



K Ě S T U T I S Z A K A R A U S K A S

**INVESTIGATION
ON THERMAL
DECOMPOSITION OF
BIOMASS AND TAR
DESTRUCTION
EFFICIENCY**

S U M M A R Y O F D O C T O R A L
D I S S E R T A T I O N

T E C H N O L O G I C A L
S C I E N C E S , E N E R G E T I C S
A N D P O W E R E N G I N E E R I N G
(0 6 T)

K a u n a s
2 0 1 5

KAUNAS UNIVERSITY OF TECHNOLOGY
LITHUANIAN ENERGY INSTITUTE

KĘSTUTIS ZAKARAUSKAS

**INVESTIGATION ON THERMAL DECOMPOSITION OF
BIOMASS AND TAR DESTRUCTION EFFICIENCY**

Summary of Doctoral Dissertation

Technological Sciences, Energetics and Power Engineering (06T)

2015, Kaunas

Dissertation is prepared during the period 2010–2014 at Lithuanian Energy Institute, Laboratory of Combustion Processes.

The research was funded by the Research Council of Lithuania.

Scientific Supervisor:

Dr. Algis DŽIUGYS (Lithuanian Energy Institute, Technological Sciences, Energetics and Power Engineering – 06T).

Dissertation Defense Board of Energetics and Power Engineering science Field:

Prof. Dr. Habil. Gintautas MILIAUSKAS (Kaunas University of Technology, Technological Sciences, Energetics and Power Engineering – 06T) – **Chairman**;

Prof. Dr. Gvidonas LABECKAS (Aleksandras Stulginskis University, Technological Sciences, Energetics and Power Engineering – 06T),

Dr. Egidijus URBONAVIČIUS (Lithuanian Energy Institute, Technological Sciences, Energetics and Power Engineering – 06T),

Prof. Dr. Habil. Eugenijus UŠPURAS (Lithuanian Energy Institute, Technological Sciences, Energetics and Power Engineering – 06T),

Prof. Dr. Saulius VASAREVIČIUS (Vilnius Gediminas Technical University, Technological Sciences, Environmental Engineering – 04T).

The official defense of the dissertation will be held at 10:00 a.m. on 12 June, 2015 at the public session of Council of Power and Thermal Engineering science trend at Dissertation Defense Hall at Lithuanian Energy Institute (Breslaujos str. 3, room No. 202, Kaunas).

The sending-out of the summary of the Doctoral Dissertation is on 12 May, 2015.

The Dissertation is available at the Libraries of Lithuanian Energy Institute (Breslaujos str. 3, Kaunas) and Kaunas University of Technology (K. Donelaičio str. 20, Kaunas).

KAUNO TECHNOLOGIJOS UNIVERSITETAS
LIETUVOS ENERGETIKOS INSTITUTAS

KĘSTUTIS ZAKARAUSKAS

**BIOMASĖS TERMINIO SKAIDYMO IR DERVŲ
DESTRUKCIJOS EFEKTYVUMO TYRIMAI**

Daktaro disertacijos santrauka

Technologijos mokslai, Energetika ir termoinžinerija (06T)

2015, Kaunas

Disertacija rengta 2010–2014 m. Lietuvos energetikos institute, Degimo procesų laboratorijoje.

Mokslinius tyrimus rėmė Lietuvos mokslo taryba.

Mokslinis vadovas

Dr. Algis DŽIUGYS (Lietuvos energetikos institutas, technologijos mokslai, energetika ir termoinžinerija – 06T).

Energetikos ir termoinžinerijos mokslo krypties daktaro disertacijos gynimo taryba:

Prof. habil. dr. Gintautas MILIAUSKAS (Kauno technologijos universitetas, technologijos mokslai, energetika ir termoinžinerija – 06T) – **pirmininkas**;

Prof. dr. Gvidonas LABECKAS (Aleksandro Stulginskio universitetas, technologijos mokslai, energetika ir termoinžinerija – 06T),

Dr. Egidijus URBONAVIČIUS (Lietuvos energetikos institutas, technologijos mokslai, energetika ir termoinžinerija, 06T),

Prof. habil. dr. Eugenijus UŠPURAS (Lietuvos energetikos institutas, technologijos mokslai, energetika ir termoinžinerija, 06T),

Prof. dr. Saulius VASAREVIČIUS (Vilniaus Gedimino technikos universitetas, technologijos mokslai, aplinkos inžinerija, 04T).

Disertacija ginama 2015 m. birželio 12 d. 10 val. viešame Energetikos ir termoinžinerijos mokslo krypties tarybos posėdyje, kuris įvyks Lietuvos energetikos instituto posėdžių salėje (Breslaujos g. 3 202 kab., LT–44403 Kaunas).

Disertacijos santrauka išsiuntinėta 2015 m. gegužės 12 d.

Su disertacija galima susipažinti Lietuvos energetikos instituto (Breslaujos g. 3, Kaunas) ir Kauno technologijos universiteto (K. Donelaičio g. 20, Kaunas) bibliotekose.

INTRODUCTION

Global Energy currently finds itself between two interrelated crises: decrease in fossil fuel resources and climate change due to greenhouse gas emissions. Population growth, automotive industry and especially large extent of consumption of goods lead toward extra consumption of fossil fuel and environmental degradation. Research on alternative ecology fuels is the trend nowadays, and gasification of biomass or other organic waste is considered as one of most promising ways for energy production. In comparison with direct combustion of biofuel, gasification process is more efficient and environmentally friendly due to lower emissions of greenhouse (CO_2) and hazardous (NO_x , SO_x , VOC) gases. The producer gases obtained are further used as a fuel for internal combustion engines, gas turbines, hydrogen production industry, and production of synthetic diesel fuel.

The main obstacle for broader utilization of gasification technologies is tar and solid particles (mainly soot and volatile metals), which are an unfavourable part of producer gas. Untreated producer gas tends to deposit and condense on turbine blades, moving parts of internal combustion engines or hydrogen separation membranes. By sticking on the surfaces, tar compounds shorten the service life of the equipment. Until now, the producer gas has been treated by simple mechanical methods: solid particles are caught on electrostatic precipitators and tars are condensed in scrubbers. These methods of producer gas treatment are quite effective, but not economically efficient since some part of calorific compounds is being discarded, as well as some of hazardous substances. Tars, sulphur, chlorine and other hazardous substances pollute process water. In order to optimize the gasification process, new ways of tar removal from producer gas are being researched worldwide. One of the methods is catalytic thermal tar destruction. During the process, tar-containing hydrocarbons are additionally gasified down to final reaction products CO and H_2 , which increases overall yield of producer gas.

By getting familiar with the present situation of scientific works performed in the field of biomass gasification, I see the importance of tar and particulate matter cleaning from producer gas question. This problem is still an outstanding issue by the essence of the process. Moreover, technological implementation of the process is diverse; efficiency of different methods is still not enough evaluated in practice. Consequently, the objective of this experimental work is the evaluation of processes for catalytic thermal destruction of tars using dolomite and used tire char catalysts at different temperatures, oxidizing environment and the amount of the catalysts.

Aim of the work

Investigation of catalytic destruction processes of tars that are present in the producer gas with dolomite and tire char catalysts. Determination of optimal process conditions for efficient cleaning of producer gas by tar destruction.

Tasks of the work

For implementation of the scientific goal, the following main tasks should be performed:

1. An experimental study of tar destruction with dolomite and activated char catalyst and comparison of the results with those of other authors.
2. Determine destruction efficiency of tars formed during biomass gasification with respect to different reaction temperatures, oxidizing environment, type and amount of the catalysts.
3. According to the experimental results, determine the influence of selected tar destruction processes on total integrated energy efficiency of gasification process.

Relevance of the work

Gasification of biomass results in producer gas, which contains tars. Tars are unwanted material in producer gas and should be removed. In order to optimize the gasification process, new ways of tar removal from producer gas are investigated. One of the methods is catalytic thermal tar destruction. During the process, tar-containing hydrocarbons are additionally gasified down to final reaction products CO and H₂. For optimization of the process, the following conditions must be determined: temperature, reaction time and type of catalyst.

Novelty of the work

Common principles of different catalytic tar destruction processes with tire char and dolomite catalysts were identified and systematized, with respect to process temperature, space velocity, type and amount of oxidizer.

Significance of research results

Optimal process conditions for catalytic-thermal destruction of tars from producer gas were determined. The obtained results may contribute to development of catalytic reactors for tar removal from producer gas by using dolomite and tire char catalysts. Also, materials and process solutions are presented for more efficient development of biomass gasification technology.

Statement presented for defense

1. Tire char and dolomite are active as catalysts at thermal destruction of tars and are suitable for producer gas cleaning; however, tire char efficiency is better in destruction of real tars consisting of heavier hydrocarbons.
2. Most efficient catalytic tar destruction method is steam reforming.
3. In integrated gasification technology, better energy efficiency is achieved with catalytic tar destruction process in comparison with mechanical tar treatment method.

Scientific approbation of dissertation

Research results presented in the dissertation were published in 2 scientific articles in refereed publications with a citation index at the “Thomson Reuters” database “Web of Science Core Collection”. Research results were also presented at 6 conferences, 5 of them international.

