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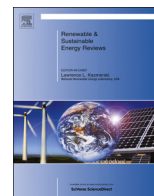
# Chemometric interpretation of different biomass gasification processes based on the syngas quality: Assessment of crude glycerol co-gasification with lignocellulosic biomass

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## ARTICLE INFO

## ABSTRACT

This paper reviews data available in the literature on biomass gasification parameters in order to elucidate the general information common for different gasification systems fueled with different biomass feedstocks by applying principal component analysis (PCA). Focus was given to the co-gasification of crude glycerol derived as by-product in biodiesel plants, with olive kernel derived from olive oil processing plants, a lignocellulosic biomass locally available in the Mediterranean region, which might be considered as an important step towards economic and sustainable biodiesel production, particularly in small and medium-scale plants. The PCA was applied for the first time on the literature-based input data sets of the thermochemical conversion processes of various biomass, aiming to: (a) characterize syngases obtained under different conditions during co-gasification of crude glycerol and olive kernel, (b) compare syngases obtained by co-gasification and co-pyrolysis of crude glycerol and olive kernel, and (c) assess general information common for different gasification systems, comparing the syngas from co-gasification of crude glycerol with olive kernel with those produced by other non-woody and woody biomass gasification processes.

PCA has evidenced the strongest correlations among the variables included in the sets, which were further used to discuss the similarities among the produced gases. Some of the major conclusions derived from PCA results concern the comparability of gases produced by co-gasification of crude glycerol and olive kernel with the published data, particularly with gases produced by gasification of olive residues with intermediate to the highest $H_2$ contents, intermediate to low $CO_2$ contents and intermediate $H_2/CO$ ratios. Even though olive-based waste gasification may result in wide range of the gas composition, the majority of the considered syngases was separated on the PCA biplots from gases produced by gasification of woody and other non-woody biomass due to higher $H_2/CO$ ratios.

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## 1. Introduction

Biomass as a typical kind of renewable energy source, which has been used for heat and power production, has become an interesting matter due to a growing concern for future energy supply and for limiting $CO_2$ emissions. Traditionally, it has been used to produce heat by combustion, but it may be also used for biofuel production through thermochemical or biochemical processing. Gasification is one of the most promising technology for utilizing renewable resources to produce fossil fuel alternatives. It is a more mature form of thermochemical conversion technology than pyrolysis; thus it is an important method to convert biomass into combustible gaseous mixture of syngas consisting mainly of hydrogen ($H_2$), carbon monoxide (CO), methane ($CH_4$) and carbon dioxide ($CO_2$) by partial oxidation of the biomass at high temperatures generally in the range 800–1000 °C in contrast to the pyrolysis that is conducted in the absence of oxygen at 300–650 °C [1]. Syngas quality is depended on its composition, heating value, and possible impurities contained. The sum of the $H_2$ and CO gas percentages ($H_2+CO$) and their ratio (i.e. $H_2/CO$) are two important measures of syngas quality for the chemical industry: a syngas with a high percentage of ($H_2+CO$) are strong reducing power, while a high value of the $H_2/CO$ molar ratio indicates a syngas useful for chemical syntheses [2].

Biomass can be divided into two big categories: woody biomass, which includes the biomass resulting from conventional forests and/or from tree energy plantations, and the non-woody, agroresidues, resulting as byproducts from various agricultural and/or agro-industrial processes [3]. Due to the low price of non-woody biomass, non-woody biomass fuels are cheap fuels, adding a high economic potential compared to the expensive woody biomass fuels [4].

