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Densification mechanisms during solid biofuels production made of sawdust, coal and cocoa husks by pressing

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Dedicated to God and my dear dad.

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ABSTRACT

Solid biofuels have become a valuable alternative for cleaner energy generation. This work aimed to identify the feasibility of using mixtures between coal, sawdust and cocoa husks for manufacturing pellets and the effect of particle size on their mechanical properties. Moreover, advanced characterization techniques such as Light and Fluorescence microscopy were used for identifying changes on the densification mechanisms due to the variation of raw materials. Cocoa husks exhibited a similar performance as sawdust for binding coal particles; compression ratio and final density of pellets made with sawdust-coal were near to values obtained with cocoa-coal pellets. Optical and fluorescence microscopy showed that coal particles crushed during the process as a result of the fragmentation stage included in the densification mechanisms; the images also reveals the incidence of lignin and protein content in the agglomeration process. The coal particles were brittle; therefore, it was necessary to add either sawdust or cocoa to increase the resilience, strength and durability of the final solids. Identification of the mechanisms taking place during densification is of great importance in order to establish the optimal conditions for producing biomass or coal-biomass pellets. The production of biomass or biomass-coal pellets might create alternatives for developing new renewable energy industries in Colombia.

Key words: Biomass, Coal, Cocoa, Densification mechanisms, Pellets, Sawdust

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INTRODUCTION

During the last decades, the world energy consumption has continuously increased due to changes in the lifestyle and the population growth. One of the most common methods for supplying, not only thermal energy, but also electricity, is the combustion of fossil fuels such as coal, natural gas and oil derivatives. This process has several advantages because the technology is well developed, reliable, and capable of producing power at different scales from kW to GW; nevertheless, the uncontrolled use of these energy resources has caused several environmental, economy, and social issues. Among the various problems, the release of greenhouse gases is the most remarkable and discussed around the world. Meanwhile, the increase of the fuel costs, the fossil fuels reserves decrease, and the energy dependency, have motivated some countries to promote the development and installation of energy systems based on renewable energy resources.

Several policies have been established by national governments aiming to support this industry. The new investment on renewable energy systems boosted up more than eightfold in the 2004-2012 period, moving from 40 to 244 billion US Dollars. As a consequence of these efforts, about 20% of the global final energy consumption was supplied by renewable energy sources in 2011. In this field, the biomass is one of the most valuable resources; about 9.3% of the final energy consumption came from traditional biomass for heating and cooking and other 2.8% from modern biomass and biofuels. Biomass is made up of a wide variety of agricultural residues growing wherever and capable of producing energy for small and large scale power systems.

Nonetheless, the biomass has some drawbacks like high moisture content, irregular shape and sizes, and low bulk density, which make it very difficult to handle, transport, store and utilize in its original form. In order to overcome these difficulties, the biomass can be densified by pressing or extrusion, resulting on uniform solid biofuels denoted as pellets or briquettes. These are cylindrical solid biofuels with standardized characteristics, dimensions, moisture content, and density. During the last years, wood pellets were manufactured and commercialized on such a way that world production has grown from 2 to 22.5 million tons per year between 2000 and 2012. Pellets and briquettes offer several advantages because they are ease to handle, can be adopted efficiently in direct combustion or co-firing with coal, and have higher energy density than traditional biomass.

Nowadays, the pellets are mainly made of wood residues from the timber industry. While the wood pellet consumption is rising notably fast, the production of wood residues could not supply this demand in the further decades. Thus, the necessity of alternative raw materials for densified biofuels will be valuable. On this field, some authors are working on the production and utilization of mixed biomass pellets, manufactured from different raw materials. Some results showed an attractive opportunity for manufacturing densified biofuels, but it is necessary to analyze how the change of raw materials properties affects the pellets final characteristics and the stages including on the densification mechanisms.

This work aims to contribute with the development of mixed biofuels production using an alternative agroindustrial resource such as cocoa pod husks mixed with either sawdust or a traditional fossil fuel like coal. Cocoa husks were chosen due to the availability of these resources in Colombia and the environmental problems caused by their wrong disposal. Coal was employed to increase the heating value of the pellets, and sawdust was used because it has demonstrated to be a natural binder. Moreover, this project has the following objectives:

- To identify the potential of cocoa husks, sawdust and coal as raw materials for solid biofuels production according with international standards

• To analyze the incidence of particle size and raw material mass fractions on the densification mechanism during solid biofuel production using mixes between sawdust, cocoa husks and coal powder by hydraulic pressing
• To identify the effect of particle size on solid bridges and intermolecular forces phenomena based on Light and Fluorescence Microscopy images
• To evaluate the behavior of physical properties such as density, durability and strength when the mass fraction of the feedstock changes

This work was divided into six chapters. The first one is a brief introduction to the state of the art; this section comprises an overview about the relationship between energy, renewable energy sources and biomass pellets. Moreover, it describes the densification mechanisms that will be analyzed in this work and some principles of the techniques applied; this chapter was extracted from the thesis proposal document written in 2012. The second chapter is a short review written, presented and published on an indexed journal. This review was done after the thesis proposal presentation; it contains a more descriptive analysis of pellets industry, the main uses of this product and the different models employed to analyze the pellet gasification on downdraft and updraft fixed bed gasifiers. It was originally submitted and published in Spanish, but translated for this dissertation. The article highlights the importance of pellets production for the energy generation sector, especially the advantages of wood pellets on gasification power systems.

The chapter three exhibits the results of the practical work performed during the initial stage of this thesis; this article was submitted and published on an international indexed journal. The document aims to explain in a more descriptive manner the methodology utilized for producing the pellets and the methods applied for analyzing the pellets physical characteristics such as moisture content, volatile matter, fixed carbon and ash content. Also, it mentions the equipment employed for performing the ultimate analysis and relates the results with international standards. This article includes some exploratory tests performed with other agroindustrial residues like oil palm shells or coconut shells. These raw materials were used while cocoa pod husks were acquired and provided by farmers from Cimitarra Santander. Afterwards, the chapter four shows the results obtained after addition of sawdust onto coal pellets. This article analyzes the variation of mechanical properties like compression ratio, impact resistance, compressive resistance and maximum load before failure for different particle size and coal-sawdust mass ratios. Sawdust acts as a natural binder for coal grinds and enhances mechanical properties. Coal finest grinds crushed more than bigger particles during the compression as observed by light microscopy.

The chapter five states the behavior of coal and sawdust pellets after addition of cocoa husks. The results are similar as presented on the chapter before. The cocoa husks grinds act as a binder for coal pellets increasing their resistance and resilience; although the coal-cocoa bonds were no as stronger as sawdust-coal bonds. This decrease of the binding force happens because cocoa husks are less fibrous than sawdust, so this biomass resulted more fragile and less resistant to compressive strains.

The chapter six includes the results obtained after analysis of solid pellets by Fluorescence Microscopy. This section exhibits the incidence of lignin and proteins during densification of sawdust-coal, sawdust-cocoa, and cocoa-coal pellets. Lignin squeezed acting as a natural binder for sawdust densification. UV-AF shows the differences between lignin embedded into the sawdust matrix in comparison with that of cocoa. Cocoa husks have less lignin and more protein; the primary mechanisms affecting densification of cocoa husks were mechanical interlocks, protein gelatinization and short-range intermolecular forces. Finally, some conclusions and recommendations for further research were summarized. This field is gaining importance around the world; Colombia has a considerable potential for pellet production, but the lack of technology and knowledge encumbers the growth of this industry. However, this work aims to identify some alternatives for harnessing this potential.

I. Brief description of the state of the art

A. Energy and renewable fuels

Throughout the history, the relationship between energy and economy has been so close for the development of the humankind. During the last 30 years, the total energy supply increased about twofold from 5800 to 12000 Mtoe [1], most of this energy came from fossil fuels. In 2008, Oil was the most important fuel for energy production. Several liquid fuels such as LPG, motor gasoline, fuel oil, and aviation fuels can be obtained from oil; this energy source was used to generate 33.2% of the world primary energy consumption. The production of this fuel has increased during the last 30 years from 2000 to 4000 Mt at a rate equals to 50 $Mtyr^{-1}$. In 2009, the countries with the highest production were Russia 494 Mt, Saudi Arabia 452 Mt, United States 320 Mt, Iran 206 Mt and China 194 Mt.

Coal produced about 27% of the 12267 Mtoe consumed worldwide. From 1971 to 2000, the production of coal rose from 2000 to 4000 Mt; although, the last ten years the production reached 6000 Mtyear-1. Nowadays, the most important coal producers are China 2971 Mt, United States 919 Mt, India 526 Mt, Australia 335 Mt and Indonesia 263 Mt. Colombia is the tenth country in terms of coal production (73 Mt) and the fourth of net exports (69 Mt).

Natural gas is the third most employed fuel for energy production; it shared 21.1% of total primary energy. The penetration of natural gas in the energy market increased thanks to the development of new technologies and new processes. The production rose up threefold from 1000 to 3000 billion cubic meters (bcm) during the last 40 years. The United States is the most important producer (594 bcm), followed by Russia, Canada, Iran, and Norway with a production of 589, 159, 144, and 106 bcm, respectively. Other sources used during the last decades for energy production are Nuclear, Hydro and renewable fuels. However, nuclear power increased from 0.9 to 5.8% of world total primary energy between 1973 and 2008. While, in 1971, the nuclear power production was no more than 100 TWh, 40 years later, the production reached about 2500 TWh. In this field, the United States has 30% of the world production producing 838 TWh; France is the second most important producer of nuclear energy (439 TWh), followed by Japan, Russia, and Korea with 258, 163, and 151 TWh, respectively.

There are several problems associated to the combustion of fossil fuels for energy generation. Some of them are worldwide known, i.e., global warming, ocean acidification, energy dependence, ozone layer depletion. Global warming is a problem caused by greenhouse gases (GHGs) emissions. These compounds go to the atmosphere absorbing the solar radiation and preventing it for going out of the Earth. As a consequence, the mean atmosphere temperature increases, changing the weather and the conditions of some ecosystems. The most hazardous GHGs are Carbon Dioxide (CO_2), Methane (CH_4), Nitrous Oxides (NO_x), Sulphur Oxides (SO_x), Chlorofluorcarbonates (CFC's) and Hydro-Chlorofluorcarbonates (HCFC's). Most of these gases resulted from fossil fuel fired systems. The CO_2 produced from fossil fuels have increased during the last 40 years about twofold; the production of CO_2 was 15000 Mt in 1971 and 30000 Mt in 2008. Coal produced 43% of CO_2 emitted in 2008, followed by Oil, 36.8%, and Natural Gas, 19.9% [1]. China and United States released one-third of the world CO_2 emitted. Figure 1 summarizes the CO_2 emissions by country in 2008[2].

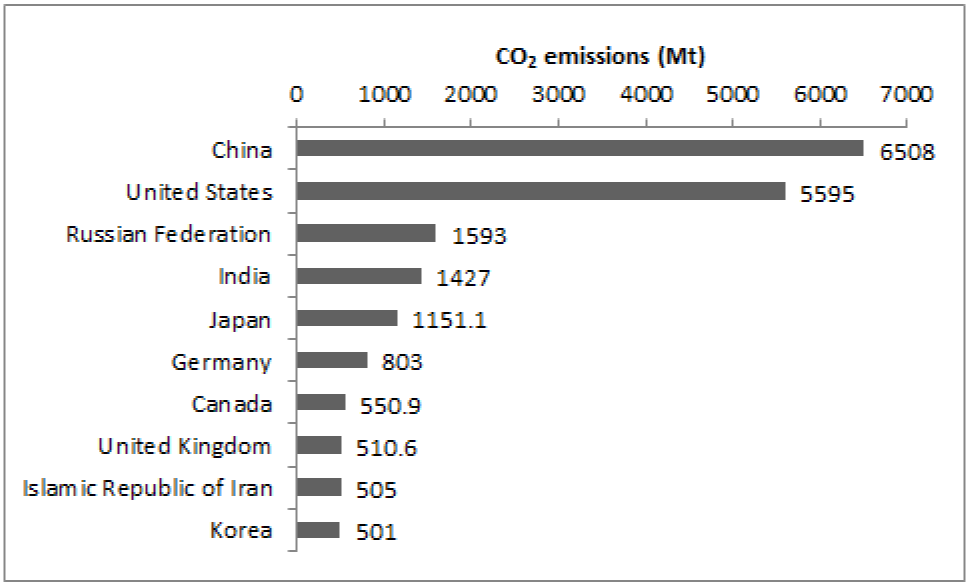

Figure I-1 Top 10 CO2 emitting countries in 2008

Meanwhile, it is also remarkable to analyze the emissions production distributed by sector. In 2008, three sectors summed up more than two-thirds of the overall emissions; these sectors were the industry, transport, and the power and heat generation sectors. The latter represented two times the production of transport and industry together. The power and heat generation sector reached about 41% of the world GHGs emissions, followed by industry 20% and transport 21%. The considerable production of CO_2 from the power and heat generation sector is based on an intensive coal-based power generation systems, e.g., countries such as Australia, China, India, South Africa or Poland produced from 69% to 94% of their electricity and heat through the coal-fired systems. The figure 2 shows the variation of CO_2 emissions by sector from 1971 to 2008[2]. The behavior of these sectors during the last decades exhibited the necessity of applying different kind of strategies in order to control these emissions.

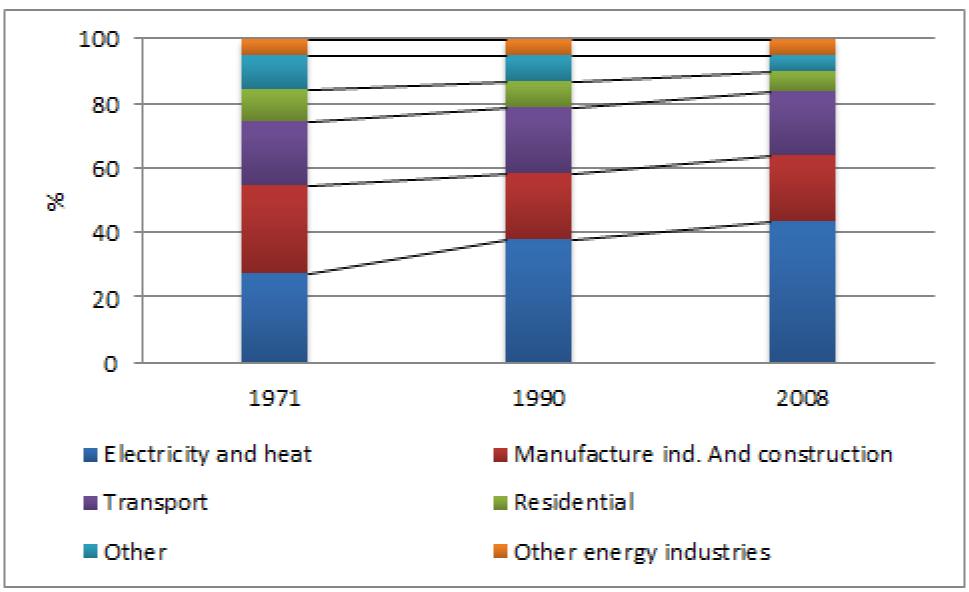

Figure I-2 CO_2 emitted between 1971 – 2008 organized by sector

Besides the environmental problems previously discussed, there is another important fact that should be taken into account regarding the use of fossil fuels for energy production. Comparing the crude oil price between 1990 and 2010 is possible to observe that it has risen up fourfold (Figure 3). The price was 20 USDbarrel^{-1} in 1980 and 80 USD/barrel at the beginning of 2010[1].

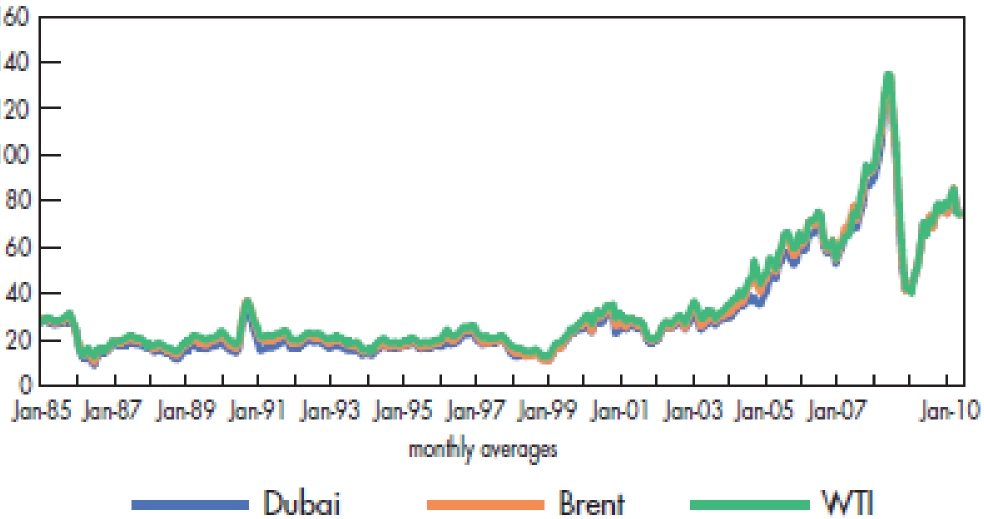

Figure I-3 Key crude oil spot prices from 1085 to 2010. Prices in USDbarrel^{-1}

Likewise, the cost of Coal also increased on the last ten years. Along the period of 1983-2003, the price was stable about 40 and 60 USDton^{-1}; nevertheless, this value has increased since 2003, reaching the highest point during 2008, 160 USDton^{-1}. Figure 4 exhibits the changes of steam coal price in the EU member states and Japan between 1983 and 2009[1].

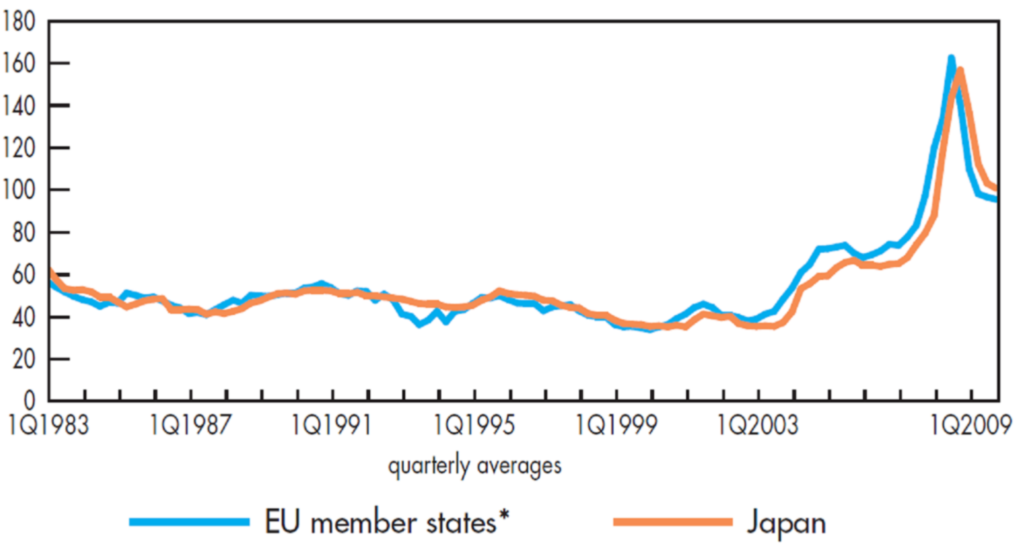

Figure I-4 Steam coal import costs from 1983 to 2009. Prices in USDton^{-1}

As a consequence of these problems, the necessity of developing different kind of technologies capable of harnessing alternative fuels has become remarkable worldwide. These technologies should be capable of generating either heat or electricity, producing fewer GHG emissions than traditional systems, and providing sustainable alternatives for the power and heat generation sector. During the last ten years, many projects have been performed in order to achieve this milestone; the annual investment on new renewable energy capacity between 2004 and 2009 has increased from 20 to more than 140 billion USD [3]. The renewable energy installed capacity was about 305 GW at the end of this period; however, the energy produced from renewable fuels represented no more than 19% of global final energy consumption and 18% of world electricity generated in 2008.

At the end of 2009, the most important renewable resource for power generation was hydropower, followed by wind and biomass-fired systems. For heating applications, biomass was the most used source rather than solar or geothermal. Table 1 gathers the installed capacity for power generation in 2009 classified by the energy source [3].

Table I-1 Renewable energy existing power capacity at end of 2009

Renewable Source	Capacity (GWe)	Renewable Source	Capacity (GWe)
Wind Power	159	Geothermal Power	11
Small hydropower <10	60	Concentrating Solar Power	0.6
Biomass power	54	Ocean Power	0.3
Solar PV- grid connected	21		

B. Biomass and Solid Biofuels

Nowadays, biomass is one of the most attractive renewable energy sources due to some advantages discussed further. Biomass has some definitions. Some considered as those organic materials mainly composed of carbohydrates and lignin; meanwhile, it is a stored form of solar energy relying on the process of photosynthesis. Several materials could be labeled as biomass. Biomass can be classified in traditional biomass, new biomass or energy crops. Traditional biomass is mainly firewood, sawdust, and other wastes coming from timber industries; about 70-75% of the global wood harvested is either used for energy generation or potentially available as a renewable fuel [4]. New biomass includes organic wastes and agriculture residues such as palm oil fruit bunches [5], rice husks [6], coconut shells [7], sugar cane [8]. Biomass utilization as an energy resource has a significant contribution to enhance energy independence, decrease greenhouse gas emissions, add value to agriculture residues [9], and promote decentralized power systems. Nonetheless, there are some problems associated with food replacement that should be taken into account.

Due to the wide variety of available materials, different processes could be applied for energy generation. When the biomass assortment has oils or fatty acids, is possible to produce biodiesel after extraction and transesterification with either methanol or ethanol. Biomass with considerable starch or sugar compounds can be harnessed to produce bioethanol by fermentation. Biomass with a valuable content of organic substances can be fed into anaerobic biodigesters to produce a gaseous fuel known as Biogas, mainly made of CO_2 and CH_4. Moreover, lignocellulosic biomass can be employed on gasification or combustion systems that are detailed discussed in further sections.

