Influence of Freeboard Temperature, Fluidization Velocity and Particle Size on Tar Production and Composition during the Air Gasification of Sewage Sludge

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Abstract

The influence of freeboard temperature, fluidization velocity, and particle size on tar production and composition during the air gasification of dried sewage sludge has been researched using a bench-scale gasifier. Of the operating variables analyzed, the results obtained from a statistical analysis (ANOVA and PCA) indicate that only the freeboard temperature has a significant influence on tar production. The results also show that freeboard temperature is the key factor that influences the tar composition. A high freeboard temperature reduces the amount of tar produced, but the tar compounds obtained are mainly PAH, which could require a more complicated secondary treatment for tar removal. Nevertheless, an increase in the freeboard temperature value implies a substantial increase in both low heating value and cold gas efficiency (6.5% and 10.8%, respectively, when the required freeboard temperature was increased from 873 to 1123 K). Future studies should focus on testing/developing catalytic materials able to degrade (in a secondary treatment) tar with a high content of PAH compounds.

Keywords

Sewage Sludge; Air Gasification; Fluidized bed; Tar; ANOVA; PCA.

Introduction

Gasification of sewage sludge has been investigated during recent years as a possible route for managing this waste safely while at the same time producing a gas with a certain heating value.[1] However, it is well known that the main drawback of this technology is related to the high tar and dust content of the synthesis gas produced. An accepted definition of tars in biomass gasification includes all organic compounds with a molecular weight heavier than benzene.[2] Tars are responsible for major operational problems due to their condensation that inhibits the use of gas obtained from gasification in engines or turbines without further expensive gas cleaning. In addition, the high toxicity level of condensate and scrubber water involves a critical increase of waste-water treatment costs if a wet gas cleaning method is used.[2] For all these reasons, tar removal has been a focus of great interest in the field of biomass gasification in recent years.

Some tar components are more problematic for gas applications than others. The condensation phenomenon depends on the total amount of tar and its composition.[3–4] Tars become more problematic during the hot gas cleaning process if the fraction of high-boiling compounds is considerable.[3] The effectiveness of measures adopted to reduce tar production could be limited if it is not known what kinds of compounds are present. For example, toluene and xylene are not very problematic for gas application; however, naphthalene is very inconvenient because this compound crystallizes at the inlet of gas engines. Heavy tars condense as the gas temperature drops causing the major fouling problems.[2] Furthermore, the presence of tar components with a large number of aromatic rings can benefit coke formation, which is also undesirable.[5]

Tar removal technologies can broadly be divided into two approaches: treatments inside the gasifier (primary methods), aimed at the production of a gas as free of tar as possible, and gas cleaning after the gasifier (secondary methods).[6] Primary methods include all measures taken within the gasifier to prevent tar formation or convert any tar formed. An ideal primary method would avoid the need for a secondary treatment.[6] Devi et al.[6] enumerate three points to be taken into account in order to develop an effective primary method: a proper selection of the operating conditions, an in-bed use of additives or catalysts and, finally, an optimal gasifier design.

One of the main current research activities of the Thermochemical Processes Group of the University of Zaragoza is focused on the first critical point suggested by Devi and coworkers. As a result of these investigations, the influence on tar production of several operating parameters (equivalence ratio, bed temperature, bed height, and transition period) have been extensively discussed in previous papers.[7–9] The specific aim of this study is to analyze the tar production during the air gasification of dried sewage sludge as a function of three additional parameters (particle size, freeboard temperature, and fluidization velocity) by means of an experimental study, which can provide useful information in order to identify operating conditions which improve tar reduction. In this scenario and taking into account the above-mentioned considerations regarding the tar characterization, the influence of these selected variables on tar composition has also been studied.

Experimental Section

Materials

Sewage sludge samples obtained from a waste-water treatment plant and previously treated by both anaerobic digestion and thermal drying processes were used in the present study. Proximate and ultimate analyses of the received sewage sludge are shown in Table 1. The low heating value (LHV) has also been determined by means of a calorimeter IKA A-2000 (standard procedure: ISO-1928-89). The value obtained for LHV was 10.77 MJ kg^{-1}. These analyses were performed by the *Instituto de Carboquímica* (CSIC, Zaragoza, Spain). The samples of dry sewage sludge (DSS) were obtained as a dried, granular product and were crushed and sieved to provide two different feed sample sizes: one ranging from 250 to 500 μm, and the other from 500 to 800 μm.

Silica sand was used as the initial bed material. Additionally, and in order to improve the fluidization process, an additional amount of silica sand (20% of the DSS flow rate) was continuously fed to the reactor system. The particle size corresponding to the sand used in both cases was in the range 250–350 μm ($u_{\mathrm{mf}} = 3.7 \pm 0.1$ cm s^{-1} at 1123 K).

Laboratory scale BFB gasifier

Experiments were performed in a laboratory scale plant operating at atmospheric pressure, feeding continuously sewage sludge and air, and with a continuous ash removal system. Figure 1 shows a diagram of the system.

The reactor is made of refractory steel (AISI 310), with an inner diameter of 38.1 mm and a height of 800 mm. Biomass is fed by a variable speed screw feeder, entering the reactor 10 mm above the distributor plate. About 33% of the gasification air is diverted to the screw feeder, thus helping the solid to enter the reactor, while the other 67% enters through the distributor plate. The bed height remains constant at 300 mm, by means of a concentric pipe which goes through the distributor plate, enabling the bed material to overflow and be collected in an ash hopper. The reactor is heated by an electrical furnace. Beyond the reactor, a small cyclone removes particles entrained by the gas produced. Then, a heated filter system is used to separate the fine particles from the sample raw gas. A glass fiber thimble is located inside a stainless steel tube. The operating filter temperature is fixed at 673 K in order to prevent tar build-up.[10] The gas leaving the heated filter is cooled in two ice condensers, where most of the tar and water are collected. Finally a cotton filter is provided. Gas production was measured by a volumetric gas meter and the gas composition was determined by means of a micro gas chromatograph (Agilent 3000A) connected online to the process.

Recovery and characterization of tars

The tar and water condensed inside the glass traps were quantified by weight difference at the end of the experiment. This mixture was recovered using 100 g of 2-propanol. Water was determined off-line using a Karl Fischer titration and tar was calculated by difference.

A sample of the mixture formed by tar, water, and 2-propanol was dried using anhydrous sodium sulfate and filtered prior to analysis of the tar composition by means of a gas chromatograph. To identify and quantify the tar components, a method has been developed using GC/MS (GC HP-5890) and GC/FID (GC Agilent-6890).[9] The same Agilent HP-5 column (30 m × 320 µm capillary column coated with 0.25 µm film of 5% phenilmethilxilosane) was used in both chromatographs. An initial oven temperature of 323 K and a ramp rate of 4 K min^{-1} were implemented to reach a final column temperature of 523 K. This temperature was maintained for 10 min. The carrier gas was helium at a linear flow velocity of 0.19 m s^{-1}. The FID gas flows (measured under normal conditions) were 40 mL min^{-1} for hydrogen, 450 mL min^{-1} for air, and 50 mL min^{-1} for nitrogen as the make-up gas. The injector and detector temperature were 523 K and 548 K, respectively. The sample was injected in splitless mode.

A large number of compounds were expected to appear in the chromatogram. GC/MS was used in order to identify the compounds contained in the tar, and GC/FID was used to quantify the different compounds obtained. The FID detector has a high sensitivity and linearity and gives a proportional response to mass for most of the typical compounds present in tar obtained from gasification.[11] In the present work, a semi-quantitative analysis was made to analyze the influence of the three selected operating conditions on the relative proportions of several compounds contained in the tar mixture. Calibration was not carried out due to the large number of compounds in the sample. This semi-quantitative approach has been followed in various studies[12–13] and is only useful for comparative purposes.

Experimental design

The influence of the experimental conditions on the gasification products of sewage sludge in a fluidized bed was studied experimentally using a factorial design. This method is suitable for studying the influence of the experimental variables and also the influence of their interactions on tar production and composition. In terms of experimental design, the experimental variables studied are called factors and the results obtained are called response variables. The chosen factors are shown in Table 2.

To reach a given freeboard temperature value, the corresponding set point is transferred to a PID controller which adjust the power supplied to an electrical resistance. The experimental value of the freeboard temperature when the steady-state is achieved is usually lower than its set point. The evolution of the experimental freeboard temperatures as a function of their set point values is illustrated in Figure 2.

For statistical computing and testing, the freeboard temperature set point values were considered as factors. The average values of the real freeboard temperatures and their respective standard deviations are shown in Table 3.

The fluidization velocity was studied as the relation between the superficial gas velocity (u_f) and the minimum fluidization velocity (u_{mf}) for the sand particles used. Both freeboard temperature and fluidization velocity ratio are numerical factors, while the particle diameter is defined as a categorical factor (is not a continuous factor): a small particle size (250–500 μm) and a bigger one (500–800 μm).

