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Title: Thermochemical assessment of Nicotiana glauca, Panicum virgatum and Elytrigia elongata as fuels for energy recovery through gasification

Article Type: Research paper

Keywords: herbaceous biomass; energy crops; thermochemical characterization; kinetics; biomass gasification syngas.

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Abstract: Production of energy from renewable biomass resources would reduce atmospheric CO2 increase associated with fossil fuels use. In this context, the objective of this study is to evaluate the energy potential of three herbaceous biomass crops (Nicotiana glauca, Panicum virgatum and Elytrigia elongata) grown on marginal lands. In order to do so, physicochemical and thermogravimetric characterization and gasification tests of each crop were performed. From the thermogravimetric analysis, it was estimated the activation energies of each energy crop using the Friedman method, obtaining values of 194.3, 224.9 and 220.6 kJ/mol for Nicotiana glauca, Elytrigia elongata and Panicum virgatum respectively. Then, in order to assess their potential as fuels for energy recovery, gasification tests were performed in a fluidized bed gasifier, using air and enriched air as gasifying agents. The ranges of experimental conditions used were the following: gasification temperature: 770-820°C; ER: 0.15-0.20; oxygen content: 21 and 27% respectively. The gasification gas obtained from these experiments had a calorific value between 3.5-5.0 MJ/Nm3, being always slightly higher for enriched air gasification. Besides, particle and tar contents were in the range of 4-17 g/Nm3 and 4-12 g/Nm3 respectively using air and 4-27 g/Nm3 and 4-18 g/Nm3 using enriched air. The results obtained showed that it is feasible to gasify the three selected crops grown on marginal lands with little differences in the gas produced offering an alternative to obtain a clean energy.

Madrid, March 2nd, 2018

Dear Editor

According to the email received from Fuel on February 2nd 2018, regarding to your decision about the publication of the manuscript titled "*Thermochemical assessment of Nicotiana glauca, Panicum virgatum and Elytrigia elongata as fuels for energy recovery through gasification*", the authors have made the corresponding revision on the manuscript following the comments made by the Reviewers.

Therefore, the authors have submitted a new version of the manuscript, uploading by separate files the new manuscript and the Figures. Furthermore, another file has been uploaded with a detailed response of each issue raised by the Reviewer.

In the authors' opinion, this new version not only covers all the weaknesses identified by the Reviewers but also improve the scientific content.

Therefore, the authors would highly appreciate if you reconsidered your decision

I look forward to receiving news from you soon.

Yours faithfully,

Dr. Yarima Torreiro Villarino et al.

*Detailed Response to Reviewers

Response to the Reviewers' Comments

Journal: Fuel
Article Ref: JFUE-D-17-04768
Title: Thermochemical assessment of Nicotiana glauca, Panicum virgatum and Elytrigia elongata as fuels for energy recovery through gasification
Authors: Yarima Torreiro Villarino; Isabel Ortiz; Gregorio Molina; Marta Maroño; Virginia Pérez; José María Murillo; Raquel Ramos; Miguel Fernández; Susana García; José María Sánchez
Article Type: Research paper

The authors wish to thank the Reviewers for their valuable comments and suggestions. All of them have been taken into account and included in the revised manuscript as long as it has been possible.

Besides, in the following lines it can be found all the issues raised by the Reviewers, and a specific response by the authors to each and every one of them.

Reviewer #2:

Issue 1:
The manuscript reports on a research about fluidized bed gasification of three herbaceous biomasses, also including thermo-gravimetric and ash characterization of the feedstock. The argument is pertinent with FUEL, but the paper suffers for originality. The inspiring idea of the authors is to study three biomass of interest for Spain, in the frame of a national project. The excessive splitting in different experiments (TG, ash analysis, gasification) hindered to focus on a single topic that would be more effective in terms of scientific progress.
For instance the enriched air gasification would be particularly appealing, but was treated in superficial way.
Therefore, the manuscript should be subjected to extensive revision before consideration for publishing in Fuel.

Discussion:
The authors agree with the Reviewer when it is said that "*The excessive splitting in different experiments (TG, ash analysis and gasification) hindered to focus on a single topic that would be more effective in terms of scientific progress*". However, in order to evaluate the feasibility of the further use theses feedstocks, it was considered that it was necessary to obtain the most complete characterization possible of each energy crop before they were used in the gasification tests.

On the other hand, it must be noticed that the gasification results here presented are only from some preliminary tests. For this reason, enriched air gasification has not been discussing more deeply. However, it must be said that a more exhaustive work on this topic will be published in next future.

Issue 2:
As reported in the author's info-pack of the journal "A concise and factual abstract is required". Current abstract does not fit the requirement. Please, reduce its size and reformulate it.

Discussion:
According to the suggestion, the abstract has been considerably modified to reduce its size, but keeping the most relevant information.

Issue 3:
The manuscript largely exceeds the page limit: "Original high-quality research papers. Preferably no more than 20 double line spaced manuscript pages, including tables and illustrations. Figures and tables can be embedded in the text or on separate page(s) at the end".
Please reduce its length by deleting not relevant content.

Discussion:
The new version of the manuscript has been reduced considerably regarding the previous one.

Issue 4:
Similarly "Conclusion" is too long

Discussion:
According to the Reviewer's suggestion, the section of "Conclusions" has been summarized.

Issue 5:
Biomass fuels: explain how such moisture value is obtained. It is strange that fresh herbaceous materials are so dry and any pretreatment have economic and environmental impact on the whole process. Explain the origin of the large ash content in Nicotiana Glauca, maybe due to heterogeneous fragments (stones, sand, etc.) that would be removed before gasification.

Discussion:
As it is mentioned in the new version of the manuscript (for example, caption of Table 1 and section 2.1) the three biomasses were characterized after the pelletization process. Therefore, they were not fresh herbaceous materials. Regarding the results obtained for the pellets of the three energy crops studied, they are very similar to other pellets of other biomasses.

The decision of analyzing the energy crops in their pellets forms was taken since the biomasses were received from the different suppliers without any information regarding to the previous treatment of these biomasses (collection, conservation method and conditions, etc.). Therefore, for these authors, this was the only way to try to analyze the three biomasses in the same conditions and compare the results with the literature already published.

Regarding the origin of the large content of the NG, it must be said that this value is perfectly normal for this biomass, and it is not due to heterogeneous fragments. In fact, depending on the part of the plant (stem, leaves, roots), the ash content is even higher as it is reported in the manuscript. New references have been added to support this statement.

Issue 6:
Table 2 and 3 can be merged, by choosing only one of possible state (element or oxide). Table 4: the behaviour of Nicotiana Glauca appears surprising and should be more deeply considered.

Discussion:
The suggestion has been accepted by the authors. In the new version, the former Table 2 has been removed and there is only a table with the composition of the oxides.

Regarding the behaviour of Nicotiana Glauca in former Table 4 (current Table 3 in the new manuscript), it has been detected an error in the shrinking temperature of NG. The correct value is 650ºC. The correction has been done. The other temperatures are correct. It has to be noticed that this temperatures have been obtained with an empirical method that used homogeneity ashes and controlled conditions (heating velocity and atmosphere). In a real gasification process these conditions may be different. Nevertheless, characteristic temperatures could indicate the possibility of bed agglomerations in the gasifier. In the case of NG, the temperatures indicate al low risk which is in line with the oxide composition reflected.

Issue 7:
Isoconversional method: please explain and discuss the derivation Eq. 4 from Eq. 2 that is not straightforward, a further assumption being needed.

Discussion:
Section 2.3 has been rewritten for a better understanding.

Issue 8:
Section 3.1.2 too long and redundant, nor innovative. Reduce it drastically

Discussion:
The section "3.1.2. Thermogravimetric characterization" has been completely rewritten to reduce and remove irrelevant content.

Issue 9:
Excessive number of references. Reduce to less than 40 by selecting only those strictly relevant for the introduction and discussion of the reported research.

Discussion:
The number of references has been reduced considerably. However, some new references have been added to clarify some weak points identified by the Reviewers. For this reason, there are 44 references in the new version.

Issue 10:
P. 21. The higher tar content could be also due to the lower dilution when enriched air is used. Please, comment. Tar on dry fuel basis would be useful so far.

Discussion:
The authors agree with the Reviewer. That point of view has been included in the revised text:
Now, in the paragraph after current Table 6 (former Table 7), referring to the tar and particle content, it is said: "*In both cases, it has to be noticed that the use of enriched air implies a lower N_2 content in the gasifying agent, and therefore, a lower dilution of the components present in the gasification gas generated*."

Issue 11:
P. 22 agglomeration could take place after several hours of operation. Provide further details for proving that the absence of bed agglomeration is not only consequence of short tests.

Discussion:
A few lines have been written in the new version of the manuscript explaining the absence of bed agglomeration. However, and as it is said now in the manuscript, it must be noticed that "*Nevertheless, the preliminary results have to be confirmed with longer gasification tests to obtain more solid and reliable results related to ash melting*".

Issue 12:
Minor remarks

Issue 12.1:
Use acronyms for the three biomasses.

Discussion:
The suggestion has been accepted. In the corrected manuscript it has been used acronyms for the three biomasses (NG, EE and PV respectively) in Tables, Figures and also in some parts of the text, trying to avoid a permanent repetition of each name.

Issue 12.2:
Several "Error! Reference source not found" are present in the paper

Discussion:
The authors apologize for these mistakes. In the original document these errors don not appear. The new version has been checked and the authors hope that this problem has been solved.

Issue 12.3:
Graphical quality of the figures is poor

Discussion:
The Figures have been uploaded in a different format to improve their quality. In this occasion, the figures are uploaded in a word document, in which the graphics has been inserted as Origin objects. The size of the Figures is similar to the size in which these figures would be published if the manuscript is accepted for its publication.

