NEW CHEMICAL SYNTHESES INSTITUTE

Preliminary study of a method for obtaining brown coal and biochar based granular compound fertilizer

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INTRODUCTION

Improving nutrient use efficiency (NUE) and reversing the loss of soil organic matter are major challenges facing farmers worldwide

- Brown coal (BC) that is characterized by very low heating value can be used as a component of organo-mineral fertilizers
- BC contains organic matter in a complex, porous, three-dimensional network, which varies depending on deposit location
- The porous structure and functional groups of BC are important for better nutrient retention and microbial activity in soil
- BC is an alternative material with properties that make it appealing for use as a N fertilizer carrier
- Brown coal – urea blended fertilizers show potential for more efficient use of N in the long term and has environmental benefits in retaining more N in the soil (Rose et al., 2016)

HUMIC ACIDS

- Humic acids are very important components of brown coal and can account 10-80% of its organic matter (Allard, 2006)
- Humic acids contain many functional chemical groups that help to physically modify and improve the chemical properties of the soil and biologically stimulate plant growth
- Humic acid products mainly as plant growth enhancers and as ingredients in fertilizer products are widely distributed throughout the world

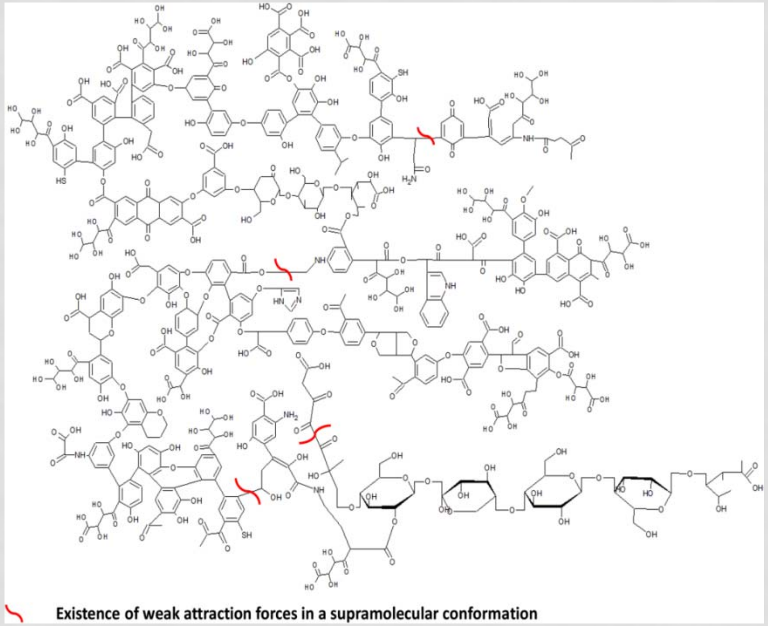


Fig. 1. Hypothetical primary structure of a leonardite humic acid

Source: Erro et al., *Chem. Biol. Technol. Agric.* *(2016) 3:18*

BIOCHAR

- Biochar can contain certain amounts of extractable humic-like and fulvic-like substances (Lin et al., 2012).
- A number of studies show that biochars can reduce nitrate and ammonium leaching from applied nitrogen fertilizers, but the effectiveness depends on the chemical characteristics of biochars and their rate of application (Manikandan and Subramanian, 2013; Rose et al., 2016; Saha et al., 2017)

PURPOSE

The aim of the research was:

- to develop a method for the production of a brown-coal based compound granular fertilizer with improved efficiency, easily available humic acids, and urea in the form of an adduct: $CaSO_4 \cdot 4CO(NH_2)_2$
- to use biochar for coating the compound granular fertilizer
- to evaluate the effect of brown coal based fertilizer and biochar coated fertilizer on wheat growth

The quality of obtained fertilizer products and the possibility of using brown coal and biochar as components of mineral USP fertilizer was evaluated.