In the present work, a full two level factorial design was selected. This means that 2^n runs were conducted, where *n* indicates the number of factors studied. For three factors considered, this design involves eight experiments. To evaluate the experimental error and the possibility of curvature during the evolution of a given response variable, two replicates in the center point were added. In this case, the number of center points is duplicated at both the low and high levels of each categorical factor. Thus, the total number of experiments carried out is equal to twelve.

The response variables can be divided between tar production and tar composition. To study tar production, the response has been defined as the relation between grams of tar and grams of DSS fed. To study the tar composition, the area percentage obtained from FID analysis has been used to compare similar compounds. As has been mentioned before, these results are not absolute and are only useful for comparing similar compounds.

Table 4 shows the scheduled operating conditions for all experiments performed at the same bed temperature (1123 K), and at an equivalence ratio value, λ, of approximately 30%. The equivalence ratio is defined as the ratio between the experimental flow rate of air and the stoichiometric flow rate required for the complete fuel combustion. In order to keep the stoichiometric flow rate constant at the same time as the superficial air velocity changes, a specific nitrogen flow rate was mixed with the air flow fed to the system.

The experimental results obtained for each response variable were analyzed statistically using Design Expert software (v. 7.0) and Minitab (v. 14.1). In a first stage, the standardized Pareto´s diagram was used to observe the estimated effects of these variables and their possible interactions. A Pareto chart is a special type of bar chart where the values plotted are arranged in descending order.[14] Analysis of Variance (ANOVA) was then used to study the influence of the variables and their possible interactions on the tar production and composition. To consider an effect as significant, a confidence level of 95% for the F-distribution was selected. A detailed explanation of the ANOVA method can be found elsewhere.[15]

Finally, Principal Component Analysis (PCA) was applied to support the interpretation of the data and obtain quick information about the similarities in a group of experiments.[16] Cluster analysis is an additional multivariate technique that allows the grouping of experiments based on similarities using several variables simultaneously.[17]

Once the analysis of which variables have a significant influence on tar composition and tar production was completed, the influence of those variables on additional gasification parameters was investigated. The parameters studied were: experimental equivalence ratio (λ_{exp}), average gas composition (dry basis), specific yield to gas obtained on a daf basis (y_{gas}), low heating value of the product gas (LHV), average cold gas efficiency based on LHV of gas and solid waste (η), average percentage of carbon in the biomass recovered in the gas (y_{carbon}), and mass products distribution based on the biomass fed.

In order to study the above-mentioned parameters, three additional experiments (13–15) were performed. The operating conditions corresponding to these additional gasification tests are also reported in Table 4.

Results and Discussion

The results presented in this section are analyzed in two parts:

1. The influence of freeboard temperature, particle diameter, and fluidization velocity on both tar production and tar composition is extensively studied. First, statistical results obtained from ANOVA analyses for the global tar production are discussed. Subsequently in order to study the tar composition, a classification by similar groups of compounds is presented. Based on this classification, the tar production within each group is also analyzed. In particular, the trends statistically deduced for the naphthalene production, which is the main tar component, are discussed. Finally, Principal Component Analysis (PCA) and Cluster analysis were applied to support the interpretation of the data.
2. Results obtained from an additional series of experiments allow us to examine the evolution of several gasification parameters as a function of the variables that resulted statistically significant for tar production and composition in the first part of this section.

Influence of freeboard temperature, particle diameter, and fluidization velocity on tar production

The first outcome studied was the tar production, defined as gram of tar obtained per gram of sewage sludge fed. Table 5 reports the corresponding results obtained from the experiments performed.

From the Pareto´s standardized chart displayed in Figure 3, it can be observed that the main influence on tar production was the freeboard temperature. Both particle diameter and fluidization velocity have opposite effects. The particle diameter produces an increase in the tar production while the fluidization velocity results in a decrease to a similar degree. Nevertheless, their influence is lower than that of the freeboard temperature.

From Figure 3 the relative importance of the variables and their interactions can be deduced. The conclusion reached from the ANOVA analysis is that only the freeboard temperature has a significant effect on tar production in the range of variable values studied. Figure 4 shows the main effect plot of the freeboard temperature on tar production, and the different values of tar obtained for each level of the selected variable. As can be seen in Figure 4, a freeboard temperature increase produces a decrease in tar production. This trend has already been observed in previous studies involving gasification of several biomass feedstocks[18–19] and could be explained by the fact that a higher freeboard temperature could improve the cracking reactions of the tar in this part of the reactor.

Nevertheless, we must remark that the quantity of tar obtained is not the only most important parameter. Tar composition is as important as tar production. The tolerance of the different applications of the gas produced with respect to the tar content depends to a great extent on the composition of tar. For this reason, the effect of the operating conditions on tar composition must also be analyzed.

Influence of freeboard temperature, particle diameter, and fluidization velocity on tar composition

Around 75% of the proportion of the tar produced that can be analyzed by gas chromatography has been identified. Figure 5 shows a typical chromatogram corresponding to a sample of tar obtained from a given sewage sludge gasification experiment. To analyze the influence of the three selected factors, the detected tar compounds have been grouped according to their chemical nature. The classification reported by the Energy Research Center of The Netherlands (ECN),[2] which is based on solubility and condensability of different tar compounds, has been taken into account in the present study to establish the groups of major components reported in Table 6.

Tars containing hetero atoms (N, S, O) are very highly soluble in water, causing waste-water problems. In general, light aromatic compounds (with a single ring) do not pose a major problem for gas application. However, the light and heavy polyaromatic hydrocarbons compounds (PAH) are the most problematic because they can condense even at very low concentrations. [11] Devi et al.[4] conclude that light polyaromatic compounds which have two or three aromatic rings are the least reactive and, consequently, need a severe treatment. Regarding heavy PAH compounds, it is important to note that some species with a large molecular weight cannot be detected by CG analysis. Because of this limitation of the applied analytical technique, the heavy PAH fraction will not be taken into account in the present work.

Table 7 shows the results corresponding to tar composition expressed as chromatogram area percentage. Unlike another types of biomass [3–4,] , the tar obtained from gasification of sewage sludge has a high percentage of nitrogen-containing aromatic compounds due to the large amount of nitrogen contained in the sewage sludge as a consequence of the presence of proteins and nucleic acids. Furthermore, additional nitrogen-containing aromatic compounds could be formed during the gasification process due to the direct incorporation of HCN into organic molecules in secondary reactions.[20] A high percentage of PAH compounds is expected taking into account the operating bed temperatures reported in the present work.[2] The low value of oxygenated aromatic compounds is in agreement with the bed operation temperature (1123 K). In this context, Kinoshita et al.[21] observed that compounds containing oxygen exist in significant quantities only at temperatures below 1073 K.

Figure 6 displays the estimated effects of the variables and their interactions on tar composition. As can be seen from this figure, the freeboard temperature has the most important effect on every parameter, except in the case of aromatics, where any variable has a relevant effect. The ANOVA analysis gives the additional information shown in Table 8, about which of these parameters affect the results in a significant way. From findings set out in this table, a preliminary consideration can be made: the particle diameter does not in itself have a significant effect on tar composition. This result is not in agreement with another work by other authors, where a higher particle size was used.[3] Padban et al.[3] assumed an influence of the particle size on the tar characterization. These authors explained that this influence could be due to the fact that a small particle suffers reactions in the higher reactor level, where the atmosphere is more reducing. In this way, the diffusion of the volatiles from smaller particles is faster and the cracking process becomes less severe than in the case of particles with a bigger size.

Figure 7 shows that an increment in the freeboard temperature leads to a sharp increase in the percentage of light PAH compounds in the tar mixture, while implying a less sharp decrease in the percentage of oxygenated aromatic compounds. In this sense, Kinoshita et al.[21] found similar trends when varying the operation temperature in the fluidized bed.

From Figure 7b it can be deduced that the oxygenated aromatic percentage could reach a maximum at a temperature close to 998 K. It would be necessary to extend the experimental design in order to find the exact maximum. Nevertheless, in the present work it is not desirable to maximize the oxygenated compound percentage, but quite the opposite. The tar poorest in such compounds is found at 1123 K as shown in Figure 7b.

In the case of nitrogen-containing compounds, the effect of the freeboard temperature varies according to the fluidization velocity. From Figure 8 it can be seen that the nitrogen-containing aromatic percentage in the mixture is affected by the freeboard temperature, the u_f/u_{mf} ratio and their interaction. The percentage is lower at the highest fluidization velocity tested for the lowest freeboard temperature tested. However, at the higher freeboard temperature, the effect of the u_f/u_{mf} ratio can be assumed negligible, as is shown by the overlapping error bars.

Figure 9 shows the different composition of tar as a function of the freeboard temperature values. The main observed difference is that operating at a high freeboard temperature means that the generated tar is richer in PAH compounds, whereas the higher percentage of nitrogen-containing compounds is found in tar produced at lower temperatures.

The collected data shown in Table 7 were also submitted to Principal Components Analysis (PCA). The PCA avoids intercorrelation between closely linked variables, and is useful in order to see if there is any grouping in the data and to visualize any relationship among the variables.[16] Components with eigenvalues higher than 1.0 were retained. The PCA solution contains 2 components and accounts for 97.8% of the total variability. The resulting score and loading plots are shown in Figure 11. The loading plot corresponding to the principal component factor analysis was obtained applying a varimax rotation.

