ENVIRONMENTAL ENGINEERING
The 8th International Conference
May 19–20, 2011, Vilnius, Lithuania
Selected papers

ISSN 2029-7106 print / ISSN 2029-7092 online
ISBN 978-9955-28-826-8 (1 Volume)
ISBN 978-9955-28-827-5 (3 Volumes)
http://enviro.vgtu.lt

COMPARISON OF STEAM REFORMING OF BIOMASS GASIFICATION TARS OVER LITHUANIAN DOLOMITE AND WASTE TIRES CHAR

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Abstract. Gasification of biomass and different types of waste now is considered as one of most perspective ways for production of heat and electricity. It is necessary to clean the synthesis gas from tar and soot particles in order to use it in turbines and micro turbines, internal combustion engines for electricity production, chemical reactors for synthetic fuel or chemicals production.

The main objective of this work is investigation of catalytic tar destruction in order to evaluate two selected catalysts, namely dolomite, available in Lithuanian as natural resource, and char derived from pyrolysis of used tires. The efficiency of these catalysts were investigated as an ability to decompose tar hydrocarbons at high temperatures and optimal process conditions were determined, which are base starting point for developing new functional material and technological solutions.

Results of catalytic steam reforming of two main tar compounds from biomass gasification – benzene and naphthalene – are presented in this article. Tar destruction was performed in fixed bed reactor changing temperature from 700°C to 900°C with constant steam volume. It was determined that thermal destruction of benzene is most intensive using dolomite as a catalyst, and destruction of naphthalene – using activated carbon at 900°C. At those conditions benzene concentration in resulting gases decreased from 47.00±3.59 down to 3.80±0.28 g/m^3, naphthalene – from 14.40±0.95 down to 0.027±0.003g/m^3. Results of the research were compared with result of other authors who used dolomite from various countries of origin and char from biomass pyrolysis for tar destruction.

Keywords: biomass gasification, tars, benzene, naphthalene, dolomite, char, tire.

1. Introduction

Nowadays gasification of biomass and different kind of waste is considered as one of most promising ways for heat and electric energy production. Comparing with direct combustion of biofuel, gasification process is more beneficial and environmentally friendly, gasification products contain less greenhouse gases CO_2 and hazardous NOx, SOx and VOC‘s. The resulting syngas may be used as a fuel for internal combustion engines, gas turbines, hydrogen production industry, and synthetic diesel production. The biggest obstacle for development of gasification process is tar and particulates (mostly soot and volatile metals) in the syngas, which tend to deposit on surfaces of turbine blades, moving parts of internal combustion engines or hydrogen separation membranes, condensates, burns-in and other ways influences long-term exploitation of the equipment. At present the syngas is cleaned by physical methods: particulates are captured with electrostatic precipitators, tar is condensed with scrubbers. These cleaning methods are quite effective but not cost-effective – part of calorific material is being captured, also, from environmental point of view, waste water is polluted with tar, chlorine and other hazardous substances (Devi *et al.* 2003). In order to achieve better gasification process new tar removal methods are researched. One of the alternative methods is thermal catalytic tar cracking, when tar hydrocarbons are additionally gasified to final reaction products CO and H_2.

Catalytic tar cracking is not a new technology and has been extensively investigated. Initial causes of tar formation, temperature, pressure, mediums, catalyst, additives, reaction time and gasification process selection influence were determined and widely investigated. It is known many chemical species of tar composition, properties and influence on destruction depending on temperature (Milne *et al.* 1998; Li and Suzuki 2009).

Varieties of catalyst metals (Ni, V, Cr, Mn, Co, Fe, Cu, Mo, Al) were investigated, but further use is complicated due to fouling or utilization problems of deactivated catalysts (Dayton 2002; Devi *et al.* 2003; Abu El-Rub *et al.* 2004; Xu *et al.* 2010). For thermal tar cracking relatively cheap natural catalysts (calcined dolomite and magnesite, natural zeolites, olivines, etc.) are widely used. Properties of these materials are strongly dependent on their age and origin. There's also plenty of dolomite in Lithuania. This carbonate rock is located in North of Lithuania, layers of devonian system. Different scientists in their research mostly investigated dolomite containing 20-30 % MgO, and depending on process conditions up to 100 % tar destruction achieved (see chapter 3. Results and discussion). Literature on Lithuanian dolomite use for gasification process was not found; therefore it would be useful to do research on use of cheap and promising catalyst.

