

TARGET COMPLEX PROGRAMME FOR RESEARCH OF NAS UKRAINE

«Development of scientific bases for hydrogen production, storage and use in autonomous energy supply systems»



Development of scientific and technological bases for synthesis gas from a mixture of hazardous organic waste

project № 8-21

Third stage: Optimization of the process of compatible gasification of sewage sludge and rubber roof of worn tires; development of proposals for the transfer of the results to a full-scale reactor; preparation of proposals for the protection of intellectual property

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DEVELOPMENT OF SCIENTIFIC AND TECHNOLOGICAL FUNDAMENTALS OF SYNTHESIS GAS PRODUCTION FROM A MIXTURE OF HAZARDOUS ORGANIC WASTE

Processing of sewage sludge obtained from municipal treatment plants as well as worn-out tires, unsorted solid waste including those already accumulated in landfills and persistent organic pollutants is the subject of this study. The purpose of the work is to develop the scientific foundations of modern technology for hydrogen production based on plasma-steam-oxygen gasification from hazardous renewable raw materials, in particular, mixture of sewage sludge from aeration stations contaminated with toxic heavy metals and rubber crumbs of worn tires.

HYDROGEN PRODUCTION BASED ON PLASMA-STEAM-OXYGEN GASIFICATION OF HAZARDOUS RENEWABLE RAW MATERIALS

Chlorine-containing waste or sewage sludge contaminated with toxic heavy metals





Plasma-steam technology



Environmentally safe slag for building Synthesis gas H2+CO for electricity production or as chemical raw material An exceptional advantage of plasma technologies used for gasification of waste is the high thermodynamic parameters of the process. That is why it has no restrictions on the quality of carbonaceous raw materials to be gasified. This advantage allows also converting even the most hazardous chlorine-containing waste. In the case of sewage sludge processing, they additionally provide vitrification (encapsulation in the glass mass of molten slag) of heavy metals. The absence of this operation creates significant environmental risks because in that case heavy metals are the part of dry ash residue compounds.

The key issue explored in this project is the achievement of maximum energy efficiency of the process of gasification of mixed raw organic waste. The idea of joint gasification of waste is the key element for solving the problem. Joint gasification or total energy gasification process allows the compensation of the high ash content of one type of raw material by high calorific value of another one. It is necessary to underline that the energy efficiency of the gasification process, and also the final cost of one of the components of syngas – hydrogen to be the target product of hydrogen energy, is fully consistent with the activity of new global coalition Clean Hydrogen Mission created by 22 countries and the European Commission in June 2021 to support a clean hydrogen economy [1].

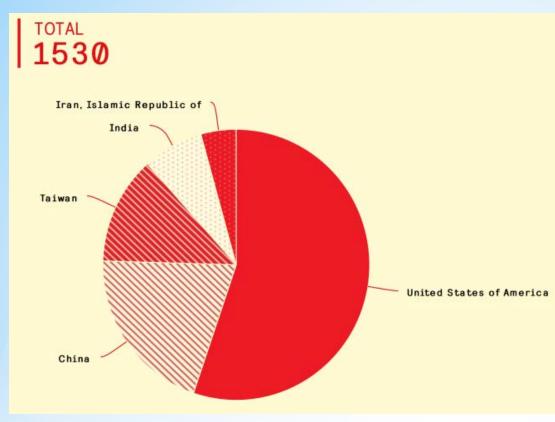
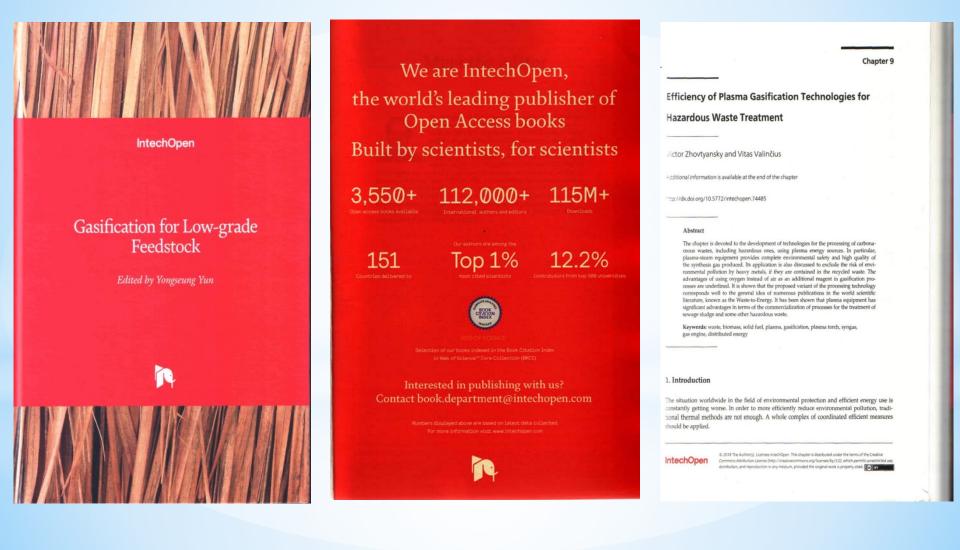


