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Concentrated Phosphorus Recovery from Food Grade Animal Bones for Agronomical Efficient Innovative Fertiliser Applications in the Organic and Low Input Farming Sectors

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Abstract: Disrupted nutrient recycling is a significant problem for Europe, while phosphorus and nitrogen are wasted instead of being used for plant nutrition. Mineral phosphate is critical raw material, which contains environmentally hazardous elements such as cadmium and uranium. Therefore, phosphorus recovery from agricultural by-product streams is critically important key priority. Phosphorus recovery from food grade animal bone by-products have been applied researched since 2002 with objective driven evolution progress towards specialized pyrolysis processing technology and animal bone char product (ABC) developments in economical industrial scale. Different animal bone by-products tested under different conditions at 400 kg/h throughput capacity in the continuously operated 3R zero emission autothermal carbonization system. The different material core treatment temperatures (between >300°C and <850°C) were combined with different residence times under industrial productive processing conditions. It has been industrial demonstrated that material core treatment temperature <850°C with 20 minutes residence time is necessary to achieve high quality ABC with useful agronomic value. The output ABC product having concentrated >30% phosphorus pentoxide (P_2O_5) and specific quality innovative fertilizer for agronomical efficient organic and low input farming applications as functional organic fertilizer, soil improver, growing medium and/or fertilizing product blend with high mineral phosphate fertiliser replacement value.

Keywords: bio-phosphate; ABC Animal-Bone-Char ; 3R pyrolysis; phosphorus recovery; animal by-products; apatite

1. Introduction

Disrupted nutrient recycling is a serious problem for Europe and all over the world. Phosphorus (P) and nitrogen (N) are lost across environmental media during food production or are wasted instead of being used for plant nutrition (European Commission 2016b [14]).

Phosphorus occurs in many minerals, of which apatite, $Ca_5(F,Cl,OH)(PO_4)_3$ is the most abundant and by far the most important group (Bartels and Gurr 1994 [3]. Apatite, a group of phosphate minerals, is in two major natural forms with concentrated P-content, such as mined mineral phosphate and biological origin animal bones. The term of phosphate rock (PR) refers to rock containing phosphate minerals, usually apatite, which can be commercially exploited, either directly or after processing, for commercial applications (Bartels and Gurr 1994 [3]. Phosphate rocks of sedimentary origin typically have 30–35% phosphorus pentoxide (P_2O_5) whereas those of igneous origin contain marginally higher P_2O_5, typically 35–40% (Schorr & Lin 1997 [34]).

Phosphate rocks by their very geological and mineralogical nature contain a host of environmentally hazardous chemical elements such as cadmium (Cd), uranium (U), lead (Pb), mercury (Hg) and arsenic (As) among others.

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The superphosphate fertilisers are particularly abundant in these hazardous elements and they contaminate the agricultural soils through the use of fertilizer. (Dissanayake and Chandrajith 2009 [6]).

U is an accompanying element of PR, particularly that of sedimentary origin. Depending on the geographical and biogenic origin of the uranium concentrations of PR may be as high as 150 mg kg-1 in sedimentary and 220 mg kg-1 in igneous PR (Kratz and Schnug 2006 [24]). In Germany, the use of P-fertilizer from 1951 to 2011 has resulted in a cumulative application of approximately 14000 t of U on agricultural land, corresponding to an average cumulative loading of 1 kg U per hectare. (Schnug E., Lottermoser B. G. (2013) [33].

Reserves of PR used to make such fertilizers are finite, especially those ones with low Cd and U content, and concerns have been raised that they are in danger of exhaustion. For long term global food security is the sustainable supply of P, a key resource for soil fertilisation that cannot be substituted (European Commission 2011a [11]). Phosphate rock, which is the main fertiliser constituents has been identified by the European Commission (EC) as a critical raw material in 2014 and upgraded in 2017 (European Commission 2017 [16]).

The estimated yearly consumption of manufactured phosphorus mineral fertilizers in the European Union (EU) 27 member states (MS) was 1.11 Mt P in 2014 based on data provided by Fertiliser Europe. (Eurostat 2016 [18]). This is equivalent with 2.55 Mt/year mineral phosphorus fertiliser expressed in phosphorus pentoxide (P_2O_5).

For phosphate fertilizers, the EU is currently almost entirely dependent on import of PR mined outside of the EU (more than 90% of the phosphate fertilizers used in the EU are imported, mainly from Morocco, Tunisia and Russia) (European Commission 2016a [13]). Concentration of phosphorus mines and gas fields outside the EU makes the EU fertilizing product industry and the European society dependent and vulnerable on imports, high prices of raw materials as well as the political situation in supplying countries (European Commission 2016b [14]). Therefore, P recycling is one of the key priorities of the sustainable agricultural systems. Trends and developments on the global PR market are putting the EU's security of supply of PR under increasing pressure (de Ridder M. et al. 2012 [28]).

The environmental, economic, and social implications of food waste are of increasing public concern worldwide (European Commission 2011b [12]). The EU alone waste 90 million tonnes of food every year or 180 kg per person. Much of this is food, which is still suitable for human consumption. (European Commission 2011a [11]). Losses from food processing mainly originate from the slaughtering of animals and the subsequent removal of P-rich rest materials (e.g. animal bones) from the biogeochemical P cycles. This loss flow equals 294 kt P yr^{-1} (van Dijk et al., 2016 [36]). The cattle, fish, and poultry industries are the largest source of animal food industry waste (Jayathilakan et al., 2012 [22]). Animal-derived food waste contains rather high amounts of protein and cannot be discharged into the environment without proper treatment (Jayathilakan et al., 2012 [22]).

