DECOMPOSITION OF TARS IN MICROWAVE PLASMA – PRELIMINARY RESULTS

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ABSTRACT

The paper refers to the main problem connected with biomass gasification - a presence of tar in a product gas. This paper presents preliminary results of tar decomposition in a microwave plasma reactor. It gives a basic insight into the construction and work of the plasma reactor. During the experiment, researches were carried out on toluene as a tar surrogate. As a carrier gas for toluene and as a plasma agent, nitrogen was used. Flow rates of the gases and the microwave generator's power were constant during the whole experiment. Results of the experiment showed that the decomposition process of toluene was effective because the decomposition efficiency attained above 95%. The main products of tar decomposition were light hydrocarbons and soot. The article also gives plans for further research in a matter of tar removal from the product gas.

Keywords: tar, gasification, microwave plasma.

INTRODUCTION

With an increasing demand for fuels and their decreasing resources at the same time, a much higher pressure is put on alternative, renewable energy sources. Biomass is definitely one of them and nowadays it is one of the most important new energy resources. Significance of biomass comes from the fact that it is easy to obtain, widely and relatively evenly available all over the world and it is relevantly cheap. In addition, biomass is considered to be neutral with respect to CO_2 emission.

There are a few ways of biomass utilization in a field of energy production i.e. fermentation, combustion, pyrolysis and gasification. Gasification is a process that has recently attracted high interest, mainly because of the fact, that it allows to transform solid biomass into much more useful (in the meaning of transport and diversity of application) products. As a result of gasification mostly gaseous products are obtained. Their concentration depends on the type of gasifier, a sort of biomass and process parameters. The produced gas may be used for a production of heat, electricity or as a raw chemical material for synthesis of liquid fuels or other chemicals.
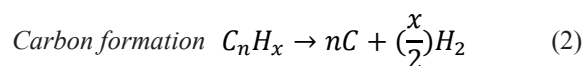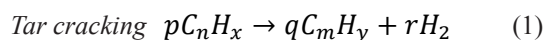
The major drawback related to the biomass gasification is a presence of solid particulates and tar in a produced gas. While the solid particles can be easily separated, the main problem is tar, which at a high temperature, is in a vapor state – what makes it difficult to separate. Upon condensation, tar blocks downstream pipelines and foul engines and turbines (1). Tar is a product of high temperature reactions of a cellulose, hemicellulose and lignin depolymerization. Tars are characterized and classified by few, similar classification's systems (1). All of them state that tar is a mixture of heterocyclic, aromatic and poly-aromatic hydrocarbons.

The amount of produced tar strongly depends on a gasification process (type of gasifier and work parameters) and it is in the range of 0.5 to 100 g/Nm^3 (2). At the same time, the allowed concentration of tars for a gas used in ICE (internal combustion engines) is stated on a level of 50 to 100 mg/Nm^3 and below 5 mg/m^3 for gas turbines (1). As a result, the presence of tar in the product gas precludes one of the most important applications of biomass gasification.

Although it is clear that the gasification process is promising, its application in larger and wider scale requires a reliable and efficient way of removal/conversion of tar from a produced gas.

Many attempts have been made in order to develop methods which allow the purification of gasification products from tar. These include primary methods, which are based on a gasifier design and biomass properties (2) and secondary methods i.e. mechanical (3), thermal (4), catalytic (5), and plasma methods (6), (7), (8). The last two methods show the highest efficiency of tar removal (9), (10). It is also worth to mention that these two methods can be matched together, showing even a higher efficiency in consequence (11) – that is a further goal for the authors of this article.

Plasma is a high temperature, strongly ionized medium with high concentration of electrons, ions, radicals and excited molecules and atoms. Such a composition makes plasma a highly reactive medium. Therefore, plasma may be considered as a coupling of a temperature source and a catalytic medium. The chemical reactions taking place during the high temperature tar decomposition can be described as follows (10):

$$\textit{Tar cracking} \quad pC_nH_x \rightarrow qC_mH_y + rH_2 \qquad (1)$$

$$\textit{Carbon formation} \quad C_nH_x \rightarrow nC + \left(\frac{x}{2}\right)H_2 \qquad (2)$$

where: C_nH_x represents tar and C_mH_y represents a hydrocarbon with a carbon number smaller than that of C_nH_x.

The lab-scale investigations were carried out on the microwave plasma application for decomposition of toluene as a tar surrogate. The preliminary results were to show the efficiency of the applied method and to identify products of the decomposition process.