1. EXPERIMENTAL SETUP AND METHODOLOGY

1.1. Preparation of catalysts

Lithuanian dolomite. For experimental investigations dolomite from Petrašiūnai mine (Lithuania, Pakruojis district) was used. Milled dolomite was sieved to a particle size range of 2.2-1.1 mm. The produced dolomite particles were placed to the stainless steel chamber and further to the thermally controlled furnace. The calcination of dolomite was carried out at the temperature of 850 °C for 2 h with constant steam flow. The properties of Lithuanian dolomite after the calcination process are presented in Table 1.

Table 1. Properties of catalysts used in the experimental investigation.

Parameter	Lithuanian dolomite	Tire char
Particle size (mm)	2.2 – 1.1	
Bulk density (g/cm ³)	0.78	0.19
BET surface area (m ² /g)	11.3	480.4
Total pore volume (mm ³ /g)	19	1435
Micropore volume (mm ³ /g)	1.5	176.1

Tire char. Waste tire parts cut into pieces were gasified in the muffle furnace at 850 °C. After about 10 min, all volatile material releases and porous coal structure is formed. From a char formed steel cords were removed, milled and sieved to particle size range of 2.2-1.1 mm. Char fraction obtained is placed into heating chamber for activation under steam atmosphere at temperature of 850 °C. Activation of coal was similar to the calcination of dolomite and took about 2 h. The properties of activated carbon after the activation process are presented in Table 1.

1.2. The methodology for investigation on catalytic thermal destruction of tar containing compounds – benzene and naphthalene

Taking into account the techniques presented in references (Abu El-Rub et al., 2008; Devi et al., 2005; Orio et al., 1997; Zhang et al., 2010), an experimental setup was designed and prepared for experimental research of catalytic tar destruction (Fig. 1). The experimental setup consists of three main parts: a system for vaporization of model tar component substances, a catalytic fixed bed reactor and tar condensers. The experiments of model thermal destruction of tar component substances are carried out as follows: nitrogen heated to 250 °C is supplied at a constant pressure to the heating chambers 2, where the evaporators 3 and 4 are installed. In the evaporators, naphthalene or benzene are vaporized at the constant temperatures of 120 °C and 20 °C, respectively, and water is vaporized at 80 °C. The flow of nitrogen saturates with a certain amount of the researched material as it flows through the evaporator. Concentrations of tars and water in nitrogen are not varied throughout the experiment. In order to avoid condensation of tars and steam, a temperature of

250 °C is maintained in the supply line all the way to the reactor *11* and the tar condenser *6*. During the thermal conversion process, the mixture of nitrogen – tars and nitrogen – steam is mixed before entering the catalytic reactor. The resulting gas mixture enters the tar conversion reactor. The reactor contains a 40 cm long and 2.1 cm diameter stainless steel pipe containing a 35 cm long catalyst bed (*10*) inside. Inside the reactor, a K-type thermocouple is installed by means of which the temperature needed for thermal destruction is controlled and maintained.

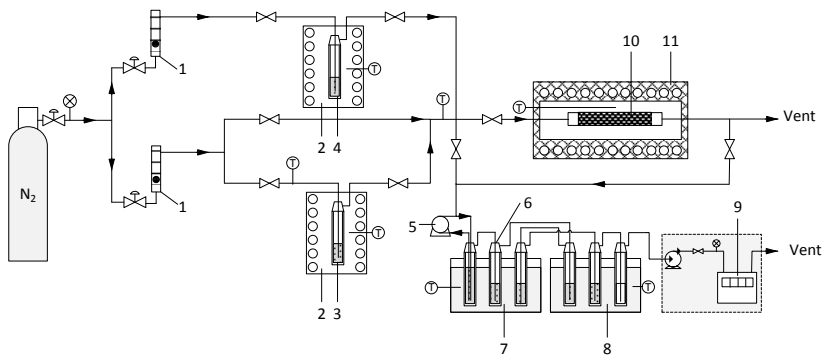


Fig. 1. Scheme of the experimental rig

1 – rotameter; 2 – heater; 3 – water evaporator; 4 – model tar evaporator; 5 – peristaltic pump; 6 – gas washing bottles; 7 – heated bath; 8 – cooled bath; 9 – gas flowmeter; 10 – catalytic bed; 11 – reactor.

The tar concentration in the gas flow at the reactor inlet and outlet is determined using the standard technique of tar condensation in a solvent (cold trapping), (Good et al. 2005). The amount of gas flow that travels during the experiment is integrated by the gas flowmeter 9. The obtained samples are weighed and analyzed, following the method of gas chromatography. Sample analysis was performed using Varian GC-3800 gas chromatograph.

1.3. The methodology for biomass pyrolysis and catalytic tar destruction

An experimental setup was designed and prepared for experimental research of catalytic tar destruction (Fig. 2). The experimental setup consists of three main parts: a biomass pyrolysis reactor, a catalytic fixed bed reactor and tar condensers. The experiments of thermal destruction of biomass tars are carried out as follows: nitrogen (0.9 l/min) is supplied at a constant pressure to the heating chamber 2, where the water evaporator 3 is installed. Water is evaporated at constant temperature in the evaporator. Nitrogen flow, flowing through evaporator, is saturated with certain water quantity. Vapour concentration is adjusted by changing the temperature of evaporated H₂O.

The steam-to-carbon ratio (H_2O/C) is defined as:

$$\frac{H_2O}{C} = \frac{V_{real}}{V_{theoretic}} ; \quad (1)$$

where G_{steam} is the real mass flow of steam to the reactor (g/min) and G_{carbon} is carbon mass in the producer gas flow (g/min).

The equivalence ratio is defined as follows:

$$ER = \frac{V_{real}}{V_{theoretic}} ; \quad (2)$$

where V_{real} is the real volume of air fed to the reforming reactor (m^3) and $V_{theoretic}$ is the theoretical volume of air (m^3) necessary for a complete oxidation of the producer gas with the concentration.

To represent obtained data the definition of space-velocity was used:

$$v = \frac{Q}{V} ; \quad (3)$$

where v – space-velocity, s^{-1} ; Q – flow of producer gas through the catalyst bed, m^3/s ; V – volume of catalyst in the bed, m^3 .

Another, measured flow of nitrogen (1.8 l/min) is supplied to the container 4 of biomass pellets. In experiments we used a commercially available biomass pellets made from softwood, mainly spruce and pine (JSC Baltwood, calorific value – 19 MJ/kg, ash content – 0.35 %, humidity – 5.2%). Screw conveyer 5 with a constant rpm delivers fixed amount of biomass pellets to the pyrolysis reactor 6. During experiments, the temperature of pyrolysis reaction was set at 850 °C. The producer gas containing 21.12 g/ m^3 of tars, before entering the steam reforming reactor is mixed with nitrogen steam flow. In order to avoid condensation of tars and steam, a temperature of 250 °C is maintained in the supply line all the way to the reactor 8 and the tar condenser 10. The resulting gas mixture enters the tar conversion reactor. Because of the variety of experiments, the reactor contains a different long catalyst bed 7 inside. Inside the reactor, a K-type thermocouple is installed by means of which the temperature needed for thermal destruction is controlled and maintained.

The tar concentration in the gas flow at the reactor inlet and outlet is determined using the standard technique of tar condensation in a solvent (cold trapping), (Good et al. 2005). The amount of gas flow that travels during the experiment is integrated by the gas flowmeter 9. The obtained samples were weighed and analyzed by gas chromatography. Sample analysis was performed using Varian GC-3800 gas chromatograph.

The analysis of gaseous samples was performed using Agilent 7890A gas chromatograph with dual channel thermoconductivity detectors (TCD) and

valve system: front channel is used for separating of O₂, N₂, CO₂, CH₄, CO and light hydrocarbons, while back channel – for hydrogen separation.

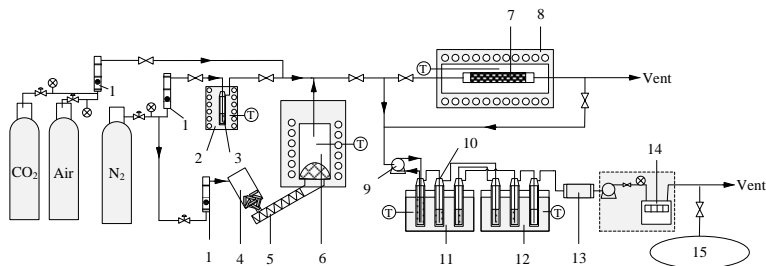


Fig. 2. Schematic diagram of experimental setup

1 – flowmeter; 2 – heater; 3 – water evaporator; 4 – biomass pellet container; 5 – screw conveyor; 6 – biomass pyrolysis reactor; 7 – catalytic bed; 8 – catalytic reforming reactor; 9 – peristaltic pump; 10 – gas washing bottles; 11 – heated bath; 12 – cooled bath; 13 – quartz fibre filter; 14 – gas flowmeter/counter; 15 – “Tedlar” gas bag.

2. RESULTS AND DISCUSSION

2.1. Investigation on catalytic destruction of tar containing compounds – benzene and naphthalene

2.1.1. Benzene decomposition

Lithuanian dolomite. Figure 3 shows benzene destruction efficiency with dolomite catalyst bed at constant steam/carbon ratio ($H_2O/C=1$) as a function of temperature. As the curve shows, with the increase of temperature, benzene destruction efficiency increases. At the value of 900 °C the efficiency reaches 90.58 %. It was determined that after increasing process temperature up to 1000 °C, particle size of the dolomite catalyst decreases, and part of it is swept away along with the gas stream. Consequently, further experimental investigations at temperatures above 1000 °C were not performed due to degradation of mechanical properties of the catalyst. Moreover, mass loss of the catalyst distorts the results by unequal conditions of the experimental research.

