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THE INFLUENCE OF FEEDSTOCK TYPE AND OPERATING PARAMETERS ON TAR FORMATION IN THE PROCESS OF GASIFICATION AND CO-GASIFICATION

WPLYW RODZAJU PALIWA STAŁEGO I PARAMETRÓW EKSPLOATACYJNYCH NA PRODUKCJĘ SUBSTANCJI SMOLISTYCH W PROCESIE ZGAZOWANIA I WSPÓŁZGAZOWANIA

Abstract: Increasing energy demand, limited resources of fossil fuels and environmental aspects are the main rationales of the research efforts aiming at wider utilization of renewable resources and waste in energy generation systems. Gasification technologies are based on thermochemical processing of solid, liquid and gaseous fuels to gas of the composition dependent on kind of gasification agent and operating parameters used. The range of applications of the product gas includes basically chemical and petrochemical industries. Its utilization in power generation systems is also of industrial interest since the environmental impact of gasification technologies is lower and the process efficiency is higher than of coal-fired power plants and it enables to utilize wide range of fuels, including fossil fuels, biomass, industrial waste and various fuel blends. One of the most important operational issues related with thermochemical processing of biomass and waste is the formation of tars, which reduces the energy efficiency of the process and causes technical problems in a system operation. The amount and quality of tars depends on the chemical composition of a fuel, a gasification agent used and its ratio to fuel flow, process temperature and pressure as well as the construction of a gasifier. In the paper review of the research on the influence of operating parameters and kind of feedstock on tar formation and composition in the process of gasification and co-gasification is presented.

Keywords: tar, gasification, co-gasification, biomass, waste, coal

Introduction

For years coal remains a considerable energy resource with stable share in the total world energy consumption of 27% expected by 2035 and approximately 37% share in the world energy consumption for power generation in years 2020-2035 [1]. However, there is a tendency to gradually replace traditional fossil fuels with alternative ones. Most of the

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European countries support utilization of biomass and various types of waste in energy production to reduce the dependence on fossil fuels, mitigate the greenhouse effect and landfills' capacities.

Biomass is considered to be a promising, zero-emission energy resource since the amount of CO₂ released in thermochemical processing is assumed to be balanced by the amount utilized by plants in their growth phase in the process of photosynthesis.

Utilization of biomass in energy sector is limited mainly to heat generation in combustion process. The share of syngas capacity produced in gasification systems fed with biomass and waste in the total syngas capacity is expected to remain as low as 0.3% by 2016 [2].

The gasification process is more environmentally friendly than combustion, which is a source of emission of NO_x and SO_x, dioxins and organic compounds. The temperature and pressure of gasification product gas are usually higher than the temperature and pressure of combustion exhaust gas, which make the removal of sulphur and nitrogen compounds technically easier and less expensive [3].

An increased interest in renewable energy resources has resulted in numerous studies on biomass gasification and co-gasification with coal and waste. Since the costs of energy crops cultivation are considerable, other sources of biomass, including food, agricultural, wood and pulp industries are of special interest [4-6]. Municipal solid wastes, sewage sludge and industrial residues are also considered as potential gasification feedstock [7, 8]. The issue of particular importance when analyzing the co-gasification process is the formation and composition of tars, slag, ash and particulates. Another important aspect, in the light of the utilization of the existing gasification plants fed with fossil fuels without major alterations to the design, is the optimization of a fuel blend composition [5, 9-13].

The gasification is the process of thermochemical conversion of carbonaceous material to a gaseous product, consisting mainly of carbon oxide, hydrogen, carbon dioxide and methane in concentrations depending on process conditions and a kind of gasification agent used. The gasification process may be represented by the following reactions:



The raw gas contains also inorganic impurities (eg H₂S, HCl, NH₃, alkali metal compounds) and tars, defined by the Directorate General for Energy of the European Commission and US Department of Energy as hydrocarbons of molecular weight higher than that of benzene [14]. Tars are therefore a complex mixture of various compounds of a wide range of molecular weight and chemical characteristics. Milne et al [15] assumed that tars are basically aromatic compounds. Some researchers [16-19] refer to the classification of tars into five groups, based on their chemical properties, solubility (or condensability) presented in Table 1 [16, 20, 21].

Table 1

Classification of tars based on [16, 20, 21]

No	Class name	Characteristics	Exemplary compounds
1	GC-undetectable	heavy tars, undetectable with GC	Determined by subtracting the GC-detectable tar fraction from the total gravimetric tar
2	heterocyclic aromatics	tars containing hetero atoms; highly water soluble compounds	pyridine, phenol, cresols, quinoline, isoquinoline, dibenzophenol
3	light aromatic (1 ring)	light hydrocarbons with single ring	toluene, ethylbenzene, xylenes, styrene
4	light PAHs (2-3 rings)	2 and 3 ring compounds; condensing at low temperature even at low concentration	indene, naphthalene, methyl naphthalene, biphenyl, acenaphthalene, fluorene, phenanthrene, anthracene
5	heavy PAHs (4-7 rings)	larger than 3 rings; condensing at high temperature at low concentration	fluoranthene, pyrene, chrysene, perylene, coronene

The content of tars in a raw gasification product depends largely on the gasification process operating parameters (a temperature, a gasification agent, and a residence time), a type of a gasifier and a feedstock composition.