To complete the multivariate analysis, the dendrogram corresponding to the Cluster analysis performed with the same data set is shown in Figure 12. A dendrogram connects similar objects by U-shaped lines. The height of each U represents the distance between the two objects being connected. This corresponds, in our case, to the squared Euclidean distances between each pair of observations using the Ward’s linkage method.

The results obtained from the statistical multivariate analyses support the considerations previously suggested in light of the ANOVA findings, and show that there is no other operational variable which may have affected the results and which have not been taken into account in the ANOVA analysis.

The dendrogram displayed in Figure 12 shows a substantial difference between the experiments performed at a set point freeboard temperature value of 1123 K and the rest of the gasification tests. Moreover, the interpretation of both the dendrogram and score plot (see Figure 11a) reveals that it is very difficult to identify similarities between the experiments as a function of the fluidization velocity ratio and/or the particle size. Concerning the loading plot corresponding to Figure 11b, a strong opposite correlation can be deduced between the light PAH compound content and the nitrogen-containing aromatic content.

Influence of freeboard temperature, particle diameter, and fluidization velocity on naphthalene percentage in tar

Naphthalene is the main compound of the tar obtained and it is also one of the most stable and hard to destroy.[5,22] In addition, naphthalene is significant because it crystallizes at the inlet of gas engines. Furthermore, naphthalene poses a great ecotoxicological problem.[23] For all these reasons, it has been analyzed separately in order to find out the influence on this compound of the variables studied in the present work. Table 7 reports the percentage of naphthalene in the mixture of tar obtained in the set of experiments performed. The corresponding ANOVA analysis shows again that the only factor that affects the response variable (in a significant manner) is the freeboard temperature. Figure 10 shows the observed effect. The trend is similar to that observed for the light PAH group, in which naphthalene is included.

From the above-mentioned considerations, it may be concluded that the freeboard temperature is the analyzed variable that has the greatest effect on the tar production and composition. A low freeboard temperature value implies a high tar production level, but the compounds contained in the tar are easier to remove. In addition, the tar obtained at low freeboard temperatures is richer in nitrogen-containing compounds. This fact could lead to a way of avoiding a part of the nitrogen contained in sewage sludge from aiding ammonia formation. Nevertheless, some of the nitrogen-containing compounds obtained have the disadvantage of high solubility in water, causing problems in water disposal. On the other hand, a high freeboard temperature reduces the amount of tar produced, but the tar compounds obtained (mainly PAH) require a more complicated secondary treatment for achieving low values of tar composition in the produced gas.

There must be a compromise between the quality of the producer gas and the amount and composition of tar. To select an appropriate freeboard temperature it is important to know the influence of this parameter on the gas composition, gas yield and cold gas efficiency. This influence is discussed in the next section.

Influence of the freeboard temperature on the gasification process

The results presented in this section show the influence of the freeboard temperature on gasification efficiency. Table 9 reports the evolution of the analyzed parameters (mentioned above in the Experimental section) with the freeboard temperature for each experiment performed.

When the freeboard temperature increases, the tar production decreases and the specific yield to gas increases, as can be deduced from the data displayed data in Figure 13a. In addition, the influence of the freeboard temperature on the gas composition was more pronounced for temperature values above 998 K, except for C_2H_6 content, which decreases over the complete temperature interval (see Figure 13b). From the same figure, an increment of both H_2 and C_2H_2 content and a decrease in CO_2 content can be observed for temperatures above 998 K. Several researchers have suggested that the formation of C_2H_2 could be due to the decomposition of C_2H_6 and to the scission of aliphatic side chains and methylene bridges contained in molecules of tar with a large molecular weight.[24–25] According to this, the observed decrease in tar production at high freeboard temperatures could be explained by the removal of heavy tar molecules, which are not detected by gas chromatography. These heavy molecules could be cracked to form light PAH, which increase with the freeboard temperature as has been shown in Figure 7.

On the other hand, Figure 13c displays the evolution of the low heating value (LHV) of the producer gas and the average cold gas efficiency (η) as a function of the freeboard temperature. The highest value for both parameters was obtained at 1123 K.

Conclusions

Of the three operating variables analyzed in this study, the results obtained from the ANOVA analysis indicate that only the freeboard temperature has a significant influence on tar production during the air gasification of dried sewage sludge in a bubbling fluidized bed.

Taking into account that the tar composition plays as important a role in tar removal as important as its absolute production, the effect of selected operating conditions on tar characterization was also analyzed. The detected tar compounds were grouped into six categories and a semi-quantitative approach was applied in order to obtain the proportion of each group of compounds in the tar. The ANOVA analysis shows that the freeboard temperature has an influence on both the oxygenated aromatic and light PAH compound content.

In the case of the nitrogen-containing compounds, the ANOVA analysis reveals that the effect of the freeboard temperature varies as a function of the fluidization velocity ratio value, which has been observed as an interaction between these two factors. In other words, there is an interaction between these two operating variables. However, the effect of the fluidization velocity becomes weaker as the freeboard temperature value increases.

The influence of the selected variables was also analyzed over the main component of the tar obtained: naphthalene. In this case, the results are similar to those obtained for light PAH, in which naphthalene is included.

To reach a more reasoned interpretation of the experimental results concerning tar characterization, the collected data were submitted to PCA and Cluster analyses. The results obtained from the statistical multivariate techniques support the idea that the freeboard temperature is the key factor that influences the tar composition. In addition, the results from the principal component factor analysis suggest opposite effects of the light PAH compound content and the nitrogen-containing aromatic content.

We should notice that a high freeboard temperature reduce the amount of produced tar, but the nature of the tar obtained under these conditions would probably require a more complicated treatment for complete tar removal as a consequence of its high light PAH compound content.

Considering that the air gasification of the sewage sludge samples used in the present work produces a gas with a reduced heating value, the operating conditions under which the producer gas exhibits a reasonable low heating value should be taken seriously. In this scenario, an increase in the freeboard temperature value implies a substantial increase in both low heating value and cold gas efficiency (6.5% and 10.8%, respectively, when the required freeboard temperature was increased from 873 to 1123 K).

Assuming that a high freeboard temperature value is of interest, future studies should be focused on testing/developing catalytic materials which are able to degrade (in a secondary treatment) a tar with a high content of PAH compounds. Moreover, further works centered on the quantification of all tar species (including the heavy PAH compounds) are required in order to obtain more reliable tar characterization.

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Nomenclature

d_p:	Particle diameter (µm)
T_f:	Freeboard temperature (K)
$T_{f,\infty}$:	Set point freeboard temperature (K)
$T_{f\ mean}$:	Average values experimental freeboard temperature in a given experiment (K)
u_f:	Superficial gas velocity at the inlet of the gasifier bed (cm s^{-1})
u_{mf}:	Minimum fluidization gas velocity at the gasifier bed conditions (cm s^{-1})
y_{carbon}:	Average percentage of carbon in the biomass recovered in the gas (%)
y_{gas}:	Specific yield to gas obtained (NTP m^3 of dry gas/kg of daf DSS fed)

Greek Symbols

η:	Average cold gas efficiency based on LHV of gas and biomass (%)
λ:	equivalence ratio, defined as ratio between the experimental flow rate of air and the stoichiometric flow rate required for the complete fuel combustion (%)
λ_{exp}:	experimental equivalence ratio, (%)

Acronyms

ANOVA:	Analysis of variance
daf:	dry ash free basis
DSS:	Dried sewage sludge
FID:	Flame ionization detector
GC:	Gas chromatography
LHV:	Low heating value of the produced gas, dry basis
MS:	Mass spectrometry

PAH:	Polycyclic aromatic hydrocarbon
NREL:	National Renewable Energy Laboratory
PCA:	Principal components analysis
PID:	Proportional integral derivative

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Table 1. Ultimate, Proximate, and Metal Analysis of Dried Sewage Sludge Samples

Proximate	Analytical standard	% by weight	*Ultimate (organic fraction)*	Analytical instrument	% by weight (daf)
Moisture	ISO-589-1981	7.06	Carbon	Carlo Erba 1108	53.27
Ash	ISO-1171-1976	41.02	Hydrogen		7.02
Volatile	ISO-5623-1974	46.59	Nitrogen		7.55
Fixed Carbon	By difference	5.33	Sulfur		1.44

Table 2. Factors Selected to Perform the Factorial Design

Factor	Studied range
Set point value for freeboard temperature ($T_{f,\infty}$)	873–1123 K
Particle size	250–500 μm and 500–800 μm.
Fluidization velocity ratio (u_f/u_{mf})	6–8

Table 3. Average Values of the Experimental Freeboard Temperatures

$T_{f,\infty}$(K)	$T_{f\ mean}$ (K)	Standard deviation
873	795	±17.9%
998	940	±4.5%
1123	1111	±12.3%

Table 4. Summary of Operating Conditions for the Experiments Performed[a]

Test no	$T_{f,\infty}$ (K)	Particle size (μm)	u_f/u_{mf}
1	873	(250–500)	6
2	1123	(500–850)	6
3	873	(500–850)	8
4	998	(250–500)	7
5	998	(500–850)	7
6	998	(250–500)	7
7	998	(500–850)	7
8	1123	(250–500)	8
9	1123	(250–500)	6
10	873	(500–850)	6
11	1123	(500–850)	8
12	873	(250–500)	8
13	873	(250–500)	8
14	998	(250–500)	8
15	1123	(250–500)	8

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[a] Experiments 1-12 were performed using air as the gasification agent. Experiments 13-15 were performed using a mixture of O_2 and Ar in similar proportions to air (20% O_2).