Fig. 1. Distribution of the basic publication[2] downloads by countries according todata of the publishing house InTechOpen,London (beginning of August 2021)

However, for specialists in hydrocarbons gasification, this area of research has a long history [2]. It should be underlined that abovementioned publication of project manager for today has more than 1500 downloads according to the information of world's leading publishing house InTechOpen half (London), more than downloads had been performed from USA (Fig.1). Later, the conclusions of the publication [2] were clarified and specified in the monograph [3] during the project activity.

V. Zhovtyansky, V. Valinčius. Efficiency of Plasma Gasification Technologies for Hazardous Waste Treatment // Gasification for Low-grade Feedstock (ISBN 978-1-78923-289-9) / Collective Monograph; Ed. Yongseung Yun. – London: InTech, 2018. – P. 165 - 189.



Experimental studies and thermodynamic calculations on the efficiency of gasification process for a mixture of sewage sludge (SS) and rubber roof of worn tires (RRWT) were performed in the process of implementation of this project as the development of the basic publication [2].

At a qualitative level, the positive effect of mixing RRWT to SS in terms of the gasification process can be shown by comparing the appearance of slag, which is formed as a result of plasma-air gasification of sewage sludge (Fig. 2) and a mixture of this raw material with RRWT (Fig. 3) under the conditions of laboratory experiment in the gasifier of small volume ~ 1 l. At the same time, these figures illustrate the exceptional advantage of abovementioned plasma technologies, which provide high parameters of thermodynamic processes and allow vitrification of heavy metals of SS, despite the high ash content of 50-60% (Fig. 2). However, the RRWT impurity further improves the quality of the vitrification process, as confirmed by the homogeneity of the slag melt in this case (Fig. 3).

Melt of slag (right), formed as a result of plasma-air gasification of sewage sludge (left)

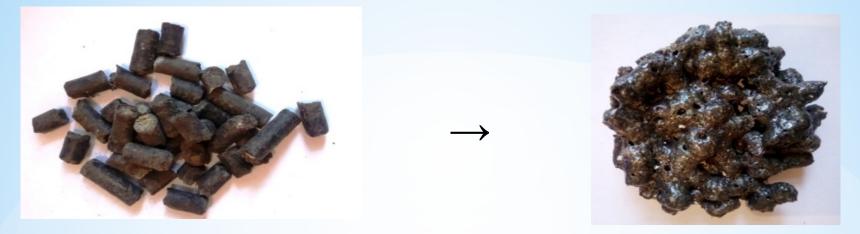


Fig. 2.

The composition of the synthesis gas obtained in the process of plasma-steam gasification of sewage sludge is as follows:

Origin of sewage sludge		The composition of the dry synthesis gas, vol. %				
		H ₂	CO	CO ₂	CH ₄	N ₂
Sewage sludge of Bortnytska aeration station in Kyiv		71,8	3,1	24,7	0,4	-
Sewage sludge of Ivano-Frankivsk water treatment plant	Sample 1	34,7	19,4	11,6	4,9	29,2
	Sample 2	39,7	20	9,6	8,3	22,3

Melt of slag (right), formed as a result of plasma-air gasification of sewage sludge (left) in a mixture with rubber roof of worn tires (middle)