Recently, tars cracking with charcoal derived from various biomass pyrolysis are widely studied and results are very similar to those obtained from tar cracking using dolomite as a catalyst. Charcoal obtained from biomass pyrolysis is mostly used in scientist research (Brandt *et al.* 2000; Abu El-Rub *et al.* 2008; Hosokai *et al.* 2008; Gilbert *et al.* 2009; Mun *et al.* 2010; Dabai *et al.* 2010).

Research group at Lithuanian energy institute (LEI) developed fast gasification reactor for used tires, which allows to achieve high gasification rate. Used tire is thermally decomposed into three main materials: volatile gases, carbonaceous residue (char) and wires. Hot synthetic gases are combusted in local combustion devices for heat energy production, and the residual carbon may be used not only as a fuel, but also for proposed thermal catalytic tar cracking.

The main objective of this work is investigation of catalytic tar destruction in order to evaluate two selected catalysts, namely dolomite, available in Lithuanian as natural resource, and char derived from pyrolysis of used tires. The efficiency of these catalysts were investigated as an ability to decompose tar hydrocarbons (benzene and naphthalene) at high temperatures and optimal process conditions were determined, which are base starting point for developing new functional material and technological solutions.

2. Experimental methodology

2.1. Preparation of catalysts

Lithuanian dolomite. For experimental investigations dolomite from Petrasiunai 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 chamber made from stainless steel and further to the thermoregulated furnace. The calcination of dolomite was carried out at the temperature of 850°C for 1 h with constant steam flow. To avoid adsorption of gas and humidity from atmosphere, calcined dolomite was kept in a closed vessel. For characterization of calcined dolomite, bulk density measurements were performed. It was observed, that the bulk density of calcined dolomite decreased about 45 % from 1.415 g/cm^3 to 0.777 g/cm^3, but granulometric composition remains unchanged. From this decreasing of weight of calcined dolomite can be stated, that bigger specific surface area and micropore structure was formed.

Waste tire char. Cut into pieces waste tire were gasified in the muffle furnace at 850 °C. After about 10 min from tires releases all volatiles material and porous coal structure are formed. From a formed char steel cords were removed, milled and sieved to a particle size range of 2.2-1.1 mm. Obtained char fraction placed to heating chamber for activation under steam atmosphere at temperature of 850 °C. Activation of coal was similarly to the calcination of dolomite and took about 2 h. After activation process produced coal was weighted and a bulk density was measured. In this case was determined that bulk density after activation decreased from 0,261 g/cm^3 to 0,187 g/cm^3, i.e. 28,4 wt.%. The same conclusion as in the case of dolomite can be done, because larger active surface area and porous structure has been formed.

2.2. Experimental setup and procedure

Taking into account the techniques presented in references (Orio *et al.* 1997; Devi *et al.* 2005; Abu El-Rub *et al.* 2008; 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 (99.6 % purity, obtained from SC „Achema“) 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 (98 %, „SigmaAldrich“) or benzene (99.7 %, „SigmaAldrich“) 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 are 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 (700–900 °C) 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 sampling system consists of six gas washing bottles filled with the solvent – isopropanol (99.5 %, „SigmaAldrich“), placed into two baths 7, 8 with different temperatures. The first condenser contains 150 ml of isopropanol, the next several – 100 ml each, and the last one is left empty. Before the gas flow enters the glass condensers, a solvent is injected for primary condensation that is circulated in a closed loop by means of a peristaltic pump (Fig 1).