Table 5. Tar Production during Experiments 1–12

Test no	$T_{f,\infty}$ (K)	Particle size (μm)	u_f/u_{mf}	λ_{exp} (%)	**Tar** (weight percentage of DSS fed)
1	873	(250–500)	6	31	10.2
2	1123	(500–850)	6	30	8.6
3	873	(500–850)	8	31	9.6
4	998	(250–500)	7	29	7.5
5	998	(500–850)	7	32	9.6
6	998	(250–500)	7	28	8.9
7	998	(500–850)	7	31	10.3
8	1123	(250–500)	8	30	8.6
9	1123	(250–500)	6	30	9.1
10	873	(500–850)	6	31	11.2
11	1123	(500–850)	8	29	8.3
12	873	(250–500)	8	28	10.0

Table 6. Major Components in the Tars Detected by GC/MS and GC/FID

Light Aromatic	Benzene, -ethenyl	**Sulfur-containing Aromatics**	Benzo[b]tiophene
	Benzene, -dimethyl		
	Benzene, -ethenyl methyl		
	Benzene, 1,3-diethenyl	**Oxygenated Aromatics**	Benzofurane
	Benzene, -ethinyl		Phenol
Light Polyaromatic Hydrocarbons	Naphthalene	**Nitrogen-containing Aromatics**	Pyridine
	Naphthalene, -2, methyl		Pyridine, 2-methyl
	Naphthalene, 1-methyl		Pyridine, 3-methyl
	Naphthalene, 1,5-dimethyl		Pyridine, 2-3, dimethyl
	Naphthalene, 1,8-dimethyl		Pyridine, 2-ethenyl
	Naphthalene, 2-ethenyl		Pyridine, 3-ethenyl
	Napthalene, 1-phenyl		Pyridine, 2-phenyl
	Naphthalene, 2-phenyl		Cyclobutapyridine
	1H-Indene		3-Pyridinecarbonitrile
	1H Indene, 1 methyl		Pyrrole
	1H-Indene, 1 methylene		1H Pyrrole, 2-methyl
	Anthracene		9H-Carbazole
	Anthracene, 2-methyl		Benzenoamine
	Phenanthrene		Benzenoamine, 2-methyl
	9H-Fluorene		Benzonitrile
	1,1 Biphenyl		Benzonitrile, methyl
	1,1 Biphenyl, 3 methyl		Benzonitrile, 2-methyl
	1,1 Biphenyl, 4 ethenyl		Benzonitrile, 4-methyl
	7H Benzocycloheptene		Benzenacetonitrile
	Acenaphthylene		1H-Indole
	Acenaphthylene, 1,2 dihydro		Pyrazine
			Pyrazine, methyl
Heavy Polyaromatic Hydrocarbons	11H Benzo[b]fluorene		Pyrazine, 2,3-dimethyl
	Benz[a]anthracene		Quinoline
	Fluoranthene		Isoquinoline
	Pyrene		1-Naphathalencarbonitrile
	Pyrene, 2-methyl		2-Naphthalencarbonitrile

Table 7. Tar Composition Obtained from Gasification Tests (1–12)

Test no	Light aromatic (% area)	Light PAH (% area)	Oxygenated aromatics (% area)	S-containing aromatics (% area)	N-containing aromatics (% area)	Naphthalene (% area)
1	6.0	24.6	2.4	1.0	44.0	11.8
2	2.9	36.9	0.8	0.8	31.2	17.4
3	3.0	30.5	3.5	0.8	36.1	11.5
4	1.8	34.0	3.3	1.0	36.0	13.2
5	3.6	29.3	3.2	0.9	37.5	12.9
6	5.7	26.6	4.8	0.7	42.0	11.0
7	5.0	31.5	2.0	1.4	36.6	15.4
8	3.9	41.1	1.2	1.5	30.7	19.2
9	3.1	48.2	0.0	1.3	26.0	14.7
10	4.1	24.6	1.5	0.9	44.4	11.9
11	1.3	44.6	0.0	1.6	29.0	19.7
12	3.0	30.8	1.3	1.1	34.4	9.1

Table 8. Significant Effects Obtained from ANOVA Analysis for Tar Composition

Compounds	**Significant effects**
Aromatics	–
N-containing Aromatics	T_f , u_f/u_{mf}, T_f-u_f/u_{mf}
Oxygenated Aromatics	T_f
S-containing Aromatics	–
Light PAH	T_f

Table 9. Experimental Results of Gasification Tests 13–15

Test no	13	14	15
u_f/u_{mf}		7.5	
λ (%)	28	28	31
$T_{f,\infty}$ (K)	873	998	1123
T_f (K)	808	932	1114
Average gas composition (% vol.dry basis)			
H_2	7.12	7.12	9.30
CO	8.45	8.20	8.03
CH_4	2.48	2.55	3.07
CO_2	15.82	16.40	13.23
C_2H_4	2.14	2.14	2.01
C_2H_6	0.19	0.14	0.07
C_2H_2	0.11	0.10	0.14
H_2S	0.12	0.11	0.07
y_{gas} (NPT m^3/kg of daf DSS)	1.83	1.89	2.00
LHV (kJ/NPT m^3)	4167	4129	4438
η (%)	53.55	51.26	59.31
y_{carbon} (%)	79.12	83.30	79.50
Product distribution based on the sludge fed (% weight)			
Produced Gas	79.57	81.66	86.77
Tar	9.36	8.73	7.52
Char	40.67	39.05	47.27
Water	11.54	13.13	12.39

Caption for Figures

Figure 1. Schematic diagram of the laboratory scale BFB gasifier.

Figure 2. Comparison between the steady-state freeboard temperature value (T_f) and its set point value ($T_{f,\infty}$).

Figure 3. Pareto´s standardized chart: effect of the operating conditions on tar production.

Figure 4. Freeboard temperature effect on tar production (The solid line represents the studied effect. The circles represents the experimental points).

Figure 5. An example of GC/FID chromatogram corresponding to a given sample of tar (experiment 4).

Figure 6. Pareto´s standardized chart: effect of the operating conditions on the tar composition; (a) aromatics, (b) nitrogen-containing aromatics, (c) oxygenated aromatics, (d) sulfur-containing aromatics, and (e) light PAH.

Figure 7. Influence of the set point freeboard temperature value on (a) light PAH percentage and (b) oxygen-containing aromatics percentage. For both graphics: the solid line represents the studied effect and the circles represents the experimental points.

Figure 8. Effect of freeboard temperature and fluidization velocity on nitrogen-containing aromatic compounds percentage. The solid line corresponds to a fluidization velocity ratio of 6 and the dashed line corresponds to u_f/u_{mf} = 8. The solid line represents the studied effect. The circles represents the experimental points obtained.

Figure 9. An example of tar composition corresponding to experiments 1 ($T_{f,\infty}$ = 873 K) and 9 ($T_{f,\infty}$ = 1123 K).

Figure 10. Influence of the set point freeboard temperature value on naphthalene percentage in the tar mixture. The solid line represents the studied effect. The circles are the experimental points obtained.

Figure 11. PC Analysis corresponding to the gasification experiments 1–12: (a) score plot and (b) loading plot obtained after applying Factor Analysis with varimax rotation.

Figure 12. Dendrogram corresponding to the Cluster Analysis performed with the data obtained from experiments 1–12.

Figure 13. Influence of freeboard temperature on (a) tar production and gas yield (square, tar; up triangle, y_{gas}), (b) gas composition, and (c) average cold gas efficiency and LHV (square, η; circle, LHV).

