

MASTER'S THESIS

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Wet Granulation of Carbonised Bio-ash

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ABSTRACT

Carbon dioxide removal from raw biogas is an expensive process step for small-scale producers of biogas with vehicle standards. Development of new efficient and cheap processes for upgrading of raw biogas to biogas with vehicle standards is a key in order to be able to take advantage of the large unused potential of biogas production from farm plants. One promising process, mainly developed at JTI in Uppsala, utilizes oxides, mainly calcium oxide, from bio-ash to remove carbon dioxide, forming carbonates. The ash product obtained possesses suitable properties as fertiliser in forests, in terms of composition and homogeneity. Thus, combining carbon dioxide removal and carbonation of bio-ash yields both biogas with vehicle standards and a suitable fertiliser product.

Accelerated carbonation of bio-ash using carbon dioxide from biogas produces a fine carbonised powder. However, using the carbonised bio-ash in its original form as a powder leads to handling problems. Dust problems is one problem as it affects the working environment, the actual spreading in the forest is another. Therefore, it is desirable to render the physical shape of the powder by physical methods to avoid these problems. One common technique to handle these problems is particle agglomeration, also called granulation.

In this project, wet granulation of carbonised bio-ash is studied to examine if it is possible to form a suitable product using granulation. Process parameters such as moisture content, binder content and binder type were used to create a statistical design using the statistical program MODDE. Response variables were chosen to be granule moisture content, dry compressive strength and conductivity, in which conductivity was measured by a method developed by the Swedish Forest Agency. A test rig for measuring the dry compressive strength was developed during the project. The results showed that wet granulation is a suitable method to use in order to agglomerate particles, forming larger aggregate with sufficient strength. The leaching properties, represented by the conductivity measurements, were not affected by the actual granulation. Bentonite may be used to increase the strength of the granules, but granules purely made by carbonised ash are also possible to produce, showing relatively high compression strengths.

Furthermore, the binding mechanisms in 100% carbonised ash granules were examined using scanning electron microscopy. The results from the analysis showed that the bonding mechanism in these granules was based on solid bridges formed by precipitation, most probably formed by calcium hydroxide precipitation.

The key finding in the project was that it is possible to granulate the bio-ash using rather simple methods. However, to fully examine the process at a larger scale, scale up tests must be performed. The results from this project are nevertheless promising, which is a big step forward in the development of the wet granulation process of carbonised bio-ash.

SAMMANFATTNING

Borttagning av koldioxid från rå biogas är en dyr process för småskalig uppgradering av biogas till biogas av fordonskvalitet. Utvecklingen av nya effektiva och billiga processer för uppgraderingen av biogas till fordongas är ett viktigt steg för att kunna utnyttja den stora potential som finns för att producera biogas från gårdsbruk. En lovande process, som framför allt utvecklas av JTI i Uppsala, utnyttjar oxider, främst kalciumoxid, för att avlägsna koldioxiden från biogasen, under bildandet av karbonater. Askprodukten som erhålls i processen innehåller lämpliga egenskaper som gör askan lämplig att använda som gödsel i skog och natur, framför allt på grund av dess sammansättning och homogenitet. Således kan uppgraderingen av biogas till fordongas samt karbonatisering av bioaska kombineras för att effektivt producera fordongas samt gödningsmedel samtidigt.

Accelererad karbonatisering av bioaska med hjälp av koldioxid från biogas producerar ett fint karbonatiserat askpulver. Problemet med askan är just dess fysiska form, ett pulver. Detta skapar problem såsom damning, som orsakar arbetsmiljöproblem, samt problem vid själva spridningen. Därför är det eftertraktat att kunna ändra den fysiska formen på pulvret genom fysiska metoder för att undvika dessa problem. En vanlig beprövat metod för att hantera dessa problem är agglomeration, även kallad granulerering.

I detta projekt undersöks möjligheterna för att granulera den karbonatiserade bioaskan för att undvika problemen som listats. Processparametrar såsom fukthalt, mängd bindemedel och typ av bindemedel användas för att bygga en statistisk design med hjälp av statistikprogrammet MODDE. Fukthalt i våta granuler, kompressionsstyrka i torra granuler samt konduktiviteten valdes till responsvariabler, där konduktiviteten mättes genom en metod utvecklad av Skogsstyrelsen. En testmodul för att testa kompressionsstyrkan utvecklades under projektets gång. Resultaten visar att vårt granulerande av karbonatiserad bioaska är en lämplig metod att använda för att agglomera ihop partiklarna i askpulvret, under bildandet av större aggregat med tillräcklig styrka. Lakegenskaperna, som i detta projekt representeras av konduktiviteten, påverkades inte av granuleringen. Bentonit visade sig vara ett potentiellt bindemedel för att öka styrkan, men styrkan ökas endast till en liten grad. Granuler gjorda på enbart karbonatiserad aska visade sig ha relativt höga kompressionsstyrkor.

Utöver granuleringsförsöken studerades även granuler gjorda på 100% karbonatiserad aska, för att undersöka hur de binds samman. Resultaten från analysen visade att granulerna hålls samman med hjälp av solida bryggor mellan partiklarna, mest troligt på grund av utfällning av Ca(OH)_2 .

Den viktigaste upptäckten i projektet var att den karbonatiserade askan var relativt enkel att granulera, med enkla metoder. Innan processen börjar användas i större skala måste dock uppskalningsförsök genomföras. Resultaten från detta projekt är emellertid lovande, och ett stort steg framåt i utvecklingen av granuleringsprocessen.

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GLOSSARY

- Absorption – A process in which one phase enters another bulk phase
- Accelerated carbonation – Enforced treatment of ash with carbon dioxide
- Adsorption – Adhesion of atoms or molecules to a solid surface
- Attrition – Process in which wearing or reduction in size occurs
- Ballability – The ability of a formulation to form granules
- Bentonite – Clay mineral commonly used as solid binder in the production of iron ore pellets, consisting of the mineral montmorillonite
- Bio-ash – Ash originating from combustion of renewable wood fuels
- Biogas – Gas mixture of mainly methane and carbon dioxide produced from organics wastes
- Bottom ash – Ash removed from the bottom of a furnace
- Capillary forces – Resulting forces of capillary action
- Carbonised ash – Bio-ash which have been treated with carbon dioxide
- Carbonation – Material treatment method using carbon dioxide
- Coalescence – Process in which two phases pull each other together
- Conductivity – The ability to transfer electrical charges
- Confidence intervals – An interval estimate of the certainty to find an observation within a predetermined limit of certainty
- Consolidation – Densification of a granular material
- Contact angle – The angle that a liquid phase gets in contact with a solid surface, in a solid-liquid-vapor system
- Deleted studentized residuals – The ratio of the residual to its estimated standard deviation
- Drop number – The number of drops from a specified height a granule can take before breaking
- Dry granulation – Granulation methods not involving liquid components, often using compression techniques
- Fertiliser – Supplies of nutrients to soils and environment
- Fly ash – Ash obtained from cleaning of exhaust gas
- Granulation – Method to agglomerate particles together, forming large aggregates
- Granule – Large grain consisting of distinguishable particles
- GROT – Swedish abbreviation for “grenar och toppar” (branches and twigs)
- Hardening – Process in which bio-ash is treated with carbon dioxide
- Interaction – A factors dependence on another factor
- Leaching – Solubilisation of inorganic compounds
- Lime effect – Alkaline effect of forest residues and ashes
- Liquid binder – Liquid used to bring particles together in wet granulation
- Main effect – The effect of changing a factor on a response
- Mixed fuel – Fuel which contains fuels of different origin

MODDE – Statistical software used in the project, created by UMETRICS AB

Model validity – Measure of the validity of a statistical model

Nucleation – Formation of a new phase by combining other phases

Outlier – An observation in a data set that is poorly explained by a statistical model

Pelletisation – Synonym to granulation

R^2 – Measure of how good a statistical model may predict future observations, also called goodness of prediction

R^2 – Measure of how well the raw data fits to a statistical model, also called goodness of fit

Raw ash – Untreated bio-ash

Reproducibility – Measure of the ability to reproduce experiments in a statistical model

Residual – The difference between an observed value and an estimated value by a statistical model

Self-hardening – Carbonation of ash using carbon dioxide from the air

Solid binder – Molecule used to enhance properties of final granules

Standard deviation – A measure of the variation in a data set around the mean value

Surface tension – The tendency of a fluid surface to minimize its surface area

Wet granulation – Granulation method utilizing liquids to bring particles closer together

Wetting – Ability of a liquid to stay in contact with a solid surface

ABBREVIATIONS

Ben	Bentonite content in formulation in weight-% in the statistical analysis
BFB	Bubbling fluidised bed
CaO	Calcium oxide
CaCO ₃	Calcium carbonate
Ca(OH) ₂	Calcium hydroxide
CFB	Circulating fluidised bed
CO ₂	Carbon dioxide
CO ₃ ²⁻	Carbonate ion
DS	Dry substance
EC	Electrical conductivity
GWh	Gigawatt-hours
H ₂ CO ₃	Carbonic acid
HCO ₃ ⁻	Bicarbonate ion
JTI	Swedish Institute of Agricultural and Environmental Engineering
kWh	Kilowatt-hours
LTU	Luleå University of Technology
MLR	Multiple linear regression
Moi	Moisture content of formulation in the statistical analysis
pH	Measure of concentration of hydrogen ions
Raw	Raw ash content in formulation in weight-% in the statistical analysis
RPM	Rotation per minute
SD	Standard deviation
SFA	Swedish Forest Agency
SEK	ISO code for the Swedish currency
SEM	Scanning electron microscopy
TWh	Terawatt-hours

1. INTRODUCTION

1.1 BACKGROUND

The Swedish Gas Association published in December 2015 their report “Förslag till nationell biogasstrategi”. In the report, they suggest that Sweden in the year 2030 should produce 15 TWh of biogas, as a step to fulfil the national target to have a fossil free vehicle fleet in Sweden in 2030. From these 15 TWh, approximately 12 TWh would be used as a fuel for vehicles. The total production of biogas was 1.8 TWh in 2014, of which 1.0 TWh was upgraded to vehicle standards [1]. This indicates that the production of biogas during the years to come has to increase significantly, if the suggested amount of biogas in 2030 is to be met.

Biogas can be produced in several different plants. These can be summarized into the following types:

- Sewage treatment plants
- Co-digestion plants
- Farm plants
- Industrial plants
- Landfills
- Gasification plants

The majority of biogas is produced in anaerobic digesters using microorganisms. The feedstock for the process is in general organic wastes, which can origin from the agricultural sector, industrial sector, municipal waste sector or aquatic sector. Traditionally, biogas production by anaerobic digestion has been related to animal manure or treatment of sewage sludge [2].

Statistics reveals that 277 biogas production facilities were in operation in Sweden in 2014, of which 37 were farm plants. Biogas in farm plants is often utilized in cogeneration of heat and power, used by adjacent buildings and facilities, but the amount of biogas is often higher than the demand for heat and power at the farm plants. The gas may then be torched, or better up upgraded to vehicle standards. The total production of biogas in farm plants was estimated to 44 GWh in 2014 [3]. However, the potential for biogas production in farm plants is estimated to 5.9 TWh [4]. This clearly indicates that farm plants have a huge unused potential to produce biogas, and more favourably, biogas with vehicle standards.

In order to produce biogas with vehicle standards, the raw biogas must be upgraded with respect to methane content. The raw biogas is composed of 50-70% methane, 30-50% carbon dioxide, and small amounts of hydrogen sulphide and ammonia [5]. Carbon dioxide is the main component that has to be removed, as it is present in the highest amount of the impurities. Commercial methods to remove carbon dioxide from methane includes:

- Adsorption

- Absorption
- Membrane separation

Unfortunately, these methods require expensive equipment, especially for small-scale producers such as farm plants. The cost for upgrading of 50-100 Nm³ raw biogas per hour, which is a common biogas flow in farm plants, has been calculated to approximately 0.35 SEK/kWh. However, the cost has also been evaluated to be as high as 0.50 SEK/kWh. This cost to produce upgraded biogas is relatively high for small-scale producers, as biogas flows higher than 200 Nm³ per hour may have an upgrading cost as low as 0.10 SEK/kWh [6].

An alternative technique under development is accelerated carbonation of bio-ash, using carbon dioxide from raw biogas. The bio-ash, which is obtained from combustion of renewable wood fuels, contains a high amount of calcium oxide, which in contact with water and carbon dioxide forms calcium carbonate. When this reaction takes place, the bio-ash is considered to be hardened, which is a key process in order to use the bio-ash as a fertiliser in the forest. Usually, the hardening of bio-ash is performed by self-hardening in piles outdoor, using carbon dioxide from the air. This gives an uneven hardened bio-ash product, often hard to utilize in an efficient way. In addition, this process may take months to complete. In practice, this means that self-hardening of bio-ash not only produce a highly heterogeneous product, but also uses up most often expensive landfill areas [7].

A clear synergic effect can be found by combining carbon dioxide removal from biogas and accelerated carbonation of bio-ash. The combination of these processes simultaneously produces a homogeneous fertilizer product for the forest, and biogas with vehicle standards. In addition, this process is much cheaper than the commercial technologies for upgrading of biogas to vehicle standards. The cost is estimated to approximately 0.24 SEK/kWh for a 1 GWh plant, which is in the range of farm plants [8].

The bio-ash produced by accelerated carbonation has a very small particle size compared to the self-hardened ash. In order to efficiently distribute the bio-ash back to the forest, the ash must be enlarged with respect to its particle size, mainly to simplify the handling of the ash. Also, the relative small particle size may possess dusting problems when dried. These problems can be avoided by for instance granulation by wet or dry methods. Thus, combining accelerated carbonization and granulation may produce an ash product suitable for fertilizer use in the forest [9].

Previous studies on the applicability of bio-ash have proven that both the carbonized ash and untreated ash is approved when considering the elemental composition of the bio-ashes. However, the conductivity measurements on the untreated ash are too high in order to be spread in the environment. The conductivity measurements on the carbonized bio-ash are however approved, which is due to the carbonation of the ash [10].

Up to this day, investigations regarding development of the process have been aimed towards accelerated carbonation of bio-ash, and the possibilities of using carbonised ash as a source of fertiliser in the forest. Now, the next step in order to present a full idea of the process is to study granulation of the carbonised bio-ash. The first step in developing a full-scale granulation process involves testing the granulation procedure in lab scale. This is the basis of this thesis.

1.2 OBJECTIVES

The objectives in this project are to:

- Investigate if wet granulation is a suitable process in order to increase the particle size of carbonised ash to facilitate a good way to handle the ash, not only after carbonation but also in the spreading of the ash in the forest.
- Study the effect of granulation in terms of compression strength and leaching characteristics by using different recipes of binders and carbonised bio-ash.

1.3 SCOPE

The scope of this project was to investigate if carbonised bio-ash is possible to granulate using wet granulation. The granulator used was of disk type, which is a tumbling granulator. The variables used as design variables were the initial moisture content, bentonite content and raw (untreated) bio-ash, all in weight-%. Bentonite and raw ash content were defined as the weight-% of the dry formulation, while moisture content was defined on the wet formulation. The liquid binder used in the project was deionized water. Several process variables, such as rotation speed of the granulator, angle of the granulator, granulation time and liquid binder delivery method, were not varied due to time constraints. Type of liquid binder and variation of ashes were also not varied for the same reason.

The response variables used in the project was dry compression strength, wet granule moisture content and conductivity in contact with water. Dry compression strength was the most important variable, as the main scope was to produce granules with sufficient strength. Wet granule moisture content was used as a response variable to act as a rough measure of porosity. Conductivity was measured to characterise the granules according to the recommendations of the Swedish Forest Agency, abbreviated SFA. The characterization of the carbonized ash and raw ash was based on particle size distribution and analysis on particle shape by scanning electron microscopy (SEM). The SEM was also used to study the bonding in the final dry granules.

2. LITERATURE REVIEW

The section on literature review covers the areas involved within the project. Firstly, a general description of bio-ash and bio-ash formation is given in order to discuss the source of bio-ash and how it is formed. Bio-ash recycling and recommendations are further discussed to present the requirements set on the final bio-ash product after granulation. The general carbonation process is further discussed, as the carbonation is the preceding process step in the process under development, followed by a thorough description of granulation theory, applications, methods and equipment. Finally, theory on the leaching characteristics of bio-ash and granulated bio-ash are discussed.

2.1 BIO-ASH AND BIO-ASH FORMATION

Whenever a fuel is combusted, residues are formed. Ash is a residue generally consisting of inorganic material and unburnt organic material originated from combustion of organic fuels such as wood, coal, wastes or other solid fuels [11]. The composition of the ash depends highly on the fuel that has been combusted, and the conditions at which the fuel was combusted.

2.1.1 Production and use of ash in Sweden

The total production of ashes in Sweden was 1.5 million tons in 2010 [12]. The ash was produced from combustion of wastes, mixed fuels, biofuels, coal, and other fuels. In Figure 1 the production of ashes from different fuels is presented as percentages of the total ash production in 2010.

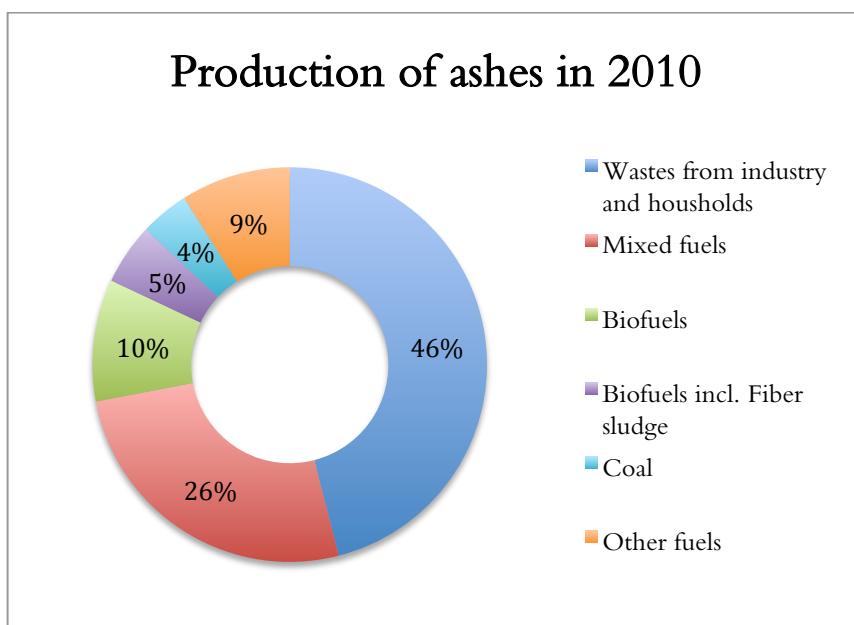


Figure 1: Production of ashes in Sweden in 2010 [12].

2. LITERATURE REVIEW

The total production of ash from biofuels was estimated to approximately 150 000 tons in 2010, and the production of ash from biofuels including fibre sludge from the pulp and paper industry was 70 000 tons. "Other fuels" in Figure 1 is represented by peat and recycled wood.

Ash is used in several applications, including as construction material at landfills, as road construction materials, or as construction materials for surfaces. These applications correspond to approximately 68% of the total use of ash in Sweden. Presented in Figure 2 are the majority of the applications in which ashes can be found.

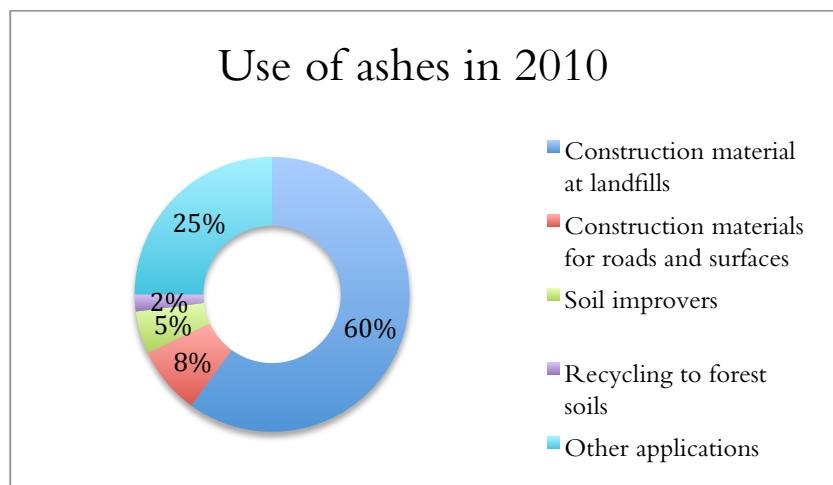


Figure 2: Use of ashes in Sweden in 2010 [12].

Worth noting from the figure is the low fraction of recycled ashes to forest soils, only about 2 %. The "Other applications" fraction includes coverage of mining wastes, filler material in oil caverns, landfill, and 10% unknown or non-reported use [12]. This fraction is rather high, compared to the others. A lot of bio-ash produced in Sweden is also not utilised in the most effective way, as several companies has to pay to dispose some amounts of the ash. This is an indication that the ash production has not fully found its appropriate customers [13].

2.1.2 Ash-forming elements in wood fuels

Ashes from combustion of wood fuels contain mainly components that originate from the combusted wood fuel. Other components may be impurities that followed the fuel into the combustion chamber, such as sand or stones. Presented in Table 1 is the composition of inorganic elements in different parts of common Nordic trees [14].

From the table it can clearly be seen that the distribution of inorganic components varies highly not only between different species of trees, but also between individual parts of the trees. In stem wood, the total inorganic content may be as low as 0.15 %, while in leaves the inorganic content may be as high as 4–5 %. The major component in all parts of the trees is calcium, with exceptions for leaves and shoots, where potassium is the major component. Also, needles of fir contain a high amount of silicon. As is evident from Table 1, combusting different species of trees and different parts of the trees may give a high variety of ash compositions.

The inorganic components in the wood fuel are either bound to organic compounds or inorganic minerals. Common compounds in which the inorganic elements are bonded to are oxalates, carbonates, sulphates, or carboxylic groups [15]. The most reactive components of these examples at the combustion conditions are the organic compounds, producing ashes as a result [16].

Table 1: Distribution of inorganic elements in common Nordic wood species [14].

Part of tree	Species	Distribution of inorganic elements [mol-%]										Total inorganic content [mg/kg DS]
		Na	Mg	Al	Si	P	S	Cl	K	Ca	Mn	
Stem wood	Fir	0.7	11.2	0.2	6.0	0.4	4.5	4.1	15.8	51.8	5.1	0.2
	Pine	1.4	16.3	0.3	9.2	2.8	6.2	5.0	21.9	33.6	3.1	0.3
	Birch	0.5	10.0	0.2	7.2	4.2	6.7	3.0	21.2	41.8	4.9	0.3
	Aspen	0.8	13.5	0.3	2.6	7.1	4.5	1.1	40.3	28.7	1.0	0.1
Bark	Fir	0.3	10.1	1.0	1.7	4.1	3.2	2.1	14.7	58.9	3.7	0.2
	Pine	0.3	9.6	9.0	0.6	10.9	2.6	1.1	12.7	42.3	1.7	0.2
	Birch	0.2	4.5	0.2	1.4	4.7	3.5	1.4	14.7	66.0	3.3	0.1
	Aspen	0.1	10.9	0.1	0.6	4.1	3.1	0.2	23.4	56.4	0.9	0.1
Twigs	Fir	1.2	10.3	2.3	9.6	9.6	6.7	2.5	25.0	29.6	2.5	0.8
	Pine	0.5	9.1	3.8	3.5	8.5	5.7	1.8	24.2	41.1	1.4	0.4
	Birch	0.7	6.8	0.3	0.9	9.8	5.7	1.2	28.5	43.5	2.4	0.3
	Aspen	0.2	5.4	0.3	1.4	4.7	3.1	0.5	30.7	53.0	0.7	0.1
Needles	Fir	0.3	6.1	0.4	33.5	7.0	3.1	2.0	15.5	28.4	3.6	0.1
	Pine	0.3	8.5	3.6	5.0	10.6	6.8	3.0	31.5	26.6	3.9	0.2
Shoot	Fir	0.1	5.6	0.2	1.6	18.6	6.2	4.6	56.1	6.3	0.7	0.1
	Pine	0.3	8.2	2.4	5.2	16.4	7.6	3.0	44.1	1.6	0.7	0.4
Leaves	Birch	0.2	11.0	0.2	1.5	13.4	7.0	0.7	31.9	30.1	3.9	0.2
	Aspen	0.0	9.6	0.1	0.4	13.2	6.3	1.1	48.8	19.4	1.0	0.1

2.1.3 Combustion of wood fuel

Combustion of wood fuel occurs in a series of steps, including heating, drying, pyrolysis and combustion. Firstly, the wood fuel is heated by the heat inside the combustion chamber, coming from the walls of the furnace or radiation from the flame. When the temperature has reached 100°C, the material will be dried and water will be boiled off, after which the temperature is steadily increasing. At 200°C, the organic compounds will start to decompose, while at 500°C the pyrolysis will start. This is the start of the actual combustion, as the organic compounds form carbon, which is gasified at this temperature. This step may produce a reductive atmosphere. The final combustion may be operated at temperatures up to 1500°C, depending on operating conditions [17].