RAW MATERIALS

- **Phosphorite** (Djebel Onk, Algeria) was bought from the Chemical Plant "Siarkopol" TARNOBRZEG Sp. z o.o. (Poland)
- **Granular urea** (46% N) - Grupa Azoty Puławy SA (GAP SA)(Poland)
- **Technical sulfuric acid** (conc. 95%) - GAP SA (Poland)
- **Gaseous ammonia** (NH_3 – min 99.8 % wt.) – GAP SA (Poland)
- **Caustic magnesite** - MAGNEZYTY "GROCHÓW" S.A. (Inc.) company (Poland)
- **Dolomite** - Dolomite Mining Company, Górnicze Zakłady Dolomitowe SA, Siewierz Mine (Poland)
- Run-of-mine **brown coal** from Brown Coal Mine "Sieniawa" (Poland)
- **Biochar 1** - plant material after extraction, Pyreg (Germany)
- **Biochar 2** - energy-crop willow, University of Limerick (Ireland)
- **Biochar 3** - wood chips, Fluid SA (Poland)
- **USP fertilizer*** (21% N, 10% P_2O_5, 15.9% CaO, and 7.9% S) – INS (Poland)

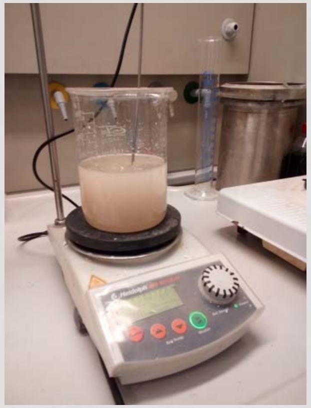
* EP Application no. EP 2 774 907 (Biskupski et al., 2014)

PHYSICO-CHEMICAL PROPERTIES

Parametr	Unit	Brown coal	Biochar 1	Biochar 2	Biochar 3
pH_{H2O}, AR	-	4.3	10.3	9.6	7.4
Electrical conductivity (EC), AR	($\mu S \cdot cm^{-1}$)	1362	2190	353	483
Loss on ignition (LOI), 550°C; 3.5h, DM	(%)	84.45	87.28	94.89	95.99
Water content, 105°C, 4h, AR	(%)	47.70	45.64	5.98	3.09
Pb, DM[1]	($mg \cdot kg^{-1}$)	<4.0	<4.0	<4.0	-
Cd, DM[1]	($mg \cdot kg^{-1}$)	<1.0	1.58	<1.0	-
Total humic acids, DM[2]	(%)	51.02	6.50	6.89	-
Free humic acids, DM[2]	(%)	49.20	4.49	3.44	-
C, DM[3]	(%)	53.46	63.5*)	85.80	84.44
H, DM[3]	(%)	4.42	0.95*)	1.36	1.99
N, DM[3]	(%)	0.76	1.80*)	0.74	0.57
Molar ratio H/C	-	0.99	0.18*)	0.19	0.28

Footnotes: [1]determined by ICP-OES; [2]humic acids determined according to BS ISO 5073:2013; [3] determined by combustion using Perkin Elmer 2400 series CHN analyzer; *) results from biochar certificate, DM – dry matter, AR – as received, - not determined

LAB GRANULATION



Hotplate

Cube mixer (ERWEKA GmbH, Germany)

Pan granulator (ERWEKA GmbH, Germany

Lab dryer

Binding agent preparation → **Bulk materials mixing** → **Pan granulation** → **Drying**

Binding agent preparation:
457 g of urea (46% N)
217 g of technical sulfuric acid (95%)
28.2 g of water

Bulk materials mixing:
1890 g of wet coal
336 g of phosphorite

Pan granulation:
Time of granulation - less than 15 minutes
Pan granulator diameter – 400 mm

