based on an application of an intermediate speed pyrolysis at the temperature range 400-600°C as the first stage of biomass processing. At an industrial scale, an incorporation of coal pyrolysis into a feeding machine – auger-reactor allows to decrease its capital cost. At a pilot scale, it permits to employ electricity to build a compact device for testing of downstream equipment. The auger-reactor (pyrolyzer) generates pyrolysis gas and char practically from any carbonaceous feedstocks but their compositions and quantities are determined by their types.

Pyrolysis gas is converted into syngas (mix of H₂ and CO) in a novel, proprietary hydrogen flame assisted non-catalytic converter which employs O₂ instead of air as an oxidizer. This reactor (converter) allows an easy adjustment to different pyrolysis gas compositions and tolerates a presence of sulfur and nitrogen contaminants. Our technology assumes carbonaceous feedstocks gasification with oxygen to allow the products H₂, CO or CO₂ to be not diluted in N₂ and ready for the following synthesis of chemicals and fuels. Due to the same reason, it permits a more efficient CO₂ capture for its transport and storage.

An implementation of our small-scale gasification process may overcome economic constraints by a flexible acceptance of coal, biomass, and plastics as well as their unsorted mixtures to make syngas for the following production of pure hydrogen, chemical and/or synthetic fuels.

Acknowledgement

The support for this project by the US Department of Energy/ National Energy Technology Laboratory (DOE/NETL) and Southern Research (SR) under Cooperative Agreement DE-FE0031531 “Small-scale engineered high flexibility gasifier” is gratefully acknowledged. As the NETL project manager, Ms. Diane Madden provided suggestions and guidance throughout the project.

The author gratefully acknowledges the Southern Research Energy and Environment Division team on this project consisting of Engineers, Chemists and Technicians including Alireza Moradi, Vincent Scott, Chansé Appling, Wesley Wilson, Yan Hong

Executive Summary

The overall objective of this project is to develop a small-scale engineered modular downdraft oxygen-blown pressurized coal gasifier that (1) can be standardized for shop fabrication to allow process scale-up via modular expansion and/or deployment at remote sites and (2) can be cost effectively deployed in an energy conversion system such as combined heat and power (CHP) scaled to 1-5 Megawatts (MW).

Entrained flow dry and slurry gasifiers, and transport gasifiers are complex, require significant energy for preparing coal feed, and cannot be cost effectively scaled down. Updraft fixed-bed and fluidized-bed gasifiers produce significant amounts of tar, ammonia, and other by-products that can plague downstream operation, requiring complex and parasitic separation operations. The large number of unit operations required renders the energy conversion system based on these gasifiers uneconomic at small-scale.

Unlike these gasifiers that cannot be deployed cost effectively at small-scale, the proposed engineered modular downdraft gasifier is simple and appropriate for small-scale, and uses three (or more) steam/oxygen inputs, located along the gasifier vertical axis based on a computational model, to optimize coal throughput and cold gas efficiency, and nearly completely crack or reform tar. Furthermore, the design allows manipulation of char make and quality and syngas make and composition. Southern Research (SR) proposes to advance the proposed oxygen-blown pressurized downdraft gasifier technology through pilot scale development and testing in order to be ready to construct a gasifier for a 1-5 MW CHP system.

Specific objectives of the project are to:

- Construct a computational model for the novel pressurized downdraft gasifier with multiple oxygen and steam (at least 3) inputs.
- Design and construct a 25-50 lb/hr pressurized oxygen-blown downdraft gasifier based on the model. Commission and test the gasifier at a range of conditions to compare its performance with that predicted by the computational model.
- Update the computational model based on the gasifier data, and use the updated model to design a gasifier sized for a 1 MW CHP system.
- Develop an Aspen-based model for a fully integrated modular oxygen-blown 1-5 MW energy conversion system, for example CHP, at a suitable site and conduct a techno-economic analysis (TEA) for the system.

SR will select two coals and measure their gasification properties at lab-scale. Based on literature information and lab-scale data such as gas evolution, char production, and char characteristics as a function of heating rate, temperature, and soak time, parameters will be estimated as input for a computational model for down-draft gasifier. Based on these parameters, a computational model will be developed to simulate a downdraft gasifier with multiple (up to 3) steam-oxygen inputs. SR will then use the model to guide engineering design of a 25-50 lb/hr gasifier. SR will then design, construct, commission, and test the gasifier. In addition to supporting the design of the

gasifier, the computational model will be used to develop an experimental plan to help optimize performance of the gasifier. In turn, the experimental data from the gasifier will be used to validate and update the computational model. Based on the data and updated computational model, SR will design a gasifier for a 1 MW energy conversion system. Finally, SR will develop an Aspen-based model for a fully integrated modular oxygen-blown 1-5 MW power system at a suitable site and conduct a techno-economic analysis (TEA) to examine its economic performance.

1. Introduction

A flexible adjustment of gasification operational parameters to accept diverse blends of coal and various renewable and waste feedstocks, especially biomass and plastic wastes may substantially extend application of gasification technologies to obtain syngas as a feedstock to produce synthetic fuels and chemicals¹. When blending biomass with coal into the feedstock and subsequently capturing CO₂ via pre-combustion capture and storage, it is possible to emit less CO₂ into the atmosphere than it took to produce the virgin biomass material, hence resulting in net negative carbon emissions².

In contrast to incineration, gasification provides a lucrative alternative to combustion and subsequent thermal power generation. It may generate a concentrated, not diluted in N₂ syngas suitable for production of chemicals and synthetic fuels. For this purpose, instead of air, oxygen (typically 90-99.9%O₂) is used as an oxidizer meaning that air is separated into oxygen and nitrogen upstream of gasification by well-established technologies (cryogenic, pressure swing adsorption, and etc.). A lot of efforts have been recently made to improve different air separation technologies to obtain oxygen³. In spite of additional expenses related to air separation, utilization of oxygen allows decreasing the cost of CO₂ capture due to a higher concentration of CO₂ in exhaust gases.

The goal of this project is to build a pilot unit to show performance of a modular gasifier to partially oxidize coal into syngas with pure oxygen. The novelty of our proposal is represented by a new method for conversion of pyrolysis gases. The overall gasification process is divided into two stages (i) pyrolysis with production of charcoal and pyrolysis gas; (ii) supplemental methane and pyrolysis gas conversion into syngas in a proprietary non-catalytic converter. It should be mentioned that charcoal could be further gasified to make additional amount of syngas or leached with appropriate alkaline and/or acid mixtures to substantially decrease its toxicity.

As it was practically demonstrated for gasification technologies, an introduction of plasma gas into a reaction mixture of hydrocarbon vapors, oxygen, and steam promotes syngas production and inhibits tars and soot formation. The thermal plasma gas (usually air with temperature up to 5000°C) is generated by an introduction of a gas flow into a gap between electrodes that form a high-voltage electric field. The oxy-hydrogen flame obtained through combustion of hydrogen and oxygen has adiabatic temperature 2800°C at which superheated steam is mixed with OH- radicals that are well-known as species substantially accelerating breakdown of hydrocarbons. An oxy-hydrogen burner is an essential part of the proposed converter and its multipurpose use can be described as follows: ignite pyrolysis gas; supply oxygen into reaction zone; stimulate decomposition of hydrocarbons containing in pyrolysis gas; promote hydrocarbons conversion into syngas through their steam reforming.

¹ G.Stiegel, R.Maxwell. Gasification technologies: the path to clean, affordable energy in the 21st century. Fuel Processing Technology. 71(2001) 79-97

² U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy (EERE), "Biomass Energy Data Book: Edition 4," ORNL/TM-2011/446, September 2011

³ S.Alavandi, J.Seaba, G.Subbaraman. Emerging and existing oxygen production technology scan and evaluation. Report issued 4/24/2018, GTI project number 22164

2. Objectives

Due to the 1990 amendments to the Clean Air Act establishing a national permits program to reduce sulfur dioxide and other toxic air emissions, 19 Alabama coal-fired power generation units were closed and 6 were converted to natural gas between the years of 2012-2019⁴. Gasification of coal into syngas to produce pure hydrogen, synthetic fuels or chemicals might be the way to suppress this trend.

The objective of the proposed project is to carry out development, testing and enhancement of the “Small-scale engineered high flexibility gasifier” representing a hybrid pyrolysis-gasification technology to produce syngas (mix of H₂ and CO).

Syngas cleaning from sulfur, nitrogen, and chlorine contaminants is regularly carried out by wet (caustic, lime) scrubbing. An implementation of an appropriate scrubbing method is out of scope of this project. A tar destruction will be done by an implementation of hot oxidation zones with a temperature range 900-1100°C as it will be described further.

The hybrid pyrolysis-gasification technology assumes coal and supplemental methane gasification and partial oxidation with oxygen (instead of air) to allow the products H₂, CO or CO₂ to be not diluted in N₂ and ready for the following H₂ separation, synthesis of fuels and chemicals as well as more efficient CO₂ collection for its transport and storage.

An economic efficiency of the proposed technology depends on commercial products manufactured from syngas (syngas represents an intermediate substance). As shown in Fig. 1, production of electricity, where syngas is used as a fuel, seems less attractive than production of pure hydrogen as well as synthesis of liquid fuels (gasoline) and industrial chemicals (formic acid).

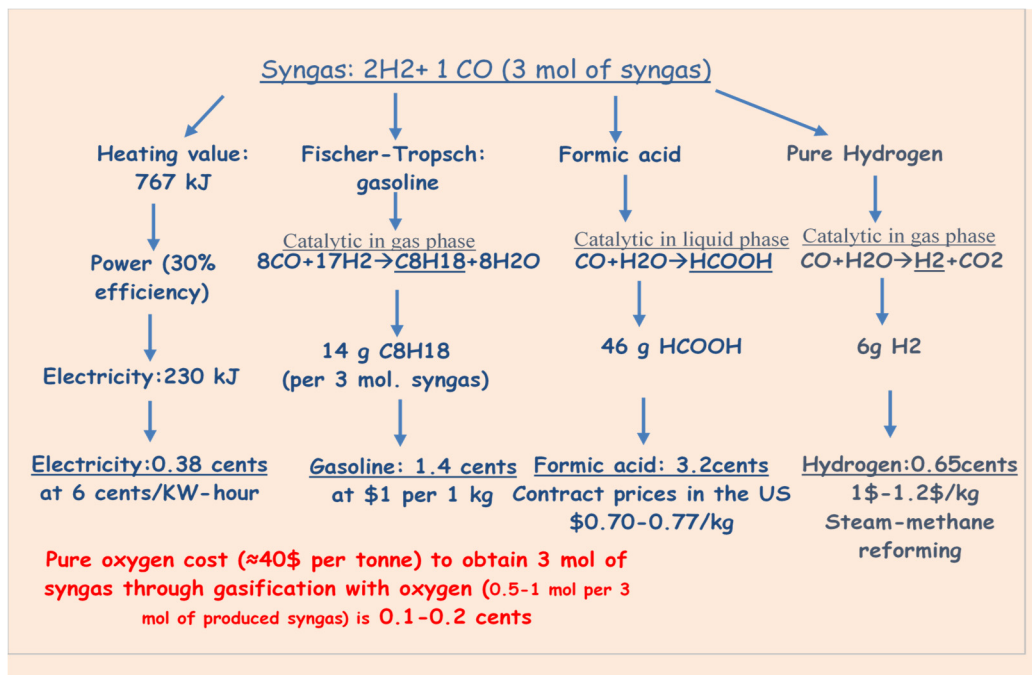


Fig.1. Potential revenues due to utilization of syngas obtained through gasification of carbonaceous materials with oxygen

⁴ Wikipedia: List of power stations in Alabama. Via https://en.wikipedia.org/wiki/List_of_power_stations_in_Alabama. Accessed June 10,2021

3. Technology Background and Description

The novelty of our proposal is represented by a new modular integration and improvement of already known technological blocks to produce hydrogen and syngas-based fuels, chemicals, and/or electricity aimed at an adjustment of capital investments based on feedstocks composition and acceptance of different carbonaceous feedstocks. A variation in syngas quantity and quality is mitigated by an optional, supplemental methane (natural gas) supply.

A process flow diagram for the proposed technology is shown in Fig.2. An overall gasification process is separated into three distinctive stages (drying & pyrolysis, pyrolysis gas partial oxidation, char gasification) with a specific device for each stage. This allows optimizing each device almost independently with a possibility to eliminate one of them depending on feedstock properties. For instance, if the unit processes only plastics with a high percentage of volatiles, char gasifier (rotary kiln gasifier) might be eliminated.

