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The Influence of Additives Upon the Energetic Parameters and Physicochemical Properties of Environmentally Friendly Biomass Pellets

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Abstract. Solid biomass fuels are economical and practical renewable energy sources. Exploitation of agricultural biomass as a fuel offers considerable advantages in different domains as energy supply as far as the climate is involved. In this study we intended to investigate the feasibility of alternative agricultural residues of grape pomace and corn cob pellets with addition of sawdust, starch, and waste rapeseed oil and to examine how these additives affects the calorific powers and pellets physical properties. Sawdust, starch, and waste rapeseed oil addition was 10 %. Pellets were produced by a manual single pellet press. The calorific powers of the biomass samples were experimentally determined using an oxygen bomb calorimeter (model 6200 adiabatic calorimeter Parr Instruments). The results show that waste rapeseed oil addition significantly increases the calorific powers in grape pomace and corn cob pellets. The highest calorific value was obtained for the grape pomace pellets containing 10 % waste rapeseed oil, 22.14 MJ/kg, compared to grape pomace control pellets, of 21.35 MJ/kg. The calorific values of corn cob control pellets were also increased when adding 10 % waste rapeseed oil, from 17.29 MJ/kg to 19.76 MJ/kg.
The results obtained in this work, related to calorific powers, moisture, ash, volatile, sulphur and nitrogen content, fixed carbon, bulk density, fuel value index, energy density and combustion efficiency, revealed that depending on additives used and their dosage, an acceptable fuel pellet could be produced.
Keywords: Biomass pellets; raw materials; combustion calorimetry; additives dosage.

Resumen. Los combustibles de biomasa sólida son fuentes de energía renovables económicas y prácticas. Al tomar en consideración el clima, la explotación de la biomasa proveniente de la agricultura como combustible ofrece ventajas considerables como fuente de energía en diferentes ámbitos. En este trabajo estudiamos la factibilidad utilizar residuos agrícolas de pastillas de orujo de uva y elote adicionándole aserrín, almidón y desperdicio de canola para analizar como estos aditivos afectan el potencial calórico y las propiedades físicas de las pastillas. El aserrín, almidón y canola se agregaron al 10%. Las pastillas se obtuvieron en una pastilladora manual. Experimentalmente, las potencias calóricas de las muestras de biomasa se determinaron con una bomba calorimétrica de oxígeno (calorímetro adiabático Parr Instruments modelo 6200). Los resultados muestran que la adición de canola incrementa significativamente la potencia calórica de las pastillas de orujo y elote. El valor calórico más alto se obtuvo con las pastillas de orujo a las que se les adicionó un 10% de canola, y fue de 22.14 MJ/kg, comparado con el control de pastillas de orujo que tiene un valor de 21.35 MJ/kg. Las potencias calóricas de las pastillas de control de elote también se incrementaron al adicionar 10% de canola, pasando de 17.29 MJ/kg a 19.76 MJ/kg.
Los resultados de este trabajo relacionados con las potencias calóricas, humedad, contenido de cenizas, volátiles, contenido de azufre y nitrógeno, carbono, densidad de bulto, índice de valor del combustible, densidad de energía

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y eficiencia a la combustión revelan que se puede obtener una pastilla de combustible aceptable dependiendo de utilizar los aditivos y las dosis adecuadas.
Palabras clave: Pastillas de biomasa; materias primas; calorimetría de combustión; dosis de aditivos.

Introduction

A solid fuel based on plant biomass could be a substitute to coal, which in comparison to this fossil fuel, is generated in nature. The expression "biomass" suggests here a diversity of plant constituents, as well as their residues and wastes [1].

In order to produce energy, biomass can be good enough for being considered an option as sustainable and carbon-neutral raw material. In the energy sector, all over the world, there is a need for a fundamental transformation, due to the changing climate circumstances and growing emissions of greenhouse gases. Consequently, biomass gained noticeable attention as a feasible stockpile. Energy from biomass is dependent on various supplies: agricultural and house-hold waste, forest wastes and energy crops. There are two classes of biomass energy production: biofuels (liquid fuels obtained from biomass, replacing petroleum production) and biopower (electricity and heat are obtained using biomass).

In Romania, a high potential is considered to have the production of biofuels and biogas. According to the Romanian National Institute of Statistics the unused technical energy production potential from renewables is of around 8000 Ktonnes, which includes 47 % biomass and biogas, 19 % solar, 19 % wind, 14 % hydro and 2% geothermal energy [2].

Romania is the second country after France regarding the agriculture sector, for both the cultivated area and production of corn [3].

The pellet market is developing constantly, the EU being directly a leader in this area. In Europe, an essential role will have the pelleted solid biofuels in achieving renewable energy objectives, as stated by European Commission. All this reveal furthermore extension in pellet manufacturing and requirement for employment of new, low-cost, substitute raw materials. Alternative supplies of notable concern are residues and by-products from agriculture and food/feed processing. Biomass constituents with high- and low-energy can be mixed in convenient amounts. Constituents generating excessive quantity of ash can be combined with constituents that produce a small amount of ash in order to obtain a good-quality pellet. Choosing the appropriate constituents and combine them in suitable ratio customize the calorific value, moisture and ash content. In order to enhance the quality parameters, biomass can be combined with constituents, such as wood or coal dust [4].

In this study grape pomace and corn cob were chosen as raw materials for obtaining alternative biofuel pellets. The demand to develop the quality of the pellets has become progressively significant. The quality of pellets is established by the end-user's specification on the combustion systems and the handling characteristics [5].

According to Grover et al [6] the first and most relevant step in the analysis into the employment of fuels obtained from waste for energy targets is the achieving of calorific values. Compressed biofuels are performed for improving the fuel properties of residues. Compressed biofuels derived from solid biomass residues, briquettes or pellets, will accomplish a better fuel homogenization, lower moisture content and a higher energy density [7].