Drying:
90°C, 1h

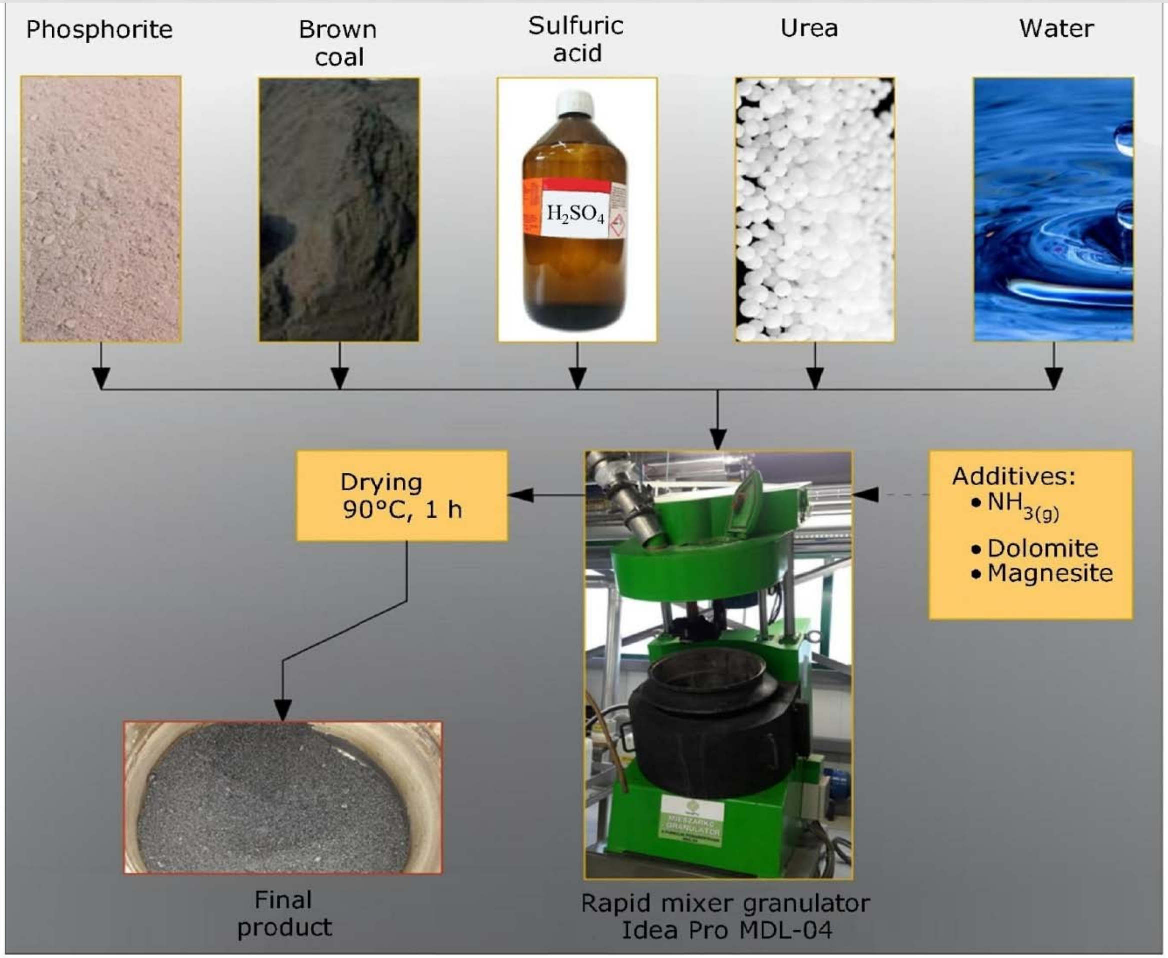
LAB GRANULATION RESULTS

Parameter	Result
Moisture content (105°C, 4h) (%)	30.2
pH of air-dried sample	2.4
pH of dried sample at 105°C	3.7

- Low particle hardness
- For the average size of granules (4.26 mm), the average particle hardness was 2.3 N
- Granules were classified as "soft" because they very easy crushed between the thumb and forefinger (UNIDO and IFDC, 1998)

The research on the binder agent selection and raw material ratios should be studied in order to increase the particle hardness of the fertilizer product.