The highest conversion rate of benzene over dolomite catalysts was found in study by Delgado et al. (1997) (Fig. 3). Dolomite used in this work originated from Cantabria region in Spain. Authors determined that at the temperature of 800 °C, tars conversion efficiency was up to 99.3 %. As seen from the figure at this temperature concentration of benzene obtained in our experiments was 80.8 %. This difference may be due to different dolomite fraction used: Delgado et al. (1997) measured high benzene conversion cracking tars over dolomite bed with particle diameter of 1.3 mm; in our work, dolomite fraction from 2.2 to 1,1 mm was used; however, the exact distribution of particles within this diameter range was unknown. In Delgado et al. (1997)

S. Hosokai et al. (2008) results (Fig. 4). The authors investigated the activity of activated char for benzene destruction during commercial gasification process and found 98 % decomposition efficiency at 900 °C or 84 % at 800 °C. S. Hosokai et al. (2008) used activated charcoal bed with bulk density 0.095 g/cm³. In this work, bulk density of activated char obtained from used tires was of double value than here, namely 0.19 g/cm³, (Table 1), and of uniform granulometric structure. Due to these differences, the performance of used tire char is considered less efficient.

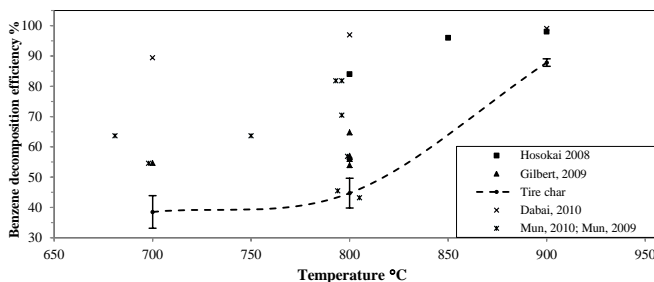


Fig. 4. Comparison of benzene decomposition efficiency over waste tire char with data obtained in literature

In their works, Mun et al. (2009); Mun et al. (2010) analyzed destruction of benzene contained in the syngas from gasification of wood waste and dried sewage sludge in a layer of commercially available activated char (Fig. 4). As seen from the results presented by the author, the resulting efficiency of benzene conversion is diverse: a higher conversion rate recorded at higher temperatures, and lower values at lower temperatures. Therefore, the results of this author and our results are comparable as similar by trends.

Gilbert et al. (2009) researched conversion of real tar from biomass gasification over wood pyrolysis char catalyst (Fig. 4). The conversion rate determined at 700-800 °C remains stable at about 55 % value; however, the author has a controversial opinion about the efficiency of the char bed and concludes that the main factor is the thermal conversion. However, as seen from both our experiments and those by others, the presence of char facilitates the tar destruction. The results obtained by Dabai et al. (2010) (Fig 4) confirm this effect as well. He noticed that increase of the temperature up to 1000 °C does not result in increase of efficiency of tar destruction, and the residual concentration in gas remains the same as that at the temperature of 900 °C.

2.1.2. Naphthalene decomposition

Naphthalene is the second most abundant tar-containing compound, and investigation of thermal destruction of naphthalene is no less important than that

of benzene. In this work, each of the catalyst was tested for naphthalene destruction efficiency at different reaction temperatures (700, 800 and 900 °C).

Lithuanian dolomite. Figure 5 shows naphthalene destruction efficiency in producer gas over dolomite catalyst bed with respect to the process temperature and at constant steam/carbon ratio ($H_2O/C=1$) conditions. As it can be seen from the results, thermal destruction of naphthalene increases with the increase of the process temperature, as it was found in the case of benzene. The experimental results also reveal naphthalene being more stable at higher temperatures; consequently, greater amount of catalyst is required for the complete destruction.

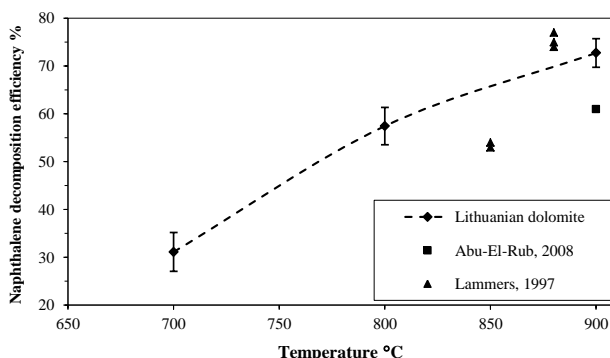


Fig. 5. Comparison of naphthalene decomposition efficiency over Lithuanian dolomite bed with data obtained in literature

In order to compare the obtained results with the works of other authors, as in the case of benzene, the resulting concentrations are recalculated into the naphthalene conversion, Fig. 5. In this graph, we present two works for comparison, Abu El-Rub et al. (2008) and Lammers et al. (1997), who performed thermal destruction of naphthalene as one of the main components of the biomass tar by using calcined dolomite as catalyst. As it can be seen, our results are very close to those obtained by other authors, and it can be concluded that the type of dolomite found in Lithuania is suitable for producer gas cleaning from tar compounds.

Tire char. Experimental results with used tire char show maximum 83.88 % efficiency of naphthalene destruction at 900 °C (Fig. 6). The results presented in Figures 6 and 5 shows about 6% more intense efficiency of naphthalene destruction using activated char bed in comparison with dolomite bed case.

Other authors (Fig. 6) also found the same tendency. As it can be seen from the figure data, naphthalene decomposition is more efficient using char bed as catalyst in comparison with dolomite. Abu-El-Rub et al. (2008) in their work investigated commercially available char obtained from biomass pyrolysis

process for efficiency on thermal decomposition of naphthalene and other tar containing compounds. The authors used finer fraction of char (from 1.4 to 1.7 mm) in comparison with this work (from 1.1 to 2.2 mm). Efficiency of naphthalene destruction reached over 99.6 % at 900°C and 99.9 % at 1000°C. S. Hosokai et al. (2008) found naphthalene conversion efficiency over 99.99 % at all three experimental points in the 800-900 °C temperature region. Similar results also were recorded by Brandt (2000), but the temperature of the process for naphthalene conversion was claimed higher, up to 1100 °C.

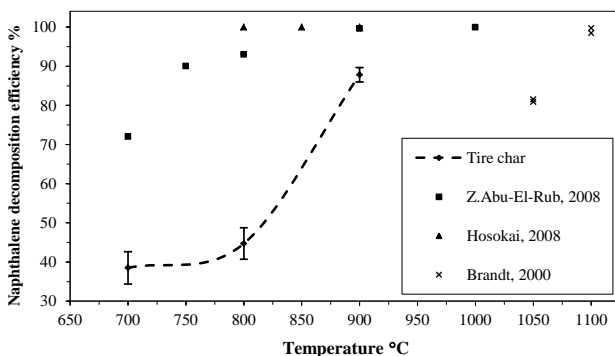


Fig. 6. Comparison of naphthalene decomposition efficiency over waste tire char with data obtained in literature

After experimental comparison of the results with the activity of calcined dolomite found in Lithuania and pyrolytic char from used tires for thermal destruction of tar containing compounds, it can be stated that both of these materials are active as an agent for tar destruction. However, dolomite performance was better for destruction of lower molecular mass hydrocarbons (C_6H_6) and char for higher structured hydrocarbons ($C_{10}H_8$).

When comparing the results presented in this work with the results from other authors, it can be stated that Lithuanian dolomite and tire char are efficient catalytic materials for thermal destruction of tar containing compounds, such as benzene and naphthalene.

2.2. Catalytic tar destruction from biomass pyrolysis process

During experimental analysis of biomass tar destruction, three types of experiments were performed, using Lithuanian dolomite and char derived from pyrolysis of used tires as catalysts, and without catalyst. The activity of a catalyst for treatment of tars was investigated at 3 temperatures, 700, 800 and 900 °C. At the beginning of experiments, the concentration of calibrated tars (21.12 g/m^3) in mixture of producer gas and nitrogen was determined.

2.2.1. Catalytic tar destruction using locally found dolomite

The first set of experiments was performed at the space-velocity of $v=0.28 \text{ s}^{-1}$. The results of concentration of biomass tars after treatment in catalytic bed of dolomite at various temperatures and at a constant steam to carbon ratio ($\text{H}_2\text{O}/\text{C}=1$) are presented in Figure 7. The effect of temperature is evident: at the temperature of $900 \text{ }^\circ\text{C}$ and mentioned time of contact, the concentration of tar after catalyst bed decreases down to 5.65 g/m^3 .

