Chemometric assessment of syngas produced by thermochemical conversion of various wastes

B.D. Škrbić*, N. Đurišić-Mladenović and J. Cvejanov

University of Novi Sad, Faculty of Technology Novi Sad, Bulevar cara Lazara 1, Novi Sad, 21000, Serbia *Corresponding author: <u>biljana@tf.uns.ac.rs</u>, Tel.: +381 21 485 3746, Fax: +381 21 450 413

Abstract

Purpose: The aim of this study was to compare different (co-)gasification processes, investigating main operating parameters that affect the produced syngas quality. Literature-derived data on the composition of the produced syngas (i.e. content of H_2 , CO, CH₄ and CO₂), concerning different systems and conditions, were summarized and assessed by chemometric technique with a final goal to analyze how well the selected parameters could explain the conversion of different waste feedstocks (e.g. biomass, polyethylene, waste tyre) and coal.

Methods: To interpret the data gathered from literature the principal component analysis (PCA) was applied. Two data sets of the literature-based data, SET1 and SET2, were created and analyzed.

Results: In accordance to the parameters of the syngas quality considered for 81 cases of (co-)gasification of different feedstocks (SET1), PCA revealed discrimination among the syngases based on the feedstock origin. Clear separation was seen between syngases produced by gasification of single feed materials and those by co-gasification of the mixed feedstocks. The main parameters of the feedstock composition that affected the syngas quality seemed to be the content of C and O.

Conclusions: PCA has demonstrated that syngas composition was primarily affected by the type of feedstock gasified. The results showed that co-gasification of coal, polymeric and/or biomass waste led to distinctive group of syngases that differed from the composition of syngases produced by single feed (particularly coal and tire) gasification. The overlapping of the syngases produced under different operating conditions suggested the possibility to substitute one another.

Keywords: gasification, pyrolysis, syngas, PCA

Introduction

Different energy sources, including biomass, municipal solid wastes, agricultural wastes and other low grade materials could be expected to have a significant role in providing the energy in future, particularly through their utilization by thermochemical conversion processes other than direct combustion. In fact, the importance of energy recovery from waste is gaining a fundamental role within the context of conventional energy source crises. Apart of using 'end of life" product for the recovery of various resources (energy, chemicals), this also provides a part of the solution for the growing problem of landfills. Additionally, such practice contributes to energy security and availability, independency from foreign oils and reduction of greenhouse gas emissions [1].

Gasification is a form of thermochemical conversion technology that provides part of the solution towards dependable renewable energy source. It is a process of the conversion of any carbonaceous fuel by partial oxidation at high temperatures (generally in the range 700–1000 °C) to a combustible gaseous mixture, so-called syngas, consisting mainly of hydrogen (H₂), carbon monoxide (CO), methane (CH₄) and carbon dioxide (CO₂). Gasification has high efficiency, low negative environmental impact and produces a gas with a wide range of applications; the significant potential of this technology is attributed to several key advantages [2-4]: it can utilize a wide range of carbonaceous materials as feedstock (e.g. coal, biomass, solid and liquid wastes), producing syngas, which can be used as fuel or as raw materials for other chemical processes; it may be considered as a pre-combustion carbon capture technology, as syngas may be converted into a CO₂ stream ready for storage and into a hydrogen rich fuel be used as fuel in hydrogen engines or fuel cells; the emission of hazardous pollutants such as dioxins, nitrous and sulphur oxides is minimized particularly if compared with the direct combustion (for example: NO_x formation is reduced due to the lower gasification temperature as compared to that encountered during the combustion); a considerable advantage of gasification over combustion is a strong reduction in the process gas volume by a factor 5 to 20, which in turn reduces the size of gas conditioning/cleaning equipment.

The quality of the produced syngas is depended on its composition that determined its heating value, downstream processing of the cleaning and the upgrading and the final application. The sum of the H₂ and CO contents in syngas (H₂+CO) and their ratio (i.e. H₂/CO) are two important measures of syngas quality for the chemical industry: a syngas with a high percentage of (H₂+CO) has strong reducing power, while a high value of the H₂/CO molar ratio indicates a syngas useful for chemical syntheses (e.g. the H₂/CO stoichiometric molar ratios required for the synthesis of methanol, hydrocarbon fuel and DME are 2, 2 and 1, respectively [5, 6].