Influence of the type of feedstock on tars formation in the processes of pyrolysis and gasification

The amount and composition of tars generated in the process of gasification depends primarily on the type of feedstock used. The effect of changing the total yield of tars and ratio of particular class of tars in the gasification by-products has been also observed when blends of various solid fuels were co-gasified.

Coal

Coal is the main energy resource used in gasification systems, with expected 62% of the total world syngas capacity (over 75,000 MW_{th}) in 2016. The majority of tars released in the process of coal gasification are decomposed under typical process conditions. The remaining tars, however; may pose a considerable problem related to their environmental impact, resulting from their chemical composition and characteristics. Tars consist mainly of extensively dealkylated aromatic structures with small amounts of oxygenates and have a carbon aromaticity of over 94% [20]. The International Agency for Research on Cancer (IARC) classified the process of coal gasification as carcinogenic to humans [21]. Tars generated in the process of coal gasification with air and steam at the temperature of 850-900°C contain over 40% of heavy hydrocarbons fraction with boiling point of 450°C and higher [20]. Dealkylated structures of 1 to 8 aromatic rings are the largest part of tars, and benzologues of heterocycles containing oxygen, nitrogen and sulphur are present in quite low concentrations [22]. Herod et al [23] reported the contents of carbon, hydrogen and oxygen in coal tars to be on the level of 82.8, 7.0 and 5.8%, respectively. The elemental composition of individual fractions of tars was similar. In the comparative study of coal derived tars, petroleum residue and coke oven tars by Pindoria et al [20] it was observed that the first group contained stable, aromatic compounds with the narrowest range of

molecular weight, which was attributed to the influence of high temperature and gasification agent. The largest number of compounds (61) was reported for coke oven tars and the smallest (50) for coal gasification tars.

The detailed quantitative and qualitative characteristics of coal tars vary depending on the type, carbon structure, coal rank and its elemental composition [24-26]. During the pyrolysis of individual coal macerals, the highest yields of liquid products were reported for exinite and the lowest for vitrinite and inertinite [24]. At the temperature of 650°C tar yields in the process of pyrolysis amounted to 22.4% for vitrinite and to 13.4% for inertinite. This trend became less visible with an increase in a temperature of the pyrolysis. Casal et al [25] studied the effect of ash, volatiles and coal macerals (vitrinite, liptinite, fusinite and semifusinite) contents on the liquid products yield and composition in the process of coal pyrolysis. The samples of ten coals of various rank and geographical origin were pyrolyzed at 450 and 550°C. The primary tars obtained in the process of pyrolysis of high rank coals of high vitrinite content were composed of aromatic hydrocarbons and heterocycles, like phenol and cresols. The presence of C₁₁-C₂₈ alkanes characterized the tars generated in the process of pyrolysis of low rank coals of the highest content of liptinite. The linear relationship between the total yield of liquid products and content of volatiles in a fuel was observed. The results indicated also that the content of aromatics and their alkyl derivatives in tars increases with an increase in aromaticity of the parent coal. The main differences between the tars generated in the process of pyrolysis at 450 and 550°C were observed in terms of the concentration of methyl-derivatives (the lowest at 550°C) and aromatics (the highest at 550°C). The composition of tars did not, however; change significantly with an increase in the temperature. The total yields of liquid products of pyrolysis at the higher temperature was about twice the amount obtained at the lower temperature and even six times higher in case of coal with the lowest content of volatiles. Watt et al [26] analyzed carbon aromaticity in three types of coal and coal tars obtained in the process of pyrolysis using ¹³C Nuclear Magnetic Resonance (NMR) method. In two cases carbon aromaticity in tars was higher than in parent coals.

Brage et al [27] compared composition of tars generated in the process of gasification of coal and biomass at 700 and 900°C in a fluidized bed reactor. The concentrations of benzene, toluene and phenol reported at lower temperature were similar, irrespective of a fuel used. Coal tars showed higher contents of naphthalene and indene. The concentrations of naphthalene, toluene and indene at 900°C were higher in coal tars and the content of benzene was higher in liquid products of biomass gasification, especially in the initial stage of the process. At both temperatures the highest tars level was observed in the beginning of the process and then decreased with time, irrespective of a type of a fuel, although the trend was more pronounced for coal. The relative char bed height increased with time in coal gasification and was almost constant in the process of biomass gasification, which was the result of the differences between coal and biomass chars' reactivity. A decrease in the concentration of coal tars with time was attributed to the catalytic activity of coal ash components in the reactions of tars cracking and reforming. The effect of enhanced tars conversion in the process of co-gasification of biomass and coal was also observed by Chen et al [28]. Liu et al [29] studied the impact of coal ash composition on the product distribution and kinetics of the pyrolysis process. Demineralized coal samples were processed with various additives, like aluminum oxide, magnesium oxide and potassium carbonate. No significant changes in products distribution and coal reactivity

were observed in the experiments with and without additives. The catalytic effect of the mineral matter components was suggested to depend not only on their content, but also on their distribution in active sites on coal surface.