GRANULATION IN LARGE SCALE



Urea-sulfuric acid solution preparation – a reactor with a heating coat (t=90°C)

Preliminary mixing of bulk materials in a intensive granulator (20 L), turbine speed – 250 rpm, vessel speed – 120 rpm

Granulation (time =20 min)

Drying

RAW MATERIAL CONSUMPTION

No. of trial	Raw material consumption (% wt.)							
	brown coal (BC), DM	urea	phosphorite	H_2SO_4, 100%	dolomite (D)	caustic magnesite (M)	H_2O	NH_3(g)
1	50.0	22.8	16.8	10.4	-	-	2.7	-
2	45.5	20.8	15.3	9.4	9.0	-	2.5	-
3	50.0	22.8	16.8	10.4	-	-	2.7	+
4	47.5	21.7	16.0	9.9	-	5.0	2.6	-

CHEMICAL PROPERTIES OF THE BROWN COAL BASED FERTILIZERS

Parameter	Unit	Trial 1	Trial 2	Trial 3	Trial 4
		BC+USP	BC+USP+D	BC+USP+$NH_{3(g)}$	BC+USP+M
Moisture content (105°C; 3h)	%	29.0	25.7	-	-
Moisture content (90°C; 1h)	%	-	-	9.3	8.3
pH	-	2.6	3.3	5.4	6.2
Ntot.	%	9.85	9.83	9.58	8.26
P_2O_5tot.	%	4.39	3.76	3.85	3.67
NAC+H_2O soluble P_2O_5	%	3.72	3.21	3.03	2.86
H_2O soluble P_2O_5	%	2.60	2.33	1.77	0.69
Mg	%	-	1.38	-	1.88
Ca	%	-	5.90	-	4.30
Loss on ignition					
105°C	%	31.32	28.70	31.50	30.20
400°C	%	72.54	64.55	74.53	70.67
1000°C	%	81.91	73.98	82.61	77.64

Footnotes: NAC+H_2O - neutral ammonium citrate and water soluble

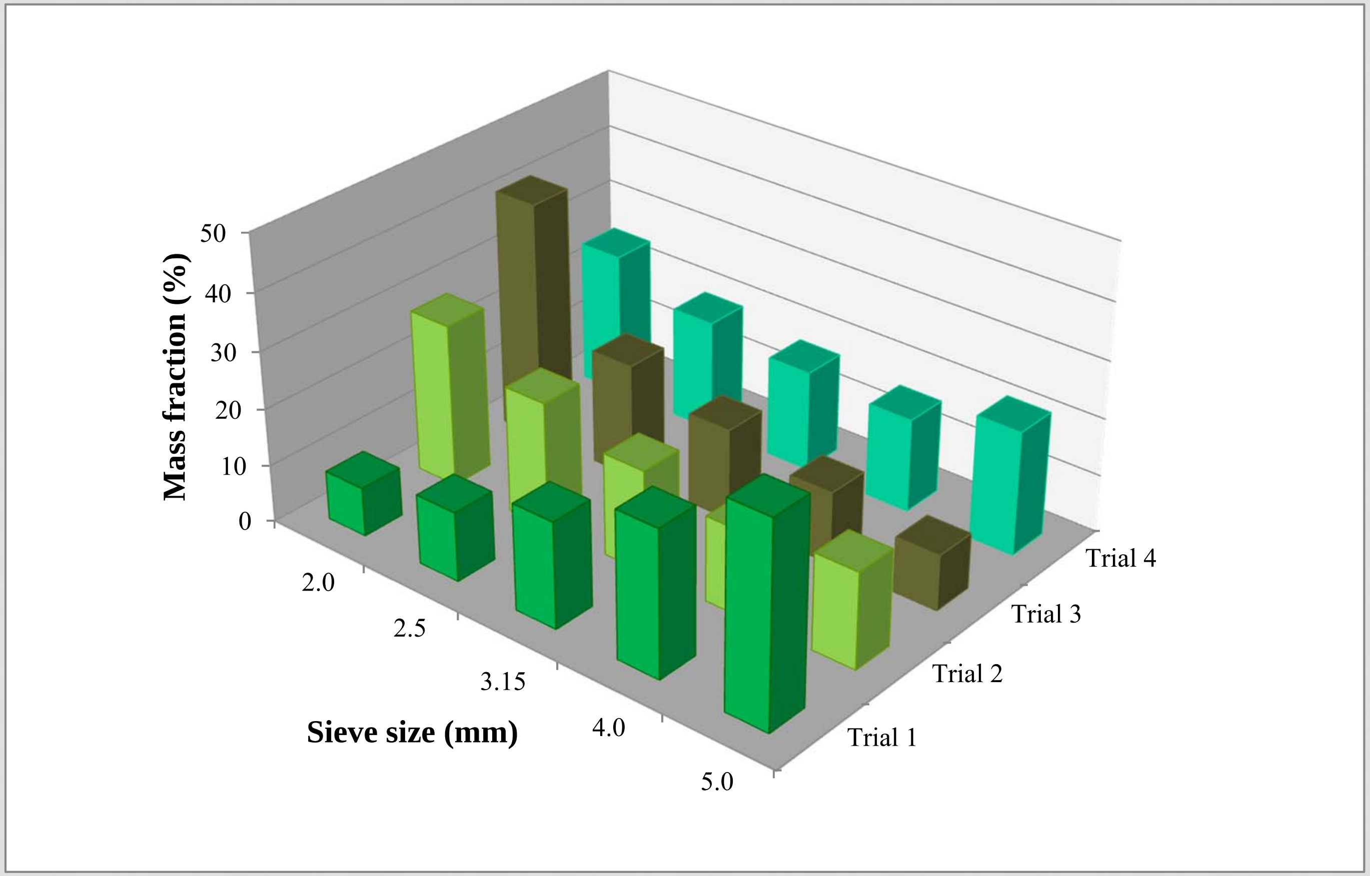
Method of nutrient determination according to the methods dedicated for the fertilizer quality analysis (EC Regulation No 2003/2003)