The Eurostat databases informing, that more than 51 million tonnes of carcass weight animals (bovine, poultries and pigs) slaughtered in the EU 28 countries (Eurostat 2016 [18]). According to Meeker and Hamilton, 2006 [26] approximately 49% of the live weight of cattle, 44% of the live weight of pigs, 37% of the live weight of broilers are materials not consumed by humans. According to the European Fat Processors and Renderers Association (EFPRA) the proportion of each animal is not used for human consumption and rendered is the highest for bovine animals (42%) followed by pig (34%) and poultry (25%) (EFPRA [8]). The European rendering industry (35 EFPRA members, 26 EU countries) processed more than 17 million raw materials in 2014 from which the category 3 processed products are 12 million t/y. EFPRA members processing the majority of the total animal by-products in the EU and additionally significant amount of material streams produced by non-member organizations (EFPRA, 2015 [9]). The skeletal system can be up to 20 percent of the carcass weight, which mean that over 4 million tons of animal bone biomass produced in the EU annually.

Biological apatite is an inorganic calcium phosphate salt. It is also a main inorganic component of biological hard tissues such as bones (Liu et al. 2013 [25]). The majority of P (85-88%) exist as bone P in the body of vertebrates (Hua et al., 2005 [21]). Animal bone by-product is characterized by very

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high P content compared to other animal waste. The P content of bone for bovine and poultry bone is about >10.5% on dry weight basis (Beighle et al., 1994 [4]; Hemme et al., 2005 [20]). Other animal by-products having far lower phosphorus content than bone grist. For example the phosphorus content of liquid pig manure, with 2-10 dry matter content, is 0.20-1.25% while the solid pig manure with 20-30% dry matter content has 1.6-5.08 % P-content (Agrotechnology Atlas, 2016 [1]).

Since 1870, the age of technological revolution, and through the 21st century, the carbon related technologies and products have been one of the most comprehensively researched sectors for energetic, steel industrial, activated carbon adsorbent, pharmaceutical, biotechnological and other wide range of applications. However, in modern age the new environmental, climate protection and output product safety aspects require significantly improved and advanced pyrolysis technology performances to better protect the environment and human health. In this context the new 3R zero emission pyrolysis technology open new technical, economical, environmental and legal opportunities for advanced production and use of safe Animal Bone Char (ABC) materials.

Pyrolysis (or carbonization process under true value reductive processing conditions) is the chemical decomposition of an organic substance by heating in the absence of oxygen. The process of pyrolysis transforms organic materials into three different components, being solid, gas and liquid in different proportions depending upon both the feedstock and the pyrolysis conditions used. (Verheijen et al., 2010 [37]).

The key objective of the pyrolysis process is to produce different types of carbon products. The organic carbon content of the pyrolysed chars fluctuates between 5% and 95% of the dry mass, dependent on the feedstock and process temperature used. For instance the carbon (C) content of pyrolysed beech wood is around 85% while that of poultry manure is around 25% and that of bone is less than 10% (EBC, 2012 [7]). Different pyrolysis technology designs have highly variating quality performances to carbonize organic materials with different heat transfer efficiency under reductive processing conditions, which is directly reflected in the remaining organic residual toxic content in the output char product, most importantly PAHs.

Pyrolysis materials are different types of reductive processed stabile carbon materials that are specifically made for different functional applications in designed quality, which chemically modified substance is produced from eligible input biomass materials via carbonization thermochemical treatment production process that fully meet the EU regulations quality, safety, environmental and climate protection requirements. Biochar products are plant or animal bone biomass origin stabile carbon pyrolysis materials with specific quality and safety parameters for explicit soil functional applications. Plant biochar is high carbon composition soil improver with no economically important nutrient content. ABC is high phosphorus and calcium concentrated innovative organic fertilizer with high agronomic efficiency and low carbon content.

ABC is Animal Bone Char, innovative phosphorus natural fertilizer made of food grade (category 3) animal bones with concentrated >30% P_2O_5 content and specific quality for agronomical efficient organic and low input farming applications, also known as Bio-Phosphate.

The Recycle-Reduce-Reuse (3R) zero emission pyrolysis technology is an autothermal carbonization process innovation, which has been specifically developed and industrial engineering designed for phosphorus recovery. 3R is processing all types of category 3 and category 2 animal bones and converting into ABC specific pyrolysis materials up to <850°Celsius material core temperature under fully reductive conditions. The 3R is an IPR protected original solution with comprehensive performance through the full life cycle of the phosphorus product.

Directive 2008/105/EC (European Parliament 2008 [17]), is listing PAHs as identified priority hazardous substances and persistent organic pollutants which are generated from the natural or anthropogenic processes, such as carbonization process. The occurrence of contaminants, such as polycyclic aromatic hydrocarbons (PAHs), Potential toxic elements (PTEs) in pyrolysis may derive either from contaminated feedstocks or from pyrolysis conditions which favor their production (Verheijen et al., 2010 [37]). It has been indicated that low temperature are unable to remove micro pollutants that were originally present or during the thermal process created in contaminated feedstocks (vom Eyser et al., 2016 [10], Weiner et al., 2013 [38], Ross et al. 2016 [30]). During

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industrialized pyrolysis process conditions PAHs are the key target and performance indicator contaminants. Generally, it is considered that adequate pyrolysis methods allow a significant reduction of the PAHs contamination and that high PAHs levels indicates substandard production conditions (Schmidt et al., 2013 [32]). If, for example, the process conditions does not separate solid residues and volatile tar components during cooling phases a high PAHs content may eventually result (Schimmelpfennig and Glaser, 2012 [31]).