Gasification systems may run on single or multiple sources of feedstock. Gasification of coal is an old technology, which is now enjoying a considerable renaissance. Namely, electricity generation has emerged as a large new market that renewed the interest in the gasification, which is seen as a means of enhancing the environmental acceptability of coal as well as of increasing the overall efficiency of the conversion of the coal chemical energy into electricity. Despite a contentious role of coal in the production of CO_2 as a greenhouse gas, it still plays an important part in the thinking of

many long-term energy strategies, as the world's coal reserves would last for about 200 years presuming current consumption rates and they are more evenly distributed than oil and natural gas [7].

In recent years, the need of using coals (also lowgrade) and wastes for energy production has led to the study of carbonaceous material co-gasification, especially blends of coal with biomass [4, 8] and polymeric waste materials (like tires and plastics) [2, 9-12], with the aim of using existing installations to process coal with diversified feedstocks [4]. Besides the feedstock diversification, co-gasification of coal and biomass has several advantages [4,13-15]: decreasing the use of fossil fuels; reduction of CO_2 emissions due to biomass carbon bio origin; reduction of the problems caused by sulfur and ash contained in coal as biomass has almost no sulfur and low ash conten, increase of volatile matter contents. However, biomass gasification is relatively high-cost and the gasification systems can often encounter the problem of unsteady source of biomass feed throughout the year: during off-season of a given biomass, another feedstock has to be mixed with the feedstock in order to maintain a steady supply of feedstock to the gasifier for seeking the desired output power from the gasification power plant. As the composition of the waste can change both temporally and spatially, the role of various input and operational parameters on the gasifier performance has to be examined [1]. Much attention has been given to evaluate the behavior of various kinds of single component materials [2, 4, 9, 11, 16] under gasification or pyrolysis conditions. There have been several studies performed to assess the quality of raw syngas poduced by co-gasification [4, 8, 10].

This study aims to contribute to such efforts and to compare quality and yield of syngas produced under different conditions of the waste and/or coal gasification in order to assess general information for various systems (different gasifier scales and types, temperatures, etc.). Literature-derived data on the composition of the produced syngas (i.e. content of H_2 , CO, CH₄ and CO₂), concerning different steam gasification systems and the conditions, were summarized and assessed by chemometric technique (principal component analysis-PCA) with a final goal to analyze how well the selected parameters could explain the conversion of different waste feedstock (e.g. biomass, polyethylene, waste tire) and coal, and to assess the produced syngases similarities and dissimilarities.

Materials and Methods

Data sets

Two data sets (SET1 and SET2) of the literature-based data on the steam gasification processes were created; steam is usually used as a gasifying agent to achieve high hydrogen yield. Brief description of the sets is given in Tables 1-2, listing the literature sources and gasification conditions. The main presumption in searching the literature for numerical values of the gasification parameters was that the more data gathered, the more reliable (general) statistical results might be obtained. The similar approach for chemometric evaluation of literature-based data was recently applied for assessment of crude glycerol co-gasification with lignocellulosic biomass [17] as well as for assessment of fatty acid profiles of vegetable oils and their influence on selected fuel properties of the obtainable biodiesel [18].

It should be pointed out that even numerous studies on the steam gasification could be found in the literature, they are not comparable with respect to the numerical variables presented; so, only those studies comparable among each other regarding the reported parameters were taken into consideration, since the input data sets should not contain empty cells if PCA is applied. It appeared that the most often presented data are volumetric percentages of hydrogen (H₂), carbon monoxide (CO), carbon dioxide (CO₂) and methane (CH₄); so, these parameters were considered in both sets, together with two derived indicators: H_2/CO ratio and (H₂+CO) content.

Thus, SET1 contained these 6 parameters for 81 cases of syngas production by steam gasification of various feed materials reported in literature (Table 1). It was analyzed in order to get as general as possible multiple correlations among the considered variables and to explore the differences/similarities in the syngases produced under different conditions of the steam gasification.