Issue 12.4:
P.17 explain "devolatilization reaction of charcoal". Charcoal by definition is volatiles free.

Discussion:
For a better understanding the sentence has been changed to: "*Although lignin activation energy is usually reported between 30-60 kJ/mol the upper activation energy values obtained in this study at higher conversions (75%) could be associated to the further devolatilization of primary products after the main reaction*."

Issue 12.5:
3.2 rename in "Isoconversional study"

Discussion:

The suggestion has been accepted and the text has been modified according to it. Therefore, in the new version of the manuscript, the section 3.2 is “ISOCONVERSIONAL STUDY”.

Issue 12.6:

Captions: report more information, e.g. temperature for Fig. 7 and 8

Discussion:

The gasification temperature for each biomass has been included in the captions of Figure 7 and 8.

Issue 12.7:

OP oxygen purity is a bit strange definition for enriched air. Better oxygen content or concentration

Discussion:

The authors agree with the Reviewer. By definition, the oxygen purity should be practically 100%.

Obviously, that parameter is referred to the oxygen content in the air used as gasifying agent: 21 % using air as gasifying agent, and 27% using enriched air.

This mistake has been corrected in the new version of the manuscript.

Issue 12.8:

Tab. 6 and 7: report temperature. Please, explain whether the temperature is controlled or it is attained by auto-thermal operation.

Discussion:

The temperature of the gasification process has been included in both Tables (now Table 5 and 6).

The experimental facility operates in an auto-thermal mode. That fact is mentioned in the manuscript, in section “2.4 Gasification test”, second paragraph: “*The facility is based on a gasifier which was operated in auto-thermal mode and at atmospheric pressure*“, and also in section 3.3.1. Operating Conditions: “*Tests were conducted under autothermal mode*”.

Issue 12.9:

Language: Some refinements are needed (e.g "impedes")

Discussion:

The English language has been improved in the manuscript. For example, it has been used “hinders” instead of “impedes”.

Reviewer #3:

Main impressions of the article: The article is interesting because it shows the preliminary results referring to the potential of three biomasses to be used as alternative fuels to fossil fuels, reducing CO2 emissions, to produce energy through gasification. Main reason of its interest and novelty is the selected crops can grow on marginal lands, i.e. unproductive or unsuitable soils, without competing with conventional food crops. This characteristic reduces one of the main concerns of biomasses grown for energy use, known as energy crops. Moreover, the gasification tests were carried out using air and enriched air for the three selected biomasses, while previous published studies were mainly related to switchgrass using steam as gasifying agent. These features imply sufficient impact and added knowledge for alternative fuels to produce energy.

Specific comments and suggestions:

Issue 1:
- ABSTRACT. It is adequate and summarized the paper's content, although it is too long and therefore it should be condensed.

Discussion:
As it has been said previously for Reviewer 2, according to the suggestion, the abstract has been considerably modified to reduce its size, but keeping the most relevant information.

Issue 2
- INTRODUCTION. It is suitable to introduce the paper, describing the current relevancy of biomass to produce energy (as alternative to fossil fuel), the reasons to select the three biomasses chosen (they are not conventional food corps but energy corps). However, in pg. 3 the sentence "Particularly, gasification is one of the most promising and diversified…." should be justified with a reference.

Discussion:
There are a lot of references which explain the main advantages of gasification regarding to other thermochemical processes. Among all of them, it has been selected the work published by Higman and van der Burgt (Gasification, 2008, Elsevier Inc., ISBN: 978-0-7506-8528-3] and also the article published by Sikarwar (Energy Environ. Sci., 2016, 9, 2939-2977).

Issue 3
- FIGURES. Figure 3 to 5 and 7 & 8 are appropriate to show main results and are well explained in the text, however:
Figure 1 should be explained in more detail showing e.g. MHV & LHV gas meaning. In addition, its reference is [10] in the text but in figure captions is [11], so this mismatch must be clarified.
Figure 2 has to be referred in the text in section 2.4.
Figure 6 should be explained with more details in the text, pg 18, 2nd paragraph.

Discussion:

Regarding Figure 1, a new paragraph has been written to explain Figure 1 and the meaning and applications of MHV gas (a gas with a medium heating value, around 6-10

MJ/Nm^3) and LHV gas (a gas with a low heating value, around 4-6 MJ/Nm^3). Besides, the mistake in the caption has been corrected, since the figure and explanation was taken from the same article published by Bridgwater in 2003 (current Reference number 9).

Regarding Figure 2, the authors wish to express their apologies for that mistake. In the corrected version of the manuscript, Figure 2 is introduced at the beginning of Section 2.4, second paragraph.

Regarding Figure 6, a few lines have been written to provide a more detailed explanation.

Issue 4
- TABLES are adequate to show main results and are well explained in the text, except for:

Issue 4.1
Table 1: to include in its caption the text underlined "…..HHV and LHV of studied pelletized potential fuels compared to wood chip (reference biomass). Chlorine content in Table 1 is 1.11% but in the text, pg 10, is 1.13%, this must be clarified.

Discussion:
The suggestion has been accepted and included in the new version. However, to simplify the caption of Table 1, it has been modified a little. In the new version, the caption is: "Table 1. Characterization of the pellets of the studied potential fuels compared to wood chips (reference biomass)". The authors hope that this new caption expresses the main idea both of the authors and the Reviewer.

The correct value of chlorine content in the Nicotiana glauca is 1.11%, as it is shown in Table 1. The authors wish to express their apologies by this mistake, which has been corrected in the new version of the text.

Issue 4.2
Table 2 is shown is section 2.1.1.2 without any comment before it, so it is suggested to move the text "Results of determination of major and minor elements in the solid biomass feedstock evaluated are shown in Table 2" (pg 11, last paragraph) before Table 2.

Discussion:
The authors accept this comment. However, in the new version of the manuscript and following the comments of other Reviewer, the former Table 2 has been deleted, and only remains the results of the inorganic species in their oxides forms (the former Table 3 which is now Table 2).

In any case, a short paragraph has been included to introduce the Table before it is shown.

Issue 4.3
Table 6: its caption is "Exit gas composition and….", suggestion change to "Syngas composition …"

Discussion:
The caption of that Table (in the new version of the manuscript is now Table 5) has been changed according to the suggestion of the Reviewer.

Issue 4.4

Table 7: In this table carbon conversion is named as Xc (%) but in the text CC is used, so these two names should be unified. Moreover, 2nd line which shows the name of the three biomasses is not necessary and therefore can be removed.

Discussion:

The authors apologize for these mistakes.

The nomenclature used to express the carbon conversion has been unified, and carbon conversion is expressed as Xc (%). The manuscript has been revised to try to avoid a possible misunderstanding.

Furthermore, according to the Reviewer's suggestion, former Table 7 (current Table 6 in the new version) has been modified, removing the second line which showed again the name of the three energy crops studied in this research.

Issue 5

- METHODS: the proposed methods to evaluate the selected biomasses as fuels are adequate, because they include studying their chemical features (proximate, ultimate and inorganic element analysis, melting behavior of ash, thermogravimetric characterization with TG and DTG analyses), and kinetic studies comparing their results with a reference biomass. Finally, some gasification tests were carried out to study its potential as fuel.

Discussion:

No comments are necessary in this issue.

Issue 6

- ANALYTICAL METHODS: all analytical methods used are developed for solid biofuels so they are appropriate to analyze the selected biomasses, being all of them specific for the features studied such as moisture, ash, total carbon content, etc. However, some of them have been replaced by new normative (as is shown in next list), so their use should be justified.

UNE-EN 14774-2:2010 Solid biofuels - Determination of moisture content-Oven dry method-Part 2: Total moisture-Simplified method by UNE-EN ISO 18134-2:2016, UNE-EN 14775:2010 Solid biofuels - Determination of ash content by UNE-EN ISO 18122:2016, UNE-EN 15148:2010 Solid biofuels - Determination of the content of volatile matter by UNE-EN ISO 18123:2016) and UNE-EN ISO 16994:2015 Solid biofuels - Determination of total content of sulfur and chlorine by UNE-EN ISO 16994:2017.

Discussion:

As it is said in the original manuscript: "*A thorough characterization of the different materials employed was carried out following the current European standards for biomass feedstock*".

To be completely honest, it must be said that the main part of the physicochemical characterization of the energy crops was carried out in 2015, and only a few complementary tests in 2016. Therefore, in 2015, the norms officially implemented for each determination were those mentioned in the original manuscript. Nevertheless, after a discussion with the experts, the new and updated norms do not modify considerably the previous ones, and consequently, the results are still completely valid. In any case, and accepting the Reviewer's suggestion, the updated norms have been included in the new version of the manuscript submitted.

Issue 7

- Section 2.4 Kinetic study pg. 8

The use of non-isothermal method compared to isothermal one should be justified (e.g. as is made in reference [14, pg. 227]), as well as the selection of Friedman method as the iso-conversional one, compared to others.

Discussion:

To justify the selection of non-isothermal method the following text has been included: "*Two types of experimental studies can be done, isothermal and non-isothermal. The advantages of non-isothermal methods lie in the possibility to obtain results in a wide range of temperatures studying the influence of different heating rates on the thermal decomposition process*."

To justify the use of isoconversional Friedman method, the following text has been included: "*For this study Friedman differential method was chosen because is the most straight forward method to evaluate the effective activation energy as a function of the extent of reaction and can be applied to any thermal history and any temperature program*".