THE LABORATORY SET-UP

Figure 1 presents a scheme of the laboratory research installation. The most important part of the installation is a microwave plasma reactor of the tubular type (4) presented in Figure 2. The main two reactor's elements are microwave generators (1) and quartz tube. Three microwave generators (Promis), each of 2 kW power, provided microwaves of 2.45 GHz frequency. Microwaves radiation was absorbed by gas providing energy into it and as a consequence, exciting and

ionizing gas molecules and creating plasma. Plasma was generated at the top of the quartz reactor and transported down the reactor by the carrier gas flow. A length of the quartz tube was 1200 mm and depending on the gas flow, the plasma can reach up to one third of the tube's length. The inner diameter of the tube was 60 mm. It is worth to notice that this type of reactor, in opposite to plasma arc for example, it was hardly ever used in a tar removal process in other research and, therefore, its impact on tar decomposition is not known very well. Its advantage is a simple and compact construction, what might be a great convenience in coupling it with a catalyst bed.

In this study, nitrogen was used as a plasma agent. It is not without a reason if we consider that nitrogen is the main ingredient in a generator gas obtained through gasification with air. It is planned to use a mixture of gases simulating syngas instead of pure nitrogen – this will prevent syngas dilution. Nitrogen was supplied from a steel bottle with pressured gas (1). Nitrogen was separated on three streams – all flow rates were controlled with a use of mass flow meters (2) (Aalborg GFM 67 and XFM 47). Two of the streams were used only for the reactor feeding purpose – one of them was to provide molecules for plasma creating (it had axial flow) and the purpose of the second one is to protect the quarts tube from a high temperature (it had swirl flow). The third stream was used as a carrier gas for toluene stored in a glass tank. The temperature of toluene was measured due to the fact that it has an influence on toluene vapors pressure.

The products of the decomposition process of toluene were analyzed with a use of two devices: gas chromatograph (6) and stationary gas analyzer (7). The chromatograph used in the research was HP 6890 with a HP-5 (Crosslinked 5% PH ME Siloxane) column and the flame ionization detector (FID). The GC analysis required sampling with a syringe (5) at the outlet of the reactor. The gas analyzer was GAS 3000 (GEIT Europe) which evaluated concentrations of CO, CO_2, CH_4 and H_2. The analyzer was connected with a computer and worked online through the whole experiment.

EXPERIMENTAL

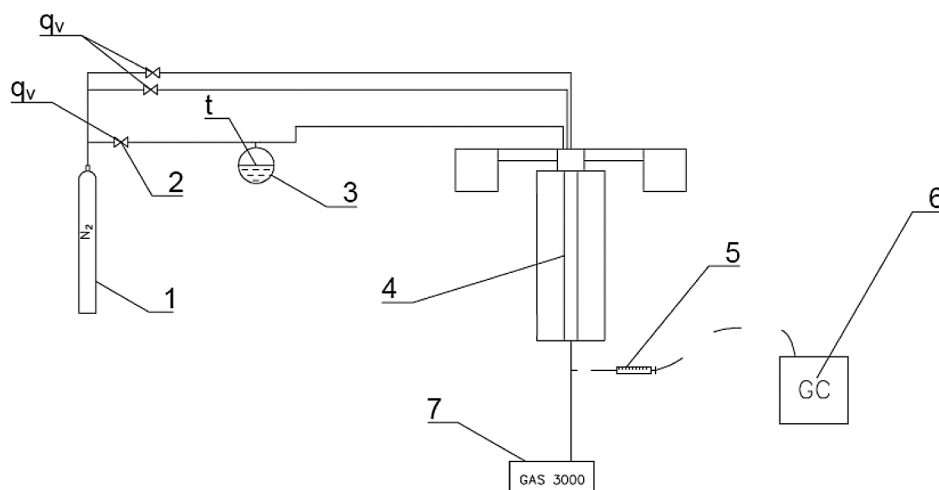Toluene was used in many studies on tar decomposition as a tar surrogate (11), (12). This de-

Figure 1. Scheme of the installation for plasma tar decomposition

Figure 2. The microwave plasma reactor: 1 – microwave generators, 2 – quartz tube, 3 – power supply

cision was mainly justified by a significant concentration of toluene in a tar from biomass gasification process – it is one of the main compounds that create tar (13). Approach like this, also simplifies analyses and clarifies measurements allowing for a more precise interpretation of results and comparison of them with other studies. Therefore, in our experiment toluene was used as a model compound.