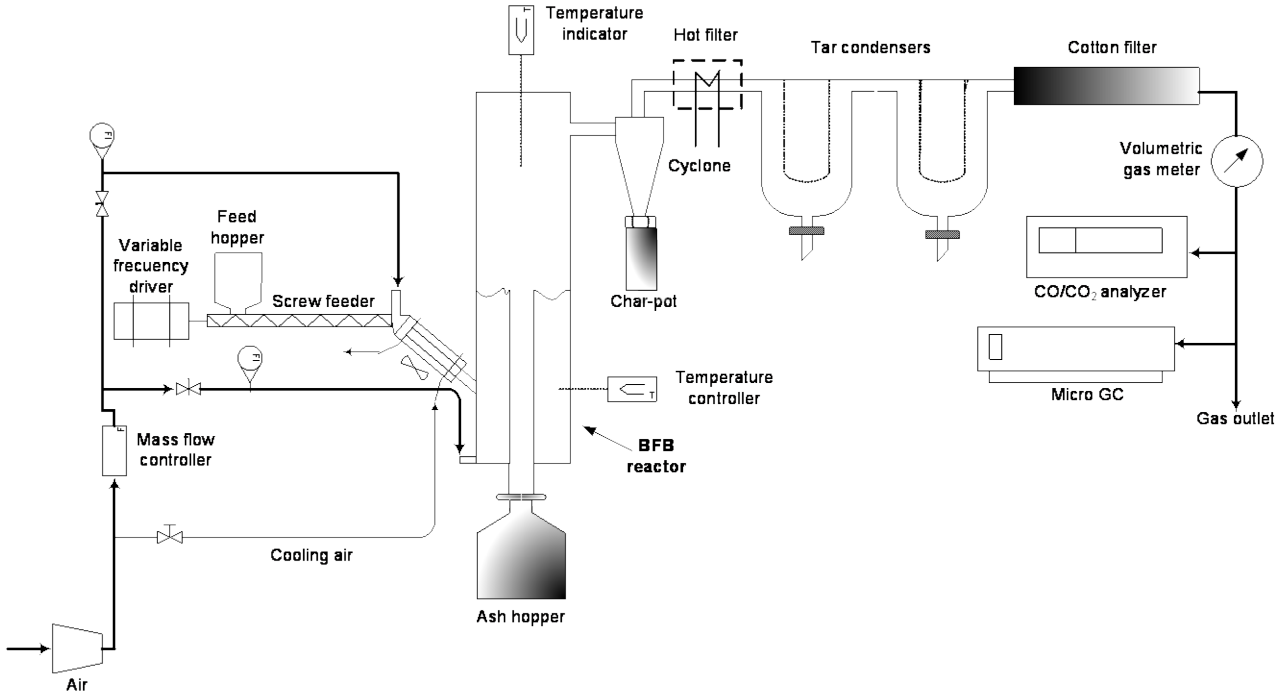

Temperature indicator
Hot filter
Tar condensers
Cotton filter
Volumetric gas meter
Cyclone
Char-pot
CO/CO_2 analyzer
Micro GC
Gas outlet
Feed hopper
Variable frecuency driver
Screw feeder
Temperature controller
BFB reactor
Mass flow controller
Cooling air
Ash hopper
Air

Figure 1

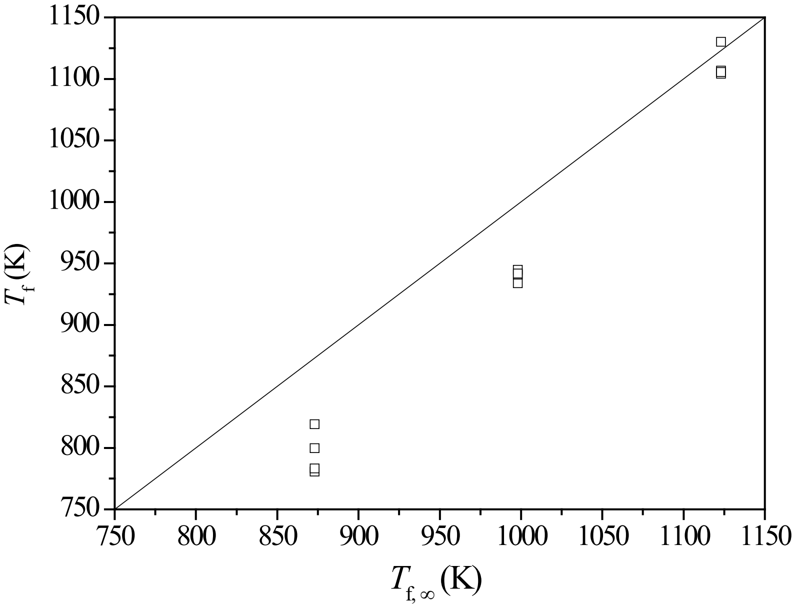


Figure 2

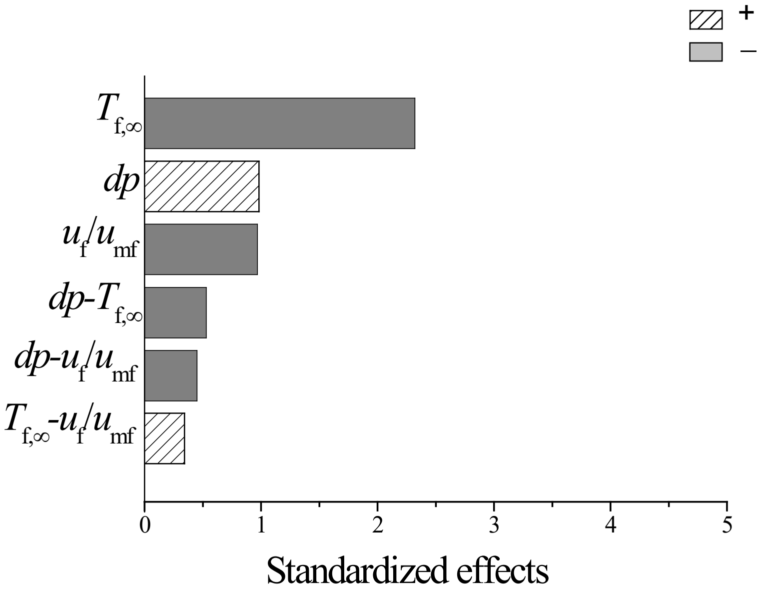
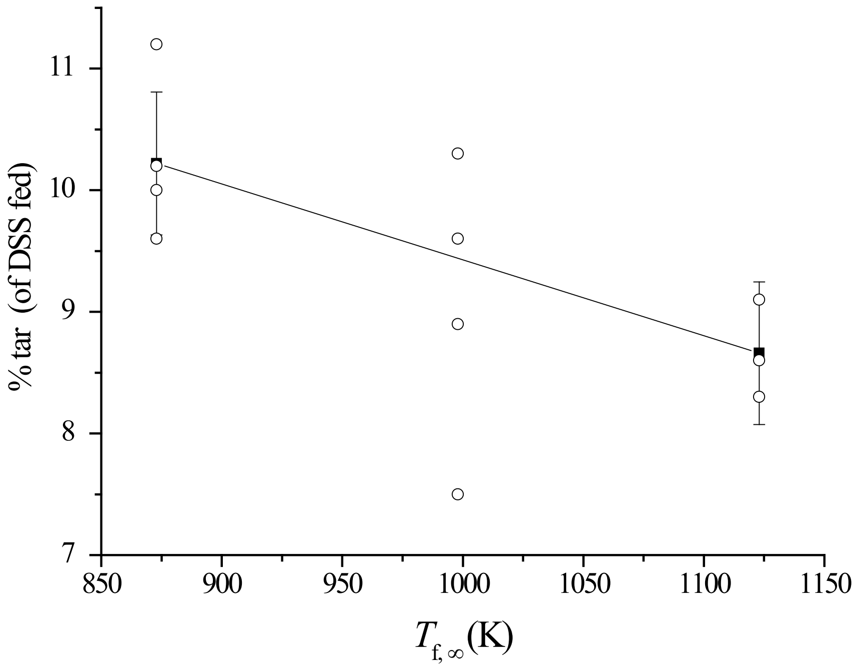
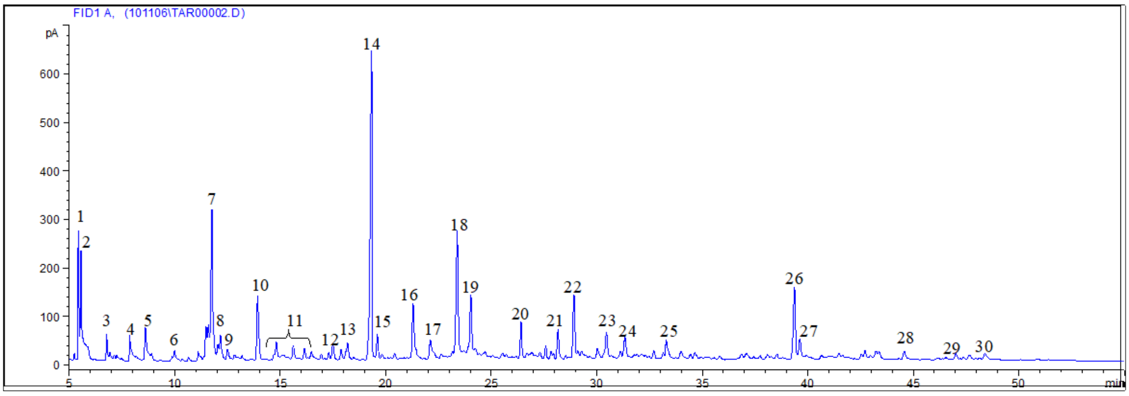

+
−
$T_{f,\infty}$
dp
u_f/u_{mf}
dp-$T_{f,\infty}$
dp-u_f/u_{mf}
$T_{f,\infty}$-u_f/u_{mf}
0
1
2
3
4
5
Standardized effects