Issue 8

In addition, the description of this section should be clarified and complete to justify the equations used, e.g. pg 6-7:

* "Friedman method" should be removed because eq. 2 to 4 are general equations that can be used for fundamental kinetic equation of thermal transformation not only for Friedman method
* add to "The rate of decomposition of a determined material is a function of temperatures and conversion" (<alpha>) that may be described as follows:

Discussion:

Section 2.3 has been rewritten for a better understanding.

Issue 9

- RESULTS/DISCUSSION:

Results are properly showed both in tables (6) and figures (8), except for the previous comments about them.

Regarding results explained in the text, main comments are:

Issue 9.1

- Please, use abbreviations to name the three biomasses, at least in the text to avoid repetition, e.g. Nicotiana Glauca (NV), Elytrigia Elongata (EE), Panicum Virgatum (PV).

Discussion:

As it has mentioned for Reviewer 2, in the corrected manuscript it has been used acronyms for the three biomasses (NG, EE and PV respectively) in Tables, Figures and also in some parts of the text, trying to avoid a permanent repetition of each name.

Issue 9.2

- Section 3.1.1.1. Proximate analyses, Pg 10, first paragraph indicates the ash content in the selected biomass has to be taken into account in order to design their removal systems during gasification of these crops. However, this is not mentioned for chlorine or nitrogen content (2nd and 3rd paragraphs), and this should be added in the text.

Perhaps, the most appropriate is to include a sentence such as The ash and chlorine contents in the selected biomass have to be taken into account in order to design their removal systems during gasification of these crops

Discussion:

Although that first paragraph was mainly related to the gasifier, the authors totally agree with the Reviewer. Following the suggestion of the Reviewer, after the paragraphs referring the chlorine content and sulphur content respectively, the next paragraph has been included in that section: "*Therefore, all these characteristics from the selected energy crops studied in this research, specially their ash and chlorine content, have to be taken into account in order to design their removal systems during gasification of these crops*".

Issue 9.3

- Section 3.1.1.3 Oxides, Pg 12, 2nd paragraph, "Equation 1 was used to predict…": The reference related biomass rake/ak value (>2) has to be added, i.e. [13].

Discussion:

The suggestion is accepted. That reference has been added in that paragraph (the article of Ramos Casado et al., Waste Manage, 2016. 47: p. 225-235, current reference number 11).

Issue 9.4

- Section 3.1.2. Thermogravimetric characterization, Pg. 14: Figure 2, 3 and 4 should be 3, 4 and 5 because figure 2 corresponds to the gasification set-up. Pg 16. The explanations given are consistent with the three figures, but in the main paragraph ("From those results….."), the last sentence ("All the crops studied presented a similar amount of residue") should be move to the following one ("Little differences…..") since the summary of residue results are again mentioned in this last paragraph. Therefore, moving this sentence could avoid content repetition.

Discussion:

Regarding the numeration of the Figures, the Reviewer is completely right and the authors apologize for this mistake. Effectively, that Figures should have been Figures 3, 4 and 5, which correspond with the TG and DTG curves for each biomass (NG, EE and PV), respectively. In the new version of the manuscript the figures have been renumbered correctly.

Furthermore, it must be said that, according to other Reviewer, this section "3.1.2. Thermogravimetric characterization" has been rewritten to reduce and remove irrelevant content.

Issue 9.5

- Section 3.2 Kinetic study (pg. 16 & 18): More explanation should be included to describe Figure 6, as well as how the results obtained in the kinetic study help to evaluate the selected biomass to produce energy.

Discussion:

Some modifications have been done in section 3.2 to improve the description of Figure 6. Moreover, a new paragraph has been written trying to explain the relevance of the kinetic parameters.

Issue 9.6

- Section 3.3. Gasification tests

Issue 9.6.1

Table 7. Particle content in Elytria Elongata using air as gasifying agent is 0, which is a quite unexpected figure due to its inorganic composition and the particle content using enriched air, so this data should be verified.

Discussion:

The Reviewer is completely right. This is an inexcusable mistake and the authors deeply apologize for it. The particle content in air gasification using Elytria Elongata as feedstock was of 4.23 g/Nm^3. That mistake has been corrected in current Table 6 (former Table 7) and also in several parts of the text.

Issue 9.6.2

Pg 21, paragraph after Table 7: the increase of particle content using enriched air should be justified, as is made for tar content.

Discussion:

According to the suggestion, a few lines has been included to explain the particle content for each biomass (results related to their ash content), and also using enriched air (results related with a lower dilution of the products in the gas).

Issue 9.6.3

Pg 22, 1st paragraph. Some data of contaminants (ammonia and sulfur hydrogen) emitted during gasification are shown, but no data of HCl is included. This pollutant is quite relevant because of biomass Cl high content and the environmental legislation applied to energy production using syngas from gasification.

Discussion:

Due to the fact that HCl determination required a specific sampling train with H_2SO_4 and NaOH, it was decided to perform these preliminary gasification tests focus on the basic analysis (gas composition, tar and particle) to achieve the best conditions prior to analyzed HCl. Therefore, no data for this compound are presented in this study but it will be present in future works.

Issue 9.6.4

Pg. 22, 2nd paragraph, last sentence "….which make feasible for several applications, especially for electricity generation due to the ease of distributing the product and the absence of product quality requirements.".

The ease of distributing the product ¿to be used as e.g. town gas?

The absence of product quality requirements: it is not completely true because e. g. syngas for gas turbines has to fulfill restrictive features referring LHV and mainly pollutants, and for fuel cell H2/CO ratio is essential. Therefore, this sentence has to be rewritten

Discussion:
The Reviewer is completely right. That part of the text has been rewritten for a better understanding.

Now, last sentence is written as follows: "*Gasification of the crops considered in this study produced a gas with a medium heating value ranging between 3–5 MJ/Nm^3 and values between 6-15, 10-14, 2-6% v/v of H_2, CO and CH_4 respectively, which make it feasible for several applications, as electricity generation which has less product quality requirements than others as chemical synthesis*."

Issue 10

- CONCLUSION: it is adequate and reflects main results of the analysis and gasification tests. However, it should be indicated in pg. 24, 2nd paragraph that these results are preliminary and have to be confirmed with longer gasification tests to obtain more solid and reliable results, mainly those related to syngas pollutants (NH3, HCl) and ash melting.

Discussion:
The suggestion is accepted, and the text has been modified according to it. Now, in that paragraph it is remarked that these are only preliminary results and an exhaustive research is still needed.

Highlights

Herbaceous crops studied show a gross calorific value and a high volatile content

They also show a fast thermal degradation essentially completed at T≈ 500°C

Preliminary characterization makes them as promising as fuels for energy recovery

Gasification tests confirm that they provided an alternative way to obtain clean energy

Thermochemical assessment of Nicotiana glauca, Panicum virgatum and Elytrigia elongata as fuels for energy recovery through gasification

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ABSTRACT:

Production of energy from renewable biomass resources would reduce atmospheric CO_2 increase associated with fossil fuels use. In this context, the objective of this study is to evaluate the energy potential of three herbaceous biomass crops (*Nicotiana glauca*, *Panicum virgatum* and *Elytrigia elongata*) grown on marginal lands. In order to do so, physicochemical and thermogravimetric characterization and gasification tests of each crop were performed. From the thermogravimetric analysis, it was estimated the activation energies of each energy crop using the Friedman method, obtaining values of 194.3, 224.9 and 220.6 kJ/mol for Nicotiana glauca, Elytrigia elongata and Panicum virgatum respectively. Then, in order to assess their potential as fuels for energy recovery, gasification tests were performed in a fluidized bed gasifier, using air and enriched air as gasifying agents. The ranges of experimental conditions used were the following: gasification temperature: 770-820ºC; ER: 0.15-0.20; oxygen content: 21 and 27% respectively. The gasification gas obtained from these experiments had a calorific value between 3.5-5.0 MJ/Nm^3, being always slightly higher for enriched air gasification. Besides, particle and tar contents were in the range of 4-17 g/Nm^3 and 4-12 g/Nm^3 respectively using air and 4-27 g/Nm^3 and 4-18 g/Nm^3 using enriched air. The results obtained showed that it is feasible to gasify the three selected crops grown on marginal lands with little differences in the gas produced offering an alternative to obtain a clean energy.

Keywords: herbaceous biomass; energy crops; thermochemical characterization; kinetics; biomass gasification syngas.

1. INTRODUCTION

The potential use of biomass for fuel and energy production has been researched extensively in recent years. In fact, biomass is currently the third largest primary energy resource in the world after coal and oil. In view of the increase in energy demand, the high costs of fossil fuels and disposal as well as the environmental concern about levels of CO_2 in the atmosphere, the use of biomass to provide partial substitution of fossil fuels for steam and power generation is of growing importance [1, 2].

The use of specifically designed crops to obtain biomass, the so-called “energy crops”, allows the resource production to be planned [3]. However, the selection of suitable energy crops and the availability of land for their cultivation are the leading concerns. Although cellulosic feedstocks are believed to have a positive environmental impact and can make up a remarkable proportion of future energy, they cannot be produced yet on arable lands due to social, environmental and economic concerns. A promising alternative is to grow cellulosic crops (traditionally called energy crops) on “*marginal lands*”, which are unproductive or unsuitable lands for crop production and that, subsequently, have no or little potential or profitability for conventional food crops. Therefore, energy crops grown on marginal lands will not only provide cellulosic biomass without competition with food crops, but also help to reclaim those lands with a substantial mitigation of greenhouse gases (GHG) [4].