As the temperature is increased, more and more reactions take place involving the inorganic components. The ash-forming elements are in an early stage in oxidic forms, except for chlorine that is present in the form of chlorine gas, Cl₂ (g), or hydrochloric acid, HCl (g). Components such as calcium, magnesium and silicon are most often present as oxides at all combustion temperatures used in industry. Potassium and sodium, on the other hand, react quickly with water to form hydroxides, NaOH and KOH, in either the gas phase or in the liquid phase, depending on the temperature. Sulphur and phosphorus produce similarly to carbon gaseous oxides. Elements such as aluminium, manganese and iron produce heavy oxides that most often are found on the bottom of the furnace [16].

The components present in the ash have all different properties. This means that they all react differently with each other and with the environment. A common way to classify the oxides is to split them into two groups: acidic and basic oxides. The definition of an acidic oxide is that it

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lowers the pH in contact with water. The definition of a basic oxide is the opposite; in contact with water the pH will increase. Table 2 presents the most common oxides while combusting wood fuel, classified as acidic or basic oxides. The position in which the compound is presented in the table gives information of the relative reactivity of the compounds. The reactivity decreases down the table.

Table 2: Classification of oxides as acidic or basic oxides [16].

Oxides	
Acidic	Basic
P ₂ O ₅ (g)	K ₂ O (s) (KOH)(l,g)
SO ₂ (g)/SO ₃ (g)	Na ₂ O (s) (NaOH)(l,g)
HCl (g)	CaO (s)
SiO ₂ (s)	MgO (s)
CO ₂ (g)	H ₂ O (g)
H ₂ O (g)	

2.1.4 Combustion furnaces

The furnace in which combustion of wood fuel is performed can be of several types. The simplest type of furnace is the grate boiler, in which the wood fuel is combusted on grates. The temperature in these boilers is usually between 1000°C and 1150°C. Powder burners are another type of burner, with operating temperatures around 1200°C.

Fluidised bed boilers are commonly used in larger plants. Basically two types of fluidised beds are used; the circulating fluidised bed (CFB) and the bubbling fluidised bed (BFB). In these boilers, wood material is finely ground and mixed with inert sand, which is used as bed material. The difference between the two types of fluidised beds are the flow pattern inside the boilers; in the circulating fluidised bed the material swirls inside the boiler, while in the bubbling fluidised bed the bed is boiling. Fluid beds are especially suitable for moist biofuels, such as wood fuel. The operating temperature in these boilers is in the range of 850 – 900°C [18].

2.1.5 Fly and bottom ash

In all types of boilers, air is added in order to combust the fuel. Produced gases are at the same time withdrawn from the boiler. While this happens, some ash may follow the gas stream, which therefore has to be removed from the exhaust gas. All boilers have some kind of cleaning device to separate ash particles from the gas stream. Common separators are cyclones, bag filters and electrostatic filters. The ash fraction that is removed from the exhaust gas is called fly ash. The ash that is left inside the furnace, however, is called the bottom ash. The fly ash has in general a much finer particle size distribution than the bottom ash [18]. Typical distributions between bottom ash and fly ash is presented in Table 3 [11].

When removing the ash from the boiler, it may be removed dry or wet. Dry ash is preferred when considering further processing of the ash, for instance hardening of the ash. Dry ash is though a source to dust, health and safety problems. Wet ash, on the other hand, decreases the dustiness of the ash, but spontaneous hardening may take place, which will render a controlled hardening process more difficult. However, addition of water to remove the ash is a much

simpler method. Thus, depending on the usage, wet or dry output of the ash must be considered [18].

Table 3: Distribution of ash to bottom or fly ash for three types of boilers [11].

Furnace type	Bottom ash (%)	Fly ash (%)
Grate boiler	70 – 80	20 – 30
Powder burner	5 – 20	80 – 95
Fluidized bed	~10	~90

2.2 ASH RECYCLING TO FOREST SOILS

Whenever woody biomass is harvested in the forest, nutrients and lime effects are removed from the forest. When logging residues are used in the industry, the factor of removal of nutrients and lime effects is raised from 1.5 to 4, over the cycle. As bio-ash includes all the nutrients that the trees have, ash is a good source for nutrients for forest soils. Ash recycling to forest soils has been recommended by the Swedish Forest Agency since 1998 [18]. Figure 3 shows the number of hectares at which ash was spread on between 2004 and 2014 [19].

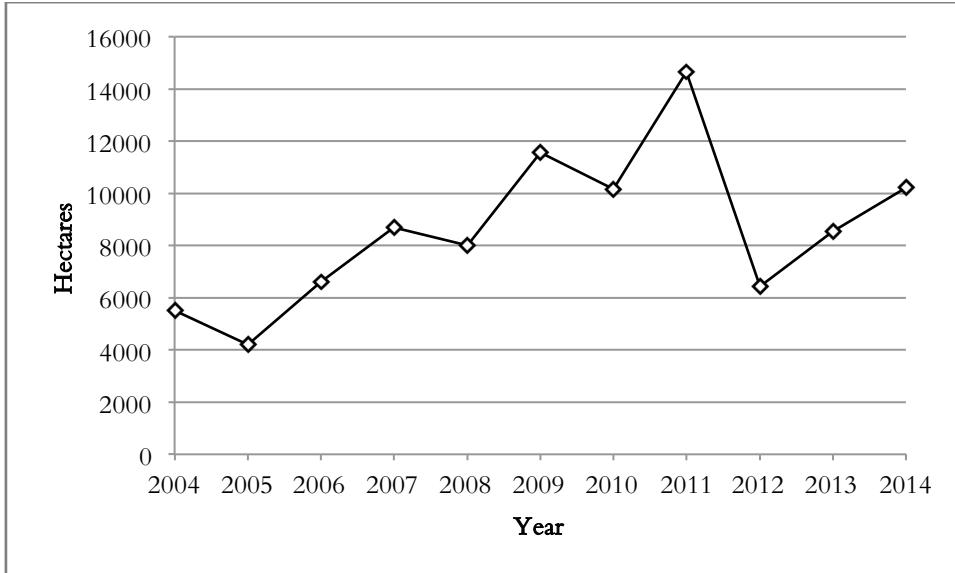


Figure 3: Diagram of the number of hectares at which bio-ash was spread on in the years 2004 – 2014 [19].

2.2.1 The bio-ash cycle

In the 90's, the use of logging residues (Swedish abbreviation GROT, which from now on will be used) increased rapidly, due to an attempt to increase the energy production from renewable sources. In recent years the amount of used GROT has been up and down, as can be seen in Figure 4, where both GROT from thinning and final felling is included. From the figure, it is clear that the amount of used GROT from final felling varies a lot, while the use of GROT from thinning has increased steadily during the years [19].

As was presented in Table 1, the majority of the nutrients in the wood exist in the twigs, needles, shoots, leaves, and bark. Only a small amount of nutrients is found in the stem wood. Twigs, needles, shoot and leaves are major parts of GROT, which makes GROT a very important nutrients source for forest soils. If GROT is removed in a high amount, the lack of nutrients and lime effects will lead to damage the soil, and in turn the ground water quality. If no nutrients is returned to the forest, the bio-ash cycle is interrupted, leading to environmental

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issues [18]. A general picture of the bio-ash cycle is given in Figure 5, in this case based on GROT as the wood source. It should be noted that the figure is only a small part of the whole forestry cycle, as the cycle presented in Figure 5 is based only on the nutrient and lime effect sources obtained from the bio-ash.

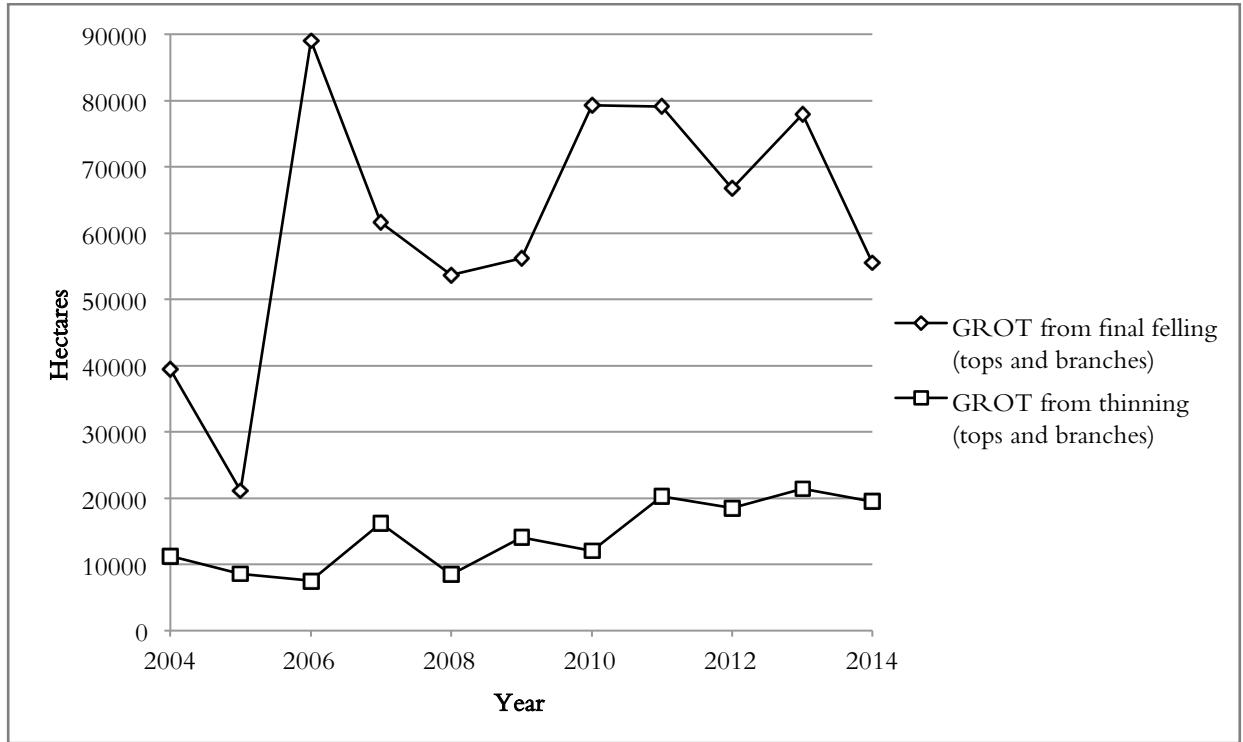


Figure 4: Number of hectares from which GROT was removed in the years 2004 – 2014 [19].

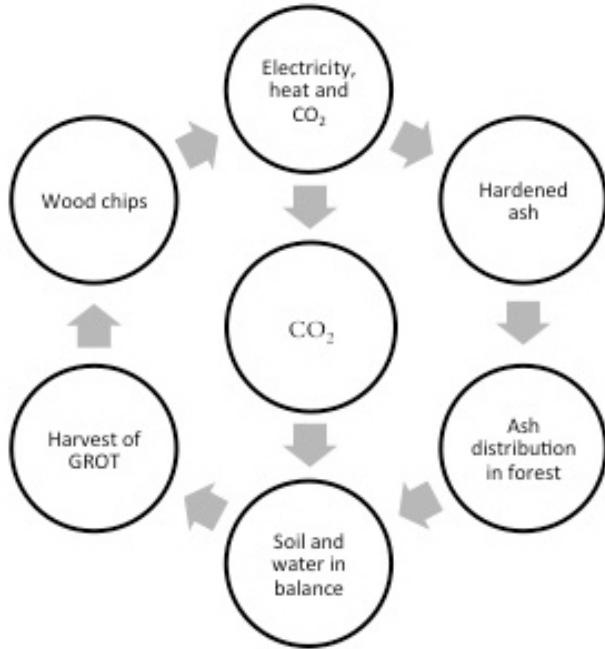


Figure 5: General picture of the bio-ash cycle [18].

2.2.2 Acidification of forest soils

Trees obtain their nutrients from the ground, and the carbon from carbon dioxide in the air. For every positive atom that the tree uses, one hydrogen atom is released to the ground. Similarly, the trees releases a hydroxide group for every negative atom or molecule it uses. As the uptake

of positive atoms or molecules often exceeds the uptake of negative atoms or molecules, the trees will acidify the ground. This, in turn, means that the tree itself has a basic character, as it contains more basic compounds than acidic compounds. However, when the tree dies the basic components in the trees will neutralize the acidified ground, leading to a more neutral pH. If the tree is harvested and removed from the forest, the neutralizing effect will disappear, as well as the nutrients. This leads to acidified grounds, which may harm not only the forest soil itself, but also ground water, as the mobility of many common metal ions is increased at lower pH values [20].

The acidification of forest soils is highly accelerated when GROT is removed from the forest. Therefore, ash recycling is a very important step at soils where a high amount of GROT has been removed from the ground [18].

2.2.3 Suitable ashes and compositions

Ash used as fertiliser in forest soils should come from combustion of wood, as these ashes most often have the appropriate compositions. The ash should not contain impurities such as sand or other contaminations, as the source of these contaminants may come from fossil sources. Therefore, bottom ashes from fluidised beds are seldom used, due to the amount of sand that can be present in these ashes. Fly ash from fluidised beds, however, is a suitable ash as it often has a suitable composition with a low content of non-combusted organics. Ashes from grate boilers are also suitable for recycling, especially bottom ash [18].

Table 4: Recommended grades in ash for ash recycling set up by SFA [9].

Element	Recommended grades	
	Lowest	Highest
Macro nutrients [g/kg DS]		
Calcium	125	
Magnesium	15	
Potassium	30	
Phosphorous	7	
Micro nutrients [mg/kg DS]		
Boron		800
Copper		400
Zinc	500	7000
Arsenic		30
Lead		300
Cadmium		30
Chromium		200
Mercury		3
Nickel		70
Vanadium		70

The composition of the ashes is a highly important property of the ash, and even though the ash may come from renewable wood sources it may be inappropriate to recycle. Therefore, composition recommendations have been set up by SFA. The recommendations are presented in Table 4.

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If the recommended lowest grades are undershot, the possibility to add the specific element should be considered. In addition to the inorganic components in the ash, the grade of uncombusted organic material, dust, sand, gravel or binder may render the grades of the elements presented in Table 4. The ash should also not contain more than 10 kBq/kg DS cesium 137 [9].

2.2.4 Recommendations in Sweden

In addition to the recommended lowest and highest grades of elements in the ash, several other aspects are included in the recommendations from SFA. First of all, the ash product should have been successfully hardened, and possess slow leaching kinetics. These are the most important properties the ashes have. In general, these recommendations are set in order to avoid chocking effects when the ash is recycled back to the forest soil. The guideline is that the ash should be dissolved in a time period of 5 – 25 years [9].

The parameters that affect the rate of dissolution are the degree of hardening of the ash and the form of the ash. Unhardened ash contains calcium oxide, CaO, which quickly reacts to calcium hydroxide, Ca(OH)₂, in contact with water. Ca(OH)₂ is easily solved in water, why unhardened ashes has quick leaching kinetics. Well-hardened ash, however, contains calcium carbonate, CaCO₃, which is much harder to dissolve, leading to slower leaching kinetics. Small ash particles have a large surface area, which will accelerate the dissolution of the ash when added to the forest soil. Bigger particles, however, possesses a much smaller surface are, if compacted enough. This leads to slower leaching kinetics. Therefore, in order to have a slow leaching ash product, the ash should be well-hardened and agglomerated by compaction or wet granulation methods [9].

The hardening of the ash is commonly checked by studying the electric conductivity (EC) of the ash when in contact with water. The guidelines for the electric conductivity are presented in Table 5 below.

Table 5: Limits for electrical conductivity (EC) for different dosages, as recommended by SFA[9].

Dosage (Tons DS/hectares)	Limit for EC (mS/m)
Clearing	2400
2–3	2800
1–2	3200
<1	3600

Worth noting from Table 5 is the fact that different dosages sets different limits on the electrical conductivity, as a smaller dosage means a wider spread of the material. The method used to determine the conductivity is presented in the experimental methodology chapter.

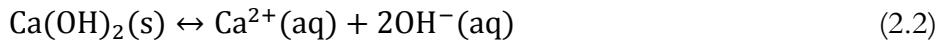
2.3 CARBONATION OF BIO-ASH

SFA recommends that the ash should be hardened before recycling, as was discussed in the previous section. As the major component in the ash is calcium, the chemical hardening, or carbonation, route of the ash will only consider calcium in this case.

First of all, the major calcium component is calcium oxide, CaO. By soaking the ash in small amounts water, CaO will react instantaneous to calcium hydroxide, Ca(OH)₂. The reaction is shown in reaction (2.1):



Calcium hydroxide is an easy soluble salt, and will thus decompose into calcium and hydroxide ions, according to reaction (2.2):



In general, reaction (2.2) is a fast reaction. Combining reactions (2.1) and (2.2) thus describes the solubilisation of CaO into calcium ions. As a result from the solubilisation, the environment will be basic, as hydroxide ions is formed in the dissolution. Worth noticing in the discussion of dissolving components including calcium is the fact that several other minerals are possible to have been formed during the combustion of the biofuel. However, CaO is the dominating form in untreated bio-ash [10].

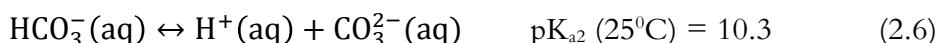
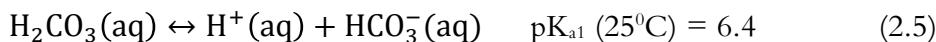
The carbonation of the calcium ions formed in reactions (2.1) and (2.2) is performed by carbon dioxide present in the raw biogas. As a first step, carbon dioxide is dissolved in water according to reaction (2.3):



When the carbon dioxide has been dissolved in water, the aqueous carbon dioxide may react with water to form carbonic acid, H₂CO₃, as is shown in reaction (2.4):



Carbonic acid is a weak acid, which can be dissolved to bicarbonate or carbonate ions depending on the pH value of the solution. The conversion from carbonic acid into bicarbonate ions and the conversion from bicarbonate ions to carbonate ions are presented in reactions (2.5) and (2.6) respectively, with pK_a values for each reaction [21].



The pK_a values in reactions (2.5) and (2.6) indicates that bicarbonate ions are the dominant compound in solutions of carbonic acid at neutral pH values, and carbonate ions at higher pH values. Figure 6 presents the equilibrium fractions of carbonic acid, bicarbonate ions and carbonate ions as a function of temperature at 25°C, made from data from [21].

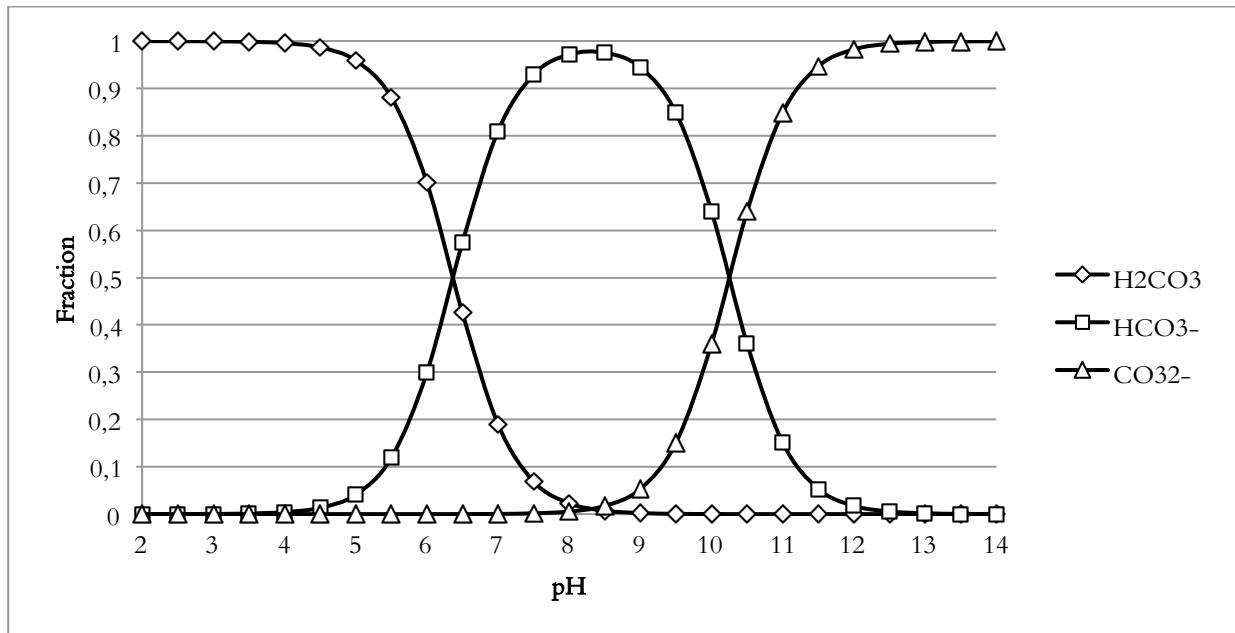
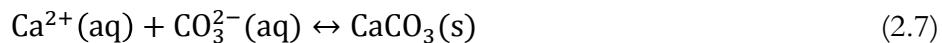


Figure 6: Equilibrium fractions of carbonic acid and its ions at different pH values at 25°C, made from data from [21].

Carbonate ions is used to carbonate the calcium ions into calcium carbonate. As can be seen from Figure 6, a high pH value is needed to have as high concentration of carbonate ions as possible. This is achieved by the calcium hydroxide itself. Calcium hydroxide in equilibrium with water gives a pH value of approximately 12.4 [22], which thus makes the carbonate ions the most abundant component. At this point, both carbonate ions and calcium ions are present in the liquid. These two components react according to reaction (2.7).



This reaction can be presented by combining reactions (2.1) – (2.7), which gives reaction (2.8):



Calcium carbonate is in general a hard-soluble mineral, which in turn means that a solid product is obtained from reactions (2.7) and (2.8). In the ash, these compounds precipitate at the surface of the ash particles.

2.3.1 Self-hardening of bio-ash

The most common way to perform chemical hardening of the ash is by using carbon dioxide from the air. The ash is first humidified to convert oxides to hydroxides, by using cement mixers. The ash is then landfilled, at which the ash is in contact with carbon dioxide in the air. This process takes approximately three months to complete. The carbonised ash is then crushed and sieved to suitable sizes.

Self-hardening is a relatively simple and cheap process. However, the product quality is hard to control and large variations throughout the ash are common. The process is also very

dependent on temperature, which makes it even harder to control the process depending on the season. Self-hardening is the dominating process used to harden the ash today [18].

2.3.2 Accelerated carbonation of bio-ash

Accelerated carbonation is a process in which the ash is much faster carbonated. The process ensures that the ash is carbonated effectively by packing a bed of ash in an effective way and by distributing the carbon dioxide homogeneously throughout the reactor. The product obtained from accelerated carbonation is more homogeneous than the self-hardened ash, and the degree of hardening is easier controlled while the process time is reduced from months to days or hours. However, the process is expensive and gives a much smaller particle size than the self-hardening process.

Accelerated carbonation has been studied by using several different substrates, commonly ash from municipal solid waste incinerator ash [23] [24] [25]. Other substrates that has been studied earlier is for instance different waste materials from the steelmaking industry, such as steelmaking slags [26]. However, accelerated carbonation of bio-ash is poorly investigated [8].

Accelerated carbonation of bio-ash using carbon dioxide from biogas was studied by Johan Andersson in his Master's thesis [8]. The ash showed varied results depending on composition and origin, and was able to adsorb up to 0.24 g CO₂/g dry ash. Thus, accelerated carbonation of bio-ash using carbon dioxide from biogas was a successful way of carbonating the bio-ash.

2.3.3 Process conditions of accelerated carbonation of bio-ash

In the process of accelerated carbonation of bio-ash, the bio-ash is firstly packed in a reactor, aiming to obtain an even packing. The ash is moistened, where after the raw biogas is fed to the reactor, running through the bio-ash bed. During the process, the liquid in the moistened ash bed absorbs carbon dioxide, while the bed is slowly dried due to evaporation of the water. The process is stopped when the carbon dioxide content increases in the outflowing gas from the reactor, indicating that the bed is saturated. At this point, the ash has obtained specific moisture contents between 10 – 25 weight-% [27]. The process is optimised using a series of ash containing carbon dioxide filters [8].

2.4 GRANULATION THEORY

Granulation is a process used to agglomerate small particles into larger aggregates, in which the individual particles still can be distinguished in the granules [28]. The process is also known as agglomeration, pelletisation or balling, words more commonly used in larger industrial processes. Granulation is used in a large variety of areas, such as the pharmaceutical industry and in the production of iron ore pellets. Granulation is used in order to:

- Enhance the flow characteristics around granules or pellets,
- Achieve better mixing properties when complex powders are mixed,
- Reduce dust-related problems,
- Get a homogeneous product with respect to shape and strength,
- Control the leaching characteristics of nutrients in fertilisers,
- Achieve a more easily handled product.

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The granules are formed in the granulation process as particles are colliding and bonds to each other. Granulation may be performed wet or dry. Wet granulation is the most common form of granulation, in which a liquid binder is used in order to form granules. Dry granulation, on the other hand, uses compression techniques, in order to press the powder together to form bonds [29]. As wet granulation is the method used in this project, only wet granulation is discussed in detail.

The wet granulation process is commonly explained in three steps, which explains the forming of granules. These steps are summarized into:

- Wetting and nucleation,
- Consolidation and coalescence,
- Attrition and breakage.

These steps are discussed more in detail below.