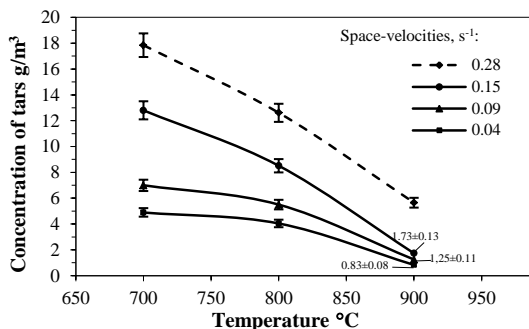


Fig. 7. Concentration of tar in producer gas after treatment over Lithuanian dolomite at different temperatures and space-velocities

In order to achieve full conversion of biomass tars, the time of contact of the producer gas with the catalyst was increased. The influence of space-velocity on tar removal is also shown in Figure 7. Doubling the time of contact of producer gases over dolomite leads to decrease of the concentration of tars at the exit of the bed from 5.65 g/m^3 to 1.73 g/m^3 , at the reaction temperature of $900 \text{ }^\circ\text{C}$. Further increase of dolomite weight does not show considerable effect on tar destruction. At the lowest tested space-velocity of $v=0.04 \text{ s}^{-1}$ and the temperature of $900 \text{ }^\circ\text{C}$, the concentration of total tar in producer gases was 0.83 g/m^3 . At this point, only two detectable tar compounds remain, benzene (0.73 g/m^3) and toluene (0.10 g/m^3).

In the previous chapter, thermal destruction of benzene and naphthalene was discussed by using dolomite as a catalyst. Activity of the catalyst was determined. Nevertheless, from the experimental results it is obvious that enough contact time with the catalyst is required for complete destruction of tars, which are present in the producer gas.

Results of tar conversion obtained at $v=0.04 \text{ s}^{-1}$ with respect to the temperature are graphically represented in Fig. 8. As it can be seen, tar conversion efficiency was 76.8% at the temperature of $700 \text{ }^\circ\text{C}$, but at $900 \text{ }^\circ\text{C}$, the dolomite becomes very reactive and the maximum conversion of 96.07% was achieved. Analysis of literature (Delgado et al., 1997; Devi et al., 2005; Gusta et al., 2009; Orio et al., 1997) also shows different results of tar

conversion over dolomite bed: from maximum tar conversion of 99.7 % at 912 °C to minimal of 44 % at 650 °C. This difference shows that dolomite from various countries has different reactivity, but it is evident that all are active at tar destruction, and only time of contact with a catalyst should be correctly selected.

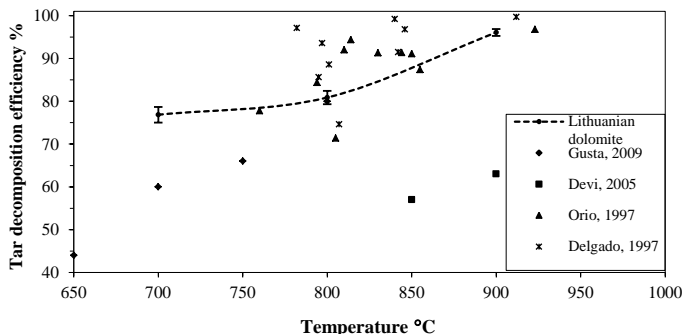


Fig. 8. Comparison of tar decomposition efficiency over Lithuanian dolomite bed at different temperatures ($v = 0.04 \text{ s}^{-1}$) with data obtained in literature

2.2.2. Tar destruction with activated charcoal

The next experimental research was performed with pyrolytic char from used tires as the catalyst for tar destruction/conversion. Initial conditions and catalyst bed load was the same as in thermal destruction case using dolomite. Figure 9 shows tar concentration in the producer gas after activated char bed at constant steam/carbon ratio ($\text{H}_2\text{O}/\text{C}=1$) as a function of temperature.

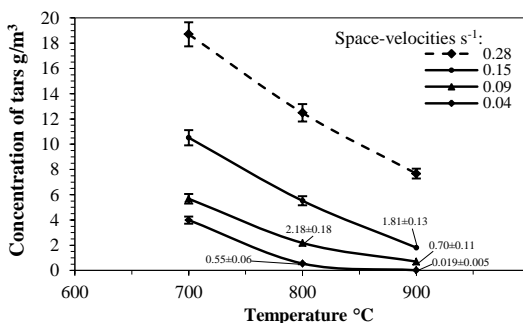


Fig. 9. Concentration of tar in producer gas after treatment over waste tire char at different temperatures and space-velocity

The first set of experiments with waste tire char, as in the case with dolomite, at the space-velocities of $v=0.28 \text{ s}^{-1}$ were performed. The influence of temperature increase was also apparent: initial tar concentration $21.12 \text{ g}/\text{m}^3$ in producer gas decreased down to $18.71 \text{ g}/\text{m}^3$ at 700°C , $12.48 \text{ g}/\text{m}^3$ at 800°C and

7.67 g/m³ at 900°C. However, at such value of space-velocity, waste tire char contribution to the tar destruction was lower than in the case with dolomite. At lower space-velocities, the concentration of tars in gas stream decreases (Fig. 9), and the full conversion of biomass tars was achieved at $v=0.04\text{ s}^{-1}$ and 900 °C. Comparison of Fig. 7 and Fig. 9 shows that with the increase of temperature, destruction of tars over waste tire char is more intense than over dolomite. This effect can be seen by different curve trends and it is more evident at lower space-velocities.

In order to compare the obtained results with the works by other authors, as in the case of dolomite, the resulting concentrations were recalculated into the tar conversion (Fig. 10). In this graph, four works for comparison are presented, Abu El-Rub (2008), Brandt et al. (2000), Dabai et al. (2010) and Gilbert et al. (2009), who performed thermal destruction of biomass tars using catalytic char bed. As it can be seen, the results obtained in these works are quite different. Brand et al. (2000) investigated the effect of char bed on tar destruction. The obtained tar conversion efficiency was up to 87.7 % at 1050 °C and 99.8 % at 1100°C.

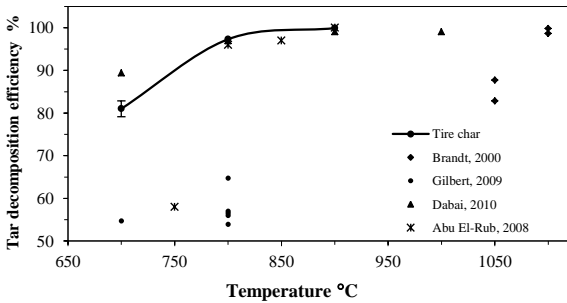


Fig. 10. Comparison of tar decomposition efficiency over waste tire char bed at different temperatures and space-velocities of 0.04 s^{-1} with data found in literature

Gilbert et al. (2009) investigated conversion of real tar from biomass gasification in wood pyrolysis char bed. The conversion rate determined at 700-800 °C remains stable at about 55-65 %; however, the author has a controversial opinion about the efficiency of the char bed and concludes that the main factor is the thermal conversion. The experimental conditions in ref. (Gilbert et al., 2009) were very close to conditions analyzed in this paper. According to author, the residual time of gases in the catalytic bed was 11.3 s, which is equal to space-velocity of $v=0.08\text{ s}^{-1}$. In the presented work, the space-velocity of $v=0.09\text{ s}^{-1}$ was also tested, and at the temperature of 800 °C the tar conversion efficiency was 89.6 %.

Dabai et al. (2010) published different experimental results. They showed that the presence of char in the heated secondary stage had significant

effect on tar destruction, to nearly to zero at 1000 °C. The main difference comparing with obtained results in this work is that authors used considerably higher space-velocity $\sim 2.7 \text{ s}^{-1}$. At similar high space-velocity of $\sim 3.3 \text{ s}^{-1}$ and at temperatures $\geq 800 \text{ }^\circ\text{C}$, almost complete conversion ($>99 \%$) of real tar was achieved in the work of Abu El-Rub (2008).

2.2.3. Steam reforming

Investigation on the temperature influence on tar destruction shows full destruction of tar containing hydrocarbons at $900 \text{ }^\circ\text{C}$ temperature and reaction conditions with space-velocity value of 0.04 s^{-1} . Consequently, further investigations on steam reforming with used tire char as catalyst were performed at $900 \text{ }^\circ\text{C}$ temperature and at the determined space-velocity of 0.04 s^{-1} . Steam to carbon ratio $\text{H}_2\text{O}/\text{C}$ was the only variable from the values of 0 to 1.

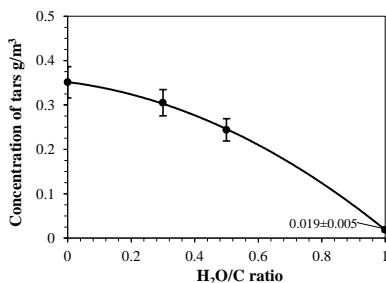


Fig. 11. Effect of $\text{H}_2\text{O}/\text{C}$ ratio on residual tar concentration in producer gas after treatment over catalyst at $900 \text{ }^\circ\text{C}$ temperature.

