IOP Conf. Series: Earth and Environmental Science **159** (2018) 012026 doi:10.1088/1755-1315/159/1/012026

Energetical Examination of Pyrolysis Carbon Black and Pine Shavings Blend Pellets

V Papp[1] and D Szalay[2] and A Vágvölgyi[3]

1 PhD candidate, MSc. Environmental researcher, University of Sopron, Sopron HU
2 PhD candidate, MSc. Energy management engineer, University of Sopron, Sopron HU
3 Assistant professor, University of Sopron, Sopron HU
E-mail: papp.viktoria@uni-sopron.hu

Abstract. Pellets for firing are not only made of wood or by-products of herbaceous plants, it can also be used for energy purposes by using different waste materials or mixtures thereof. These materials do not appear in conventional pellet firing or residential sectors. Waste pellets could be used in larger industrial facilities and in waste combustion plants. During the work pellets are produced of various proportions using furniture industrial pine-based wood shavings and carbon black from the pyrolysis of waste tires. The carbon black is purely purified by the usual wood-pellet making methods, in most places the wet materials are reused in rubber industry. The energetic utilization of wood-based and carbon black mixture pellets was only slightly explored. During the tests, pellets are prepared for pine-based wood which were analyzed by energetic and mechanical properties. In the wood industry, large quantities of contaminated byproducts also appeared: surface-treated materials, glue, paint residues, which cannot be wood pellets in residential use according to EN-14961-1 standard. The study dealt with pyrolysis carbon black (up to 20% mixing) could be used with this contaminated wood.

1. Introduction

The production and trade of wood pellets have increased significantly since 2008, the production of agripellets and industrial pellets have been also increasing [1], [2]. The United States and Canada are the main producers and exporters, primarily to the European Union. The EU wood pellets "dependence" is caused by the political directives to reduce greenhouse gas emissions and to increase the share of renewable energies. Many European electricity producers have converted or are in the process of replacing coal and gas with biomass, which is often done with wood pellets [3], [4].The production of wood pellets is also becoming more well-known in Vietnam, although the amounts produced are still small and mainly for exports. 85-90% of the pellets produced in the Hungarian wood pellet plants are sold in Italy in the domestic sector [5]. According to the Hungarian Pellet Association's 2015 data, 80% of wood pellets are exported to Italy and Austria, mainly to meet the demand for basic heating and small pellet boilers [6]. The increase in multilateral demand for wood pellets has resulted in wood of different grades, sizes and compositions being incorporated into pelletization, while clear pulp and sawdust from the wood industry do not cover the need. Since the timber industry stocks are limited, priority is therefore to expand the raw material base of the pelleting process with different materials, utilization of industrial pellets to get an increasing role in the future.
During the pyrolysis breakdown of waste-tires, I investigated the energetic characteristics of the pyrolysis carbon black and produced different proportions of soot and pine shaving pellets. The utilization of waste tires has environmentally a key role. 700 million wheel tire manufactured per year

in the world and (apart from a small increase in consumption) essentially the same amount is thrown away as garbage. These are one of the most serious waste disposal problems in the world as the proportion of recycling is very low and tire is not degraded in nature. Part of it is burned, for example, in cement factories, but there are still plenty of things to bury somehow or somewhere to accumulate. [7] The EU Decree on the disposal of waste prohibits [8] tires should now be recycled 100%. The most common way to use the material, the grinding of tires, are separated from the other components, and using this grinder with additives, they try to produce various rubber elements from it [9]. Waste is so much that at present only a fraction of the waste can be utilized by the industry. Therefore, the energetic utilization of 50,000 tons of rubber waste produced annually in Hungary is of paramount importance. In addition to the use of tire in cement factory and waste incinerators, pyrolysis technologies have been gaining an increasing role. Since rubber from tires have a higher calorific value than coal as well as considerable amount of carbon black, it seems reasonable to find a way to take advantage of its high energetic and raw material potential in order to progress in the search of alternative fuels, CO_2 emission mitigation and the reduction/recycling of raw materials [10].