Biomass and biowaste

The process of gasification of biomass gains increasing interest, as a method of generation of a versatile product utilized in energy generation and chemical synthesis, based on renewable resources. One of the disadvantages of biomass utilization is, however; release of relatively high amounts of tars in the process. Biomass is characterized by higher contents of hydrogen, oxygen, moisture and volatiles and lower content of ash when compared to coal [30]. This is also reflected in the differences in composition of coal and biomass tars. The content of carbon in tars is approximately 54.5% by weight, of hydrogen - 6.5% and of oxygen - 39%. The contents of carbon, hydrogen and oxygen in biomass tars do not seem to vary with a temperature, although the dependence of biomass tars composition on the process temperature is not entirely recognized yet [31]. High oxygen content in biomass results in a large number of polar groups present in all classes of biomass tars and thus increases their solubility in water, which is undesirable since it imposes the need for gasification waste water treatment in order to remove harmful tars components.

Milne et al [15] classified biomass tars into four classes: (1) primary products characterized as cellulose-derived, hemicellulose-derived and lignin-derived products; (2) secondary products, like phenolics and olefins; (3) alkyl tertiary products, which are mainly methyl derivatives of aromatic compounds, and (4) condensed tertiary products, which are PAH series without substituents. The tertiary aromatics can be formed from cellulose and lignin, although higher molecular weight aromatics were formed faster from the lignin-derived products. The components of tars from wood pyrolysis are listed in Table 2 [15, 32].

Table 2

Products of wood pyrolysis [15, 32]

Compound class	Compound type and examples
primary tar compounds	acids, <i>eg</i> acetic acid, propionic acid, butyric acid
	ketones, <i>eg</i> acetol (1-hydroxy-2-propanone)
	phenols, <i>eg</i> phenol, 2,3-dimethylphenol, 2,4/2,5-dimethylphenol, 2,6-dimethylphenol, 3,4-dimethylphenol, 3,5-dimethylphenol
	guaiacols, <i>eg</i> guaiacol, 4-methylguaiacol
	furans, <i>eg</i> furfural, furfural alcohol, 5-methylfurfural
secondary tar compounds	phenols, <i>eg</i> phenol, <i>o</i> -cresol, <i>p</i> -cresol, <i>m</i> -cresol
	monoaromatic hydrocarbons, <i>eg</i> <i>p/m</i> -xylene, <i>o</i> -xylene
secondary /tertiary tars *	monoaromatic hydrocarbons, <i>eg</i> benzene, ethylbenzene, <i>o</i> -methylstyrene, 2-methylstyrene, 3-methylstyrene, 4-methylstyrene, 2-ethyltoluene, 3-ethyltoluene, 4-ethyltoluene
	miscellaneous hydrocarbons, <i>eg</i> 2,3-benzofuran, dibenzofuran, biphenyl, indene
	methyl derivatives of aromatics, <i>eg</i> 2-methylnaphthalene, 1-methylnaphthalene, toluene
tertiary tar compounds	polycyclic aromatic hydrocarbons, <i>eg</i> naphthalene, acenaphthene, acenaphthylene, fluorene, phenantrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benz[e]acephenanthrylene, benzo[k]fluoranthene, benzo[a]pyrene, perylene, dibenzo[a,h]anthracene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene

* Several compounds appear also in the secondary compounds class and in one of the other two classes.

Wood and wood wastes are the type of biomass of the gasification behavior widely described in the literature. The main components of wood are cellulose, hemicelluloses and lignin. Studies on pyrolysis behavior of the above mentioned structures performed by Hosoya et al [33] showed that cellulose and hemicelluloses are precursors of primary tars released in considerable amounts in comparison with gas and char yields. The main components of this class of liquid products were anhydrosugars, aldehydes, ketones, carboxylic acids and furans. The products of lignin pyrolysis included a fraction of tars containing phenolic alcohols and their oligomers (syringil- and guaiacyl-types). The chars yield in lignin pyrolysis was two times higher than in pyrolysis of cellulose and hemicellulose and the gas yield was low. Hosoya et al [34] studied also the secondary reactions of liquid products of pyrolysis of cellulose and lignin using a closed ampoule reactor. After 120 s of the residence time the primary products from cellulose were almost entirely decomposed, while the lignin-derived primary tars were transformed into the secondary tars. Fushimi et al [35] proved that the steam gasification of the lignin-derived chars was effective only at the temperature over 650°C. Hanaoka et al [36] emphasized relatively low reactivity of lignin in the process of gasification with air and steam, even at 900°C. The conversion rates (carbon basis) of cellulose, xylan, and lignin were 97.9, 92.2, and 52.8%, respectively, proving the poor efficiency of a feedstock of high lignin content under the process parameters adopted.