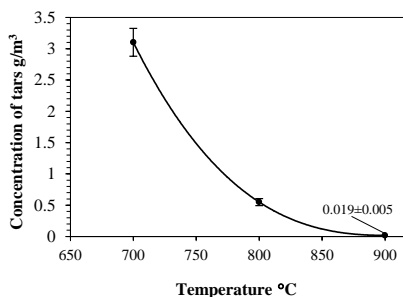


Fig. 12. Effect of temperature on total tar concentration in producer gas after treatment over catalyst at the steam/carbon ratio $\text{H}_2\text{O}/\text{C} = 1$

The results of the effect of steam/carbon ratio for tar destruction at $900 \text{ }^\circ\text{C}$ are presented in Fig. 11. The catalyst contributed to the decrease of the tars in the producer gas with the increase of the steam supplied. The influence of the process is relatively negligible. During the process of thermal tar destruction at the conditions $\text{H}_2\text{O}/\text{C} = 0$, tar concentration in the producer gas decreased from 21.12 down to 0.35 g/m^3 . During steam reforming process ($\text{H}_2\text{O}/\text{C}=1$), tar concentration decreased down to 0.019 g/m^3 .

Temperature influence on thermal destruction of tars was examined at optimal steam to carbon ratio $\text{H}_2\text{O}/\text{C}=1$ (Fig. 12). With the increase of the temperature, tar concentration decreases from initial 21.12 g/m^3 down to 3.10 g/m^3 at $700 \text{ }^\circ\text{C}$ temperature, decreased to the value of 0.55 g/m^3 at $800 \text{ }^\circ\text{C}$, and was measured 0.019 g/m^3 at $900 \text{ }^\circ\text{C}$ temperature. Experimental results show full destruction of high molecular tar containing hydrocarbons at the temperature of $800 \text{ }^\circ\text{C}$. The main compounds that are present in the tar are benzene ($\sim 63 \%$),

naphthalene (~25 %) and toluene (~6 %). Since the dew point of benzene and toluene is only 1.2 °C, the producer gas of similar composition may be directly provided for internal combustion engines (Kuhn et al., 2008).

2.2.4. Partial oxidation

In this chapter, experimental results of tar partial oxidation are presented. Air to fuel ratio optimization was selected as the start point with the respect to the results already performed at the temperature of 900 °C and space-velocity value 0.04 s⁻¹.

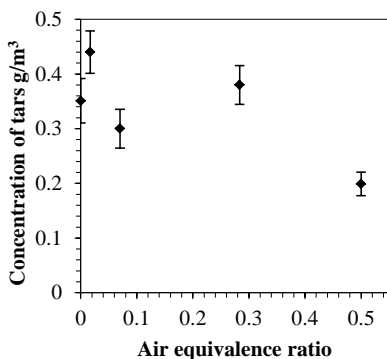


Fig. 13. Effect of air equivalence ratio on residual tar concentration in producer gas after treatment over catalyst at a temperature of 900 °C

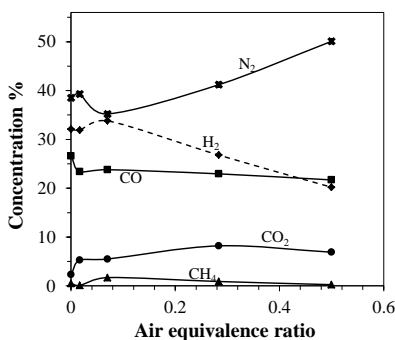
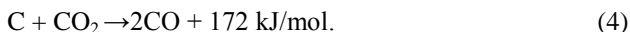


Fig. 14. Effect of ER ratio on gaseous product concentration in producer gas after treatment over catalyst at a temperature of 900 °C

Figure 13 shows results of partial oxidation of tars with activated carbon catalyst at constant temperature of 900 °C. Obviously, low influence of additional air for tar concentration, i.e., the destruction efficiency can be seen. With the increase of air supply into the catalytic reactor up to equivalence ratio ER=0.5, total concentration of tars in the producer gas decreased from 0.35 g/m³ (ER=0, the experimental point with the catalyst bed, without steam and air) down to 0.20 g/m³. With regard to the concentration of tar compounds, no significant influence of additional air for heavier tar compounds was found; however, the influence was observed in the case of steam reforming. For example, at low air equivalence ratios, heavier tar compounds starting from benz[a]anthracene disappear, but are produced and found at higher ER conditions. This effect influenced by the partial oxidation of the catalyst resulting in new favourable conditions for the formation of tars.

Gas composition after partial catalytic oxidation process of pyrolysis products shows decrease of concentration of hydrogen and methane with the increase of the amount of supplied air (Fig. 14). At higher ER conditions, concentration of carbon dioxide should increase, as found by Dogru et al. (2013).

However, CO₂ curve behaves differently and stays relatively stable. This may be due to the fact, that CO₂ produced by oxidation reaction is consumed by carbon–CO₂ reaction (Dogru, 2013):



In addition, reaction (4) results in the production of CO and compensates the losses caused by the oxidation thus maintaining relatively stable CO concentration in the gas at any ER and 900 °C temperature. Data presented by (Su Y., et al., 2011) clearly demonstrates that reaction (4) without catalyst does not occur: during partial oxidation of tars without catalyst, i.e., without C inside reactor, CO yield decreases, while the yield of CO₂ increases at higher ER conditions.

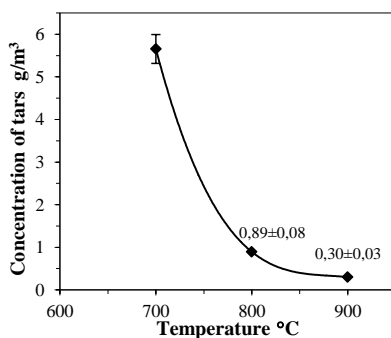


Fig. 15. Effect of temperature on the total tar concentration in producer gas after treatment over catalyst at the air equivalence ratio ER = 0.07.

Based on the total amount of tars, tar dew point and gas composition, the optimal air equivalence ratio determined in this chapter was 0.07. For this reason, further tests of the influence of reaction temperature on tar destruction efficiency with partial oxidation were performed at ER=0.07. As in the case of steam reforming, increase of temperature contributed to tar destruction efficiency (Fig. 15). Change in composition of tar compounds was minor, but the total concentration decreases. At the constant space-velocity $v=0.04 \text{ s}^{-1}$ and temperature, additional steam is more efficient for tar destruction in comparison with additional air.

Lowest concentration of tars achieved at the temperature 900 °C during tar destruction process. In the steam reforming case ($\text{H}_2\text{O}/\text{C}=1$), the total concentration of tars decreased from initial 21.12 g/m^3 value down to 0.019 g/m^3 , and in the case of partial oxidation (ER=0.5), the decrease was down to 0.20 g/m^3 value.

It was found that the impact of additional steam and air on total tar destruction efficiency over activated char catalyst was low at both processes, i.e., partial oxidation and steam reforming. As for tar destruction efficiency without

steam and air was 98.3 %, addition of steam increased the efficiency up to 99.9%, as additional air resulted in 99.0 5% efficiency. Utilization of steam and air mostly influences the destruction process of tar containing hydrocarbons of higher molecular weight.

2.2.5. CO₂ reforming

In this chapter, the experimental results of dry reforming are presented. According to the results described earlier, the experimental conditions were defined as follows: steam ratio was defined according to the rule H₂O/C=1, optimal space-velocity $v=0,04 \text{ s}^{-1}$ and the doubled amount of CO₂ gas was added before the reactor of catalytic tar destruction (from dedicated 10.8 % up to 21.0 % volume content).

Addition of CO₂ results in changes of initial composition of pyrolytic gas as follows: H₂, 15.8 %; CO, 16.2 %; CH₄, 6.5 %; C₂H₂, 0.05 %; C₂H₆, 0.02 %; CO₂, 21.0 %; N₂, 39.6 % and total tar content 18.3 g/m³. Change of the reaction temperature from 700 to 900 °C for tar destruction efficiency was monitored (Fig. 16).

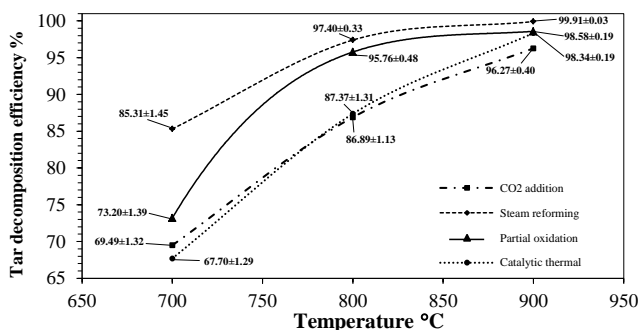


Fig. 16. The influence of temperature on tar decomposition of different processes.

Results presented in Figure 16 show obvious influence of the process temperature on tar destruction efficiency: temperature increase resulted in increase of destruction efficiency. However, comparison of different processes (Fig. 16) revealed less efficient tar destruction with the introduction of additional CO₂. At the temperature of 900 °C, the efficiency of tar destruction was lowest (96.27 %) in comparison with steam reforming (99.91 %), partial oxidation (98.58 %) and thermal catalytic destruction (98.34 %) processes. The main reason of lower tar destruction efficiency is the excess load of the catalyst by carbon dioxide gas. If the process of destruction of tar containing hydrocarbons takes place only on the surface of catalyst (Haghighi M., et al., 2007), in this case, with the increase of partial pressure of CO₂, the diffusion of tar hydrocarbons towards the catalyst is blocked.

As presented in Fig. 17, concentration of gas reaction products shows more intense CO_2 conversion into CO with the increase of the process temperature and at 900 °C amount of carbon dioxide decreases from 21.0 down to 10.8 % volumetric content. Concentration of methane reaches 2.8 % at the temperature of 900 °C.