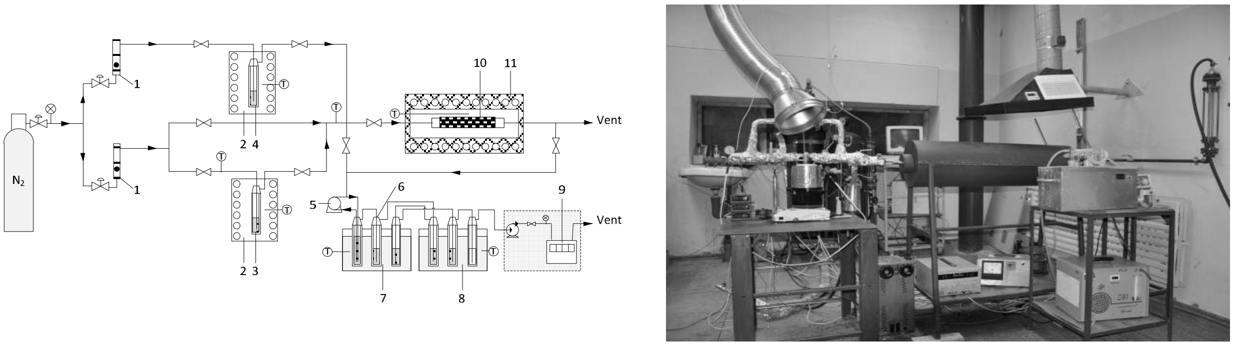

Fig 1. Scheme and photo of the experimental rig: 1 – rotameter; 2 – heater; 3 – water evaporator; 4 – model tar evaporator; 5 – peristaltic pump; 6 – gas washing bottles; 7 – heated bath; 8 – cooled bath; 9 – gas flowmeter; 10 – catalytic bed; 11 – reactor

Gas is washed in the first five bottles at different temperatures: the 1st bottle (+40°C) → 2 - (+40°C) → 3 - (-18°C) → 4 - (+40°C) → 5 - (-18°C). The sixth bottle with the temperature of - 18°C collects the remaining drops of tars and solvent carried away by the gas flow after flushing. The amount of gas flow that travels during the experiment is integrated by the gas flowmeter 9. The obtained samples are weighted and analyzed by means of gas chromatography. During analysis of each sample, the amount of extraction solvent of 1 µl is injected into the injector of the gas chromatograph. The analysis of samples was performed using Varian GC-3800 gas chromatograph equipped with flame ionization detector. For chromatographic separation of compounds general purpose Restek RXI-5ms column (60 meters long, 0.25 mm internal diameter, 0.25 µm 5%-phenol-methylpolysiloxane) was used. Other analytical conditions: injector temperature 275°C, split ratio with carrier gas 1:75, column temperature programmed from 50°C (5 min hold time) up to 325°C (at 8°C/min rate), 325°C (30 min hold time), carrier gas (helium) flow rate 1.2 ml/min and is kept constant during the chromatogram run. Several chromatograms of the same sample were performed in order to minimize method errors. Tolerable repeats of the chromatograms from the same samples were received.

For identification of polycyclic aromatic compounds (benzene and naphthalene) calibration with pure compounds specially prepared with different concentrations was performed. Compounds were identified by specific retention time of the compounds identified during calibration runs. For processing of chromatographic data Varian Workstation v6.9.1 software was used.

2.3. Experimental error

All input parameters in experimental investigations were measured at least five times. Analysis of measurements uncertainties involving all sources of uncertainty were calculated with a help of GUM Workbench (LEI license) software for analysis and calculations of uncertainty in measurement. After post processing of obtained results estimated the relative uncertainty with a level of confidence of approximately 95 % for benzene and naphthalene concentration were less than 10 %.

3. Results and discussion

3.1. Benzene destruction

Lithuanian dolomite. During analysis of benzene destruction, two types of experiments as a catalyst using Lithuanian dolomite and activated carbon derived from pyrolysis of used tires were performed. The activity of catalyst for treatment of benzene was investigated at three temperatures 700, 800 and 900°C. At the beginning of experiments the constant concentration of benzene (47.00±3.59 g/m^3) in a nitrogen flow was determined.