Methods available for harnessing biomass are broad. Some generate liquid biofuels such as biodiesel, bioethanol or crude vegetable oils; others transform the biomass into gaseous fuels like biogas or synthesis gas [10]; otherwise, some processes are based on the utilization of solid biofuels.
When biomass is employed to generate energy, there are some issues that must be faced. Some characteristics such as the non-uniform shape and size, the high moisture content, the high ash content, and the low density should be considered before defining the most suitable equipment. Frequently, the thermal efficiency of boilers and power systems decrease due to these characteristics, making the process less stable, encumbering the design of the equipment, and increasing transport, storage and handling costs. Consequently, an alternative to mitigate these problems is to pre-treat the biomass. The pretreatment aims to modify the shape, the size, reduce the moisture content and increase the density. This process is known as biomass densification, and

the final product are known as pellets or briquettes. The use of biomass pellets and briquettes have growth steadily the last five years; the annual consumption of wood pellets in Europe has increased from 0.5 to 13 Mton between 2000 and 2010. The consumption increases at a rate of 1.25 Mtonyr-1. Sweden, Denmark and Austria are forerunners in wood pellets use in Europe [11]. The European production of wood pellets is not rising as much as the consumption, giving to countries like Canada, US and China an opportunity to create new industries and provide the product demanded. Hence, pellet oversees exports of Canada varied from 100 kton in 2000 to 625 kton in 2006 [12].

Solid Biofuels have advantages that make this fuel interesting as an alternative to traditional fossil fuels. Among them, some advantages are i) simplified fuel feeding systems; ii) ease in transport and handling; iii) flexibility in accommodating a variety of feedstock including wastes; iv) uniform and controlled combustion, with low emission levels. [5, 13] Therefore, wood pellets and briquettes are employed on domestic stoves [14, 15], on gasification plants [8, 16, 17] and even on large scale power systems [18]. Despite the pellets are primarily made of wood residues, different industries are working on producing pellets from another kind of biomass such as straw, corn stalks, corn, among others. China will also develop the market of densified solid biofuels due to continued improvement and cost reduction of briquetting technology [19].

The manufacturing process for solid biofuel production implies different stages that are similar independent of the sort of biomass used. The feedstock is transported and stored. The following steps are drying, grinding, pelletizing, cooling, and screening. Finally, the products are packed and commercialized.

Drying is the first stage of this process. Often, biomass materials have high moisture contents that should be removed in order to enhance quality properties of the final solid. Drum dryers are the most common equipment used in medium and large scale industries. Drying is a very sensible stage of this process because a non-adequate design of the equipment and non-proper operational conditions might result on large quantities of energy used in the process. There is not a world standard for the moisture resulting of the drying stage, but proper values are in the range of 12 to 17%.

Following the drying stage is the grinding stage; during this step, the particle size of the biomass solids decrease. The final size depends on the mill used. The particle size is a remarkable parameter that affects the next stages and the physical properties of the solid biofuels. Frequently, the finer the particle, the more durable and resistant are the solids; nevertheless, the production of very fine grinds require more sophisticated mills increasing the energy consumption in this stage.

The ground material goes to the densification stage. In this stage, the primary objective is to compress and agglomerate the grinds in order to increase the bulk density and produce a solid biofuel with determined dimensions. When the resulting products are pellets, this stage is known as pelletizing; otherwise, it is known as briquetting when briquettes are obtained. For pellets production, the machines used could have a flat die or a rotary die. In the first case, the raw material is pressed through the top of a horizontal mounted die; on the other hand, two or more rotary presses push raw material from inside a ring die to the outside [12]. Figure 5 exhibits a scheme of the flat die and the rotary die pelletizing machine. After the densification stage, the solids are cooled. It is used to decrease the temperature of the biofuels as soon as they leave the densification machine increasing the solids strength and durability and making them more compact. According to the solids dimensions and characteristics, the solid biofuels are classified, packed and distributed to the final customer.

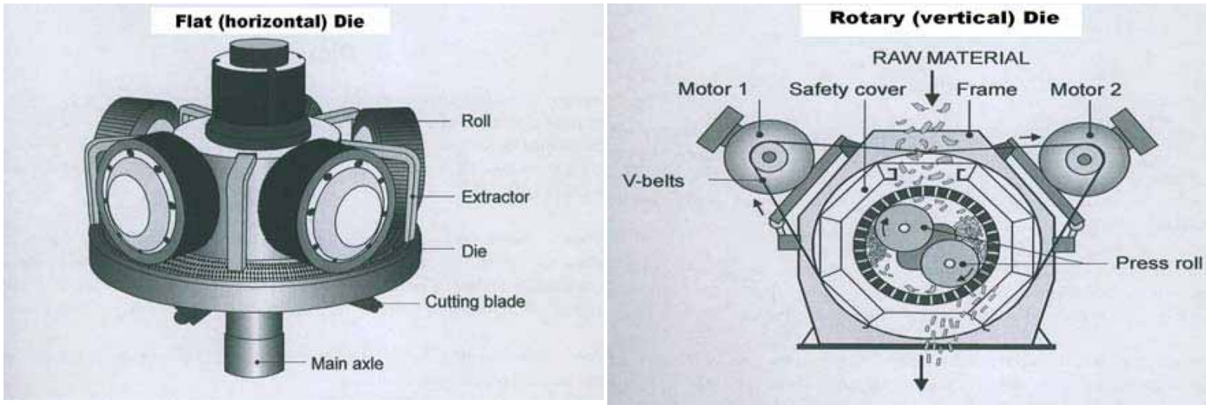

Figure I-5 Pelletizing systems employed in the industry. Flat die (left), and Rotary die (right)

C. Densification of Biomass for Solid Biofuel production

There are many factors affecting the densification mechanisms and the final characteristics of the solid biofuels. In the first stage of the densification process, the particles rearrange themselves and decrease the porosity as a result of the applied stress [20]; the energy is then dissipated due to inter-particle and particle-wall friction. Afterwards, elastic and plastic deformation of solid grinds take place as pressure and temperature increase. Likewise, the particles slide and flow into smaller void spaces, increasing the inert particle surface area [21]. Simultaneously, some compounds create new bonds due to short-range forces such as the van der Waal forces. When the raw material is brittle, it fractures as a consequence of low or medium pressures leading to mechanical interlocking bonds. At higher pressure and temperatures, some substances melt and diffuse through the matrix, creating stronger bonds denoted as solid bridges that enhance the mechanical properties of the resulting solid [22]. Figure 6 summarizes the phenomena occurring during densification of biomass pellets; these processes constituent the densification mechanisms of solid biofuel production.

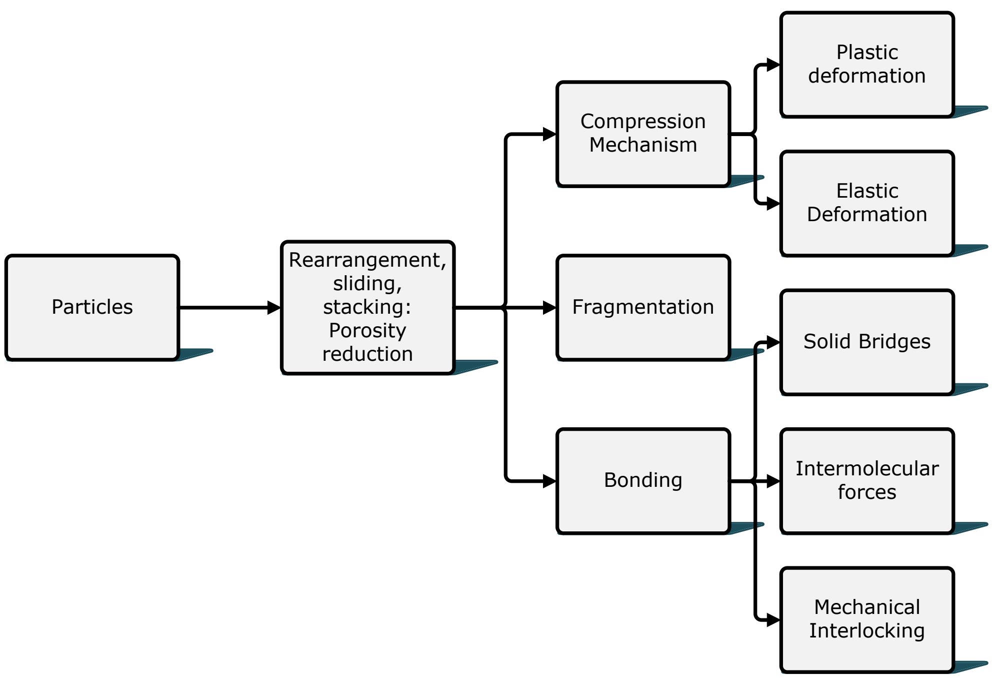

Figure I-6 Densification mechanisms of powder particles under compression

Modeling this process is complex because of the several processes taking place simultaneously during agglomeration [23]. Depending on the characteristics of the raw material, some mechanisms might be more observable than others and the properties of the solid pellets vary. The final properties of biomass pellets (such as dimensions, density, strength, and durability) are influenced by the moisture, pressure, temperature, die size, particle size, and some chemical components present on the biomass like starch, protein, fibers, oils, and lignin. Meanwhile, the characteristics of the biomass pellets affect the performance of the biofuel during combustion. The resistance of the pellet can be defined as the hardness and as the durability. Hardness describes the force needed to crush the pellet; whereas, pellets durability represents the amount of fines returning from pellets after being subjected to mechanical agitation [25].

Several studies have been reported about wood pellets production and the effect of operational conditions on the pellets physical and chemical properties. Li and Liu [26] evaluated the influence of the applied pressure on the final density, the compressive strength, and the impact resistance index, using oak sawdust, cottonwood sawdust, and oak bark mulch as raw materials. The results showed that the final pellets density could reach about 900 kgm^{-3} and stronger and more resistant solids could be produced when higher pressure is applied.

Changes on the temperature also affect the pellets density, strength and durability. The temperature of the raw material is usually increased to activate the inherent and natural binders; elevated temperatures also promote plastic and elastic deformation. In some cases, the temperature of the material is controlled by adding steam into the process; Kaliyan [27] presented results of pellets that durability grew from 79.1 to 96.5% when the temperature grow from 27 to 80°C. Meanwhile, the particle size is a remarkable parameter that should be analyzed in the process, because it not only change the final values of the density, strength and durability, but also affects the costs associated with raw material grinding. When small particles are used, higher density is achieved; pellets are more resistant and durable. Small particle size increases the inter-particle area, providing more opportunities for creating new bonds and solid bridges. Nonetheless, the most of the literature reported on this field is related with pharmaceutical products and animal feeds.

The biomass is mainly composed by carbohydrates (cellulose, hemicellulose and lignin) and other compounds such as starch, fibers, proteins, oils, and waxes. These compounds have a close relation with the final properties of the product. Some of them act as natural binders during densification. Lignin, cellulose, and hemicellulose are polymers. The glass transition temperature of cellulose, hemicellulose, and lignin is about 240, 190, and 150°C, respectively. At elevated temperatures, lignin softens and helps the binding process; the auto-adhesive action of thermally softened non- crystalline wood polymers is like that of mastic with little inner strength of its own [27]. Starch gelatinization is another process that strengthens internal bonds during agglomeration; this is possible when biomass has starch and steam is added into the pelletizing stage. Starch gelatinization supports the creation of solid bridges due to the diffusion of starch throughout the structure. Fibers can be classified as water-soluble or water-insoluble; the first group increases the viscosity of the feed and enhances the integrity of the final product. On the other hand, water-insoluble fibers act as weak spots for fragmentation because they do not make good bonding between particles and fibers [27].

Another alternative to modifying the characteristics of the solid pellets is by mixing raw materials before densification. Yaman et al. [28] found that the mechanical strength of lignite coal samples could increase by blending it with sawdust and cotton refuse. Wamukonya and Jenkins [29] analyzed the potential of mixing straw, sawdust, and shavings for high durable briquettes production; they concluded these materials can be mixed with sawdust to produce adequate solid biofuels in Kenya.

Structural analysis can be performed in order to evaluate in a microscopy scale the influence of chemical structures and operational conditions on the pellets final characteristics. It has be done using some advanced techniques such as Scanning Electron Microscopy (SEM) [6, 30, 31], Raman

Spectrometry [32], Attenuated total reflectance infrared spectrometry (ATR – FTIR) [30], Light microscopy [31], and Ultraviolet Autofluorescence (UV-AF) Microscopy [31].

SEM images, secondary electron images, backscattered electron images, and elemental X-ray images bring information about topography and morphology of the pellets surface and in some cases data about composition [33]. Stelte et al. [30] used this technique to identify the changes on the structure of solid biofuel made from beech and spruce using feed temperatures between 20 and 100^{0}C. They fractured some pellets; then, they analyzed the fracture surface with a Scanning electron microscope (FEI Quanta 200) and stated that formation of solid bridges is greater at higher temperatures. Figure 7 shows the SEM images of fracture surface of beech pellet manufactured at 20 and 100°C [30].

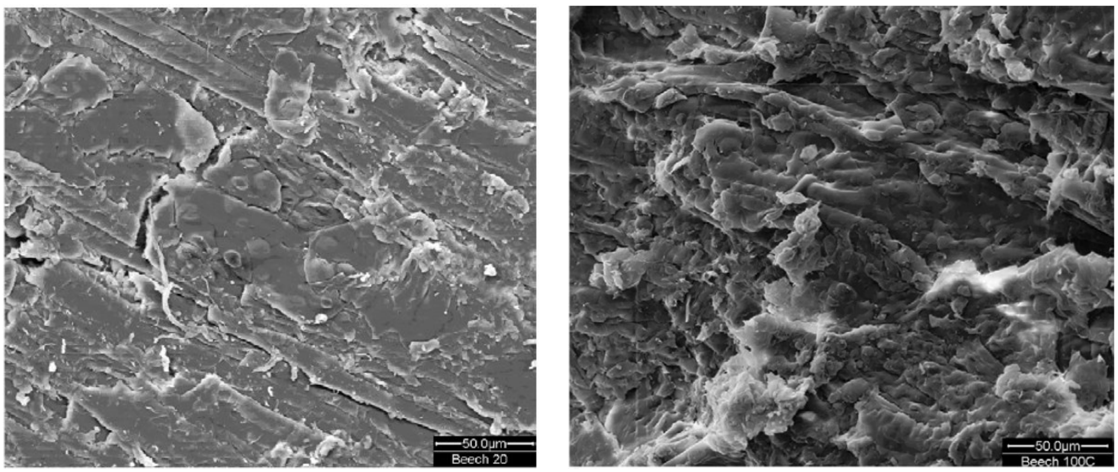

Figure I-7 SEM images of the fracture surface of beech pellets manufactured at 20 and 100°C

Fluorescence microscopy is a member of the luminescence family of processes in which susceptible molecules emit light from electronically excited states created by a physical (absorption of light), mechanical (friction) or chemical mechanism. UV-AF is based on the principle that some compounds can absorb light at a particular wavelength (ultraviolet light) and emit light with higher wavelength during a specified time interval [34]. Kaliyan and Morey [31] employed this technique in order to evaluate the influence of the lignin and proteins in the final properties of the biofuels made from corn stover and switchgrass; they evaluated the distribution of the lignin in the material before and after densification. They used the same method as Stelte [30] and fractured the solids. Thus, it was possible to see that lignin (Brilliant blue or bluish-white) and proteins (green or yellow-green) diffused during the process and created solid bridges, improving the durability of the products. Figure 8 shows the AF-UV images of corn stover before and after densification [31].

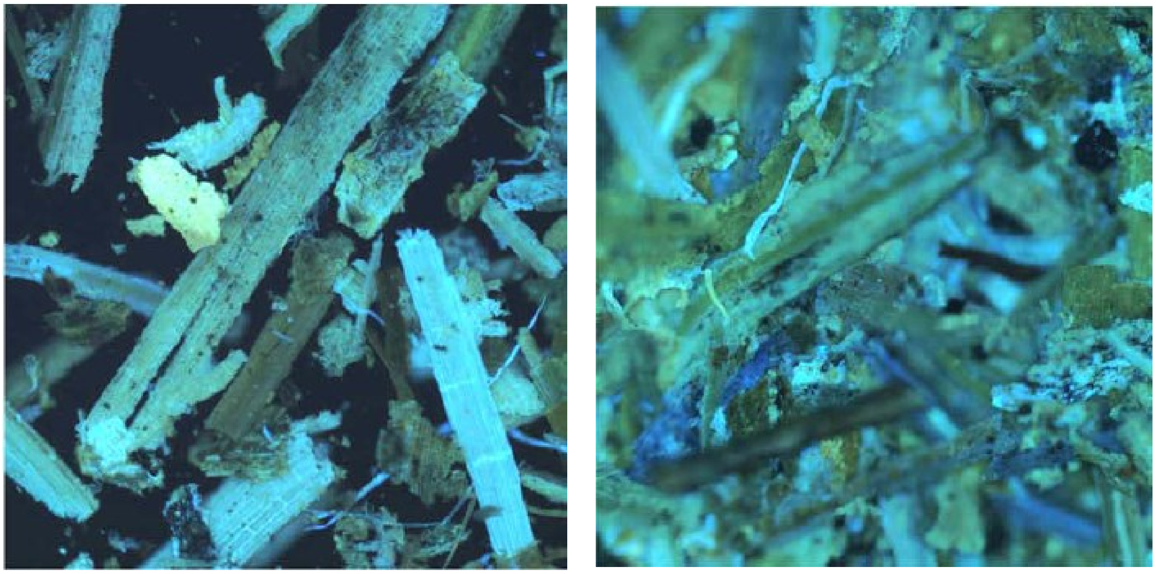

Figure I-8 AF-UV Images of corn stover grinds (particle size =0.34 mm) and fractured surface of corn stover briquette made at 150 MPa and 75°C

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II. BIOMASS PELLETS PRODUCTION AND UTILIZATION FOR THERMAL ENERGY GENERATION: A REVIEW OF THE GASIFICATION PROCESS MODELS

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Abstract

The need for producing thermal energy and electricity, the global warming caused by an increase of Green House Gas emissions, the raising of fossil fuels prices and the desire of energy independence, have created a new industry interested on generating energy by using renewable sources. Among different options, biomass is the third most important to produce electricity and the most used worldwide to produce thermal energy. Although, problems related with low biomass density, transport and storage are the main reasons why it is so important to develop products with higher density, resistance and durability, these are called pellets and briquettes. This work aims to analyze the actual situation of pellets production, their uses, and especially to summarize different models developed for gasification processes.

Keywords: Biomass, Gasification, Pellets, Pyrolysis, Renewable Energies

A. Introduction

Throughout the recent history, the humankind development has been directly related to the energy generation for either electrical or thermal applications. Nevertheless, the increase of energy production has boosted the emission of greenhouse gases (GHGs) resulting from the combustion of fossil fuels like coal, oil, and natural gas. Last 60 years, the CO_2 production up from 4 to 28 million tons [1]. As a consequence of the high levels of CO_2, the global warming, and the rise of fossil fuel prices, the necessity of using clean and renewable energy resources has become imperative. The investment on renewable energy power systems grew from 20 to 160 billion dollars between 2004 and 2010 [2], promoting the development of new technologies and the creation of new renewable energy industries [3, 4].

In 2008, the world power capacity of renewable energy systems was about 1140 GW. Hydropower systems had a power capacity about 75%, followed by wind power, small hydropower systems, and biomass with 10, 7, and 4.5%, respectively. Meanwhile, the installed capacity for heating applications from renewable energy sources was 450 GWth, from which biomass shared 56% [2].

Biomass can be defined as any organic compound generated from photosynthesis processes capable of producing energy by means of thermal or chemical processes due to its high carbon contents [5]. Some advantages of using biomass as an energy resource are the easy of handling, low GHGs resulting from energy processes and low costs of acquisition. Moreover, the utilization of biomass might result on a wide variety of solid, liquid, and gaseous intermediate fuels such as briquettes, pellets, alcohols, bio-oil, biogas, hydrogen, or syngas[6].

Biomass calculated potential is about 100 $EJyr^{-1}$ representing about 30% of global primary energy consumption. Woody biomass can produce about 41.6 $EJyr^{-1}$[7]. According to the Unidad de Planeción Minero-Energética (UPME), the biomass has an energy potential of 0.45 $EJyr^{-1}$ in Colombia and the agricultural residues are the major source representing 73.8% of this potential [8].

B. Pellets production

There are some parameters that might be considered for evaluating the biomass energy potential. Among them, the moisture content, carbon content, heating value, and density are of great importance. These parameters are useful for determining the most suitable energy process for harnessing the biomass assortment [5]. The higher heating value of biomass is always lower than parameters reported for coals; nonetheless, it is possible to produce between 10 to 25 MJ per kg of biomass. Table 1 shows the higher heating value of some biomass assortments [9]

Table II-1 Higher heating value of some typical biomass assortments

Biomass	HHV ($MJkg^{-1}$)
Charcoal	25-32
Wood	10-20
Coconut shells	18-19
Straw	14-16
Coffee husks	16
Cotton stalks	16
Cocoa husks	13-16
Oil Palm shells	15
Rice husks	13-14
Maize stalks	13-15
Sawdust	11
Sawdust pellets	20.5
Wood pellets	20.3

Density is another remarkable parameter for energy generation. The higher the density, the more material can be stored in the same space, reducing the storage and transportation costs. Despite the density of some materials like coal and coconut shells is about 220 and 330 kgm^{-3}, there are several agricultural residues such as cocoa husks, rice husks or sawdust which density is in the range of 100-112 kgm^{-3} [5]. An alternative to enhance the physical characteristics of biomass is densification; by this means, it is possible to produce uniform solids, known as briquettes or pellets, which density vary between 590 to 1000 kgm^{-3} [10].

1) Recent situation of the pellets industry

Pellets and briquettes are cylindrical solids mainly differentiated by the size. Typically, briquettes are 50-90 mm diameter and 74-300 mm length, whereas pellets are 4-10 mm diameter and 30 mm maximum length [11]. Nowadays, there is not a unique standard for pellets or briquettes. Depending on the country where the product is commercialized, the quality standard varies. Some of them are the Önorm M7135, the PVA, SS187120, DIN51731; these evaluate parameters like the diameter, length, density, water content, ash content, heating value, sulfur content, potassium, chlorine, cadmium, zinc, and lead [12]. Table 2 summarizes the physical and chemical parameters of pellets and briquettes according to DIN51731 [12].