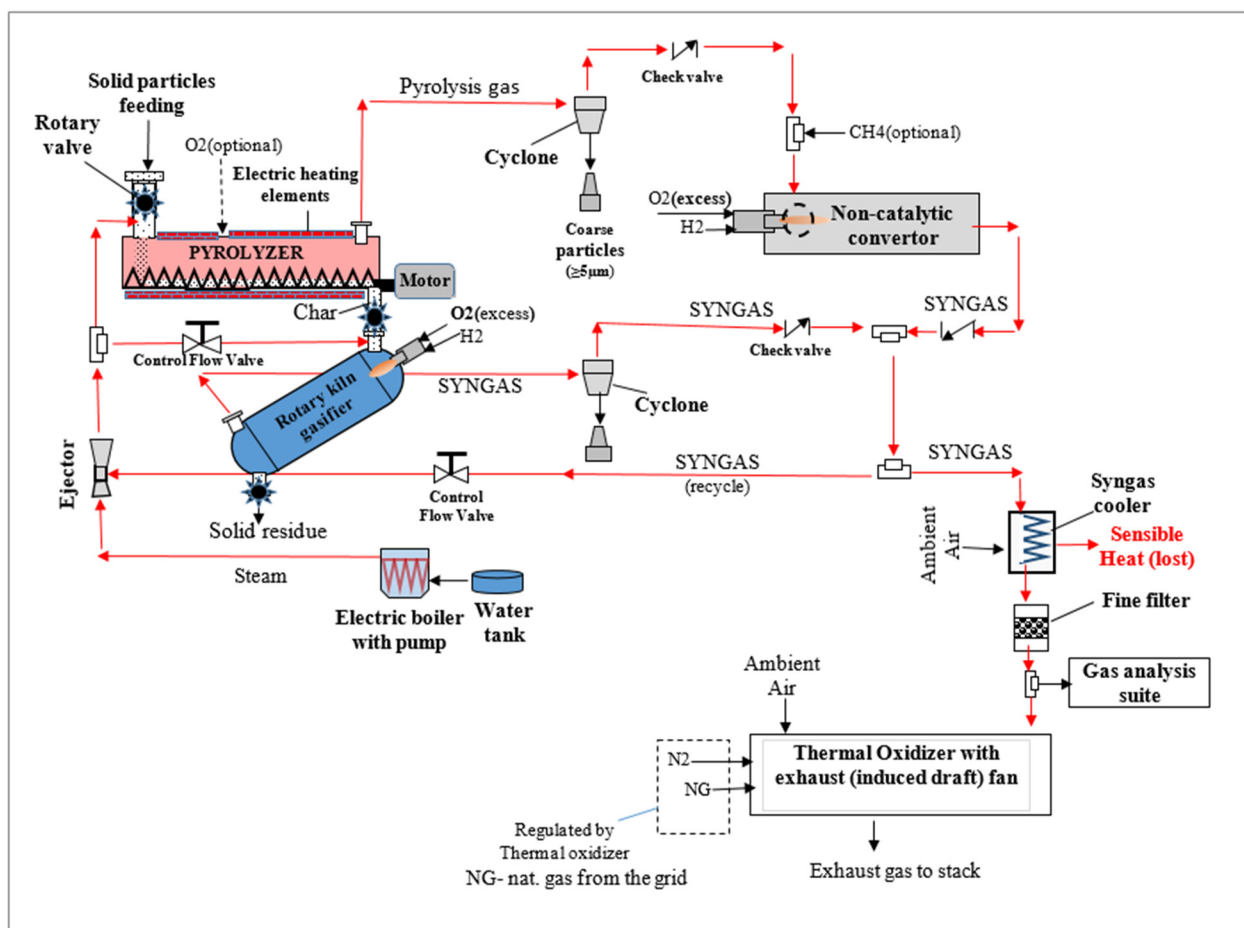


Fig.2. Process flow diagram for a pilot unit to carry out gasification in three stages (rotary kiln gasifier was removed due to budget constraints).

The process utilizes industrially pure oxygen (99.5-99.9%) as an oxidant of coal and starts with an intermediate speed pyrolysis at the temperature range 400-600°C as the first stage of biomass thermal treatment. Coal is coming into a pyrolyzer (auger-reactor) through a number of standard devices: volumetric feeder and rotary valve which separates pyrolyzer from the ambient air. At an

industrial scale, an incorporation of biomass pyrolysis into a feeding machine – auger-reactor allows to decrease a capital cost and, at a pilot scale, permits to employ electricity to build a compact device for testing of downstream equipment. Utilities, non-catalytic converter and pilot scale electric pyrolyzer are designed, purchased and utilized in the frame of this project (Fig.3).

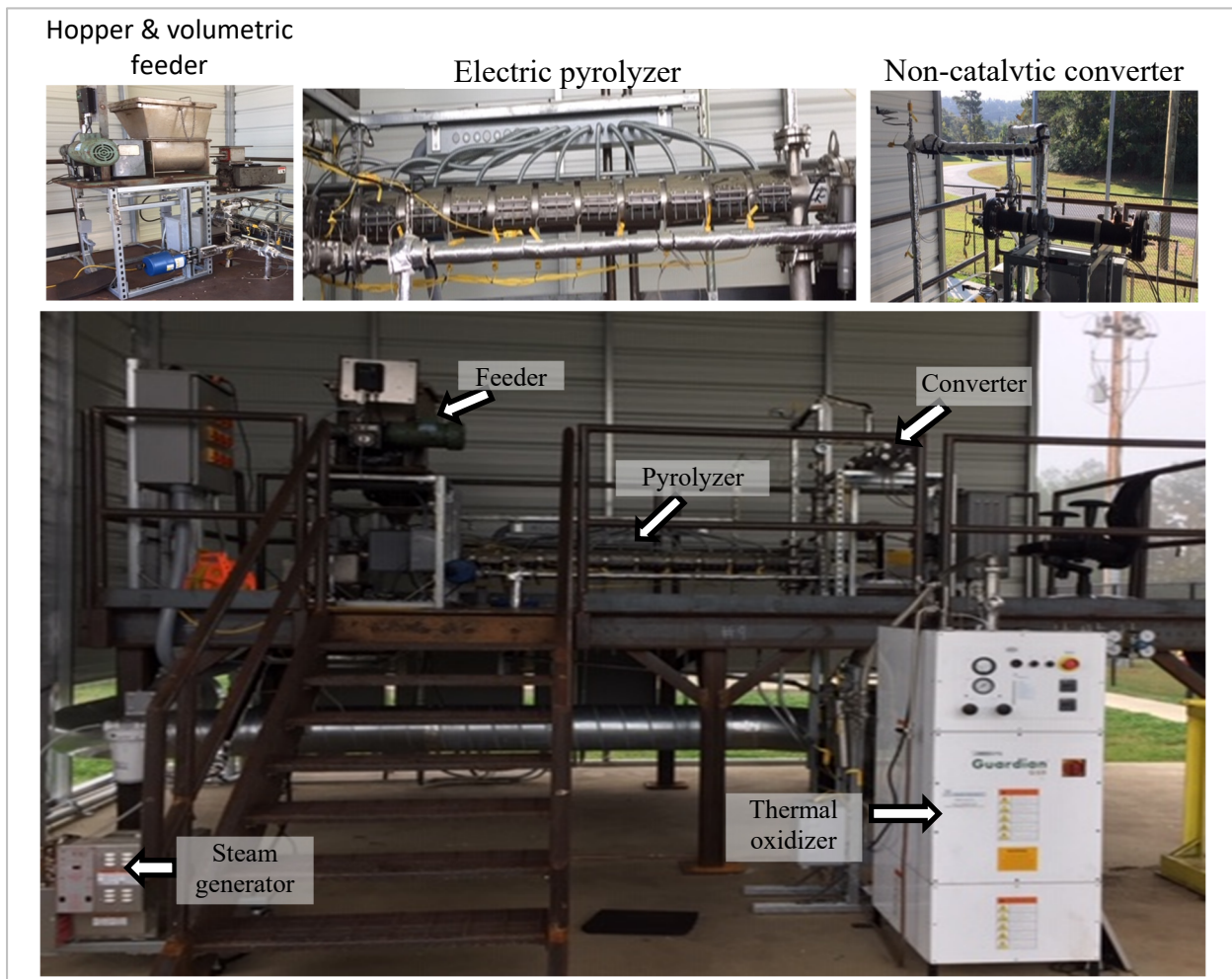


Fig 3. A pilot scale gasification unit built in the frame of DOE project (DE-FE0031531)

The released in pyrolyzer volatiles (pyrolysis gases) are directed into a proprietary (novel) non-catalytic converter (reactor) where they are converted into syngas. The pressure in the reactor is slightly negative; it is maintained by an ejector (thermo-compressor) and induced draft fan incorporated into thermal oxidizer. This ejector pulls a gas fraction out of reactor by using an aspiration force of high-pressure steam (75-85 psig) generated by an electric boiler and directs syngas-steam mixture back into pyrolyzer.

In the future, a heated syngas-steam mixture will be tested for its utilization as a sweep gas in pyrolyzer. “Sweep” gas improves rates at which solid carbonaceous particles give off volatiles during pyrolysis. Such choice allows not to dilute the obtained syngas in N₂ usually selected for that purpose. In the case of a slow indirect heat transfer (through the wall of pyrolyzer), its intensity can be improved by a combination of indirect and direct heat transfers by adding a very limited amount of oxygen to combust H₂(CO) in syngas-steam mixture.

Char from pyrolyzer could be processed in a rotary kiln gasifier where fixed carbon in char reacts with oxygen, steam, carbon dioxide to generate another stream of syngas. The choice of a

rotary kiln vs. fluidized bed gasifier is based on its better tolerance to different char particle sizes⁵. Rotary kiln gasifiers provide an interaction of char solid particles with gas in slightly tilted and rotating cylindrical chambers with abrasion resistant refractory liners on its walls. A stirring action during rotation supports exposing the new solid surfaces to the gas⁶. Direct fired rotary kilns gasifiers (Fig. 4) are adiabatic (auto-thermal) converters where the heat for endothermic reactions is provided by exothermic reactions within their internal spaces. An increase in oxygen supply intensifies exothermic reactions and allow reaching temperatures in the range 900-1100°C ensuring decomposition of most tars⁷. We were planning to apply the same multi-tubular oxy-hydrogen burner with an excess of oxygen and very limited hydrogen supply (amount of syngas produced supposed to be much higher than H₂ consumed in the burner).

Rotary kiln gasifiers are less sensitive to the fuel nature and, indeed, able to accommodate large variations in particle sizes, shapes, compositions as well as calorific values⁸.

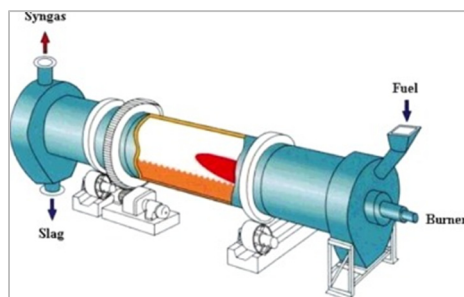


Fig.4. A principal illustration of a direct fired rotary kiln gasifier

Rotary kilns are proven thermal processing devices used for combustion or gasification of municipal solid waste as well as solid and liquid hazardous medical waste. Authors of this proposal contacted a number of manufacturers to evaluate the cost of a pilot-scale direct fired rotary kiln gasifier (Table 1). Unfortunately, due to budget constraints an implementation of a rotary kiln gasifier became impossible and it was removed from process flow diagram in Fig.2.

⁵ F. Montagnaro, C. Tregambi, P.Salatino, O. Senneca , R. Solimene. Modelling oxy-pyrolysis of sewage sludge in a rotary kiln reactor. *Fuel* 231(2018) 468–478

⁶ A.Molino,S.Chianese,D.Musmarra. Biomass gasification technology: The state of the art overview. *Journal of Energy Chemistry* 25 (2016) 10-25

⁷ H.Shi,Wen.Si,X.Li. The Concept, Design and Performance of a Novel Rotary Kiln Type Air-Staged Biomass Gasifier. *Energies* 9(2016) 67; www.mdpi.com/journal/energies

⁸ F. Montagnaro, C. Tregambi, P.Salatino, O. Senneca , R. Solimene. Modelling oxy-pyrolysis of sewage sludge in a rotary kiln reactor. *Fuel* 231(2018) 468–478

Table.1. Negotiable prices for a pilot rotary kiln gasifier

Manufacturer	Cost of a pilot scale direct rotary kiln gasifier	Web-site
Harper International	\$500,000+	https://www.harperintl.com
Harrop Industries, Inc.	\$200,000+	https://harropusa.com
Hitemp Technology Corp.	\$100,000+	https://hitemptech.com

As an example of the current emerging technologies in the field may serve the pilot “Viking” gasifier which is based on the two-stage gasification principle, where pyrolysis and gasification takes place in two separate reactors (see Fig. 5)⁹. The distinct differences of the proposed technology from “Viking” gasifier are summarized below:

- three stage process with a possibility to eliminate char gasification stage;
- oxygen as an oxidant in order to obtain a concentrated (not diluted in nitrogen) syngas to be utilized in production of biofuels or chemicals;
- syngas recycling into pyrolyzer to allow auto-thermal pyrolysis with a limited addition of oxygen;
- an oxy-hydrogen flame assisted proprietary non-catalytic converter of volatiles to generate soot and tar free syngas

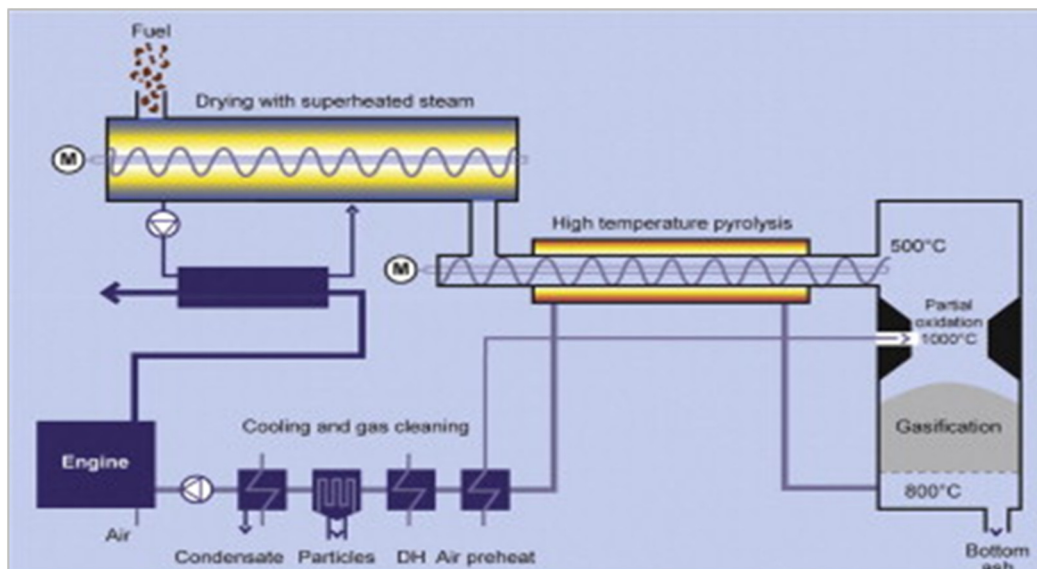


Fig 5. Two stage concept of the “Viking” gasifier

As mentioned above, our design has some similarities with successfully tested two stage “Viking” gasifier. Another example of small and middle scale two stage gasification system with a pyrolyzer - high temperature reformer combination is called STAR-MEET (steam/air reforming type multi-staged enthalpy extraction technology)¹⁰. This confirms that our endeavors comply with some trends in development of new gasification technologies. The following subsections will be

⁹ J. Ahrenfeldt, T. Thomsen, U. Henriksen, L. Clausen. Biomass gasification cogeneration – A review of state of the art technology and near future perspectives. *Applied Thermal Engineering*, 50(2013), 1407-1417.