The concentration of benzene after treatment in catalytic bed at various temperatures and at constant steam to carbon ratio ($H_2O/C=1$) is presented in Fig 2. From given results can be seen, that with increasing of the temperature destruction of benzene increases and the concentration of model tar at the temperature of 900°C remains only 3.80±0.28 g/m^3. Trying to compare obtained results with data published in scientific papers, the conversion of benzene was defined as

$$X=100(C_1-C_2)/C_1 \qquad (1)$$

where C_1 and C_2 – the inlet and outlet concentrations of benzene in nitrogen flow, g/m^3.

Obtained results in dependence of the temperature graphically represented in Fig 3. As shown in this figure, benzene conversion at the temperature of 700 °C was 60.4 % and at 900 °C – 90.6 %. Analysis of literature shows, that the first time and very detail experiments of catalytic benzene destruction over Finnish dolomite were performed in study (Simell *et al.* 1997; Simell *et al.* 1999). However obtained experimental results were described by a Langmuir-Hinshelwood type kinetic equation and to interpret these results and calculate effectiveness of benzene conversion, is needed to perform series of calculations or computer modeling works. Other researchers tested effectiveness of dolomites mined in various countries with different model tar compounds (naphthalene, n-heptane) or with real tars obtained from gasify cation of different materials. According to (Simell *et al.* 1995), typically, in biomass gasification at the temperature range of 850 – 950 °C, the major tar component is benzene, representing about 50 – 60 wt.%. Hereby, our experimental data can be compared with those studies in which real tar destruction over dolomite catalyst was tested, Fig 3.

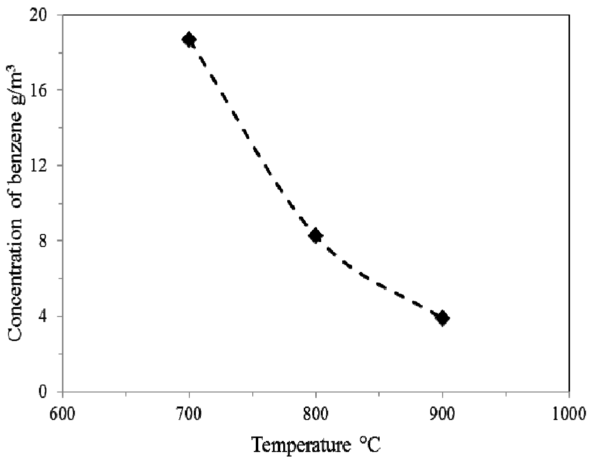

Fig 2. Concentration of benzene after treatment over calcined Lithuanian dolomite

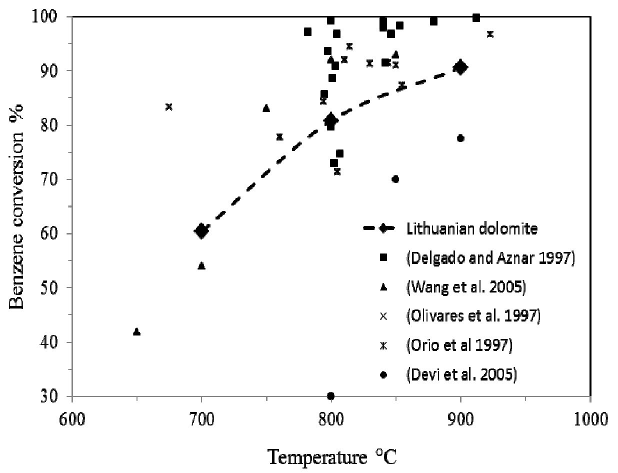

Fig 3. Comparison of benzene conversion over Lithuanian dolomite bed with data obtained in literature

The highest conversion rate of benzene over dolomite catalysts was found in study (Delgado and Aznar 1997) (in Fig 3. results pointed with marker,„■“). Dolomite used in this work originated from Cantabria region in Spain. Authors determined that at the temperature of 800 °C tars conversion can be got up to 99.3 %. As seen from the figure at this temperature concentration of benzene obtained in our experiments was 80.8 %. This difference could arise because different dolomite fraction was used: (Delgado and Aznar 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 mm was used, but exact distribution of particles within this diameter range was unknown. In (Delgado and Aznar 1997) study, the largest particle size used was 3.3 mm. At this point the tar conversion was only 73 %. After interpolation of results received in our experiments we can see that obtained benzene conversion is very similar to those like in work of (Delgado and Aznar 1997).