Grape pomace is a powerful source of biomass, being the most abundant waste from wine production [8]. The most outspread crops are grapevine, representing 50 million tonnes of grapes per year of which more than 20 million tonnes are assumed by European producers [9]. Romania recorded an increase of the grapes production since 2014, this great potential is due to its geographical position, climatic condition and sandy soils [10]. The waste that comes from wine processing (seeds, skins, leaves and stems) obtained by the winemaking industry, turn into an ecological and economic difficulty, thus, utilisation within power sector is financially reasonable and technically justified in both small and large wineries [11].

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Corn cobs are a ratio of the corn residues (corn stover), besides stalks, leaves (including tassels) and husks [12]. The capacity of corn stover for energy production are expressive since corn is one of the most expanded grown field crops worldwide [13].

Correlating to further crop residues, corn cobs have more favourable combustion properties. Hence, this fuel is a challenge to woody fuels, intending to diminish undesirable consequences after combustion. Corncob has a heating value of about 19.14 MJ/kg, thus might be employed as an alternative for coal or mixture with coal to decrease hazardous emissions which contaminate the environment. In Romania, the areas cultivated for corn and sunflower are placed in the top four along with France, Germany, and Spain. Our country was second after France for both the cultivated area and production of corn [3]. A method to handle these agricultural residues from industrial processing is to use it for solid combustion as a solid fuel in blends with various additives, due to the inconveniences with pelletization as well as with emissions of undesired by-products during combustion. This is the argument why the additives with good densification characteristics seems encouraging for preparing pellets with enhanced quality.

In the literature, there was implemented a wide range of calorimetrical measurements of combustion heat and caloric power of grape marc in its original state, grape marc after seed separation (assumption of oil pressing usage), and in seeds themselves. The results indicate that the heating power varies between 16.07-21.14 MJ/kg [14]. Although many biomass feedstocks possess natural binders, they do not have enough strength due to the limitations of binding between particles. The most used additives can be coal, lignosulphonate, starch, sawdust and sugar, dolomite, corn or potato flour, and some vegetable oils [15-16]. Additives are added to improve the combustion properties, improve durability, or to reduce wear on the pellet die. The additives and binding agents influence all the main features of the biomass pellets. Each additive has consequences in distinct physical and thermal properties when used with various biomass materials. The additives act as a lubricant and raise the production rate and lower the energy use per unit output of wood pellets. In the literature is specified that 0.5 % assay of motor oil and vegetable oil raise the calorific values and 0.5 % corn starch additive decreases calorific values by about 0.5 MJ/kg [16].

Gageanu et al. performed a series of experimental research conducted on pellets obtained from agricultural biomass, namely, wheat straws, rapeseed stalks, corn stalks as received and with additives (paraffin 5 %, paraffin 1.5 % + corn starch 5 % and dolomite 5 %). The authors demonstrated that the pellets obtained after combining different types of materials and those obtained by using additives showed good results, both during the production process as well as in terms of the quality parameters [17].

Starch is already used on some markets to achieve reduced operating costs and better durability. Obernberger and Thek found that 7 of 23 producers of pellets (mostly in Austria) used starch as a biological binding agent to reduce the operating cost and achieve higher abrasion resistance [18]. Nielsen showed by laboratory measurements that, when 5 % of potato starch was added, the strength of the pellets increased [19].

Corn starch was the most effective of the starch binders; the tensile strength of the pellets improved with up to 10 wt %. Further additions of the three starches, up to 20 wt%, made the pellets deteriorate in terms of tensile strength, even though density increased [20].

According to Demir et al., starch may function as an adhesive agent. Additives of 2.5 %, 5 %, 7.5 %, 10 % (wt/wt) starch to pellet materials were examined. Their results showed an improvement on pellet processing, calorific values and physical properties with increasing starch content [21].

Falemara et al. studied the physical and combustion properties of briquettes produced from agricultural wastes (groundnut shells and corn cobs), wood residues (Anogeissus leiocarpus), and mixture of the particles at 15 %, 20 %, and 25 % starch levels (binder). The authors concluded that briquettes containing 25 % starch level had better quality in terms of density and combustion properties, thus being suitable as feasible alternative energy source [22].

Rice husk and coconut shell have been proposed as alternative energy sources by Yuliah et al. The basic ingredients were briquettes prepared from rice husk and coconut shell charcoal with varying composition and addition of tapioca starch gradually as adhesive material to obtain briquettes in solid with the maximum heat energy content. After going through pressing and drying process, the briquettes with 50:50 percent of composition and the 6 % addition of adhesive was found to have the highest heat energy content, equal to 4966 cal/g [23].

In the literature**,** studies regarding the **e**ffects of additives on the pelletization of raw and torrefied food waste were performed using three binders; starch, lignin, and vegetable oil, at various compositions of 10 %, 15 %, and 20 % in order to obtain the raw and torrefied food waste pellets [24].

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Potato starch is another common binder that can reduce the energy needed for pellet formation, increasing the moisture content, and decreasing the lower heating value [25,26]. Concentrations of 10 %, 20 %, and 30% provided ash content of 1.45 %, 1.50 %, and 1.59 % and calorific value of 18.2, 18.1, and 18.0 MJ/kg, respectively.

The effects of paraffin, corn starch, and dolomite on the quality of wheat straw pellets were investigated by Gageanu et al. [17,27] founding beneficial effects of these binders on the pellet length, surface, shape, bulk density, and ash content.

Vegetable oils are referred in literature as additives which decrease die wall friction and reduce energy consuming for pelleting procedure as a result of lubrication effect, however there is no systemic research about the impact of oil on pelletability and physical characteristics of pellets.

Waste cooking oils (WCO) are classified among used vegetable oils (UVO), which, according to the Waste Catalogue Regulation of the Minister of Environment dated 27 September 2001, constitute waste hazardous for the environment [28].