¹⁰ K. Yoshikawa. R&D (Research and Development) on distributed power generation from solid fuels. *Energy* 31 (2006) 1656–1665

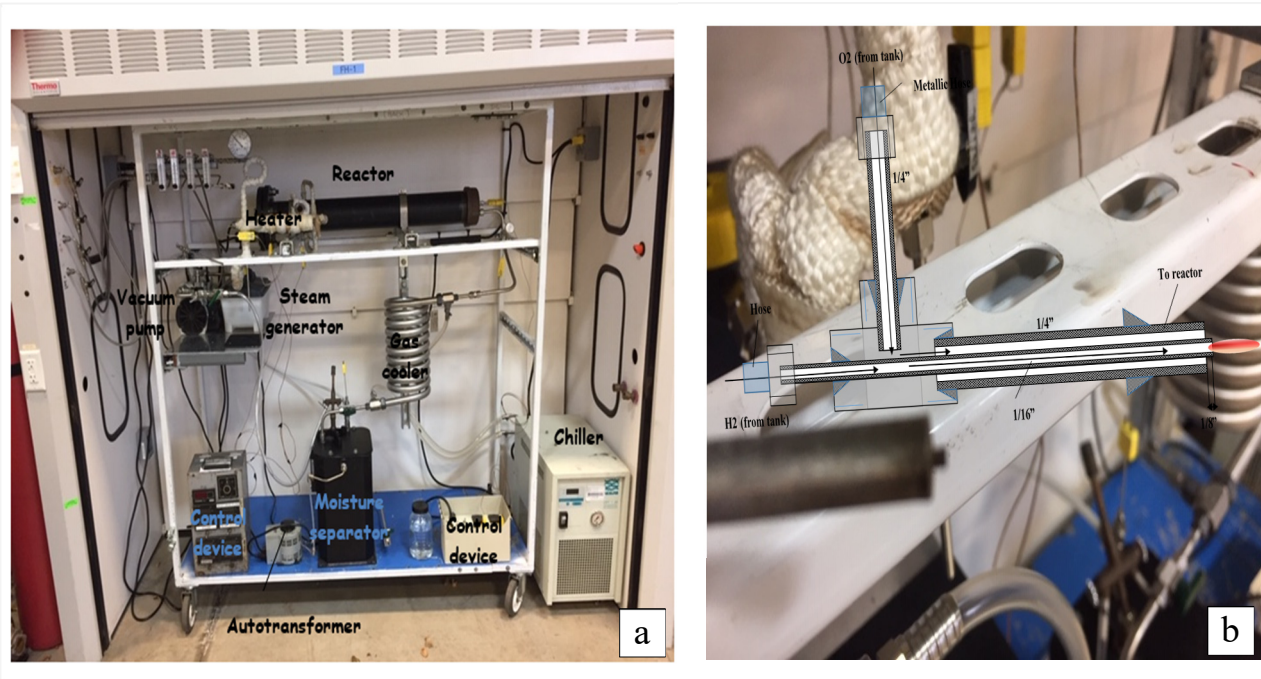
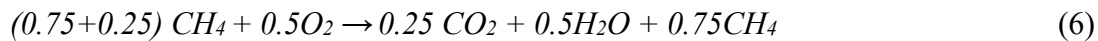


Fig.7. A picture of lab-scale unit (a); a picture and schematic of the oxy-hydrogen burner (b)

When there is a shortage in oxygen methane oxidation could be described as follows. A partial oxidation reaction:



competes with a full combustion one:



The purpose of hydrogen flame (ultra-superheated steam) is to promote methane partial oxidation through steam-methane reforming (no catalyst):



As it was mentioned above, oxygen is supplied into the burner in excess to hydrogen combustion allowing partial oxidation conditions within the reactor (converter). The basic compounds' flow rates for the test are presented in Table 2.

Table 2. Flow rates of compounds entering lab-scale reactor

Compounds	H ₂	O ₂	CH ₄	Steam
Flow rate, L/min	1.8	2.8	2.7	4.7

These flow rates provide steam:methane ratio 1.6-1.7; oxygen: methane ratio with accounting for the amount of oxygen consumed in the hydrogen burner is $2.83 - 0.9(H_2\text{-burner}) : 2.7 = 0.7$ (0.5 is a stoichiometric partial oxidation); temperature of a methane-steam mix is about 250-300°C.

In order to characterize methane reforming into syngas, the following efficiency indicators are introduced.

Methane conversion efficiency:

$$\zeta_{CH_4} = \frac{[CH_4]_{out}}{[CH_4]_{in}} \quad (10)$$

Syngas production efficiency:

$$\zeta_{sg}^{abs} = \frac{[SYNGAS(H_2 + CO)]_{out}}{3 * [CH_4]_{in}} \quad (11)$$

Two reactor configurations were tested. The first one together with the flame picture taken through the view port is presented in Fig. 8.

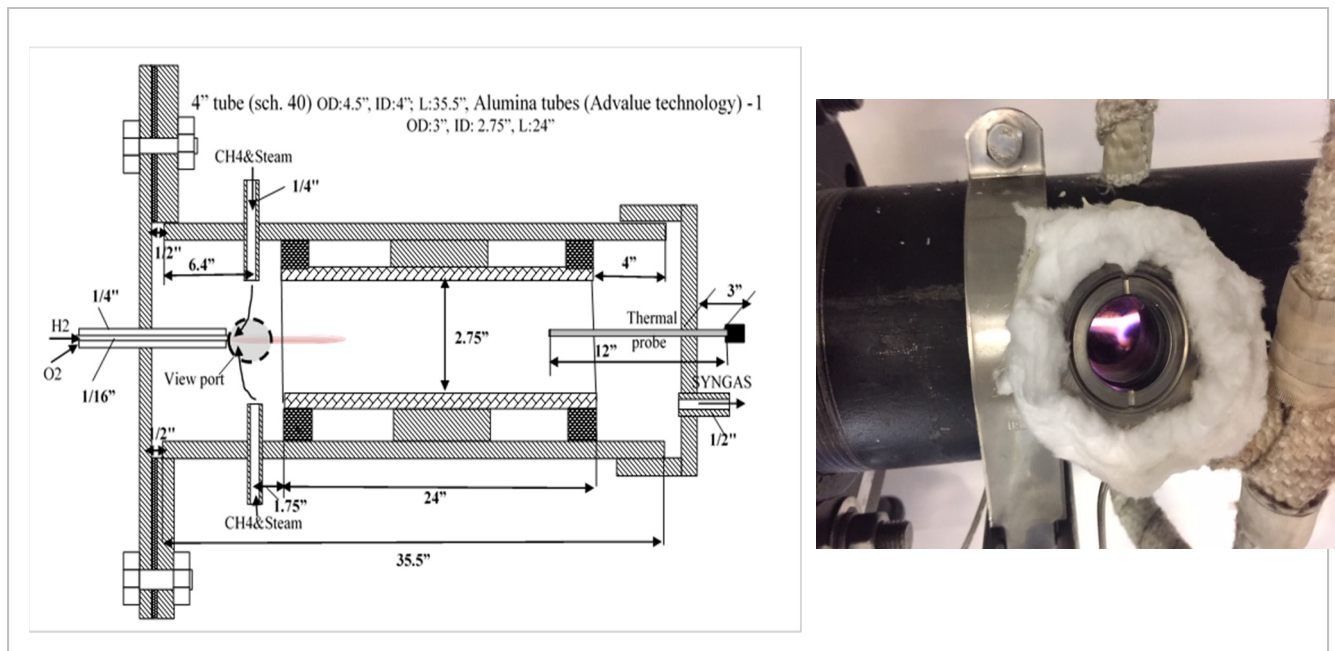


Fig 8. The first reactor configuration with the flame picture taken through the view port

The results of the test including syngas composition, its flow rate and efficiency indicators are listed in Table 3.

Table 3. The results of the test for the first reactor configuration

$H_2, \%$	$CH_4, \%$	$CO, \%$	$CO_2, \%$	$C_2H_2, \%$	syngas($CO+H_2$), l/min	ζ_{CH_4}	ζ_{sg}
38.99	28.33	12.61	18.10	0.67	2.36	52%	29%

The amount of syngas produced is pretty low, especially, accounting for 1.8 l/min of H_2 consumed in the burner. This could be explained by the flow patterns within the reactor presented in flame picture in Fig. 8 and showing that only the bottom methane is involved into the flame formation. This imperfection is eliminated in the second configuration presented in Fig. 9.

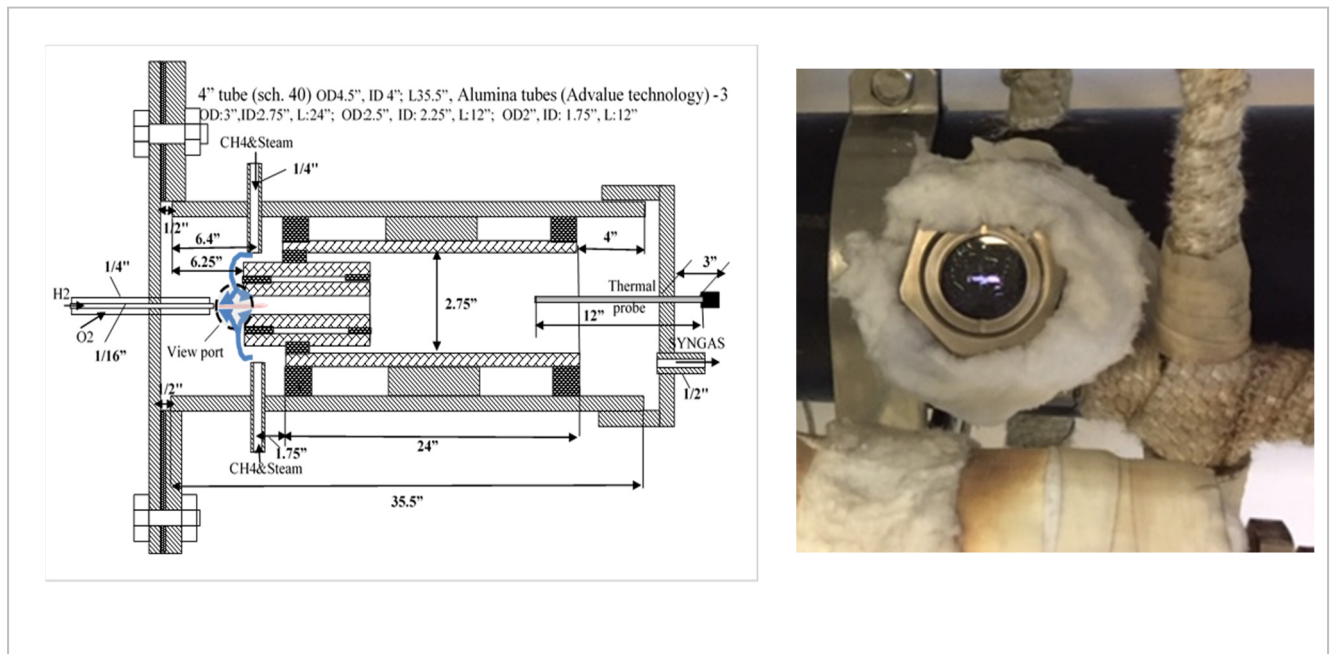


Fig 9. The second reactor configuration with the flame picture taken through the view port

The test results are listed in Table 4. A presence of CO_2 in gaseous products articulates that methane partial oxidation exists in parallel with complete combustion. Accounting for a much higher speed of H_2 combustion, the ratio $\text{H}_2 : (\text{CO} + \text{CO}_2) = 2:1$ as in the feedstock methane (CH_4) supports a conclusion that some extra H_2 comes from water through methane-steam reforming (reaction (8)).

