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Choice the Filter for Tar Removal from Syngas

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Abstract. One of devices for removing char from syngas is a cloth-based filter. Char is mainly carbon black which is a good adsorbent and can be used for removing tar from syngas. When the latter passes through the filter, the char accumulates in it and adsorbs tar. In order to study effectiveness of this way of removing tar, samples of syngas for further analysis were taken twice, before and after the filter with char. A solid-phase adsorption (SPA) method for determining concentration of tar compounds has been chosen. The research showed that the filter for removing char from syngas proved quite cheap and effective in removing tar from syngas. Concentration of the total tar in the samples taken after the filter for removing char from syngas decreased by nearly 90% comparing to the total tar concentration in the samples taken before it. A solid-phase adsorption system consisting of amino-phase sorbent and activated coconut charcoal is a very convenient and effective device for sampling tar in syngas. If its concentration in syngas is high, light tar compounds are adsorbed on both sorbents. With a low concentration of tar in syngas, all compounds might be adsorbed only on the first sorbent.

Keywords: adsorbent, analysis, char, syngas, tar removal.

I. INTRODUCTION

Biomass fuels as a carbon neutral renewable energy source can be used for the production of electricity and heat. Gasification of biomass produces lower levels of sulfur, nitrogen compounds and reduced carbon emissions, than those in coal gasification [1], which is particularly important today.

The planned 20 percent of the EU's power are to be obtained by 2020 from renewable sources such as biomass alongside with wind, solar or geothermal sources. Although it is true that clean energy technologies cost more than fossil fuels, the European Union says a low-carbon economy will create millions of new jobs, which is particularly important at the time of crisis right now (Green jobs vs unemployment, Euronews 16/06/2009 08:27 CET). So the use of biomass is not a question of purely academic importance.

Biomass gasification results in the production of a syngas that can be used as a fuel gas to power combustion engines, turbines, and fuel cells to produce electric power. The gas composition resulting from biomass gasification depends on conditions of gasification.

Gasification process generates solid char and tars whose quantities depend on the gasifier type and operating conditions. Tars are condensable in the gasifier, in downstream processing steps, or in conversion devices [2]. The amount of tars in the gas stream can be as high as several hundred g m-3 depending on the type and operating conditions of the gasifier [3]. The unwanted tar may deposit on the walls of piping and in other process units downstream of the gasifier. Tar in the gas stream hinders the removal of particulates in the gas stream, utilization of the syngas, and affects steam reforming of the syngas into hydrogen [4]. This leads to blocking and fouling of downstream processes resulting in a low cold gas efficiency of the system and low heating value of the final fuel gas produced [5].

Char removal from syngas is usually considered as a very important process where the cost of the removal device should not be high. One of such devices is a cloth-based filter which adsorbs char when syngas passes through it. The filter pores get blocked with time, and it becomes less effective. That is why regular shaking out helps remove char from the filter during gasification.

By virtue of its nature, char is mainly carbon black which, due to its large surface, is a good adsorbent. That is why the filter with char adsorbed on it can be used for removing tar from syngas. When syngas passes through the filter, the char accumulated in it can adsorb tar. In order to study effectiveness of this way of removing tar, samples of syngas for further analysis were taken twice, before and after the filter with char. Sampling was performed in different conditions of biomass gasification, i.e. the temperature of the process varied as well as the biomass – air ratio. To analyze the adsorbed tar, the char shaken out of the filter was also examined. The aim of the present research is to examine the effectiveness of removing tar from syngas with the

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help of the filter filled with char resulting from biomass gasification.

In the present work, solid-phase adsorption (SPA) method for determining concentration of tar compounds has been chosen. The SPA method was developed by The Royal Institute of Technology in Sweden [6] to measure tar compounds ranging from benzene to coronene. Traditional methods [7] are based on cold solvent-trapping (CST). They proved very impractical for light compounds and require lengthy sampling times (15–60 minutes per sample). By contrast, the SPA method is easy to handle, and one sample is typically taken in only 1 minute. According to this method, tars are sampled by collection on a column with a small amount of amino-phase sorbent. For each sample, 100 mL of gas is taken from a sampling line with the help of a syringe or a pump. The sampling line is kept at 250–300°C to minimize tar condensation. The aromatic fraction is extracted using dichloromethane, and the solution is then analyzed by a gas chromatograph (GC-MS). With a high concentration of volatile organic compounds in biomass tar, not all of them will be collected on an amino-phase sorbent. Trying to solve this problem, it was decided to install a second column with another adsorbent designed for collecting volatile organic compounds, following the column with the amino-phase adsorbent.