The total yield of biomass tars in the process of gasification depends also on a type and amount of inorganic matter present in a feedstock. Some components of biomass ash, like salts and oxides of alkali metals, alkaline earth metals and transition metals prove catalytic activity in reactions of cracking or reforming of tars, which was confirmed among the others by the results of the experimental studies performed by Skoulou et al [37]. The authors gasified olive kernels and leached olive kernels with steam at temperatures of 850 and 950°C. The ash content in a leached fuel was lower (of approximately 1%) and consequently the content of alkali metal oxides was also lower than in parent olive kernels. The yield of tars obtained in the process of steam gasification of leached olive kernels at 850°C was four times higher than the value obtained in the process of gasification of untreated biomass. The tars yields reported in the gasification process at 950°C were comparable for both fuels and slightly lower than the levels obtained at 850°C. This effect was attributed to the volatilization of the active components of biomass ash, alkali metals oxides, at 950°C, resulting in similar content of these components in treated and untreated samples of olive kernels.

Coal and biomass blends

Co-gasification of two or more various fuels offers several advantages. One of the benefits of co-gasification is the reduction in yields of tars when compared to the gasification of fuels separately [13, 38]. In general, studies on co-gasification are mainly focused on the changes in products composition under different operating conditions. The interactions taking place in the process of co-gasification are not entirely recognized mainly because of the wide variety and overlapping effects of the reactions.

Weiland et al [39] studied the process of pyrolysis of coal and biomass of grass (*Panicum virgatum*) and co-pyrolysis of coal and biomass blends of the biomass content of 15, 30 and 50% by weight. The aromatic hydrocarbons were observed in all chromatograms, but some of them, like benzenediol and chlorine compounds, were present

only in the process of biomass or biomass-containing blends pyrolysis. Dibenzotiofene was detected only in tars generated in the process of pyrolysis of coal-containing fuels. The yields of light tars increased and the yields of heavy tars decreased with an increase in biomass content in a fuel blend. The analysis of inorganic matter of coal and biomass showed significantly higher contents of calcium, potassium and magnesium in biomass than in coal and higher levels of aluminum, iron and titanium in coal. The differences in light and heavy tar yields observed in the process of pyrolysis of coal-containing and biomass-containing fuels were attributed to the number of heterogeneous reactions taking place between chars and volatiles, including catalytic cracking.

Pinto et al [9] reported that addition of 20% by weight of biomass of pine waste to coal resulted in a decrease in the total tars yield in the process of air and oxygen gasification when compared to the values observed in gasification of coal. The addition of 10% by weight of pine biomass resulted in a decrease in the total yield of tars, when Polish coal was used, and in an increase in the total gas yield, when German coal was gasified with oxygen. A decrease in the total tars yield was also observed when biomass was co-gasified with coal and polyethylene and in the process of catalytic gasification of the fuels. In the study on a two-stage co-gasification with catalytic cracking of tars formed [10] pure fuels and blends of two types of coal and wood biomass of the biomass content of 10, 20, 30 and 40% by weight as well as blends of coal and olive bagasse of 10 and 20% by weight of biomass content were used. The tars yield decreased with increasing content of wood in a fuel blend irrespective of the coal type and was the lowest in the process of wood gasification. The amount of tars reported in the process of gasification in a fluidized bed reactor with air/oxygen and steam of fuel blends containing 10% by weight of olive bagasse biomass was lower than in the process of coal gasification. Addition of 20% by weight of this biomass resulted, however; in the higher yield of tars, when compared to the value observed in coal gasification. A decrease in the total yield of tars with an increase in biomass content in a coal/biomass blend was also observed in the process of co-gasification with air and steam at 900°C by Kumabe et al [40]. The reactive structures of biomass, like alkyl derivatives and some compounds containing heteroatoms, in particularly oxygen, take part in thermal cracking at high temperature easily, and therefore the total yield of tars was lower. Mastellone et al [41] studied the distribution of products of gasification of biomass and co-gasification of blends of biomass and two types of lignite. The concentrations of tars in product gas were approximately 28 and 43 g/Nm³ in the process of co-gasification of lignite and biomass blends. In the process of biomass gasification no tars were detected. High amounts of soot and the highest concentration of hydrogen reported in the process of biomass gasification proved that the volatiles were decomposed in cracking reactions. A conclusion was drawn that high content of iron and potassium in wood biomass, that is metals exhibiting catalytic activity in cracking and reforming reactions, resulted in complex reactions between hydrocarbons and compounds of inorganic matter on char surface, resulting in a formation of soot and organic carbon nanoparticles.