Table 4. The results of tests for the second reactor configuration

$\text{H}_2, \%$	$\text{CH}_4, \%$	$\text{CO}, \%$	$\text{CO}_2, \%$	$\text{C}_2\text{H}_2, \%$	syngas($\text{CO} + \text{H}_2$), l/min	ζ_{CH_4}	ζ_{sg}
58.0	13.35	16.17	12.04	0.54	4.76	67%	59%

The experimental results confirm a promoting action of the oxy-hydrogen flame in conversion of methane into syngas.

4.2 Coal pyrolysis with steam in electric pyrolyzer. Test results

Pyrolyzer was disconnected from non-catalytic converter in order to test its ability to create pyrolysis gas. Table 5 and Table 6 illustrate the change with time in power consumption and temperature distribution along with pyrolyzer length. As seen in Table 5, we were able to decrease power to pyrolyzer from 19.1 kW to 13.0 kW. This means that steady state conditions are associated with lower power consumption and an excess of power is required to warm up equipment and reach thermal equilibrium between heat supply, heat losses to environment and heat consumption to pyrolyse coal with steam. These data are important to determine how much heat is needed when electricity is replaced by a heat transfer from hot gases (syngas from non-catalytic converter).

As seen in Table 6, the temperature of pyrolysis gas was in the range 481-532°C during the time of collecting sample 1 and 532-523°C during the time of collecting sample 2.

Table 5. Heaters power consumption along pyrolyzer (Steam(wt.): Coal(wt.) \approx 2:1; coal flow rate 15 lb/hr)

Time	Power, % of maximum (3kW)												Total Power, kW	Comments	
	1	2	3	4	5	6	7	8	9	10	11	12			
12:35	80	75	65	65	45	40	40	45	45	45	45	45	45	19.1	
12:55	80	75	65	65	45	40	35	35	30	30	30	30	30	16.8	Smpl.1
13:11	80	75	65	65	45	40	35	30	0	0	0	0	0	13.0	Smpl.2

Table 6. Temperature distribution along pyrolyzer

Time	Tin, °C (steam)	Temperature of tube outer wall in the middle of the heater length, °C												T _{out} , °C (pyrolysis gas)	Comments
		1	2	3	4	5	6	7	8	9	10	11	12		
12:35	121	581	664	707	542	692	702	712	776	768	800	810	760	481	
12:55	111	602	668	695	544	693	698	713	758	742	773	792	759	532	Sample_1
13:11	100	606	670	694	542	693	699	694	698	684	709	727	708	523	Sample_2

The proximate compositions of incoming “raw” coal and samples 1 and 2 of charcoals were compared with the use of thermo-gravimetric diagrams. The thermos-gravimetric analysis (TGA) was performed in accordance with a protocol presented in Fig 10.

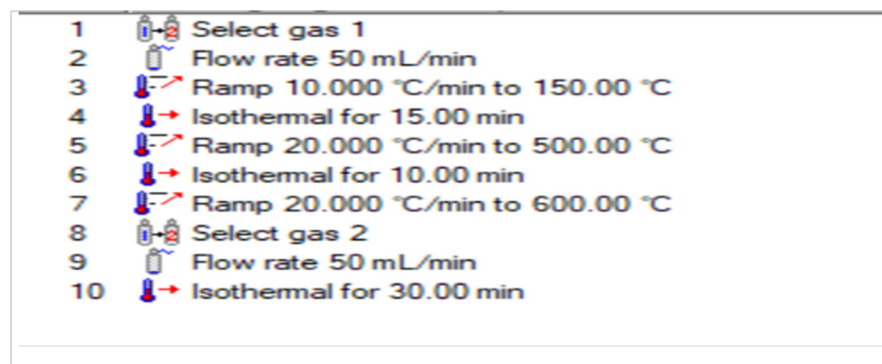


Fig 10. Protocol for TGA analysis. Gas 1 is N₂, Gas 2 is Air.

TGA analysis of raw coal and the coal composition derived from TGA diagram are presented in Fig.11 and Table 7.

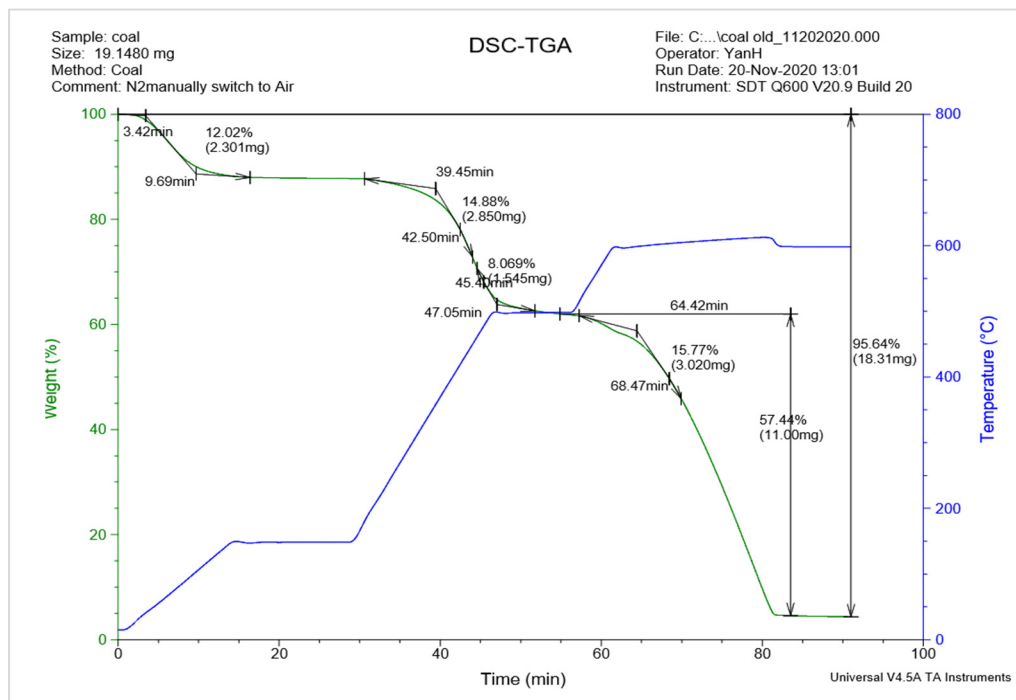


Fig. 11. TGA diagram of raw coal

Table 7. Composition of raw coal

Moisture, %wt.	Volatiles, %wt.	Fixed Carbon, %wt.	Ash, wt%	Fixed carbon, mg	Ash, mg.
12.0	26.2	57.4	4.4	11.0	0.84
Without moisture					
Moisture, %wt.	Volatiles, %wt	Fixed Carbon, %wt.	Ash, wt%	Fixed Carbon/Ash	
0	29.8	65.2	5.0	13.1	

The efficiency of pyrolysis is estimated based on TGA analysis of the samples obtained. After pyrolyser, coarse charcoal particles are separated from the gas by the cyclone. Then, they were falling into the cyclone container. In this container, char cools down and interacts with steam and volatiles (pyrolysis gas) absorbing some moisture and volatiles back. Moisture, volatiles, and fixed carbon contents may be different in raw coal and samples but we can thoughtfully assume that ash amount stays unchanged. If the ratio between fixed carbon and ash is getting lower during pyrolysis, this would mean that some fixed carbon is gasified. An inception of fixed carbon gasification means that volatiles extraction as well as pyrolysis of coal is finished. The following clarifies the way our analysis was performed.

TGA diagrams of charcoal sample 1 is presented in Fig.12. The difference between TGA diagrams is due to the sample preparation method for TGA analysis. One portion of sample_1 was dried in an ambient air, another one in an oven with temperature around 110°C. The derived proximate composition of sample 1 is listed in Table 8.

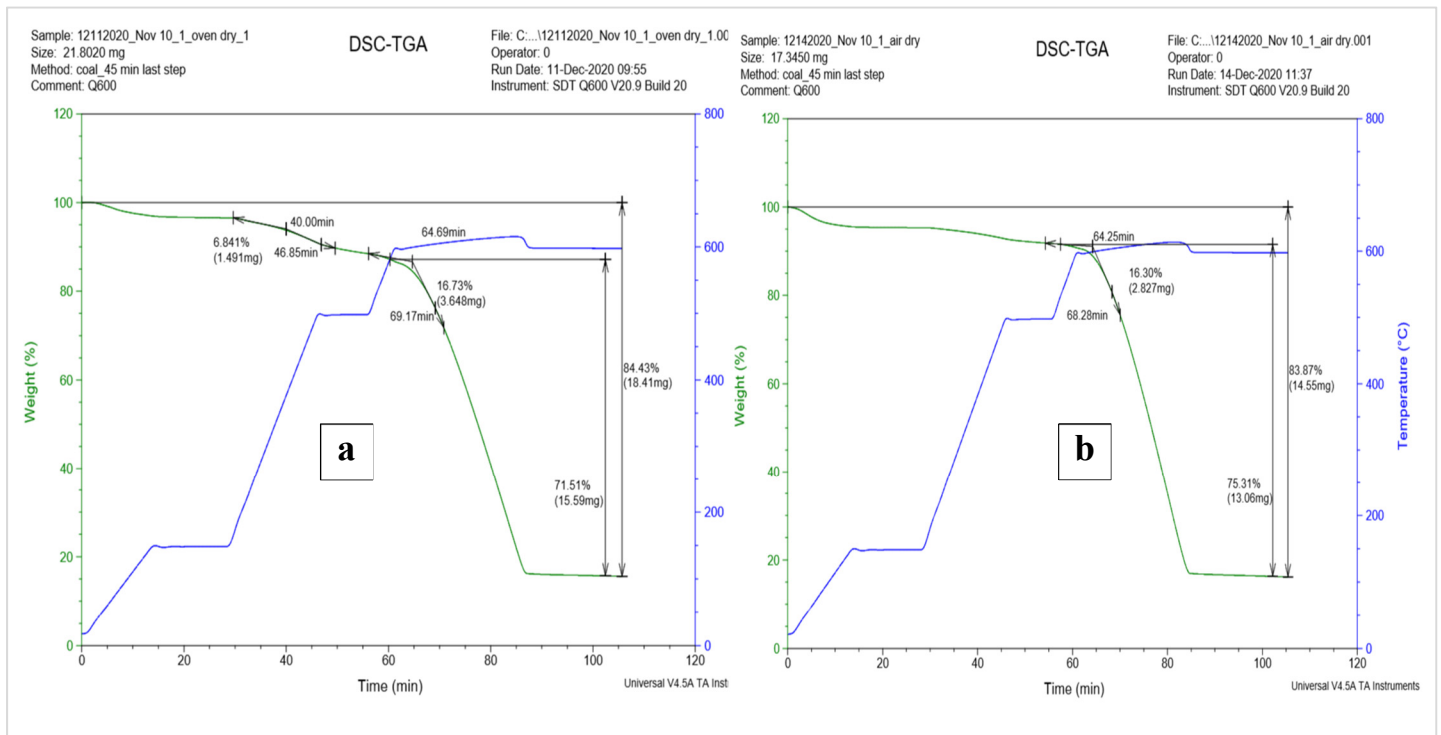


Fig. 12. TGA diagrams of oven-dried (a) and air-dried (b) coal char in sample 1.

Table 8. Composition of charcoal (sample 1)

Fixed Carbon, %wt.	Ash, wt%	Fixed carbon, mg	Ash, mg.	FC/ASh
Oven dried				
71.5	15.6	15.6	3.4	4.6
Air dried				
75.3	16.13	13.1	2.8	4.7
Average				4.65

The results of the analysis are presented in Fig.13. According to the data fixed carbon conversion reached 64% meaning that, practically, all volatiles were separated from coal particles in pyrolyzer.