2.4.1 Wetting and nucleation

The first step in the granulation sequence is the wetting of individual particles and the formation of granule nucleus. This basically means that wetting and nucleation is the process when the binder liquid and dry powder is brought into contact for the first time, in addition to the attempt to distribute the binder liquid evenly in the powder bed. Several variables, both process and formulation variables, are important in this stage. However, wetting and nucleation is hardly separated from the other processes occurring in the granulator, such as consolidation and coalescence [30].

The zone in which wetting and nucleation occurs is called the nucleation zone. There are two major processes that are important in the nucleation zone: nuclei formation, which is a function of wetting thermodynamics and kinetics, and binder dispersion, which is a function of process variables. Thus, in general, nuclei formation is based on mainly formulation properties, while binder dispersion is based on operation conditions.

One of the most important variables in the final granule product is the size distribution. The granule size distribution is highly affected by the nuclei size distribution, which in turn is highly dependent on the wetting and nucleation characteristics described earlier. In order to make the characterisation of the wetting and nucleation stage easier, a nucleation regime map is commonly used. This map is presented in Figure 7 [31].

The y-axis is based on nuclei formation thermodynamics and kinetics, and is described by the theoretical penetration time, τ_d . The equation for the theoretical penetration time is presented in equation (2.9):

$$\tau_d = 1.36 \frac{V_d^{2/3}}{\varepsilon^2 r_d^4 R_{\text{pore}}} \frac{\mu}{\gamma_{LV} \cos \theta} \quad (2.9)$$

where V_d is the total drop volume, r_d is the radius of the drop footprint on the powder surface, ε is the surface porosity of the powder bed, γ_{LV} is the liquid surface tension, μ is the liquid viscosity, θ is the solid-liquid contact angle, and R_{pore} is the effective pore radius. τ_c in Figure 7 is the particle circulation time in the granulator, which is used to make the vertical axis dimensionless. On the horizontal axis, however, is the dimensionless spray flux, which

corresponds to variables important to binder dispersion. The dimensionless spray flux is defined as equation (2.10):

$$\Psi_a = \frac{3V}{2Ad_p} \quad (2.10)$$

where V is the volumetric flow rate of liquid binder, d_p is the average drop size and A is the area at which the droplets are spread. The dimensionless spray flux is basically a measure of the binder coverage on the powder surface in the granulator.

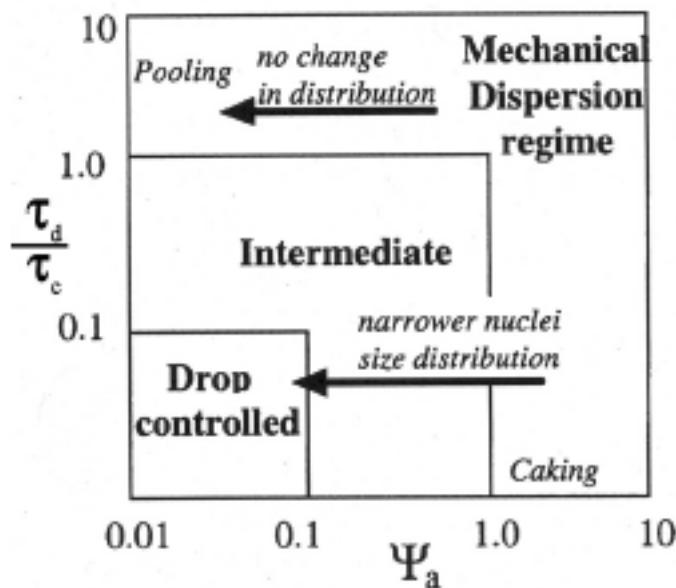


Figure 7: Nucleation regime map [31].

In order to facilitate good wetting and an effective formation of granules with a narrow nuclei size distribution, it is wanted to operate in the lower left corner in Figure 7, in the regime map called the drop controlled nucleation regime. In this regime, one droplet will form one granule nucleus. If the granulation procedure is operated in mechanical dispersion regime, however, the droplets may coalescence with other droplets creating a wider drop size distribution, in turn a much broader nuclei size distribution, leading to a broader final granule size distribution. In the intermediate regime, a combination of the two extremes will occur. This in turn means that the distribution method and addition of liquid binder to the powder bed is a highly important process in the production of granules [30].

2.4.2 Consolidation and coalescence

If wetting and nucleation has been successful, consolidation and coalescence will highly affect the final properties of the granules. In a granulator, the particles and granules continuously collide and compact, pushing liquid from the inside of the granules to the surface, while the size and porosity decreases. This process is referred to as consolidation. This phenomenon is directly dependent on process conditions, especially the degree of agitation [30].

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Coalescence of granules is the process in which two granules collides and sticks together, forming a larger granule. In general, coalescence depends on the availability of liquid binder at the surface of the granules, and the deformability of the granules [32].

Coalescence and consolidation is generally considered as the growth of the granules. There are mainly two types of growth patterns that are commonly observed in granulation: steady growth, and induction growth. Steady growth is the growth pattern observed when the granules increase in size steadily over time. This pattern is observed for weak and easily deformable granules. Induction growth is the growth pattern observed when there is a period of slow growth, followed by a period of rapid growth. This pattern is observed for hard and hardly deformable granules. The characteristics mentioned for the granules generally affect the degree of consolidation, which in turn affects the coalescence of particles. Figure 8 shows an illustration of the different growth behaviour, together with the underlying effect of granule deformability [33]. The liquid content is an important variable, as an increased liquid content increases the growth rate in steady growth behaviour, while in induction growth behaviour induction time is shortened. The effect of liquid content can also be seen in Figure 8.

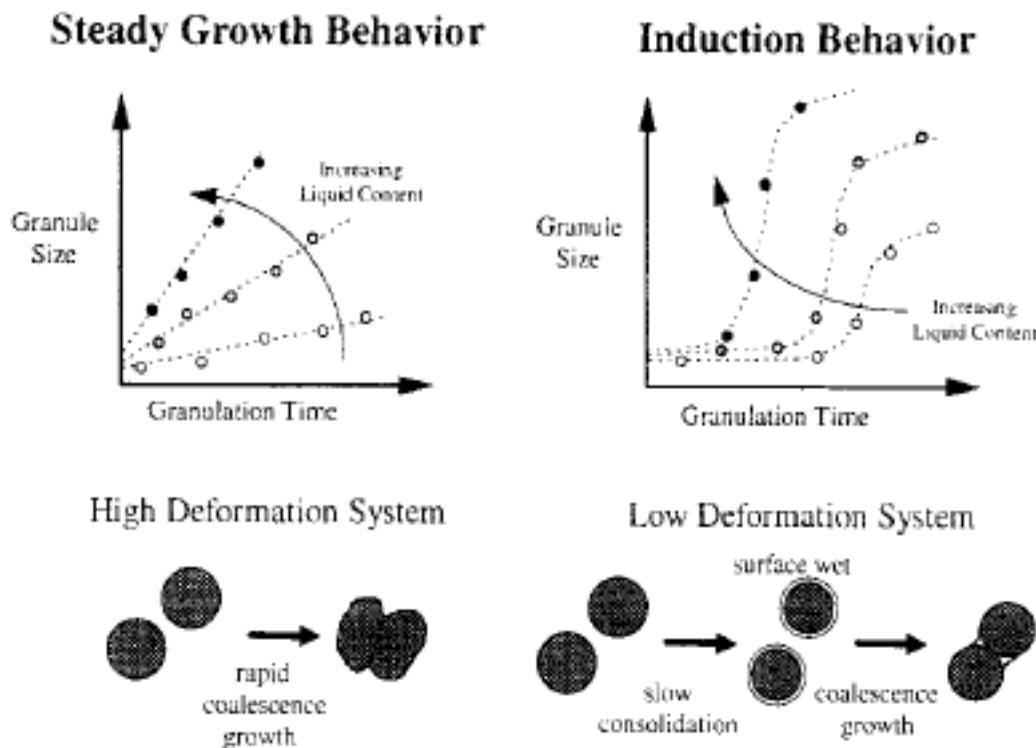


Figure 8: Illustration of growth behaviour and the underlying effect of granule deformability [33].

The discussed growth behaviours are not the only possible behaviours observed in granulators. Other types of behaviour are nucleation only, crumb behaviour, and overwetting. Nucleation only is the behaviour observed when an insufficient amount of binder liquid is added to the granulator, hindering the growth of the granules. Crumb behaviour is observed for granules that are too weak to overcome the impact forces in the granulator, producing loose crumb material that are continuously broken and reformed. Overwetting occurs when too much binder liquid is added to the granulator, producing sludge. These behaviours do not lead to the growth of the granules [33].

All discussed behaviours in the granulator are usually modelled as dependent on two variables: the maximum granule pore saturation, which is used as a measure of liquid content in the granules, and the Stokes deformation number, which is used to measure of the degree of deformation during impact. The equations for each variable are presented in (2.11) and (2.12) respectively.

$$S_{\max} = \frac{w\rho_s(1-\epsilon_{\min})}{\rho_l\epsilon_{\min}} \quad (2.11)$$

$$St_{\text{def}} = \frac{\rho_g U_c^2}{2Y_g} \quad (2.12)$$

In equation (2.11), w is the mass ratio of liquid to solid, ρ_s is the density of the solid material, ρ_l is the density of the binder liquid, and ϵ_{\min} is the minimum porosity that can be obtained for the specific formulation at the specific operating conditions. In equation (2.12), ρ_g is the density of the granules, U_c is the collision velocity inside the granulator, and Y_g is the dynamic yield stress for the granules. These variables are used in order to characterise the granule behaviour inside the granulator. Plotting the Stokes deformation number on the vertical axis and the maximum pore saturation in the horizontal axis gives the growth regime map, in a similar way as the nucleation regime map. The growth regime map is shown in Figure 9 [33].

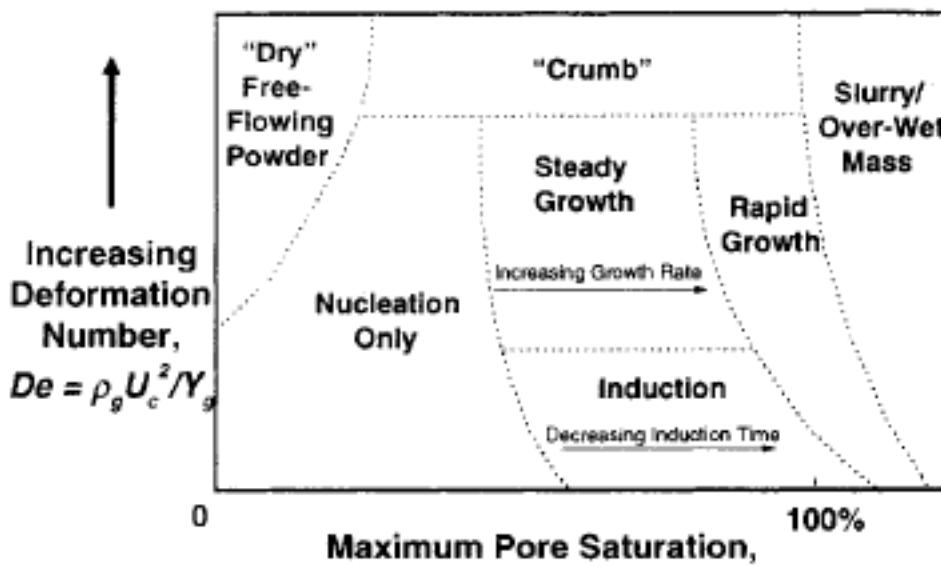


Figure 9: Growth regime map for liquid bound granules [33].

The growth regime map is an effective way of characterizing the granulation procedure, in order to get information of what may be changed in order to make the process more effective. However, the growth regime map is only valid for similar liquid binders in terms of mainly viscosity, and in the same type of granulator [33].

2.4.3 Attrition and breakage

Attrition and breakage is the final step in the wet granulation procedure. In this step the granules grows too large to overcome the agitating forces. The coalescence is in this case counteracted by attrition of the granules, or the breakage of whole granules. Basically two mechanisms are responsible for this: an uneven distribution of binder liquid or the drying of the granules [30].

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Depending on the type of granulator these mechanisms may dominate over the other or they both contribute to the breakage of the granules. In general the breakage is mostly seen when the agitation is done by high intensity.

Attrition and breakage is an important step in the granulation sequence, as it contributes the homogeneity of the final product. It affects mainly the size distribution of the final granule product, as the process sets limits on the maximum granule size possible to obtain. Secondly, it also breaks weak granules, which makes the strength distribution throughout the product narrower [34].

2.5 STRENGTH OF WET AND DRY GRANULES

The strength of particle agglomerates and granules comes from different types of forces between the particles. Depending on the medium several different forces may bind the particles together.

2.5.1 Strength of wet granules

The basic idea of granulation processes is to bring particles together to form bonds that keep the granules together. In wet granulation, a binder liquid is used to bring the particles together, before drying to form solid bridges. Forces that are the dominating forces between particles in the liquid state are mainly capillary forces, which arise as a response to capillary pressure, and viscous forces, which is a response to friction [35].

The forces in the liquid state are mainly measured as the strength of wet granules. The strength helps to determine the growth behaviour that may be observed in a granulator, as weak granules tend to grow quick and steady, while strong granules grow with induction behaviour, as was discussed earlier. The mechanical strength of the wet granules is also a very important process variable, as the granules must be able to withstand for instance a bed of granules when transferred from the granulator to the dryer. Thus, the forces between the binder liquid and the particles is not only important in order to bring the particles together, but also to keep the shape and size of the granules after granulation and following handling [35].

Wet granules can exist in several different states depending on the degree of pore saturation of the agglomerates. Figure 10 shows a schematic picture of the different states that may appear.

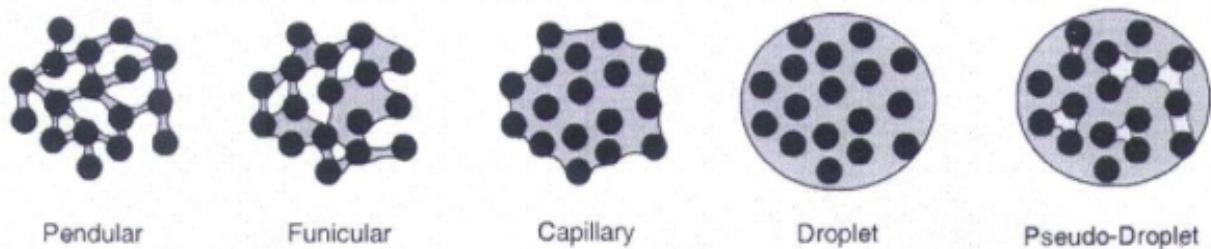


Figure 10: States of wet granules at different degrees of pore saturation [30].

If wetting and nucleation is done sufficiently, one droplet will form one granule nucleus, which means that the nucleus will have the droplet state. This nucleus is only held together by surface tension forces, which is rather weak. The pseudo-droplet state may appear in poorly wetted systems. However, when the nucleus is balled in a granulator, the granule will grow into the capillary state. The capillary state is held together by curvature effects, and not surface tension forces as in the droplet state. As the degree of pore saturation continues to decrease the funicular

state is achieved, in which liquid bridges starts to form, increasing the strength of the wet granule. In the pendular stage full liquid bridges have appeared, which forms a strong network in the granules. The particles are held together in the pendular stage by forces from the capillary pressure effect [36].

From capillary theory, it is possible to obtain an equation related to the wet tensile strength of the granules, as a function of formulation variables and the pore saturation degree. The equation commonly used is the Rumpf equation, which is shown in equation (2.13) [37].

$$\sigma_t = SC \frac{1-\epsilon}{\epsilon} \frac{\gamma_{lv} \cos \theta}{d_p} \quad (2.13)$$

In the equation, σ_t is the tensile strength of the granule, S is the liquid pore saturation, C is a material constant, ϵ is the granule porosity, d_p is the surface-average particle size, γ_{lv} is the liquid surface tension, and θ is the contact angle between the liquid and the solid.

The equation predicts that the tensile strength is proportional to the liquid surface tension and the liquid pore saturation, while it is inversely proportional to the porosity and particle size. However, the equation usually overestimates the tensile strength, for instance for large monosized particles. This is due to the fact that the equation does not take in to account for the frictional forces, which may be the dominant force in some materials. Frictional forces at increased pore saturation are usually lowered as the binder acts like a lubricant. Although the equation is not fully correct, it gives valuable information on how the strength is affected by for instance porosity [30].

2.5.2 Strength of dry granules

The liquid bridges that have formed the granules in wet granulation will eventually be removed by drying. When this is done other forces keep the particles together. In order for the particles to stick together after drying, the bonds between the particles must overcome the gravitational forces, which drags the particles away from each other.

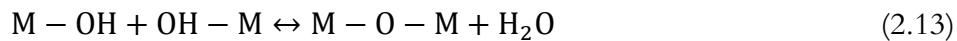
The forces that keep the granules together can be for instance attractive forces between the particles, such as van der Waals forces, electrostatic forces or magnetic forces. These forces are forces that only act at small ranges, and are only significant for small particles up to 1 μm in diameter. These forces may be significant for granules based on small primary particles, or when a powder is intimately compressed. Other forces that may hold the granule together are solid bridges, which may be formed through chemical reactions, crystallisation, binder solidification, or sintering. If these forces are present in the granules, these are most often the main strengthening mechanisms [34].

One special strength phenomena is seen when studying compounds forming hydroxides in the wet state. During drying, the hydroxides form a gel, which lead to hard granules. The reason to this effect may come from either of the following phenomena [38]:

- Hydrogen bonds between the hydroxides in the granules, or
- Condensation reactions of hydroxides.

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The second phenomena, condensation reactions of hydroxides, occurs when further drying is applied to the granules. The condensation reactions may be explained by reaction presented in reaction (2.13), where M stands for any metal ion.



Thus, further drying of the granules may produce hard agglomerates by reaction between hydroxyl groups at the particle surfaces, releasing a water molecule as a response [39].

2.5.3 Strength measurements in industry

The most common strength discussed in the literature is the tensile strength of the granules, as for instance the Rumpf equation is based on. However, the more common strength variable measured in industry is the compression strength, as this variable is less time-consuming than the tensile strength measurements [40]. The compression strength is always higher than the tensile strength. Compression strength is generally measured on both wet and dry granules, as is done for instance in the iron ore industry. These strengths are highly important in the production of iron ore, as the pellets must be able to withstand different forces in for instance transportation on conveyor belts. Another example of strength requirements is on the dry granules as they are transported through a blast furnace. In the iron ore industry, wet compression strengths above 10 N/pellet and dry compression strengths above 30 N/pellet are satisfactory [41].

Another common variable measured in industry is the drop number, which is a measure of impact strength. It is measured by dropping the pellets or granules from a specific height, and counting the number of drops before the pellet breaks. This variable is an important measure to ensure that the granules won't crack when loaded from one conveyor belt to another. A drop number above 4 is considered satisfactory in the production of iron ore pellets [41].

2.5.4 Strength-enhancing additives

Different formulations of powders possess different possibilities to form strong pellets or granules. Due to this, different strength-enhancing additives may be added to the formulations to increase the strengths. One industrial example is the use of bentonite in the iron ore industry. Bentonite majorly constitutes of the clay mineral montmorillonite, and the most common form of the mineral is the sodium activated calcium form [42].

Montmorillonite has a complex structure, which can be seen in Figure 11. Montmorillonite has two tetrahedral sheets of silica with a layer of octahedral alumina in between [41]. Sodium bentonite, which is one of the most studied types of bentonite, swells several times its original size when in contact with an excess amount of water. In wet iron ore pellets, bentonite contributes to the strength by forming a supporting network of viscous liquid in between the iron ore particles [44]. When the wet pellet is dried, however, the swelled bentonite reduces in size and is drawn to the surface of the iron ore particles and to the contact points between the grains, forming solid bridges [42]. These mechanisms are the main strengthening mechanisms of bentonite in iron ore pellets.

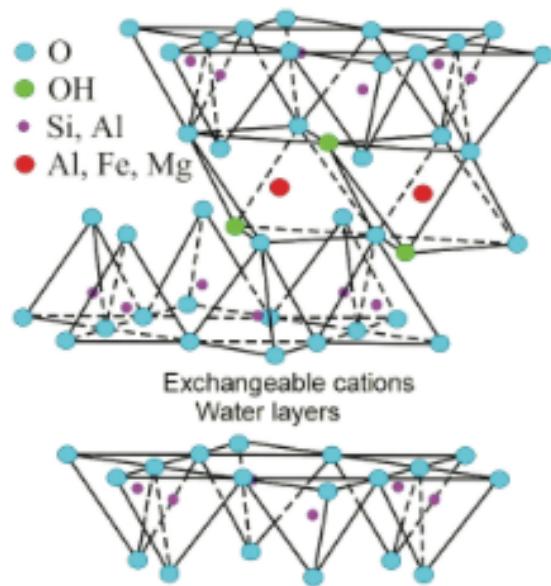


Figure 11: Structure of montmorillonite [45].

Common bentonite dosages used in the production of iron ore pellets ranges from approximately 0.5 – 0.7 weight-%. In spite the fact that even higher bentonite contents increases the wet compression strength and drop number, a higher content of bentonite is not used in industry [44].

Other strength-enhancing additives that may be used to enhance the strength may be quick reactions that form another phase during the reaction. One example of such a reaction was presented in chapter 2.3 as reaction (2.1):



Calcium oxide is a component that is found in bio-ashes of different kinds. Thus, calcium oxide may act as a potential binder in bio-ash by forming solid bridges in the granules. Also, other components may for instance be solubilized by the water addition during the granulation procedure, and recrystallized after drying. Thus, there are several potential binding mechanisms that may appear in the granules of bio-ash. Also, calcium oxide may be added by pure calcium oxide or untreated ash in order to raise the amount of calcium oxide in the formulation.

2.5.5 Strength dependence on formulation variables

As was seen in the Rumpf equation, equation (2.13), the wet tensile strength is dependent on porosity. A low porosity increases the wet tensile strength, and also the dry strength of the granules [46]. The porosity is highly dependent on the particle size distribution. A narrow particle size distribution creates voids between the particles. However, if some amount of smaller particles exists, these particles may fill the voids between the bigger particles, lowering the porosity. Packing of a bimodal particle size distribution can be seen in Figure 12 [47].

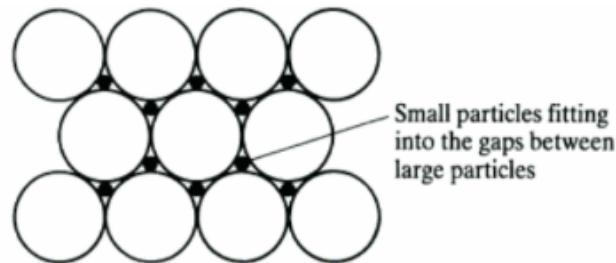


Figure 12: Bimodal packing of particles [47].

In addition to porosity originating from the voids between particles, air bubbles may also create large cavities which add to the porosity. This is seen for instance in the production of iron ore pellets, in which flotation collectors are added. The flotation collectors make the surfaces highly hydrophobic, which adsorbs air on the surfaces instead of binding liquid, entrapping air as a result [48]. A similar phenomenon may appear in granulation of bio-ash, as different compounds may be hydrophobic, for instance carbon.

As a continuation on the porosity dependence of packing, another variable is commonly evaluated as an important variable, namely the fineness of the material. The specific surface area of the material often represents the raw material fineness [40]. However, a decrease in raw material fineness (increase in specific surface area) leads to that higher moisture content is needed to be able to ball the material, due to the increase in contact points between particles. In general, there are different optimum moisture contents for every formulation, which depends on the particle size and particle size distribution, surface phenomena such as surface roughness and wettability, and inner porosity of the particles. These combined variables are commonly referred to variables that determine the ballability of the material, which indicates how easy a particular formulation can be granulated [40].

2.5.6 Strength dependence on process variables

There are mainly three general process variables that affect the final granules. These are the degree of agitative forces in the process, the time that the granules spend in the granulator, and the liquid binder delivery method. The degree of agitation highly affects the consolidation phenomena important for the granule growth, as a more intense agitation leads to more impacts in the granulator and so also a quicker consolidation. Depending on which type of equipment that is used, different degrees of agitation will occur. Moreover, the granulation time is important as an increased granulation time increases the chance for the granules to fully consolidate and to form a denser final granule [29]. Also, a longer granulation time will produce a narrower granule size distribution. The binder delivery method, including the binder distribution method, drop size distribution and binder delivery rate, is highly important for the forming of granule nucleus, as was discussed earlier [49].

2.6 WET GRANULATION METHODS AND EQUIPMENT

There are in general three different kinds of granulators used industrially. These are [50]:

- Tumbling granulators,
- Fluidized bed granulators,
- High-intensity mixer granulators.

2.6.1 Tumbling granulators

Tumbling granulators is the generic term for granulators that use a tumbling motion in order to granulate the material. In general, tumbling granulators refers to drum and pan granulators.

Drum granulators is the most common granulator used in industry. Fertilizer and iron ore production are two examples that mainly are produced in drum granulators. Drum granulation uses a tumbling motion for the particles in order to bond and form granules. Figure 13 shows a schematic picture of a drum granulator.