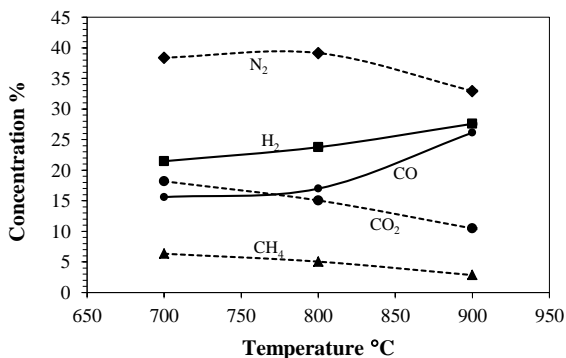


Fig. 17. Effect of temperature on the concentration of gaseous products in the producer gas after treatment over an activated char at $v = 0.04 \text{ s}^{-1}$, $\text{H}_2\text{O}/\text{C} = 1$, $\text{CO}_{2\text{in}} = 21 \text{ vol. } \%$

2.2.6. Influence of initial CO_2 concentration

Further investigations on carbon dioxide reforming process were continued at the same 900 °C temperature, which was chosen for studying the influence of initial CO_2 concentration and water steam on tar destruction efficiency. Increase of initial concentration of carbon dioxide in the gas caused increase of tar concentration (Fig. 8). With minor increase of the initial concentration of CO_2 gas (from 10.8 % up to 12.0 %) and at the same steam to carbon ratio ($\text{H}_2\text{O}/\text{C}=1$) with space-velocity value 0.04 s^{-1} full destruction of tars was not achieved. The measured residual tar concentration in the gas was 0.10 g/m^3 . At low initial concentrations of CO_2 including water steam heavier hydrocarbons are destroyed, and with the increase of CO_2 , concentration of these compound increases. Without the steam, tar decomposition process slows down. Influence of steam is noticeable at lower initial CO_2 concentrations. With the increase of CO_2 concentration, the influence of water steam disappears and similar residual tar concentration values were recorded in both cases. With the increase of initial CO_2 concentration, the partial pressure over the catalyst increases resulting in more intense *Boudouard* reaction. Consequently, additional introduction of CO_2 gases results in decrease of tar destruction efficiency.

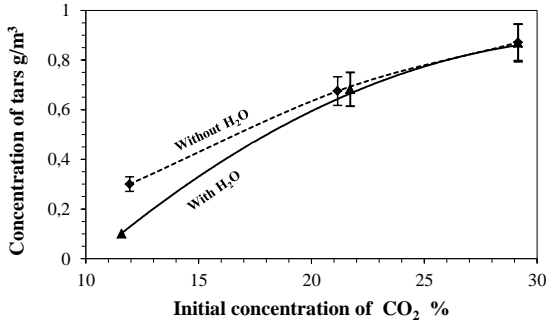


Fig. 18. Effect of the inlet concentration of initial concentration CO₂ on tar destruction over an activated char bed w/ and w/o addition of steam.

2.3. Evaluation of energy efficiency of tar destruction

In order to evaluate the energy efficiency of tar destruction, the energy balance was built for three catalytic processes: steam reforming, dry reforming, and partial oxidation. Comparison of the efficiencies with conventional mechanical cleaning method efficiency was made. Diagram for energy efficiency evaluation showed in Fig. 19. Main parameters of catalytic tar destruction process are selected: temperature 900 °C and space-velocity 0.04 s⁻¹. For evaluation of the mechanical treatment, it was assumed that the tar concentration after the process equals to zero.

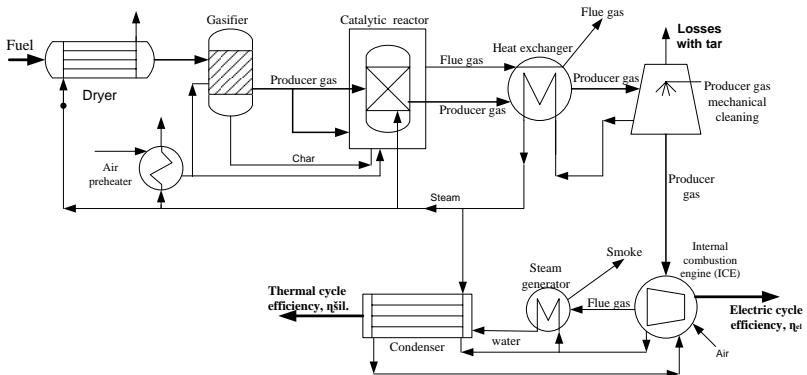


Fig. 19. Principal diagram of integrated gasification cycle

In all four cases, energy balance before the gasification process is the same (Figures 20 and 21). Wood chips with moisture content of 50 % are supplied into drying chamber (dryer) where they are dried to 7 % moisture content. For drying of the fuel, water steam obtained from the technology

process is supplied by heat exchangers or by steam generators in case of shortage.

At the next stage, dried fuel is supplied into the gasifier together with preheated air (200 °C). At the exit of the gasifier, there are two outputs: producer gas and char. Total heat energy of the producer gas amounts up to 88.3% of total fuel balance (504 kW).

In catalytic tar cleaning process case, the obtained gas is supplied to catalytic reactor where 900 °C temperature is maintained by separate combustion of wood charcoal and some part of producer gas. In mechanical cleaning case, the charcoal is additionally gasified into producer gas. The highest heating value of producer gas at the exit of catalyst was in the case of steam reforming, namely 97.3 %. In the cases of dry reforming and partial oxidation this value was 96.6 % and 94.5 %, respectively. In mechanical cleaning case, char gasification produces additional 12.6 % of gases.

Next, gas and smoke are cooled down to 145 °C in the heat exchanger. Gas is further supplied for mechanical cleaning, while flue gas is discharged as waste. For the increase of efficiency, a heat exchanger is designed to produce water steam for its further utilisation in the technology process. The usage includes air preheating, fuel drying and catalytic reactor operation in the cases of steam reforming and dry reforming processes. Excess steam, which is accumulated during the processes of steam reforming, dry reforming and partial oxidation (0.5 %, 2.4 % and 2.9 % respectively), is collected in the condensers.

After passing heat exchanger, the cooled gas is further supplied for mechanical cleaning (scrubber) where final removal of tars from the producer gas takes place. Figures 20 and 21 show tar energy losses in every case, 0% in steam reforming, 0.5 % in dry reforming, 0.2 % in partial oxidation and even 7.7 % energy loss value differs significantly in mechanical cleaning case.

After final gas cleaning, steam reforming process performance was the most efficient (83.8 %). Less effective processes were partial oxidation and dry reforming, 81.5 and 81.4 % respectively (Figures 20 and 21). When comparing overall thermal cycle efficiency values of different catalytic processes, the difference is greater than is caused by tar energy losses only. This is due to reactions of the gaseous products, not only tar destruction efficiency. In the case of partial oxidation, some part of gas was oxidized, which obviously resulted into lower calorific value of the gas. In the case of dry reforming, steam was also supplied into the reactor, but due to high concentration of CO₂, the efficiency of catalysts tended to decrease. In the case of mechanical cleaning only, energy value of the gas was up to 80.1 %. Based on the results, it may be assumed that due to heat energy, which is necessary for tar destruction, the heating value of producer gas increases only by 3.8 % in comparison with steam reforming process.

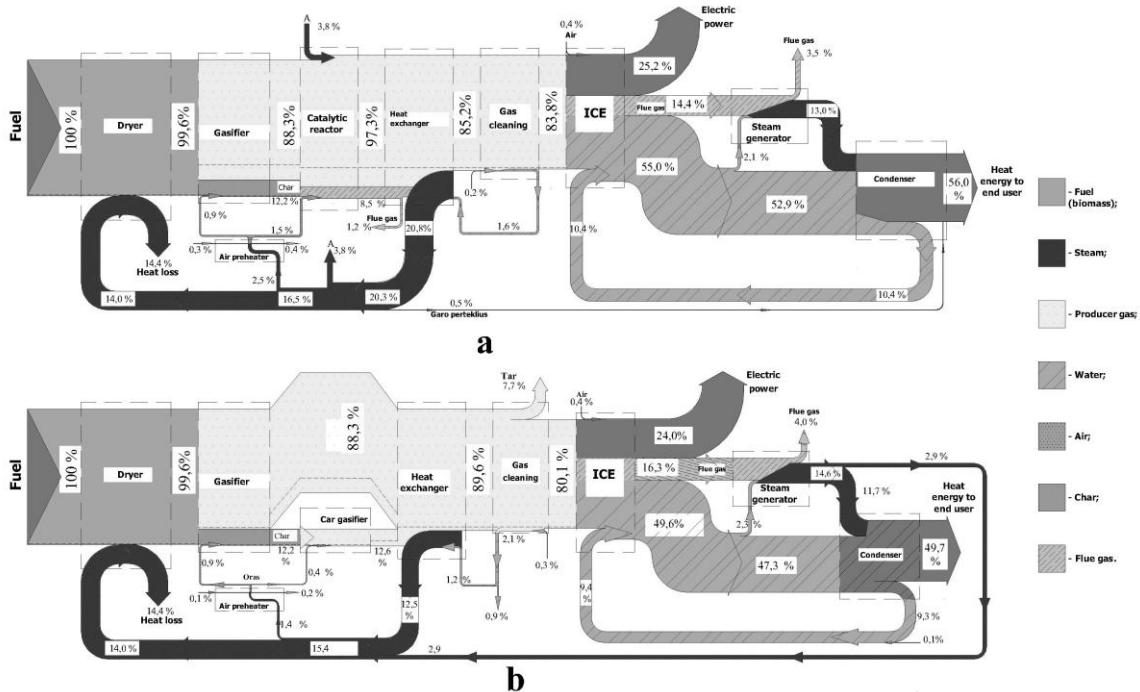


Fig. 20. Energy flow diagram (%): a – catalytic steam reforming; b – mechanical treatment.