PARTICLE HARDNESS (N)

Parameter	Unit	Trial 1	Trial 2	Trial 3	Trial 4
Average granule size	mm	4.04	3.94	4.04	3.90
Average particle hardness	N	23.30	18.18	20.05	15.80
Percentage of weak granules	%	10	20	25	30
Average particle hardness after excluding weak granules	N	24.89	21.12	23.38	19.62

Trial 1. BC+USP	**Trial 2.** BC+USP+D	**Trial 3.** BC+USP+NH_3	**Trial 4.** BC+USP+M

PARTICLE SIZE DISTRIBUTION



A vibratory sieve shaker (Retch AS 200, Germany

Fig. 2. Sieve analysis of brown coal based fertilizer

HYGROSCOPICITY

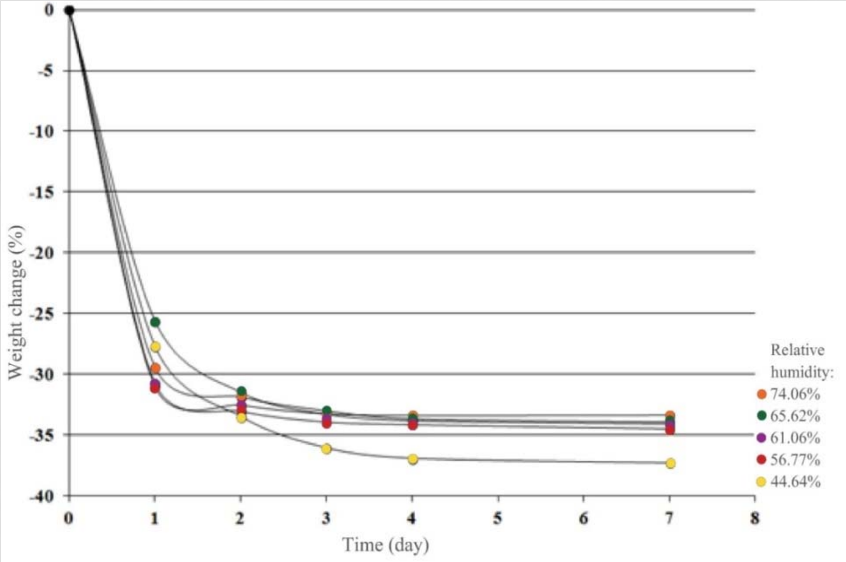


Fig. 3. Weight changes (%) of brown coal under different relative humidity

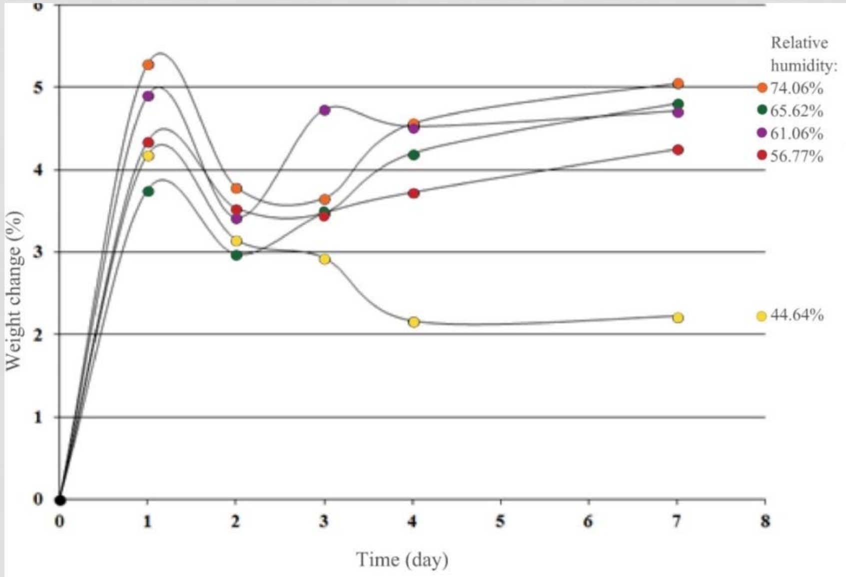


Fig. 4. Weight changes (%) of biochar 3 under different relative humidity

Brown coal sample undergoes natural drying process.
After 7 days, BC contained 10-17% of moisture.

Biochar sample is hygroscopic.
After 7 days in discicator, B3 sample stored at humidity of 56-74% , absorbs about 5% wt. of water.