Wang *et al.* (2005) in their study used natural dolomite from a Chinese mines. Tar conversion as a function of temperature achieved from 45 to 93 %, (Fig 3. „▲“). (Olivares *et al.* 1997) („×“) and (Orio *et al.* 1997) („ж“) studied activity of dolomite mined from Spanish region for destruction of biomass gasification tars. In these studies obtained results are also similar to ours and to other works. Rather, smaller conversion of tars received in study of (Devi *et al.* 2005) („•“) and according to authors, the decrease of tar conversion arises from sand who was additionally added to the bed of catalyst.

From obtained experimental results established that correctly prepared Lithuanian dolomite can be used for a thermal catalytic treatment of benzene and tars present in the producer gas from biomass and waste gasification. The calcined Lithuanian dolomite in experimental condition was tested about 12 hours. After each sample preparation, which took about one hour, dolomite was regenerated passing steam through the catalytic bed. In order to test contamination and the crystallographic structure of dolomite, the X-ray diffraction analysis in diffractometer “BRUKER D8 Advance” of new and used dolomites was performed, Fig 4. From the X-ray diffraction pattern can be seen, that crystallographic structure of calcined dolomite was unchanged and the signal intensity of main components CaO and MgO remains similar as in the beginning of work, but after multiple regeneration with steam dolomite was fully calcined: the peaks not characteristic for calcium and magnesium oxide disappeared.

Waste tire char. The following experiments have been performed using residual char from the waste tire pyrolysis as a catalyst. The initial conditions and the amount of catalyst remained the same as in the case of thermal destruction with dolomite. The changes of benzene concentration in gas after passing through the activated char bed depending on the temperature and at the constant ratio of steam to carbon in the gas ($H_2O/C=1$) are shown in Fig 5. As seen from the presented results, thermal destruction of benzene increases as the temperature grows, and concentration decreases to 5.50±0.42 g/m^3.

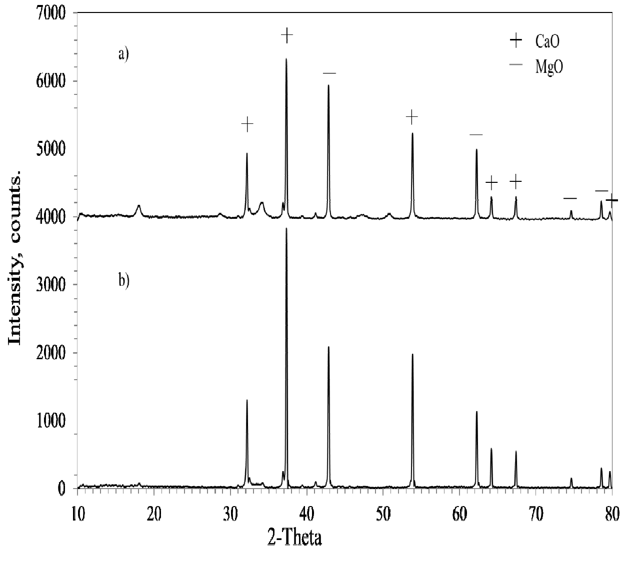

Fig 4. X-ray diffraction pattern for calcined dolomite: a – before experiments; b – after experiments