In the previous papers [8–11], an improved system for sampling tar, namely, equipped with one more adsorbent cartridge loaded with another sorbent, was suggested and described. The best results were obtained while using activated coconut charcoal as the second sorbent. So, a modified sampling device consisting of 500 mg of amino-phase sorbent and 100 mg of activated coconut charcoal was chosen as optimal for sampling tar and volatile organic compounds it comprises in synthesis gas produced in biomass gasification.

II. MATERIALS AND METHODS

A. Gasifier

For research in a real-life context, the Circulating Fluidised Bed (CFB) gasifier situated in eastern Latvia (Rēzekne region) was chosen. Peat extracted several kilometres from the gasifier was employed as biomass. The main characteristics of the gasifier are as follows: heat output is ~600 kWth, reaction temperature reaches ~800–1050°C, the mass of dry peat is ~250 kg hour^{-1}, and the mass of air ~120 kg hour^{-1}. The peat biomass has the following fuel characteristics calculated as for dry basis: gross calorific value is 20.00 MJ kg^{-1}, moisture 13.0%, C 53.23%, H 7.63%, N 0.86%, S 0.10%, O 38.18% (by difference). The product gas comprises H_2 (13.43%), N_2 (50.52%), O_2 (0.38%), CO (12.72%), CH_4 (2.41%), CO_2 (16.91%). The temperature of syngas in the point of sampling before the filter is about 250°C, after the filter about 150°C. For analysis, 100 mL syngas at the flow-rate 100 mL min^{-1} were sampled and 100 mg of the shaken-out char from the filter were sampled.

B. Tar sampling device

A tar sampling device consisting of two consecutively joined columns with adsorbents was made particularly for the present research (Fig. 1).

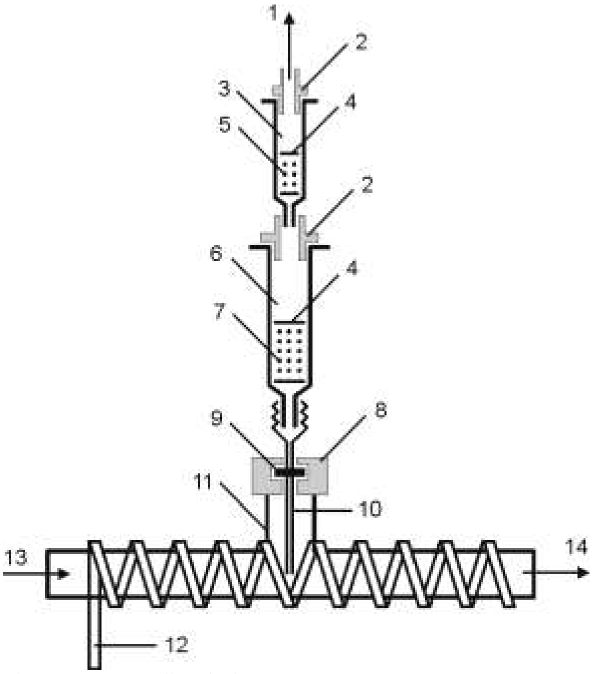

Fig. 1. A tar sampling device.
1 - connection to a pump, 2 - adapter (polypropylene), 3 - sorbent column (polypropylene, 1 mL), 4 - fritted disc (polyethylene), 5 - activated coconut charcoal, 6 - sorbent column (polypropylene, 4 mL), 7 - amino-phase sorbent, 8 - septum nut (polyethylene), 9 - rubber/silicone septum, 10 - hypodermic needle (stainless steel), 11 - glass “Tee” tube, 12 - heating tape, 13 - product gas inlet, 14 - connection to electric pump.

The first column was a 4 mL solid-phase extraction adsorbent cartridge with 500 mg of loosely packed aminopropyl-bonded silica adsorbent (the surface area was about 400–600 m^2 g^{-1}, the particle size was 50 µm, the average pore size was 60 Å, from Alltech). The second column was a 1 mL SPE adsorbent cartridge (Alltech) with 100 mg of activated coconut charcoal (the surface area was 1070 m^2 g^{-1}, the particle size was 20/40 mesh, 420–840 µm, from SUPELCO) packed loosely.