The first step in research was to find out what concentration of toluene could be achieved with a different flow of carrier gas. During scaling, as well as in the main experiment, the plasma agent and protective gas flows were on a level of 15 l/min. With this flow the plasma work was stable, the toluene concentration was not diluted and nitrogen consumption was on a low level. Flow of the carrier gas was regulated on the following levels: 3, 5, 10, 15 and 20 l/min. The results achieved for different carrier gas flow are given in Table 1. As it can be seen in Figure 3, the relationship between carrier gas flow and toluene concentration/amount is not linear. It is assumed that at the beginning of increasing gas flow, velocity of gas is too high to be saturated with toluene vapors. With further flow increase, however, the entrainment mechanism may have a greater influence on toluene transport - but at the same time it also had an impact on toluene dilution. Thus, although the amount of toluene may have slightly increased, its concentration kept decreasing. Despite that, the results show clearly that the highest concentration/amount of toluene was achieved for the lowest gas flow – that is 3 l/min. During the scaling samples were taken from an inlet port at the top of the reactor through which toluene is introduced into the reactor. During the scaling the toluene had an ambient temperature of 22 °C.

For the decomposition experiment, a carrier gas flow rate of 5 l/min was chosen. This choice was dictated by two reasons: a demand of testing the installation in conditions of high toluene concentration and a problem with stabilizing the gas flow on a lower level where every deviation may have an impact on the results. During decomposition investigations toluene stored in the bottle had an ambient temperature of 20 °C. Only two

Table 1. Parameters obtained for toluene feeder scaling

q_v l/min	Toluene concentration		F g/min
	ppm	g/Nm³	
3	49338	185.07	6.11
5	37092	139.13	4.87
10	31704	118.92	4.76
15	31291	116.31	5.28
20	27369	102.66	5.13

Explainations: q_v – volumetric flow of carried gas, F – mass flow of toluene.

microwaves generators were used in these experiments. Their power was set up on a maximum, which was 2 kW for each one.

In both, scaling and decomposition research, from three to five samples of gas were taken, depending on a repeatability of measurements.

For the determination of toluene decomposition efficiency the samples were taken at the outlet of the reactor. The temperature at the outlet of the plasma reactor was about 22 °C. Just before the principal toluene removal process, the measurements similar to those for feeder scaling were carried out in a purpose of evaluating inlet toluene concentration (C_0) – it was 131 g/m³.

Additionally, during the toluene decomposition process the GAS 3000 analyzer was measuring concentrations of CO, CO_2, CH_4 and H_2. The chromatograph program was set up on 70 °C (the column temperature) and 3 minutes (previous research shown that after the toluene's peak none other were shown up to 15 minutes). Identification of decomposition products was done with a use of GC (HP6890) with MS (HP 5973) by an external laboratory (Laboratory of Gas Chromatography, Department of Polymer and Carbon Materials, Wroclaw University of Technology).

RESULTS AND DISCUSSION

Preliminary investigations were performed to recognize a potential of the method. The carrier gas (5 l/min) was doped with toluene to bring its concentration to approx. $C_0 = 130$ g/m³. The products of toluene decomposition were identified and the effectiveness of destruction was calculated for the selected experiment.

Figure 4 shows a chromatogram obtained from the analysis of toluene decomposition products. There are four main products and marginal amounts of other compounds. Qualitative analyzes allowed to identify three products: methane, benzene and toluene. The fourth product of toluene decomposition is some light compound (with retention time of 1.507 and peak's area of 12.07 pA·s) that is hard to define because its identification is disturbed by the presence of other light compounds such as methane, nitrogen and carbon oxide. Some deeper and extended further analyses all required for identification of that compound, however, according to other observations (14), (15) it is suggested that it might be C_2 compound like ethane or ethylene.

The retention times, average concentrations of toluene, organic products of its decomposition and conversion efficiencies are given in Table 2.

The effectiveness of toluene conversion in the decomposition process was calculated with a use of the following formula:

$$X = \left(1 - \frac{C_m}{C_0}\right) \cdot 100\% \qquad (3)$$

where: X – toluene conversion efficiency, %
C_m – concentration of toluene after decomposition, g/m³
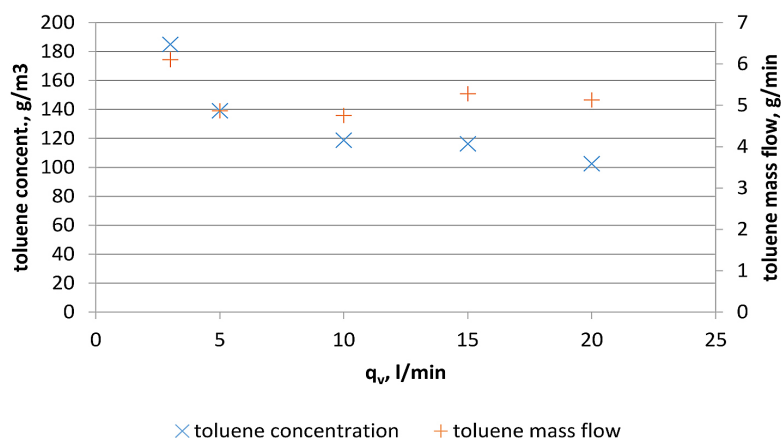C_0 – concentration of toluene before decomposition – 131 g/m³