For slow-pyrolysis processes (at least 20 minutes reaction time), most of the weight loss in plant based pyrolysis materials derived from contaminated input materials occurs over the temperature range from 250 °C to 550 °C due to burning out of organics (Deydier et al., 2005 [5], Koutcheiko et al. [23], Ro et al., 2010 [29]), at least under laboratory conditions. At 500°C, the pyrolysis reaction time to remove >90% of the organic micro pollutants was less than 5 minutes (Ross et al., 2016 [30]). However, animal bone based pyrolysis materials, due to its specific character; require far higher processing temperatures, up to 850 °C material core temperature and longer residence time, under true value industrial production conditions. In all types of pyrolysis material cases, it is important to highlight, that there is a significant difference between the processing results from laboratory tests or from true value industrial and market competitive production conditions.

There is a substantial risk for the accumulation of non-volatile pollutants such as inorganic metals and metalloids in the pyrolysis materials as these mostly remain in the solid phase and become concentrated during the production process.

When pyrolysis material is irrevocable applied to open and complex soil ecological system, there is also a direct interlink to subsurface water systems, therefore only qualified and safe biochar products must be applied. Currently there is lack of harmonized quality and safety standards at European level for pyrolysis material products. However the complex and strict criteria for safety and quality; functional application efficiency under open environmental and ecological conditions; are already unconditionally valid for all types of biochar products according to the Member State regulations. However, this is not yet law harmonized on EU level, therefore there are Member State differences. Industrial pyrolysis technology, pyrolysis material production and commercial applications, above 1 tons/year capacity) require Member State Authority permits that conform according to the European Union regulations since long time. The less than 1 ton/year pyrolysis processing capacity is counted as research quantity.

The list of 16 polycyclic aromatic hydrocarbons (PAHs), issued by the U.S. Environmental Protection Agency (EPA) in 1976 with a view to use chemical analysis for assessing risks to human health from drinking water, has gained a tremendous role as a standardized set of compounds to be analyzed, quite especially in environmental studies. (Stephen et al. 2015 [35] Anderson and Achten 2015 [2]). Although not mandated by law in most countries, it appears that the list has attained the authority of a legal document and that the 16 priority PAHs compounds are routinely investigated in a large number of environmental situations (Anderson and Achten 2015 [2]).

The new scientific recognitions and developed analytical methods expanded the list to PAH19, which might even expand in the future. As an example some Member State require Authority accredited long termed agronomic efficiency tests and maximized potential organic contamination levels <1 mg/kg for sum of 19 PAHs congeners for soil improvers since 2005, such as Hungary (FVM 2016 [19]), while other Member States does not agronomic efficiency testing the novel soil improver products and apply up to <6 mg/kg for sum of US EPA 16 PAHs congeners. For example the German Federal Soil Protection and Contaminated Sites Ordinance gives precautionary values for soil with low (<= 8%) and high humus content (> 8%) regarding the total content of 16 priority PAHs as defined by the Environmental Protection Agency of the United States (EPA 16 PAHs), namely 3 mg/kg soil and 10 mg/kg, respectively (Meyer et al. 2017 [26]).

The Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) is mandatory for all types of pyrolysis materials for import, manufacturing and placing on the market on its own or in preparation above 1 ton/year capacity that is to be applied from June 1, 2018 in the EU. REACH is to be applied above 1 ton/year capacity for all types of pyrolysis material cases, that products are all thermo chemically modified substances.

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The conditions for access to the market of fertilising products are only partially harmonized at EU level. The fragmentation of the non-harmonized part of the market is seriously hindering trade opportunities (European Commission 2016c [15]). Around 50 % of the fertilizers currently on the market, however, are left out of the scope of the Regulation. This is true for a few inorganic fertilisers and for virtually all fertilizers produced from organic materials, such as animal or other agricultural by products, or recycled bio-waste from the food chain (European Commission 2016a [13]).

Many Member States have detailed, national rules and standards in place for such non-harmonized fertilizers, with environmental requirements, such as potential toxic elements (PTEs) contaminant limits, that do not apply to EC-fertilisers (European Commission 2016a [13]). The EU Member States have been since long time regulated the agricultural use of soil improvers, organic fertilizers, such as the Animal bone char (ABC) and other organic products. However the EU Member States regulations are widely and significantly different in each EU Member States, so the Mutual Recognition concept is difficult to be applied in practice. Therefore, the new EU Fertilizers Regulation revision under the Circular Economy incentive will soon, hopefully by 2019-<2020, open full and EU wide law harmonization opportunity for many agricultural, food industrial by-products and organic material streams, including biochar and its formulated products as well.

The recent initiative on EU fertilising products (COM(2016) 157 final) is expected to: create a level playing field for all fertilising products at EU level, thereby increasing the industry's opportunities to have access to the Internal Market while maintaining the national regulations in place for products limited to national markets, hence avoiding any market disruption (European Commission 2016c [15]).

The improved and safe output pyrolysis material products enhancing the environmental, ecological and economical sustainability of the food crop production, while reducing the negative footprint and overall contributing to climate change mitigation. Terra Humana Ltd. has been science and technology coordinator and key technology designer for EU Commission co-financed biochar applied research projects since 2002, with prime specialization on ABC recovered bio-phosphate production full industrial engineering, economical field applications and market uptake evaluations. The core competence of the Terra Humana Ltd. is zero emission pyrolysis and carbon refinery science and technology developments, objective driven to the added value recycling and recovery of phosphorus and other valuable nutrient materials. In this context Terra Humana Ltd. is the EU and international knowledge center for ABC Bio-Phosphate matured research, science, technology and industrial engineering.