Table II-2 Physical and chemical parameters of wood pellets and briquettes according to DIN51731

Parameter	Units	Pellets	Briquettes
Diameter (d)	mm	4-10	40-120
Length	mm	<5*d	<400
Bulk density	kgm^{-3}	>600	
Particle density	kgm^{-3}	>1.12	>1
Moisture content	Wt%	<10	<10
Ash content	Wt%	<0.5	<0.5
Abrasion	Wt%	<2.3	
Lower Heating Value	$MJkg^{-1}$	>18	>18
C	Wt%	~50	~50.5
H	Wt%	~6	~5.6
N	Wt%	<0.3	<0.3
S	$mgkg^{-1}$	<400	<400
Cl	$mgkg^{-1}$	<200	<200
K	$mgkg^{-1}$	~490	~600
Cd	$mgkg^{-1}$	<0.5	<0.5
Pb	$mgkg^{-1}$	<10	<10
Zn	$mgkg^{-1}$	<100	<100
Cr	$mgkg^{-1}$	<8	<8
Cu	$mgkg^{-1}$	<5	<5

Despite the diversity of biomass species, the pellet industry has primarily focused on the production of wood pellets. Annually, some countries like Sweden, Canada, and the United States produce more than one million tons [13]. Wood pellets have been employed for applications like power generation with cogeneration systems [14] or residential and district heating[15]. As a consequence, the wood pellets industry is steadily increasing; however, this industry supplied about 7.5 billion tons in 2012 [16]. Some advantages of wood pellets are the decrease of environmental impact due to the use of a renewable resource, ease of storage and transportation, and mechanical durability. Based on these benefits, there are more countries analyzing the potential of biomass pellets [17]. Sweden has become one of the most valuable importers and producers of wood pellets around the world; this country leads the wood pellets market and has the most feasibility studies reported in the literature. The cause of that is their necessity of producing heating systems capable of harnessing renewable energy resources and the existence of more severe policies [18]. Finland is also another important market; the annual wood pellet consumption is about 117.000 tons [19]. Meanwhile, wood pellets have become a valuable fuel in Denmark where the Avedore power plant is located [20]. This system is considered the biggest pellet-fired district heating system in the world.

2) Biomass pellet manufacturing systems

Pellets are the resulting product after agglomeration. During the first stage, the biomass is ground producing smaller particles of uniform size; the biomass is then dried, and metallic substances are removed using magnets. Afterwards, the grinds are wet, densified using a pelletizer machine. The solid obtained from the pelletizer is cooled, increasing its durability and preparing it for storage [11, 16].

Research has been done on some of the stages of this process. The drying stage is one of the most critical because of the high energy consumption [21]. Drying processes with high residence time affect some characteristics of the final pellet, promote terpenes evaporation, and diminish the heating value of the final pellet. Meanwhile, some literature is available about the incidence of exhaust gas recirculation. This technique decreases the energy supplied to the system, increasing the energy efficiency and makes processes more feasible [22].

Some developments have been done on the pelletizing stage; pelletizers have been patented since 1948 [23]. Also, some processes have been applied using binding agents like waxes and lignosulfonates [24, 25]. Meanwhile, other authors analyzed the effect of lignin content on mechanical properties such as durability and resistance [26 - 28], or evaluated the production of biomass pellets using different species of biomass, varying pressure and compression ratio[29, 30].

3) Mixed biomass pellets

Pellets are produced from timber residues and wood; nevertheless, it is needed to employ other varieties of biomass with proper quality standards due to the fast increase of the pellets demand and the difficulties of producing wood residues at this rate. When pellets are manufactured with residues different from wood, there are denominated as mixed biomass pellets. Authors have demonstrated the possibility of producing pellets from agricultural residues with durability, resistance, and heating value similar to wood pellets [31]. The mixed biomass pellet industry has increased considerably the last years, although it is smaller than wood pellet industry. In 2008, the production capacity rose about 80% in comparison with the year before, moving from 447 to 809 million tons [32],. This production mainly focused on Denmark, Finland, and Poland; although, France has the highest installed capacity. A significant disadvantage of mixed biomass pellets is related to the high sulfur and chlorine content that might produce corrosion, blocking, and GHGs emission [33]. As an alternative to control the quality of mixed biomass pellets, a standard in France has defined some specific characteristics. Table 3 shows the main parameters that mixed biomass pellets require for being commercialized in France [32].

Table II-3 Mixed biomass pellets quality parameters according to French standards

Parameter	Units	Agro+	Agro
Diameter	mm	6-8	6-16
Length	mm	10-30	10-30
Moisture content	%wt	<11	<15
Lower heating value	$MJkg^{-1}$	>15.5	>14.7
Particle density	kgm^{-3}	>650	>650
Mechanical Durability	%	>95	>92
Fines content	%	<2	<3
Ash content	%	<5	<7
Cl	%wt	<0.2	<0.3
N	%wt	<1.5	<2
S	%wt	<0.2	<0.2
Ash melting temperature	°C	1000	800
As	$mgkg^{-1}$	<1	<1
Cu	$mgkg^{-1}$	<40	<40
Cr	$mgkg^{-1}$	<10	<10
Cd	$mgkg^{-1}$	<0.5	<0.5
Hg	$mgkg^{-1}$	<0.1	<0.1
Ni	$mgkg^{-1}$	<15	<15
Pb	$mgkg^{-1}$	<10	<10
Zn	$mgkg^{-1}$	<60	<60

Based on the chlorine and sulfur content, these pellets can be employed for energy production in big industries capable of financing the exhaust gas cleaning systems. Further research is needed in this field aiming to decrease these environmental impacts. Nonetheless, the enormous amount of agricultural residues available in several countries make of mixed biomass pellets an interesting alternative for power generation [34].

C. Gasification process

There are several thermochemical and biochemical processes capable of harnessing biomass and pellets; i.e., biodigestion, pyrolysis, combustion, and gasification. Biodigestion is based on the biomass decomposition promoted by microorganisms and absence of oxygen. The result of this process is a high energy value gaseous fuel known as Biogas, mainly composed by methane (CH_4) and carbon dioxide (CO_2) that is employed on internal combustion engines or gas turbines.

The pyrolysis is a thermochemical process by which biomass decomposes at temperatures between 400 and 800 K. Because of the temperature, big chemical chains crash releasing volatile matter, tars, and a high energy solid known as char. This solid can be afterwards used as a fuel on gasification or combustion processes. Combustion can be used for transforming the chemical energy of biomass or pellets into thermal energy. In this process, the fuel reacts with an Oxygen excess releasing CO_2, H_2O, and energy that can be either transferred to steam for producing electricity in a Rankine cycle or to water for residential and district heating. Wood pellets have been majorly employed on combustion systems for heating applications. Research have been done aiming to identify the resulting emissions [35], slag formation capable of blocking the heater burners [34], and the relationship between ash and pellets composition[36].

On the other hand, biomass gasification is the partial oxidation of a solid fuel with a gasification agent, e.g., O_2, CO_2, H_2O, or Air, at temperature between 750 to 1100 K [37]. As a consequence of this process, a gaseous fuel, known as syngas, is generated; because of the chemical composition, mainly CO and H_2, this gas has a high energy value and can be used on power generation systems or as a raw material for the chemistry industry. Nowadays, biomass gasification systems are becoming more employed in industries because of the gas energy value, the process energy efficiency, and the lower emissions emitted in comparison with traditional combustion processes. Therefore, the interest on pellets gasification is steadily increasing; research focus on identifying the relationship between the syngas quality and process operational conditions. Typical parameters considered on this field include the gasifier design, process temperature, system pressure, oxidizer agent, and pellets physicochemical characteristics. During gasification, biomass undergoes some physical and chemical changes. In the first stage, the material dries and loses humidity, followed by pyrolysis, combustion, and reduction stages. Depending on the operational conditions and the design of the reactor, these stages might occur simultaneously but have been studied separately. Some work is reported in the literature about gasification modeling; nonetheless, most is based on wood or coal pellets gasification despite the diversity of biomass species.

1) Pyrolysis stage models

During the pyrolysis, some multiple reactions take place releasing volatile matter and transforming the pellets into carbonized solids [38]. This process can be described by the following reactions.

$$Dry\ soild \rightarrow Volatile\ matter + pyrolized\ solid \tag{1}$$
$$Volatile\ matter\ \rightarrow Gases + tar \tag{2}$$

Some of the gases produced in this process are methoxyphenol, benzene, methylbenzene, phenol, naphthalene, among others [39]. However, it is considered that the primary gaseous compounds produced during this stage are H_2O, CO, CO_2, CH_4, and C_2H_6. From these, CO share is about 60%wt, CO_2 12%wt and H_2O 15%wt [40]. Using biomass pellets has some benefits in comparison with as-received biomass. Pellets are more homogeneous and stable. Based on this, some authors neglect any change of the solid volume in the radial axis during pyrolysis modeling [41].The kinetic reaction of this stage has been analyzed in terms of the activation energy, evaluated under thermogravimetric methods with the heating rate varying between 2 and 5 $Kmin^{-1}$ [42] and different pressure [43]. Likewise, other authors evaluated the kinetic of this stage based on the degradation of the solid without considering the decomposition of cellulose, lignin, and hemicellulose [44]. More detailed analysis considered the heat flux, mass and heat balances, and Darcy´s law aiming to establish the kinetic as a differential equation system that considers some competitive reactions and changes on the solid density [45].

2) Combustion and reduction stage models

Following the pyrolysis stage, the char undergoes some combustion and reduction reactions by which the final syngas composition is established. In this stage, several exothermal reactions take place, and the carbonized solid oxidizes using the oxygen fed with the gasification agent [46]. After combustion, the gaseous compounds react and reduce, generating H_2 and CO that are the principal constituents of syngas [47]. Kayal [48] considered the following homogeneous and solid-gas heterogeneous reactions in his mathematical model.

$$charcoal + O_2 \rightarrow CO_2 + H_2O \quad (3)$$
$$CO_2 + H_2O \rightarrow CO + H_2 \quad (4)$$
$$CO_2 + H_2 \rightarrow CO + H_2O \quad (5)$$
$$C + O_2 \rightarrow CO_2 \quad (6)$$
$$C + CO_2 \rightarrow 2CO \quad (7)$$
$$C + H_2O \rightarrow CO + H_2 \quad (8)$$
$$C + 2H_2 \rightarrow CH_4 \quad (9)$$

Other alternatives to model the combustion and reduction zone are based on the species thermochemical equilibrium [49] or the Gibbs free energy minimization method. The latter method exhibited a good approximation of the experimental data; although there are some limitations with the kinetic of the process due to the temperature profile and the air-fuel ratio employed [50]. Moreover, Mandl [51] analyzed these stages assuming the charcoal as a hydrocarbon made of Carbon, Oxygen, and Hydrogen expressed as $CH_{0.2526}O_{0.0237}$. Reactions considered in this model were summarized in equations 10, 11, and 12. Otherwise, Babu developed a gasification model defining the reduction reactions as a series of equilibrium reactions evaluated in terms of the activation energy and the frequency factor [52].

$$CH_{0.2526}O_{0.0237} + 0.976H_2O \rightarrow CO + 1.1026H_2 \quad (10)$$
$$CH_{0.2526}O_{0.0237} + CO_2 \rightarrow 2CO + 0.1026H_2 + 0.0237H_2O \quad (11)$$
$$CH_{0.2526}O_{0.0237} + 1.8974H_2 \rightarrow CH_4 + 0.0237H_2O \quad (12)$$

D. Analytical models based on the reactor configuration

Biomass gasification is performed in gasifiers that vary depending upon the particle size, residence time, or gasification agent. The reactors can be classified into the fluidized bed or fixed bed gasifier. The fluidized bed gasifier let the biomass to freely fluid through the reactor as a consequence of the gasification agent pressure. In the fixed bed gasifiers, the biomass remains almost static in the reactor creating a bed; the gasification agent might diffuse through the inter-particle voids reacting with the material.

1) Models defined on fluidized bed gasifier

Some authors have defined the mathematical models in these reactors by separating the solid and gaseous phase along the equipment and taking into account critical parameters during devolatilization [53], and the generation of condensable substances and tars [54]. These models have been evaluated by computational methods based on either fluid dynamics or the combination of chemical kinetic expressions together with mass and diffusion transfer mechanisms [55].

Fluidized bed gasifiers have become a valuable equipment for biomass gasification due to the alternatives to control the quality of the syngas generated; nevertheless, more research is needed for establishing accurate mathematical models capable of predicting the internal performance of the process [56]. These models might consider the differences of biomass composition and its particular performance in the reactor.

2) Models defined on fixed bed gasifier

The fixed bed gasifiers have been widely employed in developing countries because of to the low capital and operational costs and the lack of advanced control systems. Using this type of reactors is possible to evaluate the behavior of the process varying the biomass characteristics, pellets size, raw material consumption, and the air-fuel ratio. Pellets size affects the resulting syngas; the bigger the pellet, the more residence time on each stage and the more dense the fixed bed [57]. Some models have been established using H_2O and CO_2 as gasification agent and Langmuir-Hinshelwood type kinetic equations; these related the reactive surface area of the bed by means of desorption programmed temperature techniques [58]. As a result of that, the relationship between the pellets surface area and the reaction velocity has been identified.

Some models assume a stationary state process and neglect the temperature and biomass composition changes in radial and angular directions [59]. In this manner, these models can be mathematically calculated and verified with experimental data. Coal and wood pellets have been used in these models in order to avoid problems like the non-uniform particle size, low bulk density, ash sintering, and non-uniform temperature distribution along the reactor that have been observed when using pellets from agricultural residues [60]. However, Ghani [61] stated that despite the biomass employed during gasification, the resulting syngas composition would be 28-30% CO, 6-8% H_2, and 5-7% CO_2. Another alternative to simulate pellets gasification have been focused on the use of simulation software like Aspen Plus, Aspen Hysys or by neural network control systems [62].

Conclusions

Biomass is a renewable energy resource that is becoming more valuable every year. The necessity of increasing the density of timber and agricultural residues has promoted the pellets industry in Europe, Canada, and United States of America; this industry has a 10 $Mtonsyr^{-1}$ installed capacity. Nonetheless, the wood pellets demand is growing faster than the production of timber residues that could cause some problems due to the lack of raw materials for pellets industry. Production of mixed biomass and agricultural residues pellets is gaining interest as an alternative to solve this problem in the incoming years.

Nowadays, pellets are mainly used on direct combustion process for energy generation producing some emissions that need to be cleaned; likewise, pellets gasification could produce energy by transforming the biomass into a gaseous fuel with less emission than the traditional processes. In order to improve the capacity and predict the performance of gasification systems, more research on gasifier modeling is needed. The evaluation of the different stages occurring simultaneously in the gasifers (e.g., drying, pyrolysis, combustion, reduction) is of great importance for establishing accurate models. This field needs further research aiming to define particular characteristics for reactors capable of harnessing the wide variety of biomass species available in Latin America.

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III. CHARACTERIZATION AND FEASIBILITY OF BIOMASS FUEL PELLETS MADE OF COLOMBIAN TIMBER, COCONUT AND OIL PALM RESIDUES REGARDING EUROPEAN STANDARDS

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Abstract

Strong correlation between economic development, energy demand and fossil fuels utilization during last decades has caused some adverse impacts worldwide, based on it, the renewable resources for energy production should be employed to mitigate these effects. Nowadays, biomass is one of the most prominent renewable sources, but factors such as low density and high moisture content are some drawbacks. In order to overcome these problems, some companies use different types of biomass to provide solid biofuels with higher energy density, mechanical resistance and standardized dimensions. Wood pellet production increased exponentially during recent years, faster than timber industries; therefore, new raw materials should be evaluated to guarantee pellets demand in the near future. Some of them are agricultural wastes. Colombia is a country with an interesting potential for biomass production because there is a rising generation of agricultural products. This work aims to assess primary properties of Colombian timber industry residues, coconut shells and oil palm shells and compare the characteristics of pellets made from these raw materials with European standards. Pellets made from these feedstocks have an average density between 850 and 1025 kgm^{-3}, low ash contents and heating values around 18000 $kJkg^{-1}$. Coconut shell pellets have low compression ratios and problems during pretreatment; whereas, sawdust, wood shavings and oil palm shell pellets proved to be an attractive opportunity for pellet industry development in Colombia.

A. *Introduction*

The development of humankind has produced a significant increase of energy consumption. Since the industrial revolution, the demand of electricity and primary energy has augmented from 71071 PWh in 1973 to 141304 PWh in 2009. Likewise, the power generation boosted up 227%, 6115 PWh in 1973 and 20055 PWh in 2009 [1]. Large-scale hydropower systems and fossil fuel combustion power systems cover this necessity, causing a lot of environmental, economic, political and social impacts worldwide. Despite the advantages that these fossil resources have such as high energy density, stability during the combustion process and relative ease for extraction and transportation, there are some serious effects that could not be neglected. Some of them are energy dependency, wars, social displacement and maybe the most known one, global warming caused by greenhouse gases.

As a consequence of the unrestricted use of fossil fuels for energy production, CO_2 emissions have gone up [2]; in 1971 global emissions were about 15000 Mt, whereas in 2009 reached 30000 Mt. In 2009, coal produced 43% of CO_2 emissions while 37% came from oil and 20% from gas [3]. An analysis of these emissions by sector shows that the critical issue here is to control emissions produced by electricity and heat sector, its share was 43% of world emissions in 2009 while transport was 23%, industry 20%, residential 6%, and others 10%. Based on these and other problems, some countries have redirected their investments and policies on trying to increase the production of clean energy based on renewable resources.

Between 2004 and 2010 global new investment in renewable energy raised up at high rates, in 2004, it corresponded to 22 Billion USD, and seven years later the investment overpassed 210 Billion USD [4], this means an increase around 850%. Nevertheless, these investments are not enough to satisfy the world demand, in terms of electricity renewable resources support 18%, whereas these technologies supply 16% of final energy consumption. More research and development should be done on renewable resources different from big hydropower systems, based on the fact that they cover no more from 3.3% of global electricity production.

Biomass is commonly used for food, feed, fiber, and energy production such as power, heat and liquid biofuels. Among non-hydro renewable resources, biomass is the second most significant source for power production. Wind power existing capacity, at the end of 2010, was 198 GW followed by 52 GW from biomass. Some of the most attractive characteristics of biomass are: the vast variety of species with adequate characteristics for producing energy [5], decentralized location of the resources, existing technologies for direct biomass utilization such as biodigesters, gasifiers or stoves [6]. Moreover, these characteristics generate opportunities for promoting employment creation for technicians and farmers [7].

Colombia has an attractive opportunity to use biomass for energy carrier production. Several agricultural processes use a significant share of the territory, leading to large quantities of agricultural byproducts. Meanwhile, there is a necessity of electrical supply at some off-grid areas. Energy potential of coconut shells is 854 $TJyr^{-1}$ and potential of oil palm solid residues are 6921 $TJyr^{-1}$ [8] that could satisfy the energy demand of 2.1 million people, approximately.

Low-density values, non-uniform shapes and sizes, high moisture contents at production place are some of the most serious problems regarding biomass utilization, especially when solid wastes would be employed. Therefore, biomass densification might be applied; this process produces bigger structures from biomass powders; typically, the products are cylindrical solids known as pellets or briquettes with standardized dimensions and high mechanical resistance [9]. Pellet production has some benefits in terms of reduction of storage volume, transportation costs and easy handling and control of feeding systems [10]. Likewise, the lower moisture content and the decreased heterogeneity of the densified biomass also contribute to improving conversion technologies [11].

Wood pellets industry grew during last years, and different production facilities have been installed worldwide to support demand of Europe, US and Canada. Europe has the largest wood pellet manufacturing industry with 670 pellet plants under operation, producing 10 Mtons in 2009 [4]. Most of this industry operate with wood residues such as sawdust or wood shavings; although, there are more types of materials that should be explored based on the fact that the timber industry could not increase in the same rate as wood pellet, producing a deficit of raw materials. Some of these alternative materials show fascinating results such as paulownia [12], corn stover, switchgrass [10] and poplar [13]. This work aims to analyze proximate and ultimate analysis of Colombian oil palm shells, coconut shells, sawdust, wood shavings, dark coal and the feasibility of pellets produced with these materials in relation to European standards.

B. Materials and methods

In this study, two kinds of residues of the timber industry were used; the sawdust and wood shavings produced during wood cutting were gathered from carpentry of Universidad Nacional de Colombia. Coconut shells are the external part of the coconut; they were supplied by Amerteck Ltda, Colombia. During palm oil extraction, different solid residues are produced; the most notable are oil palm empty fruit bunches (EFB), fibers and shells. We used oil palm shells provided by the Colombian company “El Palmar del llano”, an oil palm extraction plant (Figure 1).

Figure III-1 Samples of oil palm shells (left) and Coconut shells (right) as received

The feedstock used needs to have small particle sizes and low water content to ensure that produced pellets have better physical characteristics such as strength, durability and final density. The pretreatment of these resources includes some stages; biomass was air dried during one week, afterwards, samples were crushed and ground. Palm oil shells required less energy while grinding because they were more fragile than coconut shells. Sawdust and wood shavings do not require cutting, just drying was done (Figure 2).

Figure III-2 Samples of the treated biomass assortments. Oil palm shells (left-up); Coconut shells (right-up); Sawdust (left-down); Wood shavings (right-down)

During physical characterization, different properties were measured. Bulk density was determined according to ASTM D5057, where a box with known dimensions is filled with the material; afterwards, the samples are weighed. The relation between samples weight and box volume gives the value of this property (Equation 1). The proximate analysis is performed; moisture content is evaluated by following ASTM E871 82, where samples are weighed before and after drying in an oven at 105°C; this test was completed when the mass difference did not change more than 0.2%. Volatile matter was determined by ASTM E872, where samples were placed in an oven during seven minutes at 950°C; the volatile matter was calculated as the ratio between the weight difference and initial dried sample. Ash content was measured by following the methodology presented on ASTM E1755 01. Samples used for volatile matter evaluation were employed and burned in an oven at 800°C; the relation of remaining mass against initial weight gives the ash content. Fixed carbon was calculated by mass balance on the samples ASTM 1756 08. Each biomass after natural air drying at environment conditions has water, volatile compounds, ash and carbon; therefore, fixed carbon is defined by the difference of initial material weight with moisture content, ash and volatile matter fraction, all of these parameters might be at wet basis.

$$\rho_{in} = \frac{m_{in}}{V} \quad (1)$$

Where m_{in} (*kg*) was the sample mass weight, ρ_{in} (kgm^{-3}) was the bulk density, and V (m^3) was the sample volume. Ultimate analysis was performed by the staff of Ingeominas Coal laboratory Colombia; carbon, hydrogen, nitrogen contents were determined according to ASTM D5373 08, where a LECO Truspec CHN analyzer is used. Sulfur content was measured with a LECO SC 32 and S 144DR analyzer based on ASTM D4239 08. Hence, it was possible to calculate elemental oxygen content.

Two methods were followed to determine heating value; the samples were analyzed in a bomb calorimeter in accordance with ASTM D 5865-04, and two analytical relations based on ultimate analysis were used [14]. The first one corresponds to Dulong Bertholot equation, and the second relates the higher heating value of lignocellulose and the ash content. Lower or net heating value (LHV) was calculated by using the Equation 2 according to Obernberger and Thek [15].

$$HHV = 339 * \%_C + 1214 * \left(\%H_2 - \frac{\%_{O_2}}{8}\right) + 226 * \%_{H_2} + 105 * \%_S \quad (2)$$

$$HHV = 20490 - 271 * \%_{ash_{db}} \quad (3)$$

$$LHV = HHV * \left(1 - \frac{\%_m}{100}\right) - 2{,}447 * \frac{\%_m}{100} - \frac{\%_{H_2}}{200} * 18{,}02 * 2{,}447 * \left(1 - \frac{\%_{H_2}}{100}\right) \quad (4)$$

Where HHV (*$MJkg^{-1}$*) is the higher heating value; %C means the Carbon mass content; $\%H_2$ represents the Hydrogen mass content; $\%O_2$ is the Oxygen mass content; %Sis the Sulphur mass content, and % ashdb means the ash mass content on a dry basis. LHV (*$MJkg^{-1}$*) is the lower heating value, and %m was the moisture content in the sample.