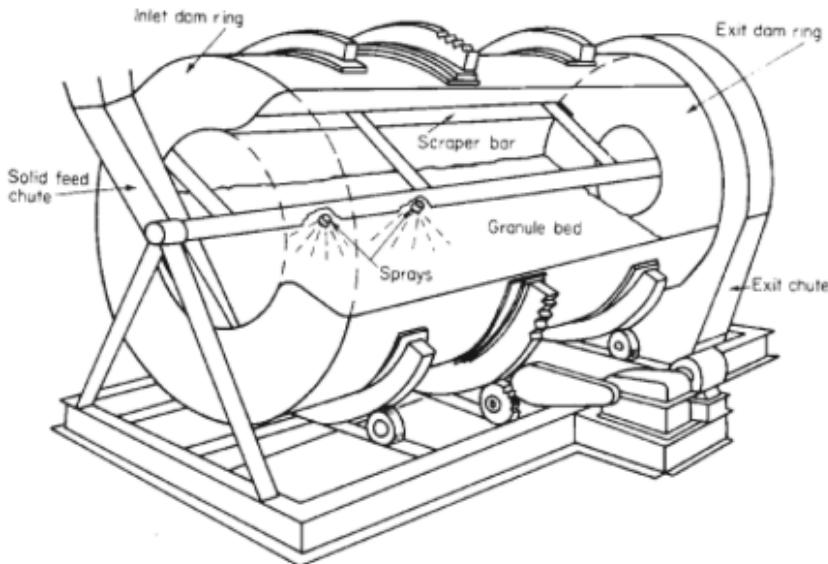


Figure 13: Schematic picture of a drum granulator [29].

The agitative forces that make the particles collide, consolidate and coalescence comes from the rotating motion of the drum. Depending on the speed of the rotation, the particles may rock forth and back, roll on top of each other, or move in a cascade motion. Figure 14 shows pictures of different moving patterns according to the rotational speed [29].

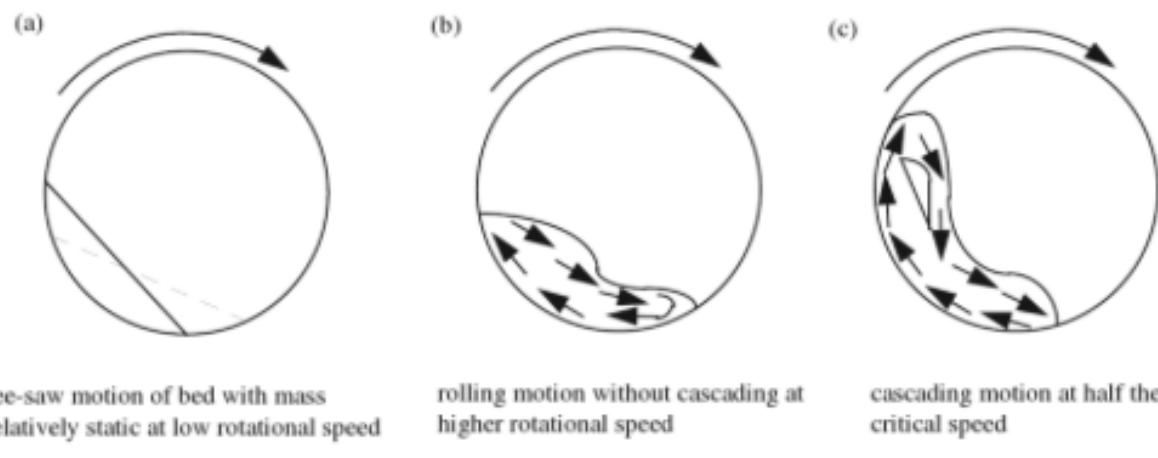


Figure 14: Motion of the particle bed inside a drum granulator at different rotating speeds [29].

The drum granulator is most often operated in continuous mode, using a slight inclination in order for the material to move down the granulator. Changing the inclination thus changes the speed of the process.

Pan granulation is similar to drum granulation, and forms granules in the same way as the drum granulator. Pan granulation is also called disc granulation. The particle bed is forced to collide by an agitative motion from the disc. However, unlike the drum granulator the disc

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granulator is operated at a much higher angle, which also can be changed and optimized. Thus, a pan granulator has one more process variable than the drum granulator available for optimization [49]. Figure 15 shows a schematic picture of a disk granulator [50].

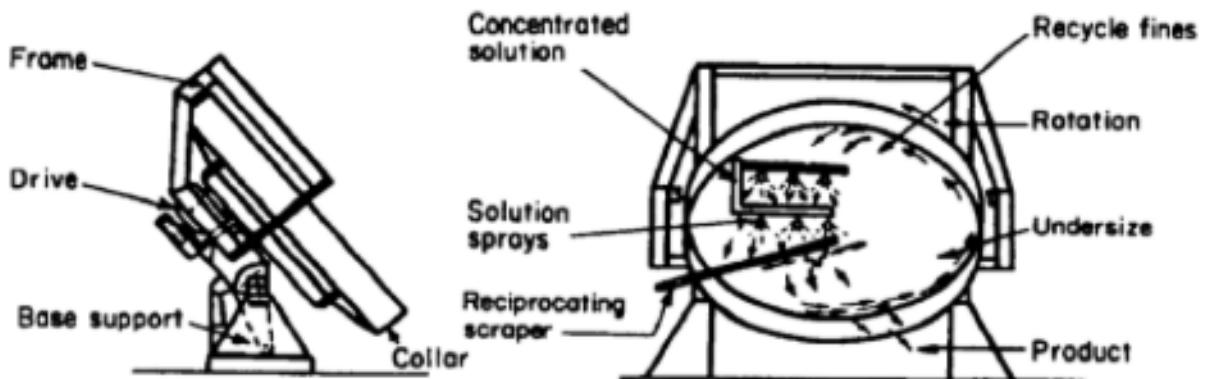


Figure 15: Schematic picture of a disk granulator [50].

2.6.2 Fluidised bed granulation

Fluidised beds are commonly used in the chemical industry in a wide variety of processes. Common processes include mixing, drying, heating and chemical reactions in general. Granulation is another common process that uses fluidised bed technologies. When using fluidised beds as granulators several processes may be performed at the same time, as for instance mixing, agglomeration and drying. A good control of mass and heat transfer is the main advantage with fluidized beds [52] [53].

Fluidisation of a particle bed occurs when the force acting from the supplied gas flow from below the powder bed exceeds the force of gravity acting on the particles. The fluidisation of the powder bed gives high area of contact between the supplied gas and particles, which improve heat and mass transfer. The fluidisation also leads to efficient mixing of the powder, which in turn induces collisions between the particles. If then a binder liquid is supplied to the granulator, liquid bonds may be formed, which in turn makes the particles agglomerate, forming granules as a response [52]. Figure 16 shows a schematic picture of a fluidised bed granulator.

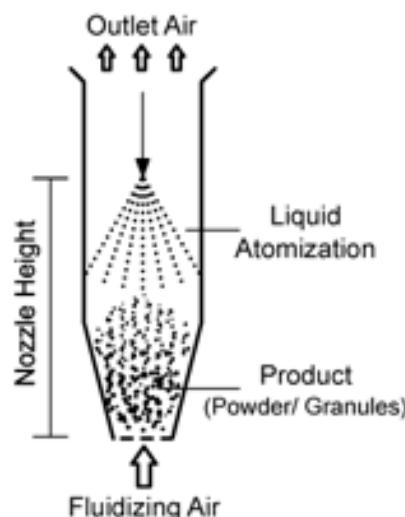


Figure 16: Schematic picture of a fluidised bed granulator [54].

2.6.3 High-intensity mixer granulation

In high-intensity granulators, a mixer operated at high intensity is used to induce particle collisions. Depending on the speed of the mixer, different product characteristics may be obtained. If the mixer is operated at a relatively low intensity, weak external forces will act on the granules, which make them porous, with low density. However, if the intensity is high, the external forces acting on the particles will be strong, leading to dense and small granules. In general, high-intensity have the following advantages over the other types [55]:

- High-intensity mixer granulators may process wet and sticky material,
- High-intensity mixer granulators can spread highly viscous binders efficiently on the powder bed,
- High-intensity mixer granulators are relatively tolerant to process variations,
- High-intensity mixer granulators can efficiently produce small and dense granules.

High-intensity mixer granulators may be operated in continuous or batch mode, depending on the process requirements. There are in general two major classes of high-intensity mixer granulators: vertical and horizontal granulators. The difference between the two classes is the orientation of the mixer in the granulator [55].

In high-intensity mixer granulators, not only the impeller acts as a mixing initiator, but also a chopper mounted on the side of the granulators, which can be seen in Figure 17. The chopper is often operated at rather high speed, which most often is used to control the final product size.

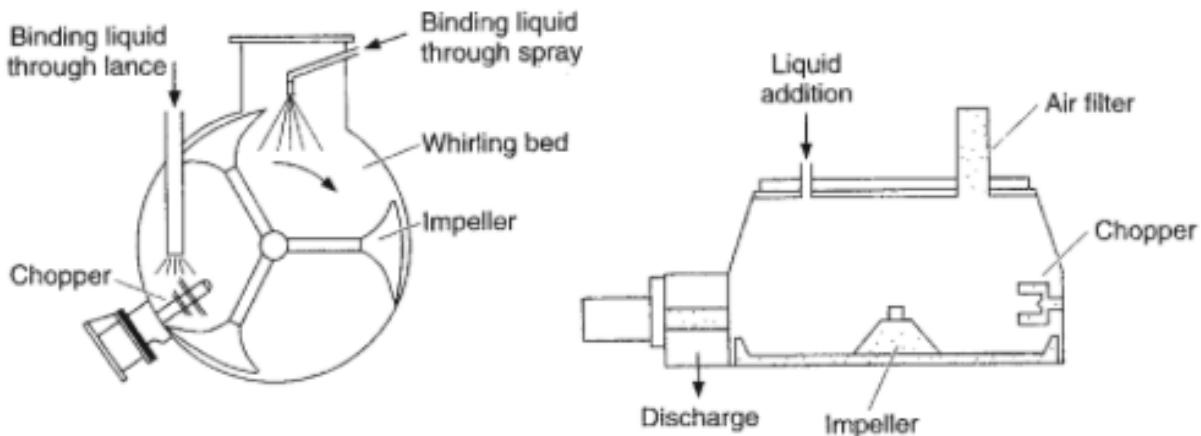


Figure 17: Schematic picture of a vertical (left) and horizontal (right) high intensity mixer granulator [55].

2.7 GRANULATION OF BIO-ASH

Granulation of ash in general is a common unit operation. Ashes from for instance coal combustion is commonly granulated in order to achieve a better product when used in construction, road and agricultural industries [56]. Bio-ash, on the other hand, is most often granulated in order to act in agriculture as soil conditioners. Different mixtures have been evaluated, for instance mixtures of ash from wooden biomass and ash from wastes from pulp production, by using press techniques [57]. Another example studied is co-granulation of bio-ash with lime and sewage sludge, using drum granulation techniques [58]. The majority of examples

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regarding granulation of bio-ash consider untreated fly ash, often granulated directly after combustion of the biofuel.

Granulation of carbonised bio-ash, however, is poorly investigated. Only one study of carbonised bio-ash was found, using disk granulation to granulate bio-ash treated with carbon dioxide [59]. However, no previous study on carbonised ash granulation from biogas upgrading was found.

2.8 LEACHING OF BIO-ASH

The Swedish Forest Agency recommends that bio-ash which is returned to the environment should possess slow leaching kinetics, as was discussed earlier. Granulation of bio-ash may not only change the bio-ash into a more easily handled product, but it may also change the leaching kinetics of the bio-ash. The leaching kinetics of granular materials may be affected by several variables.

First of all, the carbonized bio-ash contains for instance carbonates such as CaCO_3 . The bio-ash is leached by water, which may be in contact with CO_2 in the atmosphere. Thus, the leaching of the bio-ash may be modelled as the dissolution of CaCO_3 in the ternary system $\text{CaCO}_3\text{--H}_2\text{O}\text{--CO}_2$ [60]. In general, there are three rate-controlling processes in the dissolution of CaCO_3 [61]:

1. Dissolution of CaCO_3 at the mineral surface,
2. Diffusional mass transport of Ca^{2+} , HCO_3^{-} and CO_3^{2-} from the mineral diffusion boundary layer,
3. Conversion of CO_2 to H^+ and CO_3^{2-} in the liquid phase.

In general, the dissolution of CaCO_3 is diffusional dependent. This in turn means that the dissolution is dependent on the surface area in which the CaCO_3 is in contact with water. If it is assumed that the bio-ash possesses similar properties as CaCO_3 , then it is valid to assume that the dissolution of bio-ash is dependent on the contact surface area of water.

When the carbonized bio-ash is submerged in water, the leaching kinetics will be highly dependent on the particle size. However, when the carbonized bio-ash has been granulated, the surface area is significantly reduced, if the granule structure is kept and not interrupted by the water. The mass transfer of the different solutes from the granule will then highly depend on the morphology of the porous structure, which includes pore size, tortuosity and constrictivity [62]. This means that if the granule structure is sustained when immersed in water, the porosity of the granules will determine the leaching characteristics of the bio-ash. If the bonds in the granules, however, are interrupted when immersed in water, the particle size of the individual particles will determine the leaching characteristics of the bio-ash.

2.9 PROBLEM STATEMENT

Accelerated carbonation of bio-ash by using raw biogas has proven to be an efficient process both in terms of CO_2 removal and carbonation of bio-ash. However, in order to use the bio-ash as a fertilizer in the forest, enlargement of the carbonized bio-ash particles must be performed in order to more efficiently handle the bio-ash. Also, an enlarged bio-ash decreases dust problems, enhancing the work environment.

2.10 KEY QUESTIONS

The key questions in this project can be summarized to:

1. Is it possible to form granules of the bio-ash?
2. Is it possible to form granules without the addition of solid binders?
3. Does granulation change the leaching characteristics of the final product?
4. What is the binding mechanism in granules consisting of bio-ash?

3. EXPERIMENTAL METHODOLOGY

In this section, all methodologies used in the project are presented, regarding characterisation, granulation and analysis.

3.1 OVERVIEW

Within this project, mainly four parts were considered: sampling, characterisation of ashes, granulation, and granule analysis. The sampling was performed by Johan Andersson at JTI. The characterisation of the ashes was based on particle size analysis, shape analysis and conductivity measurements. The analysis of elemental and phase composition was not performed as the ash has previously been analysed on elemental and phase compositions, with the main result that the ashes possess suitable compositions for fertilising applications. The actual granulation was performed in the lab at LTU. Analysis of granules and characterisation of ashes was performed both at labs at LTU and SP Processum.

3.2 SAMPLING OF ASH AND CHARACTERISATION

The carbonized ash used in the project was firstly collected as raw ash from two 2 MW grate boilers, with separate ash removal systems. During the transportation of ash from the boilers, fly and bottom ash was mixed, creating a mixture of both fly and bottom ash. During the sampling, one of the boilers was operated more stable than the other, leading to the presence of unburned organic compounds in the ash. The sample that was carbonized consisted of approximately 50% ash from each boiler. The sample was delivered by Johan Andersson from JTI, Uppsala. Raw ash was used in the experiments from the same boilers.

3.2.1 Particle size analysis

A particle size analysis was performed on both the carbonized ash and raw ash using sieves with sizes 4 mm, 2 mm, 1 mm, 500 μm , 250 μm , 100 μm and 38 μm . Approximately 300 grams of ash was used in the analysis, and each fraction was weighed to obtain the size distribution, as well as the cumulative size distribution.

3.2.2 Analysis of particle shape

Analysis of particle shape and morphology was performed at high magnification using a MAGELLAN 400 SEM from FEI Company. The analysis was performed with an acceleration voltage of 3.0 kV. The samples were attached to test plates using carbon tape.

3.2.3 Analysis of granule bonding mechanism

To study the bonding mechanism in the dry granules, the same SEM as explained before was used to study the granules in more detail. In the analysis, same acceleration voltage was used as

in the analysis of particle shape, 3.0 kV. One granule was split into two halves, and attached to a test plate using carbon tape.

3.3 GRANULATION

The granulation generally consisted of two phases: the forming of granules and the analysis of the granules.

3.3.1 Preparation of ash mixture

The granulation procedure started by drying the carbonised ash, raw ash and bentonite overnight in order to remove moisture. Before further handling, the raw material was allowed to cool in a desiccator to room temperature. A 2 mm sieve was then used to remove large particles from the raw ash and carbonised ash.

A basis of 500 grams of solids was used during the experiments. The carbonised ash and raw ash was then mixed together with 90% of the calculated moisture for 5 minutes in an Eirich high intensity mixer, after which the bentonite and final 10% moisture was added to the mixer. The final mixture was then mixed another 5 minutes. This method was used in order to distribute the moisture as evenly as possible, and to wet the particles as efficient as possible.

3.3.2 Granule forming

When the ash mixture had been prepared, the actual granulation was started. The pelletiser used in this project was the DP-14 Agglo-Miser pelletiser from Mars Mineral. The pelletiser is shown in Figure 18. The pelletiser was operated in disk mode, with constant angle and speed set to 30° and 45 RPM respectively. This setting was chosen as a cascading motion could be achieved. The ash was firstly scattered on to the granulator in order to start the nucleation of the ash. Approximately half the weight of the ash mixture was used to create granule nucleus. Distilled water was sprayed on to the ash in order to start the nucleation. The remainder of the ash was added to the granulator as soon as the nucleation started to facilitate the growth of the granules. The granules were then allowed to consolidate for two minutes before the granules were sieved to the product size 4 – 8 mm.

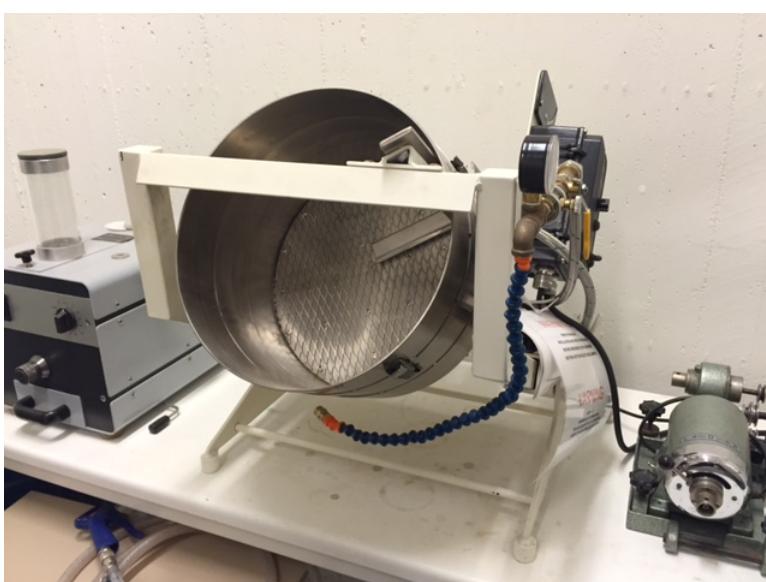


Figure 18: The DP-14 Agglo-Miser pelletizer from Mars Mineral used in the project.

3. EXPERIMENTAL METHODOLOGY

3.3.3 Moisture content measurements

When the product had been sieved and the product size range had been collected, the moisture content was measured on 10 granules from each batch to study the variation between granules in each batch. The moisture analyser was the same as described before, the MA 30 moisture analyser from Sartorius. The analysis took 5 – 10 minutes for each granule. The remaining granules were stored in a desiccator with a saturated ammonium sulphate solution in order to keep the moisture content constant throughout the measurements. The remaining wet granules, which were not used to measure moisture content, were dried in room temperature until they were dry, in order to avoid rupture of bonds due to fast drying.

3.3.4 Compression strength measurements

The strength variable used in this project was the compression strength on dry granules. A simple compression strength test rig was built, which can be seen in Figure 19. By using this test rig it was possible to determine the strength of each granule recipe, and to compare them with each other. Cast iron powder was added slowly as weight, and when the pellet broke the amount of cast iron powder was measured by weighing. The compression strength was then presented in Newton. 10 granules of each batch were analysed to facilitate a representative value on the compression strength.



Figure 19: Compression strength test rig built to measure the compression strength of the dry granules.

3.3.5 Conductivity measurements

The conductivity measurements were performed in order to see if the granulation procedure affected the leaching characteristics. Also, it was used to characterise the granules as is recommended by the Swedish Forest Agency. Firstly, approximately 10 grams of granules were analysed for moisture content, in order to more precisely compare the leaching characteristics between the recipes. The moisture content was analysed by the Moisture Analyzer MJ33 by Mettler Toledo. When the moisture content was known, an exact portion of deionised water

could be added to 25 grams of granules until the mixture consisted of one part granules and five parts water. The mixtures were mixed in E-flasks on a shaking table with a rotation speed of 3 rotations per second and a rotation of 2 cm. The mixtures were mixed for one hour. The water fraction was then filtered using Munktell 00M filters, and the conductivity was measured on the clear water phase. The conductivity was measured with a conductivity meter model LF 538 from WTW. The same procedure was performed on both the raw ash and carbonised ash, ungranulated.

3.4 STATISTICAL DESIGN

Different recipes were used to study the selected parameters between different granules. Three parameters were chosen as design variables for the statistical design used in the project, and three response variables. The parameters with ranges and units for both design and response variables are presented in Table 6 below. What should be noted is that the raw ash content and bentonite content refers to the dry weight of the formulation, while the moisture content refers to the content of moisture in the wet formulation. The range for initial moisture content was chosen to be representative of the carbonised ash properties after carbonation, which was previously discussed. The range for raw ash content was chosen to a maximum 10 weight-% as a higher content would lead to a large increase in ash handling in the process. The range for bentonite content was chosen based on dosages used in the production of iron ore pellets.

Table 6: The parameters used as design and response variables with respective ranges and units.

	Parameter	Range	Unit
Design variables	Initial moisture content	10 – 20	Weight-%
	Raw ash content	0 – 10	Weight-%
	Bentonite content	0 – 4	Weight-%
Response variables	Pellet moisture content	-	%
	Dry compressive strength	-	N
	Conductivity	-	mS/m

A statistical design was used in order to consider possible cross-correlations between the design variables. The statistical software MODDE 11 by UMETRICS AB was used to create the statistical design. The statistical design was chosen to be an optimization face centred central composite design, with three midpoints used in order to ensure reproducibility and to analyse the experimental error. The experimental plan obtained from MODDE is presented in Table 10 in Appendix I.

4. RESULTS AND DISCUSSION

In this section, the results from the characterisation of the raw materials and granulation experiments are discussed. Additional information is given in the Appendix. A summary is presented in the end.

4.1 CHARACTERISATION OF RAW MATERIALS

The characterisation of the raw materials raw ash and carbonised ash was performed with particle size distribution, conductivity measurements and SEM analysis. The results from these characterisation methods are discussed in this section.

4.1.1 Particle size distribution

The particle size analysis obtained by sieving is presented in Figure 20. The raw ash had a considerably smaller particle size, as is seen in the figure. Over 25% of the particles in the raw ash passed the 38 µm sieve. The corresponding amount of the carbonised ash passing the 38 µm sieve was approximately 3%. Both the carbonised ash and the raw ash had a rather wide particle size distribution, with d_{50} and d_{80} values for the raw ash at 100 µm and 300 µm respectively, and for the carbonised ash 220 µm and 600 µm respectively. The difference in particle size is probably due to the forming of CaCO_3 during the hardening of the bio-ash, bonding together particles as a result.

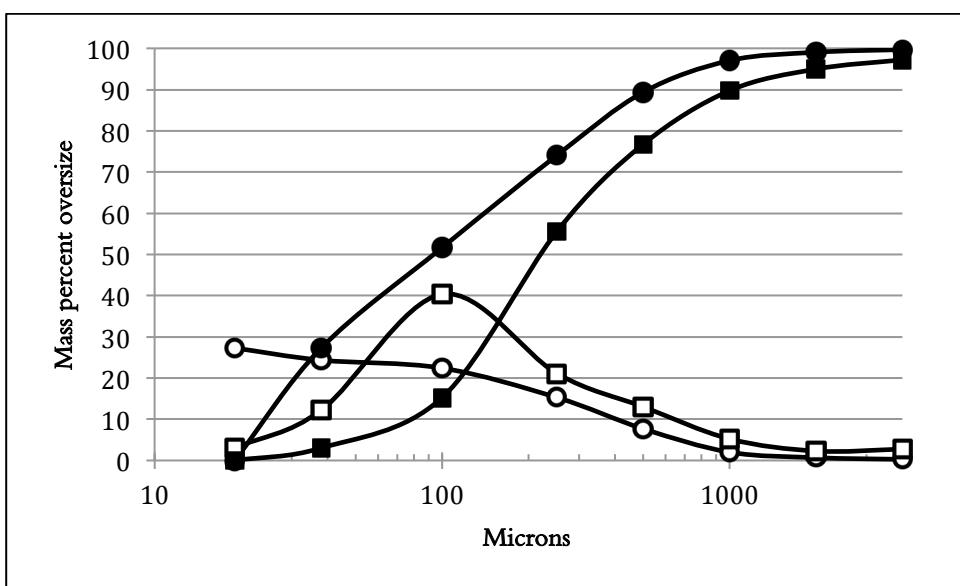


Figure 20: Particle size distribution in percent per sieve and cumulative distribution. Circles correspond to raw ash and cubes carbonised ash. Filled markings correspond to cumulative size distribution and hollow the size distribution.

4.1.2 Conductivity measurements

The conductivity measurements were performed to have a reference to compare the results with from the experimental program. The results from the three replicates for both carbonised ash and raw ash together with the mean and standard deviation is shown in Table 7.

Table 7: Results from the conductivity measurements in mS/m.