2. Characterization of pyrolysis and carbon black

Pyrolysis, also termed thermal distillation or thermolysis, is a thermochemical treatment that allows breaking apart chemical bonds [11] by means of a thermal decomposition under non-oxidative conditions (inert atmosphere or vacuum) and it is also the first step in any gasification or combustion process. Three products or byproducts are generated: pyrolysis gas, which is generally used for heating the equipment, as well as pyrolysis oil and carbon black (soot)[9]. From the recycling point of view, the main advantage of the process is that it can deal with wastes which are otherwise difficult to recycle, and consequently can create reusable products [12]. Pyrlolysis oil is also often burned and used to generate electricity or is processed by new technologies and diesel engines are used as fuel. Carbon black can be used as a fuel (coke) after the process because it has high calorific value. The LHV of the carbon black was 29,991.2 $\pm$33 kJ/kg, which is comparable with that of the good quality coal[13]. Similar results were reported by other authors using a pilot rotary kiln reactor (around 30,000 kJ/kg)[14][15] Further treatment, by increasing the active surface, it can also be used in rubber production, wholly or partly induced by the higher price industrial soot produced for this purpose. Most analyzes show that the energy balance of the pyrolysis is unprofitable without the use of by-products (carbon black and pyrolysies gas), the efficiency is 62-65%[7]. Most of the gas is used to heat the reactor. In its original form, carbon black is difficult to transport, so it would be important to make the transport more economical, before energetic utiliztaion. One option can be the wood-briquette addition or carbon black briquette production, studies are conducted since 2013 [16]. In most plants, carbon black pellets are produced in wet conditions, unlike wood pellets, generally with a smaller die hole.

In the Environmental Impact Study of the Hungarian Academy of Sciences, Homatech W has been examining Hungary's planned technology utilizing 30,000 tons of tires annually. The plant's products are pyrolysis gas (4-6.5 m / m%), sulfur disulfide gas (~ 0.2 m / m%), pyrolysis oil (20-30 m / m%), pyrolysis coke, substantially carbon black (35-45 m / m%) and steel wire (10-12 m / m%). Keeping coke wet, the dust is largely avoided. The most harmful elements in technology to health and environmental damage are mutagenicity in polyaromatic hydrocarbons (PAHs), aromatic amines in carbon black and wastewater contaminated with PAHs and amines. Among the rubber-forming polymers, chlorine and oxygen constituents, such as chlorinated or chlorosulfonated polyethylene, polyacrylate, urethane rubber, etc., may also be present. Therefore, it can not be excluded, that dioxins and furans, even trillions of parts (ppb), are generated. Potentially hazardous to health can be the inhalation of nano- and micron-sized particles of polluting carbon black substances. Successful power plant experiments have been carried out with coke. Its sulfur content is similar to the sulfur content of mineral carbon. No additional load on the coal-fired power plant flue gas treatment of tire-derived pyrolysis coke by burning. PAH compounds can be burned together with carbon [17].

In energy recovery, environmental contaminants in PM10 dust particles may be particularly dangerous. This is primarily due to the fact that the air fed to the firing can capture the smaller particles without they are sufficiently burned (especially when there is excessive air supply due to a worse setting or fire problem). It is not inconceivable that the burners used for pellet burning - due to their design - are not suited for the perfect burning of smaller crumbs [18]. Since carbon black may also be present in mutagenic compounds and during the mixing the pellet length also be significantly reduced. Therefore, these materials may be released into the environment without proper filtering equipment.

Regarding the compositon of tires (except for steel), almost all materials are flammable or pyrolysisable, with a high calorific value. The pyrolysis process also has a lot of variants and different technologies, so the output values of the different materials, main and by-products can vary considerably. The main determinant of the yield values is, of course, the composition of the input material besides the method used. At Szent István University, researchers deal with different types of pyrolysis technologies utilizing various waste materials [19]. Based on their research, the following table 1 summarizes the amount of byproduct produced by different technologies.