Some biomass waste from food industry, like oils and bagasse cause problems in gasification process due to a formation of high amounts of tars and therefore their content in a fuel blend must be carefully considered. Svoboda et al [42] reported the concentrations of BTX (benzene, toluene, xylene) and heavy tars fractions several times higher in the process of co-gasification of coal and rapeseed oil (50% by weight) with steam and oxygen mixture than the values observed in coal gasification. Pinto et al [11] studied the process of

co-gasification of coal with 2.5-10% by weight of edible oils in a fluidized bed reactor and with air and air/steam mixtures as a gasification agent. The blend required processing at high temperatures of above 850-950°C and high ratios of the gasification agent flow rate to fuel flow rate. Otherwise the existing gasification installation would require modification of the gas treatment unit, because of high tar formation. André et al [12] determined the maximum amount of bagasse in a fuel blend as 40% by weight for the same reason.

The results of some studies on coal and wood co-gasification confirm that tars obtained in co-gasification process tend to consist of lighter components and/or are released in smaller amounts. The addition of coal or lignite to biomass in gasification was also reported by some researchers to result in a decrease in tars yields, unlike in the studies by Pinto et al [10], Kumabe et al [40] and Mastellone et al [41]. Ruoppolo et al [43] studied the process of gasification of lignite and woody biomass blends at 800°C with steam as a gasification agent. The yields of tars reported in the experiments of co-gasification were lower than those observed in biomass gasification. This is in agreement with the results presented by Vreughdenhil [13]. In the process of co-gasification of fuel blends of a biomass content of 72 and 45% by weight the yields of tars were respectively 16 and 47% lower than in a gasification of wood biomass. Sjöström et al [44] studied the distribution of products of the process of gasification and co-gasification of coal and woody biomass in a pressurized fluidized bed reactor. The highest yields of light tars were obtained in the process of biomass gasification. An increase in light tars yield was observed with decreasing value of biomass/coal ration in a fuel blend. Benzene and toluene were the main liquid products of the process. The yields of light tars in gasification experiments, excluding toluene and benzene, were similar for both fuels. The heavy tars yield in coal gasification was almost twice the value reported in a biomass gasification. The highest total yield of light tars (excluding toluene and benzene) and heavy tars observed in co-gasification was the highest in co-gasification of a fuel blend of 40% by weight of biomass content. It was also lower in co-gasification than in a gasification of coal and biomass separately. The relationship between the biomass content in a fuel blend and the total gas yields and char yields was observed. The mechanism behind the observed phenomena was proposed, which assumed that the weakest bonds of biomass are decomposed first and large amounts of volatiles are released, which decompose further creating free radicals. These react with both: wood and coal, initiating decomposition and oxidation reactions of chars. In the process of devolatilization of wood hydrogen-rich molecules are also formed, being the donors of hydrogen in cracking reactions. These reactions prevent the recombination reactions and the formation of less reactive secondary chars. Also alkali metals, present in the mineral matter of biomass, may have a catalytic effect on coal and biomass char reactions with a gasification agent.

The catalytic activity of alkali and alkaline earth metals is also often considered to be the reason for tars yields reduction since they are recognized catalysts of the reactions of cracking and reforming of hydrocarbons.

Measures of tars yields reduction

All the measures taken to prevent tars formation or to convert tars formed in the gasifier into gaseous product are called the primary methods of tars yield reduction. The secondary methods of tars reduction are focused on effective removal of tars from the hot

product gas. The secondary methods can be divided into chemical (*eg* using cracking reactions) and physical (*eg* using cyclones, scrubbers, and filters) methods, both widely recognized and used. The main tools of primary methods are the optimization of operating parameters (a temperature, a pressure, a residence time, a kind of a gasification agent and catalysts) and modifications of a gasifier (two-stage process, secondary air injection). The influence of operating parameters may vary significantly depending on kind of a fuel used, because of complex interactions taking place in the process of gasification or co-gasification and the main way to achieve tars yields reduction is thermal and catalytic decomposition of hydrocarbons.

Thermal cracking

The total tars yields differ depending on a gasifier type and kind of feedstock used and it decreases with the process temperature [45-47]. The cracking reactions taking place at higher temperature convert hydrocarbons present in tars into gas and secondary chars, and therefore the yield of gaseous products also increases.

The results of the research studies on limiting tar formation in the process of gasification [27, 42, 48] showed that an increase in a temperature and long residence times facilitate thermal cracking reactions. These reactions are observed based on a decrease in the total gas yields and higher content of light components in tars [47, 49].

Jess [50] studied the kinetics of the thermal conversion of hydrocarbons at high temperatures and in the presence of hydrogen and steam using benzene, toluene and naphthalene as a model tar. Complete thermal decomposition of aromatic hydrocarbons at residence times below 10 s was possible only at temperatures above 1200°C. The thermal conversion of aromatic hydrocarbons to carbon monoxide and hydrogen required higher temperatures, of even 1400°C. The reactivity of toluene in cracking reactions was significantly higher than those of benzene and naphthalene. The proposed scheme of the thermal decomposition of tars is shown in Figure 1.