Sample	Raw ash	Carbonised ash
1	3980	1411
2	3920	1422
3	4020	1470
Average	3973	1434
Standard deviation	50	31

The results show that the carbonised ash has a much lower conductivity when in contact with water in the presented method. This agrees with the theory that a large portion of CaO has been converted to CaCO₃ in the treatment with carbon dioxide. The value for the carbonised ash is on a level that makes it possible to utilize the carbonised ash on all classes of dosages recommended by the Swedish Forest Agency, when comparing the results with Table 5. Also, the phase change alone may not have lead to the decrease in electrical conductivity, but also the particle size, as the particle size had increased after the treatment, reducing the area of mass transport.

4.1.3 SEM analysis

The SEM analysis was performed in order to study the material in more detail, especially to see the surface roughness and variations in the material. SEM analysis was performed on both the raw ash and carbonised ash.

Figure 21 shows a SEM picture with 100 times magnification of the raw ash. The ash contains generally small grains, with some amount of larger aggregates. Worth noticing in the picture are the structures seen on several aggregates, that looks like wood fibres. Especially in the upper right corner are these structures clearly seen. A picture with higher magnification on the expected wood fibre is seen in Figure 22. The structure seems to be ordered in a way that wood fibres are ordered. Thus, it is assumed that the sample contains some amounts of unburnt wood fuel. What also can be seen are precipitates of inorganic compounds on the surface of the fibres. These may come form for instance substances that was evaporated and finally recrystallized on the fibres surface when the temperature decreased in the furnace.

A high magnification picture with 50 000 times magnification can be seen in Figure 23. The surface is quite smooth, and seems to consist of elliptical particles bonded together. This in turn means that the surface roughness is low, and may affect the ballability when using raw ash in the formulations.

4. RESULTS AND DISCUSSION



Figure 21: SEM picture of the raw ash with 100 times magnification.

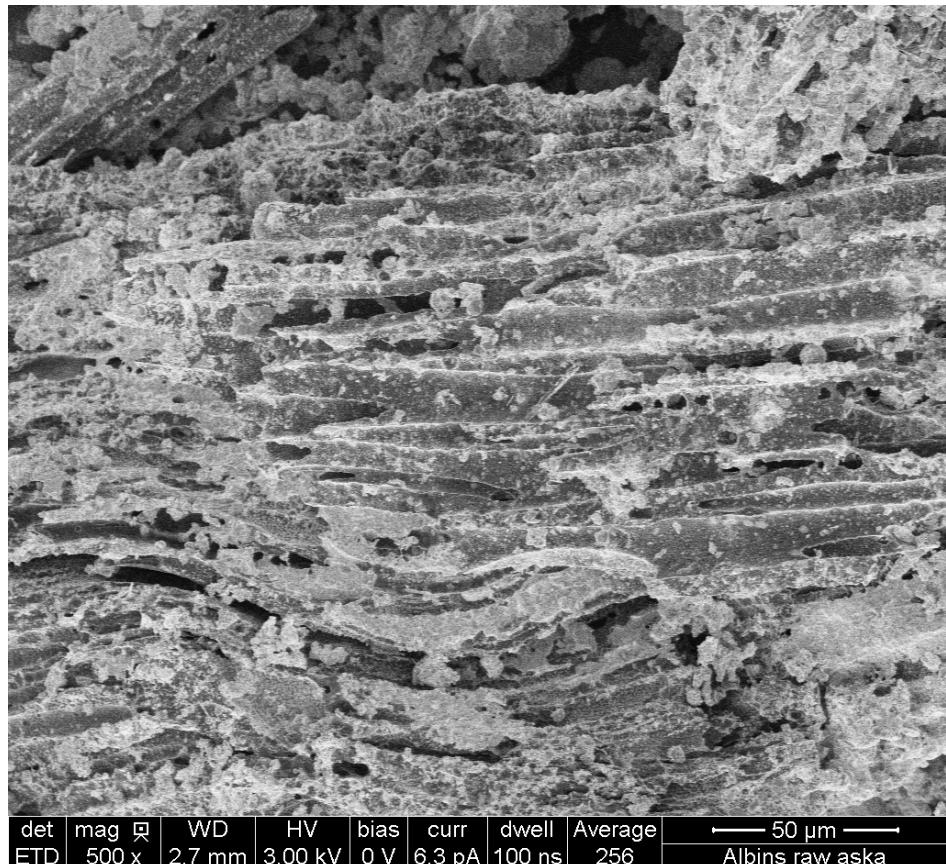


Figure 22: SEM picture of the raw ash with 500 times magnification. Zoomed in on an expected piece of wood fibre.

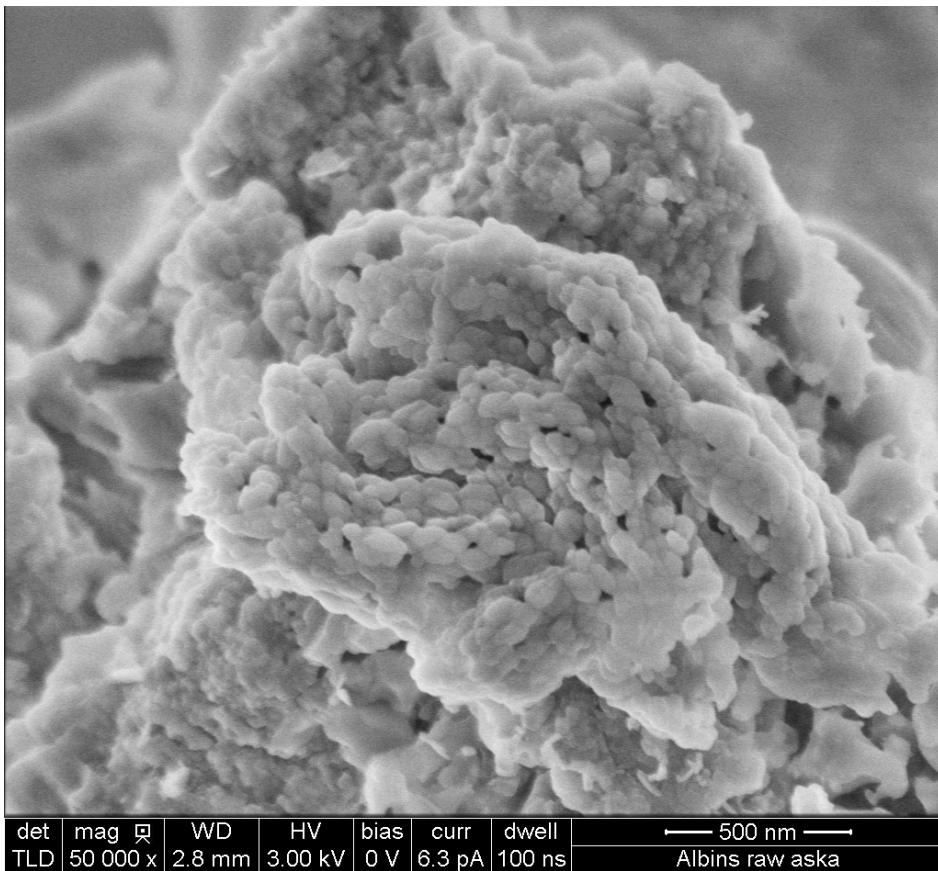


Figure 23: SEM picture with 50 000 times magnification of the raw ash.

Similar pictures of the carbonised ash are seen in the following figures. Figure 24 shows a 100 times magnification SEM picture of the carbonised ash. The particles are much bigger compared to the raw ash at the same magnification, which was presented in Figure 21. This is most probably due to the forming of calcium carbonate when the ash was treated with carbon dioxide from the biogas. The difference in particle size between the two ash samples was also found in the particle size distribution in Figure 20.

Figure 25 shows a SEM picture of the carbonised ash with 500 times magnification, zoomed in on a wood fibre. Almost the entire surface of the wood fibre is covered with some kind of coating. Compared to the raw ash, the wood fibre is coated in a higher degree for the carbonised ash, when comparing Figure 22 and Figure 25. This may also be an effect of precipitates of calcium carbonate on the surface.

To study the surface roughness of the sample, the magnification was increased considerably. Figure 26 shows a 50 000 times magnification SEM picture of the carbonised ash. As can be seen, the surface is very rough with clear edges and non-uniformity. This may be one of the major variables when considering the ballability of the ash. Especially when comparing the raw ash and carbonised ash, the carbonised has a much rougher surface.

4. RESULTS AND DISCUSSION

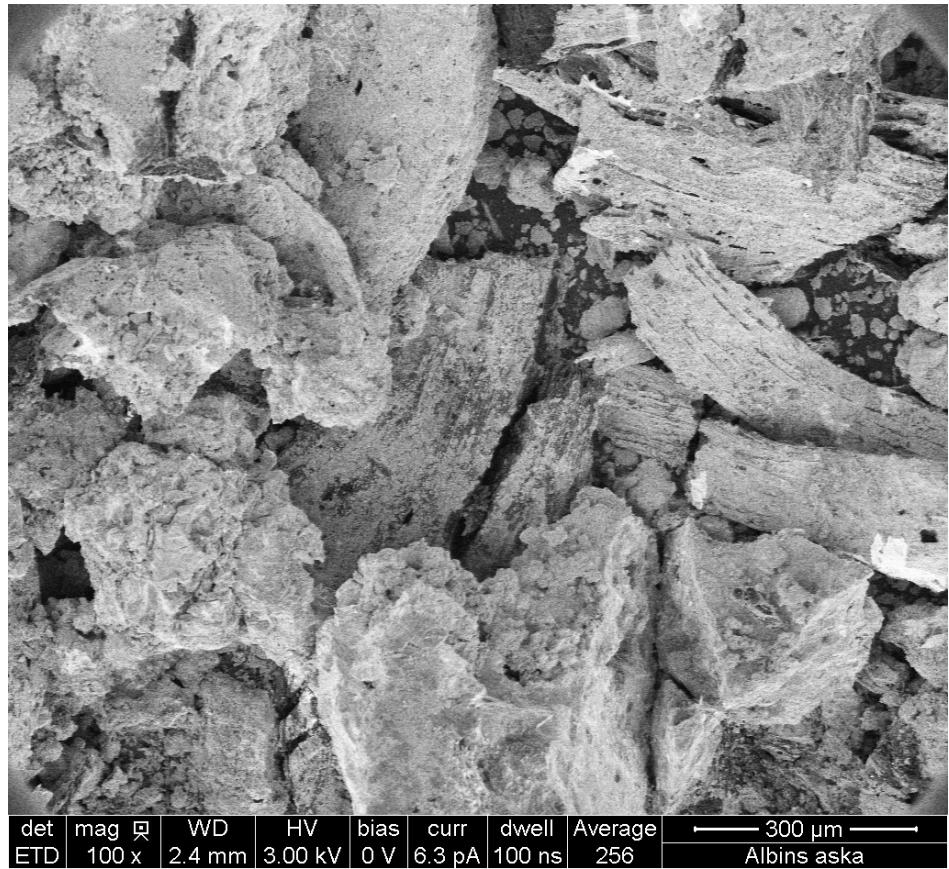


Figure 24: SEM picture of the carbonised ash with 100 times magnification. Zoomed in on a piece of wood fibre.

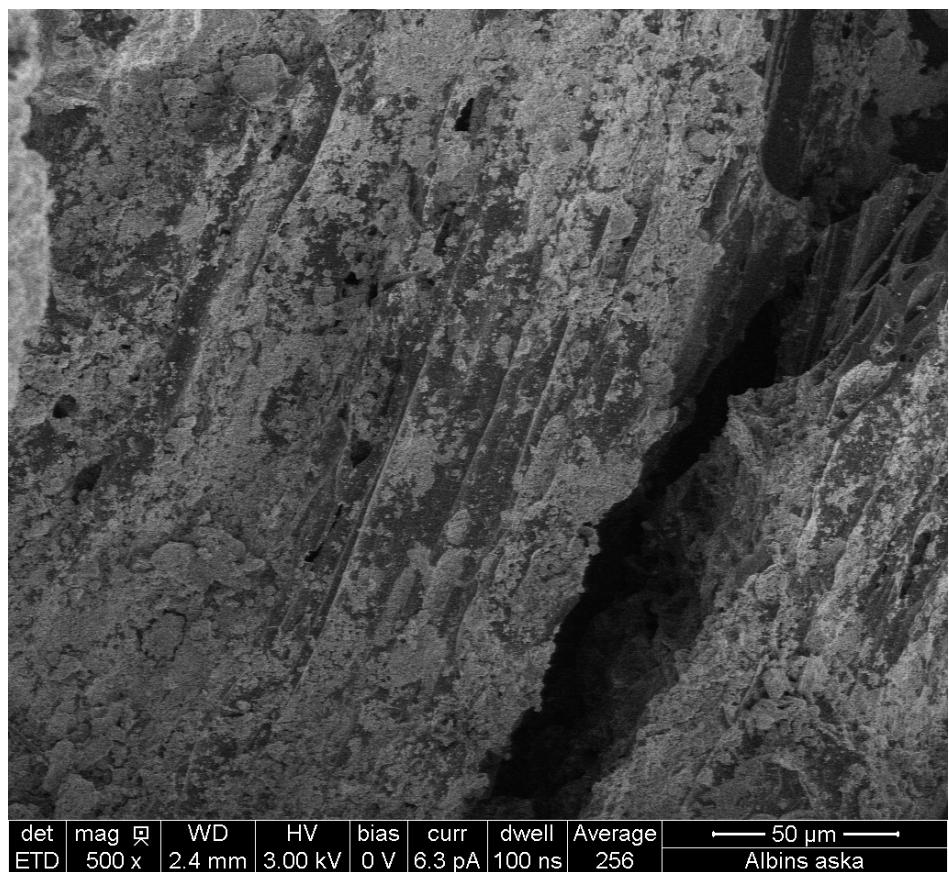


Figure 25: SEM picture of the carbonised ash with 500 times magnification.

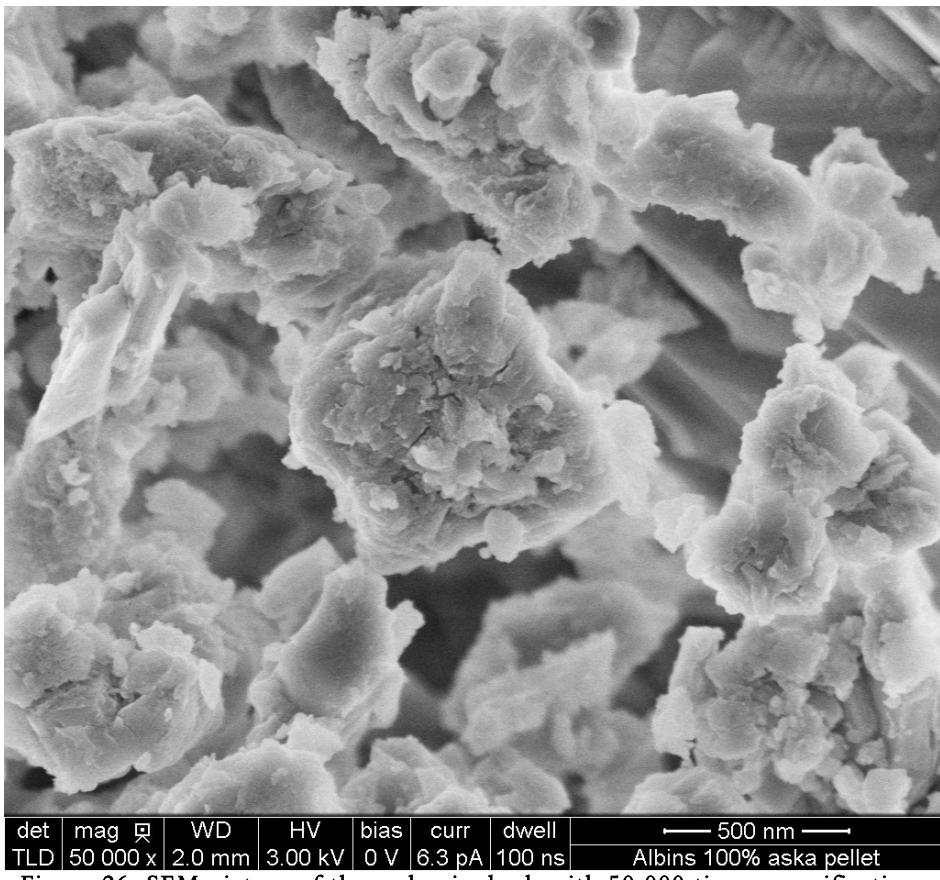


Figure 26: SEM picture of the carbonised ash with 50 000 times magnification.

4.2 GRANULATION EXPERIMENTS

The granulation experiments were performed according to the statistical plan created by MODDE. The variables granule moisture content, dry compression strength and conductivity was measured as response variables.

4.2.1 Statistical data of measured variables

The statistical data from the experiments are summarised in Table 8. The table presents statistical data such as minimum value, maximum value, mean value, and standard deviation (SD) for the measured variables for each run. As can be seen from the table, the granule moisture content and conductivity has a fairly low standard deviation. Dry compression strength, however, have much higher values on the standard deviation. The variation is probably due to the relatively broad product size range at which the test was performed on. The complete data sheets for the measured variables are found in Table 11, Table 12 and Table 13 in Appendix II.

The most important result that can be observed from Table 8 is the results from the conductivity measurements. All mean values are in the range of the conductivity measured for the carbonised bio-ash only, when comparing Table 8 with Table 7. This is one important result in the analysis, as this proves that all formulations used to produce granules are approved for fertiliser use in the forest.

4. RESULTS AND DISCUSSION

Table 8: Summary of statistical data for the measured variables.

Experimental name	Granule moisture content (Weight-%) (n=10)				Compression strength (N/granule) (n=10)				Conductivity (mS/m) (n=3)			
	Min	Mean	Max	SD	Min	Mean	Max	SD	Min	Mean	Max	SD
N1	28.1	29.9	32.6	1.2	11.5	14.9	20.5	2.7	1284	1351	1391	59
N2	21.2	23.9	25.6	1.3	16.9	20.8	29.7	4.2	981	993	1007	13
N3	24.7	26.5	28.4	1.4	12.0	17.6	27.9	5.4	1250	1254	1260	6
N4	17.8	23.8	27.5	3.8	16.9	24.4	33.9	5.3	1377	1390	1401	12
N5	26.4	28.3	31.5	1.7	4.9	5.7	6.7	0.6	1226	1273	1301	41
N6	19.4	23.1	25.8	2.3	13.2	16.4	18.1	1.6	1226	1254	1306	45
N7	24.0	26.2	28.2	1.5	8.4	12.0	14.9	1.9	1356	1361	1369	7
N8	19.2	23.5	26.0	2.3	14.5	18.7	25.6	3.5	1102	1250	1335	129
N9	26.1	27.6	29.0	0.9	7.0	9.4	14.0	2.1	1270	1297	1340	38
N10	20.6	22.1	24.6	1.2	16.8	23.9	29.0	3.8	1377	1404	1424	24
N11	23.5	25.8	30.5	2.3	9.6	13.8	18.0	2.8	1273	1315	1365	47
N12	24.5	27.0	29.3	1.8	10.2	16.8	22.7	4.5	1283	1315	1344	31
N13	20.5	26.0	30.0	2.4	15.2	17.9	22.0	2.6	1309	1321	1335	13
N14	24.9	27.2	29.1	1.1	9.6	14.2	20.5	4.0	1324	1356	1388	32
N15	23.7	26.4	28.9	1.7	11.2	14.1	19.6	2.8	1298	1325	1366	36
N16	23.7	26.1	28.1	1.3	9.6	14.6	22.5	3.6	1284	1294	1309	13
N17	22.5	26.2	28.2	2.0	10.5	15.2	21.0	3.6	1278	1289	1301	12

4.2.2 Statistical analysis of the used design

The data obtained from the measured variables were presented in Table 8, from which the mean values were used in the statistical design. A summary of the first model obtained from the data is shown in Figure 27, which shows the summary of fit for the initial model, here called model 1.

Four different bars are used in the summary to present the fit of the model. R^2 , the first bar to the left shown in green, is a measure of how good the model fits to the original data, also denoted as the goodness of fit. R^2 can have a value between 0 and 1, where a large value of R^2 indicates a good model. Q^2 , the second parameter from the left in the summary shown as dark blue bars, represents the predictive power of the model; more commonly named the goodness of prediction. Q^2 is a much more useful parameter when considering the usefulness of the model. Model validity, the third parameter from the left shown as yellow bars, gives information whether the model is of the right type, that means linear, quadratic, interaction etc. A low value of model validity indicates that the chosen formulation of the problem is incorrect, or fits badly to the experimental data. A value of 0.25 and higher indicates a suitable model. The last parameter, reproducibility, shown in the light blue bars, gives information about the variance in the measured variables, based on the measured midpoints.

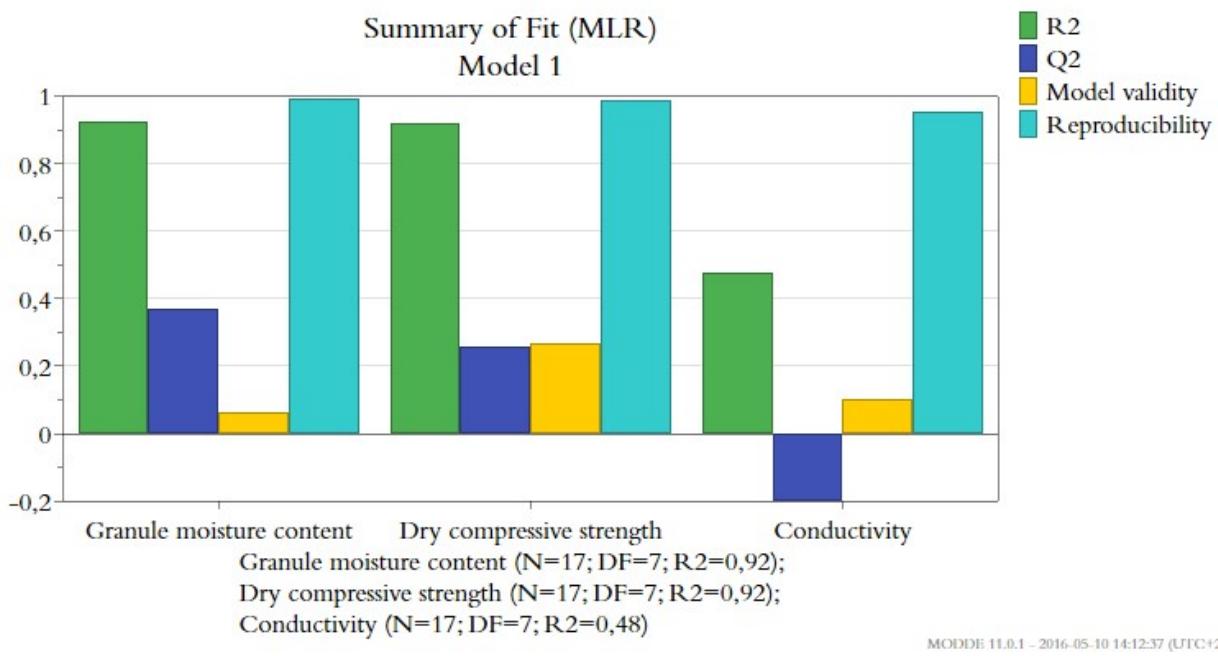


Figure 27: Initial summary of fit for the statistical design used in the experiments.

From Figure 27, it can be seen that the model fits quite good to the data for the responses Granule moisture content and Dry compressive strength. The response Conductivity, however, does not fit in at the same level. The R^2 value for Conductivity is approximately 0.45, while Granule moisture content and Dry compressive strength has values above 0.9. The Q^2 values, however, are rather low for all responses, but considerably lower for Conductivity. This indicates that the model is poorly fitted, or over-fitted by insignificant variables. Model validity shows, in a similar way as the Q^2 values, rather low values, indicating incorrect problem formulations. However, the reproducibility is very high for all responses.

To improve the statistical model, possible outliers that may impair the model may be removed. A normal probability plot was used to evaluate if outliers are present in the experimental data. Weak outliers are found in the limits $-4 SD$ to $-3 SD$ and $3 SD$ to $4 SD$, while strong outliers are found below $-4 SD$ and above $4 SD$. Weak outliers are not supposed to be removed but should be considered when evaluating the model. Strong outliers, however, indicates that the observation does not fit to the model, and may thus be removed or repeated to fit the data more efficiently to the model. The normal probability plot is shown in Figure 28.

A well-fitted model will have residuals that are normally distributed in the normal probability plots. This means that the residuals will form a straight line. As can be seen in Figure 28, the observations shows only small deviations from linearity, proposing a rather good distribution. However, for both the Dry compressive strength and Conductivity, two strong outliers are detected, observation number 10 for the Dry compressive strength and observation number 2 for the Conductivity. Observation number 2 for the Conductivity is most probably explained by the fact that these granules never dissolved when immersed in the liquid, but was held together as a granule. All other formulations fully or partially dissolved in the water. Replications of the test for observation 2 for conductivity showed similar results as the first run. Thus, this observation was removed from the data, to further develop the model. Observation number 10 for Dry compressive strength, however, is harder to explain, as no evident cause is found in the data in Table 12 in Appendix II. The standard deviation for this observation showed no abnormal value

4. RESULTS AND DISCUSSION

compared to the other, indicating that the strength analysis was not the reason to the bad fit of the observation to the model. This experimental number was however not replicated, but removed from the data set.