Waste vegetable oil is disposed by restaurants, food manufactures, households since it cannot be furthermore utilized in human or animal dietary. Improper removal of waste vegetable oil can be ecologically harmful; hence its furthermore usage is preferred. Waste vegetable oil has an appreciable capacity as a constituent of pelleted biofuels due to the fact that it is non-fossil oil, possess high calorific value and does not necessitate any preliminary treatment. Oil inclusion can enhance wood fuel characteristics, but compaction of wood with adding oil could be more complex. Utilization of oil can decrease dust generation during pelleting and afterward throughout pellet manipulation [29].

Misljenovic et al. added waste vegetable oil in two different amounts in spruce sawdust, which has been pelletized in a single pellet press under four compacting pressures. Their results led to the conclusion that oil addition significantly increases energy content in biofuel, make material less compressible, reduce pellet strength and reduce friction on the pellet – die contact area. The most important change caused by waste vegetable oil addition is reflected in increasing energy content [30-31]. Emadi et al. used plastic wastes as additives in the pelletizing process of wheat straw and barley straw. The result showed that the higher heating value and tensile strength were increased [32]. Similar results were reported by Saletnik et al. modifying the energy parameters of wood pellets using waste cooking oil. The waste cooking oil was applied at the rates of 2 %, 4 %, 6 %, 8 %, 10 % and 12 % relative to the weight of pellets, increasing the calorific value of the pellets without decreasing their durability. The highest dose of the modifier (12 %) on average led to a 12–16 % increase in calorific value. In each case, the addition of sunflower oil resulted in decreased contents of ash in the pellets; on average a decrease of 16–38 % was reported in the samples treated with the highest dose of the modifier [33].

In literature, experiments concerning fast pyrolysis of corn cob (CC) and waste cooking oil (WCO) were conducted in a fixed-bed reactor, using CC/WCO ratios (1:0.1; 1:0.5; 1:0.87; 1:1 in mass). CC/WCO ratio of 1:1 was found to be the optimum considering high bio-oil yields (68.6 wt.%) and good bio-oil properties (HHV of 32.78 MJ/kg) [34].

The benefit of oil palm and para-rubber residues, and the potential of these residues as biomass were examined by Wattana et al [35]. The biomass pellets were prepared from oil palm leaves (PL) and frond (PF), para-rubber leaves litter (PAL) and branch (PB) and their blend (mixing of 50 wt.% of two materials). These samples were the waste in the local plantation in Pathiu District, Chumphon Province, Thailand. The authors demonstrated that the characteristics of mixed biomass pellets differed from pure biomass pellets which contributed to the further improve its quality.

Waste engine oil is a type of artificial organic additive. The waste engine oil was recycled as an additive in wheat straw pelletizing process. Wang et al. focused on the reuse of wheat straw and waste engine oil by producing pellets with mixtures of the two products. The engine oil content was 5 %, 10 %, 15 % and 20 % included in biomass pellet. The higher heating value was only affected in this case by the additive content and increased linearly as the oil content increased [36].

In our study, we have demonstrated that 10 % content of starch, sawdust and waste vegetable oil applied to grape pomace and corn cob biomass, are suitable for obtaining pellets with good characteristics in term of combustion. Proximate analysis, namely, moisture content, volatile matter, ash content, and fixed carbon was performed. Combustion calorimetry method was applied for obtaining the calorific values of the studied species.

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The obtained results will complete the existing databases concerning the properties of solid biofuels from biomass containing the mentioned additives. Our investigations clearly indicate that the type of biomass used in the process has an important effect on the energy parameters.

The achieved data are helpful for both improving the value of characterized biomass pellets and for the recycling of used rapeseed oil.

Experimental

Material

Samples description

The biomass pellets resulted from grape pomace and corn cob and their mixture with 10 % waste rapeseed oil, sawdust and starch were used. The rapeseed oil was acquired from household, starch and sawdust were used from the market.

Corn cobs and grape pomace were selected as raw materials from local cultivators, in September 2021.

Fig. 1. Biomass grape pomace (GP) and corn cob (CC) before and after grinding.

Method and equipments

The pelletisation process consists of certain subprocesses such as grinding, drying, milling and pelleting. The process of pelletization is affected by the material's moisture content, particle size, density, fibre strength, lubricating characteristics and natural binders [37].

Prior to the pelleting, the samples were dried at 105 °C in the laboratory oven, until constant mass [38]. It is known that moisture content affects the energy yield of the process.

In the pelletisation process, pretreatment mainly consists of two different processes: drying_and grinding. Drying is usually required to decrease the moisture content of biomass which in many cases exceeds an appropriate value for pelletisation (between around 6 and 18% moisture content). Milling is also required in order to transform the feedstock into a more uniform material. The material after milling process consists of particles which are of equal size and similar moisture content. This homogeneity makes the pellets more durable [39]. Furthermore, milling brings size reduction which in turn leads to an increase in particle surface area facilitating interparticle bonding [40].

In raw state, up to 70-80 % mass of grape residues is water. It is necessary to dry it first to guarantee effective utilisation within most of power technologies.

According to Burg et al., to reduce a moisture content of grape pomace from 60 % to 8 %, approximately 1.5 GJ of heat need to be utilised. However, that value may be covered by renewable energy streams (solar, geothermal) or waste heat (from fumes) in integrated driers [41]. Comprehensive drying of grape pomace is essential to be introduced also for reasons of the periodicity of the grape pomace generation

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(harvesting takes place between September and October). When having a lot of water, aerobic biodegradation during storage contributes would deteriorate quality as a fuel [42].

The moisture content is determined by weighing of the sample before and after drying, the obtained difference in weight being considered for calculation, according to o EN 13183-1:2004 standard. [43].