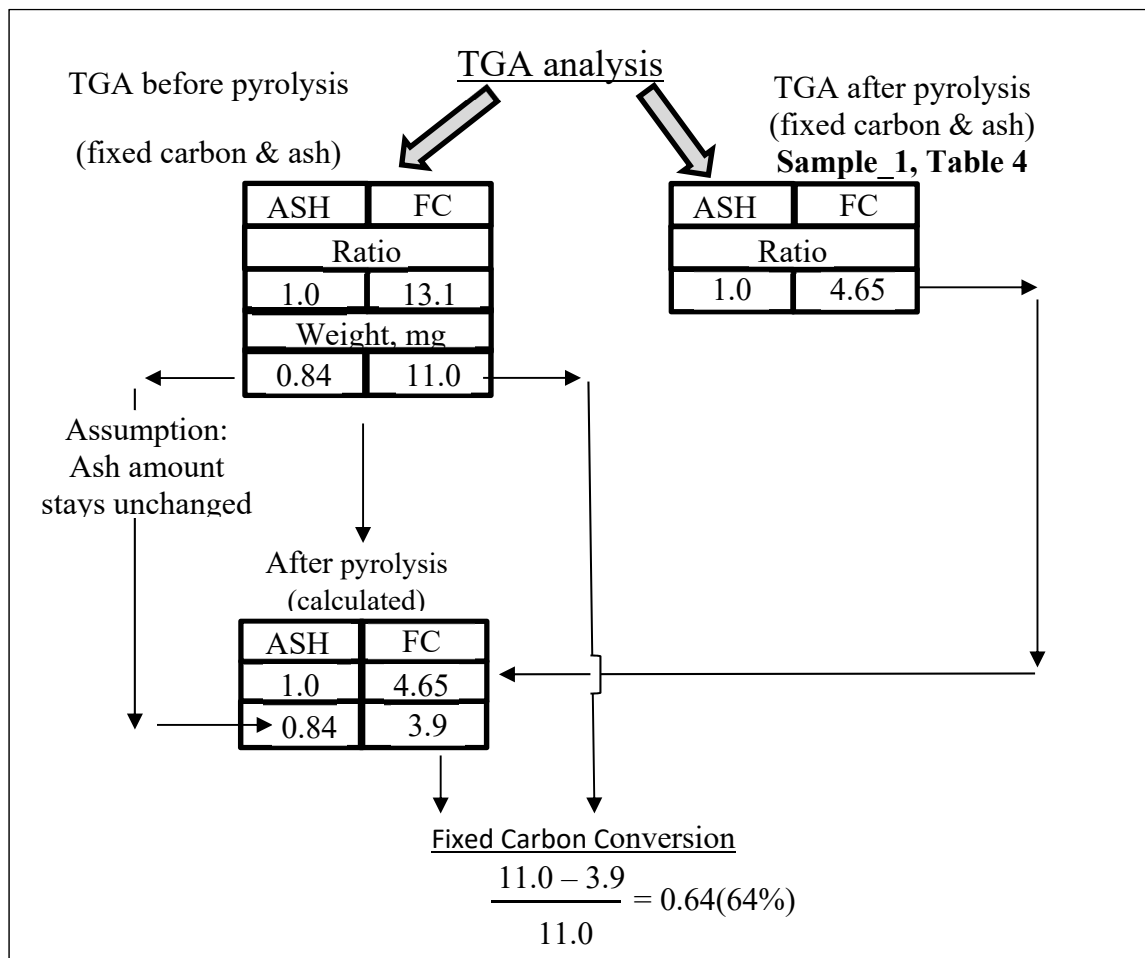


Fig. 13. The results of charcoal sample_1 analysis

TGA diagrams of charcoal sample 2 is presented in Fig.14. As seen in Table 9, the composition of charcoal in sample 2 is practically the same as in sample 1. Therefore, the results of analysis (Fig. 8) indicate the same fixed carbon conversion rate equal to about 64%.

Based on the data obtained during the test, the pyrolyzer performance meets our requirements to separate at least moisture and volatiles. The greatest part of fixed carbon (about 60%) was gasified with superheated steam. To a certain degree, an inception of steam-coal gasification was not predicted due to relatively low temperatures. Power (electricity) consumption by pyrolyzer heating elements will be optimized in the future studies.

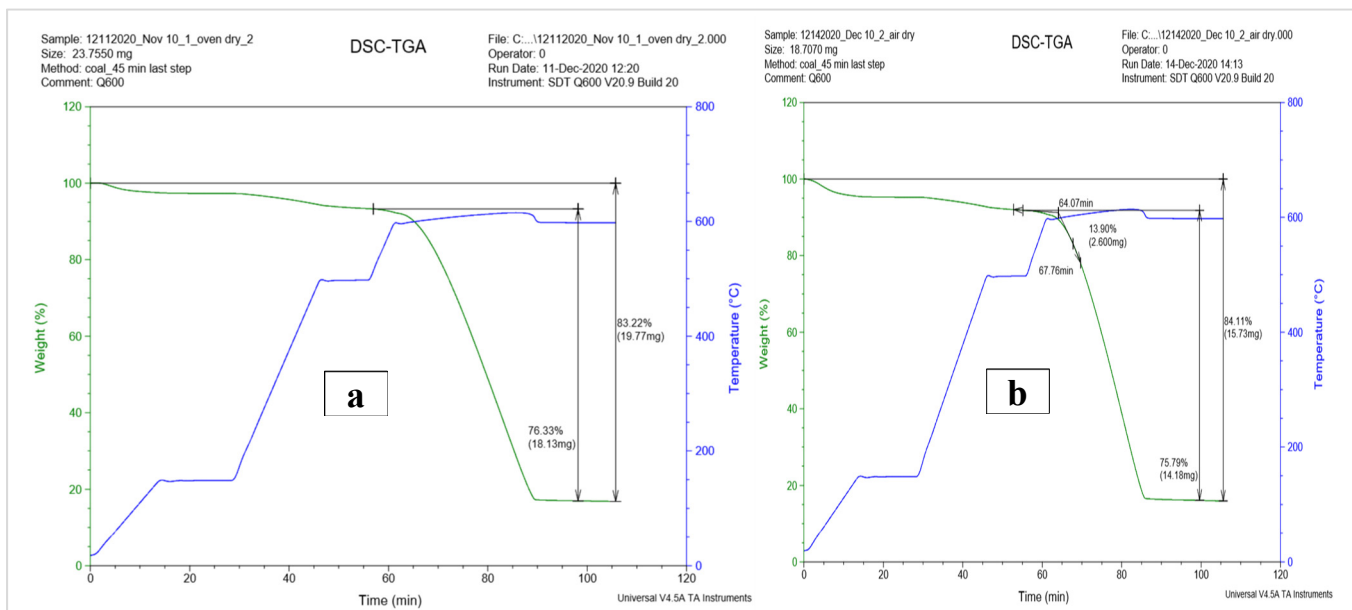


Fig. 14. TGA diagrams of oven-dried (a) and air-dried (b) charcoal in sample 2.

Table 9. Composition of charcoal (sample 2)

Fixed Carbon, %wt.	Ash, wt%	Fixed carbon, mg	Ash, mg.	FC/ASH
Oven dried				
76.3	16.8	18.1	4.0	4.5
Air dried				
75.8	15.9	14.2	3.0	4.7
Average				4.6

4.3 Pilot-scale non-catalytic converter. Test results on methane

The pilot-scaled non-catalytic converter was disconnected from pyrolyzer and tested on methane (Fig.15). After preliminary testing of our pilot-scale non-catalytic converter in March 2021 we disassembled it and found out that the internal alumina tube was broken (Fig.16).

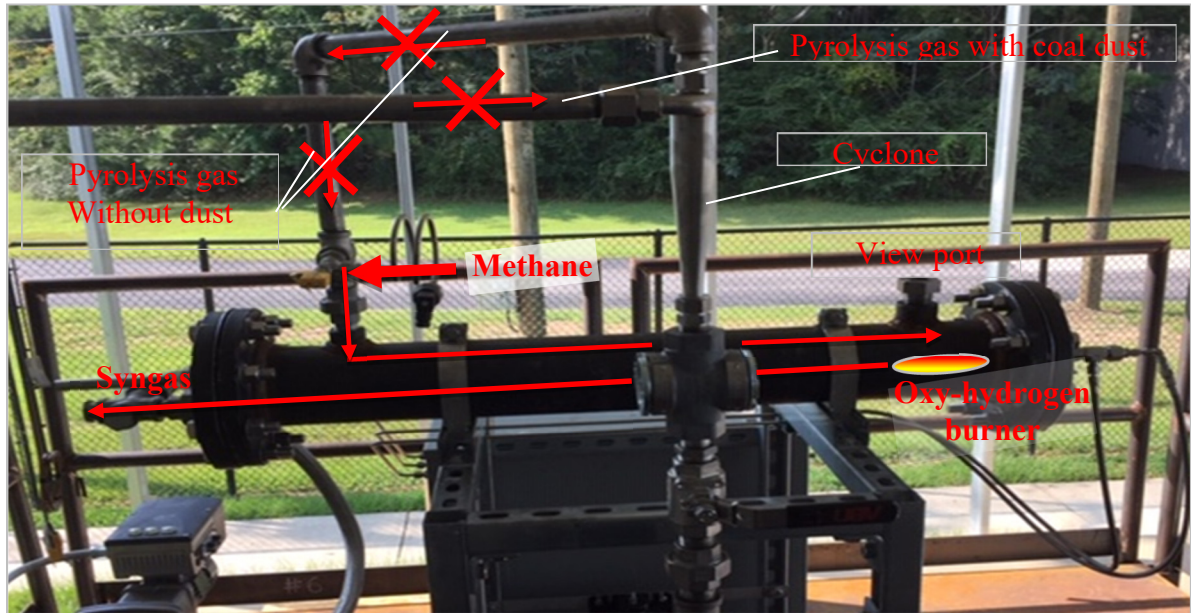


Fig. 15. Non-Catalytic converter in a test mode with methane.



Fig 16. The broken internal ceramic tube

We replaced ceramic tube with a new quartz one to improve structure integrity by eliminating contacts of different materials. Quartz is characterized with the lowest thermal expansion coefficient and, thereby, withstands severe thermal stresses.

A principle schematic and flow diagram of a patented non-catalytic converter internal structure¹¹ is presented in Fig. 17. H₂ is combusted completely in an excess of O₂ in the non-stoichiometric oxy-hydrogen burner. The rest of oxygen is taken in a sub-stoichiometric ratio to incoming methane. This amount of oxygen allows methane partial oxidation but not full combustion.

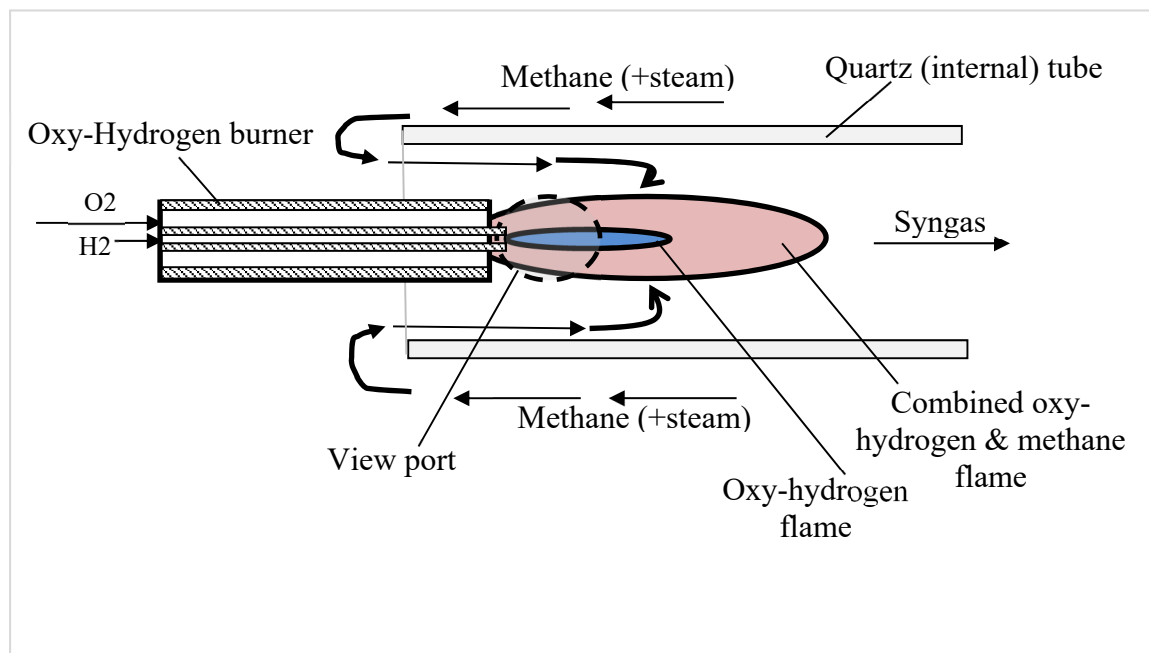


Fig 17. A schematic of oxy-hydrogen flame interaction with methane flow in non-catalytic converter

The oxy-hydrogen combustion initiates formation of a more complex oxy-hydrogen-methane flame plume. The product of the oxy-hydrogen combustion – steam at an ultra-high temperature (around 2800°C) contains a substantial amount of active OH- radicals which accelerate steam reforming of methane and thereby shift its interaction with O₂ toward production of H₂ and CO^{12,13}. This mechanism is presented in Fig.18.

¹¹ Granovskiy, M. Method and reactor to produce syngas. *Provisional patent 12 Aug 2020*, Attorney Ref. No. 19044.0445U1

¹² Granovskii M., Gerspacher R., Pugsley T., Sanchez F. An effect of tar model compound toluene treatment with high-temperature flames. *Fuel* 92 (2012) 369-372

¹³ Granovskii M., Gerspacher R., Pugsley T., Sanchez F. Decomposition of tar model compound toluene by treatment with the high-temperature hydrogen/oxygen flame. *Proceedings of 19th European Biomass Conference and Exhibition* pp. 1530-1538. 6-10 June 2011, Berlin, Germany. DOI:10.571/19thEUBCE2011-VP2.4.1.