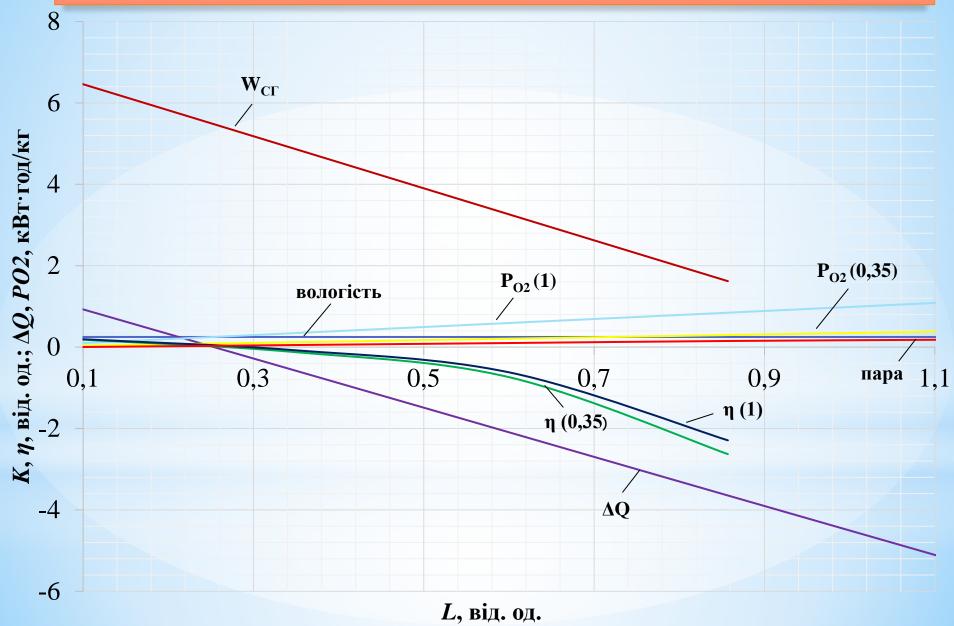
Fig.	3.
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Components	Sample 1,%	Sample 2,%	Sample 3,%	
•	for 2-3 minutes	at 7-9 minutes	at 40-42 minutes	
H ₂	44,55	56,09	44,80	
N ₂	15,68	9,04	21,30	
СО	14,42	17,16	13,88	
CH ₄	11,36	6,95	0	
CO ₂	6,34	7,94	20,02	
C_2H_4	3,43	0,92	0	
C_2H_6	3,88	1,90	0	
C ₃ H ₆	0,13	0	0	
nC ₄ H ₁₀	0,21	0	0	
	100	100	100	

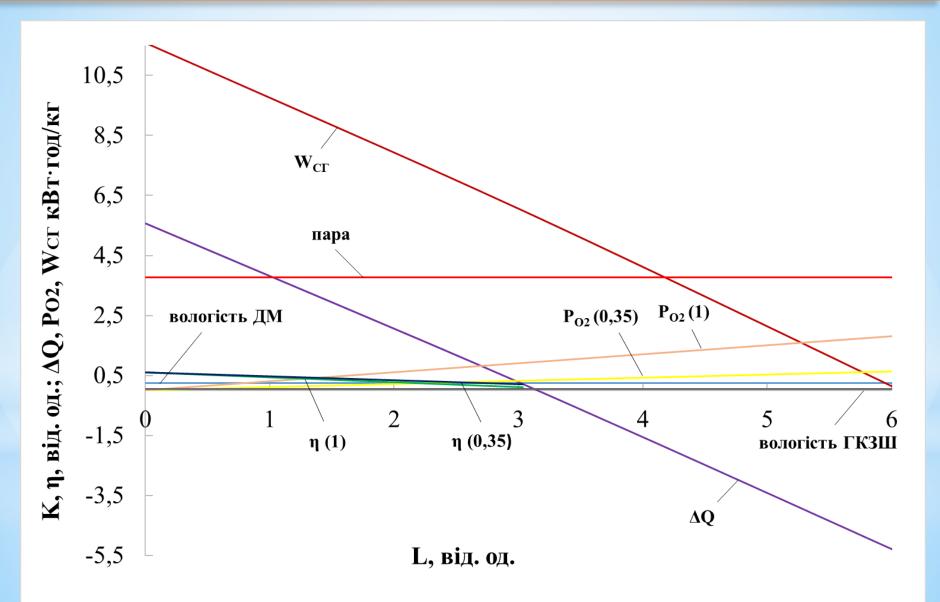
The composition of the products of compatible gasification of rubber roof of worn tires with LLC "Green Way" and sewage sludge of the water treatment plant in Ivano-Frankivsk

In the thermodynamic modeling for the processes of joint gasification of SS and RRWT, the basic thermochemical equation for plasma-vapor-oxygen conversion of carboncontaining waste was used, presented by the authors in [2, 3]. Here it is generalized for the variant of mixed raw materials processing. A positive effect was quantified in terms of improving the energy efficiency of the gasification $\eta = (P_{PI})^J +$ P_{O2} / $\eta_{EE}W_{SG}$, which takes into account the cost of electrical energy P_{PL}^{J} for the production of plasma jet with plasma torch efficiency at ~ 0.8, ie: $P_{PL}^{J} = \Delta Q_{PL}/0.8$, $P_{\Omega 2}$ – energy consumption for oxygen production, $\eta_{FF} \sim 0.3$ – efficiency of electricity production, W_{SG} – energy of synthesis gas production.