HYGROSCOPICITY

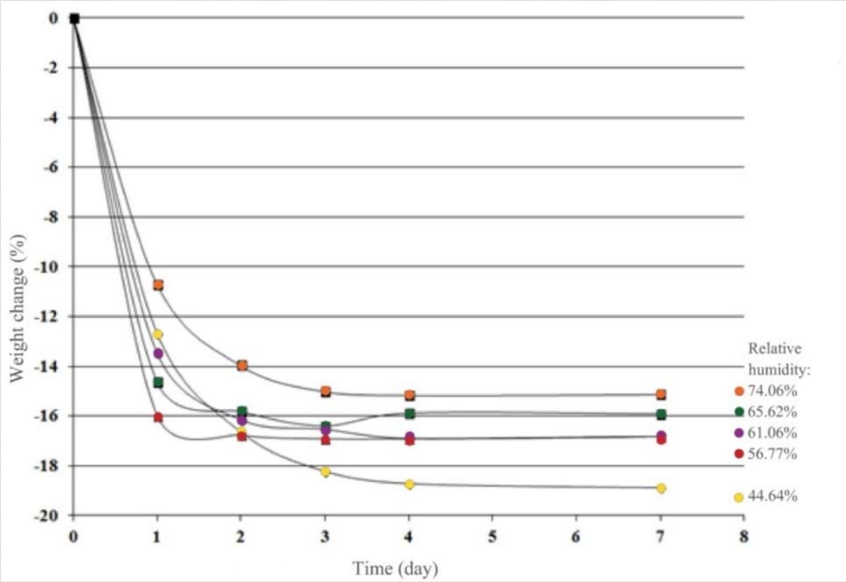


Fig. 5. Weight changes (%) of BC+USP sample under different relative humidity

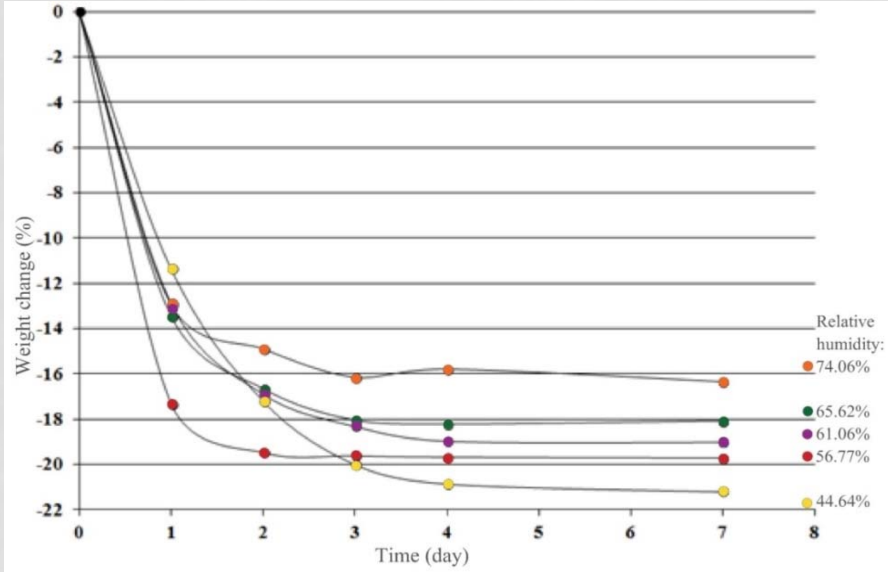


Fig. 6. Weight changes (%) of $BC+USP+NH_3$ under different relative humidity

The weight losses of brown coal based fertilizers was about 15-19% wt. because of water desorption to the environment

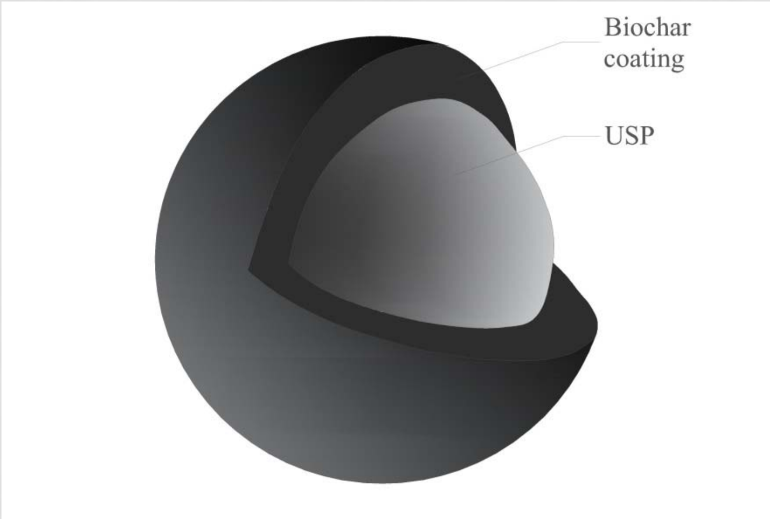
COATING OF USP FERTILIZER GRANULES

A pan granulator (ERWEKA GmbH, Germany)

While USP fertilizer granules were rotating in the pan granulator, the biochar was added and water was sprayed using a hand sprayer (Kwazar Corporation Sp. z o.o., Poland)

The samples were called:

- B1CF - biochar from a plant material after extraction,
- B2CF - biochar from energy-crop willow,
- B3CF - biochar from wood chips.