The recently closed EU project of the Terra Humana Ltd is the REFERTIL (EU contract number 289785 contracted in 2011), www.refertil.info, which complex development works covering the fields from the applied biochar, most importantly ABC, science into economical full scale industrialization and commercialization. The REFERTIL is a biochar policy support specific project for conversion of biochar applied science into economical industrial practice, for which a comprehensive biochar law harmonization proposal has been reported to the Commission.

2. Materials and Methods

All ABC pyrolysis materials have been processed by the Terra Humana Ltd, as this is the only organization in the EU who is systematically developing advanced ABC science and technology, which is objective driven towards the industrialization of the P recovery technology and products in European dimension since 2002. Different pyrolysis treatment conditions (treatment temperature and residence time) used in material treatability test with different food grade animal bone meal and bone grist by-products in the 400 kg/h throughput capacity continuously operated 3R zero emission industrial pyrolysis equipment. The different material core treatment temperatures (300-450-600 and 850 °C) were combined with different residence times (15, 20, 30, 40, 50 and 60 minutes) under industrial productive processing conditions. Representative plant based pyrolysis material samples received from the UK, Italy, France and Denmark and comparative tested for PAH16 and PAH19.

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Table 1 shows the description of pyrolysis condition (treatment temperature (T) and residence time (tres) and samples ID of different EU industrial reference plant based pyrolysis material samples which have been collected and analysed.

Table 1. List of industrial reference plant based pyrolysis material sample

Sample ID	Pyrolysis condition (provided by the technology owner)	Type of pyrolysis material	Sample origin
BCFR2	T=475^{0}C, tres=60min	Oak chips pyrolysis material	France
BCIT1	T=450°C, tres= 60min	Wood based pyrolysis material	Italy
BCUK1	T=675°C, tres= 20min	Gasification – wood material	United Kingdom
BCDK4	T= 400°C, tres=60min	Wood waste pyrolysis material	Denmark
BCDK5	T= 550°C, tres=60min	Wood waste pyrolysis material	Denmark

Careful and material specific consideration is needed for all analytical items, also which standards to be applied for investigation of the quality and safety of the pyrolysis materials especially when open ecological soil applications targeted. The Environmental Testing Laboratory of WESSLING Group is the first laboratory in Europe to be obtained accredited status for different analyses of the plant based and animal based pyrolysis materials. The accredited analysis of the different samples has been done by the WESSLING Hungary Ltd. The frequency, procedures and documentation for industrial production of ABC has been determined and EN-12079 used, which for sample pre-treatment Method CEN/TC400 - EN 16179:2012 used. The REFERTIL methodology for accredited identification of the PTEs is based on European Committee for Standardization - Project Committee - horizontal and MS mutually recognized standards. If no horizontal methods are available, than well recognized accredited methodologies has been used. The concentration of PAHs in pyrolysis material was determined according to CEN/TS 16181:2013 standard with a gas chromatography-mass spectrometry method.

3. Results

3.1. REFERTIL recommended biochar safety parameters.

The REFERTIL consortium integrated the pyrolysis applied scientific and high maturity research, industrial engineering, legal, market competitive economical aspects and user demands from the horticultural sector. Harmonized and standardized analytical measurements have been developed for determination of the physico-chemical properties, potential toxic element content and organic pollutants in all types of pyrolysis materials. A proposed quality and safety criterion system has also been set up which is maximizing the inorganic and organic pollutants for safe application.

The most important PTEs are Cd, Cr (Cr total and/or Cr(VI)), Cu, Zn, Hg, Ni, Pb and As, while the key organic parameters are polyclorinated dibenzodioxins and furans (PCDD/Fs), sum of 7 polychlorinated biphenyls (PCB7) and sum of 16 US EPA priority PAHs (PAH16) congeners.

PCB7 is a sum of seven PCBs, such as PCB 28, 52, 101, 118, 138, 153 and 180. PAH16 is a sum of the following 16 US EPA congeners: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene and benzo[ghi]perylene. Sum of 19 PAHs additionally to PAH16 are including 1-Methylnaphthalene, 2-Methylnaphthalene and Benzo[e]pyrene.

All proposed parameters are maximum allowable limits on EU level, which in justified environmental cases may be MS amended to lower limits. PAHs are key performance indicators, while PCDD/F and PCBs no any cases found as potential contamination risk. In some MS for Sum of 19 PAHs congeners (19) one mg/kg is permitted since 2005 as maximum limit for soil improvers. This low limit value requirement is already applied by some EU Member States since 2005, with special concern in the environmentally sensitive regions. In general cases 4 mg/kg PAH16 limit value

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proposed. With various pyrolysis processing conditions it has been verified that the technology is critically influences the quality of the product.

Extended producers responsibility and liability for product safety is to be applied for all types of pyrolysis material cases.

Table 2 shows the proposed REFERTIL safety criteria for organic pollutants and table 3 for potential toxic elements.