Densification of these materials was made using a hydraulic press with a 120 mm long and 21 mm diameter fixed die. It was fitted on a stainless steel base; the press plunger moves straight down with no lateral movement. Press force could vary between 113 MPa and 200 MPa; all samples were densified at the same pressure. The die has not any heating device; hence, all the solids were made at ambient conditions (18°C and 87.993 kPa).

The characteristics analyzed for the solids were their dimensions, final bulk density and the compression ratio. The dimensions of the pellets were measured according to Obernberger and Thek [15] by measuring the length and diameter of 20 randomly selected samples; thus, the ratio length/diameter was calculated. Based on the dimensions, it was possible to reckon the volume; thus, the final bulk density was defined as the ratio between green solids weight and volume. The average bulk density was calculated for ten measurement series per sample. Based on the fact that densification is a mechanical process, and no heat was added to the system final heating value, sulfur and nitrogen content were assumed constant and equal to initial values. Compression ratio was calculated as the relation between final and initial density (Equation 5).

$$CR = \frac{\rho_{fin}}{\rho_{in}} \quad (5)$$

Where CR is the compression ratio; ρ_{fin} (*kgm^{-3}*) represents the final density and ρ_{in} (*kgm^{-3}*) corresponds to the density before densification. In order to evaluate the properties of the solids, they were compared with standard parameters employed in the most influential European markets, i.e., Sweden, Austria, Germany and Italy. The Swedish pellets standard SS 18 71 20 was used since 1999; nowadays, European standard EN 14601 is used. This standard classifies solid biofuel pellets into three groups [16]; number one is designed to fit high-quality systems, especially small scale boilers for residential and private usage. Groups 2 and 3 are defined to supply larger scale systems which do not require the highest quality.

In Germany and Austria, EN 14961-2 has replaced the existing standards, DIN 51731 and ÖNORM M7135. The solid biofuel pellets are classified into three groups based on their characteristics; they are ENplus A1, ENplus A2 and EN B. Some properties, of each group are in Table 1.

Table III-1 Remarkable wood pellets characteristics according to EN-14601

Parameter	Test method	Unit	Group 1	Group 2	Group 3
Length	Measure 10 pellets	mm	Max 4*Φ	Max 5*Φ	Max 5*Φ
Bulk density	SS 187178	Kgm^{-3}	>600	>500	>500
Durability	SS 187180	Fines	0,8% <3 mm	1,5% <3mm	1,5% <3mm
Low heating value	SS-ISO 1928	$MJkg^{-1}$	>16,9	>16,9	>15,1
Ash	SS 187171	% $mass_{d.b}$	< 0,7	< 1,5	< 1,5
Moisture	SS 187170	% $mass_{w.b}$	< 10	< 10	< 12
Sulphur	SS 187177	% $mass_{d.b}$	< 0,08	< 0,08	To be stated
Chlorides	SS 187185	% $mass_{d.b}$	< 0,03	< 0,03	To be stated

Table III-2 Physical characteristics of Pellet Gold in France

Parameter	Unit	Limit
Moisture content	$\%mass_{w.b}$	< 10
Ash content	$\%mass_{d.b}$	≤ 1
Mechanical durability	%	> 97,7
Binding agents	%	< 2%
Low heating value	MJ/kg	≥ 16,9
Nitrogen content	$\%mass_{d.b}$	≤ 0,3
Chlorine content	$\%mass_{d.b}$	< 0,03
Sulphur content	$\%mass_{d.b}$	< 0,05
Lead content	$mgkg^{-1}$	< 10
Mercury content	$mgkg^{-1}$	< 0,05
Cadmium content	$mgkg^{-1}$	< 0,5
Chromium content	$mgkg^{-1}$	< 8
Formaldehyde	mg/100g	< 1,5
Radioactivity	Bq/kg	< 6

Most of the pellets used in Italy are for space heating in small scale units; the Italian market employed the Pellet Gold label to guarantee adequate pellet characteristics. Some of the required properties that pellet needs to acquire this category are defined in Table 2. However, during the next years these requirements will change according to EN 14961 in the same manner as in Germany and Austria (Table 3).

Table III-3 Wood pellets characteristics for commercialization in Germany and Austria

Parameter	Test method	Unit	ENplus-A1	ENplus-A2	EN-B
Diameter	To be stated	Mm	6-8	6-8	6-8
Length	To be stated	Mm	3,15-40	3,15-40	3,15-40
Bulk density	EN 15103	kg/m^3	≥ 600	≥ 600	≥ 600
Net calorific value	EN 14918	MJ/kg	16,5 - 19	16,3 – 19	16 – 19
Moisture content	EN 14774-1	$\%mass_{w.b}$	≤ 10	≤ 10	≤ 10
Fines (<3,15 mm)	EN 15149-2	$\%mass_{w.b}$	≤ 1	≤ 1	≤ 1
Mechanical durability	EN 15210-1	$\%mass_{w.b}$	≥ 97,5	≥ 97,5	≥ 96,5
Ash content	EN 14775	$\%mass_{d.b}$	≤ 0,7	≤ 1,5	≤ 3
Ash melting behavior	EN 15370-1	°C	≥ 1200	≥ 1100	≥ 1100
Chlorine content	EN 15289	$\%mass_{d.b}$	≤ 0,02	≤ 0,02	≤ 0,03
Sulfur content	EN 15289	$\%mass_{d.b}$	≤ 0,03	≤ 0,03	≤ 0,04
Nitrogen content	EN 15104	$\%mass_{d.b}$	≤ 0,3	≤ 0,5	≤ 1
Copper content	EN 15297	mg/kg	≤ 10	≤ 10	≤ 10
Chromium content	EN 15297	mg/kg	≤ 10	≤ 10	≤ 10
Arsenic content	EN 15297	mg/kg	≤ 1	≤ 1	≤ 1
Cadmium content	EN 15297	mg/kg	≤ 0,5	≤ 0,5	≤ 0,5
Mercury content	EN 15297	mg/kg	≤ 0,1	≤ 0,1	≤ 0,1
Lead content	EN 15297	mg/kg	≤ 10	≤ 10	≤ 10
Nickel content	EN 15297	mg/kg	≤ 10	≤ 10	≤ 10
Zinc content	EN 15297	mg/kg	≤ 100	≤ 100	≤ 100

C. Results and discussion

During raw material pretreatment, coconut shells present some problems due to their mechanical durability; the equipment required needs more power than that used for palm oil shells grinding. Initial density shows the importance for compressing some of these materials; the wood shavings had the lowest bulk density (165.37 kgm^{-3}) while coconut shells had the highest (468.58 kgm^{-3}) among examined samples. Nevertheless, these values were small in comparison with typical ranges for coal (650–800 kgm^{-3}). This parameter is a fundamental characteristic because it affects transportation costs, the necessary space for storage and the energy density.

Proximate analysis and ultimate analysis indicated the strong relation between some typical characteristics and the heating value and the potential of biomass for energy production. Coconut shells and wood shavings should be dried beforehand due to their high water content (12%), whereas sawdust and palm oil shells (>8%) could be used as received (although sawdust had a remarkably low density).

Volatile matter content and fixed carbon are parameters that affect the combustion process directly. Sawdust and wood shavings had more volatile compounds than coconut, palm oil shells or dark coal; nevertheless, the fixed carbon levels of the last materials were always bigger. Sawdust and wood shavings will release more volatile material at the first stage of the combustion process; although, these materials will add energy for char combustion. Based on proximate analysis it is possible to comprehend the performance of the material during combustion. Thus, solids like coconut shells (C.sh.), palm oil shells (P.o.sh.) or hard coal (D.c.) will release more energy due to combustion but will require more energy for reaction activation (Table 4).

Table III-4 Proximate analysis of biomass assortments compared to a sample of Colombian hard coal.

Parameter	Unit	Sd.	W.sh	C.sh	P.o.sh	D.c
Density	Kg/m^3	200,59	165,37	468,58	197,86	650-800
Moisture	$\%mass_{w.b}$	9,67	12,14	12,01	7,92	2,75
Volatile matter	$\%mass_{w.b}$	76,82	76,21	71,45	72,74	37,73
Fixed carbon	$\%mass_{w.b}$	11,71	10,56	15,28	16,87	51,02
Ash content	$\%mass_{w.b}$	1,8	1,09	1,26	2,47	8,5
Total	$\%mass_{w.b}$	100	100	100	100	100

s.d sawdust, W.sh wood shavings, C.sh coconut shells, P.O.sh Oil palm shells, D.c hard coal

The materials with high fixed carbon content have more elemental carbon than those with less fixed carbon determined in the proximate analysis. Nevertheless, there is a relevant relation between oxygen content and volatile matter. If coal results are compared against biomass analysis, it wil be possible to establish a relationship between oxygen and carbon on the solid structure with volatiles content. For instance, coal volatile matter is small (12%) due to content of oxygen; whereas, biomass has volatiles around 75% due to higher oxygen content (approximately 43%) in the structure (Table 5).

Table III-5 Ultimate analysis of the biomass assortments

Parameter	Unit	Sd.	W.sh	C.sh	P.o.sh	D.c
Carbon	$\%mass_{d.b}$	42,14	45,86	44,76	47,3	71,28
Oxygen	$\%mass_{d.b}$	45,82	43,75	44,73	39,39	12,59
Hydrogen	$\%mass_{d.b}$	9,07	9,07	8,92	9,72	5,27
Nitrogen	$\%mass_{d.b}$	0,98	0,08	0,16	0,84	1,63
Sulphur	$\%mass_{d.b}$	0	0	0,03	0,07	0,73
Ash	$\%mass_{d.b}$	1,99	1,24	1,4	2,68	8,5
Total	$\%mass_{d.b}$	100	100	100	100	100

Assortments defined as stated in Table 4

A critical parameter that should be evaluated is the ash content. Low ash content prevents multiple problems in boilers and furnaces regarding the formation of fused solids and high emissions of particulate matter. Furthermore, there is another advantage of biomass. Low sulfur and nitrogen content mean less SO_x or NO_x produced in boilers and furnaces. Analysis of heating value confirms the relation between elemental analysis with energy released during combustion; coal with significant elemental carbon and low oxygen has the highest HHV (32.3$MJkg^{-1}$); whereas, biomass HHV is similar for all these residues (approximately 20.1$MJkg^{-1}$), but 32% smaller.

Likewise, calculated higher heating values indicate that equations used and presented before are reliable for determining biomass heating values; however, this is not the case when coal heating value is found (Table 6). This occurs because the Equation (2) is based on heating value of lignocellulose that is not a component of coal structure. Moisture content is also a factor that should be considered; the difference between lower and higher heating values show that energy lost due to moisture evaporation is around 10% for biomass and no more than 3% for coals. Therefore, lower heating value should be employed during the design of household, boilers or any other biomass energy systems if a more reliable and real fuel consumption calculation is needed.

Table III-6 Experimental and calculated higher heating values.

Parameter	Unit	Sd.	W.sh	C.sh	P.o.sh	D.c
Experimental	kJ/kg	20130	21055	21300	20160	32323
Calculated eq. 2	kJ/kg	20393	21968	21234	24062	29919
Calculated eq. 3	kJ/kg	19950	20154	20110	19763	18187
Low heating value	kJ/kg	18181	18497	18740	18561	31433

After densification, solids produced had the characteristics presented below, mean length of pellets was around 29 mm, and bulk density varied from 850 to 1028 kgm^{-3} (Table 7). Sawdust compression ratio was high (5.15), and final bulk density was over 1000 kgm^{-3}. The relation between initial and final density of coconut shells and its low compression ratio were in accordance with the problems reported during biomass pretreatment. Coconut has low plastic and elastic deformation during densification due to rigid chemical structure and solid strength, which make this material less suitable for pellets or briquettes production.

Table III-7 Characteristics of the pellets obtained after densification.

Parameter	Unit	Sd.	W.sh	C.sh	P.o.sh
Diameter	mm	21	21	21	21
Length	mm	32	22	38	24
Density	kg/m^3	1028	850	902,9	1023
Heating Value	kJ/kg	17221	19425	18707	19944
Compression ratio		5,12	5,15	1,92	5,17

Figure III-3 Pellets made from sawdust, coconut shells, and wood shavings.

On the other hand, sawdust, wood shavings and oil palm shells have appropriate compression ratio, the final density and heating value. Pellets produced with these Colombian materials could be distributed in Sweden and Italy based on European standards (Figure 3). To achieve requirements for Germany or Austria it is necessary to change the die used because dimensions are oversized; however, another study is required in order to establish the influence of dimensions on physical properties.

D. Conclusions

In Colombia, it is feasible to produce pellets or briquettes using timber and oil palm solid residues. These could fulfill European standard requirements; otherwise, the production of coconut shell pellets is not a suitable option due to its low compression ratio and its high mechanical resistance, which made the product final density lower.

Measurement of timber, palm oil solid residues and coconut shells main characteristics are necessary in order to establish the potential of these materials as energy sources for further processes such as combustion or gasification. Wood shavings, oil palm shells and sawdust require to be densified in order of increasing energy density; however, coconut shells should be used without prior densification.

The utilization of these kinds of materials for energy processes and indeed on co-firing systems generates a significant impact on the environment, based on the low sulfur content and affordable heating values reported in this work. Pellets production will provide other alternatives for reducing problems caused by brown coal combustion in some areas of Colombia.
Massive production of fuel pellets from wood and other biomass assortments for small and medium scale energy systems could enhance the development of rural areas in Colombia, where there is a lot of these resources and lack of stable electrical supply. Therefore, more research on different alternatives for biomass solid biofuel production, on analysis of their characteristics and their behavior on combustion or gasification processes, should be performed.

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IV. Effect of particle size and addition of sawdust on mechanical properties of coal pellets

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Abstract

Energy demand is constantly increasing as much as the population grows, and the need for alternative and cleaner energy sources is even more remarkable nowadays. Pellets and briquettes, resulting from densification processes, offer important advantages in terms of handling, transportation, storage, cleaner combustion and feeding control. This work aims to analyze the densification capacity of coal-sawdust mixtures by characterizing the mechanical properties of final solids and the effect of particle size and mass ratio variations on the densification mechanisms. Results showed that the addition of sawdust improved the impact and compression resistance due to its resilience and lignin content. Moreover, optical microscopic images exhibited the effect of using finer particle sizes; brittle coal particles crushed during the process, mixed better with sawdust grinds creating stronger inter-particle forces and solid bonds. Addition of sawdust to coal pellets is an interesting alternative to produce cleaner solid fuels with improved mechanical properties; although, more research is needed to analyze the effect of inter-particle forces on the bonding mechanisms.

Keywords
Biomass, Coal, Pellets, Densification Mechanisms, Sawdust

A. Introduction

The continuous increase of the world population is commonly accepted as one of the most important causes for the high primary energy demand. Typical fossil resources such as natural gas, oil, and coal are the most-employed fuels with the biggest share of total primary energy. According to the International Energy Agency (IEA), these fuels provide approximately 83% of energy from 1973 to 2009. During this period, oil fell down from 46 to 32.8%, while natural gas and coal rose from 16 and 24.6 to 20.9 and 27.2% respectively [1].

Production of hard coal moves up at higher rates since 2000, rising from 4000 to 6000 Mt in ten years (200 Mt yr^{-1}). China, with 3162 Mt in 2010, leads the list of the biggest coal producers in the world, followed by US, India, and Australia (932, 538, and 538 Mt, respectively). In this field, Colombia is the tenth most important producer (74 Mt in 2010) and the country with the largest reserves in Latin America; moreover, it exported about 68 Mt in 2010, becoming the fourth biggest exporter. According to UPME [2], the production in this country is constantly increasing; it is expected that production will be about 138 Mt in 2019. Despite the fact that more than 80% of the national production is exported, much coal is still used to satisfy the energy demand in rural places. Indeed, coal and wood are the main fuels for heating and cooking at small households in rural areas. The typical stoves employed are very rudimentary and non-controlled, as figure 1 illustrates, producing hazardous effects to the population nearby, such as respiratory illnesses and severe environmental impacts due to the emission of greenhouse gases and particulate matter.

Figure IV-1 Typical household cooking stove fed with coal and wood in Cundinamarca and Boyaca areas

A worldwide feasible alternative to decrease the effects of fossil fuels combustion is by using renewable energy resources such as solar, wind, geothermal, ocean, or biomass. Several governments have strengthened their policies aiming to increase the penetration of these sources in the energy market; hence, the global new investment grew up to 257 Billion USD and the total power capacity, including hydropower, reached 1360 GW in 2011. Among different pathways to produce clean energy, biomass is the world´s fourth largest source (following oil, coal, and natural gas) [3]; this resource has many advantages because of its wide variety, location, low cost of collection, and permanent availability with large amounts of biomass growth [4]. Nonetheless, this resource has some drawbacks ascribed to the high moisture content, irregular shape and size, and low bulk density which make biomass difficult to handle, transport, store and utilize [5, 6].
Densification aims to increase density and size by agglomeration of biomass grinds. There are two techniques followed globally: tumble agglomeration and pressure agglomeration. Tumble agglomeration increases the density of materials by mixing them with binders in balling discs, cones and drums; whereas, in the pressure agglomeration, high forces are applied onto particulate materials in a confined volume to increase its density. Rising biomass density by pressure agglomeration implies the mechanical deformation of grinds, air displacement, porosity reduction and effects of short-range bonding forces. According to Kaliyan and Morey [7], during the first stage, at low pressure, several phenomena take place simultaneously. For instance, the grinds rearrange themselves, air voids are decreased, but the material retains most of their properties. Later on, when pressure increases, biomass particles undergo elastic and plastic deformation promoting inter-particle bonding forces such as i) solid bridges, ii) attraction forces between solid particles, iii) mechanical interlocking bonds, iv) adhesion and cohesion forces, and v) interfacial and capillary forces.

Depending on size and dimensions, the resulting solids could be categorized into pellets or briquettes. They offer several benefits such as higher energy density, lower moisture content, ease of handling and storage, convenience of use, suitability for co-firing in coal-fired power plants, and the option of automatic control options in small heat pants [8, 9]. Regardless, the solid fuel industry is majorly based on wood densification, different materials and mixtures are under evaluation.

Raslavicius [10] analyses the use of glycerol and wood cutting wastes to produce briquettes showing final densities in the 740-861 kg m^{-3} range. Kaliyan and Morey employ corn stover and switchgrass for making briquettes that respective density reaches 1164 and 1057 kg m^{-3} at finer particle sizes (<3mm) and grind temperature of 75.5 °C. Different British Columbia softwoods including pine, fir, spruce, and pine bark have valuable densification properties, before and after torrefaction, reaching final densities between 1410 and 1720 kg m^{-3} [11]. Likewise, Na et al. [12] analyze the pelletizing properties of torrefied oil palm mesocarp fibers, reporting several binding problems with more carbon content due to higher torrefaction temperatures.

Despite the existing potential and multiple lignocellulosic resources available in Colombia, the production of solid fuels is still stagnant due to the lack of knowledge, technology, and financial support. Nowadays, the government is trying to promote the use of alternative energy resources in rural places where needs of thermal energy are large. As a consequence, they are funding more research projects which show the possibilities of shifting, either partially or completely, traditional fossil fuels by renewable resources. In 2008, the installed capacity for energy generation with co-firing systems was 26 MW [13], but it was mainly focused on bioethanol systems that burned mixtures of coal with residues of sugar cane. Potential of oil palm residues, such as bunches and fibers, was 1923.89 GWh approximately; whereas, coconut shells and fibers could generate 237.36 GWh [14]. Forero et al. [15] evaluated the feasibility of manufacturing solid fuels with agricultural residues from timber, coconut, and oil palm industries; the density of these solids varied from 850 to 1028kg m-3, but the heating value was not competitive with traditional coal. Nevertheless, it is possible to produce solid fuels mixing biomass and coal in such a way that the resulting solid not only exhibits higher heating capacity than wood pellets, but also decreases the common hazardous emissions of traditional coal systems. In this manner, this work aims to analyze the densification capacity of coal-sawdust mixtures characterizing the mechanical properties of final solids and the effect of particle diameter and mass ratio variation onto the densification mechanisms.

B. Materials and methods

Raw materials characterization

Coal sample was provided by the Servicio Geologico Colombiano (Bogota, Colombia) coming from a mine located in Boyacá; whereas, the sawdust was gathered from the wood workshop located in the Universidad Nacional de Colombia. Coal and sawdust samples were individually ground using a hammermill. The procedure employed for making the proximate and ultimate analysis was described previously [15]; thus, moisture content was evaluated according to ASTM E871-82 [16], volatile matter was conducted following ASTM E872 [17], ash content as defined by ASTM E1755-01 [18] and fixed carbon calculated by difference. The ultimate analysis was carried out at the coal laboratory of Servicio Geologico Colombiano where an LECO Truspec CHN Analyzer determined carbon, nitrogen, and hydrogen content according to ASTM D5373-08 [19], and the sulfur content was measured by an LECO SC-32 and S-114 DR analyzer following ASTM D4239-08 [20]. Finally, the oxygen content was established by difference. Higher heating value was analyzed according to ASTM D5865-13 [21]. Likewise, lower heating value was calculated based on the proximate and ultimate analysis using some correlations available elsewhere [22, 23].

$$LHV = HHV * \left(1 - \left(\frac{X_W}{100}\right)\right) - 2.447 * \left(\frac{X_W}{100}\right) - \left(\frac{X_H}{200}\right) * 18.02 * 2.447 * \left(1 - \left(\frac{X_H}{100}\right)\right) \quad (1)$$

Where, HHV [$MJkg^{-1}$] is the higher heating value, and XH [wt% d.b.] represents the content of Hydrogen. Meanwhile, LHV [$MJkg^{-1}$] is the lower heating value taking into account the moisture content (XW) in wt% (wb).

Experimental design and statistical analysis

After characterization, grinds were sieved separately using a Sieve Shaker equipped with Mesh No 4, 16, and 50. Then, the grinds were classified into three categories: i) Big particles made of solids that particle size was between 4.76 and 1.19 mm (Mesh 4/16); ii) Intermediate particles constituted by solids that particle size was between 1.19 and 0.297 mm (Mesh 16/50); and iii) Fines made of particles remaining on the base of the Sieve shaker that particle size was less than 0.297 mm. The experiment was designed around two factors; sawdust content in the mixture, five levels (0, 30, 50, 70, 100%wt), and particle size, three levels (big, intermediate, and fines); therefore, a factorial design (3x5) was adopted as the statistical design for this study. Table 1 summarizes the assortments used in this experiment. Chauvenet´s criterion was applied for all the results in order to identify if there was any data that should be rejected. Likewise, the mean value and tolerance limits were calculated for a 95% confidence level using the Student´s t-distribution [24].