Recently perennial grasses have been chosen as promising energy crops in Europe because of their beneficial attributes over wood feedstocks for bioenergy applications. Those benefits include ease of establishment, high yields, fast growing, minimum environmental impact and low costs. However, despite there is a lot of information dealing with the cultivation, productivity and chemistry of these crops, there is a lack of information concerning to their quality as fuels and their thermal degradation behavior [1]. Therefore, the knowledge of its chemical composition and its thermal behavior and reactivity is very important for the effective design and operation of the thermochemical conversion units, since solid devolatilization is always a fundamental step during fuels thermal conversion [1, 5, 6].

Besides, the conversion of biomass by thermochemical processes such as pyrolysis, combustion and gasification is in volume the most important and efficient option to produce steam and power generation [1]. Particularly, gasification is one of the most promising and diversified technologies, due to its higher efficiency and its flexibility to use a wide range of feedstocks (biomass, coal, wastes, etc.) and to obtain a great variety of products, such as syngas, heat, power, bio-fuels, fertilizer and bio-char [7, 8]. For example, Figure 1 summarizes the range of fuel, electricity and chemical products that can be derived from the product gas obtained through biomass gasification. A medium heating value gas (MHV gas) obtained from steam or pyrolytic gasification is better suited to synthesis of transport fuels and commodity chemicals. On the other hand, a low heating value gas (LHV gas) obtained through air gasification is mainly used for electricity production [9].

Figure 1.

In this context, three herbaceous biomass are considered as promising energy crops due to their high productivity, appropriateness for marginal land quality and their low water and nutritional requirements: *Nicotiana glauca* (NG) also known as tree tobacco; *Panicum virgatum* (PV) commonly known as switchgrass, and *Elytrigia elongata* (EE) or wheatgrass. Besides, they have allowed to obtain a high biomass production from which fuel and electricity can be generated [4, 10]. Therefore, this study aims to investigate the potential of the three selected energy crops (NG, PV and EE) as fuels for energy recovery through gasification: In order to do so, this work can be divided in three parts: firstly, their thermochemical characterization by means of proximate, ultimate analysis, ash analysis, determination of calorific value and thermogravimetric analysis, (TGA); secondly, the estimation of pyrolysis kinetics of biomass materials, necessary to understand their behavior during thermal processes. Finally, short series of tests using the three crops and two different gasifying agents, air and enriched air, were conducted in a pilot bubbling fluidized bed (BFB) gasifier in order to determine gasification feasibility in terms of syngas composition, energy content, carbon conversion and tar content.

2. EXPERIMENTAL SECTION

2.1. MATERIALS

Three energy crops have been studied in this research: *Nicotiana glauca* (NG), supplied by Azahar Management S.A, and *Panicum virgatum* (PV) and *Elytrigia* *elongata* (EE) supplied by CEDER. In all the cases, the raw biomasses were received from the suppliers and pelletized as cylindrical pellets, with an average size of 6x18 mm.

2.2 CHARACTERIZATION

2.2.1 Physicochemical characterization

The three herbaceous biomasses were exhaustively analyzed to obtain a thorough characterization of each one. All the analyses were carried out following the corresponding European norms for analysis and characterization of solid biofuels.

Characterization included the proximate analysis (for the determination of moisture content, ash content, volatile matter and fixed carbon), the ultimate analysis (to determine the total content of carbon, hydrogen, nitrogen, sulphur and oxygen of the sample), and the calorific value determination.

Furthermore, the ashes of the three biomasses (NG, EE, PV) were also analysed, and the content of the different elements present in the ashes were expressed as oxides. A theoretical method based on analyzing the ratio between alkaline earth oxides and alkaline oxides (Rake/ak) was carried out to predict the tendency to sintering of each sample. The relation for the estimation of sintering is the following [11]:

$$Rake/ak=(CaO+MgO)/(K_2O+Na_2O) \qquad \textit{Equation 1}$$

To complete the ash characterization, ash fusibility temperatures were also estimated using the corresponding standard method.

2.2.2 *Thermogravimetric characterization*

Thermogravimetric analysis (TGA) was done in an inert atmosphere of nitrogen in order to predict the behavior and thermal stability of different materials during a gasification process. TGA of different samples was performed in a thermobalance METTLER TOLEDO TGA/SDTA 851. The analyzer has a sensitive microbalance with an accuracy of +/- 0.2 µg. Temperature measurements are expressed with an accuracy of +/- 1°C. In each test approximately 30 mg of sample was placed in a platinum basket and heated in N_2 flow (50 ml/min) from room temperature to up to 900-1000°C at different heating rates of (5, 10 and 20° C/min).

2.3 KINETIC STUDY

Pyrolysis is the initial step in most thermochemical conversion processes. During that stage, large complex hydrocarbon molecules break down into smaller and simpler molecules of gas, liquid and char. Knowledge of pyrolysis therefore becomes relevant due to the fact that it is a key conversion step during gasification [12-14].

For a better understanding of the pyrolysis process, many researchers have studied thermal decomposition of biomass by thermogravimetric analyses. TGA is the technique most commonly used for kinetic analysis of devolatilization processes [5]. Two types of experimental studies can be done, isothermal and non-isothermal. The advantages of non-isothermal methods lie in the possibility to obtain results in a wide range of temperatures studying the influence of different heating rates on the thermal decomposition process [14].

There are many methods for analyzing non-isothermal solid-state kinetic data from TGA. These methods can be divided into two types: model fitting and model free (isoconversional) methods. Isoconversional methods are more frequently adopted because are flexible to allow for a change of mechanism during the course reaction (not necessary to choose a specific reaction model) and mass transfer limitations are reduced by the use of multiple heating rates [15].

The rate of decomposition of a determined material is a function of temperature and conversion. Conversion (α) may be described as follows:

$$\alpha = \frac{m_0 - m}{m_0 - m_f} \qquad \textit{Equation 2}$$

where m_0 is the initial mass of the sample, *m* is the mass of the pyrolyzed sample, and m_f is the final residual mass. The general conversion-time relationship is expressed in equation 3.

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \qquad \textit{Equation 3}$$

where f(α) is the model function which describes the dependence of the reaction rate with the conversion and k(T) is a temperature-dependent reaction rate constant expressed by Arrhenius equation (equation 4)

$$k(T) = A\exp\left(-\frac{E}{RT}\right) \qquad \textit{Equation 4}$$

where *A* is the pre-exponential factor, *E* is the activation energy, and *R* is the gas constant.

By introducing the Arrhenius correlation equation 3 becomes:

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \qquad \textit{Equation 5}$$

Determination of kinetics parameters can be done by differential or integral methods. For this study Friedman differential method was chosen because is the most straight forward method to evaluate the effective activation energy as a function of the extent of reaction and can be applied to any thermal history and any temperature program [6]. Taking logarithms of equation 5, Friedman method gave the following equation:

$$ln\left[\left(\frac{d\alpha}{dt}\right)_{\alpha,i}\right] = ln[A_\alpha f(\alpha)] - \frac{E_\alpha}{RT_{\alpha,i}} \qquad \textit{Equation 6}$$

where the subscript α refers to the value related to a considered conversion, and *i* to a given heating rate.

The kinetics parameters can be obtained from the plot of $ln\left[\frac{d\alpha}{dt}\right]$ against 1/T. For example, the value of the slope gives the value of the activation energy as a function of conversion (independent of the $f(\alpha)$-model).

2.4. GASIFICATION TESTS

In order to evaluate the potential of studied crops as fuels, gasification of NG, PV and EE was studied at pilot scale in a bubbling fluidized bed gasifier (BFB). Fluidized bed reactors are the most promising types of gasifier, with excellent fuel mixing, carbon conversion and thermal efficiency. Besides they are able to operate with flexible feed specification and size [2].

Figure 2 shows the scheme of the gasification facility where the gasification tests were conducted. The facility is based on a gasifier which was operated in auto-thermal mode and at atmospheric pressure. The gasifier is 3.0 m high, with an inner diameter of 0.3 m, and it is internally coated with a layer of refractory cement with an outer diameter of 0.72 m. There is also an overflow pipe that is used to assure a constant fluidized bed height. Under the distributor, a plenum reduces the velocity of the incoming air to ensure a uniform distribution when entering the nozzles. The air for gasification is supplied by a roots blower. A preheater with propane is used for start-up. During steady state gasification stage, the temperature is maintained around 800°C, without the necessity of external heating sources. The feeding system consists of two hoppers and two screws, one between the two hoppers and the other to feed the fuel into the reactor. Another screw feeder is used to refill the bed material during the tests and a second one is used to remove the mixture of ash and bed material from the reactor [16].

Figure 2.

The produced gas leaves the reactor by the top of the freeboard and passes through a high efficiency cyclone, where most of the particles are collected. A gas pipeline connects the cyclone to the flare. The system includes two gas sampling points located after the gasifier, with the aim of evaluating the gas composition and the tar content. The gas analyzer used includes a FTIR analyzer to measure CO, CO_2 and CH_4, a thermal conductivity analyzer to determine H_2 and a paramagnetic analyzer for O_2.

Gasification performance is assessed based on the low heating value (LHV) of the syngas obtained and the carbon conversion (Xc). LHV (MJ/Nm^3) has been calculated considering the H_2, CO and CH_4 content on the producer gas. Xc (%) is defined as the ratio between the carbon weight in the produced gas and the carbon weight in the feedstock that enters the gasifier. The amount of tars obtained in each gasification test was determined following the Technical Specification CEN/TS 15439:2006 [17]. Liquid chromatography was employed as the analysis method.

3. RESULTS AND DISCUSSION

3.1. CHARACTERIZATION

3.1.1. Physicochemical characterization

3.1.1.1. Proximate and ultimate analysis. Calorific value.

The results of the proximate and ultimate analyses and calorific values for the three energy crops studied (NG, EE and PV) are shown in Table 1. As woody biomass is traditionally employed during gasification processes [18, 19], results obtained with a reference fuel (wood chips) are also included for comparison.