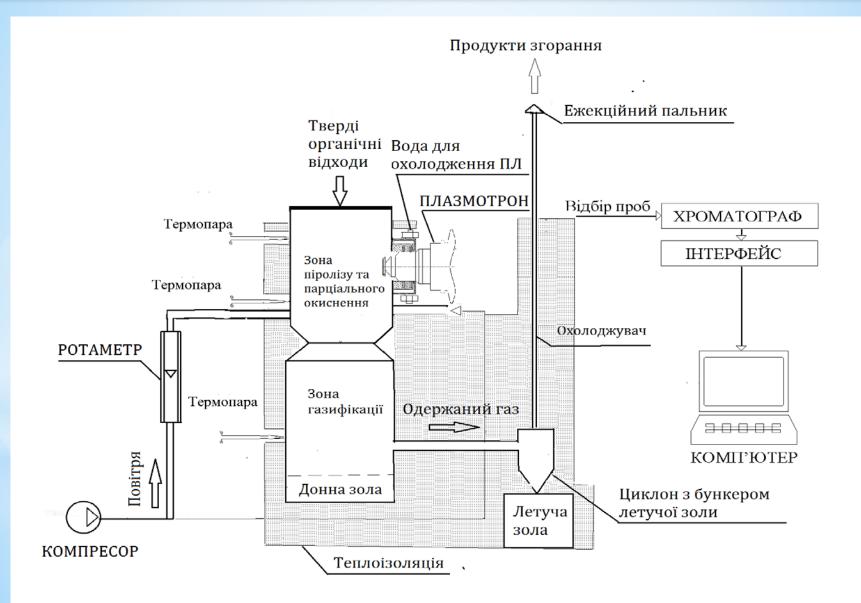
BASIC REGULARITIES THAT CHARACTERIZE THE GASIFICATION OF CARBONACEOUS RAW MATERIALS



MAIN INDICATORS OF THE PLASMA-STEAM OXYGEN GASIFICATION PROCESS



PILOT EQUIPMENT FOR PLASMA-STEAM GASIFICATION OF A MIXTURE SEWAGE SLUDGE AND RUBBER ROOF OF WORN TIRES



Indicator		Value		Dimensionality	
		2	3	4	
Consumption of the mixture		0,29	0,31	kg/hour	
Thermal capacity of the equipment in relation to the consumption of the mixture		1,41	1,51	kW	
Electric power of a steam plasma torch		1,28	1,36	kW	
Water consumption in the plasma torch		2,69	2,82	g/min	
Air consumption		0,77	0,77	nm ³ /hour	
Oxygen consumption		0,16	0,16	nm ³ /hour	
Steam consumption		0,16	0,17	kg/hour	
Molar ratio of steam / oxygen		1,24	1,30	mol/mol	
	Pyrolysis section	259	274		
The temperature of the outer	Oxidation section	416	432	°C	
walls of the reactor	Gasification section	443	413		
Dry gas yield		0,95	0,98	nm ³ /hour	
Composition of the obtained g	as				
H ₂		10,98	12,70		
	СО	8,05	8,78		
CO ₂		16,10	15,55	vol. %	
CH ₄		0,73	0,56		
N ₂		64,14	62,41		
Molar ratio H ₂ /CO		1,36	1,45	mol/mol	
Lower heat of combustion of the obtained dry gas		2,46	2,68	MJ/nm ³	
Thermal capacity of the equipment relative to the output of the obtained gas		0,65	0,73	kW	
Chemical efficiency of gasification (taking into account the electric power of the plasma torch)		24,16	25,44	%	
The yield of hydrogen in terms of the consumption of dry ashless mixture		0,653	0,648	nm ³ /kg	

POSSIBLE AREAS OF APPLICATION AND PROSPECTS FOR IMPLEMENTATION

The project "Development of scientific and technological bases for synthesis gas from a mixture of hazardous organic waste" is part of a more general project aimed for creating of full technological line of hazardous waste processing using plasma technologies with a capacity of 200 kg per hour at the Gas Institute of NAS of Ukraine (Fig. 4). The end result of these studies should be the production of electricity based on the combustion of synthesis gas $H_2 + CO$, which is obtained as a result of waste processing. This electricity should be distributed both to meet the technological line's own energy needs and to external consumers, which will facilitate the commercialization of results. For the production of electricity, the use of a gas-diesel power plant or turbine is envisaged, depending on the specific conditions of the potential user of this technology. Modern fuel cells can also use synthesis gas for direct conversion of chemical energy into electricity. If necessary, membrane technologies can be used to extract hydrogen directly from the synthesis gas mixture – similar to what was done in development [4].