The different blends of corn cob and grape pomace containing 10 % starch, sawdust and used rapeseed oil were prepared in appropriate proportions, weighting in dry basis and, by means of a mechanical blender, thoroughly mixed in order to ensure optimal homogenization that guaranteed the right composition of mixtures. The purpose was to obtain pellets that would meet the specifications established for industrial pellets. The proportion of biomass samples for each blend was configured, taking into account the N, S and ash contents of each biomass sample, since these parameters could restrict the quantity of biomass permitted in the mixture with respect to pellet quality specifications. After mixing, there have been obtained stable pellets by using a Parr 2811 Pellet Press. This pellet press provides a convenient means for compressing powdered materials into pellet or tablet form, being a compact, hand-operated press producing uniform pellets in a polished stainless-steel die and ejecting them smoothly into a stainless receiver without danger of contamination. This system is designed to provide a steadily increasing mechanical advantage up to a ratio of approximately 50 to 1 at the end of the stroke. Thus, a force of 20 pounds applied to the lever develops approximately 1000 pounds on the punch, which is adequate to produce firm pellets from most powdered materials. The obtained pellets are cylindrical in shape with flat ends and have ½ inch diameter [44]. The calorific values for all the blends studied were higher than 16.5 MJ/kg, which is the minimum value required for the industrial pellet qualities.

The calorific energy values were measured using an isoperibolic Parr Instruments 6200 Combustion Calorimeter, previously described [45]. Proximate analysis was performed to establish the standards quality of the pellets produced.

The calorific values using Parr Instruments 6200 Combustion Calorimeter were calculated following ASTM D5865 standard test for gross calorific value [46] and standard operating procedure of the calorimeter [47]. The method was detailed in previous papers [45,48]. The nitrogen was calculated from the nitric acid formed [45]. Sulphur content was performed by adding in the resulted solution of the calorimeter bomb after combustion, a diluted sodium hydroxide to convert sulphur to sulphates [49]. The obtained results are crucial in the estimating of the emission of gas contaminants generated during combustion (dioxins, furans, NO_x, SO_x, or HCN), corrosion problems in heaters and bad operation in boilers.

Bulk densities have a major impact on shipping and storage charges [50-51] and were calculated using an analytical balance Mettler Toledo, model XP6.

Volatile matter is a characteristic feature of solid fuels, which is standardized when assessing energy biomass [52-54]; biomass is characterized by a high content of volatile matter [53] which includes gaseous products and vapours produced during the thermal decomposition of solid fuel under anaerobic conditions. The amount of volatile components essential to the assessment of the energy suitability of solid fuels decreases as the degree of carbonization increases. Volatile matter content (%) is an important parameter which has a considerable influence on the combustion process [55]. Data from the literature indicate that biomass contains up to 2.5 times more volatile matter than coal, which has a significant impact on the conditions under which it is ignited and combusted [56].

The presence of volatile compounds can change the behaviour of the fuel in generating boilers, variations in efficiency and severe operational problems. Volatile matter content was calculated according EN ISO 18123:2015 standard and following the procedure stated in the literature [57].

Fixed carbon [58-59] is the mass left after the release of volatile compounds, excluding ash and moisture. This may be calculated using some of the data obtained previously in the proximate analysis. The higher the percentage of fixed carbon in a solid fuel, the higher the calorific value and consequently, the fuel is better.

The ash content (AshC, %) was derived from the difference in the weights of the bomb crucible before and after combustion. To obtain accurate results the measurements were performed in triplicate, in accordance with the protocols of the literature [60]. Similar to hard coal and lignite, biomass combustion produces solid waste, mainly in the form of bottom ash. The quantity of this waste is largely dependent on the type of biomass used [56]. Typically, biofuels have much lower ash content after combustion than fossil fuels such as coal or lignite. This has certain operational benefits, i.e., longer periods between ash disposal.

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The energy density (MJ/m^3) was derived from the bulk density and calorific value of the biomass raw materials [61-62].

The analysis of the fuel value index (FVI, GJ/m^3) shows that the materials are applicable to the energy product, a threshold value for application as fuel being 100 GJ/m^3 [63]. The procedure was previously described [64]. Each test was caried out in triplicate. The aim of the knowledge of each property under investigation is to certify the solid fuel derived from biomass in accordance with European standards for solid biofuels CEN/TS 14961/ 2005.

Combustion efficiency is a measure of how well the fuel is being burned and the main parameter to describe the performance of a biomass furnace. Essentially, it is the percentage of the energy of a fuel that has been used up in the burning process. While complete combustion (100 percent combustion efficiency) is theoretically possible, in reality it is not, mostly due to heat losses [65].

In literature, a method for calculation of the combustion efficiency is presented. The method is based on the combustion reaction and can be applied to every biofuel with given composition. The following equation is proposed [66-67]:

$$\text{Combustion efficiency } (\%) = 1 - \left[(\text{unburned fuel in botom solids}) / (\text{initial fuel placed in burner}) \right] \times 100 \qquad (1)$$

The statistical analysis of the obtained data was performed using Minitab 18 program [68]. The median of the survey and the standard deviation was determined as the main statistical parameters of tendency and dispersion, for each group of values. The entire statistical analysis was carried out with a confidence interval of 95 % and an alpha error of 0.05.

Results and discussion

Extensive knowledge of all the parameters presented above is essential for characterizing a biomass sample as a potential fuel resource. Calorimetry may be the most influential of all because it provides precise data on the heating value of each of the samples studied; data that when combined with market prices for each fuel, enable consumers to compare the energy and financial yield of each one.

Grape husk (pomace) obtained from a winery in native state cannot be used efficiently due to its size, biodegradability, and low weight. The grape raw materials has a very good caloric power, comparable with the one of fire wood and pellets obtained from beech or resinous sawdust, thus obtaining pellets of good quality from this raw material, especially when additives are used is of great interest. As other researchers stated before, the more sugar the higher calorific value will be [69].