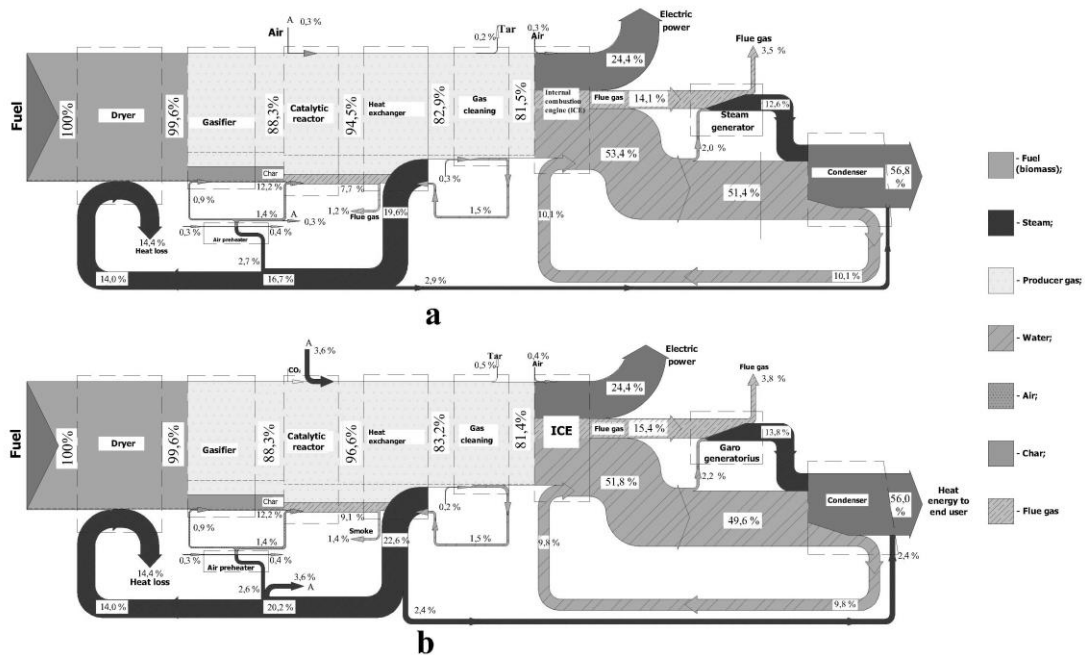


Fig. 21. Energy flow diagram (%): a – partial oxidation; b – dry reforming.

Clean gas is further supplied to internal combustion engine (ICE), loaded by electric power generator. ICE emission products (500 °C) are fed to the steam generator. Steam generator is necessary for several reasons. First, water steam is required for drying of the fuel during start-up of the technology process until heat exchanger reaches operational temperatures; second, in mechanical cleaning case (Fig. 20), additional steam is required since heat exchanger does not produce required amount of water steam. Waste steam and water from internal combustion engine cooling passes to the condenser where production of heat energy to end users takes place.

Comparison of different catalytic reforming processes shows, that most efficient process is water steam reforming with resulting electric power of 25.5 %, while partial oxidation and dry reforming produces 24.4 % each. Comparing the overall energy balance, the same final value calculated for both water steam reforming (25.2 % electric power, 56.0 % heat energy) and partial oxidation (24.4 % electric power, 56.8% heat energy) processes, namely 81.2 %. Calculated performance of dry reforming process was 80.4 % of the total fuel energy (24.4 % electric power, 56.0 % heat energy). The obvious reason for this difference is 0.5 % energy loss due to tar discharge as can be clearly seen from Figure 20.

The results of energy balance calculations presented in Figure 20 show gained 30.2% electric power and 50.5 % heat energy of total fuel balance 504 kW in the case of steam reforming, meanwhile, in the case of mechanical treatment 28.8 % of electric power and 44.9 % of heat energy is produced. Catalytic steam reforming results in higher overall efficiency by 7.0 %. It should be noted that the loss due to tar discharge during mechanical treatment is 7.7 %.

Although part of the producer gas is used for heating of catalyst and for additional heating of gas up to 900 °C, the calorific value of combustible gases (H₂ and CO) increased due to tar destruction. Specifically, if tars collected for discharge during mechanical cleaning are considered as energy loss or waste, the total calorific value of the gas decreases only by 0.7 % of the total fuel balance (504 kW). In mechanical cleaning case, overall energy efficiency decreased by 2.9 % due to additional steam demand of technology process, meanwhile, in catalytic cases, excess water steam was produced.

Summarizing the results, the four processes sorted by energy efficiency are listed (highest first): catalytic steam reforming, partial oxidation, dry reforming and mechanical cleaning.

CONCLUSIONS

Experimental research was performed on thermal destruction efficiency of tars, which are found in producer gas from biomass pyrolysis, by using two types of catalysts: dolomite mined locally in Lithuania and char obtained from gasification of used tires. The findings of the main results are summarized in the following conclusions:

- 1 It was found, that both pyrolytic tire char and Lithuanian dolomite are active as catalysts at thermal destruction of tar-containing compounds, however, tire char catalyst showed better performance on destruction of heavier hydrocarbons ($\geq C_{10}H_8$), and dolomite performed better on lower molecular weight hydrocarbons ($\leq C_6H_6$). The optimum process conditions for both catalysts were $T = 900\text{ }^\circ\text{C}$, $v = 0.04\text{ s}^{-1}$ and $H_2O/C = 1$.
- 2 It was found, that tar destruction efficiency with tire char catalyst at different processes was as follows: steam reforming 99.9 %, partial oxidation 98.6 %, thermal destruction 98.3 %, and dry reforming 96.3 %.
- 3 It was found, that at optimum process conditions using tire char as catalyst, tar destruction efficiency was most influenced by the following factors:
 - ✓ By increasing the amount of steam, tar concentration decreases and the calorific value of the obtained gas increases. At $H_2O/C=1$, tar concentration in input gas 21.12 g/m^3 decreases down to 0.019 g/m^3 value in the output gas;
 - ✓ During partial oxidation most efficient tar destruction takes place at 0.5 air equivalence ratio with efficiency reaching 99.1 %. However, most calorific producer gas is obtained at 0.07 air equivalence ratio with destruction efficiency 98.6 %, since further increase of the air equivalence ratio results in lower concentration of combustible gas;
 - ✓ With the increase of carbon dioxide concentration in input gas, carbon monoxide concentration in output gas increases. This explained by inhibition of hydrocarbon interaction with steam by CO_2 on carbon catalyst surface. Due to this calorific value of the output gas decreases, since H_2 concentration decreases and concentration of the ballast CO_2 increases.
- 4 As theoretical calculations have shown, with tire char catalyst, best energy efficiency in integrated gasification technology is achieved at steam reforming process (81.2 %), and least efficient is mechanical treatment process (73.7 %). Meanwhile, at the partial oxidation and CO_2 reforming, energy efficiency achieved are 81.2 and 80.4% respectively.