Using an insulated heating tape to minimize tar condensation, the “Tee” tube was heated to 250°C. The product gas was drawn through the heated tube with the help of an air sampling pump (SKC). A required volume (depending on tar concentration) of product gas at ~atmospheric pressure was sampled with a mass flow rate regulator and a specific gas vane-type pump at the constant flow rate of 100 mL min^{-1}. The product gas with tar was drawn into the first adsorbent cartridge with the amino-phase adsorbent. The core amount of the compounds such as indene, naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene was adsorbed in the first adsorbent cartridge, while volatile organic compounds, mainly benzene and toluene, were drawn with syngas into the second adsorbent cartridge loaded with activated coconut charcoal. After sampling, the inlet and outlet sides of the cartridges were sealed with plastic stoppers.

C. Sample preparation

There are two procedures, one for the amino-phase sorbent by column extraction with dichloromethane/acetonitrile and the second for the activated charcoal sorbent by solvent extraction. The following applies to the first column. The inlet of the adsorbent cartridge was connected to a reservoir (an empty adsorbent column). The cartridge was positioned vertically in a stand exactly above a vial (1.8 mL) placed on a laboratory jack. The internal standards dissolved in dichloromethane were added to the reservoir. The fraction containing aromatic compounds was eluted with 3×600 µL of dichloromethane. The fraction containing phenolic compounds was eluted with 3×600 µL of dichloromethane/acetonitrile (1:1 v/v). Dichloromethane or dichloromethane/acetonitrile was drawn through the amino-phase adsorbent by means of a 100 mL syringe. The sorbent from the second column was placed in separate vials, 1.8 mL each; 1.0 mL of carbon disulfide was added to each vial, and crimp caps were immediately attached to each vial. The vials were allowed to stand for at least 30 min with occasional agitation.

The char shaken out from the filter was analyzed similarly to activated coconut charcoal: 100 mg char was placed in separate vials, 1.8 mL each; 1.0 mL of carbon disulfide was added to each vial, and crimp caps were immediately attached to each vial. The vials were allowed to stand for at least 30 min with occasional agitation.

D. Analysis

A Shimadzu GCMS-QP2010 system (Shimadzu Corporation, KYOTO, Japan) was used for the analysis. The gas chromatograph was equipped with an electronically controlled split/splitless injection port. GC was carried out on a 5% diphenyl-/95% dimethylpolysiloxane fused-silica capillary column (Rtx-5SIL-MS, 30 m×0.32 mm, 0.25 µm film thickness; Restek). Helium (99.999%) was used as the carrier gas, at a constant flow of 1.6 mL min-1. The injection (injection volume of 1 µL) was performed at 250°C in the split mode, split ratio 1:10. The oven temperature program was as follows: the temperature was held at 30°C for 5 min, then 30–180°C at the rate of 10°C min^{-1}, 180–300°C at the rate of 15°C min^{-1}, and finally held at 300°C for 5 min. The mass spectrometer was operated in the electron ionization mode (ionisation energy of 70 eV). The source and transfer line temperatures were 200 and 310°C respectively. Detection was carried out in the scan mode: m/z 35–300.

E. Calibration and quantification

Calibration method with internal standards was used for analysis. For mixing standard solutions, standard compounds most common in biomass gasification tar were used: benzene, toluene, xylenes, phenol, indane, indene, cresols, naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, and benzo(a)pyrene. Deuterated compounds benzene-d_6, phenol-d_6 and naphthalene-d_8 were used as internal standards. Calibration curves were performed with five points, each of them realised in triplicate. The criteria for the linear regression (R^2) were a minimum of 0.995 according to [7]. Five calibration mixtures were made using pure standards of the compounds to be quantified and a known amount of internal standards added to each calibration mixture and to the studied samples. All areas were measured and referenced to the area of the internal standards. To determine concentrations of the tar compounds that were not among the quantified ones, the response factor of the quantified compound with the retention times closest to the unquantified compound was used. The total tar concentration (mg m^{-3}) was calculated as a sum of concentrations of all identified and quantified compounds.

III. RESULTS AND DISCUSSION

A. Sampling in different conditions of biomass gasification

The present research studied dependence of the concentration of the total tar and its individual components in syngas on the temperature of the reactor. Sampling was performed before the charred filter. While changing the biomass – air ratio, varying temperature of the reactor was obtained. Sampling was performed 30 min after the change of parameters and the following change of temperature, i.e. the time necessary for stabilization of all parameters including the syngas composition. The reactor temperature was gradually increased from 800°C to 1050°C with the interval of 50°C. Moreover, the temperature of syngas in the point of sampling was practically unchanged, about 250°C, which is connected with the fact that syngas was going through heat exchangers. 100 mL syngas was drawn through sorbents at the flow-rate 100 mL min^{-1}.