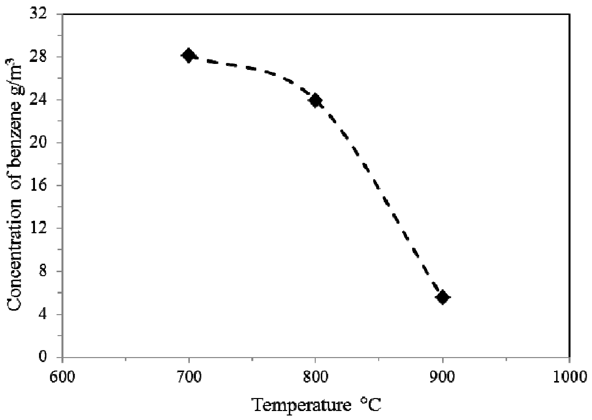

Fig 5. Concentration of benzene after treatment over waste tire char

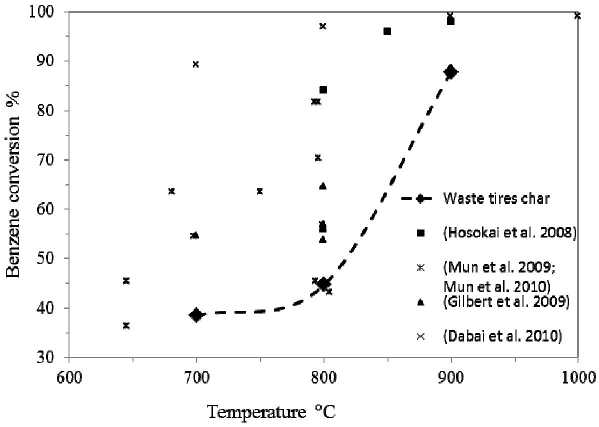

Fig 6. Comparison of benzene conversion over waste tire char with data obtained in literature

In contrast to the case with dolomite, the effect of waste tire char is exhibited only at higher temperatures at around 900°C and its activity in thermal destruction of benzene is not inferior to that of the dolomite case.

The activated char produced from biomass pyrolysis, due to its especially porous textured structure, is also used rather widely for research of tar destruction (Devi *et al.* 2003; Abu El-Rub *et al.* 2004; Xu *et al.* 2010). For comparison of the results obtained by us with those published in the scientific publications, we can plot the values of benzene conversion versus the temperature (Fig 6). As seen from the figure, the benzene conversion ratio determined in our experiments was only 38.5% at the temperature of 700°C and even twice as high at 900°C – 87.8%. For comparison of the results, a number of results from other authors were analyzed that are summarized and presented graphically (Fig 6). As in the case of dolomite, destruction of pure benzene in layers of activated char is scarcely researched. The only reference that we have found was the results by (Hosokai *et al.* 2008), Fig 6 („■“). The author analyzed the activity of activated carbon produced by commercial biomass gasification for benzene destruction: a high conversion rate of 98% was identified at 900°C and a smaller rate of 84% at 800°C. The author mentions that completeness of conversion is highly dependent upon the size of char micropores. The bulk density of activated char used in (Hosokai *et al.* 2008) was 0.095 g/cm^3, whereas in our experiments, the bulk density of activated char from waste tires was twice as high, 0.187 g/cm^3, and the granulometric composition was the same. It is possibly due to this difference that our results were somewhat lower. For optimizing the operation, this difference should be preferably compensated for by using a longer char bed thereby increasing the total surface area of the catalyst.

Mun *et al.* (2009; 2010) analyzed in their works destruction of benzene contained in the syngas from gasification of wood waste and dried sewage sludge in a layer of commercial activated char (Fig 6, „⨯ “). As seen from the results presented by the author, the resulting benzene conversion is very different: a higher conversion rate was identified in case of higher temperatures, and a lower one in case of lower temperatures, therefore, the results of this author and our results can be compared as similar to each other.

Gilbert *et al.* (2009) researched conversion of real tar from biomass gasification in a layer of char produced from wood pyrolysis (Fig 6, „▲“). The conversion rate determined at 700–800 °C remains stable at about 55 %, 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 6. „×“) confirm this effect as well. He noticed that increase of the temperature to 1000°C does not result in additional effect of tar destruction and the residual concentration in gas remains the same as that at the temperature of 900°C. Therefore, based on observations of this author, further experiments with increased temperature are not necessary.