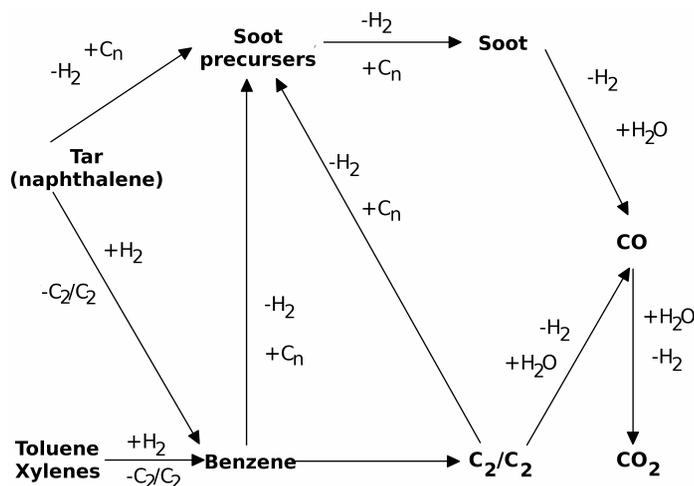


Fig. 1. Simplified reaction scheme of thermal conversion of aromatic hydrocarbons in the presence of hydrogen and steam [50]

It was also reported that the presence of steam had no influence on the conversion of aromatic hydrocarbons. Experimental results showed that soot was primarily formed from naphthalene and its formation was lower in the presence of hydrogen. These results were in line with the results by Gil et al [51] and Zeng et al [52]. A significant decrease in concentrations of polycyclic aromatic hydrocarbons, including naphthalene, was unfeasible at temperatures lower than 1000°C. Zeng et al [53] investigated thermal cracking of tars obtained from different coals. They analyzed tar components behavior in the temperature range of 650-1200°C. High-rank, bituminous coals produced high aromaticity tars of strong tendency to sooting as a result of condensation of aromatics to polycyclic aromatic compounds. The amounts of soot obtained in a pyrolysis of low-rank coals were lower. The heterocycles and alkyl-derivatives of aromatics, present in tars derived from low-rank coals, underwent thermal cracking reactions and formed gas and small amounts of soot.

Polycyclic aromatic hydrocarbons (PAHs) formed in the process of coal pyrolysis are very stable. Ledesma et al [54] gasified coal tars obtained in the process of coal pyrolysis at 600°C. The tars were processed at 1000°C with various amounts of oxygen. The concentrations of 27 PAH compounds present in tars, with 2-9 aromatic rings were measured. The maximum concentrations of some of them were observed in the process of gasification with oxygen in the amount of 0.3 of stoichiometric combustion ratio. Higher rates of oxygen resulted in a decrease in PAHs, but even in experiments of stoichiometric oxidation, three structures were still identified (9-fluorenone, cyclopenta[*def*]phenanthrene and indeno[1,2,3-*cd*]fluoranthene).

Paasen and Kiel [50] studied the influence of a temperature on composition of biomass tars. Wood was gasified in a bubbling fluidized bed reactor at temperatures of 750-950°C. Total tars yield and concentrations of heterocycles, light aromatics and GC-undetectable compounds decreased with increasing temperature, while the contents of heavy polycyclic aromatic hydrocarbons was higher and those of light polycyclic aromatics was almost constant. The most significant decrease was observed in the concentrations of heterocycles, which dropped to zero at temperatures above 850°C. The yields of heavy PAHs were quite low in samples obtained at 750°C and increased with a temperature, while concentration of light polycyclic aromatic hydrocarbons, like biphenyl or phenanthrene, slightly decreased at 900°C. Two paths of formation of heavy PAHs were considered: cracking of very heavy structures undetectable by GC and condensation of aromatic rings from light PAHs. The amount of GC undetectable components decreased with an increase in a temperature and concentrations of heavy PAHs, supporting the first hypothesis. A decrease in GC undetectable compounds was observed at 800°C, when heavy aromatic hydrocarbons were hardly present in the products. A significant increase in concentrations of heavy PAHs proceeded at temperatures above 850°C, while the concentrations of light PAHs slightly decreased. This effect proved condensation of aromatic rings to be the mechanism of formation of PAHs structures, but no explanation of high amounts of GC undetectable structures at lower temperature by condensation reactions could be given. A significant decrease in concentrations of heterocycles, even at 750°C, suggested that they may be the precursors of very heavy structures, undetectable with GC.