Table 1. The amount of solid and gas-purifying residues per technology (tons / 100000 tons) [19]

	Lurgi	Compact Power [a]	Compact Power [b]	Brightstar	Waste Gen	Foster Wheeler	Thermoselect
Technology	firing	pyrolysis	pyrolysis	pyrolysis	pyrolysis	gasification	pyrolysis-gasification
Carbon black	21353	19598	13065	23400	27090	30351	23390
Gas clearing byproduct	2265	945	630	500	2257	0	3583
Sum	23618	20543	13695	23900	29347	30351	26973

a without pretraetment
b with pretreatment

It can be seen, therefore, that the amount of coke / carbon black produced is significant, usually 20-30%, but higher in the gasification, even if the amount of carbon black (35-40%) can be higher than pyrolysis oil (30-35 %). The utilization of carbon black is therefore a crucial issue, it can determine the profitability of a technology and significantly affect the energy balance.

3. Presentation of the tests, methods

The pyrolysis carbon black and wood blend pelletization is less explored. One of the reasons for this is that the carbon black is difficult to handle and pelletize. On the other hand, due to dusting of carbon black powder, mixing is difficult to solve under operating conditions. In 2013 Liu et al. developed a special pelletizer in China for the utilization of pyrolysis carbon black and biomass blends. However, the pellet diameter of these blends is 14-20 mm, which is significantly higher than the usual 6-10 mm size in Europe [20]. There is no data on the quality of the pellets and the proportion of mixtures. An American company [21] has also developed a pelletizing technique for carbon black, with a diameter of 0.3 to 2mm of pellets of pure carbon black, which is significantly smaller than the usual sizes. In most cases, the aim was not the energy recovery, but also to facilitate delivery and reduce dusting of carbon black powder.

The process of manufacturing fuel pellets involves placing ground biomass under high pressure and forcing it through a round opening called a “die.” When exposed to the appropriate conditions, the biomass “fuses” together, forming a solid mass. This process is known as “extrusion.” Some biomass (primarily wood) naturally forms high-quality fuel pellets, while other types of biomass may need additives to serve as a “binder” that holds the pellet together. However, the creation of the pellets is only a small step in the overall process of manufacturing fuel pellets. These steps involve feed stock

grinding, moisture control, extrusion, cooling, and packaging. Each step must be carried out with care if the final product is to be of acceptable quality [22].
In the investigations, different proportions of mixtures were prepared by using a Kahl type press, experimental pelletising equipment (max. Power 22 kW, matrix thickness 28 mm, matrix bore diameter 6 mm, capacity 200-250 kg / h) for which energetic characteristics, and pellets length change are analyzed. Carbon black is not purely pelletable, at 30% shoot-mix cumbersome, it is "burned into" the press holes according to my own experience.

Figure 1. Kahl type pellet press with feeder.

Among the most important energetic properties, calorimetric measurements were performed to calculate the calorific value, the ash content by the muffle-furnace measurements, and the moisture content by automatic moisture measurement. The changes in pellet lengths were determined by caliper measurements. The energy measurements were made separately for the raw materials and the different mixture pellets.

3.1.Calorimetric mesurments
The essence of a calorimeter is that combustion occurs under certain conditions. To do this, by analytical balance measured fuel sample must be taken into a sample holder, while the sample burning machine measures the temperature change of the calorimeter water tank. The test was carried out in accordance with MSZ EN 14918 standard, using an IKA 2000C bomb scale analyzer. During the test, the instrument receives the direct heat of the combustion heat. Calculation of the net calorific value can then be determined by using the following formula.

$$\text{Net Calorific Value(NCF)} = \frac{\text{GCF} - \left(\frac{2447\cdot(\text{U}+9\cdot\text{H})}{100}\right)}{1+\frac{\text{U}}{100}} \left[\frac{\text{kJ}}{\text{kg}}\right]$$ where:

GCF: Gross calorific value (kJ/kg)
U : the gross moisture content of the test substance [m / m%]
H : hydrogen content of the test substance [~ 6 m / m%]
Calculation of calorific value is the most important issue from an energetic point of view. The energy content of the various materials and their compressions can be determined by energy efficiency, so the energy balance is always tested for the calorific value of the raw material and the finished product.