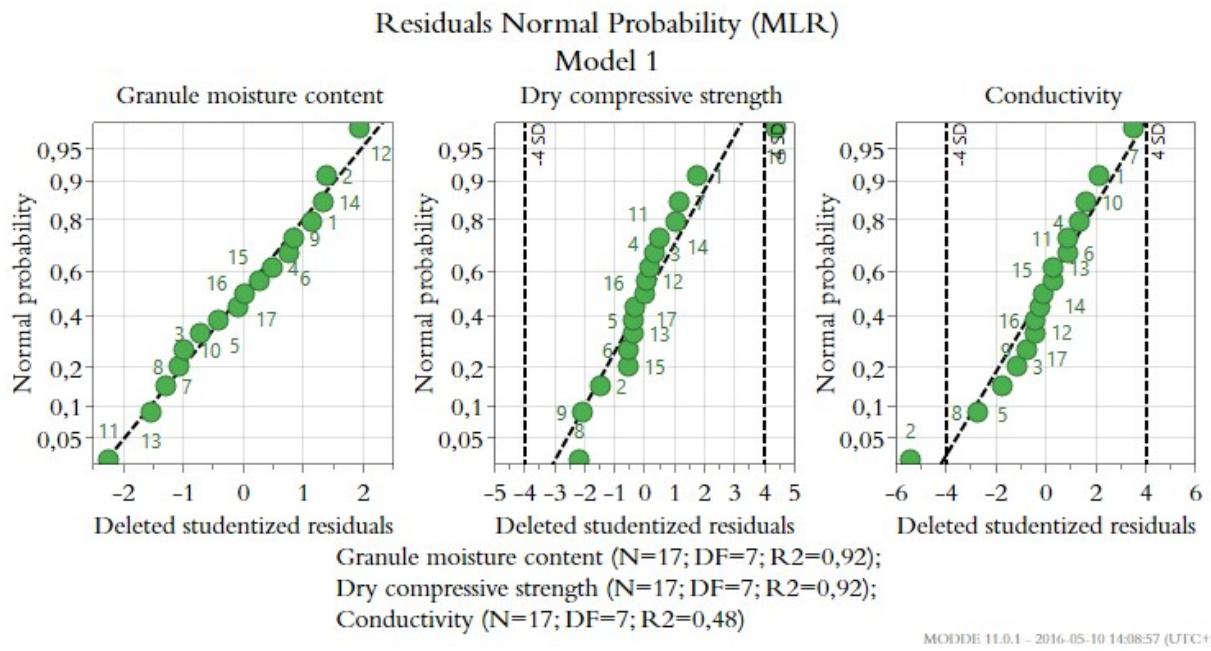


Figure 28: Normal probability plots of the deleted studentized residuals for each response of model 1. The numbers in the plots indicates the experimental number of the observation.

A second model was set up, with the strong outliers removed from the data. The summary of fit for this model, called model 2, is presented in Figure 29. The response Granule moisture content is unchanged, as no change was made for that response in model 2 compared to model 1. The other two responses, however, show big differences in the summary of fit. Especially the value of Q^2 for Dry compressive strength and model validity for both responses has increased considerably. However, the Q^2 value for Conductivity is still negative, indicating that the model is poor to use as a predictive model. The reproducibility also decreased when removing the outlier for Conductivity. R^2 , on the other hand, increased for both responses. The value of R^2 for the Dry compressive strength is close to 1 in model 2, which indicates a very good fit of the model to the original data. The R^2 value for Conductivity is approximately 0.65, which is a relatively high increase in goodness of fit, compared to model 1. Thus, it may be concluded that the removal of the two outliers strengthened the model in a positive way.

A new normal probability plot was set up to study the data that was used in model 2. This plot is shown in Figure 30. In model 2, no strong outliers are detected, according to the figure, as no observation is located below $-4 SD$ or above $4 SD$. However, one weak outlier for both Dry compressive strength and Conductivity was detected, located close to the $4 SD$ limit. As these are not strong outliers, they were kept in the model.

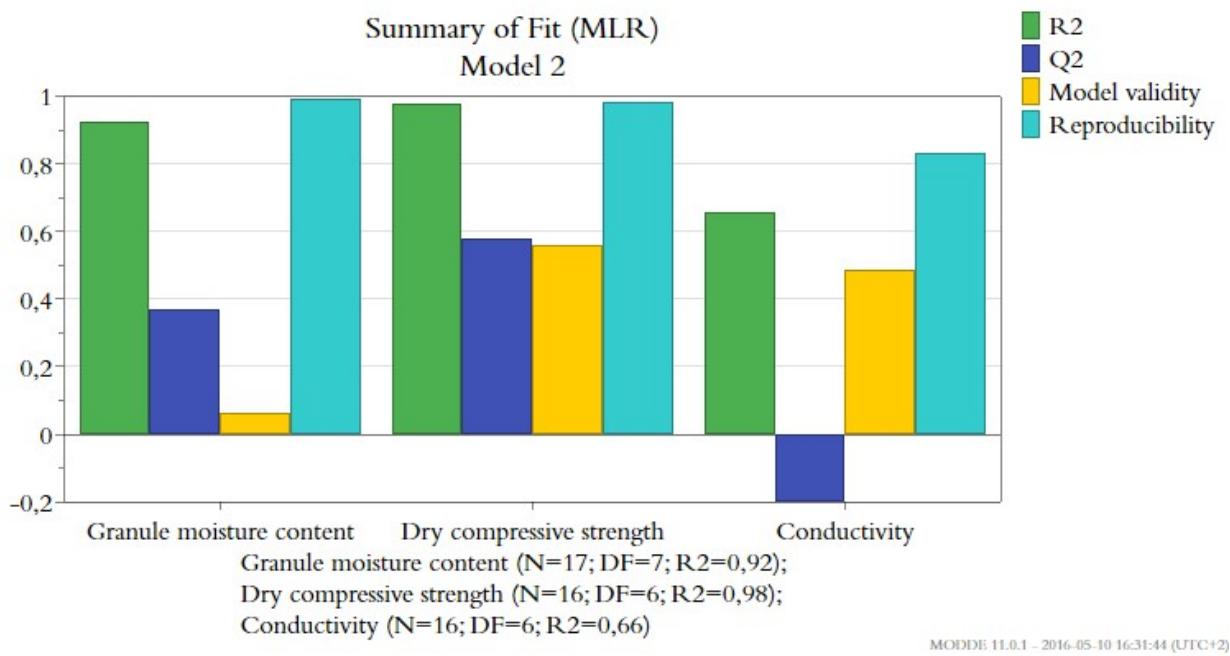


Figure 29: Summary of fit for model 2.

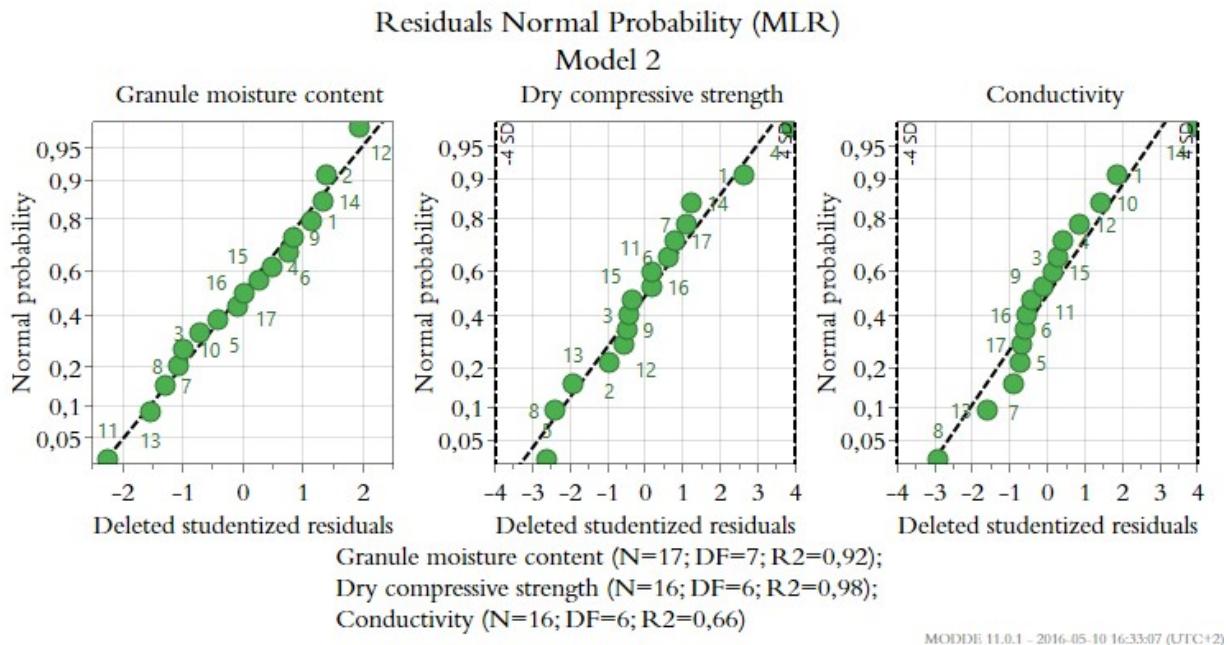


Figure 30: Normal probability plots of the deleted studentized residuals for each response in model 2.

Model 2 was an improved model compared to model 1, but may still be further improved. To improve the model more, and to study the effects of the design variables and its interactions, an effects plot was used. In the effects plot, each design variable and the interaction between them are sorted according to their significance for the model. An extreme value such as a highly positive value or a highly negative value means that the factor is of high significance in the model. What are also shown in the plot are the confidence intervals, with 95 % certainty. Small values of the effect or confidence intervals passing through the x-axis indicate factors with low or no significance. The effects plot for model 2 is shown in Figure 31.

4. RESULTS AND DISCUSSION

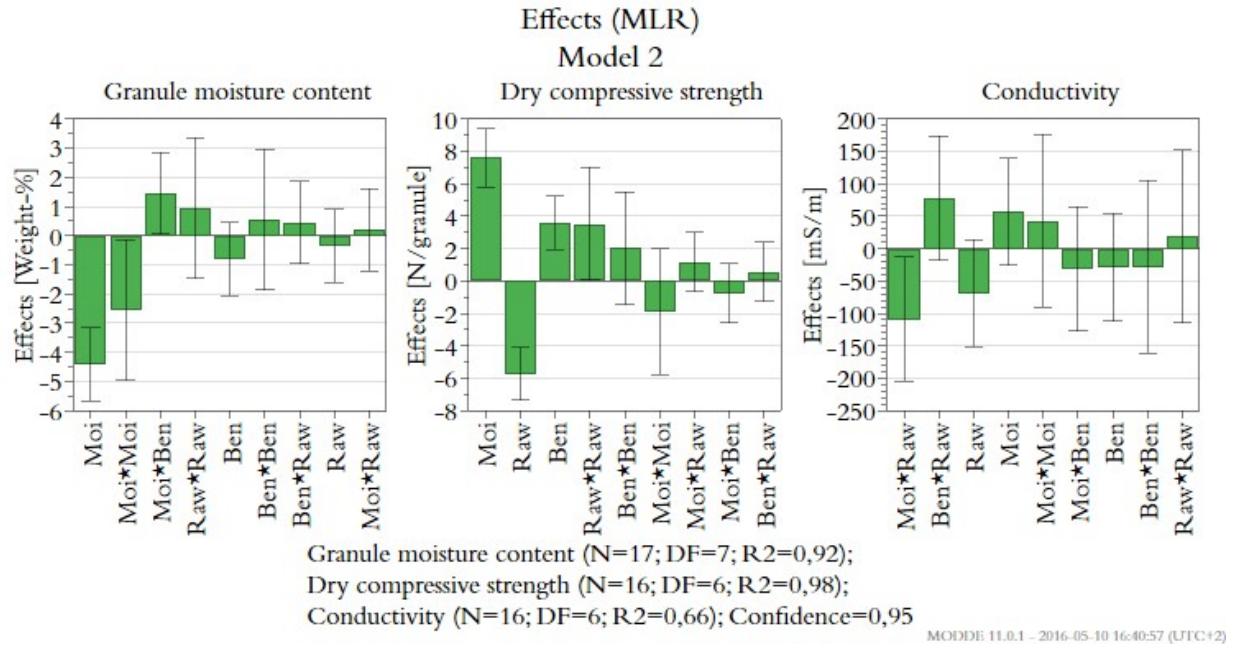


Figure 31: Effects plot for model 2. The abbreviations in the figure are the following: Moi – Moisture content; Ben – Bentonite content; Raw – Raw ash content.

From Figure 31, it is possible to see that several interactions are of low significance or no significance at all. This means that these may be removed from the model, to improve the model. Linear factors such as design variables are however not removed from the model, as these are the design variables. As the goal is to find a suitable formulation from the final model, the goodness of prediction is the main factor that should be concerned when improving the models. However, the normal probability plots are also important, as these should also be improved in the development of the model.

Improvement of model 2 in terms of R^2 and Q^2 when removing insignificant interactions are presented in Table 9. Significant improvements are made when removing several interactions from the model, which can be seen in the table. Q^2 for both Granule moisture content and Dry compressive strength increases considerably when removing insignificant interactions. This points towards the fact that the model was initially overfitted by these interactions. Conductivity, however, does not increase at all as the value of Q^2 is still negative. Thus, no improvement on goodness of prediction was possible for Conductivity. R^2 , however, decreased for all responses when reducing the model, due to a worse fit of original data to the model. Due to this result for Conductivity, this response will not be discussed further in the statistical model, as the information that the model gives will not be useful, due to the low value of goodness of prediction.

The excluded interactions presented in Table 9 forms model 3. The summary of fit, normal probability plot of residuals and effects plot form model 3 are presented in Figure 45 to Figure 47 in Appendix III. From the summary of fit plot in Figure 45, it can be seen that the Q^2 values for Granule moisture content and Dry compressive strength has increased considerably. As can be seen in the effects plot, Figure 47, all factors and interactions that are left in the model are significant. However, the normal probability plot of residuals, Figure 46, shows a decrease in linearity when comparing with the normal probability plot of model 2. Thus, model 3 is not assumed to be a good model, as the normal distribution of residuals are further away from linear

in model 3. When examining Table 9, it may be noted that only the first removed interactions significantly increase the goodness of prediction, while the following excluded interactions only result in a small increase. Thus, several of the interactions in Table 9 may be kept in the model, to better explain the variance in the model. This in turn makes the model better when considering the residuals.

Table 9: Improvement of model 2 in terms of R^2 and Q^2 when excluding insignificant interactions. Moi – Moisture content; Ben – Bentonite content; Raw – Raw ash content.

Granule moisture content			Dry compressive strength			Conductivity		
Excluded interaction	R^2	Q^2	Excluded interaction	R^2	Q^2	Excluded interaction	R^2	Q^2
None	0.92	0.37	None	0.98	0.58	None	0.66	-0.20
1 Moi★Raw	0.92	0.59	1 Ben★Raw	0.97	0.80	1 Raw★Raw	0.65	-0.20
2 Ben★Ben	0.92	0.64	2 Moi★Ben	0.97	0.86	2 Ben★Ben	0.64	-0.20
3 Ben★Raw	0.91	0.74	3 Moi★Raw	0.96	0.86	3 Moi★Ben	0.60	-0.20
4 Raw★Raw	0.90	0.76	4 Moi★Moi	0.96	0.87	4 Moi★Moi	0.58	-0.20
			5 Ben★Ben	0.95	0.88	5 Ben★Raw	0.40	-0.20

A model with the first three interactions for Granule moisture content and the first interaction for Dry compressive strength was set up (interactions from Table 9). These interactions were removed as to keep the goodness of prediction high simultaneously as the residuals were normally distributed. The summary of fit for this model, named model 4, is presented in Figure 32.

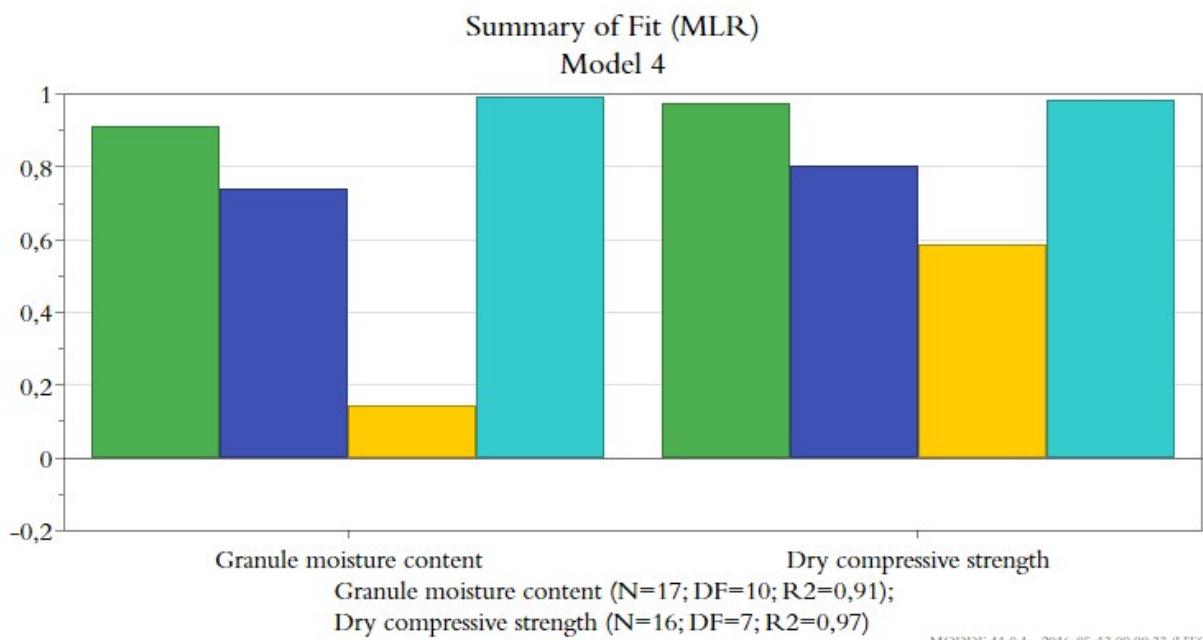


Figure 32: Summary of fit for model 4, with an alternative reduction in interactions compared to model 3.

Model 4 has high values of R^2 and Q^2 for both responses according to Figure 32. What also can be seen is the high improvement of model validity for Dry compressive strength. Granule moisture content, on the other hand, has fairly low model validity. This is probably due to a poorly formulated problem formulation in the design of the experiment.

The residuals normal probability plot is shown in Figure 33. The residuals are very well approximated as a straight line in the figure, indicating an error in the experiment that is

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normally distributed and random. Moreover, there are no outliers, neither strong nor weak. These results together with the summary of fit in Figure 32 suggests that model 4 is a fairly good model, to model Granule moisture content and Dry compressive strength. The improvements of the normal probability plots for the residuals suggests that the interaction terms gives information on the variance in the data, even though they are statistically insignificant considering the 95% confidence intervals.

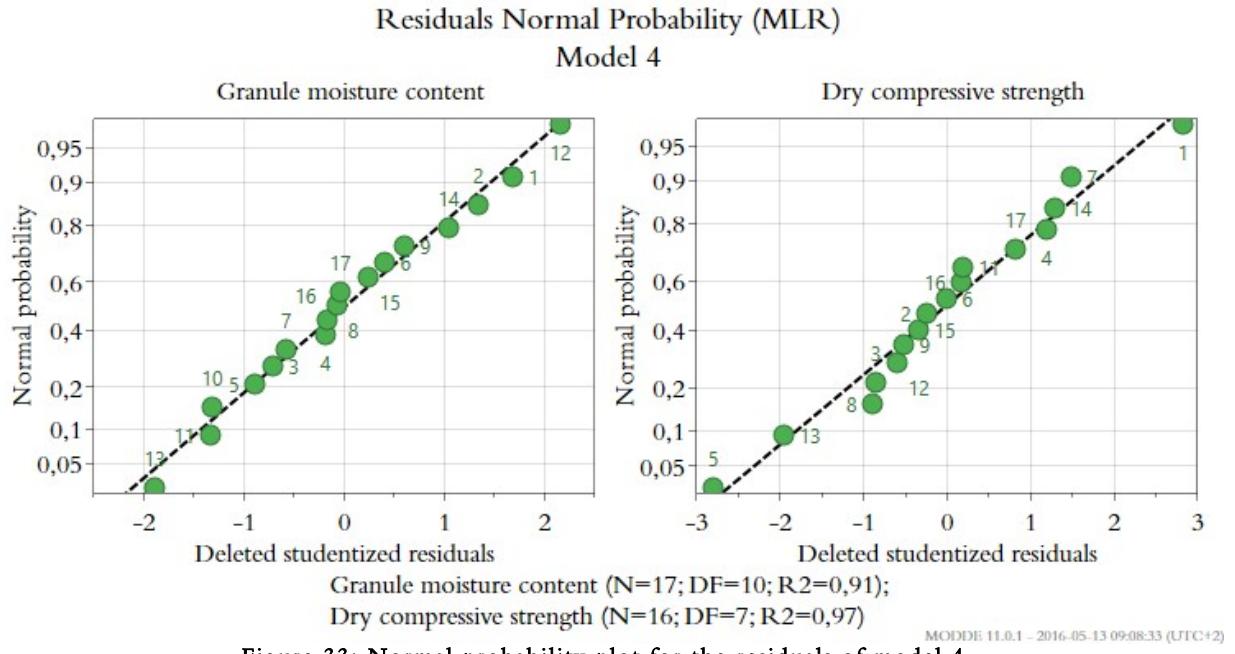


Figure 33: Normal probability plot for the residuals of model 4.

The effects that were kept in the model are shown in Figure 34. As can be seen, several interactions are kept in the model even as they have confidence intervals passing through 0, to better fit the residuals to the normal probability plot. Several main effects were also non-significant, but as they are in fact main effects they were kept in the model.

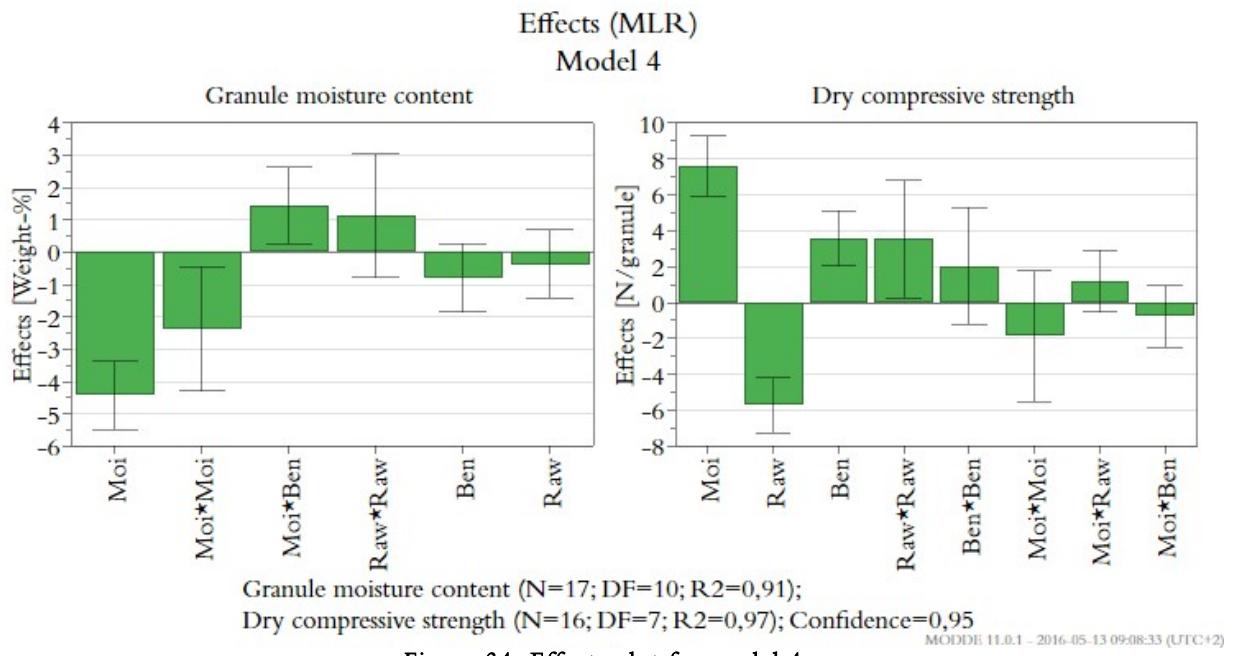


Figure 34: Effects plot for model 4.

To further study the model obtained, main effects plots are evaluated. Main effect plots shows the effect of a design variable on a specific response variable. The main effect plots are discussed for each design variable in the following sections.

4.2.3 Effect of initial moisture content

To study the effect of the initial moisture content on the response variables, a main effects plot for moisture content are used. This plot is shown in Figure 35. High moisture content decreases the granule moisture content and increases the dry compression strength. This effect is probably due to that high initial moisture content wets the particle better from the beginning, facilitating growth at lower moisture content, leading to a lower granule moisture content. High moisture content in the same size fraction indicates that the granules consist of a higher amount of water, trapped inside pores in the granule. Thus, high initial moisture content will lead to a relatively low porosity. As was seen in the Rumpf equation, equation (2.13), the tensile strength of wet granules will increase when the porosity is lowered. Thus, low granule moisture content in the granules will lead to stronger wet granules. The effect of porosity on dry strengths is found out to be similar, as a low porosity indicates large contact areas between particles that may form bonds. This is actually the result which are shown in Figure 35: a high initial moisture content leads to a low granule moisture content, and in turn stronger granules.