SET2 was formed in order to assess the influence of the feedstock composition on the syngas quality (Table 2). It contained the same 6 parameters of the syngas quality previously mentioned, together with variables defining the feedstock composition (the elemental (mass percentages of C, H, O, N, S) and the proximate (the mass percentages of volatile matter, fixed carbon and ash), but for fewer cases than in the case of SET1. In total, SET2 consisted of 44 cases comparable in 14 variables. This was the "a" version of the SET2, while "b" version contained the relative ratios of C/H and O/H instead of the C, H, and O contents. The SET2 contained data on 23 cases of the tire gasification taken from 4 studies [2, 9, 11, 19], 11 cases of the coal gasification from 3 studies [4, 8, 16], 1 case of the Refused Derived Fuel (RDF) gasification [11] and 9 cases of the biomass gasification from 4 studies [8, 11, 16, 20].

Table 1. Description of the	e input data set coded SET1	, which contained (б variables (Product	gas quality: H ₂ ,	$CO, CH_4,$
CO_2 ; (H ₂ +CO); H ₂ /CO) f	for 81 cases of the produced	syngas			

CO ₂ , (H ₂ +CC	(), 112/ CO) for of cases of the produced synge		
Data source	Gasification process description:	Feedstock	Number of
	gasification agent, process scale,		samples
	temperature, feeding ratio (FR), catalyst		(sample
			codes)
[9]	Steam lab-scale rotary kiln reactor 850	waste tire	3 (1-3)
[2]	$^{\circ}C$ 025 $^{\circ}C$ 1000 $^{\circ}C$ EP-2 no cotalyst	waste the	5 (1 5)
[0]	C, 925 C, 1000 C, 1K-2, 10 catalyst		5 (4.0)
[2]	Steam, pilot rotary kiln reactor, 850 C,	waste tire	5 (4-8)
	FR=0.33-1.3, no catalyst		
[11]	Steam, lab-scale rotary kiln reactor, 850	Refused Derived Fuel (RFD), biomass	3 (9-11)
	°C, FR=2.21, no catalyst	(poplar), tire	
[16]	Steam, lab-scale fixed bed reactor, 700 °C.	lignite (3 samples)	12 (12-23)
[-~]	no catalyst	hard coal (5 samples)	()
	no eddiyst	hiemaas (anangu anong 4 samplas)	
5.43		biomass (energy crops, 4 samples)	10 (04.0.0)
[4]	Steam+oxygen, lab-scale bubbling	100% brown (German) coal (GC),	13 (24-36)
	fluidized bed, 850 °C, FR=0.9, no catalyst	80% GC 20% pine,	
		80% GC 20% (olive oil) bagasse,	
		90% GC 10% polyethylene (PE).	
		80% GC 20% PF	
		100% sub bituminous (Puortellano) coal	
		(DC)	
		(PC),	
		80% PC 20% pine,	
		80% PC 20% (olive oil) bagasse,	
		90% PC 10% PE,	
		100% bituminous (South African) coal	
		(SAc)	
		800/ SA a 200/ mina	
		80% SAC 20% pille,	
		80% SAc 20% (olive oil) bagasse,	
		90% SAc 10% PE	
[10]	Steam, pre-pilot fluidized bed gasifier,648-	75% olive husk (OH) 25% polyethylene	19 (37-55)
	856°C, FR=0.32-1.08, without catalyst in 3	terephthalate (PET) (15 samples)	
	cases otherwise Ni/Al ₂ O ₂	75% olive husk (OH) 25% tire (4 samples)	
		7576 onve husk (on) 2576 the (1 sumples)	
[10]	Steam (avaant in two access air steam and	tiro	14 (56 60)
[19]	Steam (except in two cases, an+steam and	the	14 (30-09)
	$air+CO_2$), lab-scale bubbling fluidized		
	bed, 820°C, FR=0.273-0.52 (except in two		
	mentioned cases), no catalyst		
[8]	Steam, lab-scale external circulating	pine sawdust (PS) 100%,	9 (70-78)
_	radial-flow moving bed. 800°C. FR=1.3.	bitumenous coal (BC) 100%.	
	no catalyst	PS 25% BC 75%	
	no cutury ot	PS 50% BC 50%	
		PS 750/0 DC 30/0,	
		PS /5% BC 25%,	
		PS 50% BC 50%,	
		PS 50% BC 50%,	
		PS 50% BC 50%,	
		PS 50% BC 50%	
[20]	Steam lab-scale fluidized bed 805-815°C	biomass (almond shell)	2 (80-81)
[20]	ED-1 1 15 no cotaluct		2 (00 01)
	1 IX-1-1.1.J, 110 Catalyst		1