Table IV-1 Different assortments used in the experiment, classified by particle size (ps) and sawdust content in the mixture

Sawdust content (%wt)	Big particles (ps. 4.76-1.19 mm)	Intermediate (ps 1.19-0.297 mm)	Fines (ps <0.297 mm)
0%	Bc-100	Ic-100	Fc-100
30%	Bcs-70/30	Ics-70/30	Fcs-70/30
50%	Bcs-50/50	Ics-50/50	Fcs-50/50
70%	Bcs-30/50	Ics-30/50	Fcs-30/50
100%	Bs-100	Is-100	Fs-100

Footnote: Assortments where organized according to particle size (big (B), intermediate (I), and fine (F)), and biomass in the blend (coal (c), sawdust (s)). i.e., Bcs-70/30 indicates a blend made big particles of 70% coal and 30% sawdust.

Initial bulk density and densification process

The initial bulk density of each assortment was measured using a 10 cm side cubic box. It was filled with the grinds and weighed at near 0.001 g using a precision balance. Five repetitions were performed, and the final result was calculated as the ratio of the weight of the sample against the volume of the cubic box. The pellets were manufactured using a hydraulic press with a stainless steel fixed die (120 mm long and 21 mm diameter), installed at laboratory of thermal plants and renewable energy, located at 4,638°N-74,084°W, 2630 above sea level. The tests were performed under ambient conditions (18°C and 87.99 kPa), and neither the die nor the raw materials were pre-heated. The press plunger moved straight down with no lateral movement and constant speed (0.0205 m s-1); it applied a pressure of 170 MPa. Similar to Liu et al. [25], the end of the die is closed using a removable backstop. The grinds were loaded stepwise until filling the die, and then compressed; the backstop was removed after holding 3 s at the maximum pressure, and the solids pushed out by applying pressure. About 25 solids (i.e., pellets) were manufactured for each assortment.

Pellet characterization

Dimensions and density were measured in accordance with Liu et. al [26], Obernberger [23], and Kaliyan and Morey [5]; the dimensions were recorded with an electronic caliper. Meanwhile, ten random pellets were weighed at near 0.001 g, and the final density was calculated according to the following equations:

$$V_u = \left(\pi * \frac{d^2}{4}\right) * H \qquad (2)$$

$$\rho_{final} = \frac{m_u}{V_u} \qquad (3)$$

Where, V_u (cm^3) is the volume of the pellet, d (cm) the diameter, H (cm) the height, m_u (g) the mass weighed, and ρ_{final} (g cm^{-3}) corresponds to the final density. The compression ratio (CR) evaluated the reduction of the volume of the solid materials and the deformation of the particles during the process. It was calculated as the ratio between the final (ρ_{final}) and initial ($\rho_{initial}$) densities.

$$CR = \frac{\rho_{final}}{\rho_{initial}} \tag{4}$$

The impact resistance simulates the forces encountered while emptying of densified products from trucks onto ground [5]. It was measured as the remaining mass after dropping the samples twice from 1.83 m onto a concrete floor [27]. Moreover, the compressive resistance gives a measurement of the inter-particle bonding strength. It was recorded as the maximum load before failing on a stress-strain test. It was made by using a Shimadzu AG-Xplus 300kN Universal Tester. Finally, some samples were analyzed by brightfield optical microscopy, using an Optical Nikon Microscope at 1X and 4X, aiming to identify changes in the solid structure after densification.

C. Results and discussion

Sawdust had higher moisture and volatile matter content than the coal, whereas the coal had more fixed carbon and ash. Table 2 summarizes the results of the proximate and ultimate analysis. The most remarkable disadvantage regarding addition of sawdust to coal pellets is the decrease of heating value. Coal higher heating value was 32.32 MJ kg^{-1}, which is about 38% more than sawdust, 20.13 MJ kg^{-1}. The calculated lower heating value of coal was 30.26 $MJkg^{-1}$, and the lower heating value of sawdust was 16.13 MJ kg^{-1}. Despite these drawbacks, addition of sawdust to coal pellets represents several benefits to the pellet. Moisture in the biomass has proved to affect the densification process and the final characteristics of the solid. It promotes intermolecular bonds like Van der Waals forces and Hydrogen bonds, strengthening the resultant solid, although high moisture content in biomass raw materials can decrease compaction capabilities and final pellet densities [28]. Sawdust is a lignocellulosic material constituted majorly by cellulose, hemicellulose and lignin. According to the energy content obtained, the lignin content of sawdust can be between 35 to 44% [22]. Lignin is a complex, systematically-polymerized, highly aromatic substance which acts as a cementing matrix that holds between and within both cellulose and hemicellulose units [29]. The higher the lignin content in the raw materials, the more the chances to obtain stronger inter-particle bonds between the grinds because lignin acts as a natural binder on the densification mechanisms. Moreover, the greater content of volatile matter in sawdust makes the solid ignites faster in comparison with coal pellet decreasing air/fuel ratio and, therefore, reducing the energy losses in the flue gases. The low ash content of sawdust prevents typical slagging, fouling, and blocking problems caused by coal combustion in the equipment [30]. Addition of sawdust to the solids decrease the environmental impact caused by coal combustion; sawdust is sulfur-free and has lower nitrogen content which might decrease the synthesis of SO_x and NO_x after combustion.

Table IV-2 Proximate and ultimate analysis of raw materials used for the study

Proximate analysis (wt%)	Coal	Sawdust	Ultimate analysis (wt%)	Coal	Sawdust
Moisture content	2.75	9.67	Carbon	71.28	42.14
Volatile matter	37.73	76.82	Oxygen	12.59	45.82
Fixed carbon	51.02	11.71	Hydrogen	5.27	9.02
Ash	8.5	1.8	Nitrogen	1.63	0.98
			Sulfur	0.73	0.05

Initial densities of the raw materials varied in the range of 140-910 kgm^{-3}. Sawdust initial density changed according to the particle diameter from 148 to 205 kgm^{-3}; on the other hand, coal initial density had the contrary effect. The finest particles of coal exhibited lower densities after crushing and sizing; the initial bulk density moved down 14% from 917 to 788 kgm^{-3}. This behavior can be ascribed to stress relaxation in the coal structure after crushing, so the porosity of the finest particles increased and the void fraction in the bulk rose.

Addition of sawdust to coal promotes the densification mechanisms resulting on stronger, more uniform, and more shape-defined pellets in comparison with pure coal pellets. Figures 2 and 3 show the pellets after pressing, varying the sawdust content and using particle sizes in the range of 1.19-0.297 mm and smaller than 0.297 mm. After expelling the solids out of the die, those made of coal crashed immediately, leaving a smaller solid piece as shown in the image. This behavior can be ascribed to low cohesive bonds between the coal grinds produced probably by particle rearrangement; likewise, no solid bridges were synthesized in the agglomeration process. Nonetheless, addition of 30%wt sawdust into the mixture enhanced the properties of the solid resulting in more durable and resistant solids in comparison with coal pellets. Pellets made of finer particles exhibited a more homogeneous surface with less observable cracks resulting from stronger bonds created during the process.

Figure IV-2 Pellets made from sawdust-coal mixtures, varying sawdust content in the mixture (0, 30, 50, 70, and 100%wt from left to right), and particle size between 1.19 and 0.297 mm

Figure IV-3 Pellets made from sawdust-coal mixtures, varying sawdust content (100, 70, 50, 30, 0wt from left to right) and using fine grinds with particle size <0.297 mm

The table 3 summarizes the variation of the initial and final densities after measuring 25 random samples. The addition of sawdust in the mixture decreased the initial density due to its lower value in comparison with the density of coal; nevertheless, the sawdust is more flexible and has more resilience rising up the compression ratio.

Table IV-3 Initial (ID) and final density (FD) of the assortments

	ID	FD		ID	FD		ID	FD
Assort.	**Kg m^{-3}**	**Kg m^{-3}**	**Assort.**	**Kg m^{-3}**	**Kg m^{-3}**	**Assort.**	**Kg m^{-3}**	**Kg m^{-3}**
Bc100	917.98±2.84	1328.64±35.58	Ic100	849.93±4.41	1176.09±57.49	Fc-100	788.35±4.77	1067.45±14.88
Bcs-70/30	359.53±2.82	1015.62±4.39	Ics-70/30	385.92±3.86	992.07±17.06	Fcs-70/30	501.80±5.79	1095.49±10.19
Bcs-50/50	255.05±2.21	1018.90±13.77	Ics-50/50	285.63±1.79	934.41±16.45	Fcs-50/50	356.97±10.28	943.53±7.23
Bcs-30/70	202.01±3.49	990.92±4.28	Ics-30/70	230.39±1.34	964.80±5.59	Fcs-30/70	302.85±5.05	965.22±6.40
Bs-100	148.22±2.86	864.94±5.59	Is-100	193.53±1.94	900.09±10.80	Fs-100	215.20±4.98	934.79±2.90

Footnote: Assortments were labeled according to Table 1

The effect of the particle size differed from coal against sawdust. Final density of coal pellets decreased with the grain size from 1328 to 1067 kgm^{-3} whereas the final density of sawdust pellets moved upwards from 864 to 934 kgm^{-3}. These results are in accordance with findings reported by Arzola et al [31]. They stated that using biomass grinds with bigger particle size decreased the pellet density; nevertheless, it is also remarkable to analyze the compression ratio, defined as the capability of the material for being densified and deformed after compressing. Regardless of the particle diameter, the addition of sawdust always increased the compression ratio on a linear manner. Figure 3 exhibits the compression ratio as a function of the sawdust content in the mixture. In most cases, a linear trend line fitted the data with coefficients of determination (R^2) greater than 0.97. Moreover, higher compression ratios were observed for bigger solid particles; they moved up from 1.45 to 5.84 while the values for finest solid grains were in the range of 1.35 to 4.34. The differences between compression ratio and final density can be ascribed to the densification mechanisms. When larger solid particles were employed, the particles rearranged and crushed microscopically making it possible to achieve higher compression ratios; the displacement of the solids in the die and the porosity reduction during agglomeration are considerable.

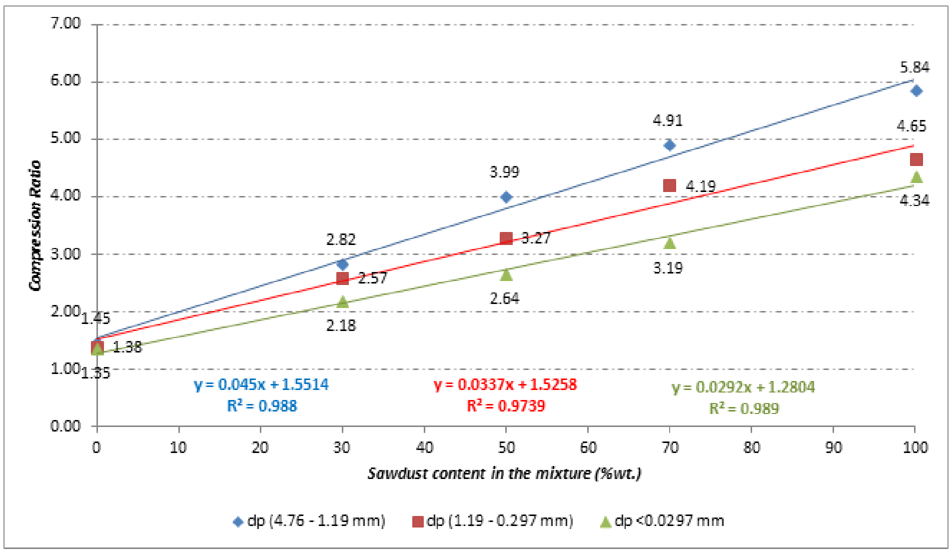

Figure IV-4 Compression ratio of sawdust-coal pellets as a function of solid particle diameter and sawdust content in the mixture

Figure 4 shows the variation of the impact resistance according to the addition of sawdust in the mixture and the correlation values of linear trendlines applied to data. The impact resistance increased with the addition of sawdust and the utilization of finer solids. For example, the solids composed of bigger particles varied their resistance from 0.79 to 40.00% with the addition of sawdust in the mixture. Likewise, those made with finest particles became more resistant; this parameter rose from 5.16 to 48.30%. The variation of impact resistance has a close relationship with the mechanical resilience of the materials and posterior stages of densification mechanisms, such as elasto-visco plastic deformation [7]. Regardless of the particle size employed, the coal pellets were more fragile, while the impact resistance of pure-coal pellets was in the range of 0.8 – 7.16%, the impact resistance of sawdust pellets was between 40% and 48.30%. The addition of sawdust increased the resistance of the solids in such a way that fitted a linear trendline with coefficients of determination around 0.97 approximately. More accurate results were found with intermediate solid particles, but the trend is almost similar in all the cases. Meanwhile, the behavior of the impact resistance as a function of the particle diameter is analogous. The resistance of the solids increased proportionally with smaller particle size despite the amount of sawdust in the mixture.

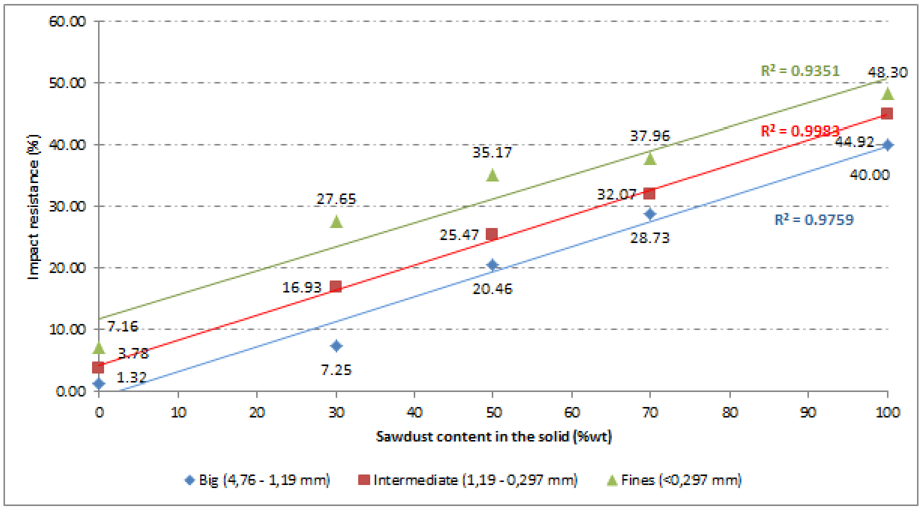

Figure IV-5 Impact resistance of pellets as a function of sawdust content in the mixture and particle size of the grinds

Table 4 provides the maximum compressive stress and strain for solids made with different mass ratios and classified by the diameter of the particles employed during densification. Variation of these parameters indicates the cohesion between solid particles in the pellets. Brittle materials, such as coal, have a lower maximum strain because the particles do not have flexible bonds between them, the structure is so crystalline and rigid, and the displacement of the stress through the structure is not possible. Addition of sawdust in the mixture increases the maximum compressive stress and strain. Solids made of coal failed immediately within a minimum stress, making impossible to measure the deformation. The more the sawdust in the mixture, the more the resistant the solid became. Thus, the maximum compressive stress of pellets made with particle diameter in the 1.19-0.297 mm range increased from 0 MPa with just coal to 2.25 MPa for a 50/50 coal-sawdust mixture and to 16.14 MPa for pure sawdust pellet. Meanwhile, the use of finer particles strengthened the final solid. The decrease of the particles diameter enhanced the resistance of the solids. For example, a solid made of 30/70 coal-sawdust mixture excelled its maximum resistance from 37.50 MPa when made of particles with a diameter between 1.19-4.76 mm to 59.55 MPa when made of finest particles of diameter smaller than 0.297mm.

Table IV-4 Maximum stress and strain resisted by solid pellets after compressive test

Assort.	Stress (MPa)	Strain (%)	Assort.	Stress (MPa)	Strain (%)	Assort.	Stress (MPa)	Strain (%)
Bc-100	0.00	0	**Ic-100**	0,00	0	**Fc-100**	0.00	0
Bcs-70/30	0.95	8.22	**Ics-70/30**	2.25	9.70	**Fcs-70/30**	6.15	13.54
Bcs-50/50	12.96	20.13	**Ics-50/50**	16.14	25.11	**Fcs-50/50**	22.24	30.05
Bcs-30/70	37.50	28.53	**Ics-30/70**	44.92	31.64	**Fcs-30/70**	59.55	38.53
Bs-100	104.46	52.09	**Is-100**	111.28	55.28	**Fs-100**	126.26	58.36

Footnote: Assortments were organized according to codes defined in Table 1

Figure 6 shows the optical microscopy images for the initial state of particles before pressing. They correspond to coal and sawdust with diameters in the 1.17-4.79 mm range and smaller than 0.297 mm; both images correspond to a 50/50 sawdust-coal mixture (assortments Ics 50/50 and Fcs 50/50).

Figure IV-6 Optical microscopic images of sawdust coal mixtures (Ics-50/50 and Fcs-50/50) before pressing. Left exhibits particle size in the range of 4.76-1.19mm; whereas right shows particle size smaller than 0.297mm

While pressing, the air is released from the structure and particles rearranged, glided and created stronger bonds due to higher inter-particle areas and close-range forces. Figure 7 shows an image of the pellets surface made with big particles (assortment bcs-50/50); coal grains and sawdust mixed and joined together. Mechanical interlocking takes place, especially between sawdust grinds; this can be identified as meeting of two or more particles at one point [32]. Nevertheless, inter-particles gaps were observable for these pellets, resulting on weaker bonds [33]. Sawdust fibers surrounded big coal structures. They moved in such a way that several layers were together, but critical changes on the solids did not occur except slight fragmentation of coal solids. Small black particles can be observed around the structures resulting from coal fragmentation and crushing after pressing. This phenomenon is more obvious in the images obtained from pellets made of intermediate particles, diameter between 1.197 and 0.297mm (Figure 8). There was a better mixing of coal solids and sawdust fibers making the resulting solid pellet stronger and more resistant. Mechanical interlocks are observable between sawdust and coal particles. Meanwhile, there are some spots with glassy coating. Formation of glassy coating layers is observable especially for sawdust grinds; this can be ascribed to possible local melting of binding components which form these solid bridges. Solid bridges due to the local melting may have been caused by plastic deformation or by primarily melting followed by resolidification of natural binding components. The rough points of contact between particles by friction may momentarily generate localized temperatures as high as 100-200°C [32]. A number of fine dark particles appeared in the solid resulting from coal crushing; this indicated that finer particles crushed easier as a consequence of the pressure added to the system. Figure 9 shows the mixing of finest particles during densification; due to the size of the solids, the particles were better-distributed uniformly. The main phenomena and bonding forces acting during the densification of sawdust-coal pellets were those related to particle rearrangement, porosity reduction, fragmentation, plastic and elastic deformation, attractive forces including H-bonding, van der Waals force, mechanical interlocking, and possibly glassy coating layers. This excels the elasticity and resilience of the solids making them more durable and resisting.

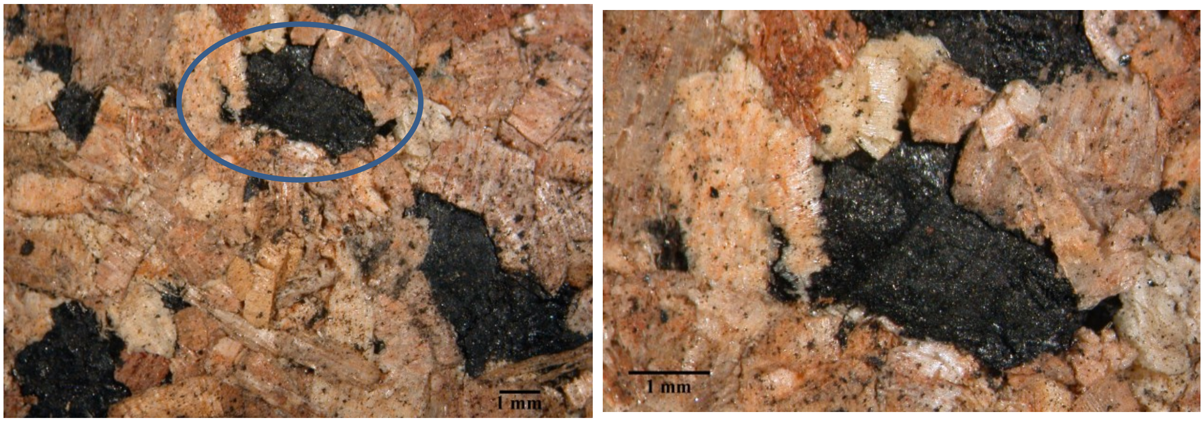

Figure IV-7 Optical microscopic images of cross surface of 50/50 coal-sawdust pellet made of particle size between 4.76-1.19mm

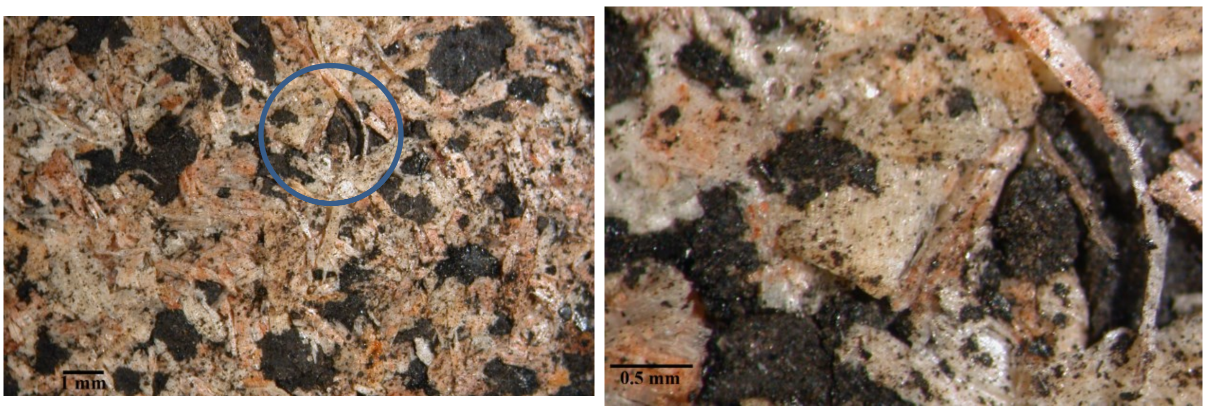

Figure IV-8 Optical microscopic images of cross section of 50/50 coal-sawdust pellets made of particle sizes between 1.19-0.297mm