3.2 Ash content
Ash content is an energetically important feature due to the design of combustion plants. Wood pellets are low, generally less than 0.5%, while pellets made of herbaceous plants or industrial materials have

a higher ash content, usually between 3-10%. The unburned slag generated during the energetic utilization of biomass, as well as the higher-capacity combustion plants, can cause special operating problems. On the one hand, it is related to the destruction of a combustion plant and, secondly, to the disposal of large amounts of ash.
Test Procedure:
- Measurement of moisture content, drying of material
- Measurement of dry matter on analytical scales
- Burning in a muffle furnace
- Weighing of ash on analytical scales

Ash content calculated with the formula: AS(%)=mo/m1*100
AS(%)- ash content, m1 (g)- weight of the dry sample, mo (g)– weight of ash.

3.3.Moisture content
From a firing point of view, moisture content is one of the most important properties, since it is closely related to the calorific value [23]. Determining the moisture content is important because of the pelletisation, if it is too high or too low the pellet is crushed and disintegrated. The optimum moisture content is about 10-12% at wood pelleting process. After pelleting the moisture content is reduced, and it must be below 10% according to regulations.
Test procedure:
The BOECO SMO 01 automatic humidity tester was used during the tests. A sample is placed on the sample holder of the moisture gauge, then dried at 105 °C to a mass flow using a heating coil in the instrument. The moisture content of samples can be determined directly by the weight before and after drying.
Theoretical definition:
$n = (m_n - m_{sz})/m_n \cdot 100$ [% v.g/g]
n-moisture content(%), mn: mass of the wet sample(g), msz: mass of the dry matter of the sample(g)

3.4.Pellet length
For pellets, it is important to have a medium length between 3.15 and 40 mm. The length of pellets may be influenced by a number of factors. Particle size, moisture, and most of all material composition. In the production of wood pellets, corn starch is often used, thereby reducing the fine fraction and adjusting the appropriate length. All pellets in 80-100 grams of samples should be tested by using a simple digital caliper.

Figure 2. Carbon black 5% and pine shaving 95% blend pellets.

The carbon black, during the work is composed of nano - and microparticles of fraction, so it was very important during the laboratory work to observe the safety regulations due to the possible dusting of powder. Before pelleting, the optimum moisture content of 12% for wood pellets was adjusted for both raw materials. The by-product of furniture industry were pine-shavings that have a calorific value of 18.6-19.2 MJ / kg due to its high resin content. Pure wood had an ash content of 0.4%, the moisture content of the finished pellet changed from 8.9 to 9.3%. The calorific value of carbon black was high, the average of calorimetric measurements was 27,9 MJ / kg. Ash content was between 3-4%.

4. Results

By increasing the rate of soot, the pellet length apparently decreased, as measured by the caliper measurements. I assumed a linear correlation between the mean average length and the rate of blend of carbonblack. The average of the length changes and the degree of mixing ratio can be written using the least squares method, the straight line closest to the points is regression line.

Thus, by increasing the mixing rate as expected, the mean average length of the pellets decreases linearly, the slope of the regression line is -0.43.