Table 2. Proposed safety criteria for organic pollutants

	PAH16[1] mg kg^{-1} dry matter	**PCB7[2] mg kg^{-1} dry matter**	**PCDD/Fs ng WHO toxicity equivalents/ kg dry matter**
Pyrolysis material safety criteria	4	0.2	20

[1] Sum of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene and benzo[ghi]perylene
[2] sum of PCB 28, 52, 101, 118, 138, 153 and 180

Table 3. Proposed potential toxic elements (PTEs) safety criteria for pyrolysis material

	As mg kg^{-1} dry matter	**Cd mg kg^{-1} dry matter**	**Cr total mg kg^{-1} dry matter**	**Cu mg kg^{-1} dry matter**	**Pb mg kg^{-1} dry matter**	**Hg mg kg^{-1} dry matter**	**Ni mg kg^{-1} dry matter**	**Zn mg kg^{-1} dry matter**
Pyrolysis material safety criteria	10	1.5	100	200	120	1	50	600

3.2. ABC yields

Table 4 shows the percentage amount of ABC product- and gas/vapour phase when food grade bone grist (category 3, pig origin) was treated at different (850, 600, 450 and 300 °C) material core temperatures (T) with 20-50-60 minute residence time (tres) at elevated material core temperature in continuously operated reductive environment under industrial conditions, when pressure (P) is under -50Pa. The total processing and residence time is longer than stated residence time (tres) at elevated temperature, such as 850°C^{20min}, which is the process efficiency key performance indicator, which is the final achieved material core temperature with associated tres. All these factors are key performance design quality parameters and specific for each pyrolysis technology designs.

Under industrial production conditions, both the material core temperature of thermal treatment and residence time have been significantly affected the yield of ABC solid products and in parallel the amount of gas/vapour phase. The lowest yield (46 w/w%) of solid ABC product was achieved at material core treatment temperature of 850°C with tres 20 minutes, while the highest yield (71 w/w%) was achieved at low treatment temperature (300^{0}C), even under as long as 60 minutes residence time. The yield of solid char phase is decreased by the increasing treatment temperature while the gas/vapour phase was increased. As majority of the ABC is produced from cattle bones, which having compact and dense character, while it is proven demonstrated for the animal bone feed stream material case, that during industrial conditions high temperature tres is needed under any circumstances, such as material core temperature 850°C under at least tres 20 minutes.

The results indicated that the lower material core treatment temperatures around 450°C generally favor ABC production, but still insufficient to get high quality products, while higher material core temperatures above 600°C – up to 850°C produce lower amount of ABC. In another word, ABC yield decreases with increasing pyrolysis temperature. The material core temperature highy effect product quality. Choosing the optimal final material core process temperature under industrial production conditions is highly depending on the pyrolysis processing design quality and performance that is finally reflected in the economical viability of the commercial production operations.

Table 4. Comparison of ABC (pig bone) yield at 850/600/450/300°C with different residence time (continuous operation, p=-50 Pa, reductive environment)

ABC sample	T (^{0}C)	tres (min)	ABC yield (%)	Gas/oil phase (%)
ABC pig bone	850	20	46	52
ABC pig bone	600	50	47	53
ABC pig bone	450	60	48,7	51,3
ABC pig bone	300	60	71	29

3.3. Total carbon and total organic carbon content

Table 5 shows total carbon and total organic carbon content of different ABC materials. The total carbon and total organic carbon content of ABC materials produced from different animal bone feedstocks was below 10 %.

Table 5. Total carbon and total organic carbon content of different Animal Bone Char samples

ABC sample[1]	Total Carbon (%)	Total organic carbon (%)
ABC cattle bone[1]	7.5	5.0
ABC chicken bone[1]	10	8.1
ABC pig bone[1]	8.4	6.6

[1] Pyrolysis condition: T=850 ^{0}C, tres=20 minute, P=-50Pa

3.4. Total primary and secondary nutrient content of different ABC bio-phosphate products

The nutrient contents and its availability from the ABC recovered bio-phosphate products can be used for evaluation of the agronomic properties. The quality parameters and agronomic value of all type of ABC products that characterize the usefulness in agricultural applications (such as the as the nutrient content) should be declared as total and requiring that information concerning nutrient content be communicated with the product. In all and any cases the nutrient specification should be considered according to the characteristics and its application performance of the product. The mineral nutrient content of the feedstock is largely retained in the resulting ABC, where it concentrates due to the gradual loss of C, hydrogen (H) and oxygen (O) during processing.

Table 6. shows the primary nutrient (N,P,K) content of different category 3 animal by-products and pyrolysed ABC samples. The phosphorus content of ABC recovered bio-phosphate materials is expressed both in the form of element and in oxide form (phosphorus pentoxide percentage by weight, P_2O_5 %). In all cases the total phosphorus content of output ABC recovered bio-phosphate products were higher compared to the relevant feed materials. The phosphorus content of animal bone is variating between 19.5-23.9 % P_2O_5 content while the final ABC product having higher concentrated 28-31.9 % P_2O_5 content.

The total N content, expressed in percentages of dry weight bases. The potassium (K) content of all ABC samples is expressed both in the form of element and in oxide form (potassium oxide percentage by weight, K_2O %). The low nitrogen content of ABC (below 1.5%) is resulting from the nitrogen loss during the pyrolysis process.

Table 7. shows the citric acid soluble P_2O_5 content of different ABC products (pyrolysis condition: T=850°C, tres=20 minutes, P=-50Pa) compared to NPK 15:15:15 mineral EC-fertiliser. In the

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case of ABC products 39-43 % of the total phosphorus contents were citric acid soluble comparing to the rapid release mineral fertiliser where 70% of the total P was citric acid soluble. In this context the ABC is controlled and/or slow release fertiliser.

In all cases the total potassium content of output ABC recovered bio-phosphate products were higher compared to the relevant feed materials. While the volatile organic compounds were removed during the reductive thermal pyrolysis process under negative pressure conditions, the inorganic elements (having higher boiling point) are enriched in the final ABC products.