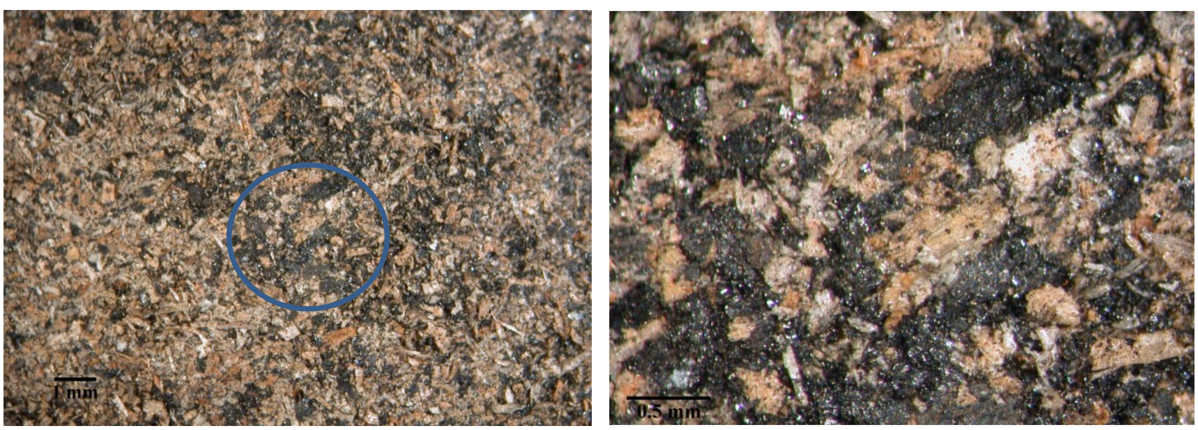

Figure IV-9 Optical microscopic images of cross section of 50/50 coal-sawdust pellet made of particle sizes smaller than 0.297mm

D. Conclusions

The effect of particle diameter was analyzed on pellets made with different mass ratios of coal and sawdust; pellets made of bigger particles had higher compression ratios than those made with finer particles for the same mass ratios. Moreover, the compression ratio had a proportional increase when more sawdust is added to the mixture. This phenomenon was described accurately by linear trendlines. Likewise, not only the diameter, but also the addition of sawdust affected the mechanical properties of the final products. The impact resistance rose when smaller particles were employed before densification, and more sawdust was in the mixture despite the higher compression ratios of the latter group. As shown by the optical microscopy images, more uniform mixing resulted from using smaller particles; as well as more coal particles crushed during the process that promotes stronger particle-particle bonds leading to higher the impact resistance and compressive strength of the pellets. Solids made with more sawdust had higher maximum strain and resisted more stress than those made with more coal. This proved the benefits of using fibrous and lignocellulosic materials such as sawdust as a natural binder, which, despite their low heating value, would have higher mechanical properties than fuels made with rigid and crystalline structures like coal. Mixing coal and sawdust for manufacturing solid fuels could result in several benefits for households placed on rural sectors. They will provide cleaner energy decreasing carbon dioxide and sulphur oxides emission; combustion will ignite faster thanks to the higher volatile matter of sawdust, and less particulate matter will be emitted due to mechanical resistance added by lignocellulosic compounds. Nonetheless, more research is valuable in order to improve some properties of the pellets, (e.g., the impact and compression resistance), determine the economic costs related to the pretreatment and production of fine particles, and identify the performance of the pellets during combustion.

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V. Effect of the particle size and the addition of cocoa pod husks on the properties of sawdust and coal pellets

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Abstract

The continuous increase of the world energy demand, the rise of fossil fuels costs, and the strong environmental policies around the globe are some reasons of the increase of the wood pellets industry. However, there are some other available biomass feedstocks capable of being densified for energy production. Among the various options, the use of mixed biomass pellets is becoming remarkable because of the wide variety of species; although, more research is needed in order to enhance the mechanical properties of these pellets. This study aims to identify the effect of the particle size on the mechanical properties of sawdust and coal pellets when cocoa pod husks are used as an additive. Cocoa pod husks have a similar composition than sawdust and less sulfur and nitrogen than coal. Thus, the use of this additive might decrease the environmental impact during coal pellets combustion. Results showed an attractive potential of cocoa grinds for pellet production, an increase of the durability of coal pellets mixed with this raw material, and similar performance between cocoa and sawdust pellets. The compression ratio, the compressive and impact resistance varied linearly with the addition of cocoa husks.

Keywords
Biomass, Coal, Cocoa husks, Densification, Pellets, Sawdust

A. Introduction

The increase of the worldwide energy demand, the global warming, and the stronger energy policies around the globe have intensified the research on alternative energy technologies capable of harnessing renewable resources such as wind, solar radiation or biomass. Biomass made up of a broad diversity of agricultural residues, is a major contributor to renewable energy, occupying about 10% of the total energy consumed approximately [1]. Biomass is classified in traditional and modern biomass; it can also be utilized by many conversion technologies such as direct combustion, thermochemical, biochemical and agrochemical processes [2]. Traditional biomass like wood, mainly used for heating and cooking, supports 9.3% of final energy consumption worldwide [3]. On the other hand, the modern biomass, consisting of the several derivatives and biofuels obtained from biomass, i.e., bioethanol, biodiesel, syngas, biogas, pellet, or briquettes, supplies about 1% of the total energy. There are some disadvantages that improved processes need to overcome in order to increase the penetration of biomass technologies in the energy market. As stated by Kaliyan and Morey [4], biomass is very difficult to handle, transport, store, and utilize in its original form because of the high moisture, irregular shape, and low bulk density. Hence, biomass

densification by agglomeration and pressing becomes a valuable alternative to solve these drawbacks. The product that results of densification processes is known as pellets or briquettes. In comparison to biomass in its original form, densified solid biofuels exhibit some advantages like (1) Efficient biomass storage; (2) Uniform and controlled combustion; (3) Low moisture content; (4) Simplified fuel feeding; (5) Ease in transport and handling; (6) Marketability; (7) Flexibility in accommodating a variety of feedstock including wastes [5].
As a consequence of these benefits, wood pellets commercialization has risen exponentially during the recent years, moving from 2 to 22.4 million tonnes between 2000 and 2012 [3]. Wood pellets are mainly manufactured with residues of timber industries; nevertheless, the rapid growth of the demand is creating a necessity of identifying new raw materials for solid biofuel industry. According to Karkania et al. [6], mixed biomass pellets (MBP) have a high potential in enlarging the use of biomass for energy conversion, particularly in central and south European countries. With the exhaustion of biomass residues for wood pellets production (particularly sawdust), the production of MBP is of growing concern for project developers and biomass producers. Hence, several authors have focused on the analysis of alternative raw materials for pellets production, the study of their mechanical properties, and their behavior during thermochemical conversion processes. Karkania et al. [6] summarized the results obtained after utilization of wood-corn and wood-cotton mixtures. LHVs for these pellets were in the range of 14 to 15 $MJkg^{-1}$. Kaliyan and Morey [7] analyzed the densification behavior of corn stover and switchgrass; they studied the effect of compression/densification conditions (particle size, moisture content, and preheating temperature) on the constitutive model parameters. Munawar and Subiyanto [8] characterized pellets made from solid wastes from oil palm industry. They used oil palm empty fruit bunch, oil palm frond, oil palm shell, and oil palm mesocarp; also, they reported adequate conditions to produce biomass pellets using these resources. Limousy et al. [9] carried out a study using pellets made of spent coffee grounds blended with pine sawdust in a boiler. Results showed a good combustion efficiency; moreover, the use of blended pellets could be a valuable alternative to replace pure sawdust pellets. Consequently, Nunes et al. [10] made an analysis of the state of the combustion models for mixed biomass pellets, they emphasized the possibility to produce mixed biomass solid fuels with sufficient hardness and resistance to transport, as well as heating values close to that of wood pellets.

Cocoa pod husks form about 70% of the cocoa fruit; the husks are generated after opening the pod for removing the cocoa beans [11]. Commonly, these wastes are unexploited and considered as a disposal problem. They are left to rot on the cocoa plantation producing foul odors and propagating diseases such as black pod rot [12]. Projects have been performed aiming to establish alternatives for adding value to these residues. Some scientists analyzed the utilization of cocoa husks as green solid base catalysts for transesterification of oils [11], as a source of proteins [13], pectins [12, 14] or other useful chemicals [15], and as a raw material of the densification process [16]. This work aims to identify the effect of using cocoa pod husks as an additive to sawdust and coal pellets, and the incidence of particle size on the mechanical properties.

B. Methods and Materials

Raw material characterization

The sawdust was gathered from the wood workshop located at the Universidad Nacional de Colombia; the coal was given by staff of Servicio Geológico Nacional, and the cocoa Husks were provided by farmers from Cimitarra Santander. Cocoa husks were air-dried until reaching low moisture content. Air-drying was needed due to the difficulties given during cocoa grinding. Figure 1 shows the changes of cocoa husks after drying; the biomass became more brittle making easy to pulverize. Typical dimensions of these husks were 20cm length and 10cm width approximately

Figure V-1 Cocoa pod husks as received (left) and one-week air dried (right)

Cocoa pod husks, sawdust, and coal were ground separately using a hammer mill. Proximate analysis was carried out for each raw material; the moisture content was calculated by following the ASTM E871-82 [17], volatile matter recorded in accordance with ASTM E872 [18], ash content determined using a furnace as indicated by ASTM E1755-01 [19], and fixed carbon calculated as balance. Meanwhile, the ultimate analysis was performed. A LECO Truspec CHN Analyzer determined the Carbon, Nitrogen and Hydrogen content according to ASTM D5373-08 [20], whereas an LECO SC-32 and an S-114 DR analyzer were employed to establish sulphur content by following ASTM D4239-08 [21]. The Oxygen content was calculated by balance. These tests were performed in the coal laboratory of the Servicio Geológico Colombiano, Bogotá, Colombia.

Experimental design and statistical analysis

The analysis was based on three factors; the particle size (three levels, particles between 4.76 and 1.19mm, intermediate between 1.19 and 0.297 mm, and fines <0.297mm), the base raw material for pellets (two types, coal and sawdust), and the cocoa content in the blend (five levels, 0, 30, 50, 70, and 100%wt). Hence, a factorial design (3x2x5) was adopted as the experimental design in this study. The mean value and tolerance limits were calculated for a 95% confidence level using the Student´s t-distribution [22]. Table 1 summarizes the assortment distribution employed in this experiment. The first letter exhibits the code of the particle size (B, I, or F); the second letter is the base raw material (coal (c) or sawdust (s)). The mass ratio between the base raw material and cocoa husks is also defined; e.g., the assortment identified by code Icch-30/70 means intermediate particles with a mass ratio 30% coal and 70% cocoa husks.

Table V-1 Assortment distribution according to particle size (big (b), intermediate (i), fine (f)), base raw material (coal (c) or sawdust (s)) and cocoa husks (ch) added in the blend

	Big particles (B) (4.76 – 1.19mm)		Intermediate particles (I) (1.19-0.297 mm)		Fines (F) (<0.297mm)	
Cocoa (ch) content	Coal (c)	Sawdust (s)	Coal (c)	Sawdust (s)	Coal (c)	Sawdust (s)
0%	Bc-100	Bs-100	Ic-100	Is-100	Fc-100	Fs-100
30%	Bcch-70/30	Bsch-70/30	Icch-70/30	Isch-70/30	Fcch-70/30	Fsch-70/30
50%	Bcch-50/50	Bsch-50/50	Icch-50/50	Isch-50/50	Fcch-50/50	Fsch-50/50
70%	Bcch-30/70	Bsch-30/70	Icch-30/70	Isch-30/70	Fcch-30/70	Fsch-30/70
100%	Bch-100		Ich-100		Fch-100	

Assortment preparation, characterization and densification

Based the experimental design, the raw materials were sieved separately using a Sieve Shaker equipped with Mesh No 4, 16, and 50; thus, the grinds were categorized in three groups according to the particle size. Big particles were those remaining between Mesh 4/16; intermediate particles were those that passed through Mesh 16 and retained by Mesh 50, and fines were those grinds remaining on the base of the Sieve shaker. Afterwards, the assortments were organized based on the raw materials combination and the mass ratio. (Table 1)

The initial bulk density of each assortment was determined by filling a cubic box of known volume and weighing it at the near 0.001g. Five repetitions were carried out, and the density was then calculated as the ratio between the weight of the sample in the box and the volume of the box. The powder was densified by using a hydraulic press with a 120mm long, 21mm diameter fixed die installed at the laboratory of Thermal Plants and Renewable Energy, located at 4.638°N-74.084°W, 2630m above sea level. Press force was constant at 170 MPa. Biomass was densified at ambient temperature without steam injection or any heating source. Similarly to Liu et. al. [23], the end of the die was closed using a removable backstop. The grinds were loaded until filling the die and compressed; after holding 3s the maximum pressure, the backstop was removed, and the resulting solids were pushed out by pressure. About 25 solids were made of each assortment.

Pellets characterization

Physical parameters like diameter and height were measured with an electronic caliper. Likewise, the solids were weighted at the near 0.001 g using a digital balance, and the final bulk density calculated as the ratio between the volume and the weight. Density was evaluated for 20 randomly samples [24]. Meanwhile, the ratio between the initial and the final bulk density was calculated and associated to the compression ratio; this parameter can be ascribed to the resilience, plasticity, and deformation capacity of the grinds during the compression.

Mechanical properties such as the maximum strain before failure, the impact and the compression resistance were measured for each group. The impact resistance was evaluated in accordance with Kaliyan and Morey [4]; ten randomly samples were dropped into the surface at 1,8m height, five times and the final weight of the samples were recorded. This parameter was calculated as the percentage of the final sample against the initial pellet weight. The compression resistance was evaluated using a universal compression machine Shimadzu AG-Xplus 300kN Universal Tester, and corresponded to the maximum load before failing on a stress-strain test. This property gives a measurement of the inter-particle bonding strength.

C. *Results*

The proximate analysis summarizes the moisture content, volatile matter, fixed carbon and ash in the samples. Each of these parameters provides elements to analyze the performance of the materials during either combustion or other thermochemical process. The moisture of raw materials affects not only the performance of the solid biofuels on thermochemical processes, but also the phenomena occurring during densification. The higher the moisture, the more energy is wasted when using the raw materials on thermochemical processes. Meanwhile, the moisture in the raw material affects the densification process; water acts both as a binding agent and a lubricant [4], moisture in the raw materials enhances the gelatinization of starch, helps develop van der Waals´ forces and diffusion of water-soluble substances throughout the matrix. Nevertheless, when the raw materials are so wet, the water might encumber short-range intermolecular forces acting as an interface between the solid grinds. Cocoa husks had the highest moisture content, about 11.53%wt; moisture was 2% larger than sawdust and 9% than coal.

The volatile matter has not a remarkable incidence on the synthesis of stronger bonds during densification; although, this parameter directly affects the performance and physical stability of the solid biofuel during thermal decomposition. The higher volatile matter in the raw material, the faster this biofuel will ignite. Because of the rapid volatile release, the solid matrix could decompose becoming powder instantaneously. The volatile matter content of cocoa was 58.46%, 20% smaller than sawdust and 20% higher than coal. Fixed carbon is the most valuable parameter in terms of the energy potential; raw materials with higher fixed carbon content have higher heating values. Fixed carbon of Cocoa is 16.8%, slightly higher than Sawdust (11.71%) but less than Coal

(51.02%). The ash in the raw materials has a remarkable effect on the heating value, combustion characteristics and equipment design. High-ash materials require a more sophisticated design to guarantee complete combustion and decrease the quantity of burnable substances remaining with ash after combustion; meanwhile, high ash content tends to produce slagging, fouling and blocking problems in the equipment. Among the raw materials employed in this study, cocoa husks have the highest ash content (13.21%), more than coal (8.5%) and sawdust (1.8%). Based on the high ash content of cocoa pod husks, the pellets made of this raw material do not accomplish the requirements defined for wood pellets and mixed biomass pellets [10]. Some alternatives to decrease the ash content of densified solid fuels are by blending cocoa husks with other low-ash materials like sawdust, or by hydrothermal carbonization (HTC) [23]. Results of proximate analysis are in accordance with findings reported by Syamsiro et al. [16].

Table V-2 Proximate analysis of cocoa pod husks, sawdust and coal employed for pelletizing

Sample (wt% w.b)	Cocoa	Sawdust	Coal
Moisture Content	11.53	9.67	2.75
Volatile Matter	58.46	76.82	37.73
Fixed Carbon	16.8	11.71	51.02
Ash	13.21	1.8	8.5
Total	100	100	100

Table 3 summarizes the results of the ultimate analysis for samples of Cocoa, Sawdust and Coal on a dry basis. Carbon and Hydrogen content have the closest relationship with the energy content; the oxidation of these elements releases the more quantity of energy during combustion. Coal has the highest carbon content (71.28%); 25% larger in comparison with cocoa and sawdust (43.87 and 42.14% respectively), whereas sawdust has the highest hydrogen content (9.07%). Nitrogen and Sulfur are components that should be taken into account due to their capability of forming pollutants such as Nitrous and Sulfur Oxides. While, nitrogen oxidation can be controlled by maintaining low reaction temperatures during combustion, sulfur reaction with air is more complicated to control. A valuable typical advantage of biomass is the low sulfur content. Sawdust has less than 0,1%, followed by Cocoa husks that have about 0.17%; fewer than the content of Coal (0.73%).

Table V-3 Ultimate analysis of cocoa husks, sawdust and coal

Sample (wt% d.b)	Cocoa	Sawdust	Coal
Carbon	43,87	42,14	71,28
Oxygen	37,20	46,13	12,79
Hydrogen	5,84	9,07	5,27
Nitrogen	1,23	0,98	1,63
Sulfur	0,17	0,05	0,73
Ash	11,69	1,63	8,3
Total	100	100	100

After compression, the pellets density varies depending upon the ratio of cocoa husks added and the particle size. Table 4 exhibits the variation of the cocoa-coal assortments density before and densification. Table 5 gathers the changes on the sawdust-cocoa assortments density during the process. Regardless the particle size, coal grinds always had a higher initial density in comparison with cocoa husks and sawdust; nevertheless, the effect of the particle size on this parameter was completely opposite. The finer the grind, the lower the coal initial density. The density decreased about 14%, from 917.98 to 788.35 kgm^{-3}. This decrease can be ascribed to the relaxation of the coal intermolecular bonds increasing the volume occupied by the particle. On the other hand, the initial density of cocoa and sawdust powder rose about 119% and 45%, from 249.53 to 547.88 and from 148.22 to 215.2 kgm^{-3} respectively.

Figure V-2 Coal-cocoa pellets made from intermediate particle size and organized by the cocoa content in the blend (0, 30, 50, 70 and 100%wt)

Low density is a typical characteristic of lignocellulosic and fibrous materials like sawdust or cocoa husks; they have void spaces throughout their structure full of air that increase the solids volume. After milling, the powder became finer releasing the air inside and raising the density. The final density of coal-cocoa pellets (figure 2) fell down due to the addition of the cocoa husks. Nevertheless, higher final density was obtained for pellets made of finer particles. Compression ratio was always larger for mixtures with higher quantities of cocoa. This behavior occurred due to the different densification mechanisms that took place during compression, e.g., air releasing, solid particles rearrangement, fragmentation, and elastic and plastic deformation.

Table V-4 Bulk initial and final density of coal-cocoa pellets made from different particle size

	ID	FD		ID	FD		ID	FD
Assort	**Kg m^{-3}**	**Kg m^{-3}**	**Assort**	**Kg m^{-3}**	**Kg m^{-3}**	**Assort**	**Kg m^{-3}**	**Kg m^{-3}**
Bc100	917.98±2.84	1328.64±35.58	Ic100	849.93±4.41	1176.09±57.49	Fc-100	788.35±4.77	1067.45±14.88
Bcch-70/30	532.37±1.14	1189.72±21.93	Icch-70/30	544.92±2.68	1141.6±5.91	Fcch-70/30	637.78±12.02	1073.17±22.55
Bcch-50/50	393.47±1.76	1187.61±29.95	Icch-50/50	455.71±4.90	1122.77±13.09	Fcch-50/50	595.92±6.64	1095.54±14.94
Bcch-30/70	345.58±2.00	1107.46±14.95	Icch-30/70	384.26±5.21	1110.89±11.85	Fcch-30/70	582.07±6.27	1099.56±11.56
Bch-100	249.53±3.18	1022.77±5.59	Ich-100	316.36±4.53	1035.23±15.28	Fch-100	547.88±5.20	1103.77±5.21

Footnote: Assortments were labeled according to Table 1

The compression ratio relates the initial and the final density; this parameter exhibits the capability that those materials have to deform with an applied stress. When coal was densified without any additive, the ratio was between 1.35 and 1.45. The more cocoa is added into the mixture, the more is the compression ratio. Hence, pellets manufactured with 70%wt. Cocoa husks have a compression ratio of 3.20 whereas those made with 30% cocoa have a lower compression ratio (2.23). Moreover, the particle size proportionally affects the compression ratio. The bigger the particle size, the more the compression ratio. Compression ratio of bcch-70/30 is about 3.22, higher than that value obtained for fcch-70/30 (1.89).

Table V-5 Bulk initial and final density of sawdust-cocoa pellets made from different particle size

	ID	FD		ID	FD		ID	FD
Assort.	Kg m^{-3}	Kg m^{-3}	Assort.	Kg m^{-3}	Kg m^{-3}	Assort.	Kg m^{-3}	Kg m^{-3}
Bs100	148.22±3.54	864.94±2.31	Is100	193.53±2.40	900.09±4.46	Fs-100	215.2±6.19	934-79±1.20
Bsch-70/30	160.72±0.77	931.26±7.16	Isch-70/30	208.37±1.43	924.94±5.91	Fsch-70/30	283.73±4.63	1027.7±7.67
Bsch-50/50	189.02±3.54	960.8±5.16	Isch-50/50	236.42±4.44	944.26±13.23	Fsch-50/50	365.14±2.77	1052.5±4.77
Bsch-30/70	218.13±4.42	1001.5±5.05	Isch-30/70	260.36±2.91	960.61±14.57	Fsch-30/70	462.65±3.49	1127.6±11.06
Bch-100	249.53±3.95	1022.8±2.31	Ich-100	316.36±5.63	1035.2±6.31	Fch-100	547.88±6.46	1103.8±2.15

Footnote: Assortments were labeled according to Table 1

Likewise, the compression ratio of pellets made of different cocoa-sawdust mixtures varies depending upon the grinds size and the mass ratio. Pellets made of 100% sawdust have lower final densities and higher compression ratios than those made of 100% cocoa. That exhibits a higher capacity of sawdust to deform and rearrange their particles in comparison with cocoa. As seen for the coal-cocoa pellets, utilizing fine particles in the pellets raises their final density but decreases the compression ratio. The figures 3 and 4 exhibit the behavior of the compression ratio as a function of the cocoa content in the mixture. Compression ratio fitted a linear trend with cocoa content in the blend. The coefficient of determination (R^2) was higher than 0.92 in all cases. The more cocoa in the mixture, the more the densification ratio of coal-cocoa assortments. On the other hand, for sawdust-cocoa pellets, the compression ratio decreases with more cocoa in the blend.