Figure 3



% tar (of DSS fed)
11
10
9
8
7
850
900
950
1000
1050
1100
1150
$T_{f,\infty}$(K)

Figure 4



1. **Pyridine**
2. **1H-Pyrrole**
3. **Pyridine, 3-methyl-**
4. **Styrene**
5. **Pyridine, 2-ethenyl-**
6. **Pyridine, 3-ethenyl-**
7. **Benzonitrile**
8. **Benzofuran**
9. **3-Pyridinecarbonitrile**
10. **1H-Indene**
11. **Benzonitrile, 2-methyl-**
12. **1H indene, 1-methyl-**
13. **Benzeneacetonitrile**
14. **Naphthalene**
15. **Benzothiophene**
16. **Quinoline**
17. **Isoquinoline**
18. **1H-Indole**
19. **Naphthalene, 2-methyl-**
20. **1,1’ -Biphenyl**
21. **Naphthalene, 2-ethenyl-**
22. **Acenaphthylene**
23. **2-Naphthalenecarbonitrile**
24. **1-Naphthalenecarbonitrile**
25. **9H-Fluorene**
26. **Phenanthrene**
27. **Anthracene**
28. **Naphthalene, 2-phenyl-**
29. **Fluoranthene**
30. **Pyrene**

Figure 5

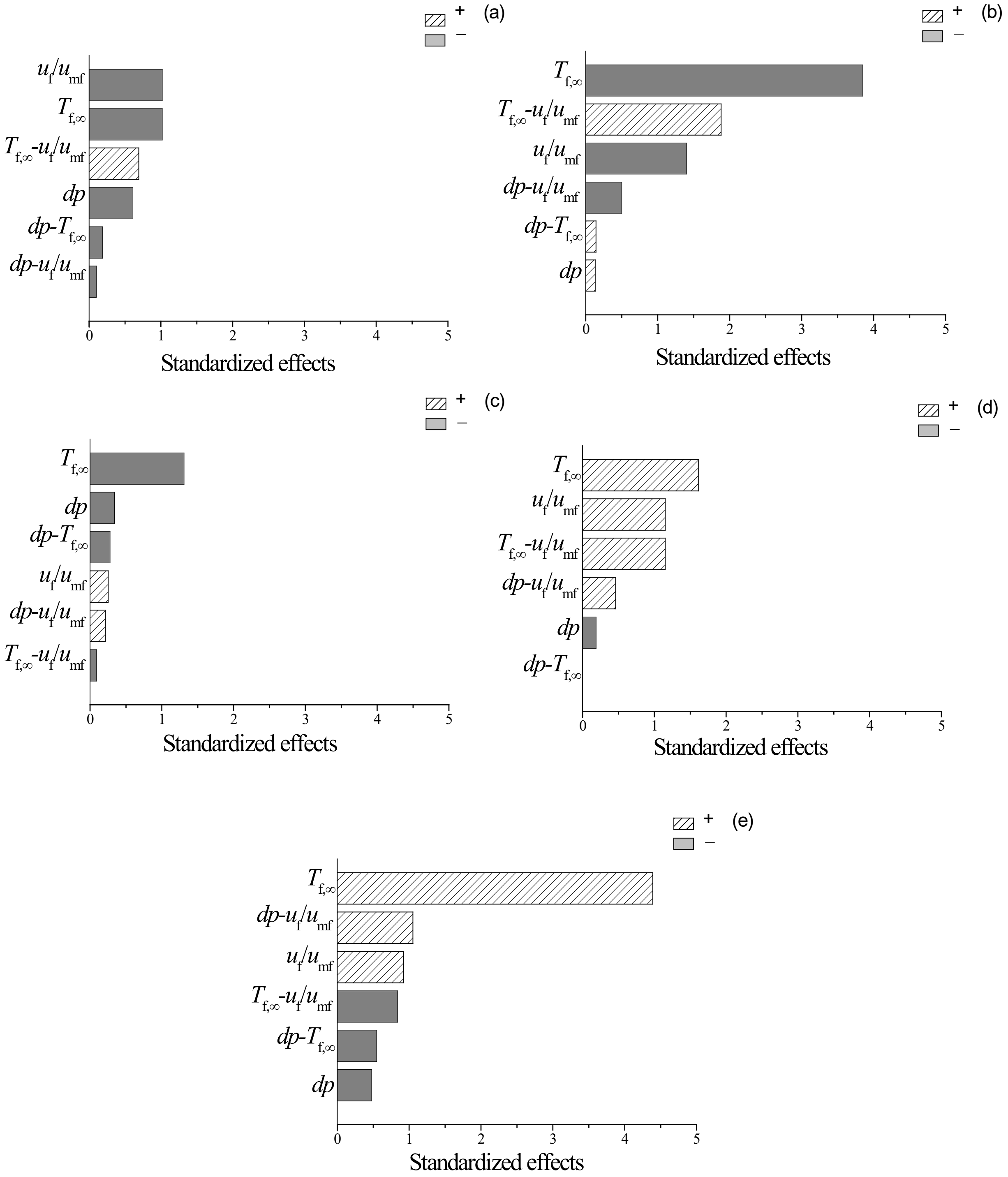

(a)
+
−
u_f/u_{mf}
$T_{f,\infty}$
$T_{f,\infty}$-u_f/u_{mf}
dp
dp-$T_{f,\infty}$
dp-u_f/u_{mf}
0
1
2
3
4
5
Standardized effects
(b)
+
−
$T_{f,\infty}$
$T_{f,\infty}$-u_f/u_{mf}
u_f/u_{mf}
dp-u_f/u_{mf}
dp-$T_{f,\infty}$
dp
0
1
2
3
4
5
Standardized effects
(c)
+
−
$T_{f,\infty}$
dp
dp-$T_{f,\infty}$
u_f/u_{mf}
dp-u_f/u_{mf}
$T_{f,\infty}$-u_f/u_{mf}
0
1
2
3
4
5
Standardized effects
(d)
+
−
$T_{f,\infty}$
u_f/u_{mf}
$T_{f,\infty}$-u_f/u_{mf}
dp-u_f/u_{mf}
dp
dp-$T_{f,\infty}$
0
1
2
3
4
5
Standardized effects
(e)
+
−
$T_{f,\infty}$
dp-u_f/u_{mf}
u_f/u_{mf}
$T_{f,\infty}$-u_f/u_{mf}
dp-$T_{f,\infty}$
dp
0
1
2
3
4
5
Standardized effects

Figure 6

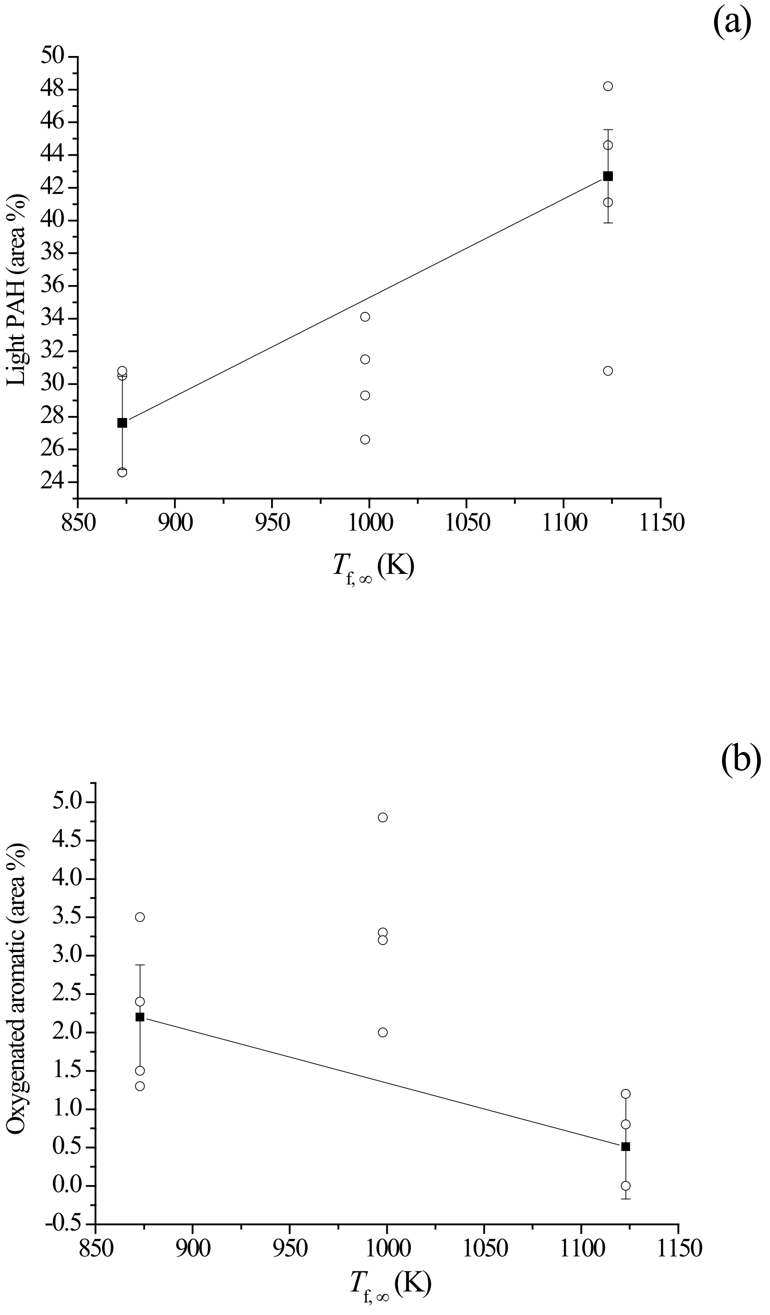

(a)
Light PAH (area %)
50
48
46
44
42
40
38
36
34
32
30
28
26
24
850
900
950
1000
1050
1100
1150
$T_{f,\infty}$ (K)
(b)
Oxygenated aromatic (area %)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
850
900
950
1000
1050
1100
1150
$T_{f,\infty}$ (K)