3.2. Naphthalene destruction

Naphthalene is the second most abundant component in the tar; therefore, research of thermal destruction of this hydrocarbon is as important as that of benzene. In order to assess efficiency of thermal destruction of naphthalene, two types of experiments were performed, using different catalysts of dolomite and char from the tire pyrolysis. Effect of each catalyst on naphthalene destruction was examined at three different reactor temperatures (700, 800 and 900°C). Before commencing experiments of catalytic naphthalene destruction, its constant concentration in nitrogen was determined, which amounted to 14.40±0.95 g/m^3.The changes of naphthalene concentration in gas after passing through the dolomite catalyst bed depending on the temperature and at the constant ratio of steam/carbon content in the gas ($H_2O/C=1$) are shown in Fig 7. As seen from the presented results, similarly to the case of benzene, increasing the temperature leads to more intense thermal destruction of naphthalene but the concentration decreases to 0,034±0.003 g/m^3.

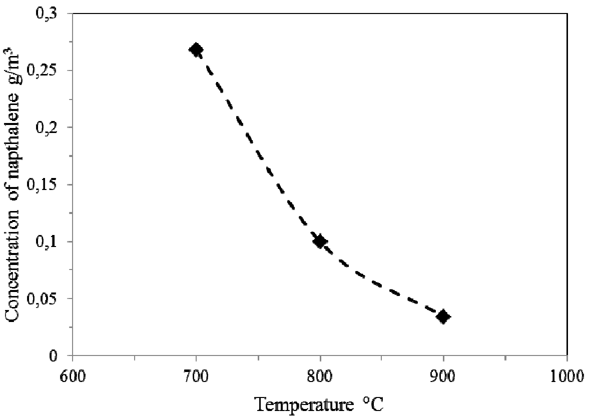

Fig 7. Concentration of naphthalene after treatment over Lithuanian dolomite

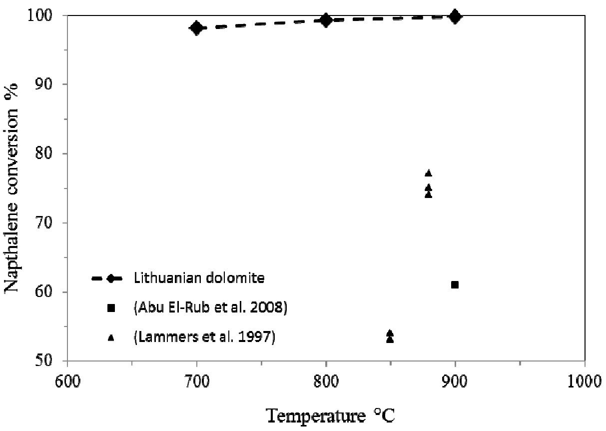

Fig 8. Comparison of naphthalene conversion over Lithuanian dolomite with data obtained in literature

It is seen from the performed experiments that naphthalene is not so stable at high temperatures as in the case with benzene. From another point of view, the initial concentration of naphthalene in nitrogen flow was smaller than with benzene and the catalyst was less loaded.

In order to compare the obtained results with the works by other authors, as in the case of benzene, the resulting concentrations are recalculated into the naphthalene conversion, Fig 8. 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, using calcined dolomite. As seen, results obtained in this work are quite different from those obtained by other authors. The difference could arise because of higher initial concentration of naphthalene used in those works.