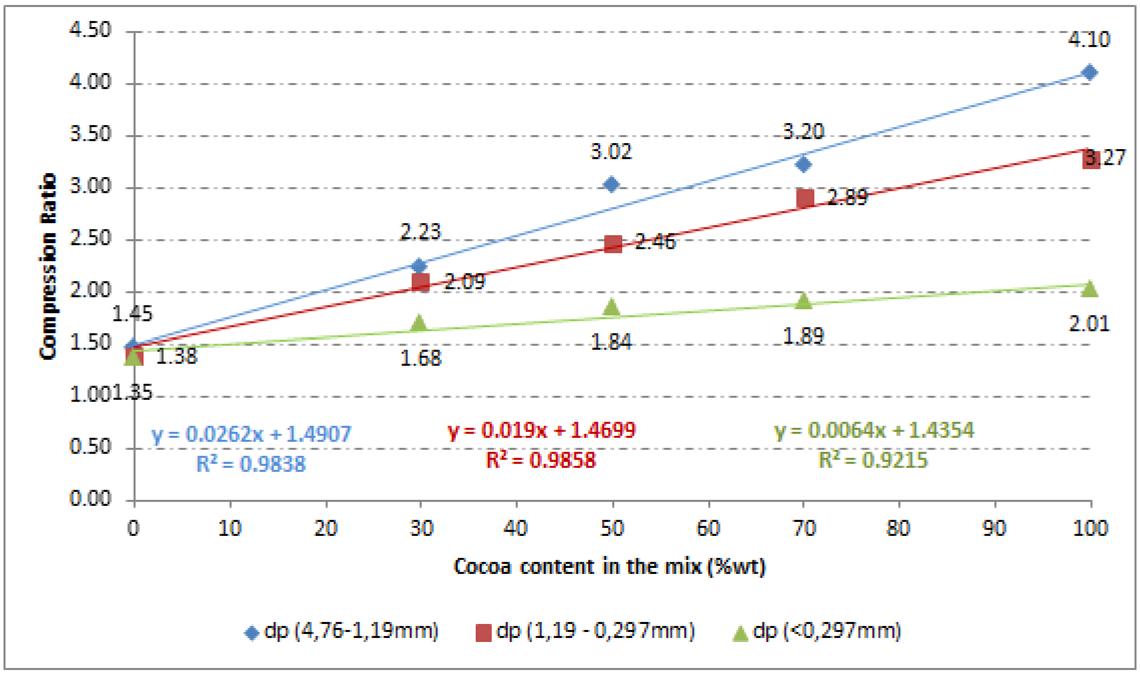

Figure V-3 Compression ratio of cocoa-coal pellets organized by raw material particle size and cocoa content in the blend

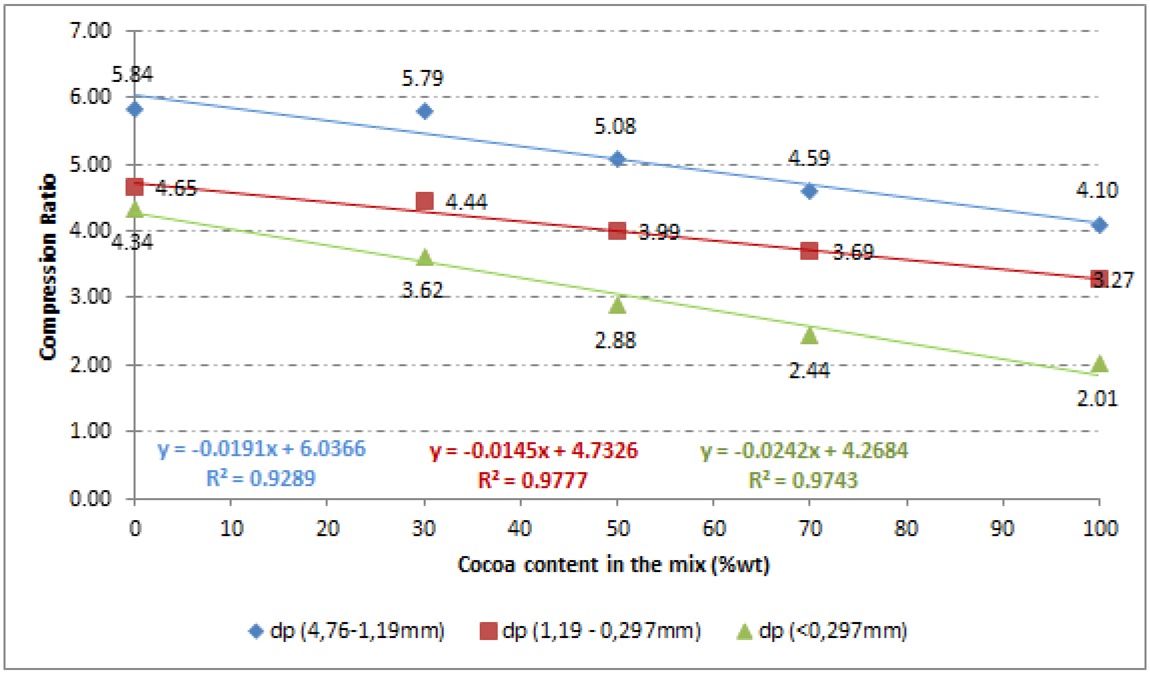

Figure V-4 Compression ratio of sawdust-cocoa pellets organized by raw material particle size and cocoa content in the mixture

The compression ratio shows the capacity of the materials to deform and occupy less space due to the applied stress, but it does not relate the cohesion of the particles. An alternative to evaluate the strength of the inter-particle bonds is by analyzing the impact resistance. This parameter simulates the forces encountered while emptying of densified products from trucks onto the ground or from chutes into bins. Several authors have used the term "durability" to report this parameter [4]. Coal pellets were so brittle and instantaneously disintegrated during the tests; their impact resistance was less than 10% despite the particle size. The addition of cocoa grinds enhanced the resistance fourfold. The impact resistance of coal-cocoa pellets proportionally increased with the cocoa content; a linear trendline fitted the results with coefficients of determination above 0.97. Likewise, the use of fine solid particles improves the resistance.

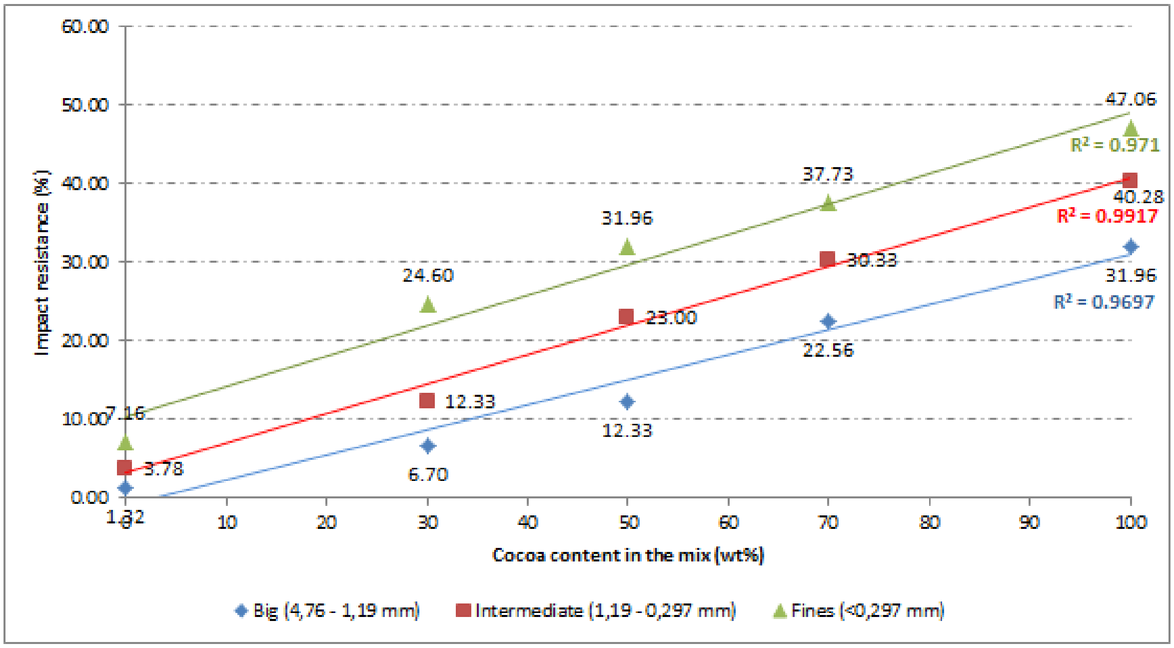

Figure V-5 Impact resistance of coal-cocoa pellets organized by raw material particle size and cocoa content in the mixture

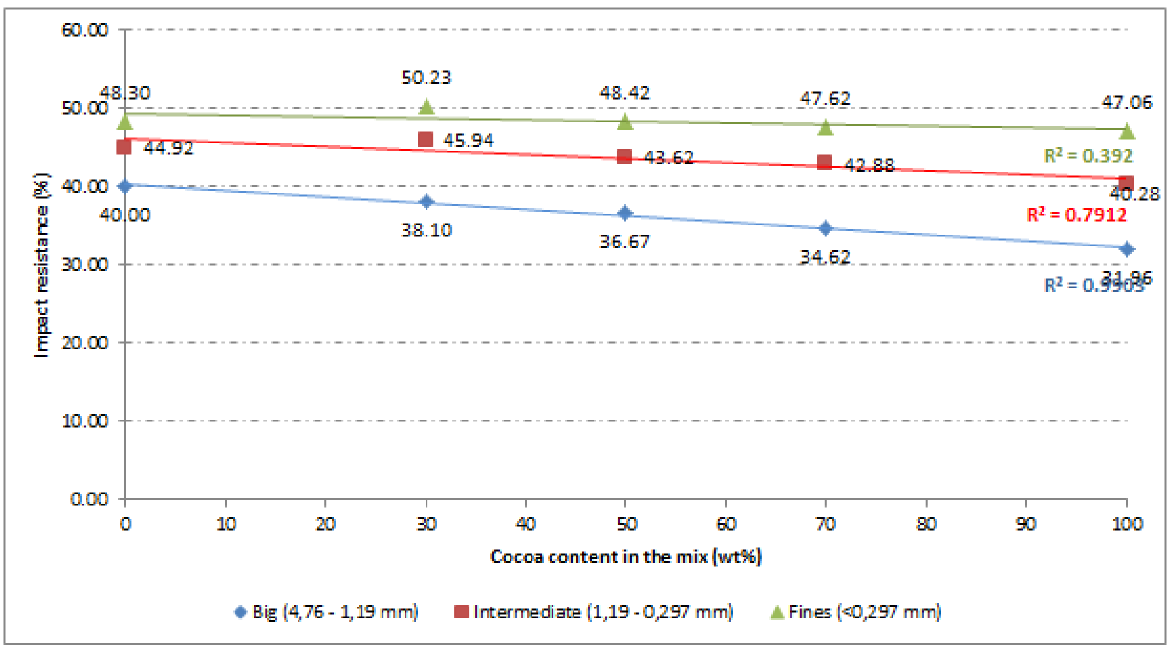

Figure V-6 Impact resistance of sawdust-cocoa pellets organized by raw material particle size and cocoa content in the blend

The compressive resistance determines the cohesion between particles and the maximum resistance against a compressive force. According to Kaliyan and Morey [4], the product may fail due to tensile forces resulting from the applied compressive force or pressure. Table 6 summarizes the results of the stress and final strain before failure for the samples. Addition of cocoa onto coal pellets enhances the cohesion of particles in the agglomerate; nevertheless, the effect is not similar to those of sawdust. Addition of cocoa to sawdust pellets makes the compression resistance to decrease. Utilization of finer particle size raises the compressive resistance as a result of the strong bonds created between particles and the large inter-particle area

Table V-6 Maximum stress and strain resisted by cocoa-coal and sawdust-cocoa pellets after compressive test

Assort.	Stress (MPa)	Strain (%)	Assort.	Stress (MPa)	Strain (%)	Assort.	Stress (MPa)	Strain (%)
Bc-100	0.00	0	**Ic-100**	0.00	0	**Fc-100**	0.00	0
Bcch-70/30	1.47	17.26	**Icch-70/30**	2.28	18.88	**Fcch-70/30**	4.93	19.07
Bcch-50/50	5.90	19.98	**Icch-50/50**	8.39	20.79	**Fcch-50/50**	10.35	21.83
Bcch-30/70	12.33	25.75	**Icch-30/70**	14.15	26.52	**Fcch-30/70**	17.57	27.03
Bch-100	17.71	32.93	**Ich-100**	20.34	34.05	**Fch-100**	25.46	36.12
Assort.	Stress (MPa)	Strain (%)	Assort.	Stress (MPa)	Strain (%)	Assort.	Stress (MPa)	Strain (%)
Bs-100	104.46	52.00	**Is-100**	111.28	55.01	**Fs-100**	126.26	58.21
Bsch-70/30	73.99	53.04	**Isch-70/30**	63.01	53.25	**Fsch-70/30**	666.8	52.66
Bsch-50/50	43.40	45.12	**Isch-50/50**	45.80	47.16	**Fsch-50/50**	47.75	45.65
Bsch-30/70	40.87	40.01	**Isch-30/70**	34.44	42.15	**Fsch-30/70**	37.15	43.25
Bch-100	17.71	32.93	**Ich-100**	20.34	34.05	**Fch-100**	25.46	36.12

Footnote: Assortments were organized according to codes defined in Table 1

D. Conclusions

Effect of particle size was analyzed for mixed pellets made of cocoa-coal and sawdust-cocoa blends. Compression ratio linearly increased with the addition of cocoa into coal pellets; whereas, in the sawdust-cocoa pellets, the behavior was opposite. Sawdust grinds exhibited better binding properties in comparison to cocoa husks possibly due to the higher content of lignin in sawdust. Sawdust is more fibrous than the cocoa particles. As a consequence of that, the sawdust pellets are more flexible and resistant against an applied stress. Nevertheless, cocoa husks pellets showed promising results; the final density was larger than 1000 kgm^{-3} with compression ratio in the range of 2 to 4.2. Thus, the densification of cocoa pod husks might mitigate problems related to waste disposal, storage, transport and management. Cocoa husks have lower nitrogen and sulfur contents than coal resulting on fewer environmental issues and less nitrous and sulfur oxides emitted to the atmosphere. Cocoa husks acted as natural binders for coal-cocoa pellets. The addition of cocoa husks to coal pellets improved their mechanical properties. Nevertheless, further research is needed in order to increase the binding capacity of cocoa husks and the mechanical resistance of the materials; preheating and steam addition could enhance mechanical properties of cocoa and coal-cocoa pellets.

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VI. DENSIFICATION OF COCOA POD HUSKS-SAWDUST-COAL BLENDS ANALYZED BY LIGHT MICROSCOPY AND ULTRAVIOLET AUTO-FLUORESCENCE MICROSCOPY

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Abstract

The research and development of alternative energy fuels for power generation and heating applications have become of increasing interest worldwide. Solid biofuels such as pellets or briquettes have proved to be reliable biofuels capable of harnessing logging residues. Nevertheless, the demand of wood pellets is rising faster than the capacity of producing such residues. Mixed Biomass pellets are an option to partially cover this market; although the use of different raw materials affects the densification mechanisms that take place during pelletization and the physical characteristics of the resulting biofuels. This work aims to identify possible changes of chemical and physical structures after densification of mixed biomass pellets made of cocoa husks, coal, and sawdust, varying the mass ratios and the particle size according to light micrograph and UV-AF microscopies. Optical microscopy images revealed the formation of mechanical interlocks and glassy coating layers between sawdust, coal and cocoa husks particles. The lignin squeezed as a result of the applied stress; nonetheless, the effect of fluorescing components is more visible on the sawdust-coal pellets than on the cocoa-sawdust pellets. Further research on this field is required in order to evaluate alternatives to promote better binding mechanisms that guarantee stronger bonds between the solid particles

Keywords
Densification mechanisms, Coal, Cocoa pod husks, Pellets, Sawdust

A. Introduction

The global investment in renewable energy has risen from 40 to 279 billion USD in the 2004-2011 period resulting on an installed power capacity capable of supplying about 1470 GW in 2012 [1]. Among the existing alternatives employed for clean energy production, biomass has been widely recognized as a renewable energy source, with increasing potential to replace conventional fossil fuels in the energy market [2]. Biomass has many advantages in comparison with other renewable resources; some of them are [3 - 5]:

- The widespread availability with a lot of materials growing
- The low levels of greenhouse gas emissions resulting from thermochemical processes
- The low cost of recollection

- Biomass can be converted into commercial products via either biological or thermochemical processes producing various types of solids, liquids and gaseous biofuels
- Diversification of fuel supply and energy security
- Rural revitalization with creation of new jobs
- CO_2 neutral conversion source for natural biomass

Nevertheless, there are some drawbacks encumbering a greater penetration of biomass in the energy market; some of them are biomass overexploitation, utilization of edible feedstocks, low density of different types of biomass, difficulty of transportation, handling, storage, and a wide range of sizes and shapes. In order to overcome these disadvantages, the densified solid biofuels, known as briquettes or pellets, have become valuable [6]. These solids are mainly produced after forcing the particles together by applying mechanical forces to create inter-particle bonding that makes well-defined shapes and sizes [7]. The production of wood pellets and briquettes has increased exponentially during the last decade. While, in 2000, two million tons were commercialized worldwide, the global production and transport of wood pellets exceeded 22 million tons in 2012. Some of the main advantages of producing solid biofuels are [8]: (i) the rate of combustion that can be comparable to that of coal, (ii) it is possible use them in grate-fired boilers, (iii) the transportation, storage, and feeding is made more efficient.

Despite the advantages mentioned before, one of the main problems facing the pellets industry is that the vast majority of these are being produced from logging company wastes. The consumption of woody residues will generate a shortage as the industry can not generate sufficient wastes to meet the global demand for wood pellets, so the development of pellets from agricultural and forestry wastes, as well as other different types of biomass will be of particular interest in the near future [3]. As a consequence of it, some researchers have carried out several studies using alternative wastes or even blends between coal and biomass for producing pellets or briquettes. They have analyzed the incidence of employing torrefied biomass during agglomeration [9, 10], and the mechanical and physical characteristics of pellets made of barley, canola, oat, wheat straw [11], corn stover, switchgrass [12], oil palm mesocarp fibers [13, 14], bamboo [15], among others.
Most of these works analyzed the characteristics of the solid biofuels and the variations of their properties according to operational conditions during manufacturing. Frequently, they pointed out the necessity of more research on the various factors affecting the densification mechanism in order to optimize the properties of the final products. Nevertheless, this is not an easy task taking into account that densification mechanisms involve several phenomena occurring simultaneously. Also, the grinds suffer different changes because of the stress applied. Physical joints can be created with or without formation of solid bridges between the particles. According to Kaliyan and Morey [7], in the first case short-range forces such as molecular, electrostatic and magnetic forces can cause solid particles to adhere to each other. On the other hand, the solid bridges may be formed between particles due to crystallization of some substances, solidification of melted components or hardening of binders.

Advanced characterization techniques such as Raman spectroscopy, Near Infrared spectroscopy, Fourier Transformed Infrared spectroscopy (FTIR), Light Microscopy, Ultraviolet auto-fluorescence (UV-AF) or Scanning Electron Microscopy (SEM) have been employed to characterize the chemical structures of different biomass and to evaluate structural changes while pelletizing or briquetting [7,16 - 19]. UV-AF microscopy has demonstrated to be a useful to technique for characterizing the densification mechanisms occurring during agglomeration. Compounds like proteins and lignin fluoresce making easier to identify the behavior of these substances on the process. This work aims to identify possible changes of chemical and physical structures after densification of mixed biomass pellets made of cocoa husks, coal, and sawdust, varying the mass ratios and the particle size according to light micrograph and UV-AF microscopies.

B. *Materials and Methods*

Biomass characterization

Sawdust was gathered from a wood workshop located at Universidad Nacional de Colombia; the coal was provided by Servicio Geologico Colombiano, and Cocoa Husks were given by farmers of Cimitarra Santander. Materials were air-dried and characterized as received. Proximate analysis was performed, so the moisture content was evaluated by according to ASTM E871-82 [20]. Volatile matter was established following the ASTM E872 [21]. Ash content was evaluated by recording the final weigh after heating the sample at 800°C during eight hours in accordance with ASTM E1755-01 [22], and fixed carbon calculated by difference.

Ultimate analysis was performed at laboratory of Coal of Servicio Geológico Nacional, Bogotá Colombia. Carbon, Nitrogen, and Hydrogen measurement was conducted following ASTM D5373-14 [23] using a LECO Truspec CHN. Sulfur content was determined according to standard ASTM D4239-08 [24]. Oxygen content was calculated by difference. Higher heating value (HHV) and lower heating value (LHV) were calculated using equations stated by Obernberger and Thek [25]. Other correlations for evaluating higher heating values based on proximate and structural analysis are available in the literature [26]

$$HHV = 0.3491X_C + 1.1783X_H + 0.1005X_S - 0.0151X_N - 0.1034X_O - 0.0211X_{ash} \tag{1}$$

$$LHV = HHV * \left(1 - \left(\frac{X_W}{100}\right)\right) - 2.447 * \left(\frac{X_W}{100}\right) - \left(\frac{X_H}{200}\right) * 18.02 * 2.447 * \left(1 - \left(\frac{X_H}{100}\right)\right) \tag{2}$$

Where, HHV [MJkg^{-1}] corresponds to the higher heating value, and X_i [wt% d.b.] represents the content of Carbon (X_C), Hydrogen (X_H), Sulfur (X_S), Nitrogen (X_N), Oxygen (X_O) and Ash (X_{ash}) respectively. Meanwhile, LHV [MJkg^{-1}] is the lower heating value which takes into account the moisture content (X_W) in wt% (wb).

Grinding, blending and pelletizing

Cocoa husks, coal and sawdust, were ground and sieved in order to have similar particle sizes. Solids with particle size between 1.19 and 0.297 mm (US Sieve 16/50) were employed. The experiment was designed around two factors, constituents of the blend (cocoa, sawdust, coal) and the mass ratio in the blend (0, 50, 100%wt). Hence, seven assortments were defined as shown in figure 1.