Feedstock	Data source ^a	Feedstocks	Variables used for PCA	Number of samples (sample codes ^b)
tire	[9]	tire	Syngas quality: H ₂ , CO,	3 (1-3)
	[2]	tire	CH ₄ , CO ₂ ; (H ₂ +CO); H ₂ /	5 (4-8)
	[19]	tire	CO;	14 (56-69)
	[11]	tire	Feedstock elemental	1 (11)
coal	[16]	lignit	composition: C and H (or	2 (12-13)
	[16]	hard coal	C/H), O (or O/H), S, N	5 (15-19)
	[4]	brown (German) coal]	1 (24)
	[4]	sub-bituminous (Puertollano) coal		1 (29)
	[4]	bituminous (South African) coal		1 (33)
	[8]	bitumenous coal		1 (71)
RDF	[11]	RDF		1 (9)
biomass	[11]	poplar		1 (20)
	[16]	not specified		4 (20-23)
	[8]	pine sawdust]	1 (70)
	[20]	almond shell]	3 (79-81)

Table 2. Description of the input data set coded SET2: 14 (or 13) variables \times 44 cases

^a For processes applied in the cited references please see Table 1.

^b Sample codes refer to those given originally for the SET1, Table 1.

Principal component analysis (PCA)

PCA was applied to identify the underlying pattern in the data sets, i.e. "hidden" correlations between the process parameters and in this way to contribute to the general interpretation of various waste steam gasification systems. It is a commonly used chemometric technique for data reduction [18, 21-24] and simplification of large sets of variables. The principal of PCA is to characterize each case (named also as object, sample or observation), i.e. syngas in this study, not by analyzing every variable (such as quantity of H_2 , CO, CH_4 , etc.), but projecting all the numerical data from the input data set(s) in a much smaller sub set of new variables called principal components (PCs), which are linear combinations of the initial variables. The algorithm of PCA can be found in the standard textbooks [25]. There are different softwares that could be used for PCA: after the formation of the input data set and the choosing of the criteria for the calculation (e.g. Kaiser's rule [26] like in this study), these softwares perform the calculations. In this study, PCA was done with Statistica 12 software (StatSoft, 1984-2015 Dell Inc.).

The main PCA results used for the interpretation of the formed data sets are loading and score values calculated for each of the retained PCs. The loadings explain the magnitude (strong or weak correlation) and the manner (positive or negative) in which the initial variables correlate among themselves and contribute to grouping (classification) of samples defined by obtained scores – coordinates of the samples in the new plane (2D) or space (3D) defined by the retained PCs [23]. The higher the loading of a variable the more that variable contributes to the sample variation accounted for by the particular PC. The sign of loading value indicates whether the particular initial variable is in positive or in negative correlation with the PC. Comparison of the score and loading plots reveals the relationship between the samples and the variables, e.g. which samples could be related with high or low levels of different parameters considered. It is also possible to view the presence of outliers – cases (syngases), which are far removed from the others in the score plot because they have exceptionally high or low levels of some parameters.

In this work, the input data sets were created by putting the cases (syngases) from different steam gasification processes into the rows and the parameters of the syngases (and also of the processed feedstocks in the case of SET2) in the columns; the exact parameters considered in each of two data sets analyzed by PCA are listed in Tables 1-2. Coefficients (loadings) between the initial variables and few new PCs retained in accordance to the Kaiser's rule were calculated and only those values (either positive or negative) greater than 60% of the maximum loading (in absolute values) per each retained PC [27] were considered for the interpretation of the links among the initial variables and syngases similarities. The calculated score values were graphically presented either in the biplots or score plots in order to visualize if groupings or separations of the syngases might be observed.

Results and Discussion

The results of the PCA application on the SET1 are graphically presented in Figs. 1-2, while those obtained for SET2 are given in Figs. 3-4.