The volatiles released in the process of pyrolysis of biomass are usually structures susceptible to thermal cracking. Yu et al [55] studied the process of pyrolysis of birch wood biomass. The concentrations of alkyl-derivatives of one- to two-ring aromatics strongly decreased with an increase in a temperature and concentrations of three- and

four-ring PAHs increased with a temperature. Brage et al [27] observed 50% decrease in the concentrations of toluene and almost complete decomposition of phenol with an increase in a temperature from 700 to 900°C in the oxygen gasification process in a pressurized fluidized bed reactor. Other experimental studies [51, 56] shown an absence of phenol in products of the high-temperature biomass gasification. The results of studies on thermochemical processing of various types of biomass [49, 52, 57] showed that phenol, cresols, toluene and xylene were the main components of tars obtained in the process of gasification at 700°C. Other alkyl-substituted aromatic hydrocarbons and heterocycles, containing nitrogen, like quinoline, isoquinoline and pyridine were also detected. An increase in a temperature resulted in a decrease in concentrations of phenol, cresols, xylene, toluene and ethylbenzene, and intense formation of dealkylated aromatics, like benzene, naphthalene and indene. The resulting composition of biomass tars obtained at 900°C was similar to the composition of coal tars, containing mainly dealkylated aromatic structures.

The process temperature is very important, however; a complete removal of tars by adjustment of this single factor, while maintaining all the other parameters values at a satisfactory level, is unfeasible. Other parameters influencing conversion of tars are a type of a gasification agent and a residence time. Umeki et al [47] reported quite high concentrations of tars in the high-temperature steam gasification of woody biomass. The amounts of tars increased from 50 to 100 g/Nm³ with an increase in a steam flow rate, which resulted in shorter residence times, insufficient to decompose hydrocarbons in thermal cracking reactions. These reactions led to formation of gas and light hydrocarbons. Increasing a temperature of the gasification process lowers the total yield of tars, but it also causes some undesired changes in tars composition.

The use of a catalyst is a very effective way to limit the concentration of tars, even in case of feedstock, which tend to form very high tars yields. Limitation of hydrocarbons yields may result from:

- cracking



- decomposition to carbon and hydrogen



- steam reforming



- dry reforming



Anis and Zainal [17] specify six groups of catalysts: nickel-based catalysts, non-nickel metal catalysts, alkali metal catalysts, basic catalysts, acid catalysts and activated carbon catalysts. Nickel-based catalysts are the most widely used in production of synthesis gas in the process of steam reforming of hydrocarbons. Nickel is characterized by high catalytic activity [17] but its resistance to poisoning, sintering and carbon deposition strongly depends on a support material, promoters and other additives. Garcia et al [58] synthesized some catalyst of this type and described their activity and stability during biomass gasification. NiMgAl₂O₅ was characterized by the highest catalytic activity and the highest resistance to deactivation. A complex preparation procedure and high price of nickel as well as the deactivation by sulphur compounds made nickel catalysts unsuitable for application

in industrial scale gasification systems. The same applies also to non-nickel metal catalysts, in particularly those containing noble metals, such as rhodium [59].

Alkali metals and alkaline earth metal catalysts proved also some activity in reduction of tars in gasification process. K_2CO_3 caused a decrease in the total yield of liquid products generated in the process of biomass pyrolysis [60]. Xie et al [61] investigated influence of calcium and potassium carbonates on tar composition in the process of steam gasification of biomass. The concentrations of saccharides, acids, aldehydes, furans and guaiacols were reduced with both additives. K_2CO_3 was also active in elimination of alcohols, while $CaCO_3$, promoted their formation. Douglas and Baker [62] observed a decrease in the amount of phenols and polycyclic aromatic compounds in gasification of wood with addition of 8% K_2CO_3 . Garcia et al [63] studied the effects of addition of calcium oxide, produced by calcination of calcium carbonate, on conversion of heavy hydrocarbon fractions from various industrial processes. The petroleum residues and coal tars generated in the process of gasification were reported to be almost completely decomposed at the temperature of 800°C and with the ratio of steam to hydrocarbons flow rate of 3.5. Alkali and alkaline earth metal compounds (salts and oxides) are natural, widely available and price competitive compounds. The catalytic activity of dolomite [16, 63-68], limestone [65], olivine [9, 64] and ilmenite [69] has been widely studied. The comparative research work [64] showed that dolomite was the most active among all the mineral catalysts, even when short residence times were applied. Narvaez et al [70] reported a decrease in the yield of tars from 11.5 g per 1000 g of a feedstock to approximately 4 g per 1000 g of a feedstock in the process of biomass gasification with air in an atmospheric bubbling fluidized bed reactor at 800°C with 3% of dolomite in a bed. Ruppolo et al [43] and Abu El-Rub et al [56] also observed high catalytic activity of dolomite and similar level of tars reduction achieved with dolomite and nickel catalyst. The dolomites from various geographical regions may differ in activity and stability, due to the presence of various substances naturally occurring in their structure [67]. Also intentional modifications like addition of iron oxides [16] may cause increase in tars conversion from 40% to over 90%. The olivine is characterized by lower activity in the removal of tars, and greater resistance to abrasion [71] and carbon deposition [72] than dolomites. Devi et al [73, 74] reported that the conversion of biomass derived model tars component - naphthalene in the process of steam gasification in a fixed bed reactor at temperatures of 750-900°C was higher in the presence of calcined olivine than in the process catalyzed by non-calcined olivine. The results of experiments performed by Pinto et al [9] showed that the activity of the non-calcined olivine was comparable with the activity of the calcined dolomite.