The shapes of the curves are different for the responses. For Granule moisture content, a curvature effect is present, seeming to be formed by quadratic interactions. When checking the effects plot in Figure 34 for Granule moisture content, it is seen that the linear term and quadratic term of the initial moisture content are the two most significant effects. Thus, the effect of initial moisture content on Granule moisture content is suggested to be modelled as a quadratic equation. This explains the curvature in the main effects plot in Figure 35. The second response, Dry compressive strength, also seems to have some curvature effects. This is probably a result of the same phenomena, as the quadratic term of initial moisture content is kept in the model. As the quadratic term has a considerably lower significance on the Dry compressive strength than the linear one, only a slight quadratic effect is affecting the dry compressive strength. This argument is considered valid as it matches both the results in Figure 34 and Figure 35.

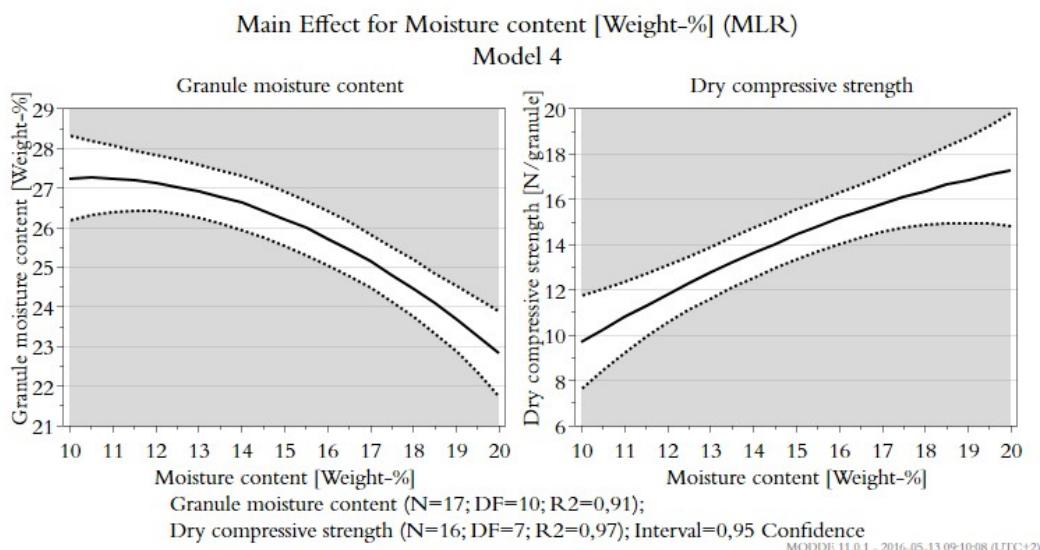


Figure 35: Main effects plot for moisture content, for model 4.

4. RESULTS AND DISCUSSION

4.2.4 Effect of bentonite content

The main effects for bentonite content on the responses are shown in Figure 36. High bentonite content lowers the final granule moisture content, while it increases the dry compression strength exponentially as a function of bentonite content. The explanation to the shape of the curve for dry compressive strength may thus be two folded. Firstly, bentonite is known to increase strength due to its interaction with solid particles, strengthening the bonding in the granule. Moreover, as the granule moisture content decreased at higher bentonite contents, the addition of bentonite reduces the porosity, leading to increased tensile strength of wet granules according to the Rumpf equation, and the dry strength as the contact area between particles increases. As a result to the decreased porosity, the bentonite can more effectively bond the particles together, as they are closer. This may be an overall explanation to the exponential increase in dry compression strength. However, as no porosity measurements were performed, this theory cannot be validated completely.

The shapes of the main effects are both linear and curved, as is seen in the figure. For Granule moisture content, the linearity is explained mainly by the interaction term between initial moisture content and bentonite content, together with the main effect of bentonite content. For Dry compressive strength, however, a curved line is seen. This curvature is based on, similar to the main effect discussion of initial moisture content in Granule moisture content, quadratic and linear terms on bentonite content, as can be seen in the effects plot of Figure 34.

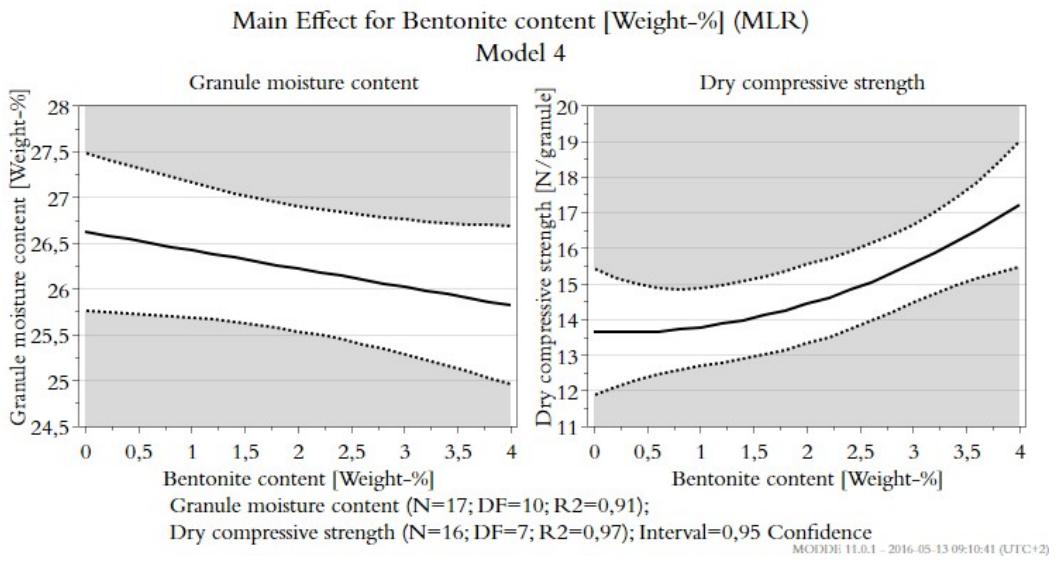


Figure 36: Main effects plot for bentonite content, for model 4.

4.2.5 Effect of raw ash content

The main effects for raw ash content are shown in Figure 37. This main effect shows some rather strange and unexpected results. The effect on granule moisture content shows a positive quadratic formula, hard to explain from theory. This may be one of the reasons to the relatively low model validity for Granule moisture content in the model.

For the dry compressive strength, however, a clear drop in dry compressive strength is seen at higher contents of raw ash. This is also an unexpected result, as the addition of raw ash was made to increase the amount of CaO in the formulation, and to theoretically increase bonding by solid bridges of Ca(OH)₂. However, as was seen from the SEM pictures on the raw ash, the surface of the raw ash particles were rather smooth, with low surface roughness, compared to the

carbonised ash. This may be the explanation to why the dry compressive strength decreased with increased raw ash content: the smooth surface interrupts the structure obtained from the carbonised ash. This result clearly indicates that an addition of raw ash to the formulation is unwanted in a future full-scale process.

The reason to the curvature of Granule moisture content due to the model is based on a positive significance of the quadratic term of raw ash content, and a negative significance for the linear effect of raw ash content. The same reason is found for Dry compressive strength, as the quadratic term has positive significance and linear term negative significance. However, they are of different absolute values compared to the effects on Granule moisture content. This difference in effects explains the difference seen in the curvature in Figure 37.

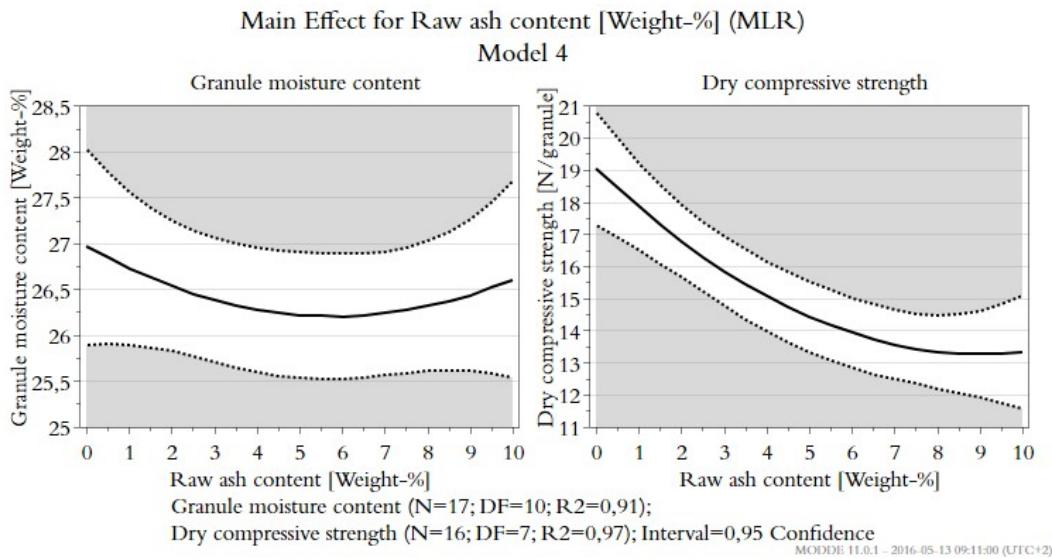


Figure 37: Main effect for raw ash content, for model 4.

4.2.6 Interaction effects

To study how the main effects interact with each other in the model, interaction plots are used. These plots show if one variable are dependent on the level of another. The interaction plot for the interaction between moisture content and raw ash content is seen in Figure 38. This interaction is used to model the Dry compressive strength. In this plot, only a weak interaction is found between the variables, as no lines are crossing each other. A lower value of raw ash content gives a slight less effect of moisture content at higher moisture contents. According to the effects plot of model 4, Figure 34, this interaction is basically insignificant for the predictive value of the model, which explains the low interaction between the variables.

The second and last interaction that was used in the model was the interaction between moisture content and bentonite content. This interaction is used to model Granule moisture content and Dry compressive strength. The interaction plot is shown in Figure 39.

The interaction between moisture content and bentonite content may be considered as a strong interaction, when discussing Granule moisture content, as the effect of moisture content on granule moisture content are highly dependent on the level of bentonite content. A higher value of bentonite content increases the importance of moisture content. For Dry compressive strength, however, almost no interaction is seen. This may be explained by the low significance of this interaction in the model, according to the effects plot of model 4 in Figure 34.

4. RESULTS AND DISCUSSION

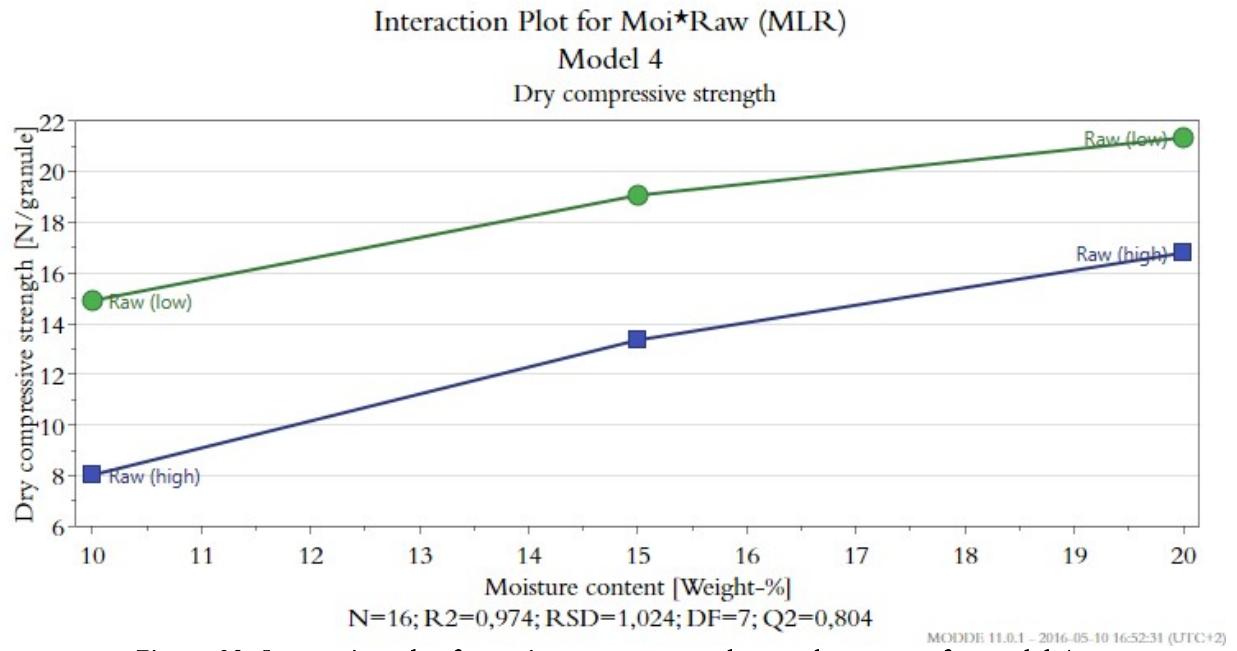


Figure 38: Interaction plot for moisture content and raw ash content, for model 4.

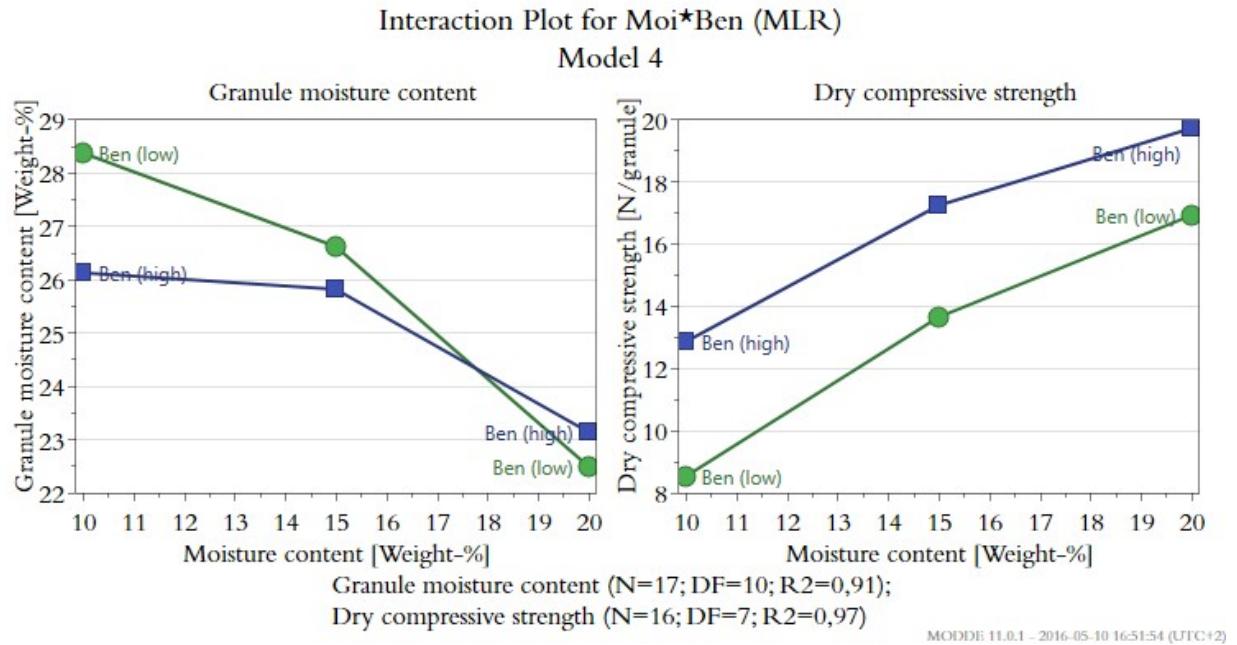


Figure 39: Interaction plot for moisture content and bentonite content, form model 4.

4.2.7 Optimisation of dry granule strength

From the response variables used in the design, Dry compressive strength is the most important as Granule moisture content was analysed to act as a measure of porosity and Conductivity was measured to see if the formulations were approved according to the recommendations made by the Swedish Forest Agency. Thus, the model created may be used to find the optimum formulation in order to maximise the dry compressive strength.

To find the optimum formulation, a 4D response contour plot was used. The contour plot is presented in Figure 40. The plot uses the design variables to study the effect on the dry compressive strength. From the figure, it is possible to see that the highest dry compressive strength is obtained at the upper right corner of the graph to the left in Figure 40. This indicates

that the highest dry compressive strength is obtained at high initial moisture content, high bentonite content, and low raw ash content. However, what can also be seen is that a fairly high dry compressive strength may be obtained at lower bentonite contents, but at high initial moisture contents and low contents of raw ash. The difference between the dry compressive strength of bentonite containing formulations and non-bentonite containing formulations are rather small, if the initial moisture content is kept at a high value. Thus, it is actually possible to form granules that possess a relatively high dry compressive strength without solid binders. The most important design variable was the initial moisture content, as is evident from Figure 40.

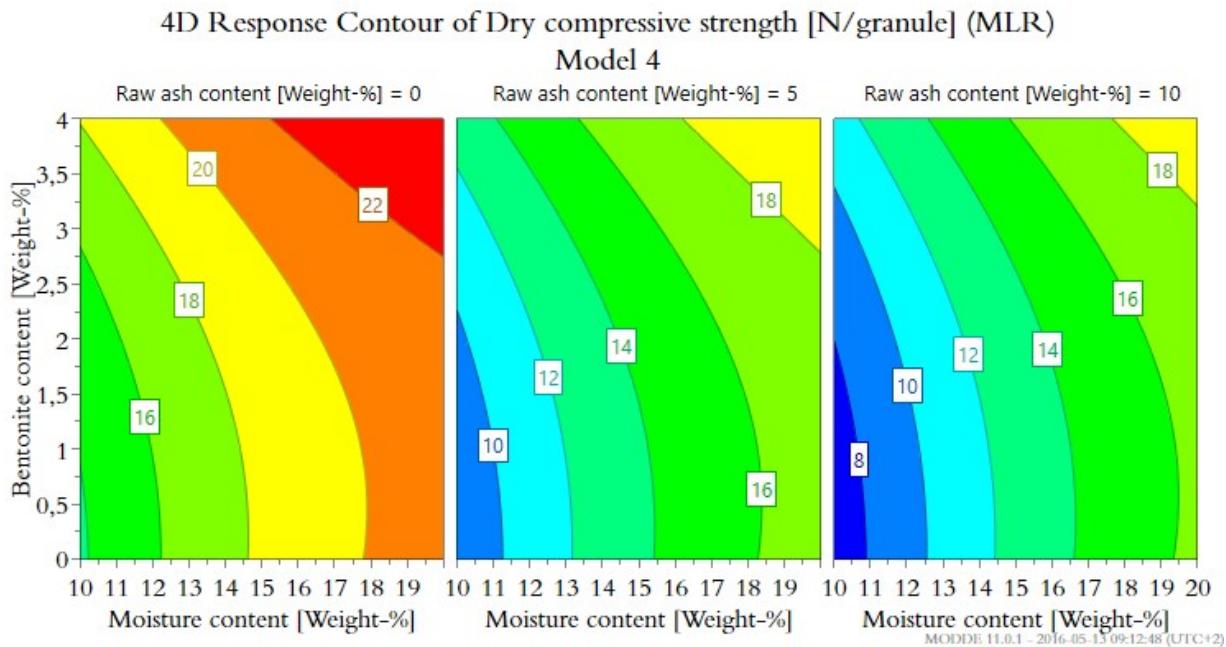


Figure 40: 4D response contour plot for Dry compressive strength, for model 4.

4.3 SEM INVESTIGATION ON GRANULES

From the contour plot in Figure 40, it was seen that it is possible to get a relatively high dry compressive strength without the addition of a solid binder. The binding mechanism of bentonite has been thoroughly investigated by several researchers, and was explained in the literature review. However, the binding mechanism in the granules consisting of only carbonised ash has not been confirmed. This is the aim of the SEM investigation, to see what kind of binding mechanism that is active in the granules of carbonised ash. Also, when using the SEM, the structure inside the granule may be revealed.

The granule that consisted of 100% carbonised ash and 20% initial moisture content was used in the SEM examination. A SEM picture with 65 times magnification is seen in Figure 41. This picture shows the whole cross section of the sample. Black dots in the picture are pores, which most probably have been produced due to enclosure of air bubbles in the granulation procedure. The structure is very dense in general.

4. RESULTS AND DISCUSSION

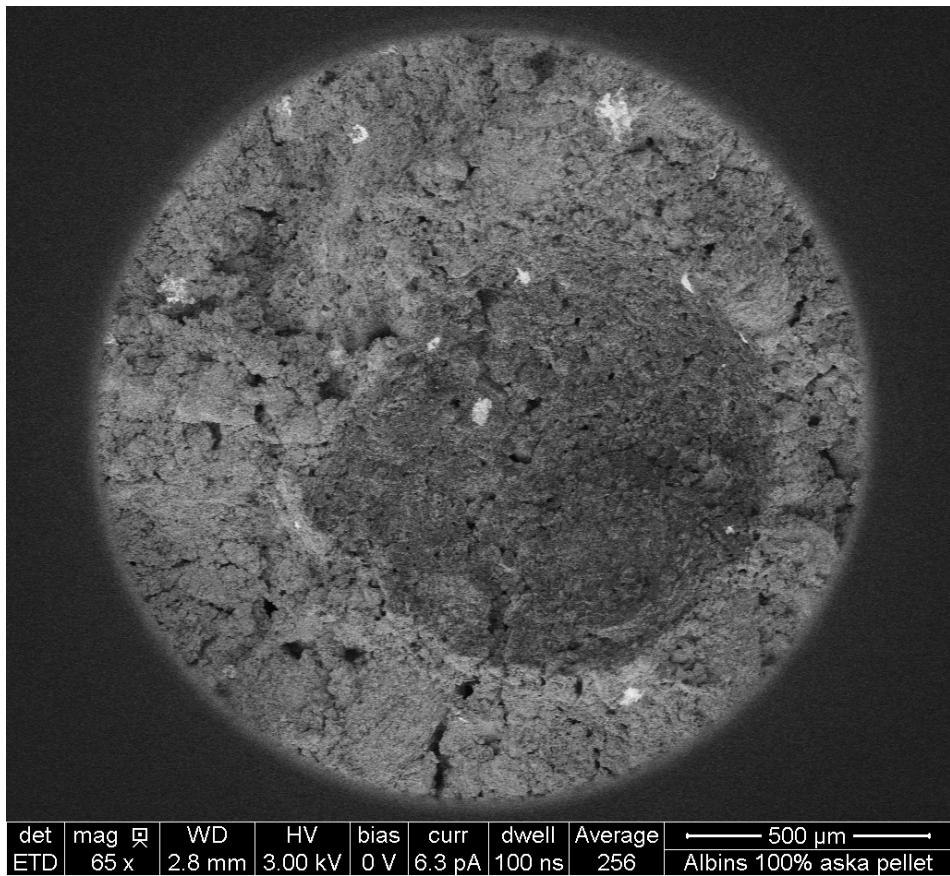


Figure 41: SEM picture of a cross section of the 100% carbonised ash granule, with 65 times magnification.

Figure 42 shows another SEM picture with higher magnification than Figure 41. Also in this image, it can be seen that the structure is highly dense. A crack is also clearly seen in the figure, probably a result from the splitting of the granule. The dense packing is probably a result of the long consolidation time used in the granulation procedure.

Increasing the magnification in the SEM shows the dense packing at particle level. Figure 43 shows a SEM picture with 10 000 times magnification. As can be seen, this structure is clearly denser than the structure of the ungranulated carbonised ash. Also, the surface is more irregular, indicating that some precipitations may have been formed in the granulation procedure. This may for instance be a result of partial solubilisation of constituents from the carbonised ash. It may also be a result from the reaction between CaO and water, eventually forming solid bridges between particles. However, a higher magnification than 10 000 times is required to study the bonding characteristics of the granule.

Figure 44 shows a 100 000 times magnification SEM picture of the 100% carbonised ash granule. At this level, it is possible to see solid bridges between the particles, which bonds them together. Thus, the forming of solid bridges is the most likely bonding mechanism in the granule. This was the expected bonding mechanism due to the reaction between CaO and water as was discussed in the literature review. This also means that the bonding mechanisms for bentonite and carbonised ash are different, as bentonite mainly binds particles together using small particles that are drawn to the particle surfaces when dried. Therefore, in granules consisting of a small portion of bentonite, the bonding mechanisms may be two-folded: by solid bridges and by electrostatic attractions due to small particles.