Experimental tests using residual char from waste tire pyrolysis shows that the lowest naphthalene concentration in gas was 0.027±0.003 g/m^3 at the reaction temperature of 900°C, Fig 9. It was observed that in case of activated char, even though insignificantly, about 16%, destruction of naphthalene is still more intense compared to the case of using dolomite. This trend is confirmed by the data of other authors, Fig 10. As seen from the data presented in the figure, naphthalene conversion is rather more intense in case when the catalytic layer of char is used than in the case of dolomite catalyst. (Abu El-Rub *et al.* 2008) („■“) analyzed utilization of char produced in the gasification of commercial biomass for thermal destruction of naphthalene and other components of tar. The utilized char fraction was finer than that used in our work and was from 1.4 to 1.7 mm. The attained naphthalene conversion was up to 99.6% at 900°C and 99.9% at 1000°C. In ref. (Hosokai *et al.* 2008) („▲“), at all the researched temperature values from 800 to 900°C, the measured naphthalene conversion ratio was >99.99%. A similar result was obtained by (Brandt *et al.* 2010) („×“), but the naphthalene destruction temperature reported there was higher and was as high as 1100 °C. Drawing the conclusions from the naphthalene conversion research, it can be stated that the activated char produced in presented work is also efficient for tar destruction. During research of naphthalene destruction over char bed one undesirable process emerges: at temperature of 900 °C coal undergoes intensive gasification and large amount of small coal particles (maybe produced soot) were bloated by flow of nitrogen to tars condenser.

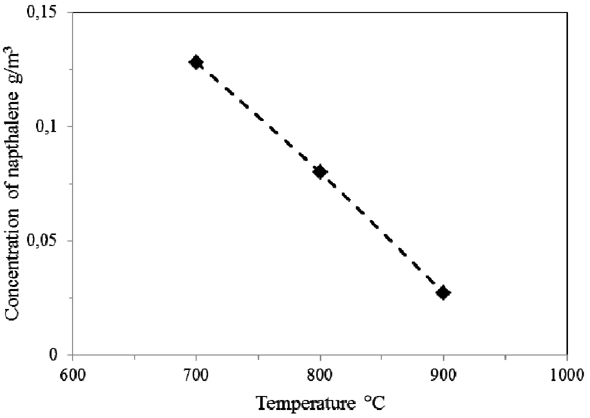

Fig 9. Concentration of naphthalene after treatment waste tire char

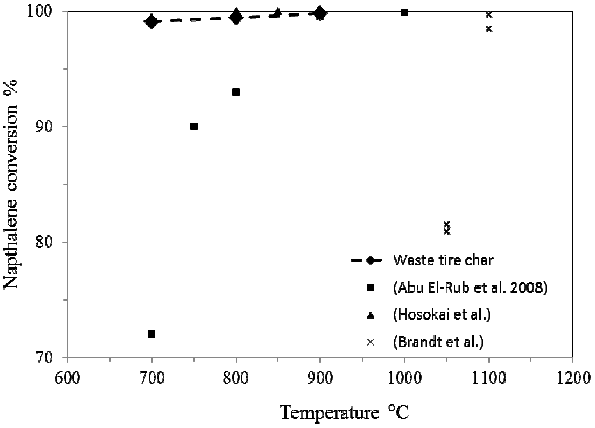

Fig 10. Comparison of naphthalene conversion over waste tire char with data obtained in literature

4. Conclusions

1. During research of thermal catalytic destruction of biomass tar elements removal compatibility the following conclusions were determined: research of catalytic thermal destruction of benzene and naphthalene at three different temperatures (700, 800 and 900°C) and constant steam to carbon ($H_2O/C=1$) ratio was carried out. It was found that thermal destruction of benzene is most intensive using dolomite as a catalyst, and destruction of naphthalene – using activated carbon at 900°C. At those conditions benzene concentration in resulting gases decreased from 47.00 ± 3.59 down to 3.80 ± 0.28 g/m^3, naphthalene – from 14.40 ± 0.95 down to 0.027 ± 0.003g/m^3.
2. Comparing activity of tar hydrocarbon destruction of calcined dolomite, which is naturally found in Lithuania, and carbon from used tire pyrolysis, it is obvious that these two materials are active in tar destruction process. Additionally it is found that dolomite is more active in destruction process of lighter hydrocarbons (C_6H_6), while carbon showed better performance in destructing heavier ones ($C_{10}H_8$).
3. Comparing results obtained in presented work and works of other authors it should be noted that Lithuanian dolomite and carbon obtained from tire pyrolysis are also suitable material as catalyst in thermal tar destruction process.

Acknowledgments

This research was funded by grant (No. MIP-112/2010) from the Research Council of Lithuania.

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