Figure 7

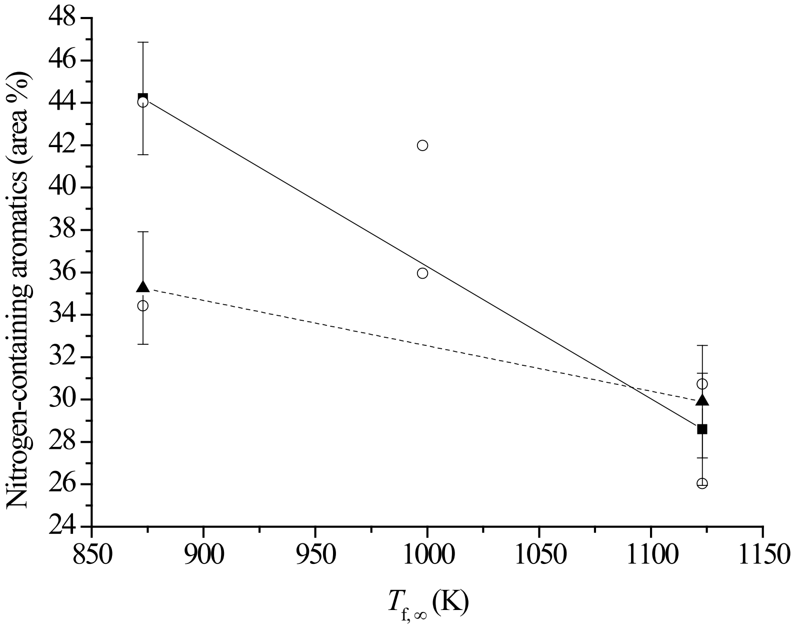

Nitrogen-containing aromatics (area %)
48
46
44
42
40
38
36
34
32
30
28
26
24
850
900
950
1000
1050
1100
1150
$T_{f,\infty}$ (K)

Figure 8

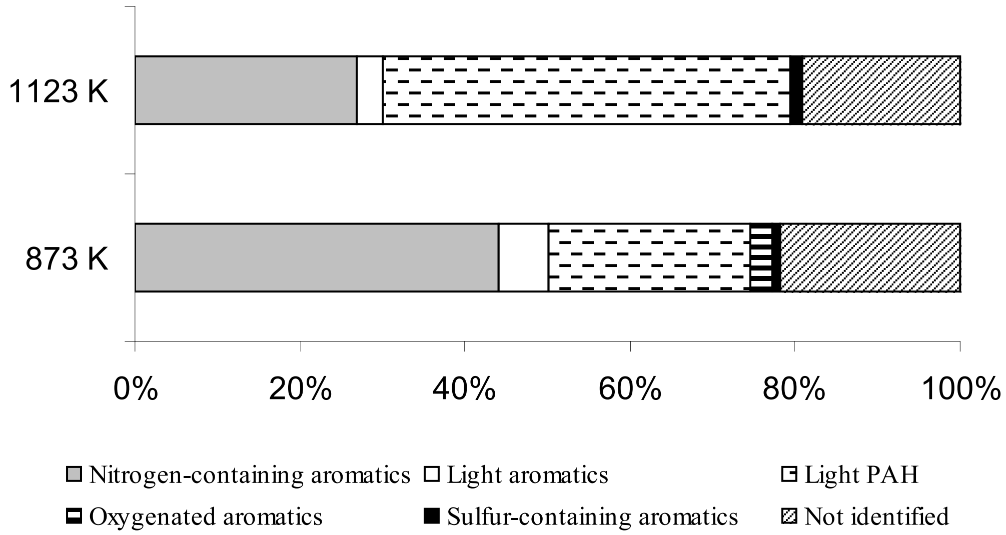
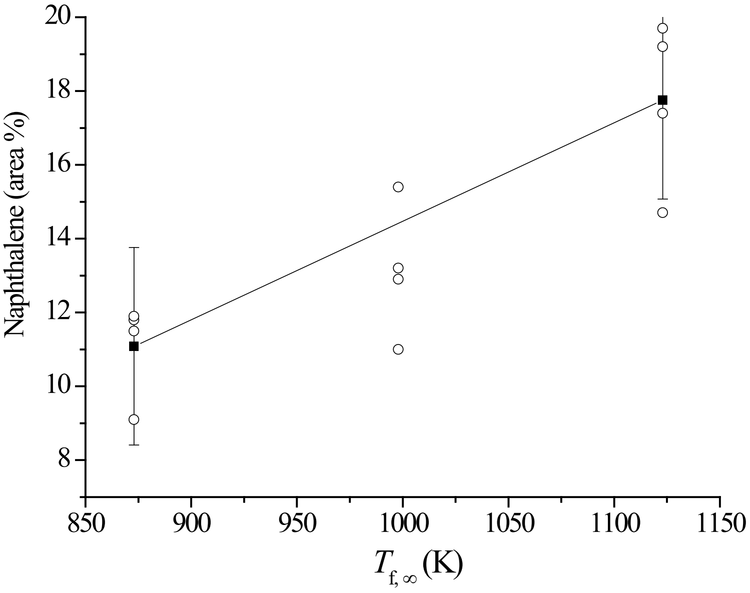

1123 K
873 K
0%
20%
40%
60%
80%
100%
Nitrogen-containing aromatics
Light aromatics
Light PAH
Oxygenated aromatics
Sulfur-containing aromatics
Not identified

Figure 9



Naphthalene (area %)
20
18
16
14
12
10
8
850
900
950
1000
1050
1100
1150
$T_{f,\infty}$ (K)