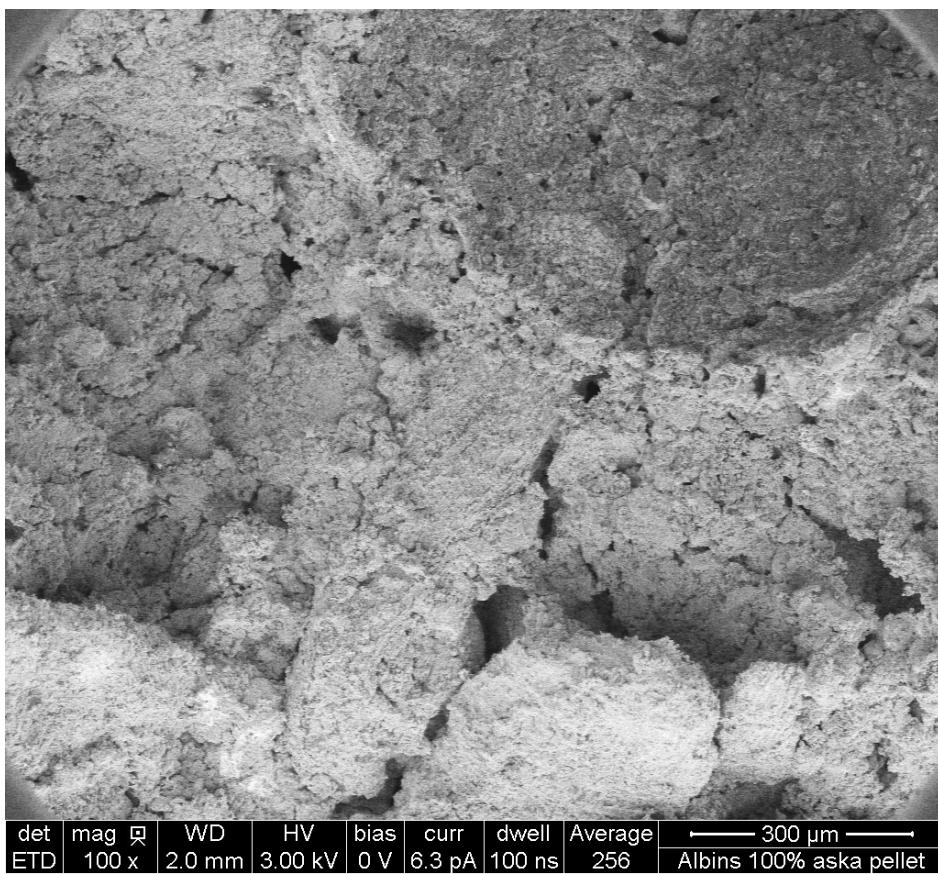


Figure 42: SEM picture of the granule with 100 times magnification.

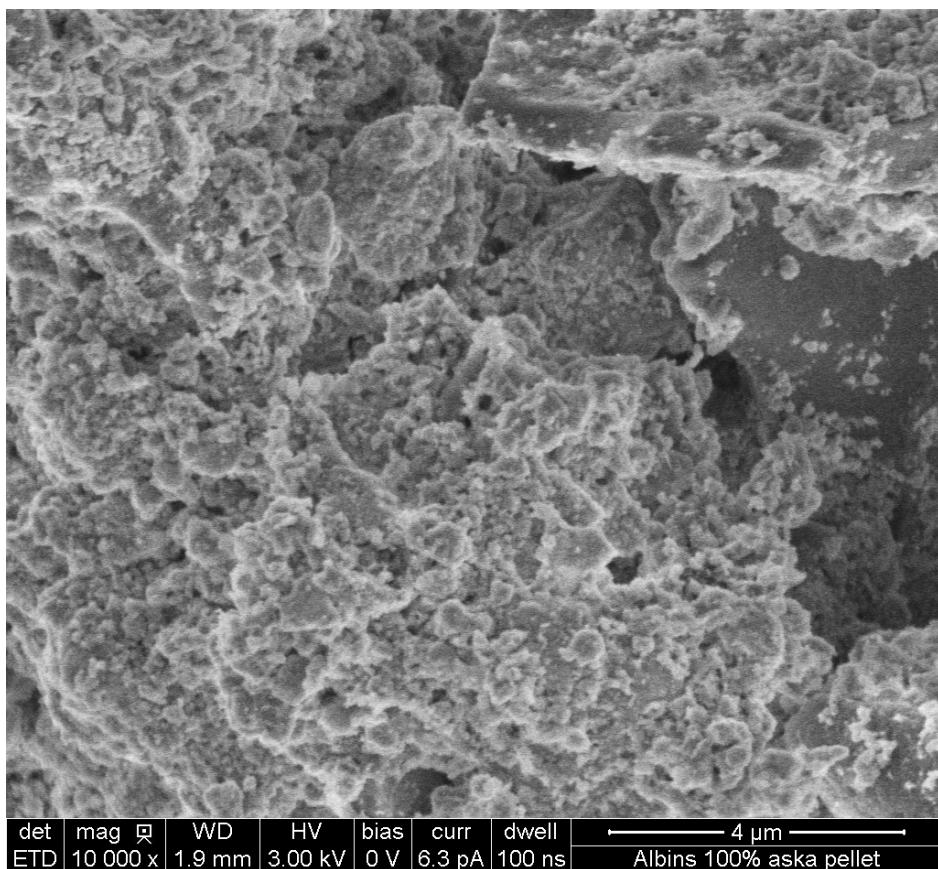


Figure 43: SEM picture of the granule at 10 000 magnification.

4. RESULTS AND DISCUSSION

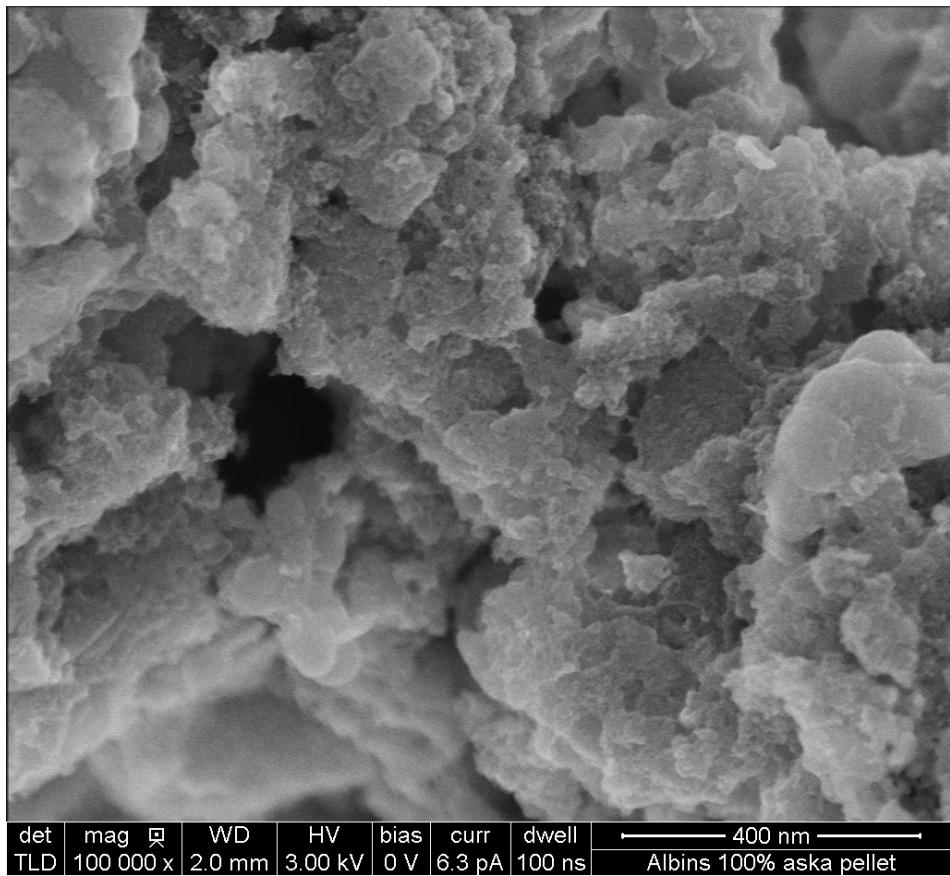


Figure 44: SEM picture of the granule at 100 000 times magnification.

4.4 SUMMARY

This section summarises the experiments made in the project.

4.4.1 Evaluation of granulation and measurement procedure

The granulation procedure developed for this project was proven to be effective, as the most important response variable, Dry compressive strength, could be modelled effectively by the proposed model created in MODDE. Two outliers were detected, from which one was hard to explain. The reason to this deviation may be some of the other variables important in wet granulation, such as viscosity of liquid binder, contact angle between the binder liquid and solids, surface tension of the liquid binder, or any process variable such as inclination, rotation speed and binder delivery method. Some of these may have been changed without noticing during the experiments, which in turn may have lead to the actual outlier.

As the other variables listed were not evaluated but kept constant, the results from this project mainly proves that it is possible to granulate the carbonised ash with or without binder depending on the requirements on dry compressive strength. Also, wet granule strength and drop number were not measured. These variables were not measured, as the main objective was to see if it is possible to form granules. Wet compressive strength is however an important process variable in full scale processes, and may thus be examined during up scaling. Process variables such as inclination, binder delivery method, and rotation speed are other important process variables to consider in full-scale processes, and may be one of the design variables during scale up of the process.

The measurement of compressive strength by the build rig is considered to be successful, as it was possible to determine the difference in strength between the formulations. However, as no correlation to more common standard measurement methods, it is hard to compare the results to existing applications in the area of granules.

The main disadvantage in the granulation procedure was the choice of product size range. As the suitable size range for granules in forestry applications are said to be 2 – 5 mm, a range of 4 – 8 mm is quite high compared to the recommendations. The higher bound in the range 2 – 5 mm was used in order to simplify the measurement of granule moisture content and dry compressive strength, and thus 4 – 6 mm or 4 – 5 mm would have been a good choice of product size span. The span 4 – 8 mm was however used as no sieves at 5 or 6 mm was available.

4.4.2 Granule moisture content results

The granule moisture content was measured as a rough indication of porosity in the granules. Therefore, this response was primarily a variable used to discuss the dry compressive strength obtained in the experiments. The granule moisture content could however quite sufficiently be modelled by the obtained model in MODDE, which was useful when discussing the dry compressive strength.

4.4.3 Dry compressive strength results

The dry compressive strength results were the most important result in this project, as the aim was to produce granules with sufficient strength. It was possible to obtain a high strength using solid binders, but also without binders, which is a successful result in particular. However, as no data is found on how high the compressive strength actually must be to overcome external forces, it is hard to determine if the strength is enough for industrial purposes. For the limits of this project however, the granules are considered to have a relatively high strength.

The measurements of dry compressive strength have a rather high standard deviation. This is believed to be caused by the broad product size range. During the measurements it was observed that the strength was dependent on size. But, as the product size was not measured as a variable, or as the dry compressive strength was not measured for several size fraction, this phenomena was not examined in more detail.

4.4.4 Conductivity results

The conductivity results in the experiments fitted badly to the obtained model. The reason to this is hard to explain, especially as no connection was found between content of raw ash and conductivity. But as all formulations showed a rather low conductivity, all formulations were approved based on the recommendations from the Swedish Forest Agency.

5. CONCLUSIONS

To summarize the conclusions in this project, each key question that was defined in the project are answered:

1. It is actually possible to form granules with sufficient strength suitable for applications as fertilizer in the forestry industry. The granules are characterised to be suitable for all kinds of areas and dosages, even clearings.
2. Solid binders may be used in the production of bio-ash granules, to increase its compressive strength. However, bentonite only to a small extent increased the dry compressive strength. Thus, it is not only possible to form granules of bio-ash together with binders, but also without binders. From an economical point of view, the best choice would be to produce carbonised bio-ash granules without the addition of binders.
3. The leaching characteristics did not fit well to the experimental model created by MODDE. Thus, no evidence is found pointing towards that granulation would change the leaching characteristics of the bio-ash.
4. The binding mechanism in 100% carbonised bio-ash granules was proven to be due to solid bridges. If bentonite was used, the binding mechanisms are believed to be caused by solid bridges and electrostatic interactions due to small particles in between larger particles.

6. FUTURE WORK

As the lab-scale tests of wet granulation of carbonised bio-ash showed positive results based on the factors used as design variables, wet granulation was shown to be a promising process. However, there are several areas of work that should be investigated to optimise the process. Some suggestions are listed below.

1. As the initial moisture content of the formulation proved to be an important variable, it would be feasible to further study the effect of initial moisture content at even higher contents than 20%. Especially to see if the strength of the granules may be improved.
2. Furthermore, process variables such as rotation speed, inclination angle and binder delivery method would be interesting to study, as these variables were kept constant in this project. Using these variables, the granule size distribution would also be a suitable parameter to measure. These variables are preferably screened firstly in lab-scale, before optimising at a larger scale.
3. Up-scaling tests of the process in general would be one major step towards a commercial process. Especially factors such as feed rate would be interesting to study.
4. Especially interesting would it be to test the granulation procedure together with the carbonised ash directly from the carbonation process.
5. Drying rate is also a parameter that should be evaluated, as it was kept constant during this project. Especially temperature of drying and final moisture content after drying should be evaluated to optimise the whole process, both in terms of product properties and process economy.
6. Phosphorous and nitrogen are two important nutrients for the growth of trees. Nitrogen is released into the atmosphere during combustion and phosphorous is an ending resource that has to be recycled. In order to use the ash more widely, it would be interesting to study the possibility to add minerals containing nitrogen and phosphorous to the ash recipe. Especially nitrogen is important to add at soils where nitrogen levels are low.

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APPENDIX

I. EXPERIMENTAL PLAN

Table 10: Experimental plan for the project.

Experimental name	Run order	Moisture content (Weight-%)	Bentonite content (Weight-%)	Raw ash content (Weight-%)
N1	14	10	0	0
N2	13	20	0	0
N3	4	10	4	0
N4	9	20	4	0
N5	12	10	0	10
N6	3	20	0	10
N7	6	10	4	10
N8	1	20	4	10
N9	10	10	2	5
N10	17	20	2	5
N11	15	15	0	5
N12	11	15	4	5
N13	16	15	2	0
N14	8	15	2	10
N15	2	15	2	5
N16	5	15	2	5
N17	7	15	2	5

II. DATA FROM MEASUREMENTS

Table 11: Results from the granule moisture content analysis, together with statistical numbers. Reported in weight-%.

Experimental name	Sample number										Statistics			
	1	2	3	4	5	6	7	8	9	10	Min	Mean	Max	SD
N1	30.4	28.6	29.4	32.6	30.6	28.1	29.7	30.2	30.3	29.6	28.1	29.9	32.6	1.2
N2	24.5	25.6	23.3	24.0	21.2	24.3	22.1	24.7	24.8	24.5	21.2	23.9	25.6	1.3
N3	28.4	26.5	25.6	25.5	25.2	24.7	27.6	28.2	25.6	27.7	24.7	26.5	28.4	1.4
N4	26.6	26.8	27.5	25.4	18.5	24.8	25.4	26.1	19.0	17.8	17.8	23.8	27.5	3.8
N5	27.6	31.5	31.4	28.3	27.2	26.4	27.9	27.9	27.1	27.7	26.4	28.3	31.5	1.7
N6	19.4	21.7	23.1	23.5	25.8	20.9	25.2	24.8	25.8	20.8	19.4	23.1	25.8	2.3
N7	27.0	24.0	26.8	27.1	25.5	28.2	25.0	25.5	28.0	24.6	24.0	26.2	28.2	1.5
N8	21.0	19.2	26.0	23.9	23.7	24.1	25.4	24.7	26.0	21.4	19.2	23.5	26.0	2.3
N9	26.6	27.1	29.0	26.1	27.8	27.8	28.4	26.9	27.9	28.5	26.1	27.6	29.0	0.9
N10	22.0	23.4	24.6	22.4	21.2	22.1	20.6	21.6	21.3	22.2	20.6	22.1	24.6	1.2
N11	23.5	29.2	24.3	30.5	23.9	25.3	23.8	25.7	26.4	25.6	23.5	25.8	30.5	2.3
N12	28.7	28.3	24.5	25.2	24.6	28.1	29.3	25.6	28.4	27.1	24.5	27.0	29.3	1.8
N13	25.1	20.5	26.5	26.5	27.5	27.3	30.0	26.3	25.6	24.8	20.5	26.0	30.0	2.4
N14	27.8	27.3	26.4	27.3	27.4	27.7	26.5	28.0	29.1	24.9	24.9	27.2	29.1	1.1
N15	23.7	28.3	26.7	23.9	28.9	27.6	26.6	25.6	27.3	25.5	23.7	26.4	28.9	1.7
N16	26.2	26.7	26.2	25.8	27.5	26.0	28.1	26.6	24.6	23.7	23.7	26.1	28.1	1.3
N17	25.1	26.2	27.2	22.5	23.4	28.1	28.2	26.4	27.3	28.0	22.5	26.2	28.2	2.0

APPENDIX

**Table 12: Results from the measurements of dry compression strength, together with statistical numbers.
Reported in N/granule.**

Experimental name	Sample number										Statistics			
	1	2	3	4	5	6	7	8	9	10	Min	Mean	Max	SD
N1	17.2	11.5	13.5	17.1	13.3	14.3	14.7	13.9	20.5	12.7	11.5	14.9	20.5	2.7
N2	22.6	16.9	22.4	19.3	17.4	29.7	25.4	17.1	19.8	17.8	16.9	20.8	29.7	4.2
N3	15.8	14.8	13.3	12.0	15.1	18.4	17.4	27.9	26.6	14.3	12.0	17.6	27.9	5.4
N4	30.8	23.7	22.9	33.9	28.9	23.4	16.9	19.2	22.8	21.5	16.9	24.4	33.9	5.3
N5	5.3	4.9	6.0	6.4	6.7	5.4	5.4	6.3	5.3	5.1	4.9	5.7	6.7	0.6
N6	16.4	18.1	17.6	16.9	13.2	15.0	18.1	17.5	15.9	14.6	13.2	16.4	18.1	1.6
N7	13.7	13.4	14.9	8.4	13.1	11.5	10.7	10.9	11.4	11.4	8.4	12.0	14.9	1.9
N8	18.5	15.4	21.8	16.8	17.1	25.6	14.5	20.8	20.4	15.5	14.5	18.7	25.6	3.5
N9	7.1	7.0	8.7	11.1	9.9	9.6	14.0	8.8	10.6	7.4	7.0	9.4	14.0	2.1
N10	22.9	25.1	24.0	28.9	29.0	26.1	23.3	23.0	16.8	19.4	16.8	23.9	29.0	3.8
N11	18.0	11.8	11.3	11.7	13.4	16.8	9.6	16.4	14.9	14.4	9.6	13.8	18.0	2.8
N12	10.2	19.7	18.8	21.8	11.6	11.7	22.7	20.1	14.3	17.1	10.2	16.8	22.7	4.5
N13	22.0	15.5	15.2	18.7	19.3	15.5	15.7	16.8	21.8	18.3	15.2	17.9	22.0	2.6
N14	18.5	10.3	11.0	20.5	18.2	10.7	9.6	16.3	13.7	12.6	9.6	14.2	20.5	4.0
N15	12.9	11.9	19.6	13.1	12.7	12.0	15.8	17.9	13.6	11.2	11.2	14.1	19.6	2.8
N16	17.7	15.6	12.0	13.9	22.5	11.7	12.5	9.6	15.4	14.9	9.6	14.6	22.5	3.6
N17	14.5	12.5	20.8	12.1	17.7	15.0	10.5	12.7	21.0	15.4	10.5	15.2	21.0	3.6

Table 13: Results from the measurements of conductivity, together with statistical numbers. Reported in mS/m.

Experimental name	Sample number			Statistics			
	1	2	3	Min	Mean	Max	SD
N1	1284	1379	1391	1284	1351	1391	59
N2	990	981	1007	981	993	1007	13
N3	1251	1260	1250	1250	1254	1260	6
N4	1377	1391	1401	1377	1390	1401	12
N5	1301	1226	1291	1226	1273	1301	41
N6	1230	1306	1226	1226	1254	1306	45
N7	1369	1358	1356	1356	1361	1369	7
N8	1102	1313	1335	1102	1250	1335	129
N9	1270	1281	1340	1270	1297	1340	38
N10	1411	1424	1377	1377	1404	1424	24
N11	1273	1307	1365	1273	1315	1365	47
N12	1344	1283	1318	1283	1315	1344	31
N13	1335	1320	1309	1309	1321	1335	13
N14	1324	1356	1388	1324	1356	1388	32
N15	1298	1366	1312	1298	1325	1366	36
N16	1289	1309	1284	1284	1294	1309	13
N17	1289	1278	1301	1278	1289	1301	12

III. STATISTICAL PLOTS FOR MODEL 3

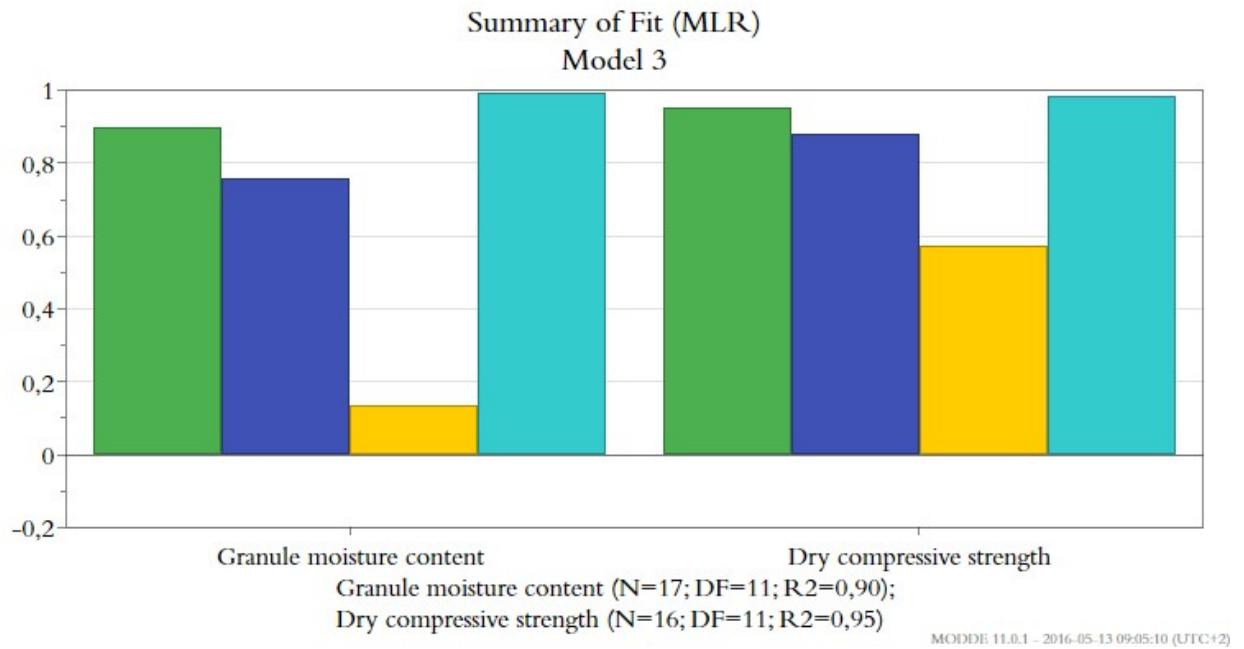


Figure 45: Summary of fit for model 3.

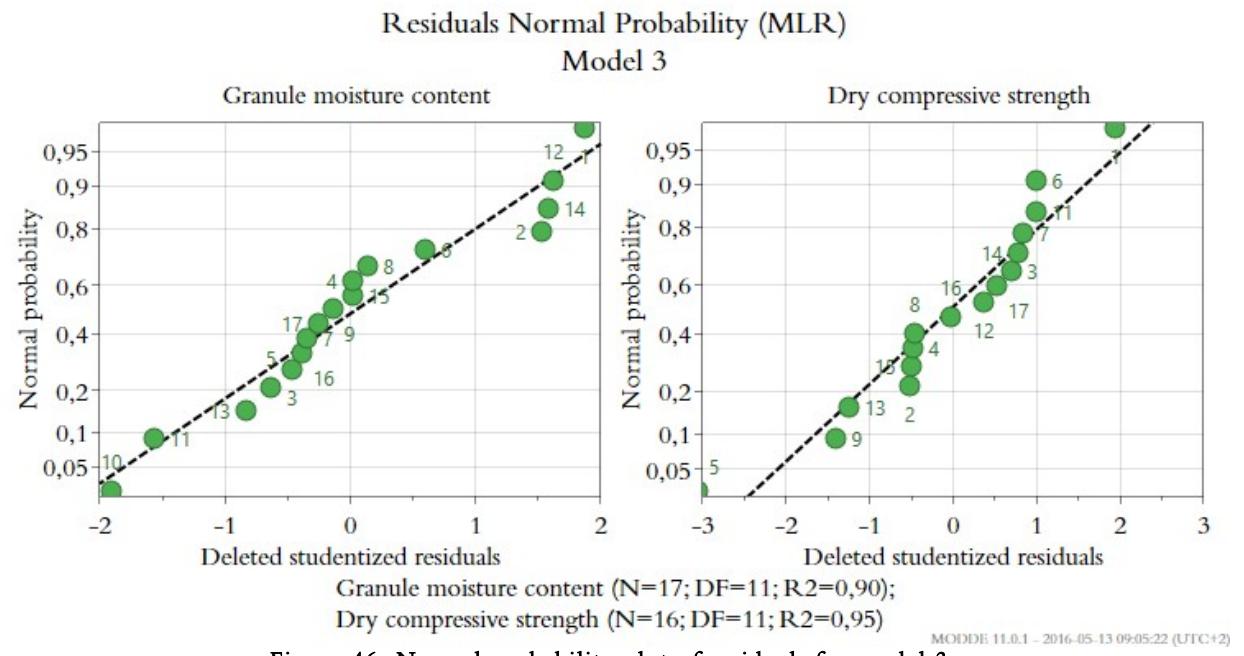


Figure 46: Normal probability plot of residuals for model 3.