Two PCs were retained for SET1, explaining 82% of the data variance: PC1 accounted for 52% and PC2 for 29% of the variance. As it could be seen from Fig. 1, the most important parameters for distribution of syngases from various studies are: the content of CO, CH_4 and H_2/CO in syngas correlated significantly with PC1 in opposite manner (CO

positively, while the other two parameters negatively with PC1); H_2 (and consequently the derived parameter (H_2+CO)) and CO₂ correlated markedly with PC2 and opposite to each other. The observed correlations implied that the higher CO contents in syngases (influencing lower H_2/CO ratios) might be linked with lower quantities of CH₄, whereas the higher H_2 contents might be indicative for the lower CO₂ levels (and vice versa). This further indicated two possible conversion routes that seemed to affect the quality of syngases considered in the SET1: a) formation of CO at the expense of CH₄ (i.e. steam cracking reactions, e.g. CH₄+H₂O \rightarrow CO+H₂), and b) the increased production of H₂ at the expense of the CO₂ reduction and vice versa. The location of points in the biplot, Fig. 1a, illustrates differences in composition of the syngases produced in different studies: the points located closely to some of the marks of the considered parameters (e.g. H₂, CO₂, CO, CH₄) are syngases with high levels of that particular parameter (e.g. syngases from study of Karatas et al. [19], with respect to their position in the plot in Fig. 1a, had quantities of CH₄ higher than other considered gases, while gases from study of Smolinski et al. [16] had exceptionally higher (H₂+CO) yields).



Fig 1 PCA results for SET1: PC1 vs. PC2 biplot with points designated according to the source reference

In order to further explore differences/similarities among the gases produced under different conditions, the gases were categorized using following criteria:

-feedstock type (tire, coal, biomass, coal and biomass, biomass and PET, biomass and tire, coal and PET; one sample of RDF was included into the group of coal),

-temperature and presence of catalyst (\geq 850°C no catalyst, <850°C no catalyst, <850°C with catalyst, <850°C with catalyst),

-type of gasifier (lab-rotary kiln, lab-bubbling, lab-fluidized, lab-ECRFM (external circulating radial-flow moving bed), lab-fixed, pre-pilot, pilot-rotary kiln), and

-fuel-to-steam ratio, FR (FR≥2, 1≤FR<2, 0.5≤FR<1, FR<0.5, and no FR specification).

These categories were used to present the syngases from SET1 in the same PC1 vs. PC2 score plots, only the way of visual identification of each gas (point in the plot) was dependent on the particular criteria. Hence, four "new" figures (Fig 2a-d), were created differing in the criteria used for syngas (point) presentation, but being in fact equivalent among each other concerning the points distribution; they are further used to point out if discrimination among the syngases could be linked with the introduced categories. It should me mentioned that all these categories represented a rough simplification of the processes described in the cited studies, as the effort was made to classify all the data in as few as possible categories of the gasification processes. Taking into account all the score plots given in Fig. 2, it could be said that discrimination among the considered syngases could be seen only when their origin, i.e. feedstock types, were taken into consideration. Namely, clear discrimination was seen among syngases produced by gasification of single feed materials and those by co-gasification of the mixed feedstocks, Fig. 2a. Namely, the syngases produced by steam gasification of coal and tire were separated from those obtained by co-gasification of the multiple materials: former were grouped within dashed line ellipse shown in Figs. 1 and 2a, while later with full line; syngases from biomass gasification were located in between these two groups. The only exception to these groupings represent the position of two cases of the coal gasification: 29 and case 71, clustered together with co-gasification syngases. It seemed that cogasification gases had higher contents of CO_2 (and CO), while the higher H_2 levels (and thus, higher H_2/CO and (H_2+CO) could be obtained by coal and tire gasification as compared to other syngases included in SET1. The basic statistics on the syngas main constituents in the observed groups are summarized in Table 3: differences observed between the mean values of the four groups (syngases from tire, coal, biomass and mixed feedstock steam gasification) were mainly significant (at α 0.05), except between mean values of the main constituents of syngases from coal and mixed feedstock.