Tables I and II contain concentration of the total tar and some of its components in the syngas in different conditions of gasification. Compounds whose concentration is not less than 1 per cent of the total tar amount were selected for comparison.

In course of experiment, concentration of the total tar in syngas varied with the change of gasification conditions which were registered as the change of reactor temperature.

Table I
Concentration of the total tar and some compounds in syngas (mg m-3) at the gasification temperature 800–900°C. Average values and standard deviations are given for three replicate runs

Compound	Reaction temperature		
	800°C	850°C	900°C
Total tar	370.3±15.3	369.2±12.7	382.9±17.2
Benzene	283.7±10.1	279.8±14.6	289.1±16.3
Toluene	21.93±1.22	21.81±1.47	22.93±0.97
Naphthalene	30.41±2.03	30.19±1.29	31.01±2.11
Acenaphthylene	5.28±0.47	5.42±0.38	5.25±0.29
Acenaphthene	3.84±0.19	4.02±0.33	4.29±0.41
Phenanthrene	3.71±0.30	3.95±0.35	4.33±0.29
Pyrene	4.21±0.22	4.48±0.40	4.99±0.21

Table II
Concentration of the total tar and some compounds in syngas (mg m-3) at the gasification temperature 950–1050°C. Average values and standard deviations are given for three replicate runs

Compound	Reaction temperature		
	950°C	1000°C	1050°C
Total tar	388.3±17.9	352.6±11.6	338.7±10.9
Benzene	291.6±19.1	262.2±15.0	252.2±12.3
Toluene	22.81±1.61	20.19±1.08	19.66±0.79
Naphthalene	31.59±1.87	29.03±1.62	27.66±1.90
Acenaphthylene	5.73±0.50	5.33±0.44	5.05±0.28
Acenaphthene	4.69±0.38	4.48±0.35	4.13±0.26
Phenanthrene	4.63±0.31	4.39±0.51	4.01±0.29
Pyrene	5.01±0.45	4.80±0.26	4.51±0.41

With an increase of temperature from 800°C to 950°C, the total tar amount slowly goes up whereas with a further temperature increase it goes down. Similarly, the temperature increase changes the ratio of volatile and heavy tar components, namely the part of volatile components decreases and that of heavy components grows. For example, the proportion of benzene slowly changes from 76% to 74% with temperature increase, the proportion of naphthalene, about 8.2%, has practically not changed whereas the proportion of pyrene increased from 1.14% to 1.33%. This proves that amount and composition of tar depends not only on the biomass composition but also on the conditions of its gasification.

B. A study of filter effectiveness

Given the results obtained from the study of the dependence of tar concentration on the reactor temperature, the following gasification parameters were selected for the investigation of filter effectiveness: reaction temperature reaches ~900°C, the mass of dry peat is ~250 kg $hour^{-1}$, the mass of air ~120 kg $hour^{-1}$. Sampling was performed simultaneously before the filter with the temperature of syngas 250°C, and after the filter, with the temperature of syngas 150°C. Only those compounds that were discovered in syngas after it passed the filter were selected for further comparison; besides, concentration of the total tar in syngas before and after the filter was analysed.

Table III shows concentrations of the total tar and selected compounds before the syngas passed through the filter, and amount of each compound in the total tar in per cent.

Table III
Concentration of total tar and some compounds in syngas before filter. Average values and standard deviations are given for three replicate runs

Compound	Concentration before filter	
	mg m^{-3}	%
Total tar	395.3±14.5	100.0
Benzene	298.5±12.3	75.5
Toluene	24.33±0.88	6.2
Indene	2.12±0.25	0.5
Naphthalene	32.46±2.45	8.2
Acenaphthylene	5.82±0.42	1.5
Acenaphthene	4.71±0.36	1.2
Fluorene	1.87±0.21	0.5
Phenanthrene	4.93±0.33	1.2
Anthracene	2.75±0.19	0.7
Fluoranthene	1.35±0.17	0.3
Pyrene	4.75±0.41	1.2

Table IV shows concentrations of the total tar and selected compounds after the syngas passed through the filter, and removal effectiveness in percent for each compound. Before the filter, 25 compounds were identified, with benzene and toluene discovered on both amino-phase sorbent and on coconut charcoal whereas all other compounds were found only on the amino-phase sorbent. In the syngas sampled after the filter, only 11 compounds were found, all of them on the amino-phase sorbent. This can be accounted for by a relatively low syngas temperature (150°C) and small concentration of tar in it.