Table 6. Comparison of primary nutrient contents of different animal by-products and ABC samples

sample	P mg kg^{-1} dry matter	P_2O_5 percentage by weight	K mg kg^{-1} dry matter	K_2O percentage by weight %	N percentage by weight
Pig bone grist (cat.3)	93600	21.5	900	0.11	5.24
Cattle bone grist (cat. 3)	104000	23.9	191	0.02	3.80
Chicken bone grist (cat. 3)	85200	19.5	410	0.05	3.85
ABC cattle bone[1]	127000	29.1	511	0.06	0.897
ABC chicken bone[1]	122000	28.0	2670	0.32	0.876
ABC pig bone[1]	139000	31.9	1100	0.13	1.20

[1] Pyrolysis condition: T=850 ^{0}C, tres=20 minute, P=-50Pa

Table 7. Comparison of total and citric acid soluble phosphorus content of different ABC samples

Sample	P mg kg^{-1} dry matter	P_2O_5 percentage by weight	2% Citric Acid soluble P mg kg^{-1} dry matter	2% Citric Acid soluble P_2O_5 percentage by weight
ABC cattle bone[1]	127000	29.1	54600	12.52
ABC chicken bone[1]	122000	28.0	64600	14.82
ABC pig bone[1]	139000	31.9	51500	11.81
NPK 15:15:15 mineral EC-fertiliser	77200	16.55	54000	12.38

[1] Pyrolysis condition: T=850 ^{0}C, tres=20 minute, P=-50Pa

Table 8. shows the secondary nutrient such as calcium (Ca), magnesium (Mg), Sodium (Na) and sulfur (S), content of different ABC samples. The results also demonstrated that ABC recovered P also having valuable calcium content expressed in Calcium oxid (CaO) (38.7- 43.6 % CaO).

Table 8. Comparison of secondary nutrient contents of different Animal Bone Char samples

sample	Ca mg kg^{-1} dry matter	CaO percentage by weight	Mg mg kg^{-1} dry matter	MgO percentage by weight	Na mg kg^{-1} dry matter	Na_2O percentage by weight	S mg kg^{-1} dry matter	SO_3 percentage by weight

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ABC cattle bone[1]	312000	43.6	3700	0.62	6800	0.92	400	0.10
ABC chicken bone[1]	277000	38.7	5180	0.86	4800	0.65	900	0.23
ABC pig bone[1]	297000	41.5	5723	0.95	7760	1.05	1000	0.25

[1] Pyrolysis condition: T=850 ^{0}C, tres=20 minute, P=-50Pa

3.5. PAHs content of animal bone chars and different industrial available plant based pyrolysis material

PAH16 and PAH19 content of 41 different ABC samples have been carefully investigated and compared. The most probable components were naphthalenes (in 24% of the samples all PAHs are naphthalanes), including most dominantly naphthalene (present in 95% of the samples in average in a concentration of 1,93 mg/kg). 1-, and 2-methylnaphthalenes, which are not listed under US EPA PAH16, are present in 70% of the samples in an average concentration of 0,7-0,8 mg/kg. Phenanthrene shows similar values to these two. Anthracene, fluoranthene and pyrene are present in 36-38% of the samples (over the benchmark), but only in an average concentration of 3 mg/kg. Summary of these most probable PAHs are shown in Table 9 and Table 10.other PAHs are negligible.

Table 9. Average concentration of PAHs compounds in ABC, 16 components, PAH19 components marked with bold and underlined letters.

Name of the PAH compounds	**Avarage concentration mg kg^{-1}**
Naphthalene	1.93
Dibenzo[a,h]anthracene	**1.00**
1-Methylnaphthalene	**0.80**
2-Methylnaphthalene	**0.72**
Phenanthrene	0.72
Chrysene	0.40
Anthracene	0.30
Pyrene	0.30
Fluoranthene	0.29
Fluorene	0.26
Benzo[a]anthracene	0.23
Benzo[e]pyrene	0.16
Benzo[a]pyrene	0.14
Acenaphthene	0.14
Benzo[b]fluoranthene	0.10
Acenaphthylene	0.10
Benzo[ghi]perylene	0.06
Indeno[1,2,3-cd]pyrene	0.04
Benzo[k]fluoranthene	0.04

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Table 10. Occurrence of the most probable PAH compounds in ABC, PAH16 components, PAH19 components marked with underlined letters.

Name of the PAH compounds	Occurrence (%)
Naphthalene	95.12
2-Methylnaphthalene	**73.17**
1-Methylnaphthalene	**70.73**
Phenanthrene	68.29
Anthracene	39.02
Fluoranthene	36.59
Pyrene	36.59
Chrysene	19.51
Benzo[a]anthracene	17.07
Acenaphthene	14.63
Benzo[e]pyrene	14.63
Fluorene	14.63
Benzo[a]pyrene	12.20
Acenaphthylene	9.76
Benzo[b]fluoranthene	9.76
Benzo[ghi]perylene	9.76
Indeno[1,2,3-cd]pyrene	7.32
Dibenzo[a,h]anthracene	**4.88**
Benzo[k]fluoranthene	2.44

Summarizing the PAHs content of all pyrolysis material cases and the results, the scientific evidences fully support that analysis of PAH19 key target contamination compounds is very important and justified, because 1-, and 2-methylnaphthalenes (measured only under PAH19) are very common. Both in the ABCs and plant based pyrolysis materials cases naphthalenes are target PAH contaminations. Naphthalane were present in 83% in the plant based samples in an average concentration of 1,2 mg/kg, while 1-, and 2-methylnaphthalenes probability is 55-66%. Sometimes PAH19 concentration can be twice as much higher as PAH16, so it is also important point to be considered during the definition of limit values, especially in the environmentally sensitive areas. A certain limit value for PAH 16 can be exceeded when measuring PAH19. Table 11 shows an examples for the difference of PAH16 and PAH19 results in different industrial available plant based pyrolysis material.