Table 1. Characterization of the pellets of the studied potential fuels compared to wood chips (reference biomass).

	NG	EE	PV	Wood chips	Norms
Proximate analysis (wt.%)					
Moisture	9.7	8.9	10.9	8.8	UNE-EN ISO 18134-2:2016
Ash (d.b)	11.0	4.1	6.5	0.5	UNE-EN ISO 18122:2016
Volatiles (d.b)	73.5	78.1	76.7	83.1	UNE-EN ISO 18123:2016
Fixed carbon[b] (d.b)	5.8	8.9	5.9	7.6	
Ultimate analysis (wt.%, d.b[a])					
C	45.1	47.2	45.7	49.55	
H	5.5	5.9	5.7	6.5	
N	1.38	0.82	0.79	0.16	
S	0.26	0.08	0.11	0.02	UNE-EN ISO 16994:2017
Cl	1.11	0.08	0.28	0.02	UNE-EN ISO 16994:2017
O[b]	35.65	41.82	40.92	43.27	
Calorific value (MJ/kg, d.b)					
HHV	17.90	18.94	18.27	19.91	
LHV	16.71	17.65	17.03	18.51	

[a] dry basis of material ; [b] by difference

As it is shown in Table 1, the moisture content in the pellets of the studied energy crops presents similar values to the reference biomass in its pellet form.

Furthermore, as shown in Table 1, as expected the ash content in the potential biomass feedstock studied is higher than that of the reference fuel. Herbaceous biomasses are usually reported to have higher ash content than woody biomass. Moreover, these results make necessary to study the risk of sintering of this fuels inside the gasifier by ash melting. Particularly interesting is the ash content in the Nicotiana glauca, much higher than it could be expected for an herbaceous biomass. However, that result is in agreement with other results found in literature since its ash content is related to the parts of the plant. For example, stem biomass of Nicotiana tabacum is reported to have an ash content between 16-26% [20], whereas leaves of Nicotiana is reported to have an ash content of 20% [21].

It is also remarkable the high chlorine content of NG (1.11%). Gasifying fuels with high chlorine content can cause corrosion, slagging and fouling in downstream piping and equipment**.** The evaluation of the corrosion potential for biomass can be performed using certain empirical indices. For example, the sulphur to chlorine molar ratio is calculated as 2S/Cl. Fuels for which this ratio is high tend to form a protective sulphate layer on the tubes. If the ratio exceeds 4, only minor corrosion is expected and with values over 8 the chlorine presence in the deposits is minimal. Molar ratio 2S/Cl for NG is lower than 1 (≈0.5), and that is the reason why corrosion problems could be expected. According to Table 1 it can be also observed the higher amount of nitrogen of biomasses studied respect to the reference fuel. Consequently, the release of nitrogen pollutants mainly as NH_3 could be expected upon gasification.

The rest of parameters considered in these analyses are close to that showed by the reference fuel except sulphur, which resulted to be slightly higher in herbaceous biomasses. Those results agree with those reported by other authors who claim that nitrogen, sulphur and chlorine tend to be present in herbaceous biomass in higher concentrations than in woody biomass.

All these characteristics from the selected energy crops studied in this research, specially their ash and chlorine content, have to be taken into account in order to design their removal systems during gasification of these crops.

In terms of heating values, the generally lower lignin/carbon content of herbaceous biomass also means slightly lower HHVs compared to woody biomass, as shown in Table 1. In addition, their higher ash content also contributes to lowering the heating value obtained per kg of fuel. Their low moisture content means that the difference between the LHV and the HHV is also slightly less than in the case of woody biomass.

Despite previously mentioned considerations, calorific value of biomasses studied is still high. This fact combined with their low moisture content and their high volatiles content make these herbaceous crops suitable to produce and acceptable fuel. On the one hand their low moisture content makes possible that devolatilization starts almost immediately after the biomass is brought in contact with a high temperature medium. On the other hand, their high volatile content also ensures a rapid release of most of the combustible matter into the gas phase.

3.1.1.2. Ashes: composition and characteristics

The inorganic species contained in the ashes of the feedstock has a huge influence in the gasification process, since some of them are involved in agglomeration phenomenon in the bed of the gasifier or present a catalytic effect on tar elimination reactions [22]. Particularly, it is important to evaluate the quantity of those elements that can have a role on the ash melting (Na, K, P, Ca, Si, Mg). The higher the content in alkaline earth oxides regarding alkaline, the higher the sintering temperature and the less the risk of sintering of each sample [23]. The results of the composition of main species in the ash of the three biomasses studied are shown in Table 2.

Table 2. Composition of the oxides present in the ashes of the crops studied (according to Norms ISO 16967:2015 and ISO 16968:20015).

Oxides (% d.b)	NG	EE	PV	Wood chips
Al_2O_3	0.88	0.55	1.8	3.4
BaO	0.008	0.062	0.026	0.06
CaO	32	9.3	9.4	36.4
Fe_2O_3	0.47	0.34	0.96	1.40
K_2O	18	23	9.4	7.6
MgO	2.4	2.7	5.3	7.3
Mn_2O_3	0.032	0.34	0.21	1.4
Na_2O	0.55	0.75	1	0.92
P_2O_5	2.2	3.5	4.5	3.4
SO_3	5	3.2	3.2	3.5
SiO_2	8.4	34	56	11.8
SrO	0.046	0.014	0.043	0.040
TiO_2	0.043	0.033	0.10	0.11
ZnO	0.023	0.038	0.089	0.082

As can be observed, the alkaline earth metals concentration is generally lower in herbaceous biomasses that in the reference fuel. Besides, their alkaline metals content is higher than that of the wood chips analyzed. Those results suggest that although the ash content of herbaceous crops considered is low, operational problems with the bed material related to the fusibility of the ashes could be expected. Because of that, a deeper study on ash behavior is presented in the following section.

As it was mentioned in section 2.2.1., equation 1 was used to predict the tendency to sintering of each sample. It can be said that in general, biomass Rake/ak values higher than 2 should not present risk of sintering [11]. Values obtained for all the biomass studied are lower than 2. That is the reason why risk of ash sintering during gasification processes may be high. In order to corroborate this information, the ash melting behavior was studied by determination of their characteristic fusibility temperatures. Results are presented in Table 3.

Table 3. Characteristic temperatures for ash melting behavior of biomasses studied (according to Norm CEN/TS 15370-1:2007)

T (◦C)	NG	EE	PV
Shrinking	650	590	720
Deformation	>1450	650	1040
Sphere	>1450	860	1120
Hemisphere	>1450	1050	1250
Flow	>1450	1050	1310

Values of the shrinking temperature, which is defined as the temperature at which the area of the sample falls below 95% are in the temperature range of fluidized bed gasification processes for NG and PV, and a bit low for EE. However, the flow temperature, which is the one at which the ash is spread out in a layer was quite high for all samples considered, being among 1050 and 1450°C for all the biomasses studied.

The low ash melting temperatures and volatilization of alkali metals from the ashes of herbaceous biomass have been reported to lead to the rapid formation of sintered glassy deposits at typical operating temperatures of thermochemical conversion processes of biomass fuels [23]. In fact, agglomeration and slag problems have been reported in fluidized bed gasification systems using similar biomasses such as wheat straw [24].

Results obtained referring to the risk of sintering indicated that a thorough control of the thermal conversion process should be carried out, especially when Elytrigia elongata is used as feedstock in gasification. The operating conditions of the BFB gasifier should be set properly in order to prevent excessive agglomeration or sinter formation and defluidization. Temperature distribution is reported to be one of the most important and dominant parameters in controlling the extent of agglomeration in fluidized beds [25]. Thus an exhaustive temperature control during gasification of the three target crops is required. On the other hand, the lower the gasification temperature, the higher is the tar formation. In this context, using bed materials that can simultaneously remove tars and avoid agglomeration could be necessary. The use of calcined olivine to decompose tar efficiently at the usual operating conditions of fluidized bed gasification has been widely reported [26].

3.1.1. Thermogravimetric characterization

Figures 3, 4 and 5 show thermogravimetric (TG) and differential thermogravimetric (DTG) analyses of studied samples at the three different heating rates evaluated (5, 10, 20°C/min).

Figure 3.

Figure 4.

Figure 5.

First of all it is important to highlight that as can be observed in all figures, temperature peaks increases with the heating rate. Increasing the heating rate shifted the TG curve to higher temperatures possibly due to a reduction in the retention time and an increase in the temperature required for organic matter to decompose [27]. This effect was observed in other studies about biomass under different heating rates [28].

All the samples show the same behavior in three stages, common between lignocellulosic biomass during pyrolysis [27, 29]. A first stage between initial temperature and 150ºC, with maximum loss weight rate around 70^{o}C, corresponding to the moisture removal of the sample by evaporation. The second stage starts between 210 and 230^{o}C and finish between 340 and 360^{o}C, depending of the sample. This stage represents the main loss mass during the whole process, with a clear defined peak around 330^{o}C. During these temperatures, cellulose and hemicellulose decomposition happens. Among these processes, it is highlighted the Panicum virgatum's profile. Instead of the common main peak, TG profile showed in Figure 5 plots a shoulder inside the main peak with a maximum rate at 245^{o}C, on the left of the main peak, corresponding to cellulose decomposition. This secondary peak corresponds to hemicellulose decomposition. This decomposition was observed in other works about biomass [13, 30]. The third stage is less evident, because of shaping as a flat tailing of the main peak of the DTG profile. This stage starts around 360^{o}C and finish at 600^{o}C with no main mass loss stage, and corresponds with the lignin decomposition. This process happens in a wide temperature range, because the complexity of the lignin structure made this process more complex than other degradations [31].