Due to their high calorific value the corn cob cores are often used as fuel, and the by-products of the combustion process are also used. The products of the corn cob core combustion process, i.e., ash, can be used as partial substitutes in cement production [70].

Starch-based and sawdust binders offer numerous advantages that are both ecologically and economically beneficial, including improving durability, reducing abrasion and dust formation, lowering the energy consumption of the pelleting plant and reducing maintenance and wear costs [71]. The possibility of using used vegetable oil in a valuable way, combined with the advantage of avoiding its dispersion into the environment and its very high availability, has encouraged scientists to look for a way to reuse waste. The most common uses of used vegetable oil are the production of bio-lubricants or fuel as animal feed, or as additives for asphalts and for energy production [28]. In Fig. 2 are shown the obtained higher heating values and moisture content for the studied samples. Moisture content is known to be one of the most important parameters for determining the quality of biopellets. The low water content will facilitate the ignition of the biopellet and extend the shelf life. High moisture levels can result in mould growth during storage [72]. From Fig. 2 it can be ascertained that single additive waste rapeseed oil has the highest heating value (40.21 MJ/Kg) and the lowest moisture content (1.32 %). The grape pomace pellets containing 10 % waste rapeseed oil have the highest heating value (22.14 MJ/kg) and the lowest moisture content (2.81 %) from the analysed samples containing

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additives, thus being in agreement with literature statements [72]. Authors demonstrated that increasing dosages of wheat and maize starch further reduces the final wood pellet moisture content [16].

An important aspect to take in consideration for obtaining good quality pellets is the method of pellet refining. Densification by means of pelletisation is considered to be a proven technology to improve biomass properties for its conversion into heat and power. Also, the torrefaction process upgrades the biomass and produce solid fuels with better quality. Torrefaction is helpful in enhancing biomass for its use in wider applications. A major advantage of torrefaction is that it can break down the fibrous character of biomass and reduce the formation of soot [73].

Torrefaction is a fast-developed technology to produce solid biofuel (biochar) or sustainable materials for several applications, but the problem induced by tar, one of the by-products formed from biomass torrefaction, is an important challenge that needs to be solved, especially in industrial systems. The torrefaction process increases the ash content in final products, and this limits the applications of combustion and gasification from torrefied biomass. Comparing the raw and torrefied biomass higher heating values (HHV) results that torrefied biomass values ranges between 16-29 $MJkg^{-1}$, higher than raw biomass values of 15-20 $MJkg^{-1}$ [74].

An alternative process for the production of biopellets is a combination of torrefaction with pelletisation and is called the TOP process for the production of TOP pellets. The TOP process integrates the advantages of both processes with respect to the quality of the biopellet, having a net calorific value of 19 to 22 MJ/kg as received. This results in an energy density of 14 to 18.5 GJ/m^3, significantly higher than conventional biopellets produced from softwood (sawdust: 7.8 to 10.5 GJ/m^3) [75].

In Table 1 are presented a summary of various biomass combustion technologies.

Table 1. Summary of various biomass combustion technologies.

Species	HHV (MJ/Kg)	LHV (MJ/Kg)	Moisture content (%)	Technologies
Grape pomace (our exp.)	21.35	21.14	23.28	combustion calorimetry
Grape seeds (lit.)	20.83	20.03	19.2	combustion calorimetry [76]
Corn cob (our exp.)	17.66	17.42	8.63	combustion calorimetry
Corn cob (lit.)	18.7	18.3	7	torrefaction in tubular furnace [77]
Maize Stalks (Corn Cobs) (lit.)	15.46	15.06	6.9	torrefaction technique / pyrolyzed samples [73]
Corn stover (lit.)	17.6	17.2	8.1	combustion calorimetry [78]
All wood fuels and most biomass (lit.)	17.9	17.5	5-60	moving grate furnaces [79]
Sorghum (lit.)	15.8	14.4	5-60	bubbling fluidized bed [79-80]
Sorghum (lit.)	17.1	15.8	5-60	circulating fluidized bed [79-80]
Sawdust (our exp.)	18.17	17.94	2.82	combustion calorimetry
Sawdust (lit.)	19.47	19.3	3.2	briquetting [81]
Starch (our exp.)	15.45	15.42	7.66	combustion calorimetry
Starch (lit.)	19.43	19.22	2.67	combustion calorimetry [82]
Waste rapeseed oil (our exp.)	40.22	40.11	1.32	combustion calorimetry
Sunflower husks (lit.)	18.83	18.44	4	combustion calorimetry [76]

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Compared with other method of biomass energy fortification like torrefaction, the addition of 10 % oil increased the final energy content similarly as torrefaction at 225 ºC. This way of increasing the energy content is definitely easier and less energy demanding compared to torrefaction [83].

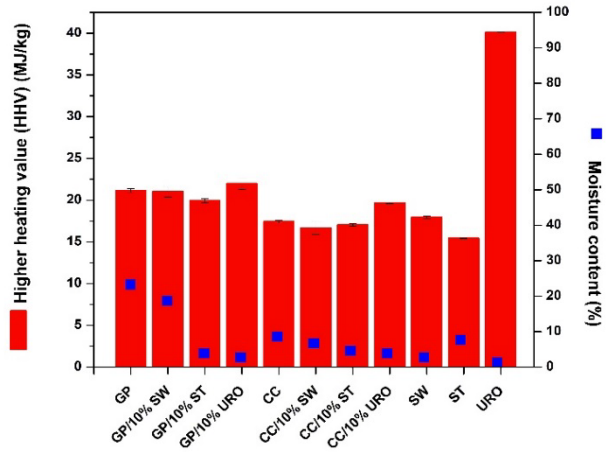

Fig. 2. Plot of the higher heating values and moisture content for the studied samples. (GP=grape pomace; CC=corn cob; SW=sawdust; ST=starch; URO=used rapeseed oil; GP/10%SW=grape pomace containing 10 % sawdust; GP/10%ST=grape pomace containing 10 % starch; GP/10 %URO= grape pomace containing 10 % used rapeseed oil; CC/10%SW=corn cob containing 10 % sawdust; CC/10%ST=corn cob containing 10 % starch; CC/10%URO=corn cob containing 10 % used rapeseed oil).