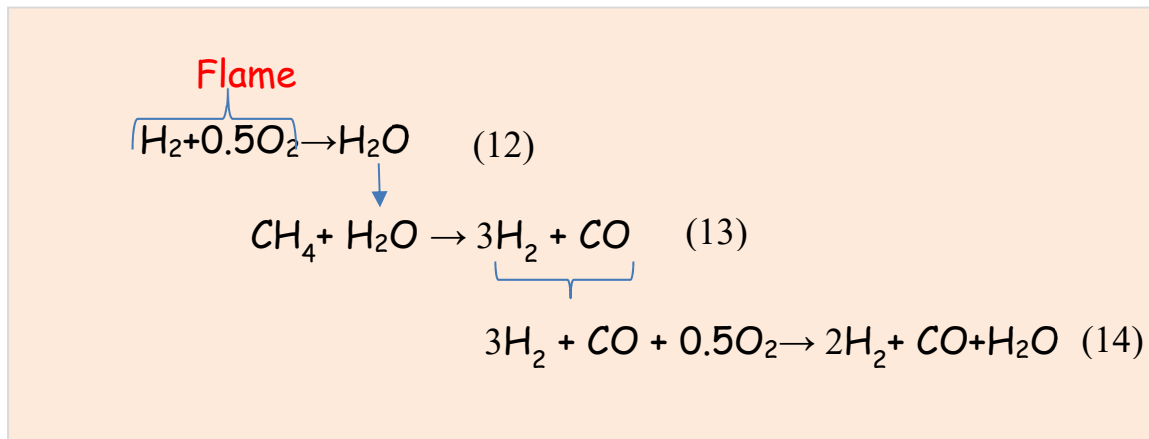
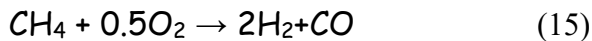


Fig 18. An activation mechanism of methane partial oxidation by the oxy-hydrogen flame.

A direct methane interaction with sub-stoichiometric oxygen represents a sum of reactions (13) and (14) as follows



A direct interaction of CH₄ with O₂ to obtain syngas following reaction (15) usually requires an appropriate catalyst. Without a catalyst, the molar ratio O₂:CH₄ lower than 1.1^{14,15} in reaction (15) induces soot formation what makes it unacceptable for a practical application. Therefore, non-catalytic partial oxidation with molar ratio O₂:CH₄=0.5 is not adapted in the practice. As molar ratio O₂:CH₄ increases, an appearance of full combustion products H₂O (steam) and CO₂ corresponds to a reduction in H₂ and CO, respectively. A higher combustion rate of H₂ compared to CO¹⁶ may imply decreasing molar ratio H₂:CO from 2 to lower values.

To analyze experimental data, the following efficiency indicators are introduced.
Methane conversion efficiency:

$$\eta_{\text{CH}_4} = \frac{[\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}}}{[\text{CH}_4]_{\text{in}}} \quad (16)$$

Relative syngas (H₂+CO) production efficiency per CH₄ converted:

$$\eta_{\text{sg}} = \frac{[\text{H}_2]_{\text{out}} + [\text{CO}]_{\text{out}}}{3([\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}})} \quad (17)$$

Absolute syngas (H₂+CO) production efficiency per input CH₄:

$$\eta_{\text{sg}}^{\text{abs}} = \eta_{\text{CH}_4} \eta_{\text{sg}} \quad (18)$$

where values in square parentheses denote flow rates of a respective component in [l/min].

¹⁴ B.Haynes, H. Wagner. Soot formation. Prog. Energy. Combust. Sci. 7(1981) 229-273

¹⁵ A. D'Alessio, A. Di Lorenzo, A. Sarofim, F. Beretta, S. Masi, C. Venitozzi. Soot formation in methane-oxygen flames. Symposium (International) on Combustion. Volume 15, Issue 1, 1975, Pages 1427-1438; [https://doi.org/10.1016/S0082-0784\(75\)80401-2](https://doi.org/10.1016/S0082-0784(75)80401-2)

¹⁶ S. Davis, A. Joshi, H. Wang, F. Egolfopoulos. An optimized kinetic model of H₂/CO combustion. Proceedings of the Combustion Institute 30 (2005) 1283–1292

Multiplier **3** in the relative syngas production efficiency (17) assumes maximum syngas amount following reactions (12-14) or (15).

In the oxy-hydrogen burner (Fig.17), H₂ is combusted with O₂ in the molar (volumetric) ratio H₂:O₂ = 1:0.5 (reaction (12)). The rest of oxygen reacts with methane. The experimental parameters are chosen so that, after H₂ is combusted in the burner, O₂:CH₄ molar (volumetric) ratios stay approximately the same 0.65:1 (13:20) for all three cases. Three sets of experimental data are listed in Table 9.

Table 9. Composition of product gas depending on H₂ and O₂ flows in the burner

	Components	H ₂ ,	O ₂ ,	CH ₄	CO	CO ₂	C ₂ H ₂
Set 1							
Input	L/min	9.76*	18.0*	20.15	----	----	----
Output	%,Vol.	57.41	----	7.22	28.86	5.59	0.92
	L/min	23.23	----	2.92	11.68	2.26	0.37
Set 2							
Input	L/min	11.71*	19.3*	19.85	----	----	----
Output	%,Vol.	58.41	----	5.73	29.43	5.61	0.81
	L/min	25.05	----	2.46	12.62	2.41	0.35
Set 3							
Input	L/min	14.25*	20.7*	19.73	----	----	----
Output	%,Vol.	60.20	0.00	4.62	28.64	5.85	0.69
	L/min	26.16	0.00	2.01	12.44	2.54	0.30
*	Supplied into burner						

As seen in Table 9 and Fig. 19, built on the data in Table 9, conversion of CH₄ reaches 90% and about 73% of converted CH₄ produces syngas (CO and H₂).

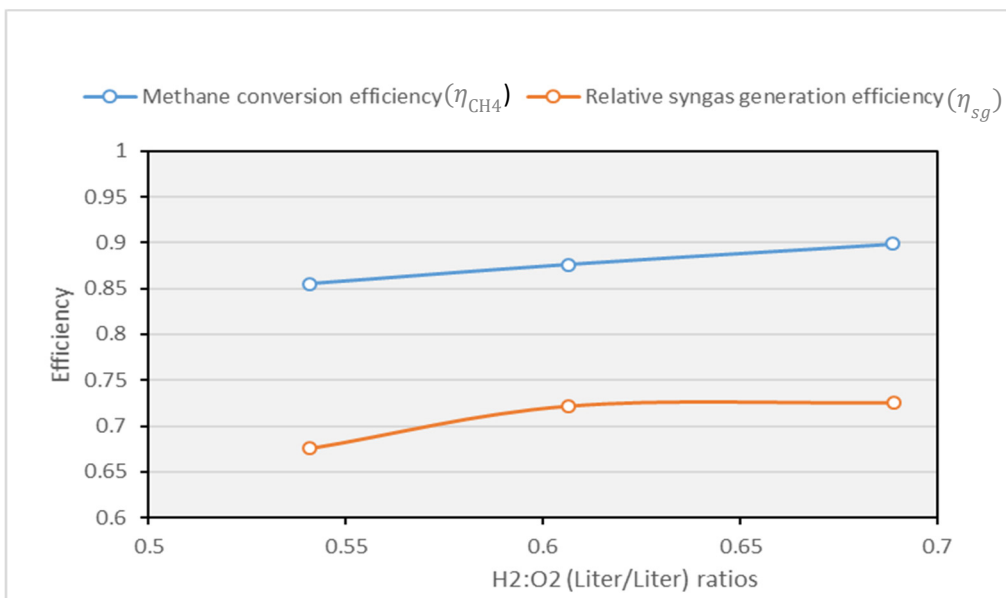


Fig.19. Variation of methane conversion and syngas production efficiencies with H₂:O₂ ratios supplied into the burner (see Table 9)

According to reactions (12) - (14), molar ratios of H₂:CO are almost equal to 2:1 in all sets as shown in Fig.20. A presence of CO₂ and CH₄ in final products implies that partial oxidation proceeds in concert with full combustion. For instance, in set 3 (Table 14), 90% of methane is consumed, about 73% of consumed amount is converted into syngas through the overall reaction (15) and the rest of used up CH₄ is completely combusted or converted into other hydrocarbons (for example, C₂H₂).

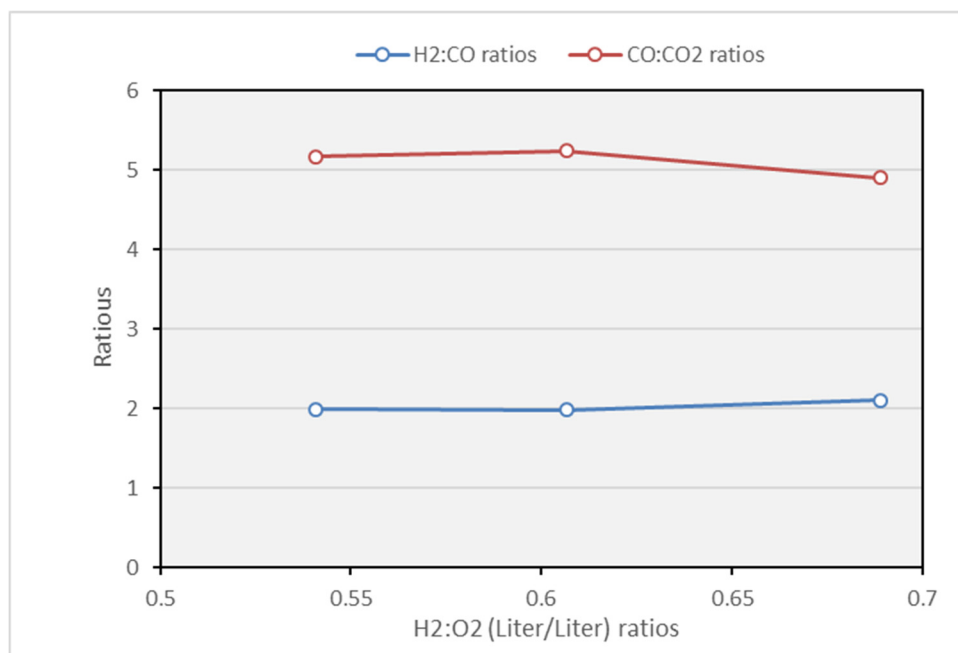


Fig. 20. Ratios of H₂, CO, and CO₂ in final products (see Table 9)

A relative syngas production efficiency η_{sg} is almost the same for Set 2 and 3, however, because methane conversion efficiency η_{CH_4} is greater in Set 3, the total syngas production efficiency η_{sg}^{abs} favors set 3 as shown in Table 10.

Table 10. Efficiency indicators for experiments in Table 14.

	η_{CH_4}	η_{sg}	η_{sg}^{abs}
Set 1	0.86	0.68	0.58
Set 2	0.88	0.72	0.63
Set 3	0.90	0.73	0.65

An application of the oxy-hydrogen burner with an excess of oxygen to convert CH_4 into syngas allows avoiding soot formation downstream of the oxy-hydrogen-methane flame (Fig.21) if molar ratios $H_2:CH_4$ are in the range 0.5-0.75 (see Table 9).

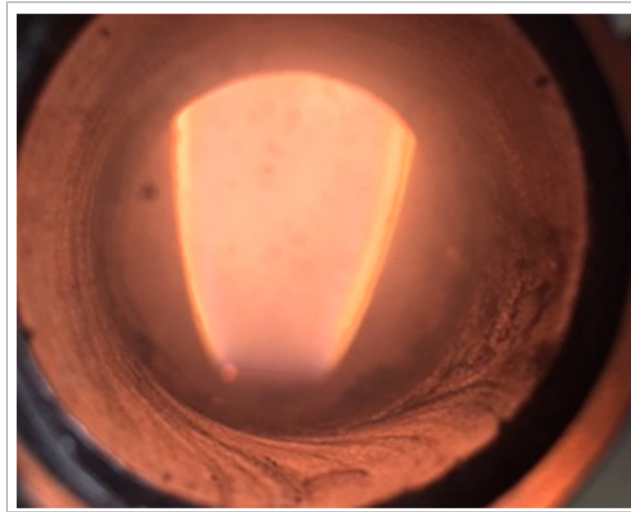


Fig.21. The oxy-hydrogen-methane flame for the $H_2:O_2:CH_4$ ratios in Table 14

4.3.1 Soot formation during methane to syngas partial oxidation at decreasing H_2 flow into the burner

With an intent to check possibility to consume less H_2 in the oxy-hydrogen burner its flow rate was reduced to 6 l/min. Accounting for O_2 to combust 6 liters of H_2 , the ratio between $O_2:CH_4$ was changed from 0.75 to 1. Comparing Fig. 19 and Fig. 22, syngas generation efficiency stays substantially in the same range.