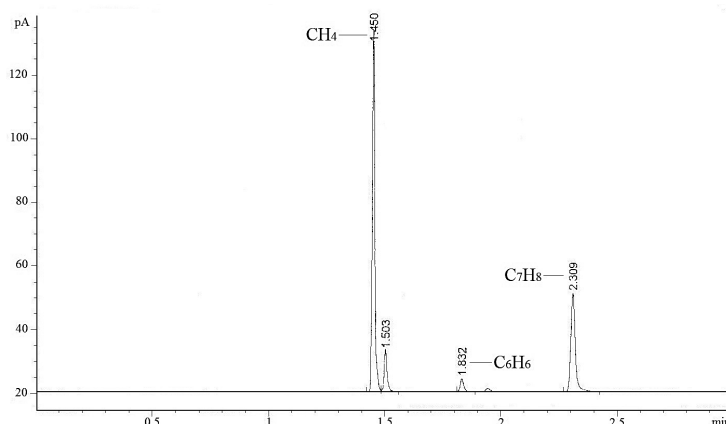**Figure 3.** Relationships between carried gas flow and toluene mass flow and concentration

Figure 4. Chromatogram of the toluene decomposition process

Table 2. Concentrations of toluene and selected products of decomposition and efficiency of conversion

Compound	Retention time [min]	Peak's area [pA·s]	Concentration C_m [g/m³]	Conversion [%]
Toluene	2.309	42.75	5.89	95.50
Benzene	1.832	5.96	0.08	0.06
Methane	1.450	97.43	2.03	1.55

The conversion degree of toluene conversion into benzene and methane was calculated as a ratio of obtained product and introduced toluene:
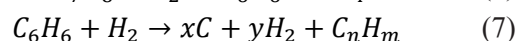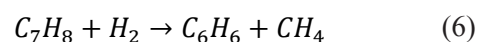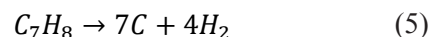
$$X_{CH_4, C_6H_6} = \left(\frac{C_m}{C_0}\right) \cdot 100\% \qquad (4)$$

No hydrogen or carbon dioxide were detected by the Gas 3000 analyzer in the produce gas in the reactor outlet. Concentration of CO was on a level of 0.06%. A presence of CO is intrigue since no oxygen was introduced – this might be explained with a small, unavoidable leaks and air sucking. Also a lack of hydrogen might be surprising. This may be explained in a few, not excluding ways. Firstly, hydrogen might have been adsorbed on soot. Secondly, considering air leaks, some of hydrogen might have been burned into water. Finally, it is possible that hydrogen was used in a process of hydrocracking of toluene and benzene.

Beside those products, it is also important to mention that noticeable amounts of soot were produced during the toluene decomposition, that is typical for that kind of process and was mentioned in other publications (16). Matching those concentrations of inorganic compounds with those for organic, shows that most of toluene was in fact transformed into soot.

If the structure of the toluene is considered, it seems reasonable and intuitive that such a compound would convert into methane and benzene. However, the results show that the amount of benzene is far smaller than methane. This may suggest that benzene was converted into methane, soot and probably some other lighter hydrocarbons. Those reactions, explaining high concentration of soot, lack of hydrogen and disproportion between benzene and methane, might be presented by the following simplified chemical formulas:

$$C_7H_8 \rightarrow 7C + 4H_2 \qquad (5)$$

$$C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4 \qquad (6)$$

$$C_6H_6 + H_2 \rightarrow xC + yH_2 + C_nH_m \qquad (7)$$

where C_nH_m represents a hydrocarbon with a carbon number smaller than benzene and which might be an unidentified compound that was previously mentioned. More precise chemical mechanism requires further researches including identification of more compounds.

CONCLUSION

The presented results of the initial lab-scale experiment leads to the following conclusions:
1. The microwave plasma is highly effective in toluene decomposition (> 95%), which indicates that this type of installation might be used for tar removal from a syngas.
2. The main product of toluene conversion is soot, which can be easily separated from a gas with a use of mechanical devices such as cyclones of fabric filters.

3. In conversion process some small amounts of hydrocarbons, lighter thn toluene were also obtained, which can increase caloric value of syngas.

Next steps in research will include water steam introduction into the reactor, what should allowed to transform soot into hydrogen and carbon monoxide, and use of a catalyst to increase the conversion even more. Besides that, the impact of plasma generator's power and plasma agent gas composition on the decomposition process will be investigated.

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