The outlying samples, i.e. syngases far removed from the observed groups due to exceptionally different levels of the considered parameters, were those produced under unique conditions: syngas no. 3 [9] – the only case of the gas produced by high-temperature gasification (1000°C), syngas no. 9 – the only case of the syngas obtained from RFD [11], and syngas nos. 68 and 69 produced by using air and CO₂ as gasification agents apart of the steam [19]. These outliers suggested the following: high temperature in the steam gasification of tires led to the enhanced syngas yields; RFD steam gasification gave syngas similar to those produced by biomass steam gasification; the additional agents in steam gasification of tire, like air and CO₂, led to simultaneous lowering of the CH₄ content and the increasing of the CO and CO₂ contents in the syngases if compared to the steam gasification of tires. No clear discrimination was seen among the gases produced under different temperature/catalyst conditions (Fig. 2b) and in various gasifier types (Fig. 2c) as there was overlapping of the gases from different categories. With respect to the feeding rate (FR), majority of the gases produced under low FRs (<0.5), i.e. 11 out of 15 gases (73%), was located in the left part of the plot in Fig. 2d, which might be linked with the highest CH₄ levels. This coincided with the known fact that the content of H₂ and CO in the syngas increase as FR increases, while CH₄ correspondingly decreases as a consequence of the steam reforming reaction of CH₄ [2].





Fig 2 PCA results: PC1 vs. PC2 *"score"* plot obtained for SET1 with points designated according to: a) the feedstock used for gasification, b) gasification temperature and presence of catalyst, c) gasifier type, and d) feeding rate (FR), i.e. steam-to-fuel ratio

Table 3. Means and ranges (in parentheses) of the main constituents of syngas produced by steam gasification of single and mixed feed materials*

	H_2	СО	CO_2	CH_4	H ₂ /CO	H ₂ +CO
tire	57 ^a (52-64)	8 ^a (3-20)	5 ^a (3-20)	29 ^a (12-38)	9 ^a (3-17)	58 ^a (44-75)
coal	55 ^b (35-68)	16 ^b (6-27)	26 ^b (18-51)	3 ^b (0-9)	4 ^b (1-7)	71 ^b (42-81)
biomass	42 ^c (38-48)	19 ^b (13-28)	29 ^b (19-37)	10 [°] (7-13)	$2^{c}(2-3)$	46 ^c (36-63)
mixed feed materials	49 ^b (35-64)	13 ^b (3-32)	21 ^b (3-51)	17 ^d (3-38)	7 ^b (1-17)	51 ^b (27-65)

*mean values followed by the same letters in superscript (either ^{a, b, c or d}) within a column indicate equal means of the particular groups at the significance level 0.05

In order to check if correlation between the syngas quality and the feedstock elemental composition could be found, SET2 (both versions "a" and "b") was analyzed by PCA. For both versions of SET2, 4 PCs were retained according to the Kaiser's rule, but only one PC, PC1, captured the correlation between the syngas and the feedstock composition (Fig. 3). For SET2a, PC1 correlated significantly with S, C, H and CH_4 in a positive manner, while with O and CO_2 in negative manner (Fig. 3a). This might be interpreted as follows: the feedstocks with higher levels of S, C, and H, showed lower levels of O and gasification of such feedstocks led to the production of syngases with higher quantities of CH_4 , and lower quantities of CO_2 ; and vice versa. Similarly, PC1, retained for SET2b, correlated positively with S and CH_4 and negatively with O/H and CO_2 (Fig. 3b).



Fig. 3 PCA results: PC vs. PC2 loading plots obtained for SET2: a) "a" version of SET2, b) "b" version of SET2