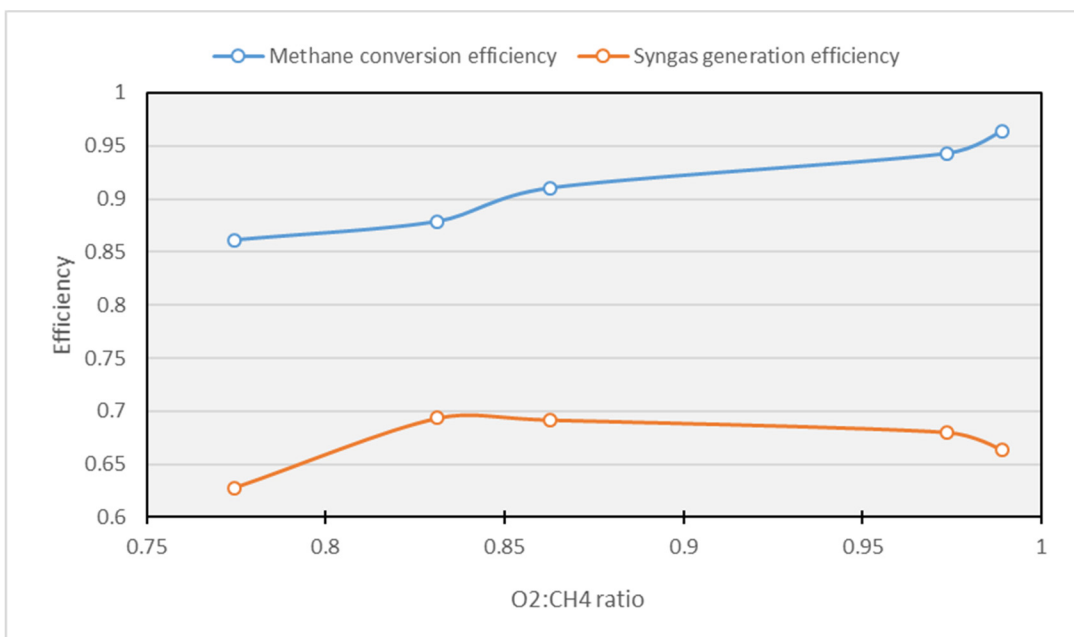


Fig.22. Methane conversion and syngas generation efficiencies at decreasing H₂ flow (6 l/min of H₂ per 20 l/min of CH₄)

However, as seen in Fig. 23, H₂:CO and CO:CO₂ ratios were steadily decreasing from 1.6 to 1.35 and from 5.8 to 4.5, respectively.

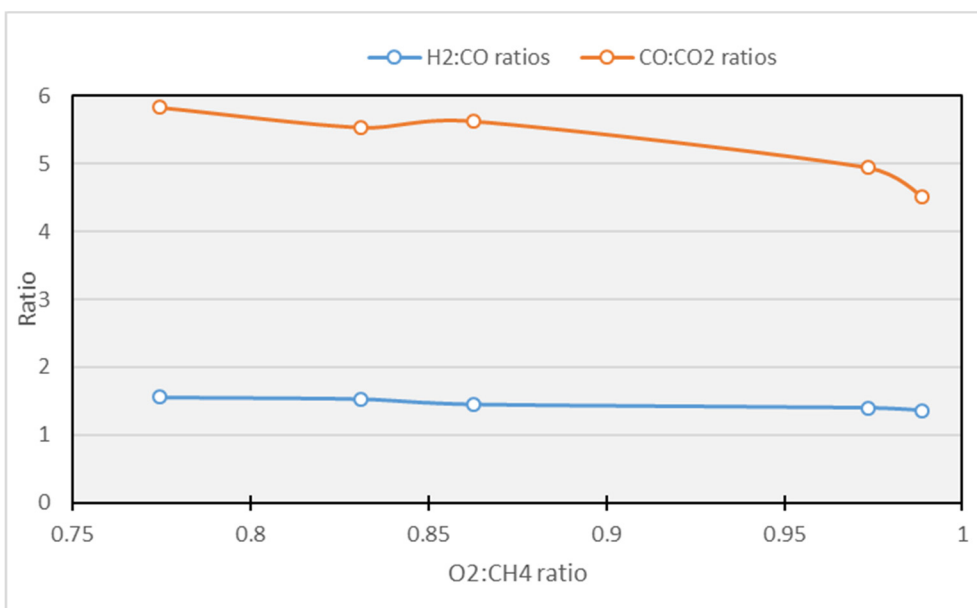
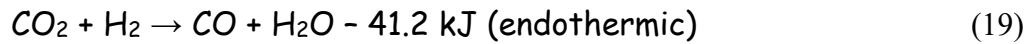


Fig.23. Ratios of H₂, CO, and CO₂ in final products at decreasing H₂ flow (6 l/min of H₂ per 20 l/min of CH₄)

A decrease in H₂:CO from 2 to lower values at substantially the same syngas (CO+H₂) amount could be explained by reaching higher temperatures which induce endothermic reaction of CO₂ conversion to CO (reversible water-gas shift reaction takes opposite direction) as follows



The same hot spots may lead to endothermic pyrolysis of CH_4 with an origination of soot:



During experiments with decreasing H_2 flow an intensive formation and deposition of soot particles were observed as presented in Fig. 24.



Fig.24. Soot origination in oxy-hydrogen-methane flame at decreasing H_2 flow [6 l/min]

4.3.2. Partial oxidation of methane to syngas by an activation with the oxy-hydrogen burner and in the presence of steam

Adding steam to methane may have positive and negative impacts on methane partial oxidation into syngas. The positive impact may be linked with steam reforming of methane (reaction (13)) but, especially without catalyst, it requires temperatures higher than 1000°C ¹⁷. The negative effect may be associated with decreasing adiabatic temperature of methane oxidation in concert with reducing concentrations of active radicals¹⁸.

Subtracting O_2 consumed by H_2 from the total O_2 flow into the burner, the ratio between the rest of O_2 to incoming CH_4 was kept around 0.5. The flow rate of CH_4 was retained around 20 l/min and temperature of steam-methane mixture before entrance to the burner was maintained higher than 300°C . The results of experiments are presented in Fig. 25 and 26. As seen in these Figures, steam addition decreases methane conversion (η_{CH_4}) and syngas generation (η_{sg}) efficiencies. No soot formation was observed. It can be concluded that application of the

¹⁷ G.Karim, M.Metwally. A kinetic investigation of the reforming of natural gas for the production of hydrogen. International Journal of Hydrogen Energy. Volume 5, Issue 3, 1980, Pages 293-304

¹⁸ K. Muller-Dethlefs, A. Schlader. The effect of steam on flame temperature, burning velocity and carbon formation in hydrocarbon flames. Combustion and Flame. 27(1976) 205-215

oxy-hydrogen burner assumes minimum or an absence of steam in the input flow. However, it doesn't contradict literature data proposing steam addition as a tool to suppress soot formation¹⁹.

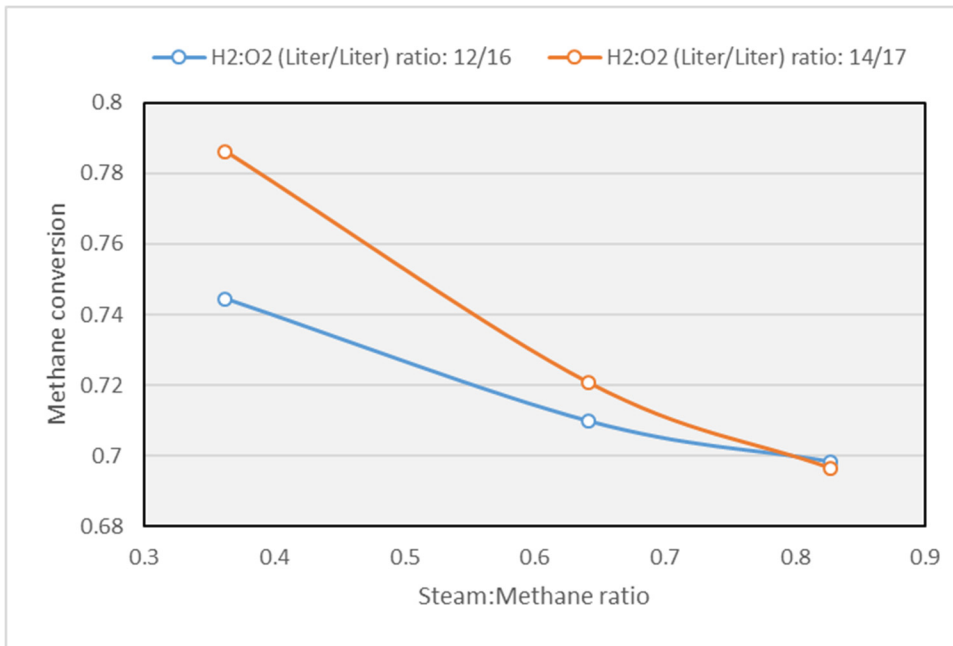


Fig.25. Methane conversion at different steam:methane ratios and H₂ and O₂ flows into the burner

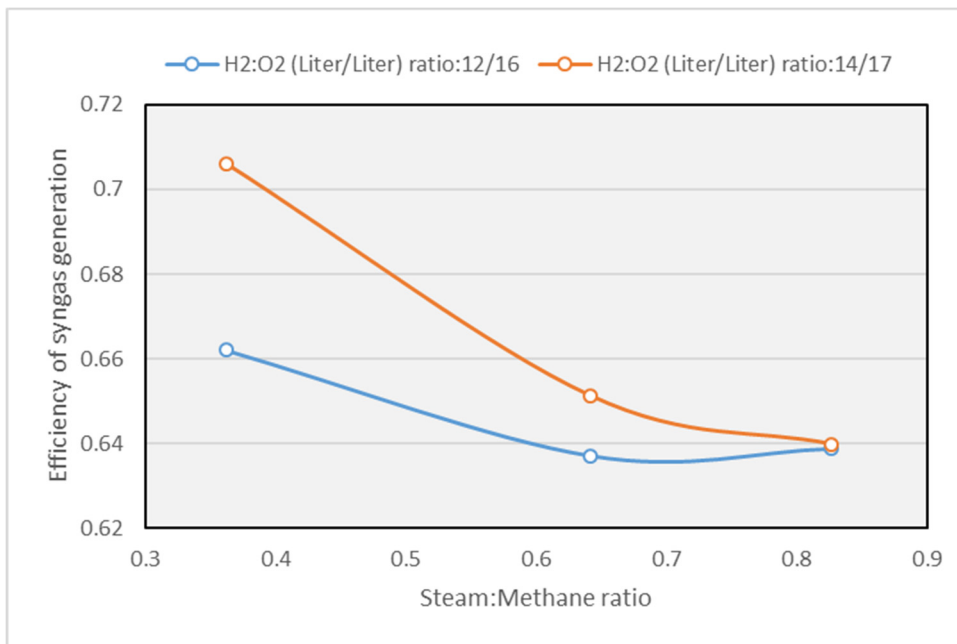


Fig. 26. Efficiency of syngas generation at different steam:methane ratios and H₂ & O₂ flows into the burner

¹⁹ Q. He, Q. Guo, K. Umeki, L. Ding, F. Wang, G. Yu. Soot formation during biomass gasification: A critical review. Renewable and Sustainable Energy Reviews.139(2021) 110710

4.4 Coal gasification in electric pyrolyzer and non-catalytic converter. Test results

The purpose of the gasification unit is to produce syngas from coal. We were doing it through pyrolysis of coal for the following conversion of its volatiles into syngas by the non-catalytic reactor (converter). We were planning to utilize steam as a sweep gas. However, an elevated pressure steam penetrated into coal feeding and measuring devices, impeded coal moving and soaked coal making coal slurry in the hopper. A more sophisticated mechanism is needed to allow steam to be a sweep gas for pyrolysis such as a customized rotary valve (airlock) or putting steam directly into pyrolyzer from its side wall at an appropriate distance from the coal feed. Nitrogen from a gas tank was utilized to maintain an elevated pressure (to avoid an air ingress) in pyrolyzer. Due to an increasing content of moisture in the coal slurry, we still can assume that steam is generated in a substantial amount to actively participate in volatiles desorption in pyrolyzer. The composition of coal slurry is presented in Fig. 27. The coal ultimate composition was determined by Energy Technical Service, LLC (Northport, AL).