An agreement has been signed with one of the production companies in Sofia (Bulgaria) on the development of these studies in the field of processing of carbon-containing waste using plasma technologies and their practical implementation based on international cooperation for their application, search for potential partners, investors and customers in Bulgaria, Ukraine and third countries.

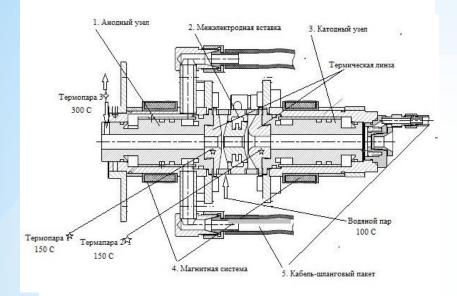
TECHNOLOGICAL LINE FOR HAZARDOUS WASTE PROCESSING







STEAMWATER PLASMA TORCH









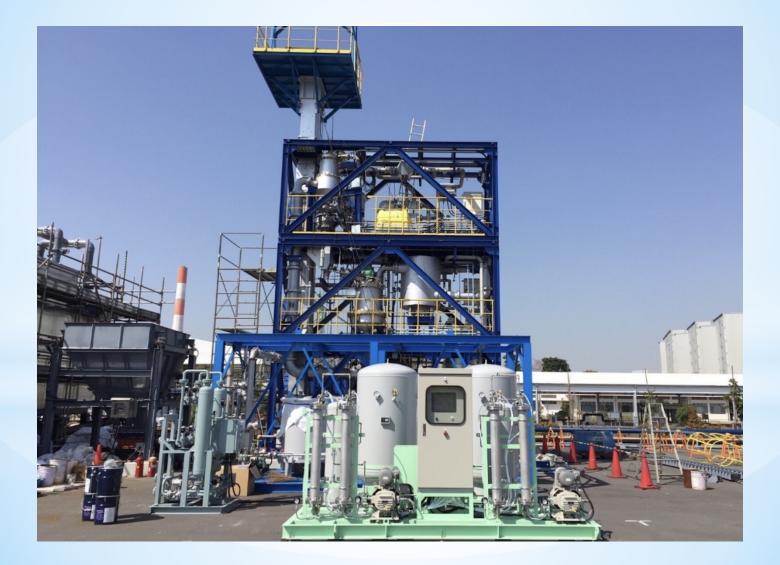
COMPARISON WITH HIGH-TECH COUNTRIES

The authors of a similar development using plasma technology [5] from company SGH2 (Washington, DC, USA) emphasize that the hydrogen produced in this process is "greener than green." The company plans to produce carbon-negative hydrogen from biogenic waste and biomass in the city of Lancaster, north of Los Angeles (USA). The hydrogen is titled carbon-negative because the waste would otherwise rot in landfills and emit methane. For 20 years period of time greenhouse gas is 84 times more potent than CO_2 . It thus calculates its carbon intensity as negative 188kg of CO_2 equivalent per megajoule, compared to 20kg for coalderived H₂ and zero for standard green hydrogen.

Another close analogue is a design solution using plasma technology, which is implemented in a joint project of the company for the production of renewable hydrogen systems Ways2H Inc. (Long Beach, CA, USA) and its shareholder and technical partner Japan Blue Energy Co. (Tokyo, Japan) [4]. It is focused, as in our case, on the processing of bottom sludge, with the main difference that membrane technology is used to extract hydrogen from synthesis gas, and the residual CO is used to the production of thermal energy, which is returned to the process. This mini-plant with a capacity of 1 ton of dried sewage sludge per day was built in 2021 in partnership with the government of Tokyo, corporations TODA, TOKYU Construction, CHIYODA Kenko and researchers at Tokyo University of Science to help Japan meet the growing demand for renewable hydrogen while demonstrating a new path to sustainable waste disposal. It converts the mentioned amount of sewage sludge into 40-50 kg of pure hydrogen fuel for cars with fuel cells.