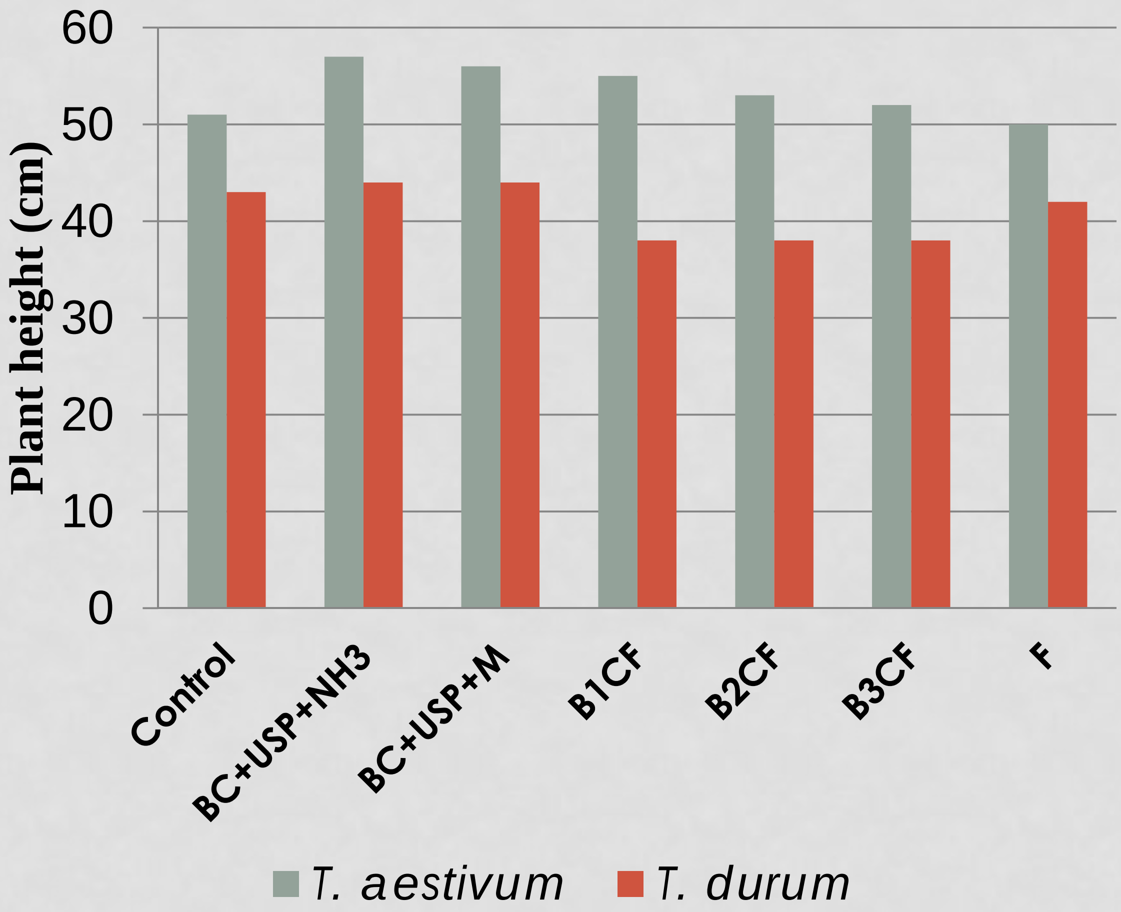
Biochar constituted 10% wt. of the total granules mass.

BIOCHAR COATED FERTILIZER

Parameter	Unit	B1CF	B2CF	B3CF	F
Average granule size	mm	4.46	4.16	4.28	4.46
Average particle hardness	N	41.65	45.20	49.50	61.90
Abrasion resistance	%	2.5	6.1	7.8	0.7

B1CF – biochar 1 coated USP	B2CF – biochar 2 coated USP	B3CF – biochar 1 coated USP	F – USP fertilizer

GREENHOUSE EXPERIMENT



Each treatment received the same dose of NPK before sowing (2.4 g N, 1.3 g P_2O_5, 2 g K_2O per a pot).

Fig. 7. Plant height (cm) at the booting stage of wheat development.

CONCLUSIONS

- Brown coal and biochar can be used as raw materials for fertilizer production
- Brown coal contained about 50% of total humic acids while biochar conatined nearly 6% of total humic-like substances
- Brown coal based fertilizer produced in lab scale using a pan granulator were classified as ’soft’ so the studies are needed to choose a special binder and appropriate raw material ratios to increase their particle hardness
- Brown coal based fertilizer granules produced in small scale using a rapid mixer granulator were characterized by promising hardness and particle size distribution
- Biochar can be used for USP fertilizer coating but the more studies are needed to choose the special binding agent in order to reduce abrasion resistance of granules

Fertilizer Research Centre, INS

Thank you!