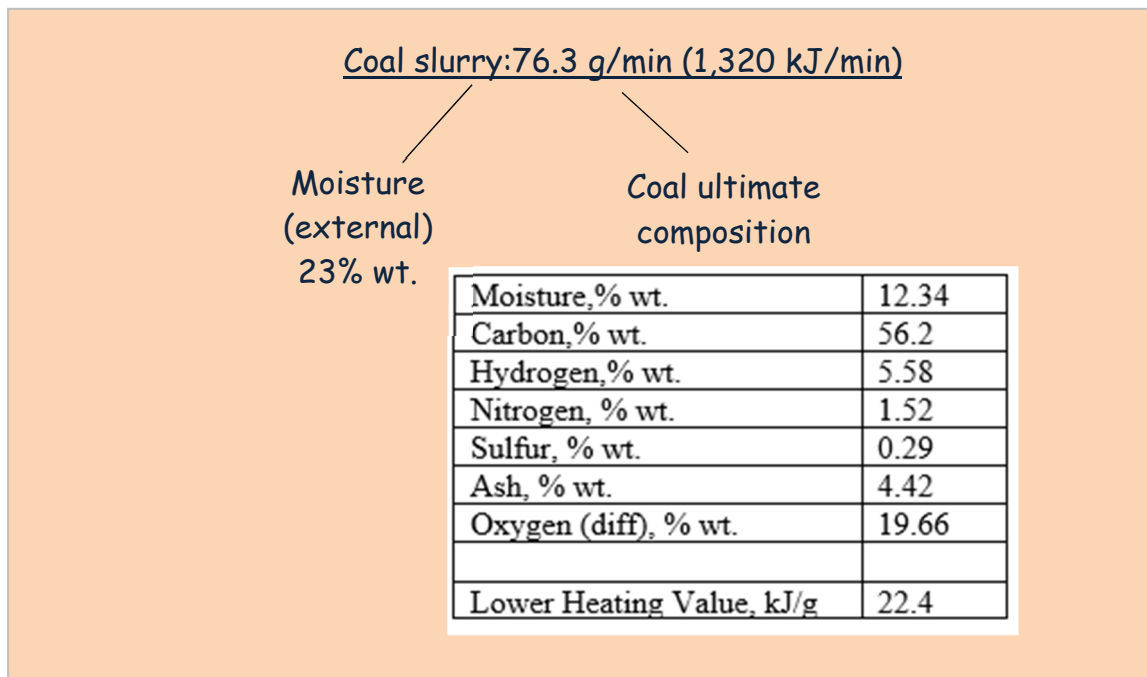


Fig.27. Flow rate and composition of coal slurry

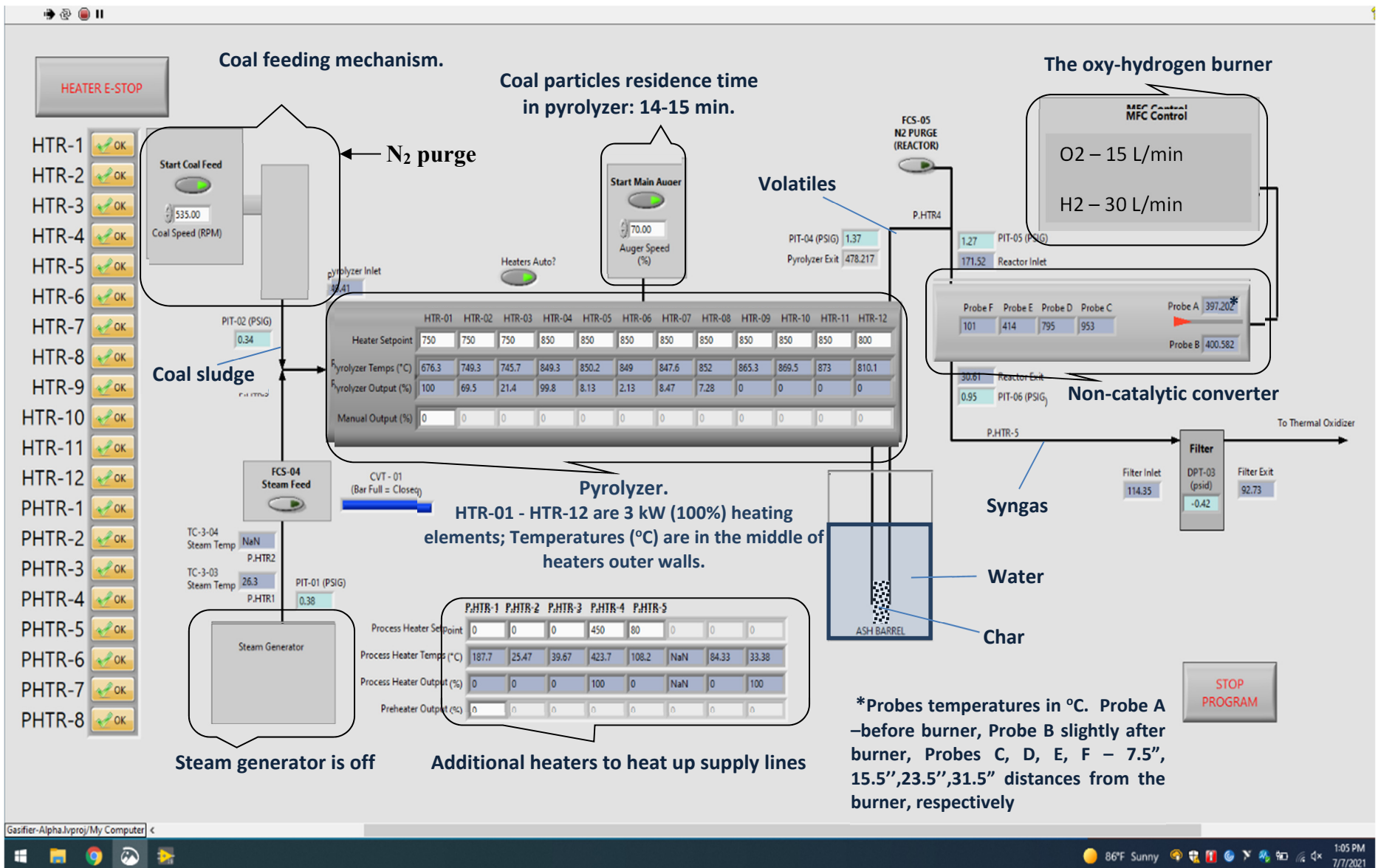


Fig.28. Lab view process flow diagram and user interface of hybrid pyrolysis-gasification unit

The results of coal slurry pyrolysis and pyrolysis gas conversion into syngas in hybrid pyrolysis-gasification unit (Fig. 28) are presented in Table 11 for three experimental sets. The input parameters are coal slurry flow rate (Fig.27) and H₂ & O₂ flows into the oxy-hydrogen burner of non-catalytic converter (Table 11).

Table 11. Composition of product gas depending on H₂ and O₂ flows in the burner

	Components	H ₂ ,	O ₂ ,	N ₂	CH ₄	CO	CO ₂	C ₂ H ₂
Set 1								
Input	L/min	30.0*	15.0*					
Output	%,Vol.	50.85	0.00	9.54	5.93	19.45	14.19	0.04
	L/min	37.40	0.00	7.02	4.36	14.30	10.44	0.03
Syngas (H₂+CO+CH₄) lower heating value (LHV):678 kJ/min								
Set 2								
Input	L/min	25*	20*					
Output	%,Vol.	44.21%	0.00%	8.78%	4.62%	19.40%	22.83%	0.17%
	L/min	33.42	0.00	6.64	3.49	14.67	17.26	0.13
Syngas (H₂+CO+CH₄) lower heating value (LHV):615 kJ/min								
Set 3								
Input	L/min	20*	25*					
Output	%,Vol.	33.00%	0	11.86%	2.76%	21.32%	30.72%	0.34%
	L/min	17.72	0.00	6.37	1.48	11.45	16.49	0.18
Syngas (H₂+CO+CH₄) lower heating value (LHV):356 kJ/min								
		* Supplied into burner						

Concentrations of combustibles (H₂+CO+CH₄) steadily decrease from 76% (Set 1) to 68% (Set 2) to 57% (Set 3). As seen in Fig. 29, this decrease is mostly attributed to a substantial decrease in H₂ and CH₄ contents; CO content is practically stays unchanged.

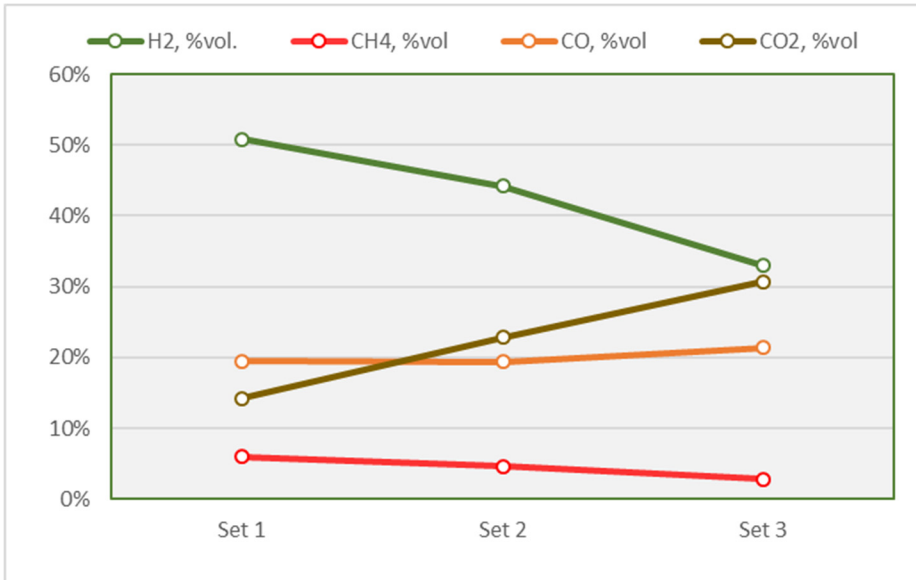


Fig.29. Primary components of the gas at the non-catalytic reactor outlet (dry basis)

As seen in Fig 30, coal processing in pyrolyzer for the following conversion of its pyrolysis gas into syngas allows to recover more than 50% of coal heating value. Accounting for around 43% of incoming carbon with coal was detected in syngas, 57% of carbon with ash can theoretically release heat 625 kJ/min. Subtracting this number from incoming coal heating value we obtain heating value of pyrolysis gas which is almost equal to heating value of the syngas obtained.

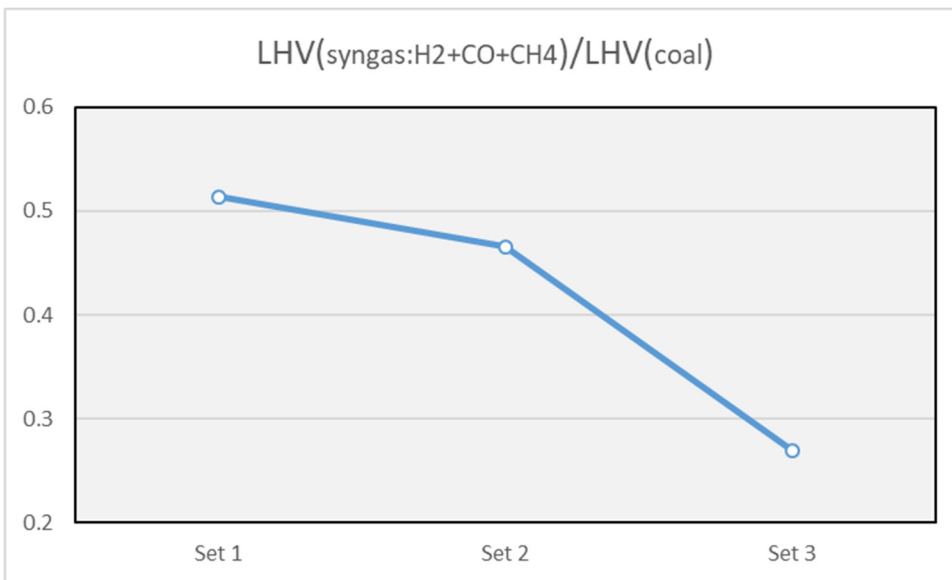
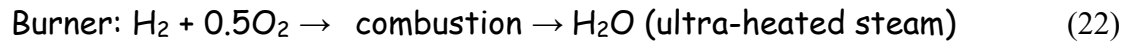


Fig.30. Recovering of lower heating value (LHV) of coal in syngas

The oxy-hydrogen flame can be conveniently obtained through electrolysis of water for the following combustion of H₂ and O₂ streams in the burner:



Set 1 is characterized by the stoichiometric combustion ratio between H_2 and O_2 implying that sole electrolysis can provide required amounts of H_2 and O_2 . The amount of syngas obtained in non-catalytic converter should be reduced by H_2 burnt in the burner to determine net-syngas production rate (see Fig. 31). The use of H_2 & O_2 in the burner ought to be minimized based on an net-syngas production rate and avoidance of soot formation. This could be a good point for the following research.

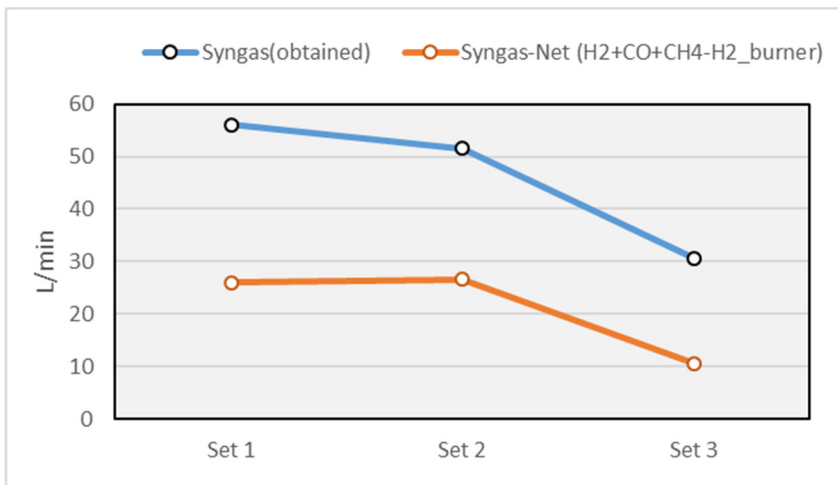


Fig. 31. Total and Net syngas production in the pyrolysis-gasification unit

5. Conclusions and Recommendation

1. A hybrid pyrolysis gasification unit with two primary devices such as pyrolyzer and non-catalytic converter was developed and commissioned in the frame of this project
2. Lab-scale and pilot-scale non-catalytic converters were built and tested on methane. Simplicity and efficiency of partial oxidation of methane into syngas in non-catalytic converter makes it attractive for an industrial practice.
3. Electric pyrolyzer was successfully tested and commissioned to generate pyrolysis gas and coal char from coal
4. A joint performance of pyrolyzer and non-catalytic converter was tested on the coal slurry: almost all pyrolysis gas was converted into syngas slightly diluted in N₂.
5. Pyrolyzer and non-catalytic converter could be effectively utilized to make syngas from solid carbonaceous feedstocks with a high content of volatiles such as biomass.
6. A complete gasification of coal could be achieved by combining of pyrolyzer and non-catalytic converter with a rotary kiln gasifier to produce syngas from fixed carbon in coal char.

6. Changes/Problems

Administration of Southern Research Institute dismissed the Laboratory for Sustainable Chemistry and Catalysis effective August 1, 2021.