Our values for high heating value of control grape pomace (21.35 MJ/kg) and corn cob (17.29 MJ/kg) are close to the values reported for bamboo biomass ranging from 18 to 21 MJ/kg. These values are higher than other commonly used biomass such as sugarcane bagasse (16.60 MJ/kg), corn cob (16.90 MJ/kg), barley straw (16.81 MJ/kg), rice straw (16.78 MJ/kg) , pine wood chips (16.81 MJ/kg), lignite (16.16 MJ/kg) and palm kernel shell (19.82 MJ/kg) [84-85].

The values of the higher heating value for control grape pomace (21.35 MJ/kg) calculated in this work are greater than the values reported by Annamalai et al [86], of about 20.34 MJ/kg. It is obvious that grape pomace is a material with a very good calorific value, surpassing the values of wood (14.6 MJ/kg) and cereals (18.00 MJ/kg) [14, 87]. The high heating values are caused by wastage of sugars. According to the literature, it is very possible to use waste corn cob as fuel in the power plant due to its calorific value of about 16.92 MJ/kg [88], close to the results reported in this study, of 17.29 MJ/kg.

Analysing the obtained results, it can be ascertained that samples containing 10 % starch present a lower heating value than the control sample (see Fig. 2), a higher value being observed for samples with 10% waste rapeseed oil. Nosek et al [89] reported for the wood pellets that a 0.5 % dosage of motor oil and vegetable oil increases calorific values, and 0.5 % corn starch additive decreases calorific values by about 0.5 MJ/kg.

The moisture content obtained in this study for grape pomace is 23.28 % and for corn cob samples 8.63 % without using additives. Adding the mentioned additives, these values decrease ranging between 2.81 % and 6.65 %, the lowest value being obtained by adding 10 % waste rapeseed oil (Fig.2). These results indicated that additives are beneficial for decreasing moisture and keeping it under 10 %, the desired value for optimal storage and use, the same behaviour being highlighted by Gageanu et al. in their study concerning wheat straws, rapeseed stalks, corn stalks and their mixtures with paraffin 5 %, paraffin 1.5 % + corn starch 5 % and dolomite 5 %. Their moisture values ranged between 8.25 % and 11.65 % for pellets obtained without using additives and between 7.48 % and 9.25 % for pellets obtained using additives [17]. Li and Liu reported that a good quality pellet has a moisture content ranging between 6 % and 12 % [90].

Kumar et al. investigated the effect of combining dry leaves, rice husk and sawdust in different proportions and concluded that the dry leaves can be used as potential source for the production of briquettes

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in India. Their higher heating value of 20.03 MJ/kg indicates that the briquette could supplement the traditional wood fuel for cooking and other purposes. Sawdust was added in proportion of 20 %, 40 % and 50 % respectively. Briquette made from equal proportions of sawdust and rice husk had the lowest heating value, of 16.52 MJ/kg, thus resulting that blending of biomass materials will not always produce higher quality briquettes [91].

Our results indicated an increase of the higher heating value by adding 10% sawdust in grape pomace and corncob samples, from 21.35 MJ/kg (control grape pomace) to 21.72 MJ/kg and from 17.29 MJ/kg (control corncob) to 17.39 MJ/kg, respectively.

Greinert et al. in their study evidenced that pellets prepared from a mixture of 80 % of straw and 20 % of wood had a low ash generation value amounting to 2.34 % and a calorific value of 18.95 MJ/kg. The pellets prepared from a mixture of 70 % of straw, 27 % of wood and 3 % of lime had a calorific value of 18.83 MJ·kg^{-1} and an ash generation amounted to 2.98 % [92]. The amount of ash generated from biomass is described as variable, depending on the origin of the material. For pure wood, it is within 0.4–1.8 %; for wood bark, it is within 6.3–10.4 %; for energy plants, it is within 2.4–7.7 %; for agricultural biomass, it is within 6.9–9.2 %; for agri-food industry wastes, it is within 1.1–9.2 % [93]. From Fig. 3 we can conclude that our ash values for corn cob and grape pomace are in agreement with the above-mentioned intervals.

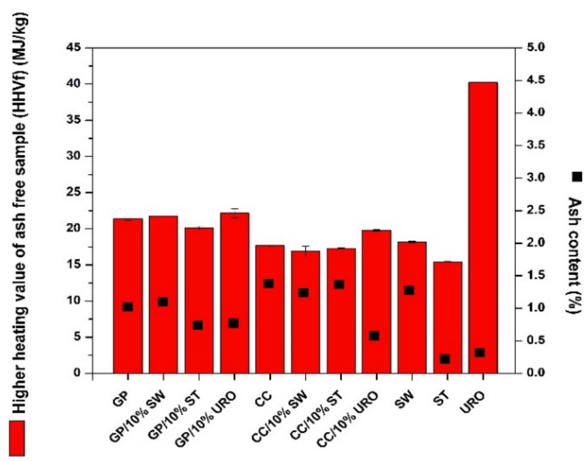

Fig. 3. Plot of the higher heating values and ash content for the studied samples.
(GP=grape pomace; CC=corn cob; SW=sawdust; ST=starch; URO=used rapeseed oil; GP/10%SW=grape pomace containing 10 % sawdust; GP/10 %ST=grape pomace containing 10 % starch; GP/10%URO= grape pomace containing 10% used rapeseed oil; CC/10%SW=corn cob containing 10 % sawdust; CC/10%ST=corn cob containing 10 % starch; CC/10%URO=corn cob containing 10 % used rapeseed oil).