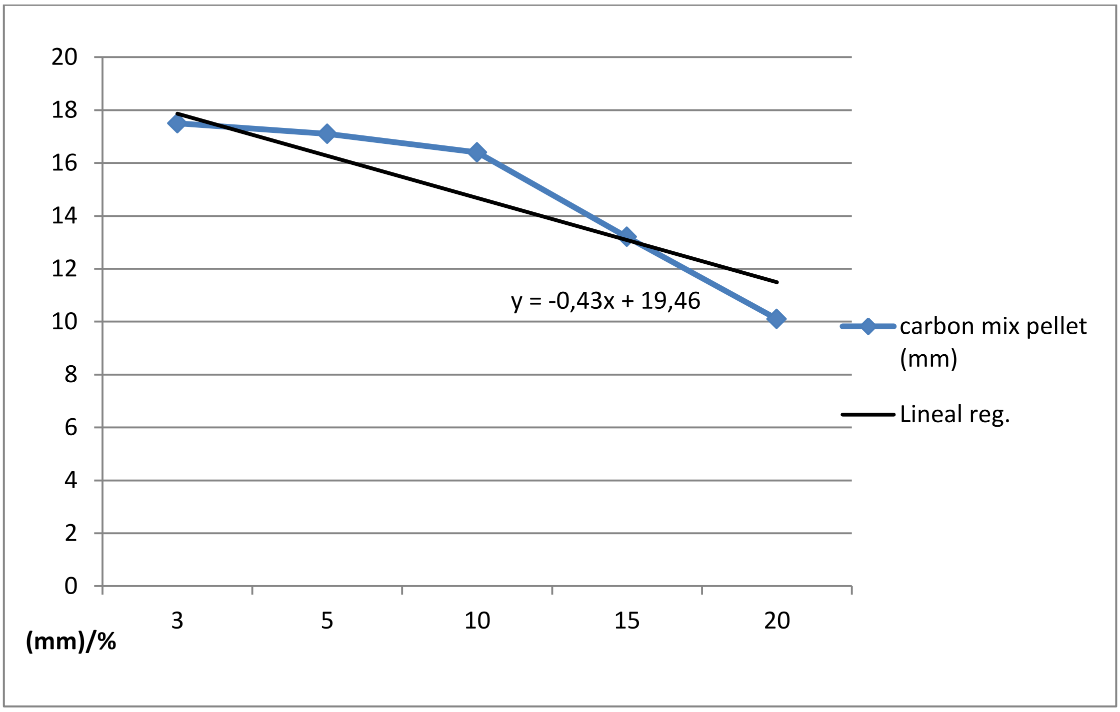

Figure 3. Medium length change of carbon black blend pellets depending of the mixing ratio.

Although the carbon black has a negative effect on the length of the pellets, due to the high 27-28 MJ / kg calorific value, the increase in the mixing rate is evident, and the calorific value of the mixture pellets also increased, which is energetically positive, as shown in table 2.

Table 2. Net calorific value changes of carbon black pine-shavings blend pellets

Carbon black ratio (%)	Calorific value (MJ/kg)
3	19,2
5	19,4
10	19,9
15	20,7
20	21,4

The ash content did not change much, the 0.4% value of wood pellets increased by 0.7% in the case of 20% mixing of carbon black. The moisture content after pelletizing process decreased from 12% to 9.2-9.5%.

5. Conclusions

During utilization, the high sulfur content of the carbon black and any mutagenic compounds (PAHs, chlorosulfonated polyethylenes, esters ppb, dioxins and furans) may be present. Therefore, it is of the utmost importance that recovery can only take place in combustion equipments with appropriate cleaning and filtering system. The reduction in the length of pellet-wood blend pellets also greatly influences combustion in pellet furnaces, as if smaller pellets are placed in the furnace - and the fine fraction is increased - it can also modify the flue gas composition and the amount of leaving solids. Based on the results, it can be said that the soot itself can not be pelletized using the usual wood pellet methods. By mixing with wood, I would recommend a maximum mixing ratio of 20% of carbon black at 6 mm diameter. Further studies could be carried out to increase the diameter, or increased the moisture content, which would probably be able to mix the soot into the wood-shavings even more. While the carbon black has a negative effect on the length of the pellets, due to the high calorific value, the heating value of the blend pellets increases as the mixing ratio increases. In the future, with the spread of the waste tire or other pyrolysis plants, in addition to industrial use and material recycling, the energetic utilization of the carbon black will be a key issue.