JAPANESE ANALOG (Tokyo, 2021)

https://www.prnewswire.co.uk/news-releases/ways2h-shareholder-japan-blue-energy-launchestokyo-renewable-hydrogen-production-facility-812077768.html.



ANALOG from the USA (California, 2021)



'Greener-than-green hydrogen to be produced at same cost as grey H2 at world's largest facility'

'It's much cheaper to produce green hydrogen from waste than renewables'

SGH2 describes its hydrogen as "greener than green" as it uses biomass-based waste that would otherwise rot in landfills and emit methane, a greenhouse gas 84 times more potent than CO_2 over a 20-year period. It thus calculates its carbon intensity as negative 188kg of CO_2 equivalent per megajoule, compared to 20kg for coal-derived H₂ and zero for standard green hydrogen.

SGH2's first commercial project, due to start construction near Los Angeles in the first quarter of next year, will have a three times larger output than any other green-hydrogen project this decade, the company states, producing 3,800 tonnes of H_2 a year.

THE LEVEL OF TECHNOLOGICAL READINESS

The above-mentioned technological line for hazardous waste processing is fully completed with plasma equipment, a reactor unit with high-quality thermal insulation and units for loading raw materials and unloading the ash residue, a system for cleaning gasification products. At the stage of completion is a system of mechanized loading of raw materials into the reactor.

INTELLECTUAL PROPERTY

1. Petrov SV, Bondarenko SG, Zhovtyansky VA, Korzhyk VM, Popov VV Electric arc plasmatron (MKP9 H05H1 / 24). Patent for invention No.98271 // Bulletin No.8 dated 25.04.2012.

2. Petrov SV, Bondarenko SG, Zhovtyansky VA, Zholudeva OS Device for steam plasma gasification of solid carbonaceous materials (IPC (2014) Patent for invention No. 111691. Bulletin No.6 from 25.03.16 and No.10 from 25.05.2016

3. Know-how for production experience in creating a technological line for hazardous waste processing.

The main publications in the frame of project "Development of scientific and technological fundamentals of synthesis gas production from a mixture of hazardous organic waste":

- S.V. Petrov, V.A. Zhovtyansky. Energy Efficient Steam Plasma Waste Recycling Technologies, - K.: Naukova Dumka, 2019. - 559 p. ISBN 978-966-00-1683-5
- V. Zhovtyansky, E. Kolesnikova, Yu. Lelyukh1, Ya. Tkachenko. Non-monotony of the volt-ampere characteristics of the arc discharge caused by effects of heat conductivity, Tekhnichna elektrodynamika, 2019, No.3, pp.12-22. https://doi.org/10.15407/techned2019.03.012

S.V. Petrov, V.A. Zhovtyansky. Energy Efficient Steam Plasma Waste Recycling Technologies, -K.: Naukova Dumka, 2019. - 559 p. ISBN 978-966-00-1683-5



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1. Mission Innovation launches a new global coalition to support the clean hydrogen economy, electronic resource, <u>https://ec.europa.eu/info/news/mission-innovation-launches-new-global-coalition-support-clean-hydrogen-economy-2021-jun-02_en#:~:text=The%20%20goal%20of%20the%20Clean,scale%20integrated%20hydrogen %20valleys%20worldwide</u>

 Zhovtyansky V., Valinčius V. Efficiency of plasma gasification technologies for hazardous waste treatment., Gasification for Low-grade Feedstock (ISBN 978-1-78923-289-9), Ed. Yongseung Yun. – London: InTechOpen, 2018,pp. 165 - 189. <u>https://www.intechopen.com/chapters/59776</u>

3. Petrov S.V., Zhovtyansky V.A. Energy-efficient steam-plasma technologies for waste processing. - Kyiv: Naukova Dumka, 2019. 559 pp.. ISBN 978-966-00-1683-5.

4. Ways2H Shareholder Japan Blue Energy Launches Tokyo Renewable Hydrogen Production Facility, electronic resource, <u>https://www.prnewswire.com/news-</u> <u>releases/ways2h-shareholder-japan-blue-energy-launches-tokyo-renewable-hydrogen-</u> <u>production-facility-301258110.html</u>

5. World's largest 'green hydrogen' offtake deal signed in California by waste-to-H2 startup, electronic resource, <u>https://www.rechargenews.com/energy-transition/worlds-largest-</u> <u>green-hydrogen-offtake-deal-signed-in-california-by-waste-to-h2-start-up/2-1-1020363</u>



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