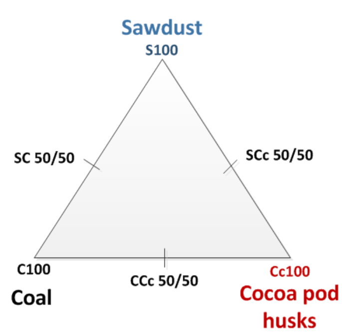

Figure VI-1 Assortment distribution based on the raw material and the mass ratio of the constituents

Densification was carried out using a single pelletizer without additional binder at room temperature. The assembly is similar as that described previously [27,28]. It is a hydraulic press consisting of two parts: (i) a press plunger moving downwards, and (ii) a cylindrical fixed die with 21 mm internal diameter and 120 mm length. The end of the die is closed using a removable backstop. The biomass was loaded stepwise until filling the die, and then compressed at a maximum pressure of 150 MPa. After holding 5 s the maximum pressure, the backstop was removed, and the solids pushed out by applying pressure.

Light microscopy and Ultraviolet auto-fluorescence microscopy

Light microscopy images were taken for the assortments using a Zoom Stereomicroscope Nikon SMZ-800 in the Laboratory of Optical Microscopy at Universidad Nacional de Colombia. After densification, images were analyzed over a cross-section of the solids. Images were analyzed to identify changes on the grinds after densification and the probable mechanisms taking place during the process. Ultraviolet autofluorescence (UV-AF) images were taken using an Olympus BX41TF Reflected Fluorescence System using the DM400 dichroic mirror (UV excitation at 360-370 nm; dichroic mirror at 400 nm; emission at 420).

C. Results

Table 1 exhibits the proximate and ultimate analysis of the raw materials. The moisture content of pellets should be controlled during densification processes based on the requirements established by commercial standards. Hence, wood pellets moisture must be less than 10% for being categorized as ENPlus A1, ENPlus A2 or ENB; meanwhile, moisture should not exceed 15% wt for Mixed Biomass pellets [3]. The volatile matter contains the constituents that burn and react at temperatures around 250-400°C; these compounds also become valuable for thermochemical processes because ignite the fuel making it easier to burn. Ash content includes several minerals embedded in the structures of the raw materials which remain after combustion. According to our results, cocoa pod husks have the highest ash content, 13.21%, followed by Coal, 8.5% and sawdust 1.8%. These results are in accordance with findings reported by Syamsiro et al. [29]. High content of ashes is a typical cause of slagging and blocking problems in the equipment. Decreasing this parameter can be possible by either mixing agroindustrial residues with woody biomass or by means of hydrothermal carbonization (HTC). As stated by Liu et al. [15], it is possible to decrease the ash content due to the dissolution of a considerable fraction of inorganics originally contained in raw biomass in water during HTC. Whereas the ash content of wood pellets must be lower than 4%; the content for mixed biomass pellets could be up to 7% [3].

Table VI-1 Proximate, Ultimate, and Heating Value of sawdust, coal and cocoa pod husks employed during densification

	Proximate analysis (%wt)					Ultimate analysis (%wt)						HHV	LHV
	W	VM	FC	Ash		C	O	H	N	S		$MJkg^{-1}$	$MJkg^{-1}$
Coal	2.75	37.73	51.02	8.50		71.28	12.59	5.27	1.63	0.73		29.66	28.68
Sawdust	9.67	76.82	11.71	1.80		42.14	45.82	9.07	0.96	0.02		20.61	16.56
Cocoa	11.53	58.46	16.80	13.21		39.87	40.98	5.84	1.23	0.17		16.28	13.91

The ultimate analysis describes the elemental composition of raw materials. An advantage of using coal as an energy source is the high carbon content and therefore the higher heating value; nevertheless, this fossil fuel has remarkable levels of sulphur and nitrogen that produce pollutants such as SO_x and NO_x. On the other hand, despite biomass resources like sawdust or cocoa husks have less carbon, more oxygen, and lower heating values, they are environmentally-friendly considering the lower levels of sulphur and nitrogen. Results of proximate and ultimate analysis are in good agreement with the findings reported by Vassilev et al. [5]. The heating value is also remarkable for designing and evaluating any energy source. This parameter represents the energy provided by the fuel after combustion. The difference between higher and lower heating value should be considered especially when working with biomass resources due to higher moisture contents in comparison with fossil fuels such as coal. Among the three raw materials analyzed here, cocoa husks provide less energy after combustion (13.91 MJ kg^{-1}). This can be ascribed to the low levels of carbon and hydrogen in the structure and the presence of more ashes than the other raw materials. Meanwhile, the heating value is strongly correlated with the lignin content of biomass fuels [26], so the lower the heating value, the lower the lignin content in biomass resources.

Densification of raw materials is a complex process by which the grinds agglomerate due to an applied stress. There are several stages occurring simultaneously that affect the final characteristics of the solid biofuels. Because of the applied stress, the grinds rearrange themselves decreasing the porosity and the void spaces; afterwards, they undergo a mechanical deformation in the plastic or elastic regime. Likewise, some friable grinds are not capable of resisting the pressure and fracture into smaller solids. Depending on the operational conditions such as pressure, temperature, and the chemical characteristics of the raw materials, some other phenomena may take place, producing stronger bonds between the grinds. These bonds, denoted as solid bridges, can be the result of the thermal softening of biomass, denaturation of proteins, gelatinization of starch, and/or solubilization and consecutive recrystallization of sugars and salts [30]. Moreover, there are other short-range molecular, electrostatic and magnetic forces causing solid particle to adhere to each other; some of them are valence forces, hydrogen bridges, and van der Waals´ forces [7].

The figure 2 exhibits the micrographs of the mixtures made of cocoa husks-sawdust, cocoa husks-coal, and coal-sawdust before and after densification using the same particle size in the 1.19-0.30 mm range. While sawdust is characterized by high levels of lignocellulosic constituents and particles seem to be more fibrous, cocoa husks have lower levels of lignin and more proteins and sugars. According to Vassilev et al. [31] mean composition of wood and woody biomass such as sawdust is 39.5% Cellulose, 34.5% Hemicellulose, and 26% Lignin on a dry ash-free basis; whereas cocoa has several other constituents such as proteins, lipids, reducing sugars, carbohydrates, soluble phenolics and lignin [32]. In the micrographs, the grinds of cocoa husks are brown non-uniform particles, while sawdust grinds are yellowish, and coal particles are the black solids. After densification, the micrographs revealed the phenomena occurring between the particles. In the first stage of the densification process, the particles rearrange themselves to form close packing and decrease void fractions [11]. This stage is appreciable if comparing distance between solid particles of sawdust-cocoa and sawdust-coal mixtures before and after densification. During the next phase of the densification mechanism, some friable materials fracture under stress becoming finer grinds which diffuse through the mixture enhancing short-range interparticle forces. This is observable in the micrographs corresponding to cocoa-coal and sawdust-coal mixtures (Figures 3, 4); in both cases, there is a fine coal powder throughout the surface.

Similarly to the analysis made by Kaliyan and Morey [7], the light microscopy images can denote points where mechanical interlocking and glassy coating layers take place. Mechanical interlocking of particles can be identified as meeting of two or more particles at one point, precisely those points where finer coal grinds mix with bigger sawdust or cocoa particles. The formation of glassy layers is observable especially on sawdust grinds; this can be ascribed to possible local melting of binding components that form these solid bridges. Solid bridges due to the local melting may have been caused by plastic deformation or by actual melting followed by resolidification of natural binding components or the asper points of contact between particles where friction may momentarily generate localized temperatures as high as 100-200°C [7]. Nevertheless, there are not solid bridges created by thermal softening or activation of biomass, denaturation of proteins, or gelatinization of starch because pelletization was made at ambient temperature. Micrographs revealed that there are some gaps and layers between the particles that can reduce the pellets resistance, leading to weak mechanical durability [27]. Further analysis about the variations of micrographs and structures due to the use of heat during pelletization could be remarkable to identify more issues about densification of solids.

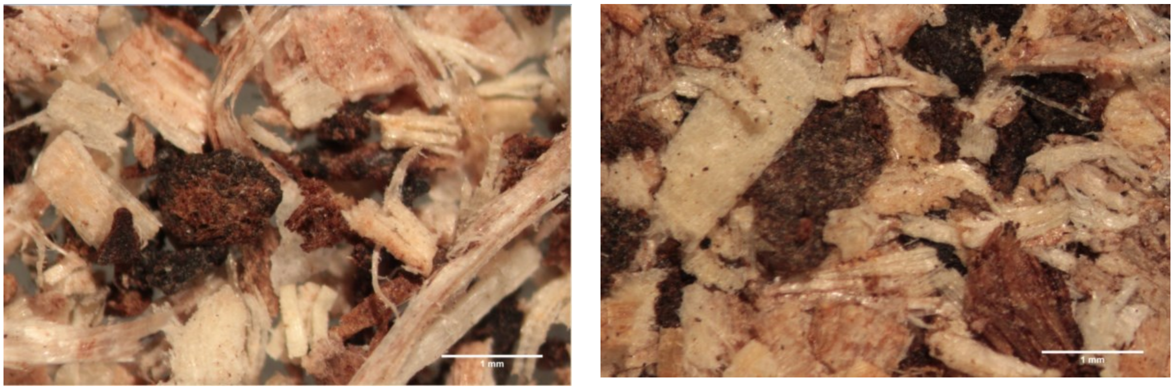

Figure VI-2 Optical microscopy images of 50/50 sawdust-cocoa pod husks assortment before (left) and after densification (right)

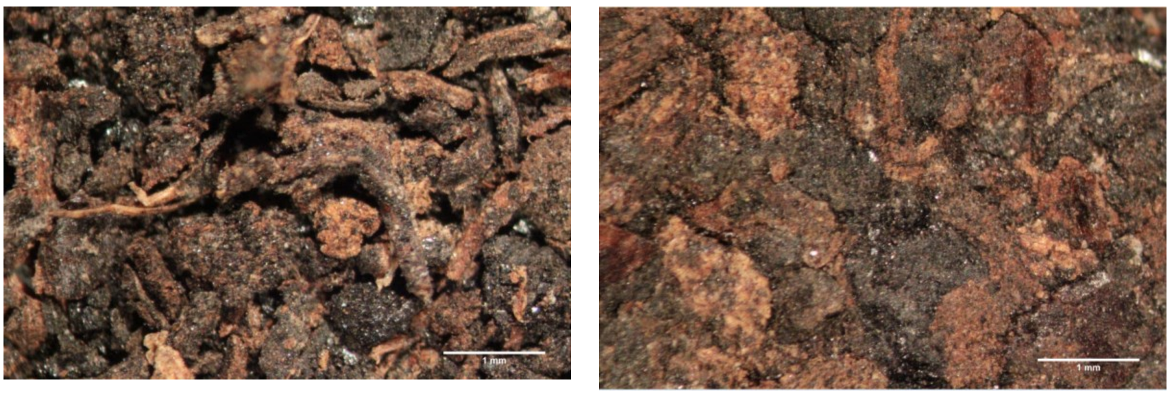

Figure VI-3 Optical microscopy image of 50/50 cocoa pod husks-coal mixture before (left) and after pelletizing (right)

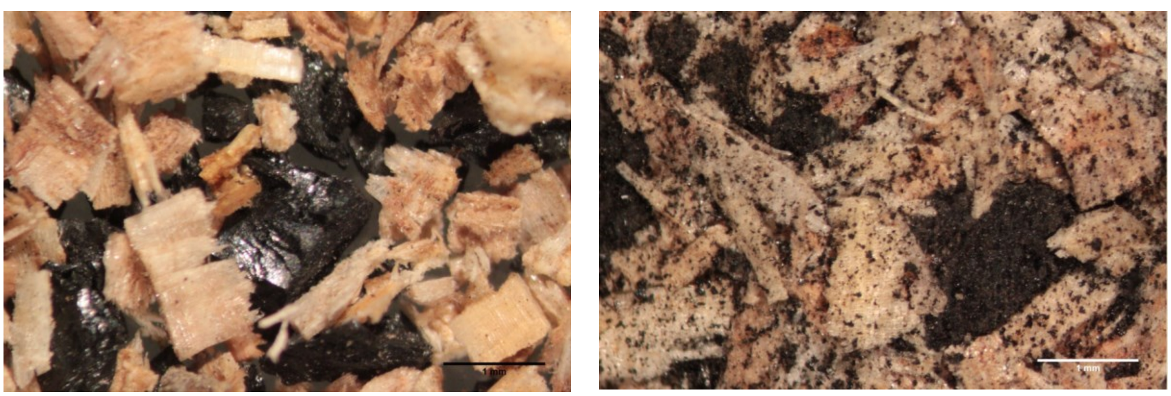

Figure VI-4 Optical microscopy image of 50/50 sawdust-coal mixture before (left) and after pelletizing (right)

Figure 5 exhibits the UV-AF micrographs of sawdust and cocoa husks, particle size between 1.19 and 0.30 mm. The micrographs obtained with short excitation wavelengths, and the DM400 dichroic mirror provides an adequate resolution to identify compounds capable or fluorescing. This technique has been thoroughly exploited in botany, biomedics and science materials, but its use in the biofuels industry, specifically in pelletization, is still in its infancy. The results of sawdust UV-AF micrographs expose the presence of aromatic molecules, which are the typical compounds capable of fluorescing under these conditions. According to Kaliyan and Morey [7], the interpretation of UV-AF is: green or yellow-green for protein compounds, brilliant blue or bluish-white for lignin, and whitish fluorescence for cutin (cuticle). Meanwhile, lipid/fat molecules and pure carbohydrates, such as cellulose, hemicellulose, and starch, do not fluoresce.

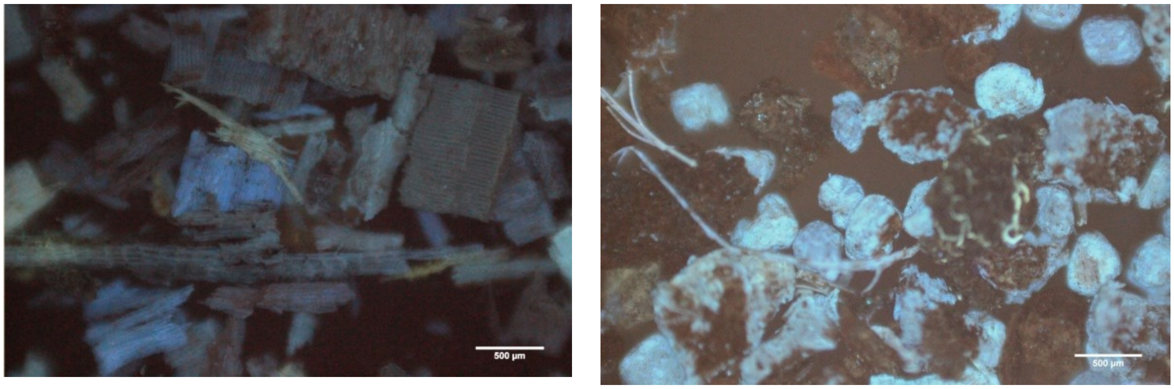

Figure VI-5 UV-AF images of sawdust and cocoa pod husks powder before densification (left, right, respectively)

V-AF micrographs revealed that the sawdust has a higher content of lignin in comparison with cocoa husks. Mostly all the sawdust grinds show brilliant blue or bluish-white fluorescence; whereas, fluorescence of cocoa grinds is scarce (figure 5). Coal grinds did not exhibit any fluorescence under same conditions as cocoa and sawdust. The high fluorescence of lignin in sawdust grinds is in accordance with the average composition reported in literature for woody biomass, where lignin represents about 20 to 35% of the biomass [26]. Whereas, the low fluorescence of cocoa pod husks can be ascribed to a lower lignin content (<20%) [33] and to the presence of more non-fluorescent compounds like cellulose, hemicellulose, fiber and ash. The UV-AF images of the cross-section of pellets made of sawdust-coal and sawdust-cocoa mixtures reveal a remarkable behavior of the grinds during pelletization. Images of sawdust-cocoa pellets shows the effect of pressure during the process; the particles become closer and the void fractions decrease. Nevertheless, the sawdust grinds maintained a similar structure during densification with cocoa husks; a natural binder such as lignin is squeezed out of the particle, so a more intense bluish fluorescence is observable but the particles seem to be just agglomerated by mechanical interlocks. Meanwhile, the appearance of some green and yellow-green fluorescing particles can be ascribed to proteins squeezed from cocoa husks as a result of the pessure applied. On the other hand, AF-UV images of sawdust-coal pellets (Figure 6) exhibits a better agglomeration between sawdust particles in comparison with the latter case. Sawdust grinds can not be easily differentiated, and shapes varied considerably. As a result of the applied stress, the particles undergo elastic and plastic deformation, increase the inter-particle contact promoting short range bonding forces such as Van der Waal forces and electrostatic forces [12]. Likewise, the lignin contained in the sawdust grinds squeeze and act as a natural binder during the process creating some solid bridges like glassy layers.

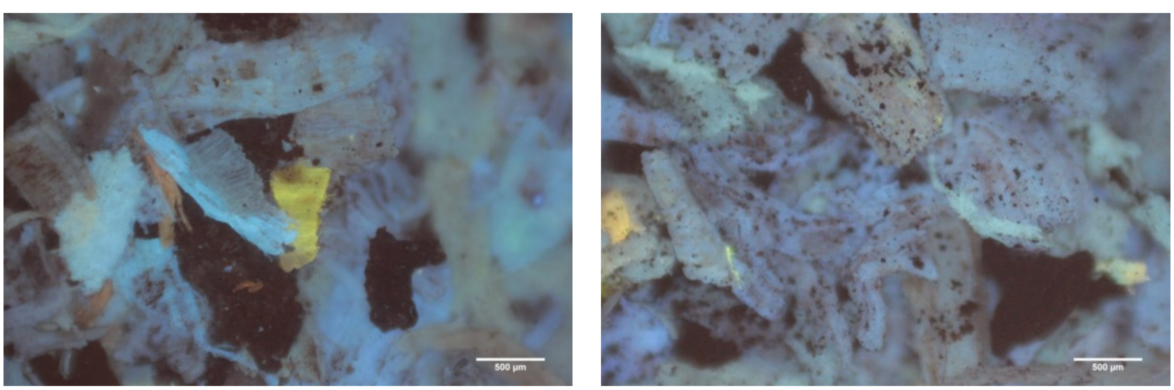

Figure VI-6 UV-AF images of sawdust-cocoa husks (left) and sawdust-coal (right) pellet cross section area

D. Conclusions

The analysis of the densification mechanisms that affect the pelletization of sawdust-coal-cocoa pod husks mixtures have been done based on optical and ultraviolet-autofluorescence microscopy images. Coal grinds exhibited to be brittle, so, the particles crashed during the process increasing the inter-particle area and promoting short-range intermolecular forces with sawdust and cocoa particles. Optical microscopy images revealed the formation of mechanical interlocks and glassy coating layers between sawdust, coal and cocoa husks particles. Sawdust acted as a natural binder on sawdust-coal and sawdust-cocoa assortments because of the remarkable lignin content. The lignin squeezed as a result of the applied stress; nonetheless, the effect of fluorescing components is more visible on the sawdust-coal pellets than on the cocoa-sawdust pellets. Further research can be performed on densification of sawdust-coal-cocoa mixtures employing heat during the process; thus, other mechanisms like lignin softening, starch gelatinization, and denaturation of proteins can be activated and observable by means of microscopy techniques. Mixed biomass pellets might result on an attractive alternative for producing a renewable energy fuel capable of replacing traditional energy sources employed for heating and cooking in rural places.

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VII. General Conclusions

Conclusions

This study aimed to identify the densification mechanisms taking place during agglomeration of solid particles for producing mixed biomass pellets. The work performed provided significant insights about the phenomena occurring simultaneously while sawdust, cocoa pod husks and coal are used as raw materials for pelletizing. According to the results of the proximate and ultimate analysis, the raw materials have potential for being used as raw materials of solid biofuels; nevertheless, some issues should be considered beforehand. Utilization of sawdust for pelletizing might result on burnable fuels that ignite easy based on the high volatile matter; moreover, sawdust has very low ash content that prevents slagging, fouling or blocking problems. When coal is employed for pelletizing, the solid biofuels might increase their heating value as a consequence of the fixed carbon of this fossil fuel, but ignition will be longer and sulfur oxides might be considered in the exhaust flue gases. Pellets made of sawdust, coal, and cocoa exhibited final density that fitted international standards, but there are some details that need to be considered beforehand.

Cocoa ash content is high; therefore, a pretreatment should be performed in order to decrease this parameter. Otherwise, the pellets do not accomplish the maximum ash level. An opportunity to modify the mechanical properties of the solid biofuels is by mixing the raw materials and varying the particle size. Pellets made of the finest grinds showed to be more resistant that those made of bigger solids. The impact and compression resistance of the pellets is opposite to the size of the grinds employed; the finest the particle, the most resistant the material is. Optical microscopy images showed that smaller particles mixed more uniformly, decreased the inter-particle space, and produced more stable solid bridges. Meanwhile, UV-AF microscopy images were employed to analyze the incidence of chemical structures like proteins and lignin into the densification of solid biofuels. Addition of sawdust to coal pellets enhances mechanical properties due to the lignin embedded in the biomass. Lignin squeezed and diffused throughout the matrix making the solid more resistant and uniform. On the other hand, despite cocoa husks had less lignin affecting the solid bridge formation, the addition of cocoa husks to coal pellets increases the mechanical properties. In this case, the mechanisms affecting that process can be ascribed to protein denaturation or short-range forces between the particles.

Future directions

This research advanced the current state of the knowledge of biomass densification mechanisms and alternatives for employing mixed biomass pellets for energy purposes. The work developed an analytical methodology to evaluate alternatives to harness a wide range of biomass assortments. It was applied not only for sawdust, coal and cocoa husks, but it was also extended to utilization of coconut shells and oil palm solid residues. Despite the extensive amount of agroindustrial residues available in Colombia, the biomass densification is still in its infancy. Therefore, further research is needed to enhance processes capable of producing biomass solid biofuels that contribute to the energy market.

An important research that needs to be pursued is to enhance the mechanical characteristics of the mixed biomass pellets. Achieving the European standards might be possible by using a pelletizer with a smaller die and adding heat and steam into the system. Likewise, an investigation on the densification mechanisms that take place during agglomeration of pre-heated solids will provide more insights about opportunities to optimize conditions when pellets are made of agroindustrial residues. There is also another issue that might be evaluated in further work. The performance of mixed biomass pellets on household stoves and thermochemical processes should be evaluated. Results of the proximate and ultimate analysis gave some predictions about the behavior of the solid biofuels, but practical analysis should be performed in order to establish the effects that biomass pellets have on typical equipment available in rural areas in Colombia.