Figure 10

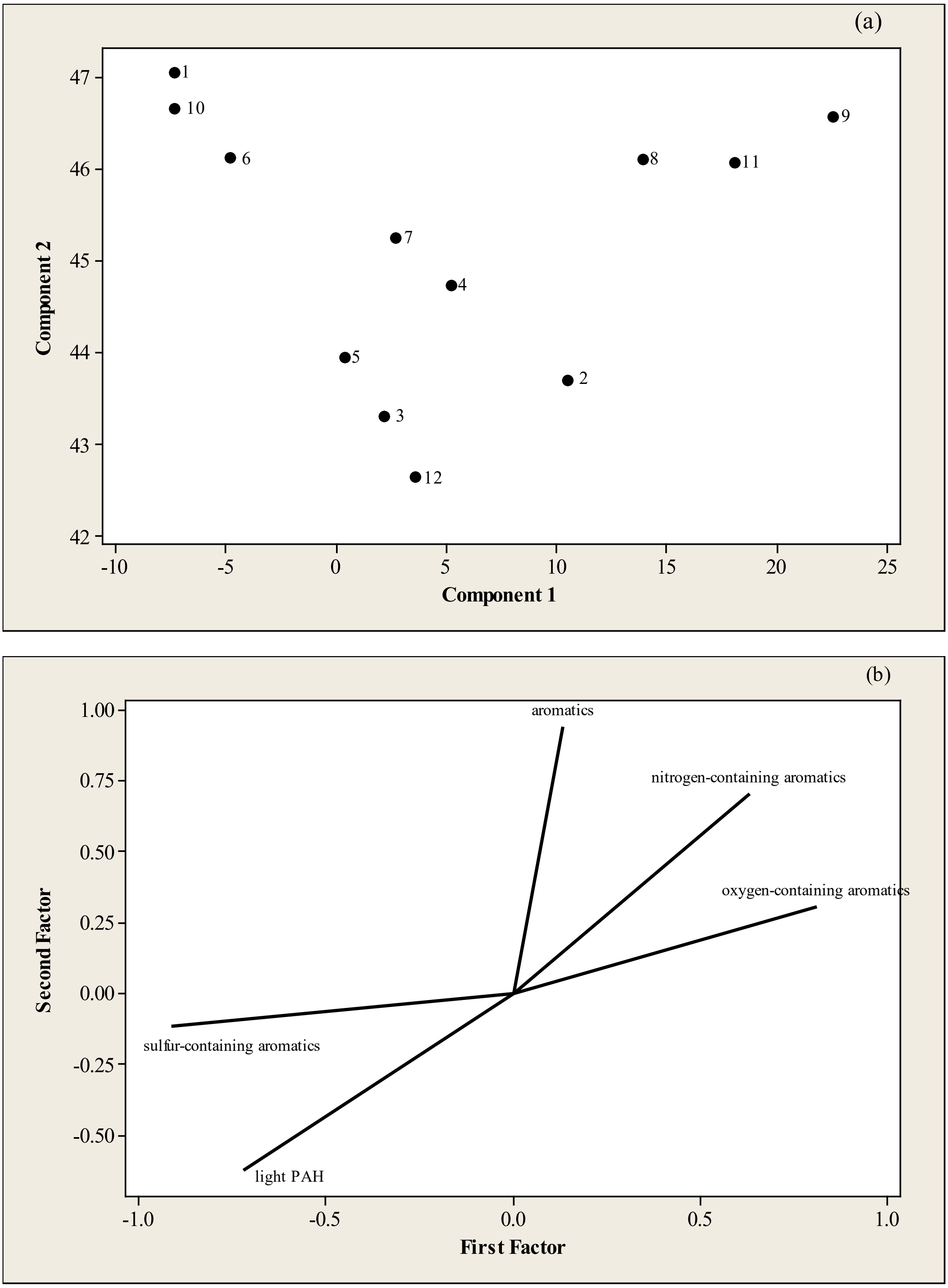

(a)
Component 2
Component 1
47
46
45
44
43
42
-10
-5
0
5
10
15
20
25
1
10
6
7
4
5
3
12
2
8
11
9
(b)
Second Factor
First Factor
1.00
0.75
0.50
0.25
0.00
-0.25
-0.50
-1.0
-0.5
0.0
0.5
1.0
aromatics
nitrogen-containing aromatics
oxygen-containing aromatics
sulfur-containing aromatics
light PAH

Figure 11

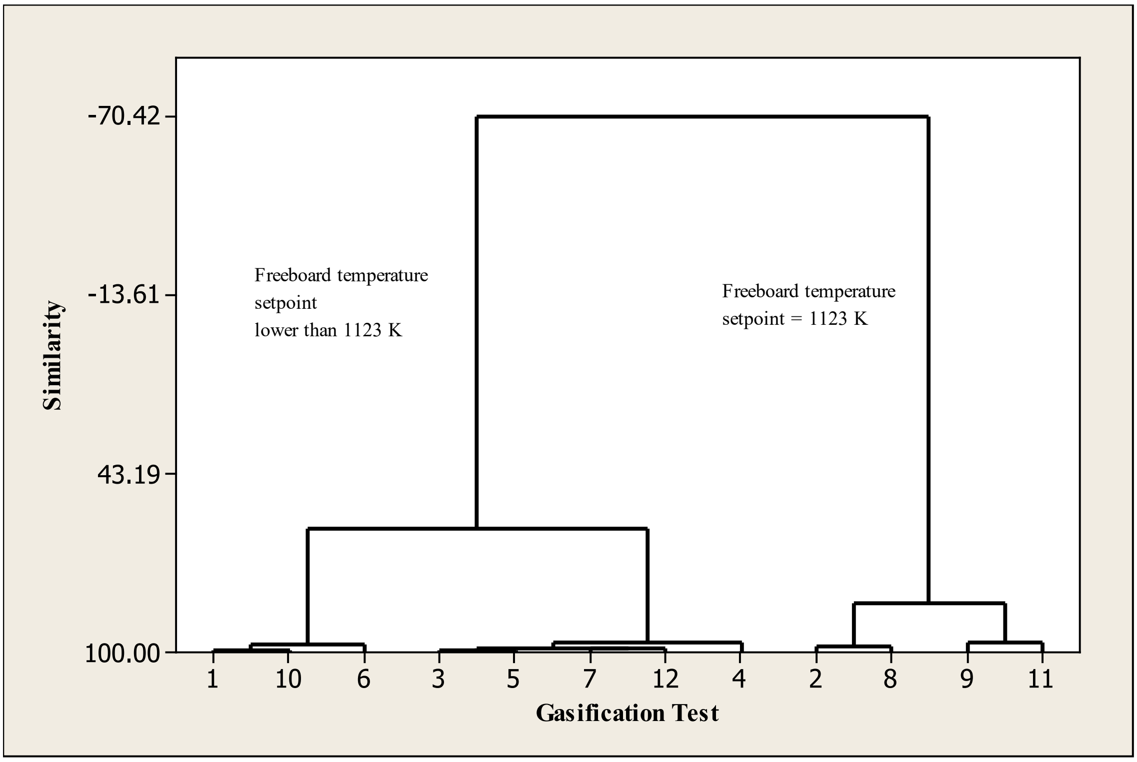

-70.42
-13.61
43.19
100.00
Similarity
Freeboard temperature
setpoint
lower than 1123 K
Freeboard temperature
setpoint = 1123 K
1
10
6
3
5
7
12
4
2
8
9
11
Gasification Test

Figure 12

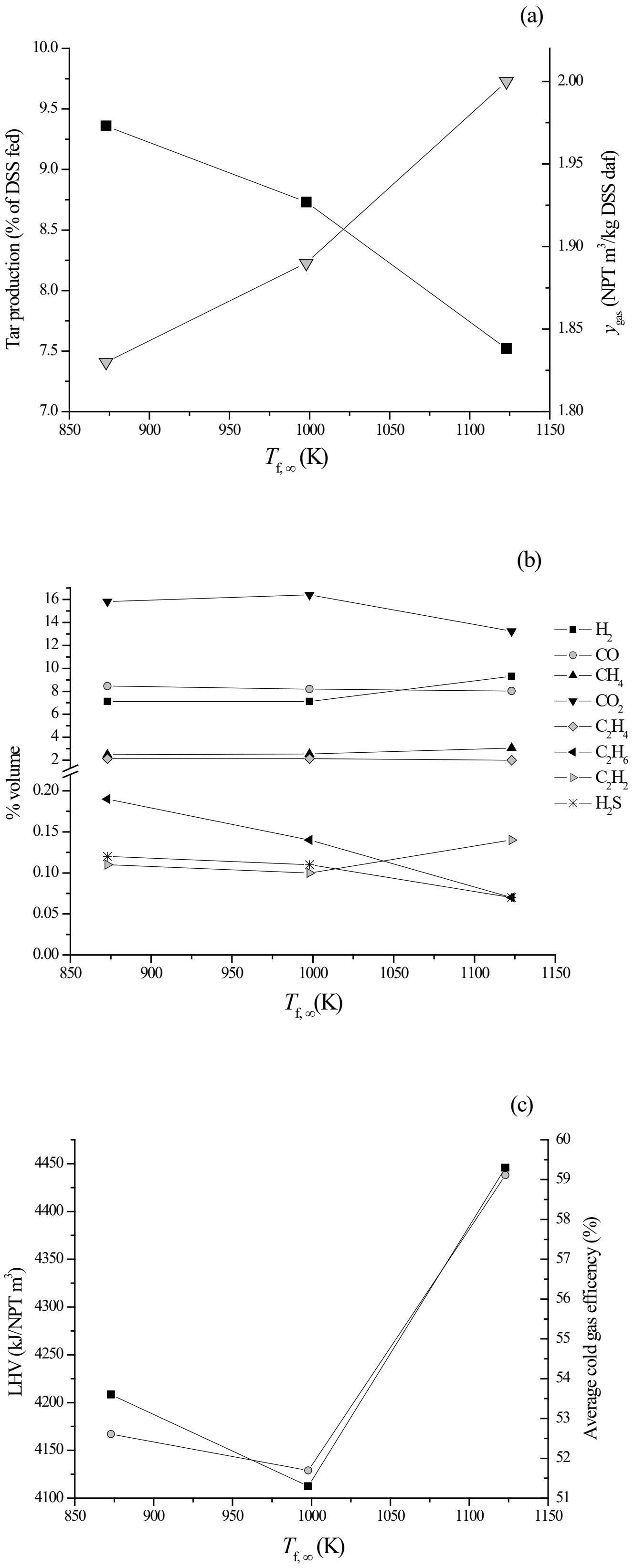

(a)
Tar production (% of DSS fed)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
y_{gas} (NPT m^3/kg DSS daf)
2.00
1.95
1.90
1.85
1.80
850
900
950
1000
1050
1100
1150
$T_{f,\infty}$ (K)
(b)
% volume
16
14
12
10
8
6
4
2
0.20
0.15
0.10
0.05
0.00
H_2
CO
CH_4
CO_2
C_2H_4
C_2H_6
C_2H_2
H_2S
850
900
950
1000
1050
1100
1150
$T_{f,\infty}$(K)
(c)
LHV (kJ/NPT m^3)
4450
4400
4350
4300
4250
4200
4150
4100
Average cold gas efficency (%)
60
59
58
57
56
55
54
53
52
51
850
900
950
1000
1050
1100
1150
$T_{f,\infty}$ (K)

Figure 13