REFERENCES

1. BRANDT, P.; E. LARSEN and HENRIKSEN. High Tar Reduction in a Two Stage Gasifier. *Energy & Fuel*, 2000, 14(4), p. 816-819.
2. DABAI, F.; et al. Tar Formation and Destruction in Fixed- Bed Reactor Simulating Downdraft Gasification: Equipment Development and Characterization of Tar-Cracking Products. *Energy & Fuels*, 2010, 24 (8), p. 4560-4570.
3. DELGADO, J., and M.P. AZNAR. Biomass Gasification with Steam in Fluidized Bed: Effectiveness of CaO, MgO, and CaO-MgO for Hot Raw Gas Cleaning. *Industrial & Engineering Chemistry Product Research and Development*, 1997, 36 (5), p. 1535-1543.
4. DEVI, L., et al. Catalytic Decomposition of Biomass Tars: Use of Dolomite and Untreated Olivine. *Renewable Energy*, 2005, 30 (4), p. 565–587.
5. DOGRU, M. Experimental Results of Olive Pits Gasification in a Fixed Bed Downdraft Gasifier. *International Journal of Green Energy*, 2013, 10 (4), p. 348-361.
6. EL-RUB, Z.A., et al. Experimental Comparison of Biomass Chars with other Catalysts for Tar Reduction. *Fuel*, 2008, 87 (10-11), p. 2243–2252.
7. GILBERT, P.; C. RYU; V. SHARIFI and J. SWITHEBANK. Tar Reduction in Pyrolysis Vapours from Biomass over a Hot Char Bed. *Bioresource Technology*, 2009, 100 (23), p. 6045-6051.
8. GUSTA, E., et al. Catalytic Decomposition of Biomass Tars with Dolomites. *Energy Fuels*, 2009, 23 (4), p. 2264–2272
9. HAGHIGHI, M., et al. On the Reaction Mechanism of CO₂ Reforming of Methane over a Bed of Coal Char. *Proceedings of the Combustion Institute*, 2007, 31 (2), p. 1983–1990.
10. HOSOKAI, S.; et al. Mechanism of decomposition of aromatics over charcoal and necessary condition for maintaining its activity. *Fuel*, 2008, 87 (13-14), p. 2914–2922.
11. KUHN, J.N., et al. Olivine catalysts for methane- and tar-steam reforming. *Applied Catalysis B: Environmental*, 2008, 81 (1-2), p. 14–26.
12. LAMMERS, G.; A.A.C.M. BEENACKERS and J. CORELLA. Catalytic Tar Removal from Biomass Producer Gas with Secondary Air. In *Developments in Thermochemical Biomass Conversion*, Vol. 2. Edited by A.V. Bridgwater and D.G.B. Boocock. London: Blackie Academic & Professional, 1997, p. 1179–1193.
13. MUN, T.Y.; B.S. KANG and J.S. KIM. Production of a Producer Gas with High Heating Values and Less Tar from Dried Sewage Sludge through Air Gasification Using a Two-Stage Gasifier and Activated Carbon. *Energy and Fuels*, 2009, 23 (6), p. 3268–3276.
14. MUN, T.Y.; P.G. SEON and J.S. KIM. Production of a Producer Gas from Woody Waste via Air Gasification using Activated Carbon and Two- Stage Gasifier and Characterization of Tar. *Fuel*, 2010, 89 (11), p. 3226-3234.
15. OLIVARES, A., et al. Biomass Gasification: Produced Gas Upgrading by In-Bed Use of Dolomite. *Industrial & Engineering Chemistry Product Research and Development*, 1997, 36 (11), p. 5220-5226.
16. ORIO, A.; J. CORELLA, and I. NARVAEZ. Performance of Different Dolomites on Hot Raw Gas Cleaning from Biomass Gasification with Air. *Industrial & Engineering Chemistry Product Research and Development*, 1997, 36 (9), p. 3800–3808.
17. SU Y., et al. Experimental and Numerical Investigation of Tar Destruction Under Partial Oxidation Environment. *Fuel Processing Technology*, 2011, 92 (8), p. 1513–1524.
18. WANG, T.; J. CHANG and L. PENGMEI. Novel Catalyst for Cracking of Biomass Tar. *Energy & Fuels*, 2005, 19 (1), p. 22-27.
19. ZHANG, Y., et al. Tar Destruction and Coke Formation During Rapid Pyrolysis and Gasification of Biomass in a Drop-tube Furnace. *Fuel*, 2010, 89(2), p. 302–309.

PUBLICATIONS RELATED TO THE DISSERTATION

Articles in journals from Thomson Reuters “Web of Knowledge” list

1. STRIŪGAS, N.; ZAKARAUSKAS, K.; DŽIUGYS, A.; GRIGAITENĖ, V. Experimental modelling of tar destruction with addition of CO₂ for application in the biomass gasification system. *Applied thermal engineering*. ISSN 1359-4311. 2013. Vol. 61, Iss. 2 p. 213-219.
2. STRIŪGAS, N.; ZAKARAUSKAS, K.; STRAVINSKAS, G.; GRIGAITIENĖ, V. Comparison of steam reforming and partial oxidation of biomass pyrolysis tars over activated carbon derived from waste tire. *Catalysis today*. ISSN 0920-5861. 2012. Vol. 196, Iss. 1, p. 67-74.

Publications at the international conferences

1. ZAKARAUSKAS, K.; STRIŪGAS, N.; STRAVINSKAS, G. Comparison of steam reforming and partial oxidation of biomass gasification tars over waste tire char. *International conference on materials and technologies for green chemistry 2011*, Tallinn, Estonia, September 5-9, 2011. P. 152.
2. STRIŪGAS, N.; ZAKARAUSKAS, K.; STRAVINSKAS, G. Experimental comparison of performance of Lithuanian dolomite and waste tires char for steam reforming of real tars from biomass gasification. *19th European biomass conference and exhibition*, Berlin, Germany, June 6-10, 2011. Germany, 2011, p. 1582-1588.
3. ZAKARAUSKAS, K.; STRIŪGAS, N.; STRAVINSKAS, G. Thermal decomposition of biomass and analysis of resin destruction. *8th international conference of young scientists on energy issues CYSENI 2011*, Kaunas, Lithuania, May 26-27, 2011. Kaunas: LEI, 2011. ISSN 1822-7554, p. 98-103.
4. ZAKARAUSKAS, K.; STRIŪGAS, N.; STRAVINSKAS, G. Investigation of thermal cracking of syngas tar from biomass gasification by catalytic steam reforming. *9th annual conference of young scientists on energy issues CYSENI 2012: international conference*, Kaunas, Lithuania, 24-25 May 2012. Kaunas: LEI, 2012. ISSN 1822-7554, p. 96-101.
5. STRIŪGAS, N.; ZAKARAUSKAS, K.; STRAVINSKAS, G. Experimental investigation of the upgrading of producer gas with CO₂ over a bed of activated charcoal made from waste tire. *21st European biomass conference and exhibition, setting the course for a biobased economy: proceedings of the international conference*, Copenhagen, Denmark, June 3-7, 2013. Denmark, 2013. ISBN 978-88-89407-530, p. 795-799.

Papers in the national Conferences

1. ZAKARAUSKAS, K.; STRIŪGAS, N.; STRAVINSKAS, G. Biomassės pirolizės metu susidarantių dervų analizė ir jų mažinimo būdai. *Šilumos energetika ir technologijos-2011: konferencijos pranešimų medžiaga*, Kauno technologijos universitetas, 2011 vasario 3,4. Kaunas: Technologija, 2011. ISBN 978-609-02-0179-4, p. 71-76

Information about the Author of the Dissertation

Kęstutis Zakarauskas was born on 03 12 1983 in Kaunas, Lithuania. Contact information: tel. (370) 37 401830, e-mail: kestutis.zakarauskas@lei.lt.

2003 – 2007 bachelor studies at Kaunas University of Technology, Faculty of Mechanical Engineering; Bachelor of Science in Thermal Engineering.

2007 – 2009 master studies at Kaunas University of Technology, Faculty of Mechanical Engineering; Master of Science in Thermal Engineering.

2010 – 2014 doctoral studies at Lithuanian Energy Institute, Laboratory of Combustion Processes.

10.2007 – 07.2010 Engineer at Lithuanian Energy Institute, Laboratory of Combustion Processes.

07.2010 – present Junior Research Associate at Lithuanian Energy Institute, Laboratory of Combustion Processes.

Padėka

Disertacijos darbo autorius dėkoja moksliniam vadovui dr. Algiui Džiugiuui ir Lietuvos energetikos instituto, Degimo procesų laboratorijos vadovui dr. Nerijui Striūgui ir visiems laboratorijos kolegoms už naudingus patarimus ir paramą, disertacijos rengimo metu.

Reziumė

Pagrindinis šio darbo tikslas katalitinio dervų pašalinimo tyrimas, siekiant įvertinti dviejų pasirinktų katalizatorių Lietuvoje randamo dolomito ir naudotų padangų pirolizės metu gaunamos anglies efektyvumą aukštoje temperatūroje skaidyti dervas sudarančius angliavandenilius ir nustatyti optimalias darbinės sąlygas, kurių pagrindu būtų galima sukurti naujas funkcinės medžiagas ir technologinius sprendimus. Darbe pateikiamas dviejų pagrindinių dervas sudarančių junginių, benzeno ir naftaleno, katalitinio terminio skaidymo vandens garų tyrimų bei biomasės terminio skaidymo ir katalitinio dervų pašalinimo tyrimų rezultatai. Sukurtas laboratorinis įrenginys, paruošti ir ištirti aukščiau minėti katalizatoriai ir jų savybės, ištirta biomasės dujinimo dujose esančių dervų sudėtis, jų skilimas skirtingose 700, 800, 900 °C reakcijos temperatūrose naudojant keturis skirtingus terminius procesus (katalitinis terminis skaidymas, garų reformingas, dalinė oksidacija, anglies dioksido reformingas), ištirta likutinių dervų bei gautų dujų sudėtis už katalizatoriaus. Nustatyta, kad aktyvintos anglies katalizatorius yra efektyvesnis dervų destrukcijai ir prie reakcijos temperatūros 900 °C, tinkamai parinkto anglinio katalizatoriaus kiekiu ($v=0.04 \text{ s}^{-1}$) ir reakcijai tiekiant vandens garo santykiu $\text{H}_2\text{O}/\text{C}=1$ pasiekiamas pilnas generatorinėse dujose esančių dervų suskaidymas. Gautų tyrimų rezultatai palyginami su kitų autorių rezultatais gautais dervų destrukcijai naudojant įvairiose pasaulio šalyse randamo dolomito bei biomasės pirolizės metu gautą anglį.

UDK 628.475+662.715.3](043.3)

SL 344. 2015-05-06. 2,25 leidyb. apsk. 1. Tiražas 70 egz. Užsakymas 158.

Išleido leidykla „Technologija“, Studentų g. 54, 51424 Kaunas

Spausdino leidyklos „Technologija“ spaustuvė, Studentų g. 54, 51424 Kaunas