There is a great amount of agricultural residues from food and energy crops that could be adequate for energy recovery, e.g. straws, hulls, pits, cobs, etc. Biowaste readily available from the biooil industry is also one of the attractive renewable energy sources that can be used for energy production via thermochemical applications [5]; for instance, olive oil production generates lignocellulosic solid by-products (olive kernel, olive tree pruning and harvest residues), which are particularly widely available in Mediterranean region. Olive kernel is the final solid residue emerging from olive oil production industries: olives are processed in an oil extracting plant to recover the oil content; after a first residue drying, residual oil is extracted by hexane, generating a residual solid product called olive kernel with a moisture content of around 10–12 mass% [6–9]. Traditionally, such kind of residue is sold as fuel for combustion in small boilers and specially designed furnaces due to its significant heating value ($\sim$21 MJ/kg) [9]. However, a more efficient and environmental friendly alternative with respect to $CO_2$ and $CH_4$ mitigation to the atmosphere is olive kernel thermochemical conversion, which produces a high heating value gas for gas engine or even gas turbine in a combined cycle of heat/power production [8].

Over the past few years some studies also considered the combined exploitation of crude glycerol (CG) with locally produced agro-residues by thermochemical treatments in order to explore a viability for the valorization of the abundant CG, which in this case is to produce high added value fuels like renewable $H_2$ production [6,7,10–13]. Crude glycerol is the only by-product of the biodiesel production by vegetable oil transesterification:

approximately 100 kg of oil reacts with 10 kg of methanol to produce 100 kg of biodiesel and 10 kg of glycerol (10 mass% of the total product) [10,14]. As it originates from biomass, this byproduct could be included in the renewable category. It contains impurities such as methanol, inorganic salts and biodiesel making it a low-value product; nevertheless, for its usage as a fuel, refining or purification is not required [15]. Glycerol has been increasingly produced in recent years as a consequence of the rapid growth in biodiesel production and its increasing availability and renewability makes it attractive to utilize as feedstock for producing $H_2$ gas or syngas [16,17]. To convert CG to $H_2$, different routes such as pyrolysis [18], gasification [19–21] aqueous phase reforming [22,23] and catalytic reforming [24–26] have been investigated in recent years. The combined thermochemical conversion of crude glycerol obtained in the production of biodiesel with the locally available biomass might be also considered as an important step contributing to the sustainability and economical production of biodiesel particularly in small and medium-scale plants, since they generally cannot afford the extra cost of crude glycerol distillation and purification as a prerequisite for the further use in food and pharmaceutical industries, so they are managing the glycerol excess as a waste because of its impurities, which further has an impact on the increasing storage and management costs [6,7].

Therefore the effect of parameters such as temperature, air ratio, and the feedstock's composition have been investigated to identify the most influential factors for the composition and quality of the gas produced by the co-gasification of CG with different biomass wastes [7,10–13]. The links among the parameters considered in these studies were investigated and most frequently presented by simple 2D graphs, not exploring the simultaneous relationships among all of them. In order to interpret large sets of experimental data, powerful multivariate data analysis techniques could be successfully applied, being able to deal with strongly collinear and numerous variables [27]. The multivariate approach provides an initial overview of the data and classification of groups, and is also useful for detection of the outliers with the extreme values of the analyzed variables. Thus, principal component analysis (PCA) is a commonly used multivariate technique for data reduction and simplification of large sets of intercorrelated variables, which are treated equally. This technique can be summarized as a tool for transforming the original variables into new uncorrelated variables, i.e. principal components (PCs). In other words, PCA reduces a set of original (initial) variables and extracts a small number of latent factors (PCs) for analyzing relationships between the observed variables and samples. The main results of PCA are presented in the terms of variable loadings (which values might be presented in tables or plots) and sample scores (most frequently presented in plots). Each PC is a linear combination of the original variables; the coefficients between the initial variables and PCs are called the loadings. Thus, loadings explain how the new PCs are composed from the original variables, i.e. how well the new extracted PCs correlate with the initial variables [28]. The loading values also show which of the initial variables are similar to each other, that is, carry comparable information, and which ones are unique. Sometimes these correlations among the variables and PCs are used in finding the physical meaning of the extracted PCs as hidden factors responsible for (affecting) the observed links [27,28]. When shown graphically on the same plot with score values (the so-called biplot), the loading values indicate the extent to which each considered variable (initial parameter)