Table IV
Concentration of total tar and some compounds in syngas after filter and effectiveness of removing these compounds from syngas with the help of a filter. Average values and standard deviations are given for three replicate runs

Compound	Concentration after filter		Adsorption efficiency
	mg m^{-3}	%	%
Total tar	41.29±3.20	100.0	89.6
Benzene	13.88±1.62	33.6	95.4
Toluene	22.39±1.93	54.2	8.0
Indene	0.23±0.03	0.6	89.2
Naphthalene	2.52±0.29	6.1	92.2
Acenaphthylene	0.57±0.06	1.4	90.2
Acenaphthene	0.53±0.04	1.3	88.7
Fluorene	0.14±0.02	0.3	92.5
Phenanthrene	0.39±0.05	0.9	92.1
Anthracene	0.24±0.02	0.6	91.3
Fluoranthene	0.11±0.02	0.3	91.9
Pyrene	0.29±0.04	0.7	93.9

Effectiveness of tar removal from syngas with the help of the filter for adsorbing char was within 90%. Effectiveness of adsorbing individual compounds on char is likewise, with no dependency of adsorption on how volatile a compound is. Effectiveness of benzene adsorption appears slightly higher, 95%, while adsorption effectiveness of toluene was abnormally low, only 8%.

Table V contains the mass in μg of the total tar and compounds under study per 100 mg of char shaken out from the filter after the syngas passed through it. It was found that the char adsorbed 36 compounds, i.e. more than the sorbents while sampling syngas. This can be explained by the fact that while passing through the filter, syngas is in contact with it for a longer period of time than it is with the sorbents during sampling. That is why it appears possible to discover on char those compounds whose concentration in syngas is very low.

Table V
Amount of total tar and some compounds per 100 mg of char shaken out from the filter. Average values and standard deviations are given for three replicate runs

Compound	Per 100 mg char	
	µg	%
Total tar	1416±117	100.0
Benzene	1264±106	89.3
Toluene	6.14±0.47	0.4
Indene	4.64±0.39	0.3
Naphthalene	62.83±3.20	4.4
Acenaphthylene	8.03±0.58	0.6
Acenaphthene	6.83±0.37	0.5
Fluorene	3.51±0.27	0.2
Phenanthrene	6.44±0.39	0.5
Anthracene	5.86±0.41	0.4
Fluoranthene	4.42±0.40	0.3
Pyrene	7.28±0.42	0.5

Table V also contains percentage of each studied compound in tar. As was expected, the amount of toluene in the total tar discovered on char is very small. It explains why concentration of toluene in syngas sampled before and after the filter is practically the same. Inability of the filter to adsorb toluene is not a big disadvantage as toluene has practically no influence on the tar dewpoint. A higher proportion of benzene in the total tar adsorbed on char in comparison to its proportion in the syngas tar had also been expected because effectiveness of removing benzene from syngas with the help of char is the highest among other compounds.

IV. CONCLUSION

The research showed that the filter for removing char from syngas proved quite cheap and effective in removing tar from syngas. Concentration of the total tar in the samples taken after the filter for removing char from syngas decreased by nearly 90% comparing to the total tar concentration in the samples taken before it. While 25 compounds were identified in the syngas sampled before the filter, only 11 compounds were identified after the filter. Toluene radically differs from other tar compounds in the ability to be adsorbed by char. Up to 95% of toluene passes through the char without being adsorbed; hence the concentration of toluene in the syngas samples taken before and after the filter is practically the same. The fact that the char does not adsorb toluene is not a disadvantage since toluene is not a problematic compound in the real biomass gasification gas. Its combustion is clean and results in no clogging, so a complete removal of toluene is not required.

An improved solid-phase adsorption system consisting of amino-phase sorbent and activated coconut charcoal is a very convenient and effective device for sampling tar in syngas. If its concentration in syngas is high, light tar compounds such as benzene, toluene, and xylenes are adsorbed on both sorbents, the other ones only on the first sorbent. With a low concentration of tar in syngas, all compounds might be adsorbed only on the first sorbent.

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