In the end of the processes, the remaining residue is between 19 and 22% of the initial biomass, except Nicotiana glauca that left a residue of between 23 and 25% of the initial mass. The variation between residues in the same sample is explained by the change of heating rate.

3.2. ISOCONVERSIONAL STUDY

The kinetics parameters are always important to optimize a process, since these parameters allow to determine some essential parameter (for example, the residence time necessary for the reaction) to design, build and operate a facility at industrial scale.

In Figure 6, isoconversional straight lines were drawn for the studied herbaceous crops in the plot of $ln\left[\frac{d\alpha}{dt}\right]$ versus 1/T. They are obtained selecting different conversion values at each heating rate (5, 10 and 20 ºC/min). The activation energies were calculated from the different slopes according to equation 6 and are presented in Table 4.

Figure 6.

Table 4. Calculated activation energy for the pyrolysis of Nicotiana glauca, Elytrigia elongata and Panicum virgatum.

	NG	**EE**	**PV**
Conversion (%)	**Ea (kJ/mol)**		
10	155.8	64.30	170.7
20	180.5	217.3	198.6
40	181.6	204.4	209.7
60	220.7	253	253.5
75	97.19	89.12	84

For the three biomasses considered in this study, the activation energy increased steadily until the conversion was about 60% and then decreased. The increase in the activation energy could be attributed to the decomposition of cellulose and hemicellulose, with an activation energy normally reported in the range from 150-250 kJ/mol [1, 12]. The apparent activation energies in the 20-60% conversion range have values between 180.5-253.5 kJ/mol and values between 84-97.2 kJ/mol at conversions close to 75%. As has been widely reported for cellulosic materials, cellulose and lignin have the highest and lowest activation energies respectively [1, 32], being the activation energy of hemicellulose an intermediate value between them [1]. Cellulose demands more energy to decompose/break compared to the other components due to its strong intra-molecular bonds, which prevent its decomposition at lower temperatures [33]. Although lignin activation energy is usually reported between 30-60 kJ/mol [29, 32] the upper activation energy values obtained in this study at higher conversions (75%) could be associated to the further devolatilization of primary products after the main reaction [32].

Even though kinetic results of the same order of magnitude were obtained for the three biomasses, differences observed in both Figure 6 and Table 4 are mainly attributed to their different chemical composition, parameter which has been reported to have a huge influence on kinetic results [1, 5].

3.3. GASIFICATION TESTS

3.3.1. Operation conditions

After completion of the thermochemical characterization work at laboratory scale, a short series of preliminary gasification tests at atmospheric pressure were conducted at pilot scale to prove from an operational point of view the feasibility of the use of Nicotiana glauca, Panicum virgatum and Elytrigia elongate as feedstock in gasification. The experimental work was carried out in a 150 kWt BFB gasifier, of 3.0 m high and an internal diameter of 0.3 m. Tests were conducted under autothermal mode, i.e. without external heating sources, which is the current operation mode at industrial conditions. ER (equivalence air ratio) was adjusted during the test to maintain the temperature around 800°C, while ensuring appropriate bed fluidization. Tests were carried out using olivine (dp: 0.4-0.5 mm) as bed material and two gasifying agents: air and enriched air.

3.3.2. Gasification performance

The effect of the gasifying agent on the gas composition obtained with each biomass was evaluated. The ranges of experimental conditions used were the following: gasification temperature: 770-820ºC; ER: 0.15-0.20; oxygen content: 21 and 27% respectively. Biomass feed rate was kept at 40-45 kg/h during all the experiments.

Figure 7, Figure 8 and Table 5 show the gas composition obtained during the gasification tests carried out with the three energy crops studied using two gasifying agents, enriched air and air. Table 5 also includes the estimated lower heating value of the syngas produced in each case.

Figure 7.

Figure 8.

Table 5. Syngas composition and LHV_{gas} obtained during each herbaceous crop gasification using two different gasifying agents.

		NG		EE		PV	
Gasifying agent		Air	Enriched air	Air	Enriched air	Air	Enriched air
Gasification Temperature (ºC)		780	780	810	810	800	800
Syngas composition (%)	H_2	12.2	14.2	9.10	10.8	6.34	7.64
	CO	11.5	14.1	10.3	12.3	10.3	12.8
	CO_2	15.5	16.4	15.44	16.5	14.8	17.1
	CH_4	2.24	3.24	3.57	5.30	4.61	4.25
LHV_{gas} (MJ/Nm^3,d.b[a])		3.66	4.60	3.70	4.83	3.81	4.14

[a] dry basis

As can be observed, enriched air gasification increases the content of H_2, CO, CO_2 and CH_4 in the produced gas for all the biomasses considered, which is consistent with information provided in literature [34-37]. The increase in the syngas components is due to not only the reduction of N_2 content in the gasifying agent but also the more production of those components. The increase of H_2 and CO using enriched air as gasifying agent is justified taking into account that all endothermic reactions involved in H_2 and CO formation are favored at higher O_2 content in the gasifying agent, due to the exothermic oxidation reactions in which oxygen is involved [36, 38]. Therefore, the higher O_2 content in the gasifying agent, more favored are the steam reforming reaction of methane and char (reaction 1 and 2) [38], and the Boudouard reaction (reaction 3) [36]. This can also turn in an increase of H_2 production via water gas shift reaction (reaction 4). Furthermore, the improvement in CH_4 yield is explained through methanation reactions due to the presence of more CO and H_2 [38].

$$CH_4 + H_2O_{(g)} \leftrightarrow CO + 3H_2 \qquad \Delta H_{298K} = +201.9\ kJ/mol \qquad \textit{Reaction 1}$$

$$C + H_2O_{(g)} \leftrightarrow CO + H_2 \qquad \Delta H_{298K} = +131.4\ kJ/mol \qquad \textit{Reaction 2}$$

$$C + CO_2 \leftrightarrow 2CO \qquad \Delta H_{298K} = +172.6\ kJ/mol \qquad \textit{Reaction 3}$$

$$CO + H_2O_{(g)} \leftrightarrow CO_2 + H_2 \qquad \Delta H_{298K} = -41.2.6\ kJ/mol \qquad \textit{Reaction 4}$$

The observed increase in the amount of CO_2 in the gas produced was also expected, since the higher amount of O_2 present during enriched air gasification enhanced CO conversion to CO_2. During gasification with enriched air the difference between CO and CO_2 content became smaller which could imply that some CO_2 react with char through Boudouard reaction to produce CO, thus limiting the final CO_2 output. Besides, oxygen is also a possible candidate for reacting with chars to produce CO_2 and CO as shown in reaction 5.

$$\text{Char} + O_2 \rightarrow CO_2 + CO \qquad \textit{Reaction 5}$$

In order to further evaluate the gasification process, the lower heating value of the syngas obtained (LHV_{gas}, Table 5 and the carbon conversion (Xc, Table 6) were determined. From those tables it can be observed that values of LHV_{gas} and Xc also increased using enriched air as gasifying agent on comparing with values obtained using air (20% of increase in LHV_{gas} values and 15% of increase in Xc results). This trend has been observed by several authors [34-37]. The observed increase in the conversion efficiency is explained due to the extra oxygen available to enhance the exothermic oxidation reactions, which allow gasifying the char generated and as a result, there is an increase in the total carbon content in the syngas.

Using enriched air gasification produces a gas with a heating value close to 5 MJ/Nm^3 and carbon conversions between 70-90%, being Panicum virgatum the crop which the highest value of Xc obtained. Those values agree with those calculated in similar works reported on literature carried out with switchgrass [39]. The total tar and particle content obtained in each gasification test was also determined (Table 6).

Table 6. Carbon conversion and total tar and particle content obtained with each crop as a function of the gasifying agent employed.

	NG		**EE**		**PV**	
Gasifying agent	Air	Enriched air	Air	Enriched air	Air	Enriched air
Gasification Temperature (ºC)	780	780	810	810	800	800
Xc (%)	69.8	80.7	61.2	71.6	80.0	91.3
Tar content (g/Nm^3)	3.99	4.51	5.34	10.5	12.2	18.1
Particle content (g/Nm^3)	17.2	26.8	4.23	5.70	4.54	4.38

As can be observed in Table 6 the tar content obtained with biomasses employed in this work is found in the range 4.0-12.2 g/Nm^3 using air as gasifying agent and 4.5-18.1 g/Nm^3 using enriched air. Enriched air gasification also increases the particle content (values between 4.2-17.2 g/Nm^3 using air and between 4.4-26.8 g/Nm^3 using enriched air). In both cases, it has to be noticed that the use of enriched air implies a lower N_2 content in the gasifying agent, and therefore, a lower dilution of the components present in the gasification gas generated. Furthermore, it is expected that enriched air gasification increases the tar content in all cases on comparing with air gasification, due to polycondensation reactions which are favored by the presence of oxygen [35, 37]. Nicotiana glauca is the biomass which presents the lower tar content in the syngas produced. Panicum virgatum is the one with the highest tar content. Regarding the particle content, the results obtained are related to the ash content in each biomass. The higher particle contain in the gas was obtained using Nicotiana glauca as feedstock, the crop with the higher ash content (11.0 %, see Table 1). For Elytria elongate and Panicum virgatum, with an ash content much lower (4.1 and 6.5 respectively), the particle content is also significantly lower.