Due to similarity of the loading values and the variables' correlations found for SET2a and SET2b, only SET2b has been further discussed, not SET2a. According to the score values obtained for PC1 and PC2, the cases included in SET2b were clearly discriminated taken into account the feedstock types. Namely, three distinctively separated groups could be observed in the score plot, Fig. 4b: tire, coal and biomass. This differentiation was governed by the variables found to be the most influential for PC1 and PC2 (Fig. 3b), thus it could be ascribed to the difference in the elemental composition of these three groups of feedstocks: tire contains more sulphur than coal and biomass, and syngases from steam gasification of tires had the highest quantities of CH_4 , which were the reasons why all gases from tire steam gasification were located in the right (positive) part of PC1 (Fig. 4b); syngases from coal gasification were located in the upper part of PC2 (Fig. 4b), as a consequence of the higher C/H ratios and fixed carbon levels (Fig. 3b) in the coals than in biomass and tire; samples obtained from biomass steam gasification were located in the third quadrant (Fig. 3b), as a consequence of the highest levels of volatiles and O/H (as well as the lowest fixed carbon level) if compared to coal and the lowest S content if compared to tire. It is interesting to note that within the "coal" group, gradual separation of low- and higher-rank coals might be observed with later being "above" former along PC2. There were three outlying samples not belonging to any of three observed groups: sample no. 9 - RDF [11], sample no. 29 -sub-bituminous (Puertollano) coal [4], and sample no. 71 – bituminous coal [8]. According to the position of RDF in the score plot in Fig. 4, it might be concluded that its composition (particularly O/H ratio, the level of volatiles and S) and the resulted syngas (i.e. its CH_4 content) were intermediate to those of the biomass and tire. The seen outliers among the coal samples obviously differed in the composition and the produced gas quality compared to lignite, hard coal, brown (German) and bituminous (South African) coal. Discrimination of cases in accordance to the feed origin was not observed along PC3 and PC4 (data not shown).



Fig 4 PC1 vs. PC2 score plot for SET2b with syngases (points) designated according to: a) cited references, and b) feedstock type

Conclusion

Although a direct comparison of gas composition produced under different conditions of the gasification is not possible due to variation of many operating conditions, comparison of literature-based data on steam gasification made by PCA in this study provided a general insight into the similarities of different (co-)gasification systems. Namely, PCA has demonstrated that syngas composition was primarily affected by the type of feedstock gasified. The results showed that co-gasification of coal, polymeric and/or biomass waste led to distinctive group of syngases that differed from the composition of syngases produced by single feed (particularly coal and tire) gasification. The overlapping of the syngases produced under different operating conditions suggested the possibility to substitute one another. All of these statements are valid within the scope of the investigation, i.e. sets that are formed and analyzed here; data other than that used in this study might behave differently.

Acknowledgement. This work is a part of the project 172050 of Serbian Ministry for Education, Science and Technological Development.

References

[1] Ahmed, I.I., Nipattummakul, N., Gupta, A.K.: Characteristics of syngas from co-gasification of polyethylene and woodchips. Appl. Energ. 88, 165-174 (2011)

[2] Donatelli, A., Iovane, P., Molino, A.: High energy syngas production by waste tyres steam gasification in a rotary kiln pilot plant. Experimental and numerical investigations. Fuel 89, 2721-2728 (2010)

[3] Gomaa, I.A.: High temperature steam gasification of solid wastes: characteristics and kinetics. Dissertation submitted to the Faculty of the Graduate School of the University of Maryland, College Park, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 2011;

[4] Pinto, F., André, R.N., Carolino, C., Miranda, M: Hot treatment and upgrading of syngas obtained by co-gasification of coal and wastes. Fuel Process. Technol. 126, 19–29 (2014)

[5] de Filippis, P., Borgianni, C., Paolucci, M., Pochetti, F.:Gasification process of Cuban bagasse in a two-stage reactor. Biomass Bioenerg. 27, 247–52 (2004)

[6] Kumabe, k., Hanaoka, T., Fujimoto, S., Minowa, T., Sakanishi, K.: Co-gasification of woody biomass and coal with air and steam. Fuel 86, 684–689 (2007)

[7] Higman, C., van der Burgt, M.: Gasification, Elsevier Science, Burlington, MA (2003)

[8] Tursun, Y., Xu, S., Wang, C., Xiao, Y., Wang, G.: Steam co-gasification of biomass and coal in decoupled reactors. Fuel Process. Technol. 141, 61–67 (2016)

[9] Portofino, S., Donatelli, A., Iovane, P., Innella, C., Civita, R., Martino, M., Matera, D.A., Russo, A., Cornacchia, G., Galvagno, S.: Steam gasification of waste tyre: Influence of process temperature on yield and product composition, Waste Manage. 33 672–678 (2013)