Table 11. Examples for the difference of PAH16 and PAH19 results in different industrial available plant based pyrolysis material

Name of pyrolysis material sample	PAH16 mg kg^{-1}	PAH19 mg kg^{-1}
BCFR2 (oak chips, France)	5.27	10.33
BCIT1 (wood, Italy)	8.72	10.12
BCUK1 (wood, UK)	7.73	10.51
BCDK4 (wood, Denmark)	6.71	9.36
BCDK5 (wood, Denmark)	6.09	6.76

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Despite the medium temperature processing and long residence time the output product PAH content is still over-high from these different types of pyrolysis technologies. The results are clearly indicating that production technology performance industrial design is one of the most important and critical factor that is ultimately impacting all types of pyrolysis material product quality with low end product quality related to biochar soil applications. It is generally experience that carbonization of plant materials in industrial scale is faster and less energy transfer demanding than carbonization of animal bone materials, due to the significant character difference of the organic content.

Table 12 shows the sum of EPA PAH16, sum of PAH19 contents of the 3R technology produced ABC samples produced at low, medium and high temperature at equal tres conditions, in industrial scale carbonization process at 400 kg/h throughput capacity. The results clearly indicating that both of the two major types of economically interesting animal bone types, but especially the cattle bone, require higher processing temperature down to the material core. The PAH16 and PAH19 concentrations show decreasing tendency in all ABC samples produced from 300°C to 850°C material core temperature at same tres. It is demonstrated, that the high heat transfer efficiency 3R and the thermodynamics of the 3R pyrolysis process do not support formation of PAHs, while the targeted rapid tres in higher material core temperature is the fully safe and economically productive solution to process ABC.

Table 12. PAH16, PAH 19 contents of different Animal Bone Char samples ---

ABC sample[1]	**PAH16**[5] **mg kg^{-1} dry matter**	**PAH19**[6] **mg kg^{-1} dry matter**
ABC cattle bone[1]	0.06	0.06
ABC chicken bone[1]	0.42	0.53
ABC pig bone[1]	0.07	0.07
ABC cattle bone[2]	3.39	4.20
ABC pig bone[2]	3.02	3.94
ABC cattle bone[3]	6.35	7.18
ABC pig bone[3]	5.22	6.43
ABC cattle bone[4]	11.15	13.01
ABC pig bone[4]	8.86	9.92

[1] Pyrolysis condition: T=850 ^{0}C, tres=20 minute, P=-50Pa
[2] Pyrolysis condition: T=600 ^{0}C, tres=20 minute, P=-50Pa
[3] Pyrolysis condition: T=450 ^{0}C, tres=20 minute, P=-50Pa
[4] Pyrolysis condition: T=300 ^{0}C, tres=20 minute, P=-50Pa

[5] Sum of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene and benzo[ghi]perylene

[6] Sum of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene and benzo[ghi]perylene, 1-Methylnaphthalene, 2-Methylnaphthalene and Benzo[e]pyrene.

PAHs content of any biochar is primarily depending on the carbonization processing technology performance design quality that is ultimately defining the processing conditions. Within the REFERTIL project 41 ABC recovered P samples have been investigated, also large number of different other types of plant based pyrolysis material as well. The results clearly justified that all the high quality ABC contained less than 1 mg/kg PAH19. In this context, it has been demonstrated that the advanced thermodynamics of the modern and high quality engineering designed pyrolysis process performance do not support formation of PAHs and dioxins.

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The 1 mg/kg maximum allowable limit of PAH19 is key performance indicator, which under commercial production driven industrial processing conditions can be reached only at high material core temperature, especially in the cattle bone case. The advanced processing condition requirements for plant based pyrolysis materials are far less versus the animal bone case. Therefore, manufacturing and application of ABC Animal Bone Char recovered phosphorus fertiliser require far higher technological level than plant based biochar soil improver. In all pyrolysis material cases under industrial production conditions the analytical characteristic of any biochar products quality performance is the identified fingerprint of the pyrolysis/carbonization processing technology engineering design quality performance and also reflecting the feed material characteristics as well.

3.6. PCBs content of different animal bone chars

Table 13 shows the PCB7 content of different ABC samples. PCBs were not detected from any ABC case, but high chlorine content of the input material was also not expected. As in no any case have been dioxins detected, we have concluded that PCBs presence is a good and under any circumstances safe indicator of these persistent and bio-accumulative chemicals.

Table 13. PCB7 contents of different Animal Bone Char samples

ABC sample[1]	PCB7 mg kg^{-1} dry matter
ABC cattle bone[1]	Not detectable
ABC chicken bone[1]	Not detectable
ABC pig bone[1]	Not detectable
ABC cattle bone[2]	Not detectable
ABC pig bone[2]	Not detectable
ABC cattle bone[3]	Not detectable
ABC pig bone[3]	Not detectable
ABC cattle bone[4]	Not detectable
ABC pig bone[4]	Not detectable

[1] Pyrolysis condition: T=850 ^{0}C, tres=20 minute, P=-50Pa
[2] Pyrolysis condition: T=600 ^{0}C, tres=20 minute, P=-50Pa
[3] Pyrolysis condition: T=450 ^{0}C, tres=20 minute, P=-50Pa
[4] Pyrolysis condition: T=300 ^{0}C, tres=20 minute, P=-50Pa

3.7. PTEs content of different animal bone chars

Certain Potential Toxic Elements (PTEs) such as Mercury, Cadmium, Nickel, and Lead are included in the list of priority substances. Directive 2008/105/EC listing Cadmium and Mercury are identified as priority hazardous substance.