In order to guarantee a combination of efficiency and comfort for the consumer of pellets in the home heating sector, a high ash content should be avoided, as this would eliminate the necessity of emptying the ash box at regular intervals, minimize the risk of slag formation in the furnace and lower soot emissions [18]. Taking these risks into account, the 10 % waste of rapeseed oil corn cob samples seems to be the most suitable raw materials for pellet production, with an ash content of 0.578 %. The low ash content indicates the good quality of the pellets, the values obtained from this study are less than 4 % (Fig. 3), considered as the tolerance level for the ash content in the fuel [94]. Ebeling et al. reported 1.4 % ash content for corn cob, which is lower than for other agricultural biomasses., e.g. the corn stover has 6.7 % ash content and the wheat straw 5.7 %, but higher than the woody biomass with an average ash content of 0.9 % to 1.2 % [95]. The control grape pomace sample has an ash content of 1.017 % and corn cob 1.374 %. The lowest content of ash was calculated for pellets containing 10 % waste rapeseed oil, grape pomace (0.77 %) and corn cob (0.578 %) respectively. In literature it was demonstrated by Saletnik et al that addition of waste cooking oil, even at a rate of 2 %, resulted in a statistically significant decrease in ash contents in beech wood pellet from the Pomorskie Region, in coniferous wood pellet from the Swietokrzyskie Region and in coniferous and deciduous wood pellet from the Podkarpackie Region [33].

Regarding the wood pellets, Kuokkanen et al. found that a supplement of 1 % potato flour does not affect ash content, but 2 % dosage of the same additive increases ash content from 0.5 % (native wood) to 0.6 % [96].

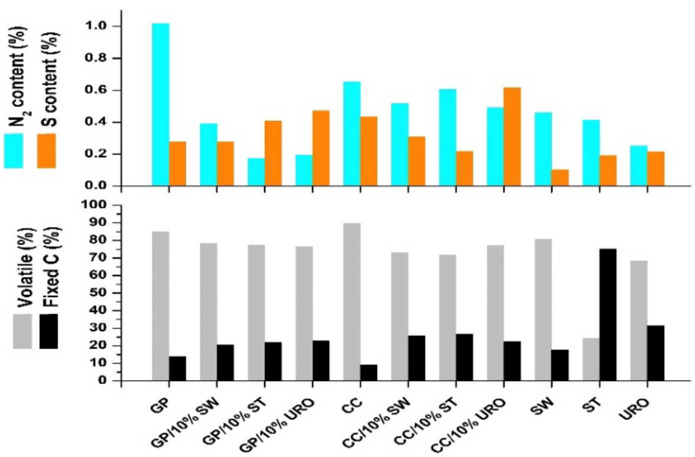

Fig. 4. Plot of the fixed carbon (%), volatile matter (%), sulphur and nitrogen content (%) for the investigated sample.
(GP=grape pomace; CC=corn cob; SW=sawdust; ST=starch; URO=used rapeseed oil; GP/10%SW=grape pomace containing 10% sawdust; GP/10%ST=grape pomace containing 10% starch; GP/10%URO= grape pomace containing 10% used rapeseed oil; CC/10%SW=corn cob containing 10% sawdust; CC/10%ST=corn cob containing 10% starch; CC/10%URO=corn cob containing 10% used rapeseed oil).

Grape pomace and corn cob have very low nitrogen and sulphur levels compared to coal (nitrogen 0.8-1.9 % and sulphur 0.7-1.2 %) [97]. In this study, control grape pomace has a nitrogen level of 0.517 %, the lowest level being obtained for grape pomace with 10 % starch, about 0.172 %. Corn cob presents a nitrogen level of 0.653 %. Knowing the nitrogen content of biomass is important to assess nitrogen oxides (NO_x) that are air pollutants. From Fig. 4 it can be ascertained that the presence of additives of 10 % results in decreasing the nitrogen content of the investigated samples.

Malat'ák et al in their study on white and red grape pomace as well as grape stems, added straw of Miscanthus sinensis (in proportion of 25 %, 50 % and 75 %) in order to verify the possibility of a reduction in emissions of NO_x. In their study, NO_x concentrations decreased significantly in stems and gradually in pomaces. The mixtures with 50 % and 25 % red grape pomace indicate the effect of addition of cleanly burning biomass on the emissions of CO and NO. With an increasing proportion of Miscanthus straw, the emission concentrations of nitrogen oxides decreased [7].

The sulphur levels for control samples are lower compared to coal, this making them emit less sulphur oxides (SO_x) than fossil fuels. Control grape pomace sample has 0.279 % sulphur content and control corncob 0.436 %. Greinert et al. reported a low content of sulphur for the studied mixtures of straw and wood, about 0.3 % comparing with our mentioned results. The authors stated that the content of biomass components is strongly related to the species of energy plants and particular parts of these plants [92].

Sulphur is a major problem because of the accumulation of sulphates on the heat transfer surfaces of the combustion chamber [98]. Research has demonstrated that the biomass tested contains a quantity of sulphur that meets the standards for wood pellets. Moreover, the presence of sulphur is a natural consequence of the sulphur content of vegetable proteins, which is a building material for the biomass tested.

The percentage of fixed carbon content in pellets is a critical factor in determining the calorific value of the fuel [99]. From Fig. 4 it can be seen that the samples containing additives have a high level of fixed carbon than the control samples, thus a high calorific value, which is in agreement to literature statements [50].

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The approach of volatile matter assigns the components released when fuel is heated at a high temperature, eliminating moisture, being part combustible gases (C_xH_y gases, CO or H_2) and part incombustible (CO_2, SO_2 or NO_x). Usually, biomass has a very high volatile level, with common biomass values at about 75 %, but they may increase to 90 %, depending on the sample [100]. The lowest volatile sample should have the highest energy content. Corn cob pellets without additives have the highest volatile content of 89.6 %; this means that more energy will be needed to burn the volatile matter before releasing its thermal energy. By comparing the volatile matter content of the samples containing 10 % starch with pristine ones, results that this additive produces the decreasing of the volatile matter content. This is caused by the presence of volatile substances contained by an adhesive, such as CO, CO_2, H_2 and CH_4 [23]. The most volatile matter is contained by pristine samples of corn cobs and grape pomace as it can be observed from Fig. 4.