[10] Brachi, P., Chirone, R., Miccio, F., Miccio, M., Picarelli, A., Ruoppolo, G.: Fluidized bed co-gasification of biomass and polymeric wastes for a flexible end-use of the syngas: Focus on bio-methanol. Fuel 128, 88–98 (2014)

[11] Galvagno, S., Casciaro, G., Casu, S., Martino, M., Mingazzini, C., Russo, A., Portofino, S.: Steam gasification of tyre waste, poplar, and refuse-derived fuel: A comparative analysis. Waste Manage. 29, 678–689 (2009)

[12] Pinto, F., Franco, C., Andre, R.N., Miranda, M., Gulyurtlu, I., Cabrita, I. Co-gasification study of biomass mixed with plastic wastes, Fuel 81, 291-297 (2002)

[13] Brown, C.R., Liu, Q., Norton, G.: Catalytic effects observed during the co-gasification of coal and switchgrass. Biomass Bioenerg. 18, 499–506 (2000)

[14] Chmielniak, T., Sciazko, M.: Co-gasification of biomass and coal for methanol synthesis. Appl. Energ. 74, 393–403 (2003)

[15] McLendon T.R., Lui, A.P., Pineault, R.L., Beer, S.K., Richardson, S.W.: High-pressure co-gasification of coal and biomass in a fluidized bed. Biomass Bioenerg. 26, 377-388 (2004)

[16] Smolinski, A., Howaniec, N., Stanczyk, K.: A comparative experimental study of biomass, lignite and hard coal steam gasification. Renew. Energ. 36, 1836-1842 (2011)

[17] Đurišić-Mladenović, N., Škrbić, B.D., Zabaniotou, A.: Chemometric interpretation of different biomass gasification processes based on the syngas quality: Assessment of crude glycerol co-gasification with lignocellulosic biomass. Renew. Sust. Energ. Rev. 59, 649–661 (2016)

[18] Škrbić B., Cvejanov, J., Đurišić-Mladenović, N.: Chemometric characterization of vegetable oils based on the fatty acid profiles for selection of potential feedstocks for biodiesel production. J. Biobased Mater. Bioenerg. 9, 358-371, (2015)

[19] Karatas, H., Olgun, H., Akgun, F.: Experimental results of gasification of waste tire with air&CO2, air&steam and steam in a bubbling fluidized bed gasifier. Fuel Process. Technol. 102, 166–174 (2012)

[20] D'Orazio, A., Rapagna, S., Foscolo, P.U., Gallucci, K., Nacken, M., Heidenreich, S., Di Carlo, A., Dell'Era, A.: Gas conditioning in H_2 rich syngas production by biomass steam gasification: Experimental comparison between three innovative ceramic filter candles. Int. J. Hydrogen Energ. 40, 7282-7290 (2015)

[21] Škrbić, B., Szyrwinska, K., Đurišić-Mladenović, N., Nowicki, P., Lulek, J.: Principal component analysis of indicator PCB profiles in breast milk from Poland. Environ. Int. 36, 862–872 (2010)

[22] Škrbić, B., Đurišić-Mladenović, N.: Chemometric interpretation of heavy metal patterns in soils worldwide. Chemosphere 80, 1360–1369 (2010)

[23] Škrbić, B., Đurišić-Mladenović, N.: Principal component analysis for soil contamination with organochlorine compounds. Chemosphere 68, 2144–2152 (2007)

[24] Škrbić, B., Đurišić-Mladenović, N.: Distribution of chlorinated organic pollutants in a wide variety of soils from Europe and Asia: a multivariate statistical approach. Arch. Environ. Contam. Toxicol. 52, 466–474 (2007)

[25] Vandeginste, B.G.M., Massart, D.L., Buydens L.M.C., Jong, S.D.E., Lewi, P.J., Smeyers-Verbeke, J.: Handbook of chemometrics and qualimetrics: part B. Elsevier, Amsterdam, The Netherlands (1998)

[26] Kaiser, H.F., Rice, J.: Little jiffy, mark IV. Educ. Psychol. Meas. 34, 111–117 (1974)

[27] Jolliffe, I.T.: Principal component analysis. Springer-Verlag, NewYork, USA (1986)