Despite ash composition of the feedstock anticipated sintering problems could be expected upon actual gasification due to alkaline species content such problems did not happen during the performed tests using olivine used as bed material. Precisely, this bed material was selected to minimize the presence of silica in the bed, due to the combination between silica and alkaline species is considered one of the main causes of agglomeration problems [40]. Nevertheless, the preliminary results have to be confirmed with longer gasification tests to obtain more solid and reliable results related to ash melting.

However as expected due to the nitrogen and sulphur content, NH_3 and H_2S were emitted during gasification with values in the range between 580-4000 ppm (NH_3) and 1.5-40 ppm (H_2S). HCl was not analyzed since these gasification tests were considered as preliminary tests. Nevertheless, although HCl is mostly removed with water in downstream stages, this compound must be taken seriously into account in future works due to the significant Cl content in the biomasses studied and the environmental legislation applied to energy production using syngas from gasification.

Therefore, results obtained from these preliminary experiments suggested that it is feasible to gasify the three selected biomasses with little differences in the composition of the gas produced, LHV, Xc and particle and tar content. Gasification of the crops considered in this study produced a gas with a medium heating value ranging between 3–5 MJ/Nm^3 and values between 6-15, 10-14, 2-6% v/v of H_2, CO and CH_4 respectively, which make it feasible for several applications, as electricity generation which has less product quality requirements than others as chemical synthesis.

Biomass oxygen-rich air gasification increased in all studied cases the heating value of the syngas and the % v/v of syngas components. However, the need of a large investment for oxygen production equipment hinders its massive implementation. On the other hand, excessive O_2 may cause more CO_2 to be produced, which could result in an increase of undesirable components. This makes desirable to study the oxygen/biomass ratio to be employed in each case [41].

Few studies of those crops gasification on similar conditions have been found. Most of investigation was carried out with switchgrass using steam as gasifying agent [2, 39, 42] or air [42]. However, in all the studied cases in this work a syngas with acceptable hydrogen and CO content was obtained, really close to that obtained through other herbaceous biomass gasification under similar conditions [43]. Besides, results obtained are quite similar in terms of gas composition, LHV, Xc and tar content obtained during air gasification [44] and during enriched air gasification [36, 37] in similar tests performed with woody biomass, the most widely used biomass for energy production.

4. CONCLUSIONS

The three herbaceous crops studied in this research are promising candidates to be used as fuels according to their gross calorific value, low moisture content and high volatile content. Nevertheless, the chlorine content and the ash composition (high content of alkalis and silica) in those herbaceous biomass ashes are the most significant issues for their gasification.

All the biomasses studied show a similar thermal behavior with a fast degradation in three steps associated to the loss of humidity, cellulose and hemicellulose decomposition (main degradation step which occurs at 200-400ºC) and lignin degradation. The process is essentially completed in all cases by 500°C. The activation energies determined by the Friedman method were between 180.5-253.5 kJ/mol in the 20-60% conversion range and values between 84-97.19 kJ/mol at conversions close to 75%.

Results obtained during the preliminary gasification tests show that it is feasible to gasify the three selected crops with minor differences in the composition of the gas produced, LHV, Xc and particle and tar content, obtaining an acceptable syngas especially when enriched air was used as gasifying agent. Despite of preliminary results obtained on behalf fuel characterization no sintering problems were detected during performed tests. Therefore, this study confirms that the use of three energy crops grown on marginal land could provide an alternative way to obtain clean energy without competition with food crops. Nevertheless, the preliminary results have to be confirmed with longer gasification tests to obtain more solid and reliable results, mainly those related to syngas pollutants (NH_3, HCl) and ash melting.

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FIGURE CAPTIONS

Figure 1. Applications for gas from biomass gasification [9].

Figure 2. Scheme of the gasification experimental set-up.

Figure 3. TG and DTG curves of Nicotiana glauca under inert conditions at different heating rates.

Figure 4. TG and DTG curves of Elytrigia elongata under inert conditions at different heating rates.

Figure 5. TG and DTG curves of Panicum virgatum under inert conditions at different heating rates.

Figure 6. Isoconversional lines for predefined conversion values in an inert atmosphere at different heating rates for biomasses studied.

Figure 7. Syngas composition in the gasification tests using air as gasifying agent. (Gasification temperature: 780ºC for NG, 810ºC for EE and 800ºC for PV).

Figure 8. Syngas composition in the gasification tests using enriched air as gasifying agent. (Gasification temperature: 780ºC for NG, 810ºC for EE and 800ºC for PV).

Figure

Figure 1

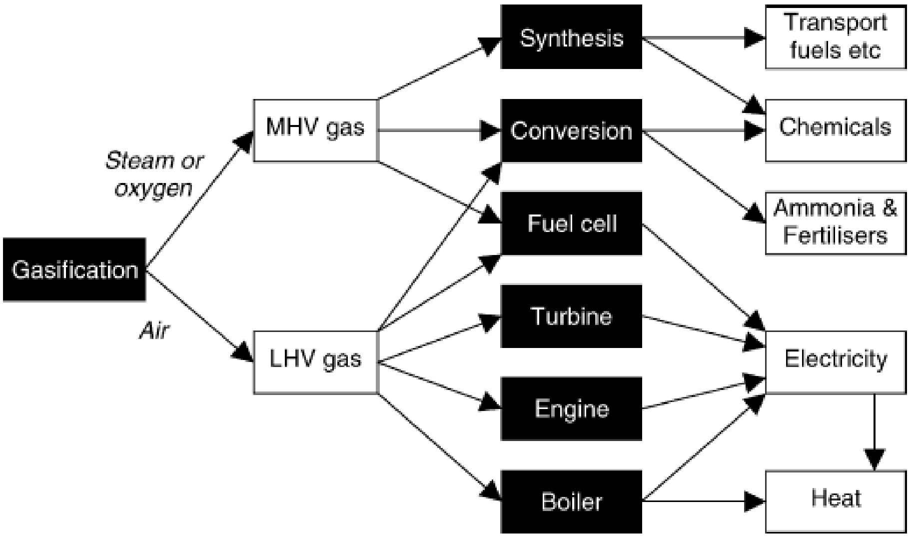


Figure 2

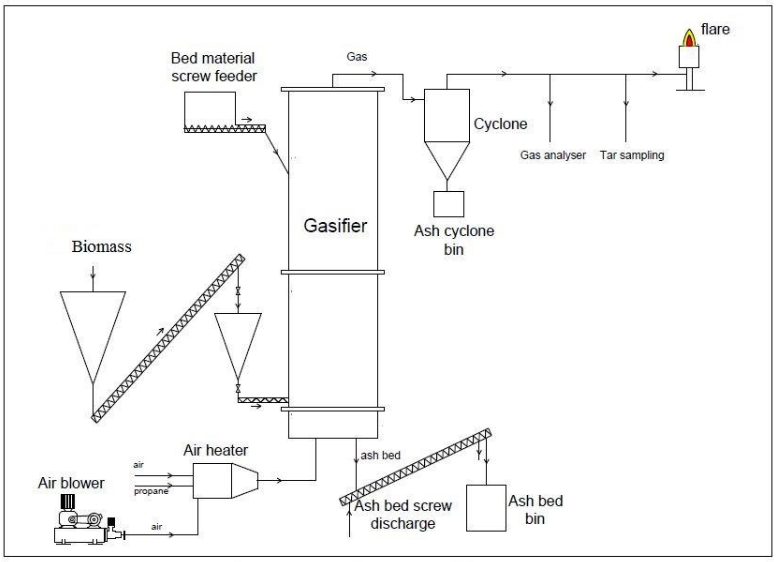
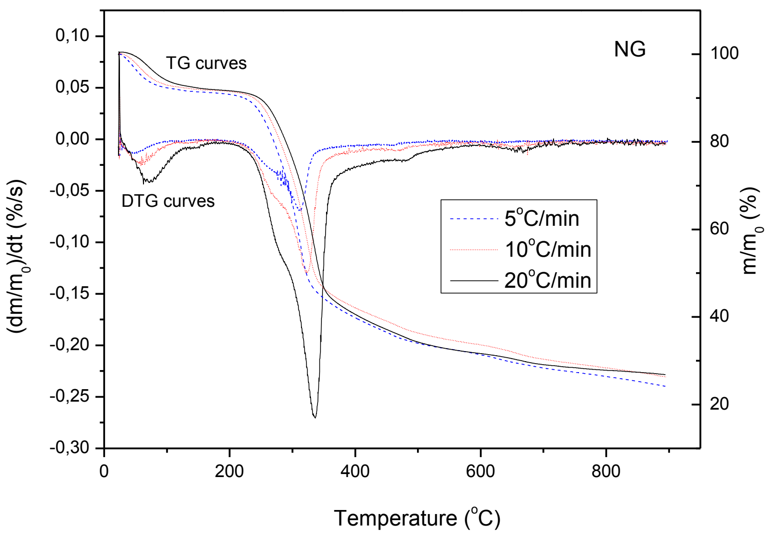
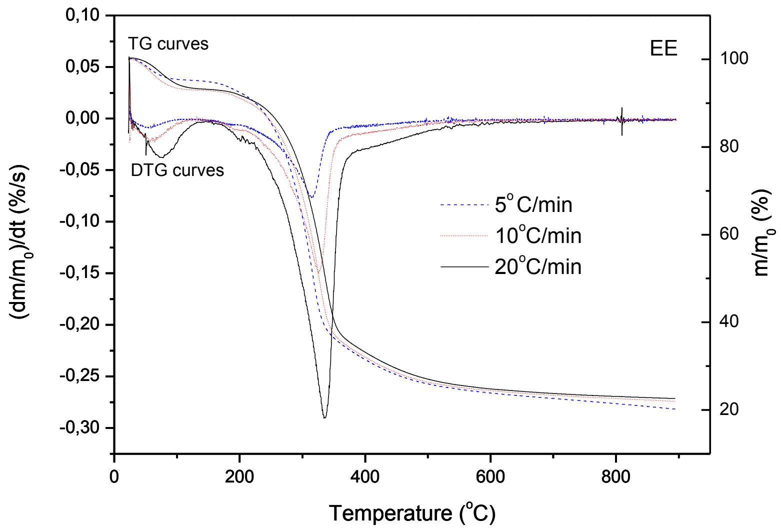

flare
Bed material
screw feeder
Gas
Cyclone
Gas analyser
Tar sampling
Gasifier
Ash cyclone
bin
Biomass
Air heater
air
propane
Air blower
air
ash bed
Ash bed screw
discharge
Ash bed
bin