There are also some reports on application of acid catalysts, like *eg* zeolites in the removal of tars. Some authors [75-77] investigated catalytic activity of commercial FCC (*Fluidal Catalytic Cracking*) catalysts. Y-zeolite in the ten-hour test showed almost 100% effectiveness in removal of tars, similarly like NiMo catalyst, and no signs of deactivation. Millini et al [77] reported also that complete restoration of zeolite catalyst performances is possible even after several reaction/regeneration cycles.

Activated carbon and coal or biomass derived chars were also used as catalysts of good activity in hydrocarbons conversion [56, 79-82] or as catalysts' support in tars removal [78] due to their porous structure and content of mineral matter. Brage et al [27] observed that presence of char accumulated in a fluidized bed was advantageous in terms of reduction of tars yields. Abu El-Rub et al [56] compared the activity of two biomass chars and other

catalysts, like calcined dolomite, olivine, FCC catalysts, biomass ash, and commercial nickel catalyst in tars removal. The conversion of tars at 700°C and in the presence of chars was lower than in the processes with addition of nickel, dolomite and zeolite. At 900°C chars showed, however; higher activity than other substances, except for nickel-based catalyst.

The catalytic cracking, decomposition and reforming of hydrocarbons enable a complete destruction of tars. The catalytic reactions enable to decompose even relatively stable compounds, like aromatics and polycyclic aromatic hydrocarbons. The improvements in known catalysts and development of new ones are considered to be promising options for removal of tars from gasification and co-gasification processes.

Conclusions

Tars are undesired by-products of the gasification and co-gasification processes. Selection of suitable feedstock and operating parameters are important in terms of reduction of tars yield. The main objective of the optimization of the process parameters is, however; the gas composition and heating value meeting the requirements of the final user and the satisfactory total process efficiency. The total yield and composition of tars strongly depend on a type of a feedstock. Biomass feedstock is proven to generate large amounts of primary tars, usually more reactive and easily decomposed in thermal cracking and catalytic reactions. The process of coal gasification results in various yields of tars produced, including considerable amounts of stable, dealkylated aromatic structures. The recognition of the conditions and mechanisms of tars formation and their reactivity is continuously being increased, which results in the development of primary methods of tars abatement. The thermal and catalytic cracking and catalytic steam reforming of hydrocarbons are the methods most commonly used in decreasing the total yield of tars and changing their composition.

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WPLYW RODZAJU PALIWA STAŁEGO I PARAMETRÓW EKSPLOATACYJNYCH NA PRODUKCJĘ SUBSTANCJI SMOLISTYCH W PROCESIE ZGAZOWANIA I WSPÓLZGAZOWANIA

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Abstrakt: Rosnące zapotrzebowanie na energię, ograniczone zasoby surowców energetycznych oraz aspekty środowiskowe stanowią główną przyczynę prac badawczych, których celem jest szersze użytkowanie odnawialnych źródeł energii oraz odpadów do celów energetycznych. Technologie zgazowania oparte są na procesie termochemicznej przeróbki paliw stałych, płynnych i gazowych do gazu o składzie zależnym od zastosowanego czynnika zgazowującego i wartości parametrów eksploatacyjnych. Zakres zastosowania produktu gazowego z procesu zgazowania obejmuje głównie przemysł chemiczny i petrochemiczny. Jego zastosowanie w produkcji energii elektrycznej również jest interesujące z uwagi na mniejszy negatywny wpływ technologii zgazowania na środowisko i większą sprawność procesu w porównaniu z systemami kotłów węglowych. Technologie zgazowania umożliwiają również użytkowanie różnych surowców energetycznych, począwszy od paliw kopalnych poprzez biomasę, odpady przemysłowe i różne mieszanki wsadowe. Jednym z najbardziej istotnych aspektów eksploatacyjnych związanych z przetwarzaniem termochemicznym biomasy i odpadów jest tworzenie się substancji smolistych, co obniża sprawność energetyczną procesu i powoduje problemy techniczne w eksploatacji instalacji. Charakterystyka ilościowa i jakościowa substancji smolistych uwarunkowana jest składem chemicznym paliwa, rodzajem czynnika zgazowującego i wartością stosunku natężenia przepływu tego czynnika do nadawy paliwa, temperaturą oraz ciśnieniem procesu, a także rodzajem zastosowanej konstrukcji reaktora. W pracy przedstawiono przegląd badań w zakresie wpływu parametrów eksploatacyjnych oraz rodzaju paliwa na ilość i skład substancji smolistych w procesie zgazowania i współzgazowania.

Słowa kluczowe: substancje smoliste, współzgazowanie, biomasa, odpady, węgiel