6. References

[1] Sikkema R. 2016 - The European wood pellet markets: current status and prospects for 2020 - *Biofuels Bioproducts and Biorefining vol.* 5. 250 – 278p.
[2] PellCert Project 2014 – *European pellet markets* – European pellet report
[3] Calderón C, Gauthier G, Jossart J.M. 2015, *AEBIOM- Statistical report*- European Bioenergy Outlook
[4] European Comission 2015 - Bioenergy Report, *Study on impacts on resource efficiency of future EU demand for bioenergy*
[5] Papp V, Szalay D, Gaál L, 2016 – Agripellet előállítás alapanyagbázis vizsgálata Magyarországon – *Journal of Central European Green Innovation* – 4. vol.
[6] MaPe 2014 – Hungarian Pellet Assosiation, *Wood pellet Trends Report.*
[7] Nagy B, 2011 – *Újrahasznosítási ismeretek –Gumiabroncs* –Digitális tankönyvtár
[8] Council Directive - 1999/31/EC- European Union directive - waste management
[9] Farkas H, 2015 Gumiabroncs hulladék újrahasznosítása, *Waste tire utilization* http://www.hirado.hu/2016/03/03/evente-otvenezer-tonna-gumihulladek-keletkezik-magyarorszagon/
[10] Martínez J. D., Puy N, Murilloa P,García T, Navarroa A, Mastrala M, 2013 Waste tyre pyrolysis – A review. *Renewable and Sustainable Energy* Reviews, vol. 23, 179-213p.
[11] Wampler T.P, 2007 - *Applied pyrolysis handbook* (2nd ed.), CRC, 23. p.
[12] Scheirs J., Kaminsky W, 2006 - *Feedstock recycling and pyrolysis of waste plastics: converting waste plastics into diesel and other fuels*, John Wiley & Sons Ltd.
[13] Sienkiewicz M, Kucinska-Lipka J, Janik H, Balas A. 2012 *Waste Manag*. 2012 32 vol. 1742-51p. Progress in used tyres management in the European Union: a review.
[14] Li S, Yao Q, Chi Y, Yan J, Cen K, 2004 *Pilot-scale pyrolysis of scrap tires in a continuous rotary kiln reactor*, Industrial & Engineering Chemistry Research, 43 p..
[15] Galvagno S, Casu S, Casabianca T, Calabresem A, G. 2002 Cornacchia Pyrolysis process for the treatment of scrap tyres: preliminary experimental results,*Waste Manage*., 22 v. 917-23pp.
[16] Kovács O. 2013 Pirolízis korom brikettálása, Carbon black briquette https://www.slideshare.net/eco-gumm/pirolzis-12652833
[17] MTA Environmental Impact Assessment 2016 - Scientific Opinion of the Institute of Materials and Environmental Chemistry of the Hungarian Academy of Sciences, Institute of Natural Sciences on the environmental adequacy of HOMATECH-W (TM) technology

[18] Németh G. (2014) – Kis teljesítményű faalapú pellet tüzelő berendezés környezeti hatásainak vizsgálata, Faipar, 62.vol.
[19] Lakatos K. 2013 – *A pirolízis elve és folyamata, pirolízis technológiák – Különböző alapanyagok és hulladékok pirolízise – Pyrolysys of different waste materials*- SZIE Konzorcium.
[20] Mars Mineral Ltd. 2015 *Carbon black pellets*, Company description
[21] Liu Y, 2014 *Carbon black and biomass pellets*, Product solutions, Company description
[22] USAID 2014 – Vietnam Clean Energy Program, *Woody biomass energy generation*, Final report
[23] Marosvölgyi B, 2006 *Szilárd, biomassza alapú tüzelőanyagok energetikai tulajdonságainak vizsgálata*- Egyetemi jegyzet.

Acknowledgment
The described work was carried out as part of the „Sustainable Raw Material Management Thematic Network – RING 2017”, EFOP-3.6.2-16-2017-00010 project in the framework of the Széchenyi 2020 Program. The realization of this project is supported by the European Union, co-financed by the European Social Fund.