Figure 3



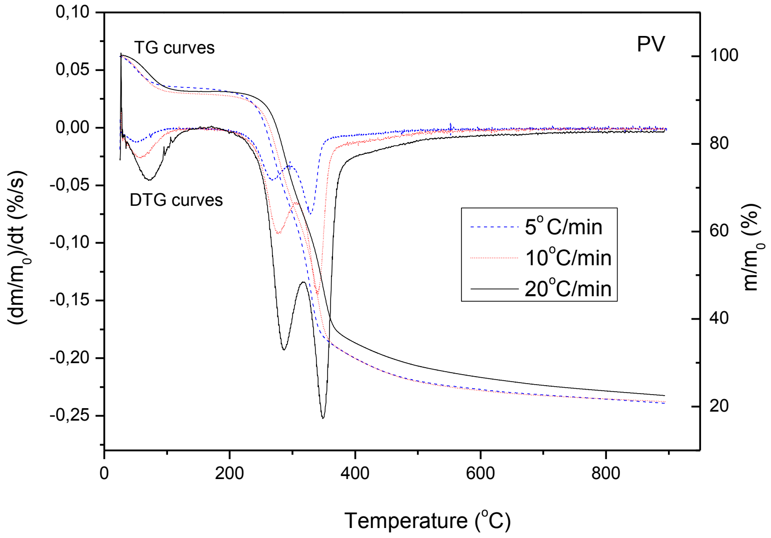
NG
TG curves
DTG curves
5°C/min
10°C/min
20°C/min
(dm/m0)/dt (%/s)
m/m0 (%)
Temperature (°C)
0,10
0,05
0,00
-0,05
-0,10
-0,15
-0,20
-0,25
-0,30
0
200
400
600
800
100
80
60
40
20

Figure 4



TG curves
EE
DTG curves
5°C/min
10°C/min
20°C/min
(dm/m0)/dt (%/s)
m/m0 (%)
Temperature (°C)
0,10
0,05
0,00
-0,05
-0,10
-0,15
-0,20
-0,25
-0,30
0
200
400
600
800
100
80
60
40
20

Figure 5



0,10
0,05
0,00
-0,05
-0,10
-0,15
-0,20
-0,25
(dm/m$_0$)/dt (%/s)
TG curves
DTG curves
PV
5°C/min
10°C/min
20°C/min
100
80
60
40
20
m/m$_0$ (%)
0
200
400
600
800
Temperature (°C)

Figure 6

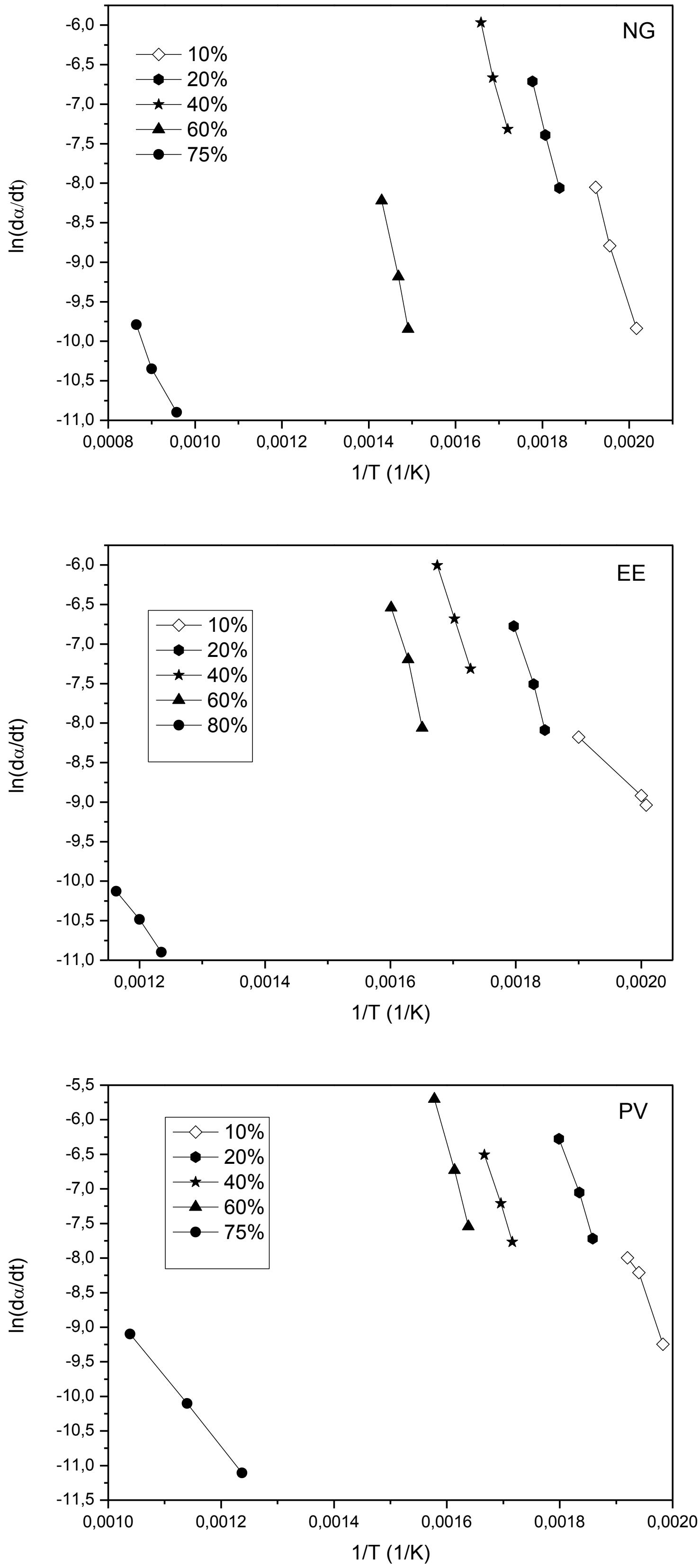

NG
10%
20%
40%
60%
75%
ln(dα/dt)
1/T (1/K)
EE
10%
20%
40%
60%
80%
ln(dα/dt)
1/T (1/K)
PV
10%
20%
40%
60%
75%
ln(dα/dt)
1/T (1/K)

Figure 7

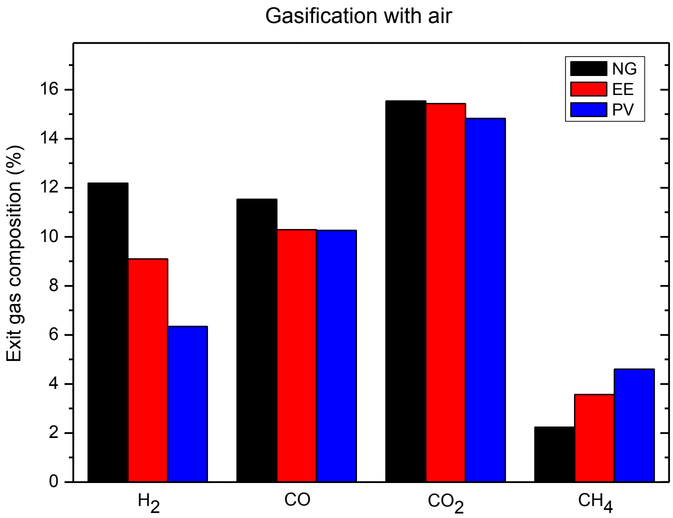
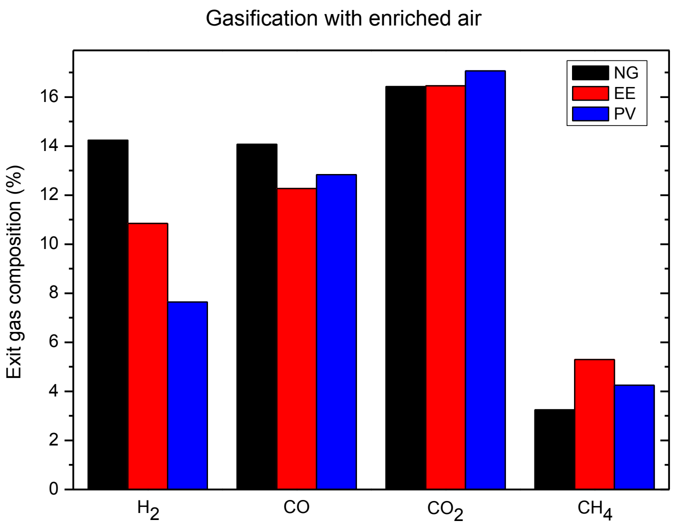

Gasification with air
NG
EE
PV
Exit gas composition (%)
16
14
12
10
8
6
4
2
0
H_2
CO
CO_2
CH_4

Figure 8


Gasification with enriched air
NG
EE
PV
Exit gas composition (%)
0
2
4
6
8
10
12
14
16
H2
CO
CO2
CH4