For comparison, Maj et al. [101] indicated that the volatile content in the corn cobs cores from seed production was 69.24 %, below than the values reported in the analyses performed in this study. On the other hand, Lu et al. [54] carried out studies on the volatile matter content in 66 types of biomasses and stated that their levels range between 70.39 % - 83.92 %. This analysis shows that the volatile components reported in the literature are typically lower than the values obtained in the experiments performed in this work.

The high heating value (HHV) was found to be ranged between 16-21 MJ/kg for the two types of biomasses studied. Among the used additives, the waste rapeseed oil presented the highest HHV values (40.21 MJ/Kg), which indicated that it would be the most appropriate additive for improving the combustion characteristics of biomass. It should be pointed out that the calorific value of pellets obtained from agricultural biomass is extremely important for professional energetics because this index affects the price of the product delivered.

The combustion efficiencies for all types of the studied pellets were calculated using equation (1) and ranged between 98 up to 99.91 % (see Table 2). Our results in terms of combustion efficiencies are close to the values obtained by Chen et al. for pellets made from wood and coal residues at various ratios (0, 25, 50, 75, and 100 % wood, and 50 % wood-plus-limestone). The authors stated that the obtained combustion efficiencies, ranging from 96 to 100 % of all types of investigated pellets were excellent [67].

Well-designed pellet-fired systems can achieve efficiencies of over 80 per cent. Many pellet stoves operate with a very high excess air level, which reduces their efficiency to 50–60 per cent. Technology to reduce emissions and improve combustion efficiency is being developed continuously. Thus, the negative environmental impacts of biomass combustion that exist today will be reduced in future plants [102].

Table 2. Determination of bulk densities and energetic features of grape pomace and corn cob with different additives.

Species	Bulk density (kg/m^3)	FVI (J/cm^3)	Energy density (MJ/m^3)	Combustion efficiency (%)
Grape pomace (GP)	431.5	388.9	9212.5	99.07
10% sawdust-GP	382.4	396.9	8121.11	98.71
10%starch-GP	462.8	3266.5	9293.5	99.27
10% waste oil-GP	422.5	4317.9	9354.7	99.05
Corncob (CC)	217.2	438.05	5194.3	98.45
10% sawdust-CC	159.24	326.66	4687.17	98.59
10% starch-CC	294.13	587.87	5755.38	98.96
10%waste oil-CC	191.4	1681.08	5784.0	99.30
sawdust	175.2	882.13	3183.03	98.76
starch	640.8	5874.8	9900.3	99.76
Waste rapeseed oil	939	75707.3	33977	99.91

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From Table 2 it can be observed that the studied biomass has low bulk density, which consists of pieces of different shapes and sizes. For this reason, the low energy density was increased by converting the free biomass to dense pellets. The pellet bulk density was increased when 10 % starch was added, from 431.5 kg/m^3 to 462.8 kg/m^3 (grape pomace) and from 217.2 kg/m^3 to 294.13 kg/m^3 (corn cob), although that required by the ENPlus Bquality (600 kg/m^3) was not reached. It was demonstrated that other additives, such as lignosulphonate and different types of starch, also decrease the moisture content of wood pellets, thereby increasing the bulk density of the product [16].

Stahl M. et al investigated how white sugar, molasses and spent sulphite liquor additives affect the energy needed by the pellet press, the durability and oxidation of the produced pellets. They found that using sugar additive, the bulk density (7 to 15 %) and durability (10 to 20 %) of the pellets were increased [103].

The FVI is a relevant parameter for the screening of biomass species, and it can be concluded that the samples with the highest FVI possesses better biofuel properties [104].

The amount of heat that can be "pulled" through the combustion of biomass is referred to as the energy density. Different fuels have different levels of energy density, which can be calculated using the equivalent energy released during combustion. The amount of energy that can be released by a specific mass or volume of fuel is known as its energy density. The quality of the fuel increases with increasing energy density. From Table 2 it can be ascertained that the samples with the highest energy density and fuel value index were 10 % waste rapeseed oil-grape pomace and 10 % waste rapeseed oil-corn cob, demonstrating that waste rapeseed oil is the best additive for enhancing the quality of the pellets. Pellets made from 10% waste rapeseed oil-grape pomace and 10 % waste rapeseed-oil corn cob appear to be particularly well suited for a clean and effective combustion. We were able to draw conclusions concerning energy efficiency and measures for environmental protection thanks to the analysis of additive properties.

Conclusions

To improve the quality of the pellets made from grape pomace and corncob and to lower the concentration of harmful emissions, three additives, namely, sawdust, starch and used rapeseed oil in addition of 10 % in dry solids, were used. In comparison to most types of wood, the results of proximate analysis and their calorific values are significantly higher. In comparison to pristine grape pomace and corncob, the nitrogen and sulphur content decreases when 10 % sawdust, starch, and waste rapeseed oil are added. Addition of waste rapeseed oil (from cooking) applied at a rate of 10 % relative to the weight of the pellets, increased their calorific value. Each time, the pellets ash contents decreased when the waste rapeseed oil was added. The biomass pellets from this study have a calorific value ranged between 16 to 22 MJ/kg. Pellets made from agricultural waste are some of the most popular biofuels. Scientists started looking for novel solutions to make it possible to improve pellets heating value because of the rising interest in them and the need to increase their efficiency. In this study, the most favourable effect upon the investigated parameters was obtained when waste rapeseed oil was added. The method of pellet refining suggested in this study may be competitive in comparison to other technologies available, according to the obtained results.

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