Measuring PTEs in pyrolysis materials is very important, because of the 3x – 5 x re-concentration tendencies during phase separated processing and even higher re-concentration of the PTEs in the final products versus feed material is rather common. This results much higher PTEs concentration in solid output products than in original input average.

PTE content of 41 different ABC samples has been carefully investigated. Table 14. shows the potential toxic elements (PTEs) contents of three different ABC samples. All the 41 different ABCs samples were well below a strict member state regulations and REFERTIL recommended safety limit value.

Table 14. Potential toxic elements (PTEs) contents of different Animal Bone Char samples

ABC sample[1]	As	Cd	Cr total	Cr (VI)	Cu	Pb	Hg	Ni	Zn

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	mg kg-1 dry matter	mg kg-1 dry matter	mg kg-1 dry matter	mg kg-1 dry matter	mg kg-1 dry matter	mg kg-1 dry matter	mg kg-1 dry matter	mg kg-1 dry matter	mg kg-1 dry matter
ABC cattle bone[1]	<1	<0.3	<1	<0.25	2	<1	<0.02	<1	75
ABC chicken bone[1]	<1	<0.3	2	<0.25	12	2	<0.02	1	310
ABC pig bone[1]	<1	0.03	2	<0.25	2	<1	<0.02	1	198

[1] Pyrolysis condition: T=850 ^{0}C, tres=20 minute, P=-50Pa

4. Discussion

For each types of pyrolysis (carbonization) processing technology full industrial production engineering design quality and efficiency performance is the critically important element that will be reflected as unique and recognized fingerprint in the output pyrolysis product quality and safety performance characteristics in all pyroylsis material cases. In this context, application of schlock pyrolysis production technology under market competitive production conditions resulting schlock pyrolysis material output products with low quality, safety and low market value, if any at all. Another important impact factor is the input material characteristics that are also reflected into the output product characteristic.

The developed new generation "3R" Recycle-Reduce-Reuse pyrolysis is a zero emission thermo-chemical decomposition autothermal process that is long term proven field demonstrated under industrial production conditions. The "3R" is specifically developed and designed for high efficient industrial carbonization of animal bone by-product streams in absence of oxygen, under material core temperature up to 850°C.

The residence time important factor to maintain economical industrial productivity during short processing time, while it is unconditionally important to assure equal quality for the processed ABC products. In this context tres is so much important for the technical, economical and legal guarantee management for the Extended Producer Responsibility certification and product labeling documentation, specified as of EU regulations and Customers “right to know” information.

All biological materials might have variations in its natural compositions and character, which is diversified by the nature. The advanced carbonization processing must be able to fully compensate these variations and assure equal quality for the output ABC products. The animal by-product rendering pre-processing sterilization of protein content input material animal bone by-products at 133°C$^{20min, 3bars}$ is upgraded into 3R carbonization final processing 850°C^{20min} performance, which is providing an fully safe and constant quality ABC product stream, while exclude any biological re and trans-contamination risks at later agricultural applications, under any variating climatic and soil conditions.

The 3R is an original solution and specific industrial design for economical Recycling, Reuse and Reduce of organic by-product streams for added value conversion into refined carbon and mineral products with targeted application functionality and total safe character.

The rendering industrial origin, food grade category 3 and industrial grade category 2 animal bone grist processed ABC Bio-Phosphate is a macro porous bio-based fertiliser with as high as 92% pure calcium phosphate and 8% carbon content only and high nutrient density (30% P_2O_5).

The ABC is providing multiple product functionalities in the organic and low input farming sectors, such as organic fertiliser (soil improver, growing medium and/or fertilising product blends. The substitution of mineral phosphate import by recovered Phosphorus is an important goal for the European agriculture already in short term, where the ABC is a high efficient and safe alternative in large extent in European industrial dimension. The fully safe ABC is used at low doses (100–600 kg/ha, in average 300 kg/ha) and in few cases when justified even up to 1,000 kg/ha.

The imported mineral Phosphorus Fertiliser Replacement Value (PFRV) substitution potential in the overall agriculture by ABC bio-phosphate in European dimension is at least >5% (>125,000 t/y

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P_2O_5) in short term (<2025) and continuously over >20% (>500,000 t/y P2O5) in long term (>2030), while 100% in the organic farming sector already in short term and 100% in the low input farming sector in long term.

5. Conclusions

Disrupted nutrient recycling is a problem for Europe and all over the world. The food-safety importance of the Phosphorus content product applications in food-crop productions is critically important. Phosphorus and nitrogen, instead of being used for plant nutrition, are lost across environmental media during food production or are wasted. For phosphate fertilisers the EU is currently highly dependent on import of phosphate rock mined outside of the EU. There is no any possibility to substitute the phosphorus materials with any other alternative materials in the agricultural food crop and animal productions. The Animal Bone Char and generally the biochar case is estimated to be included in the Fertilisers Regulation revision EU law harmonization, whereas the recent initiative on EU fertilising products (COM(2016) 157) will create a level playing field for all fertilising products at EU level, thereby increasing the industry's opportunities to have access to the Internal Market while maintaining the national regulations in place for products limited to national markets, hence avoiding any market disruption. The high nutrient dense Animal Bone Char is product functional organic fertiliser, soil improver, growing medium and/or fertilising product blend. The ABC is one of the few economical product options that can provide safe and long term sustainable solution with high nutrient concentration and agronomical efficiency that is providing economical industrial scale mineral phosphate import substitution potential in the EU28 already before 2030.

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